HALOGENATION AND ISOMERIZATION REACTIONS OF AROMATICS OVER K-L, H-BETA AND H-ZSM-5 ZEOLITE CATALYSTS

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CERTIFICATE

Certified that the work incorporated in the thesis, **“Halogenation and isomerization reactions of aromatics over K-L, H-beta and H-ZSM-5 zeolite catalysts”** submitted by **Mrs. Sushama Mohan Kale**, for the degree of ***Doctor of Philosophy***, was carried out under my supervision in the Catalysis Division, National Chemical Laboratory, Pune-411 008, India. Such materials as has been obtained from other sources have been duly acknowledged in the thesis.

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……..Dedicated to my beloved parents

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Chapter 1

Introduction

1.1. Introduction

Zeolites form an extraordinary diverse and exciting class of advanced inorganic materials, which are attracting increasing attention owing to their ion exchange, molecular sieving and above all their wide-ranging shape-selective catalytic properties. These in turn, arise from their acidity, from their ability to accommodate a wide range of different species and from their microporous crystal structure.

Structurally, the zeolite is a crystalline aluminosilicate with an extensive three-dimensional network of oxygen atoms. Situated within the tetrahedral sites formed by the oxygen can be either a Si^{+4} or Al^{+3} ion. The AlO_2^- tetrahedra in the structure determine the framework charge. This is balanced by the cations occupying non-framework positions. If H^+ ions are the charge balancing species, Bronsted acid cites are generated. The Al^{3+} ion itself has a tendency to acquire a pair of electrons to fill its vacant p orbital resulting in the formation of a Lewis acid site. Similarly the framework oxygen atoms in a zeolite give rise to Lewis basicity while the –OH groups present form the Brönsted basic sites. A representative empirical formula for a zeolite is written as:[1]

$$M_{2/n}O.\ Al_2O_3\ .\ xSiO_2\ .\ y\ H_2O$$

M represents the exchangeable cation, generally from the group I or II ions and n represents the cation valence. These cations are present either during the synthesis or through post-synthesis ion exchange. The value of x is 2 or greater than 2 because Al^{+3} does not occupy adjacent tetrahedral sites. Zeolites are synthesized hydrothermally by the combination of cations (both organic and inorganic), a source of silicon, a source of aluminium and water. Different chemical phenomena such as achievement of supersaturation, nucleation and crystal growth are found to occur during the complicated zeolite synthesis procedure[2]. The central atoms of the tetrahedra in the zeolite lattice can be replaced in an isomorphous manner by a large number of other tri- and tetravalent atoms (B, Fe, Cr, Sb, As and Ga[3-8] in place of Al while Ti, Zr, Hf, Ga[3-10] instead of Si) resulting in altered lattice constants and affecting the catalytic properties of zeolites. The use of organic cations[11-13] is an important step in the hydrothermal synthesis of silica rich types of zeolites whose characteristic features are high acidity, high resistance to water and acids and high thermal stability. Amongst the large number of organic compounds called templates, which control the crystallization of new zeolite structures, the organic amines have a dominating position[11, 14-29]. Synthesis in alcohol[30, 31], ethers[30, 32] and water[33] are also known. Further, important structure determining parameters are the Si/Al ratio and the condition of the silicate present in the synthesis mixture, which can be described in terms of the amount and degree of polymerization of the dissolved silicate anions[34, 35].

Zeolites can be classified on the basis of their morphological characteristics [14,36-38], crystal structure[14,36,39], chemical composition[14,36,40], effective pore diameter[14,36,41] and natural occurance[14,36]. On the basis of their morphology, zeolites are classified as fibrous, lamellar and those having framework structures. Depending upon the differences in the secondary building units, structural classification of the zeolites has been proposed. With the addition of new synthetic and natural zeolites, they have grouped into ten classes: Analcime, Natrolite, Chabazite, Philipsite, heulandite, Mordenite, Faujasite, Laumonite, Pentasil and Clantharate. Zeolites are classified as low silica zeolites; Si/Ai = 1-1.5 (e.g. Sodalite, A X), medium silica zeolites; Si/Al = 2-5.0 (e.g. L, Mordenite, Omega), high silica zeolites; Si/Al = 10 to several thousands (e.g. ZSM-5, EU-1) and silicalites; Si/Al = several thousands to ∞ (e.g. Silicalite-1 and silicalite-2), according to their chemical composition. Zeolites are also classified according to their pore sizes, namely, small pore zeolites; 3-4.5 Å (e.g. Erionite), medium pore zeolites; 4.5-6.3 Å (e.g. ZSM-5), large pore zeolites; 6.3-8 Å (e.g. Y, Beta, ZSM-12, L) and extra-large pore zeolites; ~ 12 Å (e.g. VPI 5, JDF – 20).

1.2. Shape-selective catalytic properties of zeolites

Shape selectivity is a unique property of zeolites and related molecular sieves. Weisz and Frillette[42] coined the term "Shape selective catalysis" more than three decades ago. The intra-crystalline surface area of zeolites is an inherent part of the crystal structure and hence they are topologically well defined. As a consequence, zeolites are able to restrict or prevent the passage of organic molecules based on the size and steric effects. The principles and applications of shape selective catalysis have been comprehensively reviewed and critically discussed by several authors[43-50]. Shape selectivity consists of a combination of shape, size and configuration of reactants, transition states and products with dimension, geometry and tortuosity of the channels and cages of the zeolite. Shape selectivity can occur either on the products, or the reactants or the transition states.

1.3. Catalysis by zeolites

Zeolites have advantages over conventional homogeneous and heterogeneous catalysts in many applications involving acid, acid-base, base, oxidation, reduction and polyfunctional catalysts as well as ion-exchange, drying and separation processes. The important unique properties that make them attractive as heterogeneous catalysts are[51]: well defined crystalline microporous structure, high internal surface area, high thermal stability, ease of regeneration, ion-exchange properties as well as non-corrosive and environmentally friendly nature. As catalysts, zeolites exhibit appreciable activity with shape selective features not available in compositionally equivalent amorphous catalysts. In addition, these materials can act as supports for numerous catalytically active metals and metal oxides.

The industrial use of zeolites as catalysts started in the early 1960's with the replacement of cracking catalysts based on amorphous aluminosilicates[52-55]. As catalysts, zeolites have found the greatest use in the hydrocarbon processing field in petroleum and petrochemical industries. Some major zeolite based processes involving petroleum, petrochemical and oil refining industries include selectoforming[56], M-forming[57], catalytic cracking[58], Jet fuel dewaxing[59] and M-2 forming[60].

Compared to successful use of zeolites in hydrocarbon processing, their use in the synthesis of organic intermediates and fine chemicals started in a later stage, but the progress of research in this field is significant in recent years. At the beginning of the 1970's P.B. Venuto and P.S. Landis indicated how zeolites- at that time principally X and Y- zeolites and mordenites could be used for the synthesis of organic compounds[61,62]. The discovery of ZSM-5[63] and its employment as a highly acidic, exceptionally shape selective and thermally stable catalyst in new technical petrochemical processes has continued to influence and stimulate zeolite chemistry right up to the present day. The applications of zeolites in organic reactions have been comprehensively reviewed by many authors[64-66]. The potential of zeolites in this field has been demonstrated for a variety of organic reactions such as alkylation[67], transalkylation[68], isomerization[69-71], halogenation[72-75], rearrangement[76], oxidation[77], reduction[78], condensation[79] and acylation[80].

1.4. Halogenation over solid catalysts/zeolites

1.4.1. Introduction

The use of heterogeneous, solid catalysts in the manufacture of fine chemicals is an area of growing importance. Halogen–containing compounds constitute an important segment of fine and specialty chemicals. Hydrofluorocarbons and hydrochlorofluorocarbons are extensively used in the refrigeration industry. Commodity chemicals like vinyl chloride monomer (for the manufacture of PVC) and intermediates like chlorobenzenes and chlorotoluenes are widely used material in the chemical industry. Chloro compounds also constitute a significant part of agrochemicals used as pesticides, insecticides, herbicides and weedicides. Bromo compounds, like tetrabromo bis phenol-A, are used as fire–retarding/extinguishing chemicals. Iodine-containing compounds find use in the pharmaceutical industry, especially in thyroid gland therapies. Even though the hydrofluorocarbons (HFCs) are manufactured using solid catalysts, many of the industrial halogenations of organic compounds are, at present, performed by free halogens either in the absence of catalysts or in the presence of Lewis acid catalysts such as halides of aluminium and iron (aromatic nuclear halogenations). The latter catalysts have certain shortcomings:

(1) Strict anhydrous conditions are required to avoid corrosion problems;

(2) In the case of nuclear halogenations of aromatic compounds, the operation has to be carried out in the absence of light to avoid side chain halogenation; and

(3) The halides of iron and aluminium, being strong Lewis acids, also catalyze other undesirable side reactions like alkyl isomerization and transalkylation or displacement of the alkyl group by the halogen. The latter are accentuated by increase in temperature, the degree of substitution on the adjacent carbon atom and the acidity of the catalyst. An additional major handicap of the Lewis acid catalysts like $FeCl_3$ or $AlCl_3$, is the difficulty

of their disposal, after use in the halogenation reaction, in an environmentally acceptable manner. The use of solid catalysts in halogenation processes will avoid corrosion and disposal problems. Work-up procedures to isolate and recover the desired product will also be easier leading to simpler and cleaner process routes. In addition, if zeolites are used as the solid catalysts in nuclear halogenations, one may expect enhanced yields of the *para* isomer due to the shape selectivity of the zeolite.

1.4.2. Halogenation and halogenating agents

A comprehensive account of the properties of halogens and their intermediate derivatives is given by Downs and Adams[81] and electrophilic halogenation is reviewed by de la Mare[82]. Halogenation reactions can be, broadly, classified into two categories, namely, halogenation of aliphatic compounds and halogenation of aromatics. Important industrial and fine chemicals like vinyl chloride monomer, HFCs, HCFCs, CFCs, chloromethanes, chlorosilanes, fluoro- and chloro acetic and sulfonic acids etc fall in the first category while chlorotoluenes, chloroxylenes, chlorophenols, chloroanilines, bromo bis phenols, the chlorine–based pesticides and insecticides, chloramphenicol etc., belong to the second category. The halogen derivatives of aliphatic compounds may be prepared by a variety of methods: (1) By direct halogenation with dihalogen i.e. by substitution reactions (of H or other halogen atoms) brought about by light, heat or catalysts; a free radical chain mechanism operates. In both photo–and thermal halogenations, no carbon skeleton rearrangement occurs at low temperatures and halogenations beyond the monohalo derivatives may be suppressed by controlling the ratio of the substrate to halogen ratio. The order of ease of substitution is tertiary hydrogen > secondary > primary; (2) by the addition of halogen acids to an alkene, (3) by halogen–halogen exchange; this route is especially important in the replacement of chlorine by fluorine in the manufacture of fluorochemicals. And (4) by direct chlorination of alkanes using sulphuryl chloride in the presence of light. Major advances have been made in the last decade in the manufacture of fluoroaliphatic compounds required in the fine chemicals industry using solid catalysts. Ever since the establishment of a relationship between ozone depletion and chlorofluorocarbons (CFCs) in the early seventies, the industrial production and use of chlorinated aliphatic compounds has been strongly discouraged. Hence, most of the research efforts in the halogenation of aliphatic compounds in recent years have been in the discovery and use of solid catalysts for the manufacture of fluoro–and hydrofluorocarbons.

Halogenation of aromatic compounds can lead to (1) addition compounds, (2) nuclear substitution products and (3) side-chain substitution products. When treated with Cl_2 or Br_2 in presence of sunlight; benzene forms the addition compounds $C_6H_6Cl_6$ and $C_6H_6Br_6$. Nuclear substitution occurs in the presence of Lewis acid catalysts, like $AlCl_3$ or $FeCl_3$, by an electrophilic substitution mechanism. Solid acid catalysts as will be shown later can replace these homogeneous catalysts. Side–chain halogenation proceeds by a free radical mechanism and is, hence, favoured by high temperatures and light and the absence of Lewis acid catalysts. Solid catalysts like silica and Na-Y zeolite also catalyze such halogenations. When the aromatic ring also contains e^- donating groups like –OH or NH_2, then the side-chain chlorination is suppressed.

A variety of compounds have been used as halogenation agents[82]. Fluorination can be carried out by molecular fluorine (F_2), HF, fluoroxy compounds (hypofluorites such as $F.CO(CF_3)_3$, $(FO)_2CF_2$ and $F.OC(CF_3)$), XeF_2, perchloryl fluoride ($FClO_3$) and metallic fluorides (especially CrF_3 and AlF_3 or their mixtures). Apart from molecular chlorine and HCl, other popular chlorination agents include hypochlorous acids, t- butyl hypochlorite, sulphuryl chloride and metallic chlorides like $InCl_2$ and $SbCl_5$. Similarly, apart from Br_2, brominations can also be carried out using hypobromous acid (HOBr), bromine acetate (BrOAc), t-butyl hypobromite and N- bromosuccinimide. The iodine molecule is the least reactive of all the molecular halogens in effecting addition to or substitution in organic compounds. Apart from I_2, other iodination agents like iodine chloride (ICl, mainly for aromatic substitutions) and iodine acetate are also used, commonly, as iodination agents.

1.4.3.Halogenation over solid catalysts

The beneficial effects of solid surfaces on the rates of halogenation reactions were observed more than 75 years ago. Stewart and Edlund[83] as well as Norrish[84] and Williums[85] studying the bromination of ethylene on glass showed that the polarity of the glass surface enhanced significantly the rates of bromination. Studies in halogenation over zeolites are of more recent vintage, starting from the early seventies. Hölderich et al. have reviewed the halogenation of arenes over zeolite catalysts[86]. A summary of halogenations over solid catalysts is given in Table 1.1

Table 1. 1 Halogenation over solid catalysts

Sr. No.	Reactant/ Halogenating agent	Product	Catalyst	Remarks	Ref
			A. FLUORINATION		
1	1,1,1 Trifluoro-2-chloroethane (HFCF–133 a)	HFC-134 a	Cr/MgO;Cr/Al_2O_3; Cr/MgF_2; Cr/TiO_2; Cr/ZrO_2	Most active catalyst Cr MgO	87
2	1,1,1 –Trifluoro-2-chloroethane (CF_3CH_2Cl)	1,1,1, 2 – tetra-fluoroethane	CrF_3 / MgF_2-AlF_3 CrF_3/MgF_2, CrF_3 / AlF_3	CrF_3 / MgF_2 or AlF_3 are more active than CrF_3 / MgF_2-AlF_3	88
3	1,1,1 – Trifluoro-2-chloroethane (HCFC-133a)	HFC-134a	MgO, Al_2O_3, AlF_3, MgF_2,TiO_2, ZrO_2 or supported chromium oxides	Best activity with CrO_x/ MgO	89
4	CFC-113,CFC-113a, CFC-114,CFC-114a, CFC-115 / HF and Cl_2	Hexafluoroethane	Cr_2O_3	300 – 500^0 C Vapour phase	90
5	HCFC-133a	HFC-134a	Chromium oxide	Selectivity to HFC –134	91

				a is independent of the O/F ratio on the Cr surface	
6	$ClCH:CHF_3$ (chlorotrifluoro-propene) / HF	1,3,3,3 – tetrafluoro-propene	Cr_2O_3 / carbon	400^0C Sel = 73.0%	92
7	$CCl_3CH_2CHCl_2$ / HF (Pentachloro-propane)	1,3,3,3 – tetrafluoro-propene	Cr_2O_3/carbon	Sel = 28.8%	93
8	2-Chloro-1,1,1,2-tetrafluoro-ethane (CF_3CHClF)	1,1,1,2 - tetra-fluoro-ethane (CF_3CH_2F)	Metal catalysts / carbon	100 - 250^0 C	94
9	CH_2Cl_2 / HF	CH_2F_2	Supported Cr catalyst	$300\text{-}450^0C$	95
10.	CH_2Cl_2 / HF	CH_2F_2	AlF_3 on a Cr-Ni	Catalytic gas phase fluorination	96
11	Chlorohydro-carbons / HF	Fluoro-hydrocarbons	Chromium-hydroxide	$100\text{-}550^0C$; conv. = 90 %	97
12	Hydrochloro-carbons / HF	Hydrochloro-fluorocarbons	Fluorinated metal oxides	Room temp.	98
13	1,1,1-trifluoro-2-chloroethane	1,1,1,2-tetrafluoro-ethane	transition metals on a γ-AlF_3	Vapour phase catalytic fluorination	99
14	SO_3	$S_2O_6F_2$	AgF_2 on Copper turnings	Product yield in substantial quantities	100
15	Fluoroalkenes, fluoroanhydrides, polyfluoroalkenes / F_2	Perfluorinated liquid compounds	Supported NiF_2	Vapour phase, high selectivity for products	101
16	1,1,1 Trifluoro-2-chloroethane (CF_3CH_2Cl) / HF	CF_3CH_2F	Cr_2O_3	-	102
17	$CF_3CF_2CHCl_2$ by fluorination and reduction of CF_3CF_3CHClF	$CF_3CF_2CH_2F$	halides or oxides of Al,Cr,Mg,Ca,Ba, Sr,Fe,Ni,CO	280^0C Sel = 73%	103
18	Chloropentafluoroethane / HF	Hexafluoroethane	Cr_2O_3,Ni-Cr alloy	Purification of pentafluoro Ethane its major contaminant	104
19	Acetylene / HF	Ethylenedifluoride (HFC-152a)	Al_2O_3-Bi-Mn	Gas phase catalytic fluorination	105
20	Hydrocarbon or halogenated hydrocarbon/HF	Fluorinated hydrocarbons	Zn supported on aluminium,Ni,CO, Mn,Fe or Cu	Vapour phase	106
21	1-chloro-1,2,2,2-tetrafluoroethane (HCFC-124)/HF and HCl	1,1dichloro-2,2,2-trifluoro-ethane(HCFC-123)	HF treated $COCl_2$ on Al_2O_3	-	107
22	1,1,1-Trichloroethane/ HF	Fuoro-hydrocarbons	$MeCCl_3$,C_2Cl_4 or $MeCCl_2Me$ supported on SF_4-	-	108

			fluorinated γ - alumina		
23	CF_3CHCl_2 or $CClF_2CHClF$ or CF_3CHClF or CHF_2CClF_2	Pentafluoro-ethane	Cr_2O_3	350^0C conv = ~ 85.9%	110
24	CF_3CH_2Cl/HF	Fluorinated hydrocarbons	Cr_2O_3	350^0C conv = 26.9%	109
25	Tetrahaloethylene /HF	2,2-dichloro-1,1,1-trifluoro-ethane,2-chloro-1,1,1,2-tetraluoroethane	Metal fluoride on γ-alumina	250-450^0C , gaseous phase	111
26	Trichloro-acetaldehyde/H_2O_2/HF	Trifluoro-acetaldehyde (hemiacetal)	Cr-zeolite	Gas - phase	112
27.	1,1,1-Trichloroethane/ HF	Chlorofluoro-hydrocarbons	Fluorinated γ - alumina	Room temp.fluorination	113
28	CCl_3CF_3/HF	$CFCl_2CF_3$	Cr_2O_3-Fe_2O_3	320^0C; conv=85%, Sel=98%	114
29	Perchloro-ethylene (C_2Cl_4)/HF	Freon substitutes (R-122,R-123,R-124,R-125)	Cr_2O_3-MgO-Al_2O_3	350^0C, gas-phase	115
30	$CF_2ClCHCl_2$ (R-122)/HF	CF_3CHCl_2(R-123)	Cr_2O3/γ -Al_2O_3	280^0C; conv=84.4%, Sel=82.6%	116
31	$MeCF_3/F_2$	C_2F_6,CF_4	Cu-Sn alloy	200^0C, Sel.,C_2F_6=87.2% CF_4=7.0%	117
32	$C_2Cl_3F_3/F$	$(ClF_2C)_2$,$ClCF_2CF_3$, C_2F_6	FeF_2/C	553^0C, vapour phase	118
33	CCl_3CHO/HF	$CF_3CH(OH)O$-C_2H_5	Cr_2O_3/Al_2O_3 Cr-zeolite	250^0C HF is fixed by H_3BO_3	119 221
34	C_2Cl_6/HF	$C_2F_4Cl_2$	Fluorinated N_2O_3 &$CuCl_2$ coated Al_2O_3	400^0C,gas-phase	120
B. CHLORINATION					
35	Ethylene / Cl_2	1,2 – dichloroethane	$CuCl_2$-Al_2O_3	-	121
36	o-Chlorotoluene / Cl_2	o-chlorobenzyl chloride	-	o-chlorophenyl-acetamide is obtained by cynation and hydrolysis of product	122
37	Toluene /Cl_2	Benzyl chloride	Composite catalyst	Benzyl chloride produced by direct, catalytic and photochlorination of toluene	123
38	Allylic sulfones / hexachloro ethane or CCl_4	Mono or dichlorinated products	Phase-transfer catalyst	High yields	124

39	CH_3Cl/HCl and air	CH_2Cl_2, $CHCl_3$	Alkali metal chlorides or earth chlorides or rare earth chlorides on γ alumina	360 ^{0} C, conv. = 31.9 %, sel. for CH_2Cl_2 = 78.8 % $CHCl_3$ = 3.5 %	125
40	CH_3Cl/HCl and air	CH_2Cl_2, $CHCl_3$	Cu-chlorides on γ alumina	330 ^{0} C, conv. = 10.5 %, sel. for CH_2Cl_2 = 81.1 % $CHCl_3$ = 5.2 %.	126
41	Chlorobenzene/ Cl_2	Dichlorobenzene	Silica-alumina, zeolite, bentonite with $FeCl_3$	Sel. to dichlorobenzenes higher over zeolites	127
42	CH_4/Cl_2	CH_3Cl	SO_4^{2-}/ZrO_2, Pt/ SO_4^{2-}, ZrO_2, Fe/Mn/ SO_4^{2-}/ZrO_2	Continuous flow reactor, atm. Pressure, CH_4/Cl = 4; 200^0 C, Cl conv. = 30 %, Sel. CH_3Cl = > 90 %.	128
43	Trichloroacetic acid	Acid chloride	Silica support	130^{0}C, 5h , Yield = 92%	129
44	[14C]-UL-Dicyamo-benzene/C_{l2}	[14C]-UL-2,4,5,6-tetrachloro-1,3-dicyanobenzene (chlorothalonil)	Activated carbon	Tubular reactor,300^{0}C, Yield=90%	130
45	Tetrafluoro-ethylene/HCl	Chlorotrifluoro-ethylene	Cr_2O_3	150-350^{0}C, conv=52% Sel=53%	131
46	Saturated hydrocarbons (CH_4)/HCl	CH_3Cl	Cr(VI)-Cl/SiO_2 and Cr(VI)-Ru(IV) – Cl/SiO_2	120^{0}C, Yield = 30%	132
47	Propene/HCl/O_2	1-chloropropene 1,2-dichloro-propane	MCl/$PdCl_2$/$CuCl_2$/ SiO_2	Oxy-chlorination	133
48	C_6H_6 or C_6H_5Cl/Cl_2	$C_6H_4Cl_2$	γ- Al_2O_3	70^{0}C, Sel. for para=75.5%	134
49	Phenol and alkylphenols / Cl_2	p-and o- chloro-phenols, chloro-alkylphenols	$CuCl_2/Al_2O_3$	50^{0}C, p-/-o chlorophenol = 22	135
50	m-Dicyano-benzene/ Cl_2	Tetrachloro-isophthalonitrile	Activated carbon supported catalyst	280-320^{0}C,gas-phase	136
51	Ethylene/Cl2/air	Dichloroethane	$CuCl_2$-KCl/γ-Al_2O_3	Gas-phase	137
52	CH_4 or chlorinated CH_4/Cl_2	CCl_4	CO/CrO_2	Gas-phase	138
53	Phthalic anhydride/Cl_2	Tetrachloro-phthalic anhydride	$COCl_2$,$BaCl_2$/active carbon	320^{0}C, Yield=82.8 mol%	139
54	Propylene/Cl_2	CH_2=$CHCH_2Cl$	LiCl/Silica gel, $AlCl_3$, $FeCl_3$/carborundum	Vapour phase	140
55	C_2H_6/Cl_2	$ClCH_2$-CH_2Cl	$CaCl_2/Al_2O_3$	Vapour phase	141
56	$C_6H_5CH_3/Cl_2$	$C_6H_5CH_2Cl$,C_6Cl_6	Al_2O_3 supported MoO_3,Fe_2O_3,CuO and $CuCl_2$, MoO_3	260-430^{0}C	142

			and $MgCl_2$ on silica gel		
57	CH_4/Cl_2	CH_3Cl	Tantalum oxy-fluoride/Al_2O_3	235-300^0C,higher yield for CH_3Cl	143
58	$C_6H_6/HCl-O_2$	C_6H_5Cl	Cr_2O_3	400C,Yield=35%	144
59	Cumene/Cl_2	Chloro-cumenes	Chemically modified silica	Para/ortho ratio higher	145
60	C_6H_6 or $C_6H_5CH_3/Cl_2$	C_6H_5Cl,$C_6H_5Cl_2$,$C_6H_5CH_2Cl$	Activated carbon	250C,liquid phase	146
61	Propene/HCl/O_2	CH2:$CHCH_2Cl$	$SnCl_3$,$PrCl_3$,$MnCl_2$, $CrCl_3/Al_2O_3$	325-525^0 C, vapour phase	147
62	C_2H_4/HCl or NH_4Cl/O_2	$ClCH_2CH_2Cl$	$CuCl_2$/TeO & TeO_2	150-230^0 C	148
63	Benzene/Cl_2 + O_2	Para-dichlorobenzene	L-zeolite	solvent = 1,2-dichloroethane	149
64	C_6H_5Cl/Cl_2	Para-dichlorobenzene	Na-Y	para-dichlorobenzene is the major product	150
65	CH_4/Cl_2; $CH_4:Cl_2$ = 4.1	CH_3Cl	H-mordenite	3350^oC, GHSV = 600; sel. = 99.2%	151
66	toluene/t-butyl hypochlorite, SO_2Cl_2	(i)p-and o-chlorotoluene (ii)$C_6H_5CH_2Cl$	H-X, Na-X	temp.25^oC, conv.98%, para sel = 82%, solvent = acetonitrile	152-155
67	CH_2=CH-CH_2Cl /Cl_2	1,3-dichloropropenes	zeolite containing 1.5-2% $ZnCl_2$ or $TiCl_4$	450-500^oC	156
68	CH_3Cl/Cl_2	CH_2Cl_2	zeolite contg. Ag and Mn	400^oC; sel.=97.5%	157
69	2-halobenzotrichloride/Cl_2	2,5-dihalobenzotrichloride	K-L zeolite	145-150^oC for 14hrs; sel. = 89% vs 11% for $FeCl_3$ as catalyst	158
70	o-ClC_6H_4F or p-ClC_6H_4F/Cl_2	2,4-dichlorofluorobenzene	Na-Y	70^oC for 4hr. conv. = 74% and sel. = 80% vs 55 and 70% for $FeCl_3$	159 160
71	C_2H_6/Cl_2	sym.tetrachloroethanes (33.6%), 1,1,2-trichloroethane (25.8%), pentachloroethane (15.5%)	SK-400	300^oC	161
72	Biphenyl/Cl_2	4,4'-dichlorobiphenyl	K-L zeolite + $ClCH_2COOH$	temp. = 40^oC; conv.. = 100%; sel. = 96%; dichloromethane	162
73	C_1-C_4 alkylbenzenes/ Cl_2	4-XC_6H_4R (R=C_{1-4} alkyl: X=halogen)	L-zeolite	70^oC; conv = 97%; sel. = 63%; 2-/4-isomer ratio = 0.5	163
74	C_6H_5Cl/Cl_2 in presence of N_2	4-$Cl_2C_6H_4$	zeolite ECR-2	100^oC; conv=92%; sel.=91%	164
75	-ditto -/Cl_2	-ditto -	various zeolites	Gas phase	165
76	-ditto -/Cl_2	-ditto -	L-zeolite	3h at 70^oC; sel. = 87.6%	166
77	-ditto -/S_2Cl_2	-ditto -	Na-Y with sulphur	100^oC for 3h: conv.=	167

			compounds	64%; sel. 86%	
78	-ditto -/Cl_2	-ditto-	L zeolite treated with NaOH	100^{o}C; conv.67%; sel. = 92%	168
79	$C_6H_5CH_3/Cl_2$	4-$ClC_6H_4CH_3$	zeolite with $ClCH_2COOH$	70^{o}C; sel = 75%	169
80	C_6H_5Cl/Cl_2	4-$Cl_2C_6H_4$	Na-Y with NaCl	100^{o}C, conv = 78%; sel. = 85%	170
81	C_6H_5R (R=Me, Et, Me_2CH, Me_3C, Ph, Cl, Br)/Me_3COCl	-ditto -	Zeolite X	97% para-sel; conv. = 92%	153
82	C_6H_5Cl/Cl_2	-ditto -	L-zeolite	100^{o}C; conv.57%; sel. = 88%	171
83	$C_6H_5CH_3/Cl_2$	4-$ClC_6H_4CH_3$	L-zeolite with $ClCH_2COOH$	98.3% conv.; 74.2% para-sel.	172
84	-ditto-/Me_3COCl	4- and 2-$ClC_6H_4CH_3$	X,Y,ZSM-5, mordenite or L-type zeolite with amorphous SiO_2	35% para	173
85	-ditto-/Cl_2	-ditto-	LZ-Y 52	conv. = 82%; 4-/2-isomer ratio = 1:0.85	174-176
86	-ditto-/Cl_2	4-$ClC_6H_4CH_3$	L-zeolite	sel. 81.4%	177
87	C_6H_5Cl/Cl_2	4-$Cl_2C_6H_4$	L-zeolite	conv. = 66%; sel. = 87%	178
88	1,2-$Cl_2C_6H_4$	1,2,4-$Cl_3C_6H_3$	zeolite-Y	sel. = 64.7%	179
89	$C_6H_5CH_2C_6H_5$/ Cl_2	Mono- and dichloro	TSZ-500 KoA (KL zeolite)	sel. for 4,4'-dichloro = 34%	180
90	C_6H_5-C_6H_5/Cl_2	4,4'-dichlorobiphenyl	zeolite L with $ClCH_2COOH$	100^{o}C for 5 h; sel. = 81.7%	181
91	C_6H_5Cl/Cl_2	4-$Cl_2C_6H_4$	zeolite L type	very high sel. for p-dichlorobenzene	182
92	$C_6H_5CH_3/Cl_2$	4-$ClC_6H_4CH_3$, 2-$ClC_6H_4CH_3$	zeolite containing K_2O and Na_2O	-	183
93	$ClCH_2CH_2Cl$, CH_3Cl/Cl_2	chlorinated prods.	L-zeolite	-	184
94	$C_6H_5CH_2Cl$ /Cl_2	4-ClC_6H_4CHCl	K-L	Conv=55.7%; isomer, 4 -/2- ratio = 3.53	185
95	4 –Chloro-toluene /Cl_2	2,4-dichlorotoluene	K-L	95^{0}C, conv = 57.3% isomer ratio, 2,4/3,4=3.5	186
96	1,2- Dichloro benzene	1,2,4- tri-chlorobenzene	K-L + $ClCH_2COOH$	Conv=92.1%, isomer ratio,1,2,4-/1,2,3 = 14.0	187
97	Chlorobenzene/ Cl_2	1,4-dichlorobenzene	K-L zeolite + $ClCH_2COOH$	70^{o}C; conv. = 26%; sel. = 86%	188
98	Toluene/Cl_2	para-chlorotoluene	-ditto-	conv. = 45%; sel. = 76.8% vs 44.1% and 32.9% resp. for $FeCl_3$	189, 190
99	-ditto-	-ditto-	-ditto-	conv. = 58.7%; sel. = 86%; solvent = 1,2-dichloroethane	191
100	o-xylene/Cl_2	4-chloro-o-xylene	K-L zeolite	conv. 39% and sel. = 92% vs 38.8% and 50% for $FeCl_3$	194 193
101	m-xylene/Cl_2	2-chloro-m-xylene	-ditto-	80^{o}C, conv. =38% and	ditto

				sel. = 86%	
102	p-xylene/Cl_2	2-chloro-p-xylene	-ditto-	80^oC; conv. = 41% and sel. = 100%	ditto
103	Naphthalene/ Cl_2	1-chloronaphthalene	-ditto-	80^oC; conv. = 27% and sel. = 95%	195 192
104	para-chloro -toluene/ Cl_2	2,4-dichlorotoluene	-ditto-	85^oC; conv.= 50%; sel. = 74.9%	196

C. BROMINATION

105	$C_6H_5CH_3/Br_2$	para-bromotoluene	Na-Y	Rapid deactivation; sel. = 81%	197
106	-ditto-/Br_2	-ditto-	-ditto-	liquid phase; initial reaction rates higher than in Lewis acids	198
107	-ditto-/Br_2	-ditto-	-ditto-	sel. = 64.2%	199-201
108	-ditto-/Br_2	para-bromotoluene (98%)	-ditto-	zeolite-bromine-oxirane system; rapid deactivation	202
109	-ditto-/Br_2	-ditto-	y type zeolites exchanged with di- and trivalent cations	Adsorptive bromination	203
110	isoprene-isobutylene copolymer (Butylrubber) /Br_2	Brominated butyl rubber (2%Br)	Na-X saturated with 45% Br_2	Bromination in benzene solution	204
111	Aromatics (C_6H_6)/Br_2	Addition prods.	Zeolites	Raman spectral study	205
112	Chlorobenzene, toluene, Xylenes (o,m,p)/Br_2 and NBS	Bromochloro benzene,bromo-toluene, bromoxylenes	H-beta, H_2SO_4	nuclear and side-chain products	206
113	1,3,3-Trimethyl-1-phenylindan / Br_2	Octabromo-1,3,3-trimethyl-1-phenylindan	Fe powder	Yield=97.2%	207
114	CH_2Cl_2/HBr	Chlorobromo-methane and dibromomethane	Al_2O_3	$180\text{-}250^0C$	208
115	CHF_3/F_2	$CBrF_3$	Quartz rings	600^0C, yield=72 %	209

D. IODINATION

116	Benzene/HI_3 in presence of O_2	C_6H_5I	Na-X	34^oC; conv. = 98%	210, 211
117	Benzene/I_2	iodobenzene	Cu-ZSM-5	97.5% sel. at 100% conv.	212
118	Toluene / ICl	Para-iodotoluene	H-beta, H-K-L	90^0C, conv.ICl=51.5%, isomer ratio PIT / OIT	213

				=2.88	
119	Naphthalene and aromatic compds / I_2 and O_2	Iodonaphthalene and iodoaromatics	K-X	250^0C, conv. Naphthalene = 20% conv.I_2= 80-90%	214

1.4.3.1. Fluorination using solid catalysts

In general, fluorination of organic compounds can be accomplished by various methods[215]

1) Halogen exchange

$RX \xrightarrow{KF} RF + KX$ The relative ease of replacement is I > Br > Cl

2) Replacement of hydrogen

1) $\text{->C-H} + F_2 \longrightarrow \text{->C-F} + HF$

2) $\text{->C-H} + AgF_2 \text{ or } CoF_3 \longrightarrow \text{->C-F} + HF$

3) Direct fluorination with molecular F_2

4) Reaction with a metal fluoride

$2CoF_2 + F_2 \longrightarrow 2CoF_3$

$RH + 2CoF_3 \longrightarrow RF + 2CoF_2 + HF$

5) Electrochemical fluorination

The electrolysis of an organic substrate in liquid anhydrous HF at a voltage below that for the liberation of F_2 leads to fluorinated organic products.

A major impetus to research in this area during the past two decades (especially after the 1987 Montreal Protocol) has been the necessity to discover catalysts for the synthesis of alternatives for chlorofluorocarbons, specifically hydrofluorocarbons[216]. 1,1,1,2 – Tetrafluoroethane (HFC –134a; CF_3CH_2F) is a typical example of such a HFC alternative to CFCs like CFC-12 (CF_2Cl_2). HFCs can be synthesised by a variety of methods including HF addition to olefins, halogen exchange, isomerisation, disproportionation, chlorofluorination and hydrogenolysis. Solid catalysts have been reported for these reactions in both the liquid and vapor phase processes. For liquid phase processes, homogeneous catalysts like SbX_5, BF_3, TaF_5, NbF_5 and $MoCl_5$ had been proposed[217,218]. Vapor phase processes often use the fluorides or oxyfluorides of chromium or aluminium or their mixture[219]. Compared to the liquid phase processes using homogeneous catalysts, the vapor phase fluorinations are less polluting and corrosive. The catalyst preparation involves two separate stages: preparation of the oxide and conversion of the oxide partially into an oxyfluoride phase using HF or other fluorinating agents. Oxides of chromium either unsupported or supported on high surface area supports like Al_2O_3 or MgO are used. In the fluorination of 1,1,1–trifluoro–2- chloroethane (HCFC-133a to HFC134a) over fluorinated chromium catalysts, Cho et al[220] reported that conversion increases as the crystallinity of the chromia (both unsupported and supported on various solids) decreases. The conversion over supported chromia decreased in the order $MgO > Al_2O_3 > AlF_3 > MgF_2 > TiO_2 > ZrO_2$. The selectivity to HFC –134a was not strongly dependent on the support type, but highest with MgO.

There are not many reports of the use of zeolites in fluorination reactions. Tasaka and Nakasora[221] have claimed the fluorination of trichloroacetaldehyde (CCl_3CHO) to trifluoroacetaldehyde hemiacetal ($CF_3CH(OH)OC_2H_5$) over zeolites containing impregnated chromium ions using HF as the fluorinating agent. Boric acid was used to 'fix' HF (HF : H_3BO_3 = 1: 2.7) to form borofluoric acid. It is probable that fluorides of chromium formed "in situ" in the zeolite by reaction of borofluoric acid with Cr^{3+} ions are the actual fluorinating agents, especially, since fluorides of chromium are known fluorinating agents [222].

1.4.3.2. Chlorination using solid catalysts

1.4.3.2.1. Catalytic chlorination of aliphatics

Catalytic chlorination of aliphatic compounds using solid catalysts is carried out in either of two ways: Electrophilic chlorination over acidic catalysts[128] or oxychlorination in the presence of dioxygen over copper–based catalysts[121]. Even though aliphatic compounds can be easily chlorinated by a radical mechanism (in the presence of light, for example), the reactions are rather non-selective. When alkanes containing different carbon-hydrogen bonds are chlorinated, all possible monochlorinated isomeric products are obtained. Similarly, chlorination of hydrocarbons with a single type of carbon-hydrogen bond, such as methane, leads to a mixture of mono- and polychlorinated products. Chloromethane is an important industrial fine chemical. Olah et al[128] have reported the selective catalytic monochlorination of methane to chloromethane over superacidic sulfated zirconia solid catalysts, like, SO_4^{2-}/ZrO_2, $Pt/SO_4^{2-}/ZrO_2$ and $Fe/Mn/SO_4^{2-}ZrO_2$. The reactions were carried out in a continuous flow reactor under atmospheric pressure. At 200^0C with 30% chlorine converted the selectivity to chloromethane was above 90% .The selectivity could be enhanced by adding platinum. The only byproduct was CH_2Cl_2. The latter is formed by the subsequent chlorination of chloromethane. No chloroform or carbon tetrachloride was formed. The authors postulated that chlorination occurs by an electrophilic insertion of an electron deficient, metal co-ordinated, chlorine molecule into the C-H bond of methane. One drawback of the process was that above 225^0 C, part of the metal was removed as the metal chloride[128]. Formation and subsequent loss of volatile metal chlorides is one of the major pitfalls one should avoid during vapor phase chlorination over solid catalysts.

The $CuCl_2$ supported on alumina-catalysed, gas phase, oxychlorination of ethylene with HCl to 1,2-dichloroethane (ethylene dichloride or EDC) followed by the dehydrochlorination of EDC to vinyl chloride monomer (VCM) is a major industrial process for the manufacture of polyvinyl chloride, a commodity polymer.

$$H_2C{=}CH_2 + 2HCl + 0.5\ O_2 \xrightarrow{\hspace{2cm}} Cl\text{-}CH_2\text{-}CH_2\text{-}Cl + H_2O$$

In a recent study of the $CuCl_2$-Al_2O_3 catalyst system, Finocchio et al[121] discovered that, at 250^0 C, while the oxychlorination reaction occurs on copper sites, the alumina surface not covered by the copper species dehydrochlorinates the desired product, EDC, further, to byproducts like vinyl chloride, trichloroethane and dichloroethylene.

1.4.3.2.2. Molecular chlorine as the chlorinating agent

Molecular chlorine is the traditional reagent for chlorinating aromatic compounds. However, in the absence of added catalysts, it reacts readily in an electrophilic manner only with activated aromatic compounds. Weakly activated or non-activated substrates are generally reacted with Cl_2 in the presence of a Lewis acid such as $AlCl_3$ or $FeCl_3$. The Lewis acid complexes the chlorine to form a highly polarized species, which, in its extreme form may be represented as a chlorinium salt ($Cl^+FeCl_4^-$). It is this highly polarized complex which is thought to be the active electrophilic reagent.

Levina et al.[223] were one of the first to use zeolites in the halogenation of benzene. The zeolite contained Fe^{3+} ions in cation-exchange positions. The composition of the product was not mentioned. In 1974 Van Dijk et al.[152] reported the interaction of aromatic compounds, preadsorbed from CCl_4 solution in the pores of NaX, CaX or Ca-Fe-X, with molecular Cl_2 or Br_2. An excess of zeolite (by wt.) was used so that more than 95% of the substrate was adsorbed on the zeolite. After reaction with the halogen at 298 K, the zeolite was separated from the solutions and destroyed with acid and t reaction products were extracted and analyzed by GLC.

Table 1.2. Chlorination with Cl_2 of pre-adsorbed aromatics in zeolites at 298 K (Ref. 152)

Substrate	Catalyst	Conv. (%)	Ring chlorination (%)	Side-chain Subs.(%)	Polyhalog. (%)	Para/ ortho
$C_6H_5CH_3$	none	100	21	79	-	0.6
	$FeCl_3$	92	87	5	-	0.5
	CaX	54	42	7	6	5.0
	FeX	98	95	3	-	1.0
C_6H_5Cl	$FeCl_3$	95	95	-	-	2.0
	CaX	80	76	-	4	24.0
	FeX	86	85	-	1	6.0
C_6H_5Br	$FeCl_3$	90	88	-	2	1.7
	CaX	68	68	-	0.5	23.0
	FeX	84	82	-	2	4.1

Both alkylbenzenes and halogenobenzenes were studied. Alkylbenzenes gave mainly and halogenobenzenes almost exclusively the para isomers. Some representative results are given in Table 1.2. It may be seen that the use of zeolites leads to a significant increase in the para/ortho ratio. To our knowledge, these are the earliest results illustrating the beneficial use of zeolites in controlling the regioselectivity in halogenation reactions using molecular halogen.

In one of the earliest reports on the vapor phase chlorination of benzene with Cl_2 over zeolite catalysts, at 175^0 C, with a Cl_2:C_6H_6 molar ratio ranging from 5:1 to 10:1, after 3 h of reaction time, Huizinga et al reported[224] the formation of significant quantities of addition products (presumably by a free radical mechanism) rather than substitution products. Contrary to expectations, the medium pore zeolite H-ZSM-5 gave more addition products (87%) than the large pore zeolite, RE-Y (3%) as well as zeolite L (11%). Evidently, H-ZSM-5 induces a free-radical reaction which takes place mainly on the external surface and/or at the pore opening of the zeolite. Also another large pore zeolite H-mordenite and silica catalyst gave higher yields of addition products (84% and 72%, respectively) than the substitution products. Similarly, in the chlorination of toluene in the gas phase[225], a comparison of aluminosilicate, silica gel, faujasite and montmorillonite shows that the yield of monochlorotoluene is 10 % higher with montmorillonite than faujasite. The para/ortho ratio of the chlorotoluenes was also comparable over the various catalysts. These early studies indicated that significant yields of nuclear substitution products in halogenation over zeolites is more likely to be achieved under liquid phase conditions rather than in the gas phase.

In the liquid phase chlorination of monochlorobenzene by Cl_2 in the presence of alkali cation-exchanged zeolites (NaY, Na-ZSM-5, Na-A, Na, K, Cs-offretite/erionite, K-L), Sekizawa and co-workers[150,226] reported that para-dichlorobenzene was the major product. The para selectivity was improved further on decreasing the acid strength of the zeolite by exchange with alkali cations. The zeolite was used in only catalytic quantities (1-5 wt.%). The same authors also reported[226] the chlorination of monochlorobenzene on various zeolite catalysts in the vapour phase (Table 1.3).

Table 1.3. Vapour phase chlorination of monochlorobenzene with Cl_2 (ref. 226)
MCB/Cl_2 = 2.0 mole/mole; 473K; W/F = 124g-cat.hr/MCB mol

Catalyst	Cl_2 conv (%)	DCB[a] sel (%)	Para sel (%)
Na-A	16.1	96.3	68.8
H-Y	99.9	92.2	64.5
Na-Y	99.8	92.7	70.2
K-L	87.9	94.5	77.4
Na-ZSM-5	74.7	95.0	78.3
H,K-O/E[b]	94.5	95.0	64.4
Na,K-O/E	99.2	96.4	78.4
K-O/E	96.3	99.3	93.1
Cs,K-O/E	78.2	99.5	92.2
SiO_2-Al_2O_3	92.7	91.0	62.5
MgO	82.7	92.0	54.9

[a] DCB = dichlorobenzene
[b] = O/E: mixed crystals of offretite and erionite

The low activity of Na-A is probably due to its smaller pore width. Most of the reaction occurs on the external surface with a para selectivity similar to the amorphous SiO_2-Al_2O_3 and MgO as well as homogeneous catalysts like $FeCl_3$. In the offretite/erionite series, the para selectivity increases with the radius of the non-framework cation. The authors ascribed[226] the high paraselectivity in K, Rb, Cs- exchanged O/E zeolites (Table 1.3) to the steric effect of the large cations (shape selectivity) in addition to decrease of the acid strength. It is probable that chlorination occurs by an electrophilic substitution mechanism, the electrophile being a polarised chlorine molecule.

The critical role of exchanged cations in influencing the para selectivity in the chlorination of aromatics using Cl_2 was later confirmed by Botta et al.[162] in the chlorination of biphenyl to 4,4'- Dichlorobiphenyl (species C, Fig. 1) in L-zeolites. This reaction is also of significant industrial interest since 4,4'-Dichlorobiphenyl is a precursor for some high performance polymers. Chlorination with conventional Lewis acid catalysts like $FeCl_3$ gives[162] a complex mixture of mono and dichlorobiphenyls [Fig 1].

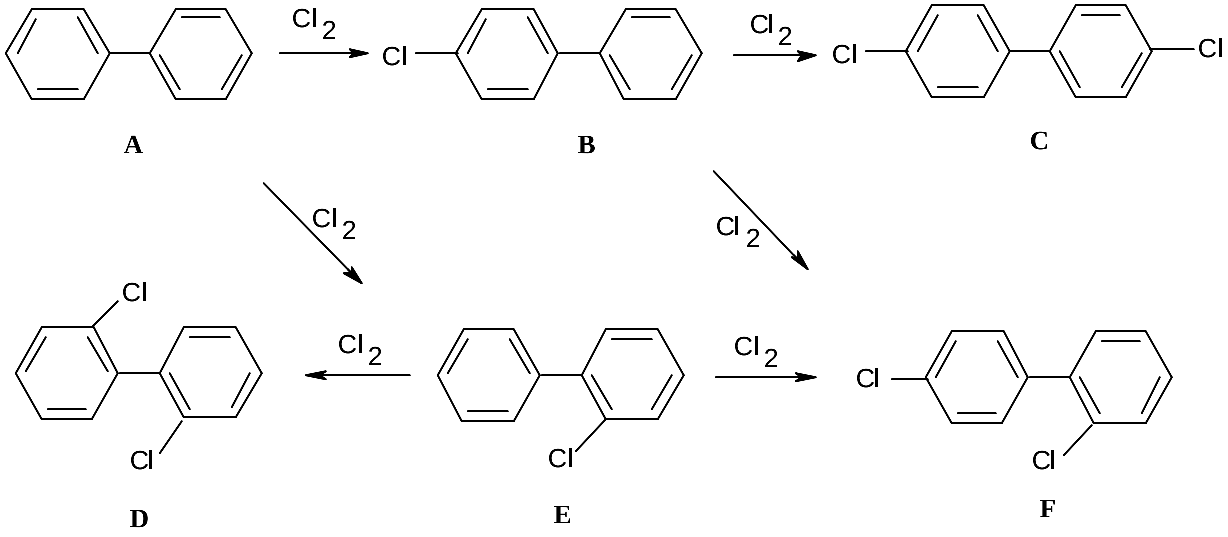

Figure 1.1. Chlorination of biphenyl with Cl_2: Reaction Scheme (Ref. 162)

Botta et al. performed the chlorinations with acidic and metal-exchanged zeolites of various structure and pore diameters. The reactions were carried out in both the molten state and various solvents (Table 1.4 and Table 1.5, respectively). It is obvious from the results of Table 1.4 that the conventional concept of geometry-related shape selectivity cannot be invoked to explain the variations in para selectivity; zeolites of similar pore diameter but of different structural types behave in different ways. The authors concluded[162] that the factors that actually direct the substitution are the ionic radius, charge and spatial arrangement of the exchanged cations and their force fields. It may be remarked from Table 1.4 that when monochloroacetic acid is added to the reaction mixture, the para selectivity is enhanced significantly (from 69.2 to 86.4%)

Table 1.4. Chlorination of molten biphenyl (ref. 162) with Cl_2

	Product Distribution (wt%)[a]							
Catalyst	A	B	C	D	E	F	Others	(B+C)
$FeCl_3$	1.0	6.4	9.1	13.2	15.4	23.7	31.2	15.5
Clay	0.1	4.0	26.5	7.4	18.1	31.8	12.1	30.5
Na-X	-	0.6	34.0	8.3	11.8	34.9	10.4	34.6
k-Omega	-	1.2	47.0	3.2	16.5	25.5	6.6	48.2
H-mordenite	-	3.1	45.0	2.4	13.4	27.6	8.5	48.1
H-L	-	2.9	45.	6.5	7.5	25.4	11.9	48.7
Na,K-L	-	8.8	60.3	1.1	12.2	12.6	5.0	69.1
K-L	-	2.7	66.5	2.2	5.0	16.8	6.8	69.2
K-L + $ClCH_2COOH$[b]	-	2.7	83.7	0.4	2.1	8.1	3.0	86.4

[a]: See Fig 1 for A-F
[b]: 13% based on K-L zeolite

Table 1.5. Chlorination with Cl_2 of biphenyl at 293K over zeolite L; Influence of solvent (ref. 162)[a]

Solvent	A	B	C	E	F	Others	(B+C)
CH_2Cl_2	-	3.0	89.0	1.9	4.9	1.2	92.0
$CHCl_3$	0.3	26.8	37.0	16.6	9.7	9.6	63.8
CCl_4	-	5.7	66.5	10.0	14.7	4.1	72.4
CH_3COOH[b]	2.7	31.9	13.0	28.9	8.8	14.7	44.9
$C_6H_5NO_2$[b]	-	19.2	29.5	18.1	4.4	28.8	48.6
$CH_3CHClCH_2Cl$	0.7	35.9	39.7	10.1	5.4	8.9	75.6
CCl_3CH_3	29.8	33.0	2.9	10.2	1.0	23.1	35.9

[a] See Fig 1 for A-F
[b] 313 K

The ability of aliphatic carboxylic acids or their salts in significantly enhancing para chlorination during chlorinations using K-L zeolites as catalysts had been claimed earlier by Ihara chemical industry[227] in the chlorination of various aromatic compounds using Cl_2 as the chlorinating agent. Aromatic carboxylic acids like benzoic acid do not possess this ability. In the chlorination of toluene, for example, the para isomer content amongst the monochlorotoluenes was about 50 % in the absence of any catalyst. When a conventional Lewis acid catalyst like $FeCl_3$, was used, the para selectivity varied between 50 and 60%. When the same reaction was carried out in the presence of K-L zeolite and monochloroacetic acid (about 1wt-% of zeolite), the para selectivity reached 74.2 wt. % at a toluene conversion of 98.3%. Other aliphatic carboxylic acids like acetic acid, propionic acid, chloropropionic acid, dichloroacetic acid, difluoroacetic acid etc or their metal salts also behave similarly in enhancing para selectivity. This effect was seen in the chlorination of aromatic substrates containing electron withdrawing substituents also. In the chlorination of chlorobenzene with Cl_2 using K-L zeolite as the catalyst and in the presence of dichloroacetic acid, the selectivity for para dichlorobenzene reached 92.7 % in contrast to 60-70% obtained with conventional Lewis acid catalysts. Similar para selectivity enhancement was observed in the chlorination of other aromatics containing electron-withdrawing groups like fluorobenzene or anisole.

In the chlorination of inactivated aromatics like benzene with Cl_2, the formation of addition products (rather than substitution products) is a significant feature[224]. If free radical intermediates are responsible for this, then the addition of free radical scavengers like O_2 should lead to enhanced selectivity of substituted products. Nakamura et al.[149] chlorinated benzene with Cl_2 using K-L zeolite in the liquid phase at 343 K in the presence of O_2. Both the degree of nuclear chlorination and para selectivity (amongst the dichlorobenzenes) was increased by the presence of O_2. This effect was seen both in the absence of solvents and in the presence of solvents like ethylene dichloride.

Singh et al.[190-193] have recently studied, in detail, the selective chlorination of toluene[190,191] naphthalene[192] and ortho, meta and para xylenes[193] with Cl_2 using zeolite catalysts in the liquid phase. Chlorotoluenes are used as intermediates in the pesticide, pharmaceutical, peroxide and other industries[228-245]. The major use of parachlorotoluene is in the manufacture of para chlorobenzotrifluoride, a key intermediate in the manufacture of dinitroaniline and diphenyl ether herbicides. In the presence of conventional homogeneous catalysts like $TiCl_4$, $SnCl_4$, WCl_6, $ZrCl_4$, $FeCl_3$ etc, the selectivity for para-chlorotoluene is rather poor Chlorination of toluene over various zeolite catalysts using Cl_2 is shown in Table 1.6[190]. Singh et al. found that the para selectivity decreased in the following order: K-L (with $ClCH_2COOH$) >> K-L (without $ClCH_2COOH$) >> H-K-L = K- Beta > K-Y > K-X = K-Mordenite = K-ZSM-5 > $FeCl_3$ > no catalyst.

Table 1. 6. Chlorination of toluene over various zeolites[a] (ref. 190)

Catalysts	Unconverted toluene (wt%)	Yield (wt%)[b]				p/o[c] isomer ratio
		PCT	OCT	BC	others	
K-ZSM-5	56.4	16.1	23.3	2.6	1.6	0.69
K-mordenite	57.3	15.2	21.9	3.9	1.7	0.69
K-X	60.0	11.0	16.0	11.1	1.9	0.69
K-Y	55.5	18.1	23.2	2.3	0.9	0.78
K-beta	55.5	20.4	23.6	0.5	-	0.86
K-L	55.0	33.5	10.1	1.4	-	3.32
K-L[d]	54.7	27.1	15.4	2.1	0.7	1.76
H.K-L	59.2	17.7	20.2	0.7	2.2	0.87
$FeCl_3$	55.9	11.7	23.9	5.6	2.9	0.49
None	51.5	0.5	1.2	45.0	1.8	0.42

[a] Reaction conditions: Catalyst = 5g/mol toluene: reaction temperature (K) = 353; $ClCH_2COOH$/catalyst (by weight) = 0.2; toluene = 0.32 mol; Cl_2 flow (mol)/h = 0.04

[b] PCT: para-chlorotoluene; OCT: ortho-chlorotoluene; BC: benzyl chloride; others: polychlorinated toluenes (di-, tri-, and tetrachlorotoluenes).

[c] p/o = PCT/OCT

[d] Reaction in the absence of $ClCH_2COOH$

The above order does not correlate, in any simple manner, with the pore width of zeolites confirming the results of earlier studies (Table 1.4) that the conventional concept of geometry-related shape selectivity alone cannot be invoked to explain the variation in para selectivity in chlorination reactions over zeolites. This crucial point is brought out in more detail in Table 1.7, which illustrates the major influence of solvents on the para selectivity in the liquid phase chlorination of toluene with Cl_2 over a single K-L zeolite[190]. The ratio of para to ortho isomer varies six fold (from 0.65 for $CHCl_3$ to 4.05 for $ClCH_2CH_2Cl$) at similar conversion levels and reaction conditions over the same catalyst and chlorinating agent.

Factors like the competitive adsorption, diffusion and counter diffusion of substrate vs. solvent and Cl_2 in the zeolite evidently play a major role in determining the selectivity. Para selectivity in liquid phase halogenations over zeolites cannot be predicted in a simple manner from the pore structure or the nature/ content of the exchanged cation, nor from, gas phase adsorption/diffusion studies.

Table 1.7. Solvent effect in the chlorination of toluene over K-L zeolite[a] (. ref. 190)

Solvents	Reaction temp (°C)	Unconverted toluene (wt%)	Yield (wt%)[b]				p/o ratio
			PCT	OCT	BC	Others	
CH_2Cl_2	40	48.0	21.6	21.5	8.6	0.3	1.00
$ClCH_2CH_2Cl$	80	48.5	39.3	9.7	1.6	0,9	4.05
$ClCH_2CH_2Cl$	40	53.8	18.1	22.0	0.4	5.7	0.82
$CHCl_3$	55	59.0	17.1	18.6	3.8	1.5	0.92
$CHCl_3$	40	52.9	14.7	22.6	3.6	6.2	0.65
CCl_4	70	56.3	32.4	10.1	0.8	0.4	3.21
CCl_4	40	51.4	19.2	21.2	7.8	0.4	0.90
No solvent[c]	80	55.0	33.5	10.1	1.4	-	3.32
No solvent[c]	40	55.4	17.4	16.5	8.0	2.7	1.05

[a] Reaction conditions; catalyst = 10g/mol toluene; $ClCH_2COOH$/catalyst (by weight) = 0.2 toluene = 0.16 mol; solvent = 15ml; Cl_2 flow (mol/h) = 0.04

[b,c] See footnotes to Table 1.6

[d] Reaction conditions are the same as those given in Table 1.6.

4-chloro ortho xylene is a desired industrial intermediate in the production of thermoplastics, pharmaceuticals and agrochemicals. Lewis acid catalysts, like $AlCl_3$, $FeCl_3$ and $SbCl_5$ produce a large amount of less valuable products like the 3-chloro isomer as well as the polychloro xylenes[246-249]. The results of the chlorinations of ortho xylene with Cl_2 in the liquid phase over various zeolite catalysts are shown in Table 1.8[193]. At comparable conversion levels, there is a ten-fold increase in the selectivity for the 4-chloro isomer over the K-L zeolite (4-Cl/3-Cl isomer ratio = 11.73 compared to 1.2 in the absence of catalyst). The authors found following decreasing order for the 4-Cl/3-Cl selectivity over various zeolite catalysts[193] K-L >> K-X > K-beta > K-Mordenite > K-ZSM-5 = silica gel > H-k-L > no catalyst > $FeCl_3$. This order is different from that seen earlier for the chlorination of toluene (Table 1.6) even though K-L zeolite is the most selective in both cases.

Table 1.8. Chlorination of o-xylene over various zeolites[a] (ref. 193)

				Prod.(wt%)				
Catalyst	SiO_2/ Al_2O_3	K^+ exch. (%)	o-xyl. (%)	4-Cl-ox	3-Cl-ox	2-MBC	others	4/3
No catalyst	-	-	61.6	13.2	10.7	5.2	9.3	1.2
Silica gel	-	-	65.2	19.7	13.8	0.2	11	1.43
$FeCl_3$	-	-	61.2	16.1	16.1	-	6.6	1.00
K-ZSM-5	41.0	96.0	63.3	20.3	14.1	0.3	2.0	1.44
K-Y	4.1	92.8	59.2	21.2	14.2	0.6	4.8	1.49
K-mordenite	22.0	89.8	57.7	24.5	15.8	0.3	1.7	1.55
K-beta	32.7	85.9	59.8	24.0	14.7	0.4	1.1	1.63
k-X	2.4	92.6	58.8	17.3	9.8	3.8	10.3	1.76
H-K-L	6.3	23.4	56.5	23.0	17.9	0.3	2.3	1.28
K-L	6.3	98.6	60.6	35.2	3.0	0.1	1.1	11.73

[a] Reaction conditions: catalyst = 21.2g/mol o-xylene; reaction temperature = 80°C; o-xylene = 0.08 mol; solvent ($ClCH_2CH_2Cl$) = 30ml; Cl_2 flow = 0.04 mol/h

[b] Degree of K^+-exchange (%) = 100 x moles of K/moles of Al

[c] 4-Cl-ox, 4-chloro-o-xylene; 3-Cl-ox, 3-chloro-o-xylene; 2-MBC, 2-methyl benzyl chloride; others, polychlorinated-o-xylenes (di-, tri-, and tetra-chloro-o-xylenes).

The influence of solvent and temperature in the chlorination of ortho xylene over K-L zeolite is shown in Table 1.9[193].

Table 1.9. Influence of solvent in the chlorination of o-xylene over K-L zeolites[a] (ref. 193)

	Product (wt%)						
Solvent	React. temp. (°C)	o-xyl.	4-Cl-OX	3-Cl-OX	2-MCB	others	4/3
$ClCH_2CH_2Cl$	80	60.6	35.2	3.0	0.1	1.1	11.73
$ClCH_2CH_2Cl$	40	58.3	2-6.7	10.3	0.2	4.5	2.59
$CHCl_3$	40	58.8	26.6	11.3	0.4	2.9	2.35
CCl_4	70	58.6	30.4	8.4	0.3	2.3	3.61
CCl_4	40	58.0	21.3	15.9	0.5	4.3	1.34
No Solvent[c]	80	56.8	24.5	12.1	5.3	1.3	2.02
No Solvent[c]	40	55.6	24.6	12.9	3.8	3.1	1.91

[a] Reaction conditions as in Table 1.10.

[b] Abbreviations as in Table 1.10.

[c] Reaction conditions: catalyst = 5.7g/mol o-xylene; o-xylene = 0.28 mol; Cl_2 flow = 0.04 mol/h.

The selectivities are compared at similar conversion levels. The 4-Cl/3-Cl isomer ratio increases twofold (1.34 to 2.59) when the solvent is changed from CCl_4 to $ClCH_2CH_2Cl$ at 313 K. However, a more dramatic five-fold increase in selectivity is seen when the temperature is increased to 353 K (2.59 to 11.73, Table 1.9) at the same conversion level. In other words, in addition to its effect on the rate of chlorination, temperature also affects the regioselectivity of chlorination, probably, through its influence on the solubility of Cl_2, the relative adsorption, diffusion/counter-diffusion of substrate/solvent molecules, etc. Negligible quantities of side chain chlorination products were seen in these reactions. A similar trend was also seen in the chlorination of meta- and para- xylenes.

The selective monochlorination of polynuclear aromatics, like naphthalene, with Cl_2 in the liquid phase, over zeolite catalysts has been reported by Singh and Kumar[192] (Table 1.10).

Table 1.10. Chlorination of naphthalene[a] (ref. 192)

					Prod. (wt%)		
Catalyst/	SiO_2/Al_2O_3	K^+exch.[b] (%)	Naph. Conv. %	1-CN	2-CN	PCN	1-CN + 2-CN
K-ZSM-5	41.0	96.0	32.1	76.3	5.6	18.1	81.9
K-L	6.3	98.6	27.9	87.6	7.6	4.8	95.2
K-beta	32.7	85.9	31.1	87.1	7.6	5.3	94.7
K-Y	4.1	92.8	26.6	76.8	6.1	17.1	82.9
K-X	2.4	92.6	30.5	62.6	4.7	32.7	67.3
$FeCl_3$	-	-	28.1	72.1	5.4	22.5	77.5
silica gel	-	-	35.0	75.1	3.5	21.4	78.6
no catalyst	-	-	30.3	49.3	7.0	43.7	56.3

[a] Reaction conditions: catalyst = 25.4g/mol naphthalene; reaction temperature = 80°C; naphthalene = 0.06 mole; solvent ($ClCH_2CH_2Cl$) = 30 ml; Cl_2 flow = 0.03 mol/h

[b] K^+ -exchange in zeolites (%) = 100 x moles of K/moles of Al.

[c] 1-CN = 1-chloronaphthalene; 2-CN = 2-chloronaphthalene; PCN = polychloronaphthalenes

Monochloronaphthalenes are used in dyes, fungicides, insecticides, wood preservatives and as ingredients in special cleansing agents. Lewis acid catalysts ($AlCl_3$, $FeCl_3$, $SbCl_5$) have traditionally been used producing 1-chloronaphthalene and large amounts of polychlorinated naphthalenes. The chlorination of molten naphthalene with molecular chlorine in the absence of any catalyst also results in the formation of a large amount of polychlorinated products. The use of $FeCl_3$ as a catalyst leads to a selectivity of about 75 % for monochloronaphthalene[250].

The results in Table 1.10 show that using zeolites like K-L or K-beta a selectivity for monochloronaphthalene up to 95 % (87 % of which consists of the 1-chloro isomer) can be achieved. The corresponding values for $FeCl_3$ are 77.5 and 72.1%, respectively. This is a significant yield/selectivity advantage over and above other process advantages like ease of catalyst separation, product recovery, absence of acid sludge disposal, handling of corrosive material, etc., when compared to the conventional processes using $FeCl_3$/$AlCl_3$/$SbCl_5$ catalysts.

Miteni (Italy), Ihara Chemicals (Japan) and Toray (Japan) utilize zeolite catalysts in the synthesis of monochlorotoluenes (Ihara)[174] and dichlorotoluenes (Miteni and Toray). The latter process involves chlorination, isomerisation and separation and includes recycle of unwanted isomers. In the isomerisation towards the equilibrium mixture, Toray researchers use[175,176]acid-type MFI zeolites for isomerisation of chlorotoluenes and dichlorobenzenes and mordenite for isomerisation of dichlorotoluenes.

More progress has been reported on the halogenation of aromatics over zeolite catalysts. Jang et al.[127] studied the vapour phase catalytic chlorination of chlorobenzene using various solid-acid catalysts such as silica-alumina, alumina, zeolites and modified clay (bentonite) impregnated with $FeCl_3$. The selectivity to dichlorobenzenes was higher over the zeolite catalysts.

1,2,4-Trichlorobenzene (1,2,4-TCB) is used as a dye carrier (via 2,4,5-trichloronitrobenzene) in the production of dyes. 1,2,4–TCB and 1,2,3-TCB (1,2,3-trichlorobenzene) were the primary products, while small amounts of tetra- and penta-chlorobenzenes arise from secondary consecutive reactions of trichlorobenzenes[251]. Zeolite K-L and K-beta exhibit comparable activity and selectivity. Further, the selectivity for 1,2,4-TCB is strongly enhanced by the addition of $ClCH_2COOH$ to K-L (1,2,4-TCB/1,2,3-TCB = 15.0). A similar effect was also reported earlier in the chlorination of biphenyl[162]. Compared to $FeCl_3$ catalyst (1,2,4-TCB/1,2,3-TCB = 2.1), all zeolite catalysts show higher selectivity for 1,2,4-TCB.

The liquid phase chlorination of para-chlorotoluene[186] (4-CT) over zeolites H.K-L, K-L, K-beta, K-mordenite, K-ZSM-5, K-Y, K-X and in the absence of the catalyst at 353 K produces a mixture of 2,3-dichlorotoluene (2,3-DCT), 2,4-dichlorotoluene (2,4-DCT) and the side-chain chlorinated product (α,4-DCT). Zeolites H.K-L, K-L and K-beta produce predominantly nuclear chlorinated products while K-ZSM-5, K-mordenite, K-Y and K-X exhibit mainly the side chain chlorinated product. The later was also the main product in the absence of zeolite. The highest yield of α,4-DCT was observed over the zeolite K-X. The results confirm that zeolite K-L is more active and selective than the other zeolites.

The oxychlorination and oxybromination, under near-ambient conditions, of benzene, toluene, phenol, aniline, anisole and resorcinol, using as catalysts the phthalocyanines of Cu, Fe and Co encapsulated in zeolites X and Y were reported by Raja and Ratnasamy[252]. Both H_2O_2 and O_2 were used as oxidants. HCl and alkali chlorides/bromides were used as sources of halogens. The metal phthalocyanines wherein the aromatic rings were substituted by –Cl or NO_2 groups were more active. There was a dramatic increase in specific activity when the complexes were encapsulated in the zeolites. The oxyhalogenation of both the aromatic nucleus and the alkyl side chain occurred. Oxidation of the aromatic ring (to phenols or cresols, for example) did not occur. Alkyl side chains, however, were oxidized by the oxidant H_2O_2 or O_2 to alcohols, ketones and acids. Halogen molecules, formed by oxidative liberation from the corresponding hydrogen or alkali halides, hydrogen peroxide, were presumably the halogenating agents.

1.4.3.2.3. other chlorinating agents:

Apart from Cl_2, other chlorinating agents like SO_2Cl_2[253-257], t-butyl hypochlorite [253], $PhICl_2$ in trifluoroacetic acid[258], alkyl and acyl hypochlorites[259], Cl_2O[260] and Nchloroamines[261-264], -amides and sulfonamides[265] have also been used to chlorinate aromatic substrates. Delaude et al.[253] have recently reviewed the chlorination of organic compounds using SO_2Cl_2 and t-butyl hypochlorite over solid catalysts. One advantage of sulphuryl chloride, especially in the lab, is that being a liquid, it is more easily handled than Cl_2. It is, however, less reactive than Cl_2 and reacts readily only with activated substrates such as phenols. At low temperatures, SO_2Cl_2 itself acts as an electrophile[254-257]. At higher temperatures it may decompose to SO_2 and Cl_2. The latter may, then be the true chlorinating agent.

Delaude and Laszlo[266] found that zeolites catalyze efficiently both the ring and side-chain aromatic chlorination by sulphuryl chloride. They demonstrated that while faujasites with significant BrÖnsted acidity favour nuclear chlorination by an electrophilic mechanism, the non-acidic Na-X favoured the free radical chlorination of the side chain. The latter is enhanced by the presence of light or a radical chain initiator. The side chain selectivity (in the chlorination of toluene, for example) stems from the greater stability and lifetime of benzyl as compared to phenyl radicals. The electrophilic ionic mechanism, on the other hand, will be favoured in polar solvents which facilitate the formation of ion-pairs, such as $Cl^+FeCl_4^-$ that are responsible for the regioselective chlorination. In an effort to achieve a clean, selective side chain chlorination of toluene avoiding ring chlorination, Delaude and Laszlo[266] found that aluminium-rich zeolites like Na-A, Na-X and Na-Y, gave very high (about 80%) yields of benzyl chloride. The yield of chlorotoluenes was negligible (0-0.3%). Photochemical irradiation and high temperatures enhanced the yield of benzyl chloride still further. Free radical traps like O_2, I_2 or benzoquinone suppressed the reaction thereby confirming that the side-chain halogenation, indeed, proceeded by a free radical mechanism. Among the small amount of chlorotoluenes, the ratio of ortho to para isomer was 58:42. The relative rates of chlorination of substituted toluenes followed the following decreasing sequence: p-

$CH_3C_6H_4CH_3$ > $C_6H_5CH_3$ > p-$ClC_6H_4CH_3$ > m-$CNC_6H_4CH_3$ > m-$ClC_6H_4CH_3$ > p-$CNC_6H_4CH_3$

Table 1.11. Chlorination of toluene by SO_2Cl_2 over Na-X - Influence of solvent (ref. 266)

Solvent	Yield %		ortho:para
	Side-chain	ring	
CH_2Cl_2	81	0	-
$CHCl_3$	78	0	-
CCl_4	74	0	-
C_6H_6	83	0	-
C_6H_5Cl	79	0	-
CS_2	70	0	-
CH_3NO_2	1	55	53:47
$C_6H_5NO_2$	3	35	54:46

Conditions: Reflux for 1 hr; toluene/SO_2Cl_2 = 2 (mol)

Nuclear chlorination of toluene vis-à-vis side chain chlorination can be favoured either by increasing the polarity of the solvent or the Brönsted acidity of the zeolite. In the chlorination of toluene with SO_2Cl_2 over NaX[266], it was found that the use of polar solvents like nitromethane or nitrobenzene dramatically increased the nuclear chlorination (Table 1.11). In the absence of any added solvent, exclusive side chain chlorination took place. Similarly, increasing the Brönsted acidity of the zeolite (exchanging the alkali cation for either H^+ or Fe^{3+}) enhanced[266] the nuclear chlorination (Table 1.12)

Table 1.12. Chlorination of toluene by SO_2Cl_2 over zeolite X - Influence of Brönsted acidity (ref. 266)

Catalyst	Yield %		ortho:para
	side-chain	ring	
NaX	80	0.2	59:41
HX	23	22	58:42
Fe(III)X	0.5	12	59:41

Conditions: Reflux for 30 min; toluene/SO_2Cl_2 = 4(mol); no solvent.

The use of *tert*-butyl hypochlorite as the chlorinating agent for para-selective chlorination of monosubstituted benzenes (C_6H_5R) in the presence of H-Na-X zeolites was reported by Smith et al in 1985[153] (Table 1.13). There is a distinct enhancement in para selectivity with the zeolite catalyst. Acetonitrile was found to be especially suitable as a solvent in chlorinations using *tert*-butyl hypochlorite as the chlorinating agent. The chlorination was most effective for alkyl-, phenyl and halobenzenes giving high para selectivity in all cases.

Table 1.13. Chlorination of C_6H_5R with t-butyl hypochlorite over H-Na-X. Comparison with homogeneous reaction (ref. 153)

R	Yield % (p+o)	para/ortho	Homogeneous[b] para/ortho/meta
CH_3	100	82/18	42/58/0
C_2H_5	100	90/10	48/52/0
i-C_3H_7	90	80/20	63/37/0
t-C_4H_9	99	98/2	76/22/2
C_6H_5	86	86/4	50/50/0
Cl	95	97/3	53/39/6
Br	75	97/3	55/42/6

a. Solvent for zeolite catalyzed reactions is acetonitrile

[b] Chlorination in the homogeneous phase was carried out with Cl_2/CH_3COOH.

Benzenes with deactivating substituents (for example benzonitrile, benzoic acid, methyl benzoate and nitrobenzene) could not be chlorinated even at elevated temperatures. Phenols reacted with t-butyl hypochlorite even in the absence of the zeolite. Hence no regioselectivity was observed. Similarly anisole was chlorinated in acetonitrile at the same rate whether in the presence or absence of a catalyst. However, in this case, considerable regioselective control was possible using H-Na-X in CCl_4 to give a para/ortho ratio of 82/18. When silica was used as the catalyst, the ratio was 70/30. One distinct advantage in using t-butyl hypochlorite as the chlorinating agent in the presence of zeolites is that, since no HCl is evolved as a by-product of the chlorination reaction, structural damage to the zeolite (due to the extraction of Al from the lattice framework positions) is minimal. That the chlorination reaction was occurring inside the pores of the zeolites was indicated by the fact that larger crystals of the zeolite produce higher selectivities (94% para in the chlorination of toluene) under otherwise comparable conditions[267]. The reaction mechanism probably involves t-butyl hypochlorite oxonium ions[268,269].

Photochlorination of n-alkanes adsorbed on pentasil zeolites using UV light (from a low pressure Hg lamp) as the chlorinating agent was investigated by Turro et al[269]. Very interestingly, the selectivity for the monochlorination of the terminal methyl groups was 20-fold greater in the presence of the zeolites compared to the selectivity observed when the same reaction is carried out in a homogeneous solution. This enhanced selectivity was found to be a function of the percent loading of the alkane on the zeolite, the zeolite's silicon to aluminum ratio, the percent conversion of the starting material and the water content of the zeolite.

1.4.3.3. Bromination using solid catalysts

The reactions of bromine and other brominating agents with organic compounds generally resemble those of chlorine[270, 271]. The differences are due to: (1) the larger size of bromine compared to chlorine leading to a greater influence of steric effects on product formation; (2) the greater ability of bromine to bear a positive charge; (3) the weaker C-Br bond (compared to C-Cl bond); molecular bromine is, hence, less reactive than Cl_2. De la Vega and Sasson272 had reviewed the literature on the bromination of aromatic compounds over zeolite catalysts upto 1988. Non-zeolitic catalysts (like ($FeCl_3$) exhibit a low para-selectivity[272]. By contrast, zeolites exhibit a much higher para-selectivity (Table 1.14, [ref.272])

Table 1.14. Bromination with Br_2 catalyzed by zeolites (ref. 272)

Zeolite	Substrate	Phase	para/ortho	Yield (%)
Fe-X	Toluene	liq.	4.1	21
Fe-X	C_6H_5Cl	liq.	33.0	58
Y	C_6H_6	gas	11.0	100
LZ-Y	C_6H_5Br	liq.	19.0	76
Ca-Y-82	C_6H_5Br	liq.	16.5	77
Ce-Y-89	C_6H_5Br	liq.	26	91

In 1966, Levina et al.[223, 273, 274] showed that bromination of benzene is catalyzed by Fe-containing zeolites. In 1974, Van Dijk et al[152] reported the liquid phase bromination of alkyl and halogenobenzenes with Br_2/CCl_4 using NaCaX and NaCaFeX zeolites.

Table 1.15. Bromination of halobenzenes with Br_2 over zeolite X (ref. 274) at 298 K

Substrate	Catalyst	Conv. (%)	p/o ratio
C_6H_5Cl	$FeCl_3$	89	7.0
C_6H_5Cl	Ca-X[a]	96	106.0
C_6H_5Cl	Fe-X[b]	58	33.0
C_6H_5Br	$FeCl_3$	96	3.8
C_6H_5Br	Ca-X[a]	91	80.0
C_6H_5Br	Ca-X[b]	59	11.0

[a] excess zeolite
[b] catalytic amounts of zeolite

When the aromatic compound was completely preadsorbed in the pores of the zeolite (excess zeolite) before contact with Br_2/CCl_4, high para/ortho ratios were observed. However, when using these zeolites in catalytic quantities, much lower conversions and para/ortho ratios were observed[274] (Table 1.15). In the bromination of alkylbenzenes in the presence of excess zeolite X, no side chain halogenation took place. The enhancement in para selectivity was diminished at higher temperatures.

Wortel et al.[203] studied the bromination, by Br_2, of halobenzenes at 298 K in the presence of Y-type zeolites, partially exchanged with di- and trivalent cations. Catalyst activity and para/ortho ratio depended upon the crystallinity of the zeolite, type of cation, the extent of cation exchange, the activation temperature, the solvent and the amount of catalyst used. In all cases, the para/ortho ratio was substantially higher than in the absence of catalysts or conventional catalysts like $FeCl_3$. Catalyst deactivation by HBr, liberated during the reaction, was suppressed by adding $NaHCO_3$ and zeolite K-A. The highest para/ortho ratios were obtained in a solvent-free system. The authors considered that the active sites were the BrÖnsted acid sites of the zeolite:

$$\text{Zeol-OH} + Br_2 \longrightarrow \text{Zeol-OBr} + HBr$$

The activities of different NaCaY zeolites could be correlated with their acidity, which was mainly of the Brönsted type. The order of reactivity decreased in the following order: toluene > benzene > fluorobenzene > chlorobenzene > bromobenzene. Both electronic and steric factors determine the rate of bromination. The larger size of bromine (compared to chlorine) leads to a lower extent of ortho substitution. In an elegant example of the shape selectivity of zeolites in the competitive addition of bromine (in CCl_4) to a straight chain and cyclic alkene (2-octene and cyclohexene, respectively), Smith[267] reported that, under conditions when the reaction occurs inside the pores of a zeolite, the linear dibromooctane was formed to the extent of 83%. Its concentration was only 35 % in the absence of the zeolite. An interesting feature of the results of Wortel et al.[203] is the catalyst deactivation by HBr, liberated during the reactions, and its suppression by addition of $NaHCO_3$ and zeolite K-A (Table 1.16). The former absorbs the HBr liberated (by conversion of HBr to NaBr) and the latter (K-A) by selectively absorbing the H_2O formed in the reaction of HBr with hydrogen carbonate. In the absence of the additives, there was a decrease in the activity and p/o selectivity of the zeolite catalysts both during the bromination reaction and on reuse.

Table 1.16. Bromination of bromobenzene by Br_2/CCl_4 over zeolite catalysts - Influence of $NaHCO_3$/K-A zeolite absorbants (ref. 203)

Catalyst	additive	Conv.after 5 hrs (%)	p/o ratio
Na-Y	none	12	14.0
Na-Y	$NaHCO_3$, KA	37	19.9
Na-X	none	<2	21.7
Na-X	$NaHCO_3$, KA	4	15.9
Ca-X	none	13	9.5
Ca-X	$NaHCO_3$,KA	38	13.2

Reactions at 298K; $C_6H_5Br/Br_2 = 0.67$ (mole)

In an attempt to find a better HBr scavenger without the formation of H_2O or solid salts, de la Vega and Sasson[275] found that propylene oxide addition dramatically improved the selectivity of Na-Y zeolite-catalyzed toluene bromination to yield almost pure p-bromotoluene (98 %). In the absence of propylene oxide the initial rate of bromination was approximately double but the para-selectivity was only 81 %. In more recent studies on the bromination of toluene in a bromine-propylene oxide-zeolite system[276-278] de la Vega et al. found that the selectivity to the para bromotoluene increases due to two factors: first, the propylene oxide deactivates the sites located on the external surface of the zeolite and second, a bromine-oxirane complex is formed that is less active and bulkier than bromine. The increased bulkiness of this complex leads to an increase in steric restriction within the zeolite, which favours the formation of the para isomer. A major disadvantage of the system was the rapid deactivation of the catalyst due to epoxide polymerization on the catalyst surface.

In addition to their influence on para/ortho selectivity, zeolites affect the rates of bromination also; de la Vega and Sasson[272] had compared the initial rates of bromination of toluene on various zeolites with that observed in the absence of zeolite. The conversion, yield and para/ortho isomer ratio levels were similar. Zeolites had a catalytic effect on the reaction, increasing the initial rates 3 to 20-fold times in comparison with the uncatalyzed reaction. For example, initial rates of bromination of toluene over Na-Y, LZY-52, 5A, Na-X and in the absence of any catalyst were 0.98, 0.37, 0.14, 0.32 and 0.05 (mol/min g $_{cat}$.) x 10^3, respectively. In addition to the structural type of the zeolite, the charge of the exchanged, non-framework cation also exerts an enormous influence on the rates of bromination (Table 1.17, ref.[272]). The initial rates are compared at similar conversion and yields. The concentration of benzyl bromide was also negligible. The increase in the initial rate on going from the monovalent (Na^+, Li^+) through the divalent (Cu^{2+}, Ca^{2+}, Co^{2+}) to the trivalent ions (La^{3+}, Fe^{3+}) is quite striking.

Table 1.17. Initial rates of bromination of toluene over Y-type zeolites - Influence of non-framework cation (ref. 272)

Zeolite	Cation charge	Na^+ Exchange (%)	Initial rates[a]			
			ortho	para	Total	p/o
Na-Y	1	-	0.34	0.64	0.98	1.88
Li-Na-Y	1	89.1	0.71	1.36	2.07	1.95
Cu-Na-Y	2	81.8	1.43	2.60	4.03	1.82
Ca-Na-Y	2	56.6	1.54	3.79	5.33	2.43
Co-Na-Y	2	45.4	2.03	3.47	5.50	1.72
La-Na-Y	3	51.9	6.50	18.9	25.4	2.91
Fe-Na-Y	3	53.7	9.20	14.7	23.9	1.59

[a] (mole/min/g cat.) x 10^3

H-beta is catalytically active in the bromination of chlorobenzene to the 4- and 2-bromo derivatives[279]. The solid catalyst is less active but more selective to the 4- bromo isomer than H_2SO_4. There was no conversion in the absence of the catalyst. The conversion of NBS, rate of NBS conversion and isomer ratio (4-BCB/2-BCB) over H-beta is 11.2 wt.%, 0.61 m mol $g^{-1}h^{-1}$ and 7.0, respectively.

The bromination of toluene with NBS over H-ZSM-5, H-mordenite, H-beta, H-Y, conventional catalyst H_2SO_4 and in the absence of any catalyst yield 2-bromotoluene, 4-bromotoluene and the side-chain product, α-bromotoluene[279]. Zeolite H-beta and H_2SO_4, produce predominantly the bromo aryl products while H-ZSM-5, H-mordenite and H-Y yield mainly the side-chain brominated product in the bromination of toluene. Zeolite H-beta is more para selective (para / ortho = 5.5) than other catalysts. The acidic H-Y gave a higher rate of N-bromosuccinimide conversion for the side-chain product. H_2SO_4 is found to be more active but less para selective than H-beta.

The bromination of xylenes (o-, m-, p-) with NBS over H-beta leads to nuclear as well as side-chain products whereas H_2SO_4 exclusively gave nuclear products. A higher yield of consecutive reaction products is also obtained over H_2SO_4. In the absence of any catalyst, only the side-chain products from the corresponding xylenes are obtained. The bromination of o-xylene over zeolite H-beta leads to the formation of 3-bromo-o-xylene (3-BOX), 4-bromo-o-xylene (4-BOX) and α-bromo-o-xylene (α BOX). With m-xylene the reaction gives 5-bromo-m-xylene (5-BMX). Similarly, bromination of p-xylene gave mainly a single monobrominated product, 2-bromo-p-xylene (2-BPX). Some amount of α- bromo-p-xylene is also detected in the bromination of p-xylene. The measured product ratio of 4-BOX/3-BOX and 4-BMX/2-BMX are found to be 5.14 and 2.73, respectively.

The selective para-bromination of phenyl acetate over the sodium forms of zeolites X and Y has, recently, been reported by Smith et al.[280]. The removal of the HBr formed by the sodium ions prevents the formation of phenol. Bases, acetic anhydride and some metal acetates also improve the selectivity.

1.4.3.4. Iodination using solid catalysts

Iodination by molecular iodine in the liquid phase occurs only with phenols and anilines due to the weak electrophilicity of iodine. However, in the presence of oxidizing agents, like nitric acid, H_2O_2 or peracetic acid, iodination of benzene, alkylbenzenes and even benzene rings with deactivating groups occurs readily. ICl is an additional popular iodination agent. Electrophiles like I^+ or I_3^+, formed " in-situ" are the probable iodinating species.

The concept of direct oxyiodination of benzene in the gas phase over zeolite 13-X was suggested in a Japanese patent[278]. Some typical results are shown in Tables 1.18 and 1.19. It may be noted that oxidation of benzene was negligible under the reaction conditions. Significant para selectivity is observed in the di-iodobenzene fraction. More importantly the catalytic activity was claimed to be stable for more than 800 h of continuous operation in the case of K-13X wherein more than 75% of the Na^+ has been replaced by K^+.

Table 1.18. Iodination of benzene over zeolites (ref. 212)[a]

Zeolite	Benzene conv.(%)	Products (wt%)			
			PhI_2		
		PhI	m	p	o
Li-X	79	60.7	16.7	17.7	4.9
Na-X	98	56.8	12.4	27.5	3.3
K-X	15	57.7	12.0	30.3	0
Cs-X	54	56.9	19.3	23.8	0
Mg-X	62	72.4	12.1	11.4	4.1
Ba-X	44	50.5	12.4	34.1	3.0
Na-Y	10	62.9	7.5	25.2	4.4

[a]Reaction conditions: O_2:benzene:HI_3 = 2.5:2.3:0.8 (molar); 345°C; GHSV = 1280hr^{-1}.
The concentration of CO_2 in the reaction effluent was negligible in all cases except Na-Y.

Surprisingly, the iodination of naphthalene (Table 1.19) occurred predominantly in the 2-position. Conventional iodination techniques in the liquid phase using I_2 and nitric acid or other strong oxidants preferentially produce iodination in the 1-position. The ability of the zeolite to iodinate the 2-position preferentially is of commercial significance in the manufacture of 2,6-naphthalenedicarboxylic acids or esters. The latter are used in the manufacture of polyesters with excellent barrier properties when fabricated into films, bottles or coatings.

Table 1.19. Iodination of naphthalene (ref. 212)[a]

Zeolite	Napht.conv. (%)	Products (wt%)				
		Mono-		Diiodo-		
		2-iodo	1-iodo	2,6	2,7	others
Li-X	8	30	70	0	0	0
Na-X	61	53.4	16.9	10.5	11.0	8.2
K-X	74	43.2	13.8	19.8	14.5	8.7
Rb-X	57	34.4	21.7	25.8	11.2	6.9
Cs-X	66	36.2	18.8	18.3	13.8	12.9
Ca-X	4	100	0	0	0	0
Mg-X	8	33.9	66.9	0	0	0
Ba-X	1	100	0	0	0	0
Sr-X	7	100	0	0	0	0
L	20	29.2	67.9	0.3	0.4	2.2

[a] Reaction conditions: O_2:Napht.:I_2 = 1.0:1.0:0.5 (molar)

It may be seen from Table 1.19 that zeolites like Rb-X possess a high selectivity for the 2,6-isomer amongst the di-iodonaphthalenes (about 70%). The concentration of CO_2 in the reaction effluent was negligible in all cases except Sr-X, Li-X and Ba-X.

The use of ICl in the iodination of aromatic compounds is illustrated in Table 1.20, ref.[281]. The iodination of toluene with ICl over various acidic and basic zeolites is accompanied to some extent by simultaneous chlorination[282-286]. The main products of the reaction are the para- and ortho isomers of iodotoluene and chlorotoluene. The absence of side-chain products (benzyl iodide and benzyl chloride) suggests that halogenation of toluene by ICl occurs by an electrophilic rather than a homolytic process. H-beta and H-.K-L zeolites are more para selective than other acidic or basic zeolites.

Table 1.20. Iodination of toluene with ICl over zeolite catalysts[a] (ref. 281)

Catalyst	ICl conv. (wt%)	Product (wt%)[b]					PIT/ OIT[c]	CT/IT[d]
		PCT	OCT	PIT	OIT	Others		
No catalyst	37.5	9.4	14.1	40.0	31.8	4.7	1.26	0.33
SiO_2[e]	56.5	10.6	18.6	38.1	28.3	4.4	1.35	0.43
H-ZSM-5	53.5	7.5	15.0	42.1	29.9	5.5	1.41	0.31
K-ZSM-5	63.0	8.7	15.9	37.3	30.0	8.1	1.24	0.40
H-mordenite	68.5	9.6	17.5	37.9	29.2	5.8	1.30	0.40
H-beta	51.5	6.9	10.7	59.6	20.7	2.1	2.88	0.22
H-beta[f]	97.5	4.4	8.8	47.9	36.8	2.1	1.30	0.15
K-beta	57.0	8.8	14.9	46.5	27.2	2.6	1.71	0.32
H-Y	41.5	8.4	13.3	49.4	24.1	4.8	2.05	0.30
K-Y	56.5	8.8	15.9	42.5	25.7	7.1	1.65	0.36
H.K-L	52.0	5.8	12.6	55.3	21.4	4.9	2.58	0.24
K-L	55.0	9.1	15.4	40.9	29.1	5.5	1.41	0.35
H_2SO_4	72.5	7.7	12.0	43.4	34.3	2.6	1.27	0.25

[a] Reaction conditions: Catalyst = 4.9g/mol toluene; reaction temperature(K) = 363; Toluene/ICl (molar ratio) = 5; toluene (mole) = 0.11; reaction time (h) = 0.25;

[b] PCT = para-chlorotoluene; OCT = ortho-chlorotoluene; PIT = para-iodotoluene; OIT = ortho-iodotoluene; others = dichloro- and diiodotoluenes;

[c] PIT/OIT = isomer ratio;

[d] CT/IT = ratio of chlorotoluenes/Iodotoluenes;

[e] fumed silica;

[f] Reaction conditions: Solvent (nitrobenzene) = 5ml; catalyst = 4.9g/mol toluene; reaction temp. (K) = 363; toluene/ICl (molar ratio) = 5; toluene (mole) = 0.055; reaction time (h) = 0.25.

1.5. Isomerization over acidic zeolites

Isomerization is a shift in the conjugation of the molecule without change in the number of atoms present. Commercial applications of isomerization generally reflect structure changes in order to create a molecule that is more reactive, has a higher performance level or has a more desirable property than the other isomers. The examples of major commercial isomerization reactions are[287]:

Feedstock	Product objectives
Aromatic isomerization	
Xylene isomerisation	Modify natural distribution to meet market demands
Paraffin isomerization	
C_4 paraffins	Tertiary carbon which is more reactive
C_5 / C_6 paraffins	High octane motor fuel

In isomerisation reaction of aliphatic compounds a distinction must be drawn between rearrangement of carbon skeleton, in which C-C single bonds are broken and formed, and double bond isomerization reactions, in which the carbon skeleton remains unchanged. The shape selectivity of the zeolites is intended to cause the reactions to take the desired path.

Isomerization may also occur as part of a complex reaction mechanism (such as naphtha reforming) and can be used to control the ultimate product distribution. There are many other examples of isomerization in the specialty chemical production and in the pharmaceutical industry such as iosmerization of dichlorobenzenes, dichlorotoluenes and chlorotoluenes etc.

Zeolites have a substantial potential for the catalysis of isomerization reactions. In some industrial isomerization processes relatively large quantities of non-regenerable, liquid acid catalysts ($AlCl_3$, H_2SO_4) are used which can be replaced by zeolite catalysts leading to clean technology. In addition, the use of solid catalyst introduces many advantages such as possibility to perform the reaction at higher temperatures than with homogeneous acids, the reduction of corrosion and environmental problems and the possible regeneration of the catalyst.

1.5.1. Isomerization of chloroaromatics

1.5.1.1. Isomerization of dichlorobenzenes

Isomerization of dihalobenzenes is interesting for the production of the meta-isomer, which cannot be obtained directly and thus the industrial processes follow more complicated procedures. For these reasons the attractive route could be the selective isomerization of o-dichlorobenzene (odcb) or p-dichlorobenzene (pdcb) to get the m-dichlorobenzene (mdcb). The iosmerization of odcb has claimed to occur readily on a series of acidic zeolites, preferably, faujasites, mordenites, ferrirites and other pentasil zeolites.

J. Pardillos, B. Coq, F. Figueras[288-290] have reported the gas phase isomerization of odcb over a number of acidic zeolite catalysts such as H-ZSM-5, H-beta, H-mordenite and H-offretite having a varied range of the aluminium content. It was observed that the initial activity of all these zeolites depends upon the silicon-to-aluminium ratio of the zeolite. A volcano-type relationship is observed between the activity of the zeolite and the Al-content of the zeolite i.e. whatever may be the zeolite, the activities go through a maximum value of Si/Al 10, as is generally observed for most of the acid catalyzed reactions. All the zeolites deactivate by coking and pore blocking, the extent of which depends upon the type of the zeolite. The selectivity of the reaction products depends, for the main part, upon the conversion level of odcb, according to the consecutive reaction scheme, as found in homogeneous $AlCl_3$-catalyzed reaction. However, coke deposition on H-mordenite and the size of the crystals for H-ZSM-5 enhances the yield of the final product, pdcb.

1.5.1.2. Isomerization of dichlorotoluenes

The direct chlorination of chlorotoluene gives 2,4- and 2,5-dichlorotoluenes as the main products, 2,6-, 2,3- and 2,4-dichlorotoluene isomers are present in low amounts and the 3,5- isomer is absent. The isomerization of these dichlorotoluenes is achieved over large pore zeolites such as beta, omega and mordenite in H-form at temperatures 300-350^0 C in hydrogen[291, 292]. In one process, 2,4-dichlorotoluene (2,4-DCT) was passed over an acid form of beta zeolite at 300^0 C for 4 h to give a product containing 4.72 %, 2,3-DCT, 2.18 % 2,6-DCT and 3.88 % 3,5-DCT[291]. In another process[292], a mixture of dichlororoluenes was passed over the acidic omega catalyst to increase the content of 2,3-DCT, 2,6-DCT and 3,5-DCT from 4.01, 1.00 and 0.00 %, respectively, to 4.25, 3.25 and 0.65, respectively. The gas phase iosmerization of 2,4-dichlorotoluene has also been reported over a Zr-containing pentasil type of zeolite at a temperature of about 250-340^0 C range with hydrogen as the carrier gas[293].

1.5.1.3. Isomerization of chlorotoluenes

Chlorotoluene form an important intermediate for the synthesis of insecticides, pesticides, fungicide, etc. It is prepared, in general, by the chlorination of toluene, in which the ortho- and para-isomers are formed owing to the directing effect of the methyl group. Accordingly, when the meta-isomer (MCT) is required in large amounts, it is desirable to isomerize the o-chlorotoluene (OCT) or p-chlorotoluene (PCT).

Conventionally, iosmerization of halotoluenes have been shown to occur only in the presence of a strong acid catalyst such as HF-BF$_3$[294] and $AlCl_3$ in HCl[295] or with water promoted Al_2Cl_6[296]. However, these homogeneous acid catalysts are highly unstable, very much difficult to recover and are highly corrosive. Acidic zeolites such as proton-exchanged mordenites and Zr-containing pentasil type zeolites have been reported to be useful as catalysts for the iosmerization of chlorotoluenes.

Isomerization of o-chlorotoluene (OCT) with acidic zeolite H-mordenite[297] with the Si/Al ratio of 3.6 and the Na/Al ratio of 0.03, mixed with 10 % Al_2O_3, at 320^0 C, gave 25.1 % m-chlorotoluene (MCT). The catalytic activity of H-mordenite was appreciably enhanced by the treatment with CF_3Cl and other chlorofluorocarbons such as CF_2ClCF_2Cl, CF_2ClCF_3, in the vapour phase isomerization of OCT as well as MCT and PCT. Enlargement of the H-mordenite pore size on treatment with CF_3Cl and other chlorofluorocarbons may contribute to increasing the catalytic activity and then maintaining it[298].

The isomerization of OCT in the presence of H as the carrier gas[299], has been reported with Zr-containing pentasil type zeolite at 250-340^0 C; the reaction product after 20 h gave 15.3 % OCT, 82.2 % MCT and 12.1 % PCT along with 5.1 % toluene with a slow catalyst deactivation [293, 300].

1.6. Conclusions

There are significant environmental advantages in the use of solid catalysts during the manufacture of fine chemicals especially in para–selective nuclear halogenations and isomerizations of aromatics instead of the Lewis acid catalysts (e.g. $AlCl_3$ and $FeCl_3$) used at present. The use of zeolites in such cases leads to enhanced yields of the para isomer in case of halogenation and the required meta-isomer in the isomerization reaction thereby lowering the formation of byproducts and cost of separation. There is a need for a better understanding of the mechanism of halogenation over zeolite catalysts in the liquid phase. Compared to the wealth of information available on halogenation in the homogeneous, gaseous and liquid phases, our knowledge about the details of solid catalyzed halogenation is meagre. An additional prerequisite for the greater use of zeolites in such applications is the solution to the problem of physical and structural damage to the zeolite by the hydrogen halide liberated during halogenations using molecular halogens. The use of acid-resistant zeolites (like mordenite, L etc.) can in some circumstances lead to viable solutions. In view of the increasing general tendency in the chemical industry to replace corrosive and toxic homogeneous catalysts (like HF, H_2SO_4, $AlCl_3$ and $FeCl_3$) by solid catalysts, activity in this field is expected to grow in the coming years.

1.7. Objectives of the thesis

The use of the solid heterogenous catalysts, especially zeolites, in various halogenation reactions has been reviewed. The literature on the isomerization of chloro-aromatic compounds is also presented in brief. It should be noted that the product selectivity depends on many reaction parameters such as reaction temperature, reaction time, catalyst concentration, type of the solvent, halogenating agent in addition to the composition and structure of the zeolite catalyst. Even though, in general, zeolites are unstable in the presence of the halo-acids liberated during the halogenation, recent developments like the use of L-zeolite could lead to the industrial use of zeolites in halogenation reactions. Therefore, it could be of importance to carry out highly selective halogenation reactions over zeolites. Similarly, the isomerization of o-chlorotoluene, which is an industrially important reaction, for the production of m-chlorotoluene, could also be optimized for giving the highest activity and selectivity as well as for reducing the deactivation of the H-ZSM-5 catalyst.

The chemical industry in the present scenario is facing an increasing pressure to reduce its impact on the environment; looking forward to replace corrosive and toxic homogeneous catalysts by solid catalysts, which are more eco-friendly. Most of the industrial halogenations and isomerizations are, at present, performed in the presence of mineral acids or Lewis acid catalysts such as the halides of aluminium and iron. Such reactions often require large quantities of mineral or Lewis acid catalysts that are destroyed or diluted during the aqueous work-up procedures, leading to problems with equipment corrosion and to effluent streams that are difficult and expensive to treat. Furthermore, the reactions frequently use excess of reagents and are poorly selective producing undesired side-chain products resulting in the need for costly separation processes and wastage of valuable resources. The overall result is the excessive energy consumption, wastage of large quantities of materials and excessive impact on the environment. On the other hand, the use of solid catalysts like zeolites can avoid the above mentioned problems. Zeolites due to their shape selectivity, thermo stability, regenerability as well as ease of separation from the products and their non-corrosive and environmentally friendly nature, have been widely used in the field of petrochemistry. However, the use of zeolite catalysts in fine organic synthesis, particularly, in the halogenation and isomerization reactions of aromatics is limited.

Halogen-containing compounds constitute an important segment of fine and specialty chemicals. Chloro-compounds form a significant part of agrochemicals used as pesticides, insecticides, herbicides and weedicides. Bromo-compounds are used in the preparation of fireproofing or fire retarding/extinguishing chemicals whereas Iodo-aromatic compounds find their use in pharmaceutical industry especially in the thyroid gland therapies. The isomerization of chloro-aromatics is also an industrially important reaction producing the meta-isomer, which is difficult to obtain in the normal chlorination reactions. Thus, the large volume of application of these materials has prompted us to develop highly efficient shape-selective zeolite catalysts for making these valuable products.

Thus, the primary objective of the thesis is to compare the surface properties and catalytic activity of some medium and large pore zeolites (H-ZSM-5, K-L, K-beta, RE-Y and

H-beta) and their modified forms in some halogenation and isomerization reactions, thus, replacing the presently used hazardous, conventional, homogeneous catalysts such as $AlCl_3$, $FeCl_3$ and H_2SO_4.

Another objective of this work is to develop a selective solid catalyst for the production of some industrially useful chemicals such as 4-chlorobenzyl chloride, 4-chlorocumene, 4,4'-dichlorodiphenylmethane, 4-bromoethyl benzene, 4-iodochlorobenzene and m-chlorotoluene.

The next objective is to improve the selectivity for the desired product in the halogenation and isomerization reactions by the use of zeolites and to compare the effect of pore structure of different zeolites on the selectivity in the above reactions.

One more objective regarding the development of solid zeolite catalysts for the halogenation and isomerization of aromatics is to study the effect of following parameters on the conversion as well as the selectivity for the desired product in these reactions:

The type of the zeolite, Influence of solvent, Influence of reaction time, Influence of reaction temperature, Influence of catalyst concentration, Molar ratio of the reactants, Halogenating agent, Influence of SiO_2/Al_2O_3 ratio of the zeolite, TOS/catalyst deactivation and Catalyst recycling.

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Chapter 2

Experimental

2.1. Materials

The materials used in the synthesis of zeolites along with their purity are summarized in Table 2.1.

Table 2.1. Specification of the materials used in the synthesis

Reagent and source	Chemical formula	Purity
Sodium hydroxide, s.d. fine Chem. Ltd., India	$NaOH$	97 %
Potassium hydroxide, s.d.fine Chem. Ltd., India	KOH	85 %
Catapal B, Vista Chem., Oklahoma.	Al_2O_3	65 %
Fumed silica (for K-L synthesis) Bhavnagar, India.	SiO_2	95 %
Ammonium nitrate, LOBA Chemie, India.	NH_4NO_3	98.5 %
Tetraethylammonium hydroxide, Aldrich Chem. Company, USA.	$(C_2H_5)_4NOH$	35 wt.% sol. in water
Fumed silica (for beta synthesis), Sigma Chem. Company, USA.	SiO_2	99.8 %
Aluminium sulphate, LOBA Chemie, India.	$Al_2(SO_4)_3$, $16H_2O$	98 %
Potassium nitrate, LOBA Chemie, India.	KNO_3	99 %
Sodium silicate	Na_2SiO_3	28.9 %
Sulfuric acid	H_2SO_4	98 %
Tetrapropyl ammonium bromide	$(CH_3CH_2CH_2)_4NBr$	98 %

Zeolite	Source
Na-X	Laporte Inorganics, Cheshire, UK.
Na-Y	Laporte Inorganics, Cheshire, UK.
Na-mordenite	Laporte Inorganics, Cheshire, UK.

2.2. Procedures

2.2.1. Synthesis of zeolites

Synhtesis of the zeolites was carried out in stainless steel autoclaves under hydrothermal conditions. Autoclaves were cleaned with aqueous hydrofluoric acid (40 wt.%) and polished with a carbon brush, prior to the synthesis. Typical synthesis procedures for the catalysts used in the study are presented below:

2.2.1.1. K-L and H.K-L

The synthesis of zeolite K-L was carried out according to the literature procedure[1]. In a typical procedure, 8.96 g of KOH and 1.55 g of Catapal B were taken in a 250 ml polypropylene beaker to which 20 ml warm, deionized water was added and the gel was stirred for half an hour. 12.44 g fumed silica in 15 ml warm deionized water was added gradually under stirring and the resulting gel was stirred for 1 h. The gel was then transferred in a stainless steel autoclave and subjected to hydrothermal treatment at 413 K. Full crystallinity was achieved in 64 h. The catalyst was then removed from the autoclave by filteration, washed with deionized water, dried at 383 K for 12 h and the resulting catalyst was then subjected to characterization.

H.K-L was prepared by conventional ion-exchange method in which 5 g of K-L was treated with 50 ml of 0.1 M aqueous solution of NH_4NO_3 at room temperature for 24 h. The resulting NH_4K-L sample was separated by filteration, washed with deionized water, dried at 373 K for 6 h and calcined at 773 K for 12 h.

Various HCl treated (dealuminated) K-L zeolites were prepared by treating fresh zeolite K-L (10 g each) with 100 ml aliquots of 0.05, 0.1, 0.3, 0.5, 0.7 molar aqueous solutions of HCl at room temperature with continuous stirring. The dealuminated zeolites thus obtained were further treated with 1 M KNO_3 solution to get their K-form.

2.2.1.2. K-beta and H-beta

In a typical synthesis[2], 0.5 g NaOH, 0.3 g KOH and 18.4 g tetraethyl ammonium hydroxide were taken in a 250 ml polypropylene beaker to which 6 g fumed silica and 10 ml water were gradually added and the gel was stirred for 1 h. 2.1 g aluminium sulphate in 15 ml deionized water was added to the gel over a period of half an hour after which the stirring was furhter continued for 1 more hour. 11 ml of deionized water was further added to the resulting gel. This final gel with a pH 12.5 was transferred into a stainless steel autoclave and subjected to hydrothermal treatment at 413 K. Full crystallinity was achieved in 7 days. The zeolite was then separated from the mother liquor, washed with deionized water, dried at 383 K for 12 h and calcined at 783 K for 16 h.

K-beta was prepared by three exchanges of the calcined beta sample with aqueous potassium nitrate solution (1 M; solid/solution (g/ml)= 1:10) for 8 h at 353 K.

H-beta was prepared by ion-exchange during which 5 g of calcined beta catalyst was treated with 50 ml of aqueous solution of 1 M NH_4NO_3 at 353 K. The process was repeated twice. The resulting NH_4-beta was separated by filteration, washed with deionized water, dried at 383 K for 12 h and calcined at 783 K for 16 h to get the H-form of beta.

2.2.1.3. K-ZSM-5 and H-ZSM-5

Zeolite ZSM-5 was synthesized as per the procedure described in the literature[3]. Appropriate amounts of aluminium sulphate and sulphuric acid were dissolved in distilled water to yield solution A. A calculated quantity of tetrapropyl ammonium bromide (TPABr) was added to a solution of sodium silicate of required strength to get a solution B. The solutions A and B were then mixed in a stainless steel autoclave with continuous stirring to form a free gel which had the molar composition as follows:

4.38 $(TPA)_2O$: 27.6 Na_2O : Al_2O_3 : 44.2 SiO_2 : 32.62 H_2O.

The autoclave was then tightly closed and kept at the desired temperature (453 K) under autogeneous pressure for about 24 h. The reactor was cooled, the contents were filtered, washed with deionized water, the catalyst dried at 393 K overnight. It was then calcined at 823 K for 8 h to decompose the organic template. Thus, Na-ZSM-5 was obtained.

The H-form of the sample was prepared by repeated exchange with 1 M NH_4NO_3 solution at 353 K to get NH_4-ZSM-5 which was then calcined at 823 K to get H-ZSM-5.

The K-form of the sample was prepared by three exchanges of the Na-form with aqueous KNO_3 solution (1 M; solid/solution (g/ml) = 1:10), for 8 h at 353 K.

2.2.1.4. K-X, K-Y, H-Y & RE-Y and K- mordenite

Na-X, Na-Y and H-mordenite were obtained from Laporte Inorganics, Cheshire, UK. They were converted into their respective K-forms by repeated (three times) exchange with aqueous 1 M solution of KNO_3 in which 5 g of the sample was treated with 50 ml of the solution at 353 K with stirring for 8 h, filtered and then dried at 423 K to get the catalysts K-X, K-Y and K-mordenite.

H-Y was prepared from Na-Y by the ion-exchange with 1 M aqueous solution of NH_4NO_3 thrice (1 M; solid/solution (g/ml) = 1:10, 8 h) and the resulting sample was then calcined at 773 K for 12 h to get the H-form.

RE-Y was prepared from Na-Y by exchange with 1 M NH_4NO_3 (three exchanges, 353 K, 8 h) and thus the resulting NH_4-Y was treated with 5 % rare earth nitrate solution followed by the analogous procedure employed for NH_4-Y exchange.

2.2.2. Catalyst Characterization

2.2.2.1. Chemical analysis

A known weight of the sample was placed in a platinum crucible, covered with a lid and heated over a Mekker burner. The crucible was then kept in a desiccator for cooling. The anhydrous weight of the sample was noted and this procedure was repeated until a constant weight was obtained. This residue was then dissolved in 10 ml hydrofluoric acid (40 wt.%) and evaporated. This procedure was repeated to ensure that all the SiO_2 has been evaporated as H_2SiF_6. The remaining part of the sample was heated again and the weight of the sample was noted after cooling it in a desiccator. The difference between the weight of the residue and the original weight (weight after initial heating) yielded the weight of SiO_2 in the sample. The residue was then dissolved in 1:1 HCl till a clear liquid was formed and this solution was diluted to a known volume by adding doubly distilled water. Chemical analysis of this solution was then performed by Atomic Absorption Spectroscopy (Hitachi, model Z-8000) to estimate other components.

2.2.2.2. Powder X-ray Diffraction (XRD)

The catalyst samples were analyzed by XRD for phase identification. The XRD patterns of the samples were recorded using a computer automated diffractometer (Model D-Max III VC, Rigaku, Japan) using Ni-filtered CuKα radiation (λ = 1.5404 Å). The samples were equilibrated over a saturated $CaCl_2$ solution at room temperature for 6 h prior to the measurement. The samples were then packed on glass sample holders. Data were collected in the 2 θ range of 5 to 40 ^{0} with a step size of 0.02^0 and a step time of 10 s with continuous rotation of the sample during the scan. Silicon was used as an internal standard to calibrate X-ray line positions.

2.2.2.3. Scanning Electron Microscopy

The morphology and crystal size of the samples was studied using a scanning electron microscope (JEOL, Stereoscan 440). The samples were slurried with ethanol and deposited as a thin film over a brass sample holder. All the samples were sputtered with Au before conducting the SEM analysis to avoid surface charging of the sample in the electron beam.

2.2.2.4. Surface area measurement

A commercial adsorption apparatus Omnisorb 100 CX, (Coulter Corporation, USA) was used for measuring the BET surface area of the samples. The sample was evacuated at 673 K for 2 h under high vacuum (10^{-6} mm). The anhydrous weight of the sample was measured. The sample was then cooled to 94 K using liquid nitrogen and then allowed to adsorb nitrogen gas. Surface area of the sample was calculated by using BET method. The general form of the BET equation may be written as follows:

$1/V_{ads}(P_0-P) = 1/V_mC + [C-1/V_mC]\ P/P_0$ ------------- {eq. 1}

Where,

V_{ads} = volume of the gas adsorbed at pressure P,

P_0 = saturated vapour pressure,

V_m = volume of the gas adsorbed for monolayer coverage,

C = BET constant

By plotting left side of equation 1 against P/P_0, a straight line is obtained with a slope of C-1/V_mC and an intercept 1/V_mC. The BET surface area is calculated using the formula

$S_{BET} = X_M.N.A_M.10^{-20}$

Where, N is the Avagadro's number, A_M is the cross-sectional area of the adsorbate molecule (N_2, 16.2 Å^2) and X_M is the moles of N_2 adsorbed.

2.2.2.5. X-ray fluorescence Spectroscopy (XRF)

Silica to alumina ratios and other metals (Na^+, K^+ etc.) of the zeolite samples were verified by XRF using a wavelength dispersive X-ray spectrometer (Rigaku, 3070) with rhodium target energized at 45 KV and 40 MA. The borate fusion technique was applied for sample preparation. For the calibration of silica and alumina, a penta erythrital (PET) crystal was used. For the analysis $K\alpha$ lines were selected and pulses were collected for 40 s using flow-proportional detector. A background correction was applied.

2.2.2.6. Acidity measurement

The acidity and the acid strength distribution of the zeolites were measured by the temperature programmed desorption (TPD) of ammonia on a fixed bed flow type apparatus attached to a HCl solution trap (4,5,6). Approximately 1.0 g of the sample was activated in flowing N_2 at 773 K for 4 h, and then ammonia was passed over the sample at 303 K for 30 min. The sample was subsequently kept in the flow of N_2 (50 ml/min) at 303 K for 15 h in order to eliminate the physisorbed ammonia. Acid-strength distribution and NH_3 chemisorbed at 303 K were obtained by raising the temperature with a ramping rate of 10^0 C /min, from 303 to 773 K in a number of steps in the flow of nitrogen (10 ml/min). The NH_3 evolved was trapped in HCl solution and titrated with a standard NaOH solution.

2.2.2.7. Catalytic reactions

The liquid phase catalytic halogenation of aromatics was performed at atmospheric pressure in a glass reactor equipped with a magnetic stirrer and a reflux condenser kept in a thermostat at the required reaction temperature. The aromatic substrate, activated catalyst, solvent if used and the halogenating agent were introduced into the reactor in the order mentioned. The mixture was then stirred and heated to attain the required reaction temperature. Samples were taken periodically from the reaction mixture by a syringe for the product analysis.

The vapour phase isomerization of o-chlorotoluene (OCT) was carried out in a fixed bed reactor with a continuous flow system under atmospheric pressure. The zeolite catalyst (0.2-0.3 mm size range) was packed in a glass reactor (1.4 I.D.) along with inert ceramic material for support and placed in a vertical furnace. Prior to the reaction, the catalyst was activated in a flow of air at 773 K for 12 h. The catalyst temperature was then brought down to the required reaction temperature and allowed to stabilize in a flow of nitrogen gas (10 ml/min) for at least 30 min. The reaction was started by passing the feed (OCT or OCT + diluent) through the catalytic bed by a syringe pump with a required feed rate. The product mixture was condensed at the reactor outlet and the samples were collected at different time intervals.

The reaction products were analyzed by a gas-chromatograph (HP 6890 GC) equipped with a FID and a Capillary column (50m x 200µm x 0.33 µm) with phenyl methoxy silicone gum. The authentic samples as well as the GCMS (Shimadzu, QP 2000 A) analyses confirmed the products of the reaction.

2.2.3. Results and Discussions

The X-ray diffraction pattern of all the synthesized as well as modified zeolites matched with those in the literature. In addition, the crystallinity and phase purity of the zeolite samples as well as the absence of any amorphous matter within the pore structure were confirmed by XRD. Also, the XRD examination gave no evidence of structure damage or change (except for HCl treated zeolite K-L) of the zeolite as a result of various treatments. The surface area and scanning electron micrographs showed the absence of amorphous matter inside the channels and on the external surface of the zeolites, respectively. All the samples consisted of particles of about 0.2 – 1.0 μm size. The properties as well as chemical composition of the zeolites used in the present study as obtained by a combination of wet chemical analysis and atomic absorption spectroscopy (AAS) and X-ray fluorescence spectroscopy (XRF) are reported in Table 2.2.

Table 2.2. Physico-chemical properties of the zeolites

Zeolites	SiO_2/Al_2O_3 (molar ratio)	Cation composition (wt.%)[a]			Surface area[b] (m^2 / g)	Crystal size (μm)
		H^+	Na^+	K^+		
K-X	2.4	-	7.4	92.6	615	1.0
K-Y	4.1	-	7.2	92.8	606	1.0
K-mordenite	22.0	7.5	2.7	89.8	542	1.0
K-ZSM-5	41.0	2.5	1.4	96.1	410	0.5
K-beta	26.0	9.8	4.3	85.9	743	0.5
H(26.1)K-L[c]	6.8	26.1	-	73.9	221	0.2
K-L	6.8	-	1.4	98.6	215	0.2

[a] Na^+ and K^+ ions were analyzed by XRF. H^+ was obtained by the difference between the Al content and the sum of the alkali metal values. Values are reported as percent of the total cation sites with Al content taken as 100%.

[b] Measured by N_2 adsorption.

[c] Value in parenthesis represent the percentage of H^+ in K-L.

The results of the stepwise thermal desorption of ammonia from the zeolites are presented in Table 2.3. The total amount of NH_3 desorbed at 303 K is also given in the same Table. The results reveal that the total acid sites and the site energy distribution are dependent on the type of the zeolite.

Table 2.3. Properties of acidic zeolites

Catalyst	SiO_2/ Al_2O_3 molar ratio	Degree of H^+ or RE^{+3} Exchange (%)	Crystal size (μm)	Surface area[a] (m^2/g)	NH_3 desorbed (mmol/g) at different temp (K)					NH_3 chemis -orbed
					303-353	353-433	433-513	513-653	653-773	
H-ZSM-5	41.0	>98	0.4	413	0.55	0.16	0.05	0.26	0.21	1.23
H-mord.	22.0	>98	1.0	552	0.20	0.17	0.15	0.12	0.07	0.71
H-beta	26.0	>98.7	0.5	745	0.14	0.24	0.05	0.16	0.16	0.75
H-RE (70.6)Y[b]	4.1	>70.6	1.0	659	0.17	0.10	0.26	0.11	0.10	0.74

[a] N_2 adsorption

[b] The percentage of RE^{3+} exchange in H-Y is given in the parenthesis.

2.3. References

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Chapter 3

Halogenation over Zeolites

3.1. Chlorination

Chlorination reactions of aromatic compounds are industrially important reactions producing a variety of valuable chemicals. The uses of chlorinated products are numerous. Many chlorinated aromatics are excellent insecticides, herbicides and fungicides. Perhaps, the most important use of chloro-compounds is its function as a raw material for hundreds of other useful chemicals.

Conventionally, these industrial chlorinations are carried out by using homogeneous Lewis acid catalysts such as $AlCl_3$, $FeCl_3$, $SbCl_3$, $MnCl_2$, $SnCl_4$ and $TiCl_4$ in the presence of a halogenating agent. But there are certain disadvantages associated with these catalysts such as: requirement of stoichiometric amount of the catalyst, the formation of polychlorinated products in substantial amounts, lower regioselectivity and difficulty in separation of the catalyst from the final product. Therefore, the need is to develop a new solid catalyst for the selective chlorination of aromatics. The use of a heterogeneous catalyst in liquid phase offers several advantages over the homogeneous ones, such as ease of recovery, enhanced selectivity and stability, recycling of the catalyst and environmentally friendly nature. Zeolites are well-defined microporous crystalline materials and, because of their large diversity of composition and structure, can display outstanding catalytic properties. They are widely used as selective catalysts, particularly in the field of petrochemistry[1,2]. Zeolite catalysts are also known to catalyze many organic synthesis reactions much more efficiently and selectively than the Lewis acid catalysts. However, few reports are available on the selective chlorination of aromatics using zeolites [3-20]. With this in mind, the catalytic liquid phase chlorination of different aromatics such as benzyl chloride, cumene and diphenylmethane was investigated over a number of zeolite catalysts for producing industrially important chemicals.

3.1.1. Selective chlorination of benzyl chloride to 4-chlorobenzyl chloride.

3.1.1.1. Introduction

4-Chlorobenzyl chloride (4-ClBC) is an intermediate in the manufacture of rice herbicide, 'Saturn' ((S-4-chlorobenzyl) N, N-diethylthiol carbamate)[21,22]. The ring chlorinated benzyl chloride (BC) is also used in the preparation of quaternary ammonium salts and as intermediate for pharmaceuticals and pesticides[22]. Conventionally, the 4-chlorobenzyl chloride is produced by the direct side chain chlorination of para-chlorotoluene (PCT). Further, in the presence of an iodine catalyst, chlorination of benzyl chloride yields a mixture consisting mostly of the 2-chloro-and 4-chlorobenzyl chlorides (2-ClBC and 4-ClBC) in equal amounts[22]. With strong Lewis acid catalysts such as ferric chloride, chlorination is accompanied by self-condensation[22]. Industrially, these reported methods for the production of 4-ClBC are not attractive owing to the use of expensive PCT and lower regioselectivity of iodine catalyst. In view of the above, it was of interest to develop a new solid catalyst for the selective synthesis of 4-chlorobenzyl chloride. The aim of the present work is to enhance the yield of 4-ClBC and to reduce the formation of side- chain and consecutive products in the chlorination of BC over zeolite catalysts. We report herein, for the first time, a catalytic method for the regioselective chlorination of BC to 4-ClBC under mild reaction conditions using zeolites as catalyst and chlorine gas as the chlorinating agent. The effect of solvent, catalyst concentration, reaction temperature, reaction time, SiO_2/Al_2O_3 ratio of zeolite K-L (obtained by HCl treatment), catalyst recycling etc. is also investigated on the conversion of BC, product yields and the selectivity for 4-chlrobenzyl chloride (4-ClBC/2-ClBC isomer ratio).

3.1.1.2. Experimental

(a) Catalyst preparation and characterization

The zeolites used, their synthesis, modification and physico-chemical characterization have already been reported in Chapter 2. Some important properties of these zeolites are listed in Chapter 2, Table 2.2.

(b) Catalytic reaction experiment

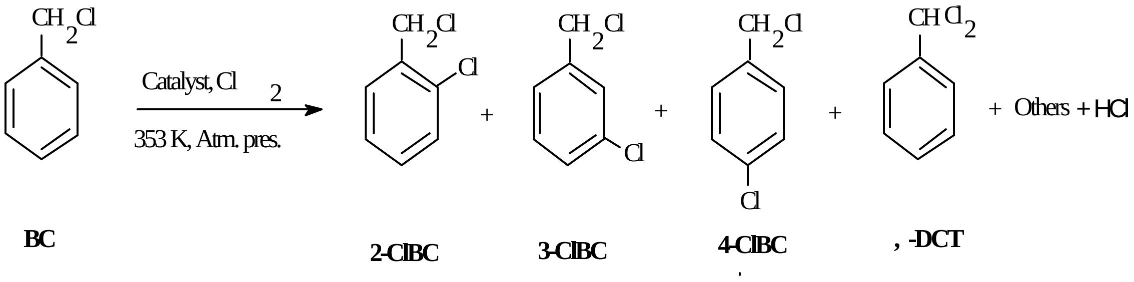
The catalytic runs were carried out batch wise in a mechanically stirred, closed 100 ml glass reactor fitted with a reflux condenser, a thermometer, a N_2/Cl_2 gas-line and a septum for withdrawing the samples. In a typical run, an amount of benzyl chloride (0.158 mol in the neat chlorination and 0.08 mol in the presence of 10 ml solvent) was charged in the reactor along with the appropriate amount of activated catalyst. The reaction mixture was heated to the required temperature under stirring in the presence of N_2 (20 ml/min) for 30 min. Then N_2 gas was stopped and the reaction was started by passing Cl_2 gas (0.09 mol/h). Aliquots were removed at various time intervals, filtered, neutralized with $NaHCO_3$ and analyzed by gas- chromatograph (Blue-star Model 421, equipped with a flame ionization detector and a capillary column, (50 m x 0.2 mm with methyl silicone gum). Products were identified by GC-MS and with reference to standard samples.

The conversion is defined as the percentage of BC transformed. The rate of BC conversion (mmol g^{-1} h^{-1}) was calculated as the amount of BC (mmol) converted per h over per g of the catalyst. The yield percentage of a product represents the amount of the product calculated from the selectivity multiplied by the conversion.

3.1.1.3. Results and discussion

3.1.1.3.1 Influence of various catalysts

Table 3.1 compares the rate of benzyl chloride conversion, product yields and the ratio of 4-ClBC/2-ClBC over various zeolites such as H(26.1)K-L, K-L, K-beta, K-mordenite, K-ZSM-5, K-Y, K-X and in the absence of catalyst in the chlorination of benzyl chloride at 353 K under similar reaction conditions. The reaction produces a mixture of 2-chlorobenzyl chloride (2-ClBC), 3-chlorobenzyl chloride (3-ClBC), 4-chlorobenzyl chloride (4-ClBC) and side chain chlorinated product, α,α-dichlorotoluene (α,α-DCT). The small percentage of consecutive products (others) is also detected (Scheme 3.1).



Scheme 3.1

The formation of mono-chlorobenzyl chlorides takes place by parallel reaction while di- and tri-chlorobenzyl chlorides are obtained by consecutive reactions of the mono-chlorobenzyl chlorides[14,23]. The most interesting feature of the reaction is that the rate of benzyl chloride conversion, product yields and the 4-ClBC/2-ClBC ratio depend on the type of zeolite used.

As can be seen from the Table 3.1, zeolites H(26.1)K-L, K-L and K-beta produce predominantly nuclear chlorinated products while the blank experiment (without catalyst), zeolites K-ZSM-5, K-mordenite, K-Y and K-X exhibit mainly the side chain chlorinated product in the chlorination of benzyl chloride. The highest yield of α,α-DCT was observed over the zeolite K-X (Table 3.1) which is in agreement with the previous literature and may be ascribed to the lower SiO_2/Al_2O_3 ratio than the other zeolites[6,15]. In addition, side chain chlorination of BC in the absence of any catalyst and poorly dark reaction conditions may be attributed to the photochlorination (by the free radical mechanism) of -CH_2Cl group of benzyl chloride[6,24].

Table 3.1. Chlorination of benzyl chloride [a]

Catalyst	Reaction time (h)	BC conv. (wt.%)	Conv. rate[b] (mmol $g^{-1}h^{-1}$)	Product yields (wt. %)[c]					4-/2-[d] ratio
				A	B	C	D	E	
K-ZSM-5	1	11.3	37.2	0.5	0.1	0.5	9.4	0.8	1.0
	3	35.2	-	1.0	0.3	1.0	32.5	0.4	1.0
K-mordenite	1	11..3	37.5	0.5	0.1	0.5	10.2	0.1	1.0
	3	46.5	-	0.8	0.2	0.7	44.0	0.8	0.9
None	1	15.1	-	-	-	-	15.1	-	-
	3	41.7	-	-	1.3	0.2	40.2	-	-
K-X	1	15.2	50.0	0.1	0.0	0.0	14.6	0.5	-
	3	61.3	-	0.2	0.0	0.1	59.1	1.9	-
K-Y	1	14.4	47.4	0.3	0.1	0.3	13.6	0.1	1.0
	3	48.1	-	0.8	0.1	0.5	46.0	0.7	0.62
K-beta	1	14.3	47.1	3.5	1.1	7.8	1.7	0.2	2.20
	3	34.4	-	7.1	2.1	13.5	11.2	0.5	1.90
H(26.1)K-L[e]	1	29.9	98.4	6.8	3.5	15.5	4.1	-	2.30
	3	70.1	-	10.5	4.5	37.2	14.1	3.8	3.54
K-L	1	23.2	76.4	3.3	1.4	12.2	5.9	0.4	3.70
	3	55.7	-	6.6	2.7	23.3	21.5	1.6	3.53

[a] Reaction Conditions: Catalyst = 3 g/mol of BC; Reaction temperature = 353 K; BC = 0.158 mol; Cl_2 flow = 0.09 mol/h; Reaction time = 3 h.

[b] Rate of BC conversion in mmol$g^{-1}h^{-1}$ is expressed as, amount of BC converted/ weight of the catalyst x reaction time (h).

[c] A= 2-chlorobenzyl chloride; B = 3-chlorobenzyl chloride; C = 4-chlorobenzyl chloride; D = α,α-dichlorotoluene;E.= di- and trichlorobenzyl chlorides.

[d] Isomer ratio of 4-ClBC/2-ClBC.

[e] Value in parenthesis represent the percentage of H^+ in K-L.

The results demonstrate that zeolite K-L is more active and highly selective and both, the rate of benzyl chloride conversion (76.4 mmol$g^{-1}h^{-1}$) and the isomer ratio (4-

ClBC/2-ClBC= 3.7) are found to be far superior over K-L compared to the other zeolites except H(26.1)K-L after one hour of reaction time. The acidic H(26.1)K-L gave higher rate of BC conversion (98.4 mmolg^{-1}h^{-1}) and lower amount of the side chain chlorinated product (α,α-DCT)[6] compared to the K-L (Table 3.1).

3.1.1.3.2. Influence of duration of the run on the conversion of BC over various catalysts

The effect of duration of run on the performance of various catalysts, under identical reaction conditions in the chlorination of BC is also tested. Increasing reaction time increased the conversion of BC over all catalysts (Figure 3.1).

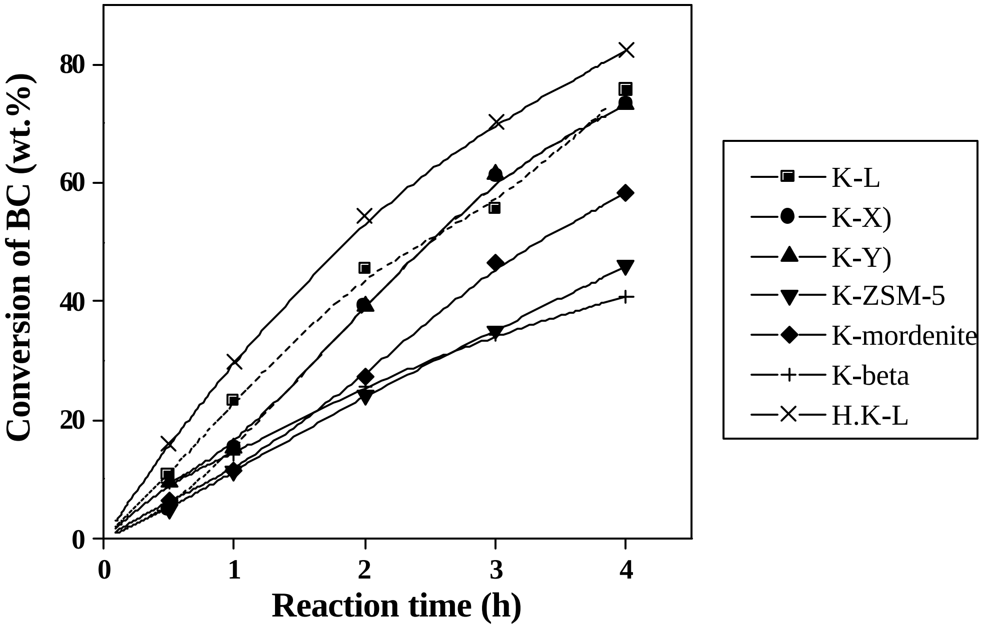


Figure 3.1. Conversion of BC over zeolite catalysts versus reaction time: reaction conditions: catalyst = 3.0 g/mol BC, BC = 0.158 mol, reaction temperature = 353 K, Cl_2 flow rate = 0.09 mol/h.

H(26.1)K-L yielded a considerably superior performance through out the reaction and its activity is found to be higher compared with other zeolite catalysts. The reason could be the higher acidity of H(26.1)K-L[6,15]. The activity order of various zeolite catalysts after 3 h of reaction time is as follows: H(26.1)K-L > K-L > K-X > K-Y > K-mordenite > K-ZSM-5 > K-beta

3.1.1.3.3. Influence of reaction time using zeolite K-L

A typical reaction course according to the time is pointed out in Figure 3.2 for the transformation of BC over zeolite K-L at 353 K.

The conversion of BC increased almost linearly with the reaction time. BC leads mainly to ring (4-ClBC, 2-ClBC) and side-chain (a,a-DCT) chlorinated products. Trace amounts of 3-ClBC and others (consecutive products) are also observed in the reaction. The results show that the reaction time influenced the conversion of BC, but did not affect the 4-ClBC/2-ClBC ratio to a greater extent.

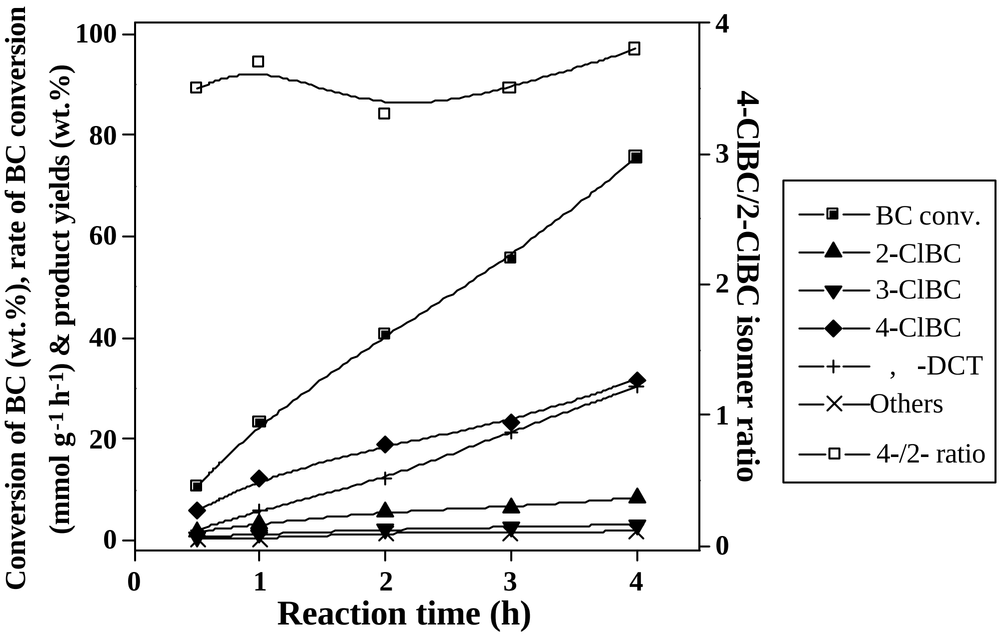


Figure 3.2. **Effect of reaction time on the conversion of BC, rate of BC conversion and product yields: reaction conditions: catalyst (K-L) = 3.0 g / mol BC, BC = 0.158 mol, reaction temperature = 353 K, Cl_2 flow rate = 0.09 mol/h.**

3.1.1.3.4. Influence of solvent

The course of the liquid phase chlorination of aromatics over zeolite catalysts is greatly affected by the type of the solvent used in the reaction[4,8,15,23]. The rate of benzyl chloride conversion (mmolg^{-1}h^{-1}), product yields and the isomer ratio of 4-ClBC/2-ClBC obtained in the chlorination of benzyl chloride using zeolite K-L in 1,2-dichloroethane (EDC), chloroform, carbon tetrachloride and in the absence of any solvent are shown in Table 3.2.

Table 3.2. Solvent effect in the chlorination of BC over zeolite K-L[a]

Solvent	Reaction Temp. (K)	BC conv. (wt.%)	Conv. rate[b] (mmol g^{-1}h^{-1})	Product yields (wt. %)[c]					4-/2-[d] ratio
				A	B	C	D	E	
EDC	313	13.4	13.2	1.4	0.3	3.1	6.6	2.0	2.21
EDC	353	52.6	51.9	5.7	3.5	41.1	1.8	0.5	7.21
$CHCl_3$	313	2.8	2.8	0.6	0.2	0.5	1.0	0.5	0.83
$CHCl_3$	333	9.2	9.1	1.1	-	5.6	2.2	0.3	5.09
CCl_4	313	6.8	6.7	1.8	-	1.5	3.5	-	0.83
CCl_4	348	23.2	22.9	4.7	1.3	13.3	3.9	-	2.82
No Sol[f]	313	14.8	48.7	3.0	0.6	8.4	2.1	0.7	2.80
No Sol[f]	353	23.2	76.4	3.3	1.4	12.2	5.9	0.4	3.69

[a] Reaction Conditions: Catalyst = 10.1 g/mol BC; BC = 0.08 mol; Cl_2 flow = 0.09 mol/h; Reaction time = 1 h; Solvent = 10 ml.
[b,c,d] see footnotes to Table 3.1.
[f] Reaction conditions similar as in Table 3.1.

Among the solvents used, the higher activity (rate of BC conversion) and selectivity (4-ClBC/2-ClBC) is observed in EDC. The rate of BC conversion and the 4-ClBC/ 2-ClBC isomer ratio at 313 K in the presence of 1,2-dichloroethane are found to be 13.2 mmolg^{-1}h^{-1} and 2.21 respectively. The use of other solvents ($CHCl_3$, CCl_4) has led to a lower selectivity for 4-ClBC and product yields when compared with EDC at similar reaction conditions at 313 K (Table 3.2.).The rate of BC conversion at 313 K decreases by changing the solvent in the following order: $ClCH_2CH_2Cl > CCl_4 > CHCl_3$

The over all trend of the isomer ratio (4-ClBC/2-ClBC) in these solvents at 313 K is found to be in the order: $ClCH_2CH_2Cl > CCl_4 \cong CHCl_3$

A significant enhancement in the rate of BC conversion and the 4-ClBC/ 2-ClBC isomer ratio is observed with the increase in the reaction temperature in the presence of all solvents. In addition, twofold increase in the 4-ClBC/ 2-ClBC isomer ratio is noticed when the reaction is performed in EDC instead of neat chlorination at 353 K (Table 3.2). When the temperature is raised from 313 to 353 K in the presence of EDC, the rate of BC conversion and the isomer ratio of 4-ClBC/ 2-ClBC increased. Side-chain chlorination of BC to α,α-DCT to some extent is observed to be dependent on the reaction solvent. The more selective reaction in 1,2-dichloroethane at 353 K is found to yield lower concentration of α,α-DCT at higher conversion level of BC, whereas a higher amount of α,α-DCT, is obtained at lower conversion level of BC in the neat chlorination at 353 K (Table 3.2).

3.1.1.3.5. Influence of catalyst concentration

In order to clarify the effect of catalyst concentration on the conversion of BC, product yields and the ratio of 4-ClBC/2-ClBC, the catalyst (K-L) concentration was increased from 3.0 g/mol of BC to 5.0 g/mol of BC (Figure 3.3).

The total surface area available for the reaction depends on the catalyst loading. The conversion of BC increased and the formation of a,a-DCT is decreased when 5.0 g catalyst per mol of BC is used in the reaction because of the increase in the number of basic sites available for the reaction. However, the change in the isomer ratio is not observed. In the absence of catalyst mainly the side-chain chlorinated product (a,a-DCT) is noticed. These results indicate that K-L catalyzes mainly the ring chlorination of benzyl chloride.

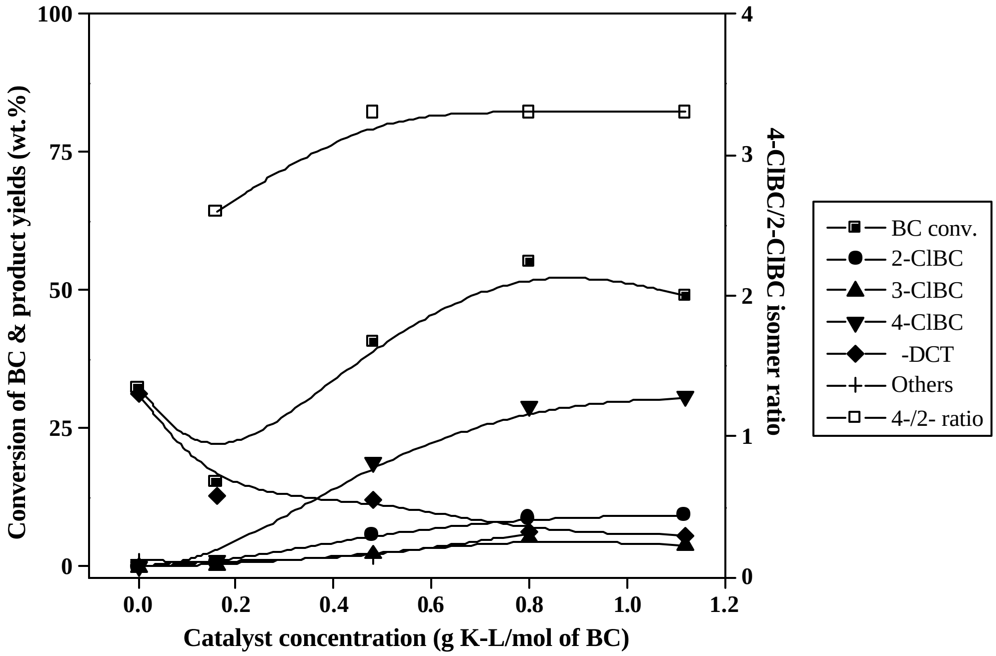


Figure 3.3. **Effect of catalyst (K-L) concentration on the conversion of BC, product yields and 4-ClBC/2-ClBC isomer ratio: reaction conditions: BC = 0.158 mol, reaction temperature = 353 K, Cl_2 flow rate) = 0.09 mol/h, reaction time = 2h.**

3.1.1.3.6. Influence of reaction temperature

The effect of the reaction temperature is studied on the rate of BC conversion, product yields and the isomer ratio of 4-ClBC/2-ClBC in the chlorination of benzyl chloride. The results are depicted in Figure 3.4.

When the temperature is increased from 333 K to 388 K, both the rates of BC conversion and formation of 4-ClBC increased significantly. In addition, the formation of consecutive products (others), a,a-DCT, 2-ClBC and 3-ClBC is also favoured at higher temperatures (Figure 3.4) and hence a decrease in the isomer ratio is noticed[6,14].

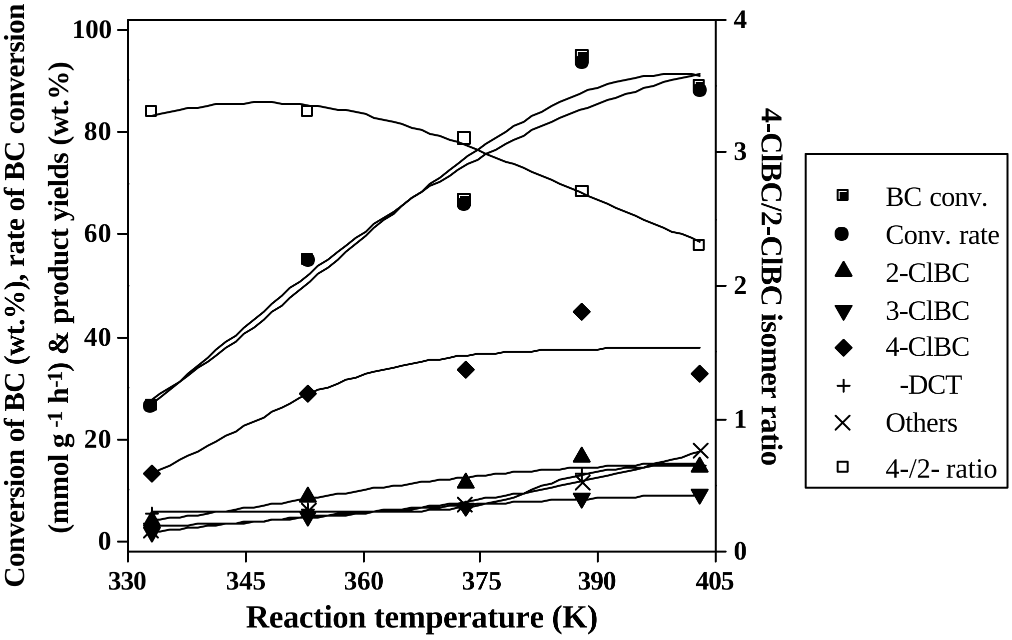


Figure 3.4. **Effect of reaction temperature on the conversion of BC, rate of BC conversion, product yields and 4-ClBC / 2-ClBC ratio: reaction conditions: catalyst (K-L) = 3.0 g / mol BC, BC = 0.158 mol, Cl_2 flow rate = 0.09 mol/h, reaction time = 2 h.**

3.1.1.3.7. Catalyst recycling

In order to check the stability and catalytic activity of zeolite K-L in the chlorination of benzyl chloride, three reaction cycles are carried out using the same catalyst. The results are presented in Table 3.3. After workup of the reaction mixture, the zeolite K-L was separated by filtration, washed with acetone and calcined for 16 h at 773 K in the presence of air before use in the next experiment. Thus the recovered zeolite after each reaction was characterized for its chemical composition by atomic absorption spectroscopy (AAS) and crystallinity by x-ray diffractometry (XRD). All data refers to calcined samples. AAS and XRD studies showed a downward trend in the content of aluminum and potassium and crystallinity of zeolite K-L after each recycle. The activity of zeolite K-L decreases progressively on recycling and it lost about 40% of its original activity after using three times in the chlorination of benzyl chloride. The hydrogen chloride liberated during the reaction probably promotes the extraction of aluminum and potassium to some extent from the framework positions of the zeolite K-L. Such type of extractions and decrease in crystallinity of the K-L may be attributed for the decrease in catalytic activity after each cycle. The results reported here are in good agreement with the earlier reported data on the halogenation of aromatics using zeolite catalysts[6,15,25].

Table 3.3. Catalyst recycling[a]

Run	SiO_2/ Al_2O_3 ratio	Degree of K^+- in K-L	BC Conv. (wt.%	Conv. rate mmol $g^{-1}h^{-1}$)	Product yields (wt.%)					4-/2- ratio	K-L crystnty %
					A	B	C	D	E		
0	6.82	98.6	59.8	59.0	9.5	3.7	30.1	12.7	3.9	3.2	100
1st	6.97	96.7	53.0	52.3	8.1	3.5	32.2	7.1	1.7	4.0	89
2nd	7.09	95.0	44.8	44.2	7.0	2.8	20.1	13.5	1.4	2.9	64.7
3rd	7.21	93.2	35.5	35.1	4.2	1.3	8.2	20.8	1.1	2.0	46.9

[a] Reaction conditions: catalyst = 5 g/mol BC; reaction temperature = 353 K; BC = 0.237 mol; Cl_2 flow = 0.09 mol/h; reaction time = 2 h.

[b,c&d] see footnotes to Table 3.1.

3.1.1.4. Conclusions

Zeolite K-L catalyzes the chlorination of benzyl chloride selectively to 4-chlorobenzyl chloride with Cl_2 gas as the chlorinating agent and is superior to other zeolite catalysts. Acidic H(26.1)K-L and higher concentration of K-L are favorable for better BC conversion and formation of the lower amount of α,α-DCT. 1,2-dichloroethane is found to be a good solvent and gives the highest selectivity for 4-ClBC at 353 K and lower yield for the side-chain chlorinated product (α,α-DCT). Increase in the reaction temperature in the presence of 1,2-dichloroethane (solvent) increases the rate of BC conversion and the ratio of 4-ClBC/2-ClBC. The conversion of BC increases with the increase in duration of run and reaction temperature. The selectivity for 4-ClBC (4-ClBC/2-ClBC) is found not to be influenced by the increase in BC conversion. Recycling of the catalyst progressively decreases the rate of BC conversion due to the extraction of small amounts of aluminum and potassium by HCl (produced in the reaction) from the catalyst.

3.1.2. Selective chlorination of cumene to 4-chlorocumene

3.1.2.1. Introduction

Chlorinated aromatic compounds are excellent insecticides, herbicides and fungicides[26]. Chlorocumenes act as important raw materials for many other useful chemicals. Conventionally, 4-chlorocumene (4-ClCm) is prepared by the chlorination of cumene (Cm) in the presence of homogeneous Lewis acid catalysts like ferric chloride or aluminium chloride, which produce 2-chlorocumene (2-ClCm) as the major product and also give higher amounts of polychlorinated products. Further, in the presence of Fe and FeS, Se, S, CS_2 or $FeCl_3$ and PtO_2[27,28], the chlorination of cumene with chlorine yields chlorocumenes, but with a lower selectivity (65 %) for 4-chlorocumene. Another method for the preparation of 4-chlorocumene involves the use of chemically modified silica gels in the presence of Cl_2 in CCl_4[29-31]. About 75% 4-chlorocumene is obtained by reacting cumene with chlorine by means of a $SbCl_3$-modified catalyst[32]. Furthermore, the chlorination of cumene was carried out by organic chlorine-containing compounds like Me_3COCl in CCl_4 in the presence of silica[33]. However, industrially, these reported methods for the preparation of 4-chlorocumene are not suitable, owing to poor para-selectivity as well as higher cost of preparation. Thus, the main purpose of this study is to enhance the selectivity for 4-chlorocumene and to reduce the formation of side-chain and polychlorinated products in the liquid phase chlorination of cumene over zeolite catalysts in the presence of sulfuryl chloride (SO_2Cl_2) under mild reaction conditions. The chlorination of cumene using gaseous chlorine as the chlorinating agent has been already reported by us in a U.S. Patent, where a combination of zeolite K-L, a co-catalyst chloroacetic acid and 1,2-dichloroethane serves as the best catalyst for the synthesis of 4-chlorocumene[20]. But the detailed study of the chlorination of cumene has been carried out by using sulfuryl chloride as the chlorinating agent. Sulfuryl chloride, by virtue of its being a liquid, is more easily metered and handled in batch reaction studies than molecular chlorine. However, it is a milder reagent and reacts readily only with the most activated substrates like phenol. Even then the reactions are sluggish. In cases of activated compounds, molecular sulfuryl chloride itself can act as an electrophile[34]; it undergoes an incipient heterolytic dissociation into $Cl^{\delta+}$-$SO_2Cl^{\delta-}$, thus giving the electrophilic substitution at room temperature. In addition, since it is bulkier than chlorine, it produces higher p-/o- ratios with little dichlorination. On the other hand, in cases of less activated compounds like toluene, chlorobenzene, ethylbenzene and isopropylbenzene (cumene), sulfuryl chloride decomposes into sulfur dioxide and molecular chlorine at elevated temperatures, the latter being the chlorinating agent for the electrophilic substitution. Thus, the p-/o- ratios obtained in this case are identical with those for either molecular chlorine or sulfuryl chloride[35].

The present work describes the use of various catalysts in the selective chlorination of cumene with sulfuryl chloride and also compares their activity with the conventional catalyst, $AlCl_3$. The effect of solvent, catalyst concentration, reaction temperature, reaction time, cumene to SO_2Cl_2 molar ratio, SiO_2/Al_2O_3 ratio of zeolite K-L (obtained by HCl treatment), catalyst recycling etc. is also investigated on the conversion of cumene, product yields and the selectivity for 4-chlorocumene (4-ClCm/2-ClCm isomer ratio). In addition, a few reactions using molecular chlorine (Cl_2 gas) as the chlorinating agent in the chlorination of cumene are also discussed.

3.1.2.2. Experimental

(a) ***Catalyst preparation and characterization***

The zeolites used, their synthesis, modification and physico-chemical characterization have already been reported in Chapter 2. Some important properties of these zeolites are listed in Table 2.2.

(b*) Catalytic reaction experiment***

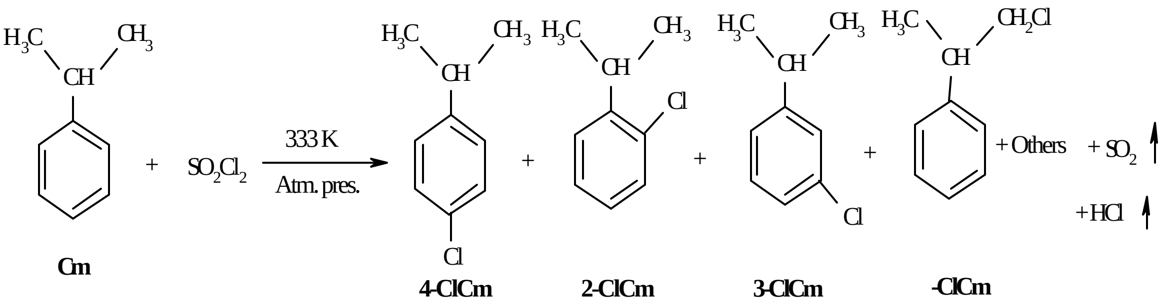
All the chemicals employed in this study were of high purity. Sulfuryl chloride was freshly distilled to a clear fraction (bp.69.5 ^{0}C) before each and every reaction. A typical batch reaction procedure was as follows: A sample of activated catalyst (0.5g), cumene (0.04 moles) and sulfuryl chloride (0.02 moles) were taken in a mechanically stirred 50 ml closed glass reactor fitted with a reflux condenser, a thermometer and a septum for withdrawing the samples. This filled reactor was placed in a thermostat at the required reaction temperature. The samples were taken out periodically, degassed thoroughly, neutralized by $NaHCO_3$ and analyzed on a Gas-chromatograph (HP GC 6890) equipped with a capillary column (50 m x 200 μm x 0.2 μm) with Phenyl methoxy silicone gum. Product identification was done with reference to standard samples and GCMS (Shimadzu, QP 2000A).

Conversion is defined as the percentage of cumene transformed. The rate of cumene conversion (mmolg^{-1}h^{-1}) is calculated as the amount of cumene (mmol) converted per h per g of the catalyst. The yield percentage of product represents the amount of the product calculated from selectivity multiplied by the conversion and divided by 100.

3.1.2.3. Results and Discussion

3.1.2.3.1. Influence of various catalysts

Table 3.4. compares the rate of cumene conversion, product yields and the selectivity i.e. the 4-ClCm/2-ClCm ratio over various zeolites such as K-X, K-Y, K-ZSM-5, K-L, K-beta as well as in the presence of conventional Lewis acid catalyst $AlCl_3$ and also in the absence of any catalyst in the chlorination of cumene at 333 K with sulfuryl chloride (SO_2Cl_2) under identical reaction conditions.



Scheme 3.2

Table 3.4. Chlorination of cumene with sulfuryl chloride[a]

Catalyst	Cm. conv. (wt.%)	Conv. rate[b] (mmol $g^{-1}h^{-1}$)	Product yields (wt.%)[c]					4-/2-[d] ratio
			2-ClCm	3-ClCm	4-ClCm	α-ClCm	others	
K-X	6.2	5.2	0.3	0.1	0.5	2.9	2.4	1.6
K-Y	7.0	5.8	1.3	0.2	2.5	1.7	1.3	1.7
K-ZSM-5	8.8	7.3	3.3	0.2	3.4	1.1	0.8	1.3
K-L	27.7	23.0	6.4	0.2	20.3	0.1	0.7	3.2
K-beta	18.9	15.7	5.2	0.4	11.4	1.2	0.7	2.2
K-mord.	7.5	6.2	1.7	0.1	3.4	1.5	0.8	2.0
$AlCl_3$	23.8	19.8	2.7	0.5	3.4	2.3	14.9	1.9
No catalyst	2.4	-	-	-	0.5	1.1	0.8	-

[a] Reaction conditions: Catalyst = 12.5 g/mol of cumene; Reaction temp.= 333 K; Cumene = 0.04 mol; Sulfuryl chloride = 0.02 mol; Reaction time = 1 h.

[b] Rate of cumene conversion is expressed as amount of cumene converted / wt. of the catalyst x reaction time.

[c] 2-ClCm = 2-chlorocumene; 3-ClCm = 3-chlorocumene; 4-ClCm = 4-chlorocumene; α-ClCm = α-chlorocumene; Others = di- and trichlorinated cumenes.

[d] 4-/2- ratio = Isomer ratio of 4-chlorocumene to 2-chlorocumene

The reaction produces a mixture of 2-chlorocumene (2-ClCm), 3-chlorocumene (3-ClCm), 4-chlorocumene (4-ClCm) and the side-chain chlorinated product (α-ClCm). Small quantities of di- and tri-chlorinated products (others) are also detected in the reaction (Scheme 3.2).

The monochlorocumenes are formed by the parallel reaction, while the di- and tri-chlorinated products are obtained by the consecutive reactions of the monochlorocumenes[14,23]. Table 2 shows that zeolites K-L and K-beta give higher rates of cumene conversion than the other zeolites studied, but K-L is found to be more active and selective than K-beta. The rate of cumene conversion and the 4-ClCm/2-ClCm ratio over zeolite K-L is found to be 23.0 mmolg^{-1}h^{-1} and 3.2, respectively, after 1h of reaction. Zeolite K-X and blank experiment (without catalyst) give the side-chain product α-ClCm as the main product with a little activity whereas the other zeolites, viz. K-Y, K-ZSM-5, K-mordenite, give both nuclear as well as side-chain chlorinations, which are neither active nor selective. The highest amount of side-chain chlorinated product is obtained over zeolite K-X; this result is in agreement with the previous literature and may be ascribed to the lower SiO_2/Al_2O_3 ratio[6,15]. Also the side-chain chlorination of cumene in the absence of any catalyst and poorly dark reaction conditions may be attributed to the photochlorination by the free radical pathway[6,24].

The activity of the conventional Lewis acid catalyst is found to be nearly comparable with that of zeolie K-L, but gives a lower ratio of 4-ClCm/2-ClCm. $AlCl_3$ mainly gives the di- and tri-chlorinated products (others) and a substantial amount of the side-chain chlorinated product (α-ClCm) is also obtained.

Thus, from the results it is clear that zeolite K-L is far superior to the other zeolites and that the conventional $AlCl_3$ catalyst can be replaced by highly active and selective catalyst K-L in the chlorination of cumene with sulfuryl chloride.

3.1.2.3.2. Duration of the run over various catalysts

Figure 3.5 compares the influence of reaction time on the performance of various catalysts at 333 K under atmospheric pressure in the liquid phase chlorination of cumene with sulfuryl chloride.

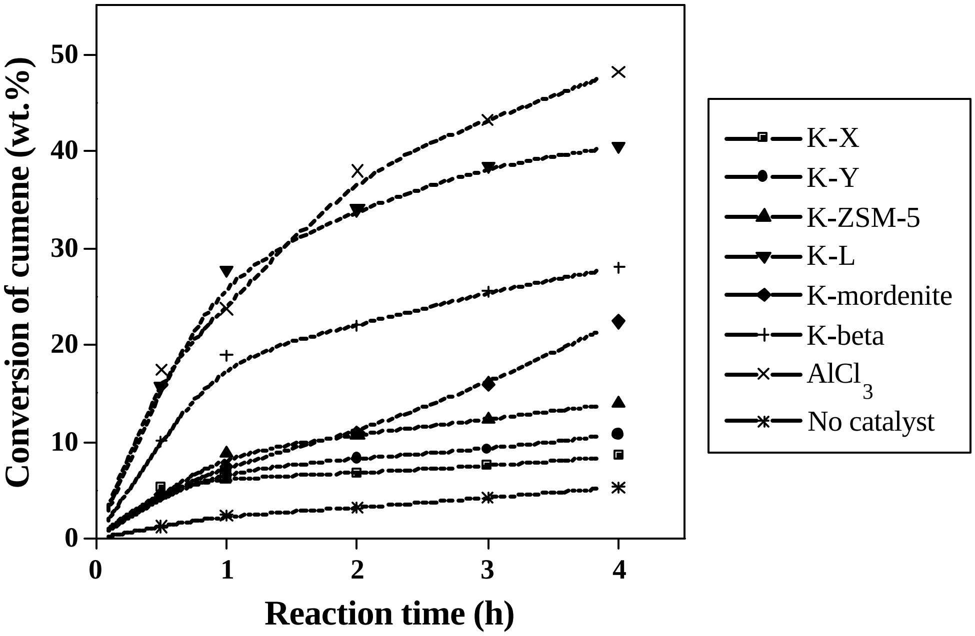


Figure 3.5 Chlorination of cumene with SO_2Cl_2: Effect of reaction time on the performance of various catalysts. Reaction conditions: See the footnotes to Table 3.4.

As can be seen from the figure, the conversion of cumene has been increased with the reaction time over the catalysts K-L, K-beta, K-mordenite and $AlCl_3$, whereas the activity of the other catalysts (K-X, K-Y, and K-ZSM-5) is found to be very much less. Zeolite K-L and $AlCl_3$ are the most active catalysts giving 40.5 and 48.2 wt.% conversion of cumene, respectively, after 4 h of reaction time. Various catalysts used in this study can be arranged according to their decreasing order of catalytic activity after 4 h of reaction time as follows: $AlCl_3$ > K-L > K-beta > K-mordenite > K-ZSM-5 > K-Y > K-X > None.

3.1.2.3.3. Influence of reaction time using zeolite K-L

The performance of zeolite K-L catalyst at 333 K in terms of cumene conversion, product yields and selectivity to 4-ClCm (4-ClCm/2-ClCm ratio) as a function of time of stream is presented in Figure 3.6.

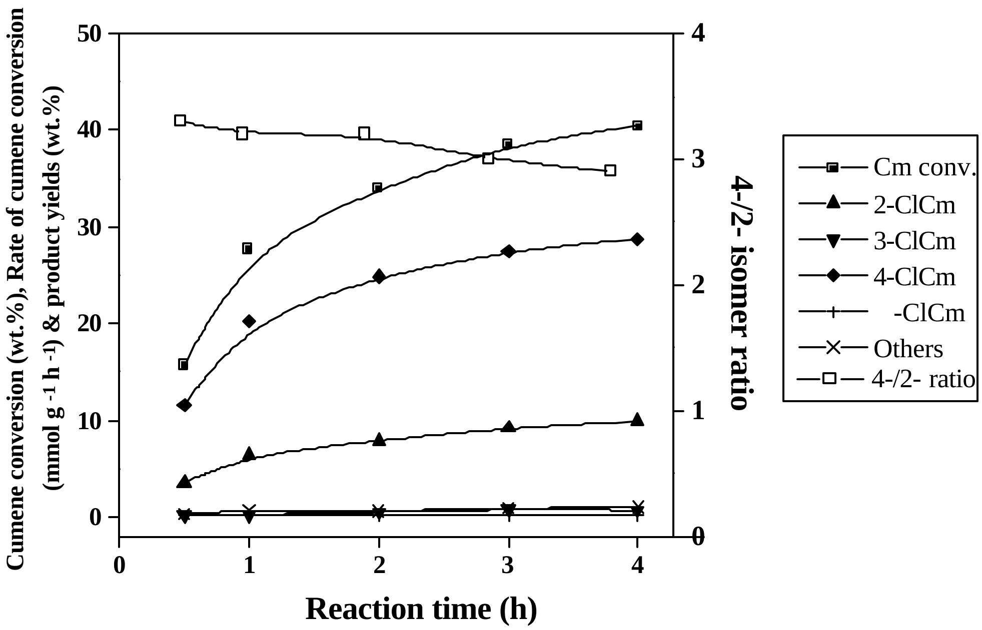


Figure 3.6 Effects of reaction time on the conversion of cumene, product yields and 4-ClCm/2-ClCm ratio over zeolite K-L. Reaction conditions: See the footnotes to Table 3.4.

Both the conversion of cumene and the product yields increase with the duration of run, whereas the 4-ClCm/2-ClCm ratio remains almost constant. The initial rate of cumene conversion, however, is found to decrease with time. The concentration of the side-chain chlorinated product (α-ClCm) is very much less and remains constant, but the di- and tri-chlorinated products (others) are found to increase with time because of increased conversion.

3.1.2.3.4. Influence of reaction temperature

The effect of reaction temperature on the conversion of cumene, rate of cumene conversion, product yields and 4-ClCm/2-ClCm ratio is studied after 1 h of reaction time; the results are shown in Figure 3.7.

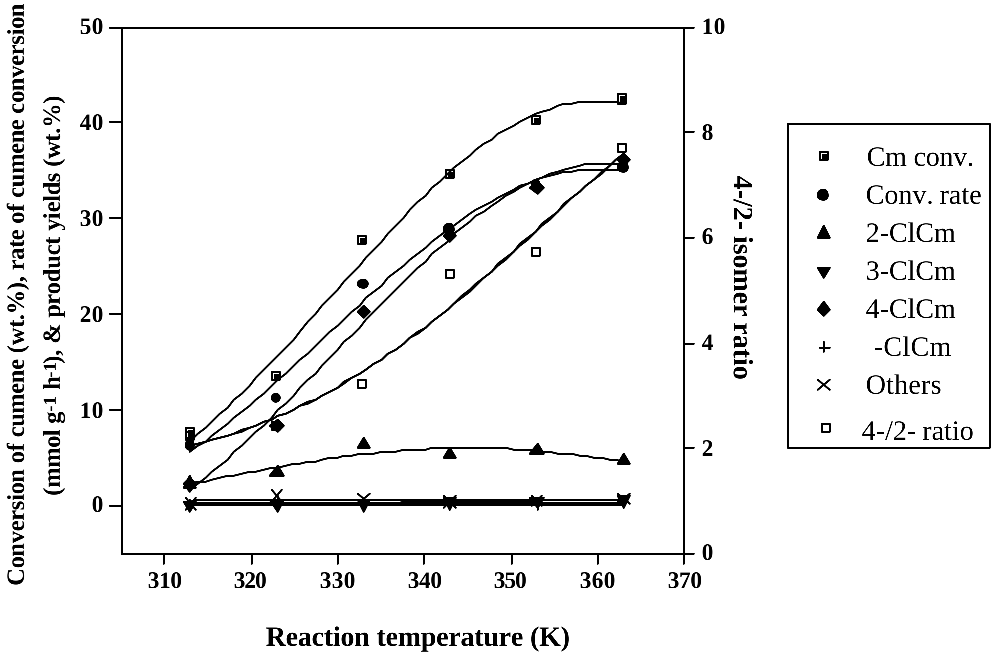


Figure 3.7 **Effects of reaction temperature on the conversion of cumene, rate of cumene conversion, product yields and 4-ClCm/2-ClCm ratio over zeolite K-L. Reaction conditions: Catalyst (K-L)) = 12.5 g/mol of cumene; Cumene = 0.04 mol; SO_2Cl_2 = 0.02 mol; Reaction time = 1 h.**

It is evident that the rate of cumene conversion increases sharply with increase in the reaction temperature from 313 to 343 K and thereafter only a marginal increase in the rate of cumene conversion is observed up to 363 K. It is interesting to note that most of the increase in the conversion of cumene is due to the increase in the yield of 4-ClCm. The yields of 2-ClCm, 3-ClCm, α-ClCm and others (di- and tri-chlorinated cumenes) remain almost constant, even in the region of higher temperature. The selectivity, i.e. 4-ClCm/2-

ClCm isomer ratio also increases from 2.2 to 7.7 with increase in the reaction temperature from 313 to 363 K.

3.1.2.3.5. Influence of solvent

Table 3.5. records the conversions of cumene, rates of cumene conversion, product yields and the isomer ratios of 4-ClCm/2-ClCm obtained in the chlorination of cumene using zeolite K-L with sulfuryl chloride, in the presence of various solvents such as 1,2-dichloroethane (EDC), carbon tetrachloride, chloroform, 1,1,1-trichloroethane and dichloromethane.

Table 3.5. Effect of solvent on the chlorination of cumene over zeolite K-L[a]

Solvent	React. Temp	Cm. conv. (wt.%)	Conv. rate[b] (mmol $g^{-1}h^{-1}$)	Product yields (wt.%)[c]					4-/2-[d] ratio
				2-ClCm	3-ClCm	4-ClCm	α-ClCm	Others	
EDC	353	37.7	31.4	1.1	0.3	36.3	-	-	33.0
	313	6.1	5.1	0.8	0.1	2.8	0.9	1.5	3.5
CCl_4	348	20.1	16.7	4.8	0.4	11.6	1.0	2.3	2.4
	313	5.7	4.7	1.2	0.1	2.5	0.7	1.2	2.1
$CHCl_3$	333	9.5	7.9	1.4	0.1	3.1	1.4	3.5	2.2
	313	4.5	3.7	0.5	0.1	1.0	1.2	2.0	2.0
CH_3CCl_3	345	15.7	13.1	4.2	0.3	9.1	0.6	1.5	2.2
	313	5.5	4.6	1.1	0.1	2.4	0.9	1.0	2.2
CH_2Cl_2	313	6.7	5.6	1.1	0.1	4.6	0.1	0.8	4.2
No Solvt	353	40.2	33.4	8.5	0.5	30.5	0.2	0.5	3.6
	313	7.5	6.2	2.3	0.1	4.6	0.1	0.2	2.0

[a] Reaction conditions: Catalyst (K-L) = 12.5 g / mol of cumene; Cumene = 0.04 mole; Sulfuryl chloride = 0.02 mole; Solvent = 10 ml; Cumene/solvent (wt./vol.) ratio = 0.5; Reaction time = 1 h.

[b,c,d] Same as in Table 3.4.

The effect of these solvents is studied at their reflux conditions as well as at 313 K for comparison. As can be seen from Table 3.5, the conversion of cumene at 313 K over all the solvents is found to be less compared with the neat chlorination (without solvent) at 313 K; the selectivity, however, is higher in the presence of dichloromethane as a solvent than in the presence of other solvents at 313 K. The rate of cumene conversion at 313 K decreases by changing the solvent in the following order: CH_2Cl_2 > $ClCH_2CH_2Cl$ > CCl_4 > $Cl_3C\text{-}CH_3$ > $CHCl_3$.

Also the order of 4-ClCm/2-ClCm in these solvents at 313 K is

CH_2Cl_2 > $ClCH_2CH_2Cl$ > $Cl_3C\text{-}CH_3$ > CCl_4 > $CHCl_3$.

The rate of cumene conversion and the 4-ClCm/2-ClCm isomer ratio are found to increase significantly with an increase in the reaction temperature (reflux temperature of that particular solvent) in the presence of all the solvents. In addition, the selectivity has been found to increase drastically when the reaction is performed in the presence of 1,2-dichloroethane at 353 K instead of neat chlorination at 353 K (Table 3.5.). When the temperature is raised from 313 to 353 K in the presence of EDC, the rate of cumene conversion as well as the selectivity is increased many-fold. The side-chain chlorinated product (α-ClCm) as well as the others (di- and trichlorinated products), which are observed in the neat chlorination at 353 K are not obtained in the presence of EDC at 353 K. Thus, the side-chain chlorination of cumene and also the formation of polychlorinated products to some extent are found to be dependent on the solvent used in the reaction.

3.1.2.3.6. Influence of cumene/ EDC molar ratio on the isomer ratio

Table 3.6. lists the effect of the concentration of the solvent, 1,2-dichloroethane, on the isomer ratio of 4-ClCm/2-ClCm at 353 K. It is clear from the Table that the isomer ratio increases with increase in the EDC amount up to a cumene to EDC ratio of 0.5, and then further increase in the EDC concentration has not shown any significant effect on the isomer ratio, which remains almost constant.

Table 3.6. Influence of cumene to EDC (wt./wt.) ratio on the isomer ratio[a]

Cm/EDC ratio	Cm Conv. (wt.%)	Conv. rate[b] (mmol $g^{-1}h^{-1}$)	Product yields (wt.%)[c]					4-/2-[d] ratio
			2-ClCm	3-ClCm	4-ClCm	α-ClCm	Others	
2	40.0	33.3	2.9	0.3	36.6	0.1	0.1	12.6
1	40.2	33.5	1.5	0.3	38.2	0.1	0.1	25.5
0.67	39.7	33.0	1.2	0.3	38.2	-	-	31.8
0.5	37.7	31.4	1.1	0.3	36.3	-	-	33.0
0.4	36.9	30.7	1.1	0.3	35.5	-	-	32.3
0.33	34.4	28.6	1.0	0.3	33.1	-	-	33.1

[a] Reaction conditions: Catalyst (K-L) = 12.5 g/mol of cumene; Reaction temp. = 353 K; Cumene = 0.04 mol; Sulfuryl chloride = 0.02 mol; Reaction time = 1 h.

[b,c,d] Same as in Table 3.5.

3.1.2.3.7. Influence of catalyst concentration

In order to study the effect of catalyst (K-L) concentration on the conversion of cumene, rate of cumene conversion, product yields and the selectivity (4-ClCm/2-ClCm isomer ratio), the concentration of the catalyst is increased from 6.25 g/mole of cumene to 25.0 g/mole of cumene (Figure 3.8). It is clear from the figure that the conversion of cumene increases with increase in catalyst concentration up to 12.5 g/mole of cumene. The rate also has increased with increase in the catalyst concentration up to 12.5 g/mole of cumene. After this optimum catalyst concentration (12.5 g/mole of cumene), however, the increase in the catalyst concentration has not shown any noticeable effect on the conversion of cumene. In the absence of catalyst K-L, the side-chain chlorinated product (α-ClCm) is mainly observed. The isomer ratio is increased from 2.4 to 38.1 when the catalyst concentration is increased from 0 to 25 g/mole of cumene. Thus, maximum selectivity for 4-ClCm (96.7%) is obtained when 25 g catalyst K-L /mole of cumene is used. In addition, the side-chain product (α-ClCm) as well as the others (di- and trichlorinated products) have disappeared with increase in the catalyst concentration. Thus, the catalyst K-L is highly active as well as selective in the liquid phase chlorination of cumene, giving exclusively ring chlorination.

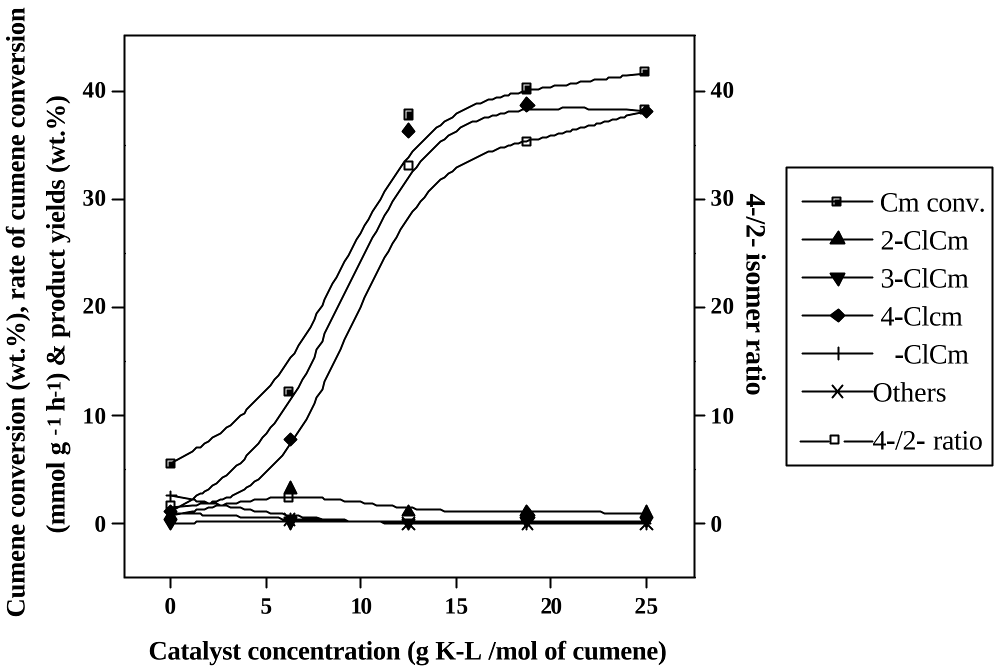


Figure 3.8 **Effects of catalyst (K-L) concentration on the conversion of cumene, product yields and 4-ClCm/2-ClCm ratio. Reaction conditions: Cumene = 0.04 mol; SO_2Cl_2 = 0.02 mol; EDC = 10 ml; Reaction temperature = 353 K; Reaction time = 1 h.**

3.1.2.3.8. Influence of HCl treated zeolite K-L

The chlorination of cumene was studied with zeolite K-L with different SiO_2/Al_2O_3 ratios obtained by the treatment of parent K-L with various molar solutions of HCl (0.05 to 0.7 M HCl). The results are depicted in Table 3.7. As can be seen from the results, the conversion of cumene and 4-ClCm/2-ClCm isomer ratio decreases from 37.7 wt.% to 28.8 wt.% and 33.0 to 4.2, after 1 h of reaction time, when the framework SiO_2/Al_2O_3 ratio of zeolite K-L increased from 6.82 to 9.01, respectively, because of dealumination. The higher catalytic activity of fresh zeolite K-L compared to the treated zeolite K-L may be due to the lower SiO_2/Al_2O_3 ratio, thus giving a higher concentration of aluminium, which in turn gives a higher number of basic sites for the reaction. The lowest activity of 0.7 M HCl treated zeolite K-L may be attributed to a combined effect of higher SiO_2/Al_2O_3 ratio and lower crystallinity of zeolite K-L. Thus, higher numbers of basic sites as well as good crystallinity of zeolite K-L are the most important factors for the liquid phase chlorination of cumene.

Table 3.7. Influence of HCl-treated zeolite K-L[a]

Catalyst K-L	SiO_2/Al_2O_3 ratio	Degree of K^+- in K-L	Cm Conv. (wt.%)	Conv. rate[b] (mmol $g^{-1}h^{-1}$)	Product yields (wt.%)[c]					4-/2-[d] ratio
					2-Cl Cm	3-Cl Cm	4-Cl Cm	α-Cl Cm	Others	
K-L	6.82	>98	37.7	31.4	1.1	0.3	36.3	-	-	33.0
K-L (0.05)[e]	7.43	>98	37.2	31.2	1.2	0.3	35.8	-	-	29.8
K-L (0.1)[e]	8.02	>98	36.0	30.0	1.7	0.3	34.1	-	-	20.1
K-L (0.3)[e]	8.63	>98	33.7	28.0	3.7	0.5	29.5	-	-	8.0
K-L (0.5)[e]	8.73	>98	30.2	25.1	3.6	0.3	26.2	-	-	7.2
K-L (0.7)[e]	9.01	>98	28.8	24.0	5.4	0.4	22.8	-	0.2	4.2

[a] Reaction conditions: Catalyst = 12.5 g/mol of cumene; Reaction temp. = 353 K; Cumene = 0.04 mol; Sulfuryl chloride = 0.02 mol; EDC = 10 ml; Cumene/solvent (wt./vol.) ratio = 0.5; Reaction time = 1 h.

[b,c,d] Same as in Table 3.4.

[e] Values in parentheses correspond to the molarity of HCl solution taken for K-L treatmemt.

3.1.2.3.9. Influence of cumene/sulfuryl chloride molar ratio

Figure 3.9. represents the effect of cumene/SO_2Cl_2 molar ratio on the conversion of cumene, rate of cumene conversion and product yields. As expected, the conversion of cumene decreases from 92.8 to 16.1 wt.% with an increase in the cumene/SO_2Cl_2 molar ratio from 0.33 to 4. It is to be noted that the increase in the conversion of cumene with an increase in the SO_2Cl_2 concentration is mainly because of the increase in the concentration of 4-ClCm. The side-chain product (α-ClCm) as well as others (di- and trichlorinated products) are detected only at cumene/SO_2Cl_2 molar ratio of 0.5 and 0.33 i.e. at higher concentrations of sulfuryl chloride.

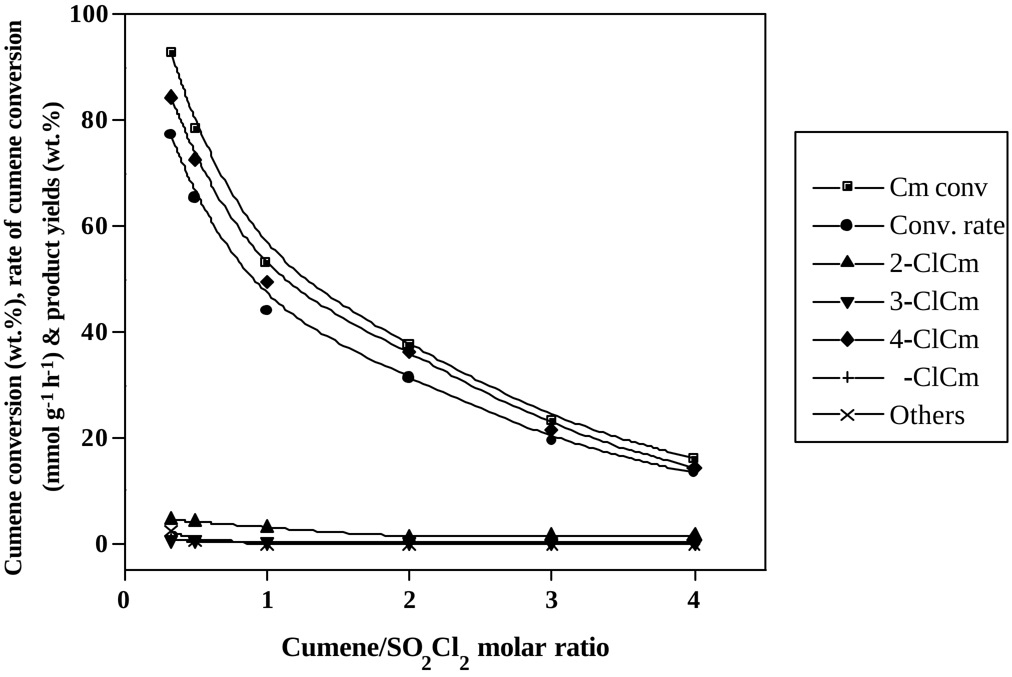


Figure 3.9 **Effects of Cumene/SO_2Cl_2 molar ratio on the conversion of cumene, rate of cumene conversion and product yields over zeolite K-L. Reaction conditions: Catalyst (K-L) = 12.5 g/mol cumene; Cumene = 0.04 mol; EDC = 10 ml; Reaction temperature = 353 K; Reaction time = 1 h.**

3.1.2.3.10. Recycle of zeolite K-L

The results of the catalytic recycling experiment using zeolite K-L in the chlorination of cumene at 353 K are shown in Table 3.8.

Table 3.8. Recycle of the catalyst K-L[a]

Run	SiO_2/Al_2O_3 ratio	Degree of K^+-in K-L	Cm Conv (wt. %)	Conv. rate[b] (mmol $g^{-1}h^{-1}$)	Product yields (wt.%)[c]					4-/2-[d] ratio	K-L Crys tnty %
					2-Cl Cm	3-Cl Cm	4-Cl Cm	α-Cl Cm	Others		
0	6.8	>98.6	37.7	31.4	1.1	0.3	36.3	-	-	33.0	100
1	7.0	>96.7	29.4	24.5	2.0	0.3	27.1	-	-	13.6	75
2	7.9	>94.8	6.4	5.5	1.1	0.1	3.1	0.9	1.2	2.8	Amp.

[a] Reaction conditions: Catalyst = 12.5 g/mol of cumene; Reaction temp. = 353 K; Cumene = 0.04 mol; Sulfuryl chloride = 0.02 mol; EDC = 10 ml; Cumene/solvent (wt./vol.) ratio = 0.5; Reaction time = 1 h.

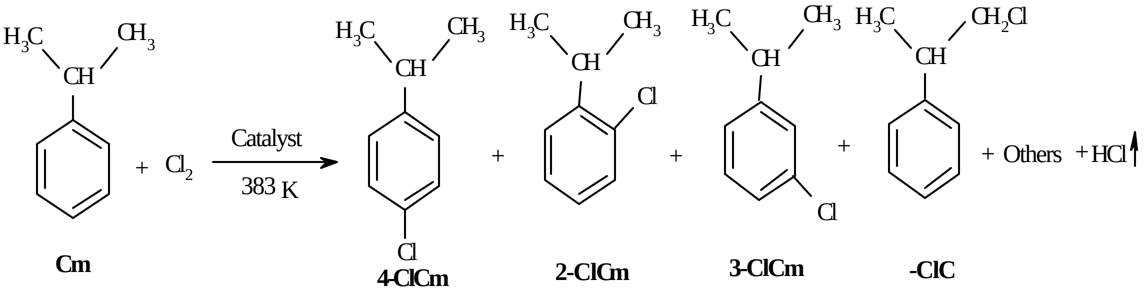
[b,c,d] Same as in Table 3.4.

Amp. = amorphous

After the completion of each reaction, the zeolite K-L was separated from the reaction mixture by filtration, washed with acetone and calcined in air at 773 K for 12 h. Each sample is then characterized for the chemical composition and crystallinity. All the data refers to the calcined samples. The aluminium and potassium content as well as crystallinity of K-L samples have been found to decrease after each recycle. The activity of zeolite K-L decreases progressively on recycling and the sample lost almost all its activity after the 3rd recycle. The sulfur dioxide and hydrochloric acid evolve continuously during the reaction, which affects the catalyst activity. In addition, the HCl formed in the reaction extracts aluminium and to some extent potassium from the framework positions of zeolite K-L. Such type of extractions and the decrease in the crystallinity of zeolite K-L leads to the decrease in the catalytic activity of zeolite K-L in the chlorination of cumene after each recycle.

3.1.2.3.11. Chlorination of cumene with molecular chlorine in presence of K-L

Table 3.9. illustrates the results of the liquid phase chlorination of cumene at 383 K under atmospheric pressure with molecular chlorine as the chlorinating agent (Scheme 3.3).



Scheme 3.3

Table 3.9. Chlorination of cumene with molecular chlorine[a]

Catalyst	Cm. Conv. (wt.%)	Conv. Rate[b] (mmol $g^{-1}h^{-1}$)	Product yields (wt.%)[c]					4-/2-[d] ratio
			2-ClCm	3-ClCm	4-ClCm	α-ClCm	Others	
K-L+ $ClCH_2COOH$	66.6	66.8	5.3	1.2	58.0	0.5	1.6	10.9
$FeCl_3$	22.2	22.3	10.5	1.7	7.6	-	2.5	0.7
No catalyst	11.6	11.6	1.3	0.1	1.9	4.5	3.7	1.5
K-L+ $ClCH_2COOH$ + EDC[e]	68.8	23.8	2.9	0.8	64.5	-	0.6	22.6

[a] Reaction conditions: Catalyst = 5 g/mol of cumene; $ClCH_2COOH$ = 0.2 g/g K-L; Cumene = 0.166 mol; Cl_2 flow = 0.09 mol/h; Reaction temperature = 383 K; Reaction time = 2 h.

[b,c,d] Same as in Table 3.4.

[e] Reaction conditions: Catalyst = 10 g/mol of cumene; $ClCH_2COOH$ = 0.2 g/g K-L Cumene = 0.08 mol; Cl_2 flow = 0.09 mol/h; EDC = 10 ml; Cumene/ EDC (wt./vol.) ratio = 1; Reaction temperature = 353 K; Reaction time = 2 h.

The reaction is performed in the presence of a combination of zeolite K-L and chloroacetic acid ($ClCH_2COOH$) as a co-catalyst, with the conventional Lewis acid catalyst $FeCl_3$ and without any catalyst under similar reaction conditions. In addition, the chlorination of cumene is also carried out in the presence of 1,2-dichloroethane at 353 K along with K-L + $ClCH_2COOH$.

As can be seen from Table 3.9., the combination of K-L and $ClCH_2COOH$ is found to be highly active and selective and the rate of cumene conversion and the 4-ClCm/2-ClCm isomer ratio are found to be 66.8 mmolg^{-1}h^{-1} and 10.9, respectively, at 383 K after 2 h of reaction time. The conventional catalyst, $FeCl_3$ mainly gives higher amounts of polychlorinated product with a very poor selectivity. The chlorination without any catalyst produces side-chain product (α-ClCm) predominantly with a substantial amount of polychlorinated products, with much less activity and selectivity.

In the presence of 1,2-dichloroethane at 353 K, the combination of K-L + $ClCH_2COOH$ gives a drastic increase in the isomer ratio of 4-ClCm/2-ClCm. The isomer ratio is increased from 10.9 to 22.6 with a conversion of 68.8 wt.%. Further, no side-chain product is formed and only a trace amount of consecutive products is detected.

Thus, the combination of zeolite K-L, $ClCH_2COOH$ and 1,2-dichloroethane serves as the best catalyst for the selective chlorination of cumene to 4-chlorocumene with molecular chlorine. Presumably, the interaction of $ClCH_2COOH$ with the basic sites (K^+) of the zeolite produces hindrance in the zeolite channels for the diffusion of the products due to formation of Zeol-OH-K^+OOCCH_2Cl, resulting in higher para-selectivity of the reaction[36].

3.1.2.4. Conclusions

Zeolite K-L catalyzes the chlorination of cumene selectively to 4-chlorocumene with sulfuryl chloride and is found to be superior to other zeolite catalysts as well as to the conventional Lewis acid catalyst $AlCl_3$. The conversion of cumene and the isomer ratio of 4-ClCm/2-ClCm increase with increase in the reaction temperature with zeolite K-L. Among the solvents, 1,2-dichloroethane is found to be the best solvent; it gives the highest selectivity for 4-chlorocumene (4-ClCm/2-ClCm = 33.0) at 353 K without formation of any side-chain (α-ClCm) or polychlorinated product. Higher concentration of zeolite K-L in the presence of 1,2-dichloroethane increases the conversion of cumene and produces still higher selectivity for 4-chlorocumene. The conversion of cumene decreases with the increase in the SiO_2/Al_2O_3 ratio (obtained by HCl treatment). Increase in the concentration of the chlorinating agent (lower cumene/SO_2Cl_2 molar ratio) increases the conversion of cumene. The side-chain as well as polychlorinated products are detected at higher concentration levels of sulfuryl chloride. The activity of zeolite K-L decreases progressively on recycling due to the changes in chemical composition and crystallinity of zeolite K-L by HCl (produced in the course of the reaction as a by-product.

Zeolite K-L in combination with chloroacetic acid is found to be highly active and selective in the chlorination of cumene with molecular chlorine at 383 K under atmospheric pressure. 1,2-dichloroethane is the best solvent and gives higher isomer ratio when used along with zeolite K-L and chloroacetic acid at 353 K in the chlorination of cumene with molecular chlorine.

3.1.3. Selective chlorination of diphenylmethane to 4,4'-dichlorodiphenylmethane

3.1.3.1. Introduction

Ring chlorinated dichlorodiphenylmethane (DCDPM) is useful in the preparation of agricultural and pharmaceutical chemicals or as a plasticizer for vinyl resin[37]. Traditionally, it is known that, on chlorinating diphenylmethane (DPM) with molecular chlorine, methylene group chlorinated compounds are formed: When DPM is chlorinated in the presence of azobisisobutyronitrile in CCl_4 solvent, then 66-67 % α-chlorodiphenylmethane and 32-33 % α,α-dichlorodiphenylmethane (α,α-DCDPM) are obtained[38]. DPM in the presence of PCl_5 with chlorine gas gives only the side-chain chlorinated product[39]. Furthermore, DPM when chlorinated in the presence of $FeCl_3$ as catalyst in CCl_4, gives monochlorodiphenylmethane (MCDPM) with a low yield and selectivity for the para-product[40]. In another method, DPM in the presence of CCl_4, azobisisobutyronitrile and ammonium molybdate at 333 K gives MCDPM with molecular chlorine[41]. Thus, these methods are not suitable for the preparation of 4,4'-DCDPM. Also the homogeneous Lewis acid catalysts pose many problems in the chlorination reaction as discussed earlier in this chapter. The use of heterogeneous catalyst, on the other hand, offers several advantages compared to their homogeneous counterparts. Zeolite based catalysts are effective in meeting current industrial processing objectives and more stringent environment pollution limits which require the development of new more active and selective catalysts. The chlorination of diphenylmethane in the presence of zeolite catalysts is limited to patents[42,43]. The main purpose of this study, therefore, is to enhance the selectivity for 4,4'-dichlorodiphenylmethane in the liquid phase chlorination of diphenylmethane with sulfuryl chloride (SO_2Cl_2) as the chlorinating agent using zeolite K-L as the catalyst under mild reaction conditions. Sulfuryl chloride, though a milder reagent than molecular chlorine, is more easily metered and handled in batch reaction studies, by virtue of its being a liquid.

The present work describes the use of various catalysts in the liquid phase selective chlorination of diphenylmethane with sulfuryl chloride and also compares their activity with the conventional catalyst, $AlCl_3$. The effect of solvent, catalyst concentration, reaction temperature, reaction time, DPM to SO_2Cl_2 molar ratio, SiO_2/Al_2O_3 ratio of zeolite K-L (obtained by HCl treatment), catalyst recycling etc. is also investigated on the conversion of DPM, product yields, DCDPM/MCDPM ratio and the selectivity for 4,4'-dichlorodiphenylmethane (4,4'-DCDPM/2,4'-DCDPM isomer ratio).

3.1.3.2. Experimental

Table 2.2. summarizes some physico-chemical properties of the zeolites used in the study.

The experimental set up and the procedure for the catalytic batch reactions consisted of a sample of activated catalyst (0.3 g), DPM (0.006 mole), sulfuryl chloride (0.012 mole) and 1,2-dichloroethane (EDC) with the rest of the things being similar to that described in Section 3.1.2.2. (b).

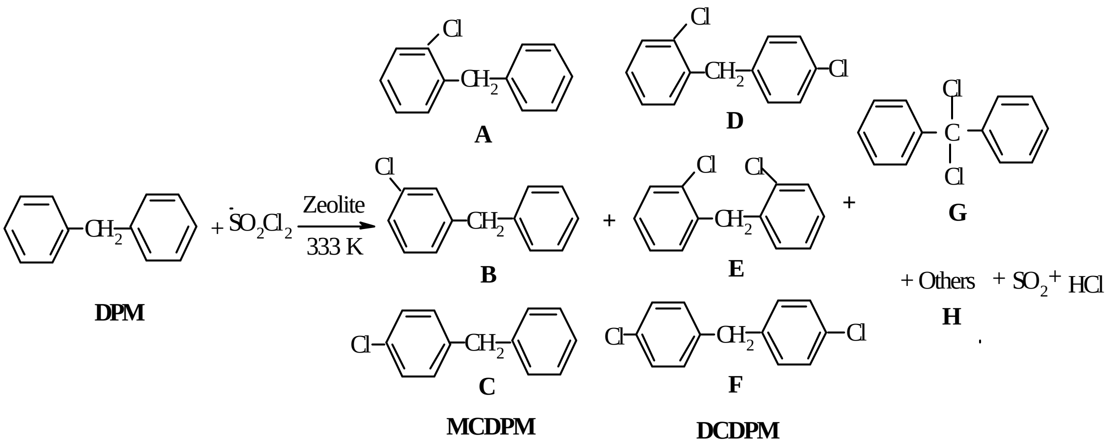
Conversion is defined as the percentage of DPM transformed. The rate of DPM conversion (mmol$g^{-1}h^{-1}$) is calculated as the amount of DPM (mmol) converted per h per g of the catalyst. The yield percentage of product represents the amount of the product calculated from selectivity multiplied by the conversion and divided by 100.

3.1.3.3. Results and Discussion

3.1.3.3.1. Influence of various catalysts

Table 3.10. compares the conversion of DPM (wt.%), rate of DPM conversion (mmol$g^{-1}h^{-1}$), product yields (wt.%), DCDPM/MCDPM ratio and the selectivity for 4,4'-dichlorodiphenylmethane (4,4'-DCDPM/2,4'-DCDPM isomer ratio) over various catalysts such as K-X, K-Y, K-L, K-ZSM-5, K-beta, K-mordenite, H.K-L and also the Lewis acid catalyst, $AlCl_3$ and without any catalyst (blank), in the chlorination of diphenylmethane with sulfuryl chloride at 333 K under identical reaction conditions. The reaction produces a mixture of MCDPM such as 2-chlorodiphenylmethane (2-CDPM) or (A), 3-chlorodiphenylmethane (3-CDPM) or (B) and 4-chlorodiphenylmethane (4-CDPM) or (C) and DCDPM like 2,4'-DCDPM (D), 2,2'-DCDPM (E) and 4,4'-DCDPM (F). Smaller amounts of the side-chain chlorinated product (α,α-DCDPM) (G) and polychlorinated products (others) (H) are also obtained (Scheme 3.4). The MCDPM are formed by the parallel reaction by an interaction of an electrophile (Cl^+) with DPM whereas the DCDPM

are obtained by the consecutive reaction of the MCDPM[14,23]. It is clear from the results that zeolite K-L is highly active as well as selective in this reaction compared to the other catalysts and the conversion of DPM, the rate of DPM conversion, DCDPM/MCDPM ratio and 4,4'-DCDPM/2,4'-DCDPM ratio over zeolite K-L are found to be 96.8 wt.%, 19.2 mmolg^{-1}h^{-1}, 0.7 and 7.4, respectively, after 1 h of reaction time.



Scheme 3.4

Table 3.10. Chlorination of diphenylmethane over various catalysts[a]

Catalyst	DPM Conv (wt. %)	Conv Rate[b] mmol g^{-1}h^{-1}	Product yields, (wt.%)[c]								DC/ MC[d] ratio	4,4'/ 2,4'-[e] ratio
			MCDPM			DCDPM						
			A	B	C	D	E	F	G	H		
K-X	13.7	2.7	4.9	0.6	6.2	-	-	-	0.3	1.7	-	-
K-Y	20.0	4.0	5.8	0.7	8.3	-	-	-	0.1	5.1	-	-
K-L	96.8	19.2	2.5	2.0	52.7	4.6	0.8	34.0	0.1	0.1	0.7	7.4
K-ZSM-5	14.0	2.8	4.7	4.3	4.3	0.1	0.1	-	0.4	0.1	0.02	-
K-mord.	17.7	3.5	6.9	2.0	8.1	0.8	0.2	0.2	0.3	0.3	0.07	0.3
K-beta	34.9	7.0	8.1	4.8	17.4	2.4	0.2	1.4	0.4	0.2	0.13	0.6
H.K-L	48.5	9.7	11.9	4.1	29.4	1.8	-	1.1	0.2	-	0.06	0.6
$AlCl_3$	34.1	6.8	12.2	2.0	12.3	1.6	-	-	0.7	5.3	0.06	-
Blank	12.2	-	-	10.5	1.7	-	-	-	-	-	-	-

[a] Reaction conditions: Catalyst = 50.5 g/mol of DPM; DPM = 0.006 mol; SO_2Cl_2 = 0.012 mol; 1,2-dichloroethane = 2 ml; Reaction temperature = 333 K; Reaction time = 1 h.

[b] Rate of DPM conv. is expressed as the mmol of DPM converted per gm of catalyst per hour.

[c] MCDPM = monochlorodiphenylmethanes; DCDPM = Dichlorodiphenylmethanes; A = 2-chlorodiphenylmethane; B = 3- chlorodiphenylmethane; C = 4-chlorodiphenylmethane; D = 2,4'-dichlorodiphenylmethane; E = 2,2'-dichlorodiphenylmethane; F = 4,4'- dichlorodiphenylmethane; G = α,α-dichlorodiphenylmethane; H = Others (polychlorinated diphenylmethanes).

[d] DC/MC ratio = dichlorodiphenylmethanes/ monochlorodiphenylmethanes ratio

[e] 4,4'/2,4' ratio = 4,4'- dichlorodiphenylmethane/2,4'- dichlorodiphenylmethane isomer ratio.

Zeolites K-X, K-Y and K-ZSM-5 and the conventional Lewis acid catalyst, $AlCl_3$, are found to be less active giving only MCDPM and higher amounts of polychlorinated products (others). Zeolites K-beta, K-mordenite and H.K-L are also less active and give little dichlorination. Blank reaction also gives very less conversion with monochlorinated products. Thus, the conversion of DPM and product yields mainly depend upon the type of the catalyst used in the chlorination reaction.

3.1.3.3.2. Duration of run using various catalysts

The conversion versus reaction time in the chlorination of DPM over various catalysts under similar reaction conditions is given in Fig. 3.10.

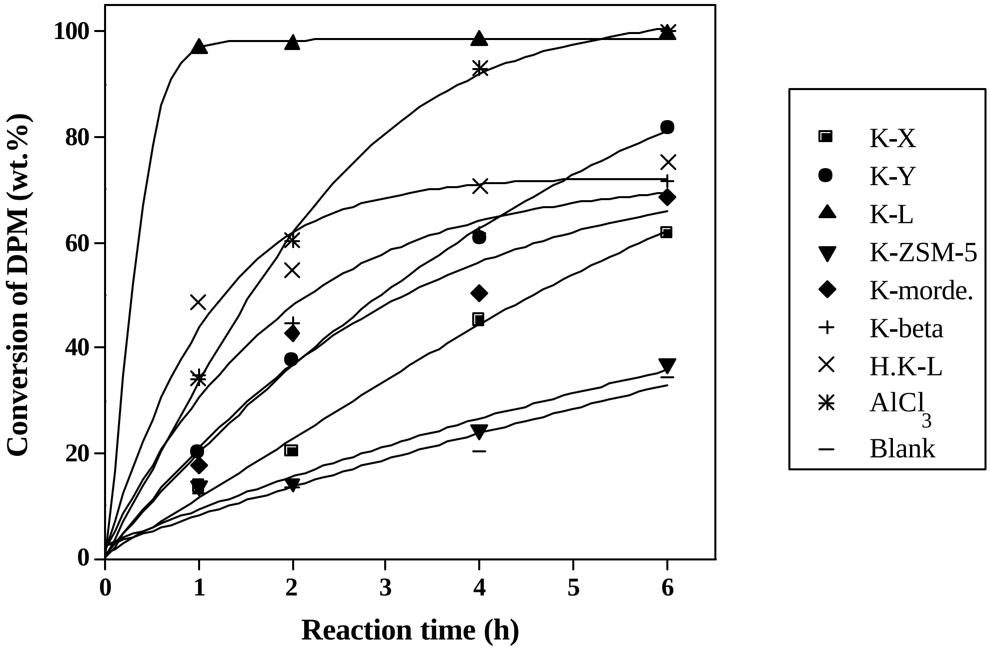


Figure 3.10. Chlorination of DPM with SO_2Cl_2: Effect of reaction time on the performance of various catalysts. Reaction conditions: See the footnotes to Table 3.10.

The conversion of DPM increases over all the catalysts with the progress of the reaction. However, zeolite K-L is highly active giving 96.8 wt.% conversion of DPM after 1 h which increased to 99.4 wt.% after 6 h of reaction time. Thus, the reaction is very fast in the presence of zeolite K-L. The conversion of DPM over the Lewis acid catalyst, AlCl$_3$ is found to be lower initially but increased slowly with time giving 100 wt.% conversion after 5 h.

Based on the conversion of DPM after 6 h of reaction time, the trend in the activities of the catalysts studied is as follows:

AlCl$_3$ > K-L > K-Y > H.K-L > K-mordenite > K-X > K-ZSM-5 > Blank.

3.1.3.3.3. Effect of reaction time using zeolite K-L

The performance of zeolite K-L catalyst at 333 K in terms of DPM conversion (wt.%), product yields (wt.%), DCDPM/MCDPM and 4,4'-DCDPM/2,4'-DCDPM ratios as a function of time on stream is presented in Figure 3.11.

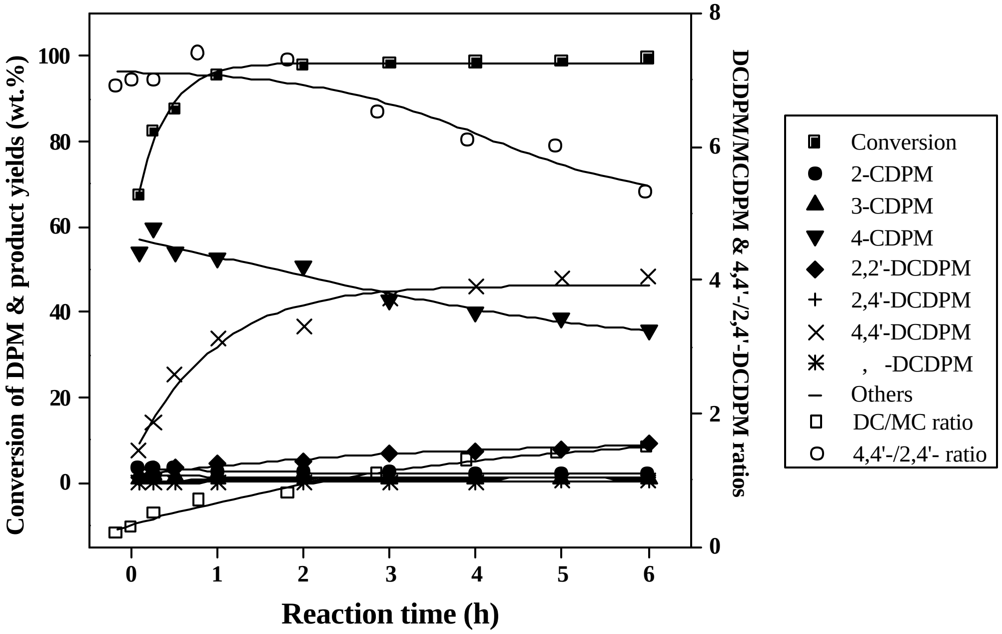


Figure 3.11. **Effect of reaction time on the conversion of DPM (wt.%), product yields (wt.%), DCDPM/MCDPM and 4,4'-DCDPM/2,4'-DCDPM ratios over zeolite K-L. Reaction conditions: See the footnotes to Table 3.10.**

The conversion of DPM and product yields increase with the duration of the run. The concentration of DCDPM increases with reaction time at the expense of MCDPM and hence the DCDPM/MCDPM ratio increases with time. It is interesting to note that the yield of 4-CDPM decreases and simultaneously the yield of 4,4'-DCDPM increases with the time which suggests that the formation of 4,4'-DCDPM takes place by the consecutive reaction of 4-CDPM. The level of DPM conversion (wt.%) and the yield of 4,4'-dichlorodiphenylmethane (wt.%) are found to be 99.4 wt.% and 48.5 wt.%, respectively, after 6 h of reaction time. The selectivity for 4,4'-DCDPM (4,4'-DCDPM/2,4'-DCDPM ratio) shows a slight decrease with time on stream. The polychlorinated products (others) are found to increase with time due to the increased conversion of DPM. The side-chain chlorinated product (α,α-DCDPM) remains almost constant throughout the reaction.

3.1.3.3.4. Influence of solvent

Table 3.11. presents the conversion of DPM (wt.%), rate of DPM conversion (mmolg^{-1}h^{-1}), product yields (wt.%), DCDPM/MCDPM as well as 4,4'-DCDPM/2,4'-DCDPM ratios obtained in the chlorination of DPM using zeolite K-L in the presence of dichloromethane (CH_2Cl_2), 1,2-dichloroethane (EDC), 1,1,1-trichloroethane (Cl_3CCH_3) chloroform ($CHCl_3$) and carbon tetrachloride. The nature of the reaction medium (solvent) plays an important role in the course of the liquid phase chlorination of aromatics over zeolite catalysts[4,8,15,23,]. Among the solvents used, the highest activity (rate of DPM conversion) is observed in CH_2Cl_2 whereas the highest selectivity (4,4'-DCDPM/2,4'-DCDPM ratio) is obtained in EDC at 313 K. The other solvents led to a lower activity as well as selectivity under similar reaction conditions at 313 K. Thus, the activity of K-L using these solvents can be arranged in the decreasing order of their activity at 313 K as follows:

$CH_2Cl_2 > CH_3CCl_3 > EDC > CHCl_3$ » CCl_4

The overall trend of the isomer ratio over these solvents at 313 K is found to be as follows:

EDC > CH_2Cl_2 > CH_3CCl_3 > $CHCl_3$ » CCl_4

Table 3.11. Solvent effect[a]

solvent	React. Temp (K)	DPM Conv (wt. %)	Conv. Rate[b] (mmol $g^{-1}h^{-1}$)	Product yields (wt.%)[c]								DC/MC[d]	4,4'-/2,4'-[e] ratio
				MCDPM			DCDPM						
				A	B	C	D	E	F	G	H		
EDC	313	67.4	13.4	3.2	0.7	50.8	1.5	0.3	8.3	0.3	2.3	0.2	5.5
	353	98.1	19.4	1.9	0.8	44.3	4.6	1.3	44.4	0.4	0.4	1.1	9.7
CCl_4	313	3.6	0.7	1.1	0.4	0.8	-	-	-	-	-	-	-
	348	47.1	9.3	12.1	4.2	28.0	2.3	-	0.8	0.3	0.6	0.1	0.3
$CHCl_3$	313	50.2	9.9	7.1	2.8	33.8	2.3	0.3	3.1	0.2	0.6	0.1	1.3
	333	50.4	10.0	15.7	3.9	25.9	2.5	-	1.0	0.9	0.7	0.1	0.4
CH_3CCl_3	313	72.3	14.3	7.5	1.6	49.5	3.6	0.6	7.9	0.4	1.3	0.2	2.2
	345	69.8	13.8	10.7	1.4	46.4	3.7	0.5	6.3	0.4	0.4	0.2	1.7
CH_2Cl_2	313	75.8	15.0	4.1	1.6	55.3	3.2	0.4	10.7	-	-	0.2	3.3

[a] Reaction conditions: Catalyst = 50.5 g/mol of DPM; DPM = 0.006 mol; SO_2Cl_2 = 0.012 mol; Solvent = 2 ml; Reaction time = 1 h.

[b,c,d,e] See the footnotes to Table 3.10.

EDC = 1,2-dichloroethane; CH_3CCl_3 = 1,1,1-trichloroethane.

The rate of DPM conversion has increased markedly on increasing the reaction temperature to the respective reflux temperatures in case of all the solvents except $CHCl_3$. Thus, EDC is found to the best solvent and the conversion of DPM (wt.%) and the 4,4'-DCDPM/2,4'-DCDPM isomer ratio obtained are 98.1 wt. % and 9.7, respectively, with a DCDPM/MCDPM ratio of 1.1, at 353 K after 1 h of reaction time. The other solvents give less selectivity at higher temperatures as compared to EDC.

3.1.3.3.5. Influence of catalyst concentration

Figure 3.12. shows the effect of concentration of zeolite K-L in the range of 0 to 117.8 g/mol of DPM on the conversion of DPM, product yields, DCDPM/MCDPM and 4,4'-DCDPM/2,4'-DCDPM ratios at 333 K for 0.083 h (5 min) of reaction time in the chlorination of DPM with SO_2Cl_2.

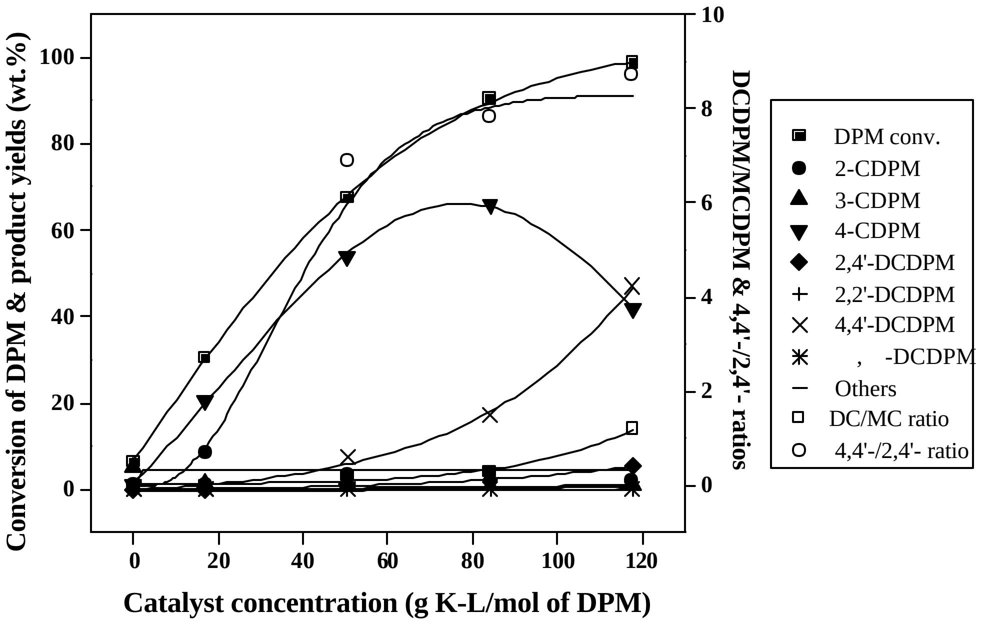


Figure 3.12. **Effect of catalyst (K-L) concentration on the conversion of DPM (wt.%), product yields (wt.%), DCDPM/MCDPM and 4,4'-DCDPM/2,4'-DCDPM ratios. Reaction conditions: DPM(mol) = 0.006; SO_2Cl_2 = 0.012 mol; EDC = 2 ml; Reaction temperature = 333 K; Reaction time = 0.083 h.**

Only MCDPM is formed with a very low conversion of DPM when no catalyst is used. The conversion of DPM increased from 30.4 to 98.6 wt.% when the catalyst loading is increased from 16.8 to 117.8 g/mol of DPM, respectively. Also, the yield of 4,4'-DCDPM increases with a decrease in the 4-CDPM yield as the concentration of catalyst K-L is increased. Thus, 47.1 wt.% 4,4'-DCDPM is obtained at 98.6 wt.% conversion level of DPM after 0.083 h of reaction time at the catalyst concentration of 117.8 g/mol of DPM. The DCDPM/MCDPM as well as 4,4'-DCDPM/2,4'-DCDPM ratios also increase with an increase in the catalyst concentration.

3.1.3.3.6. Influence of reaction temperature

The effect of reaction temperature on the conversion of DPM (wt.%), rate of DPM conversion (mmolg^{-1}h^{-1}), product yields (wt.%), DCDPM/MCDPM as well as 4,4'-DCDPM/2,4'-DCDPM ratios over zeolite K-L in the liquid phase chlorination of DPM with SO_2Cl_2 is illustrated in Figure 3.13.

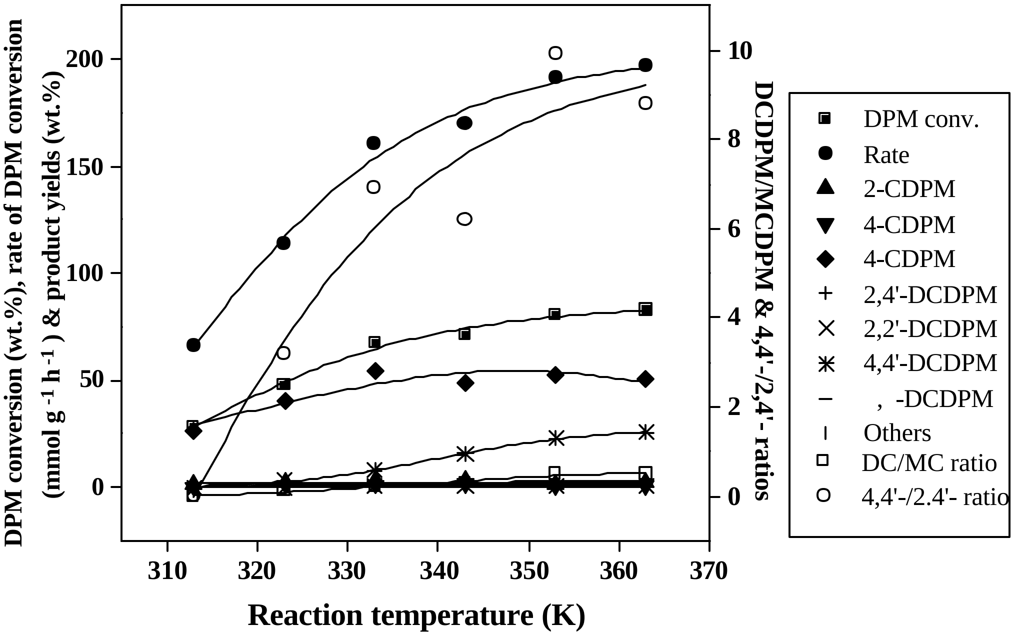


Figure 3.13. Effect of reaction temperature on the conversion of DPM (wt.%), rate of DPM conversion (mmolg^{-1}h^{-1}), product yields (wt.%), DCDPM/MCDPM and 4,4'-DCDPM/2,4'-DCDPM ratios over zeolite K-L. Reaction conditions: Catalyst (K-L) = 50.5 g/mole of DPM; DPM = 0.006 mol; SO_2Cl_2 = 0.012 mol; Reaction time = 0.083 h.

As expected, the rate of DPM conversion increases from 66.3 to 196.6 mmolg^{-1}h^{-1} when the reaction temperature is increased from 313 K to 363 K, respectively, after 0.083 h (5 min) of reaction time. At lower temperature (313 K) no DCDPM is detected. The DCDPM/MCDPM as well as the 4,4'-DCDPM/2,4'-DCDPM ratios increase with an increase in the reaction temperature.

The formation of 4,4'-DCDPM is favoured at higher temperature. The yield of 4-CDPM decreases thus increasing the required product (4,4'-DCDPM) with an increase in the reaction temperature. Thus, 25.5 wt.% 4,4'-DCDPM is obtained at 82.7 wt.% conversion level of DPM after 0.083 h of reaction time at 363 K.

3.1.3.3.7. Influence of HCl treated K-L catalysts

The chlorination of DPM was studied with zeolite K-L with different SiO_2/Al_2O_3 ratio obtained by the treatment of parent K-L with various molar solutions of HCl (0.05 to 0.7 M HCl). The results are presented in Table 3.12.

Table 3.12. Influence of HCl-treated zeolite K-L [a]

K-L	SiO_2/Al_2O_3 ratio	Deg of K^+-	DPM conv (wt. %)	Conv. Rate[b] (mmol g^{-1} h^{-1})	Product yields (wt.%)[c]								DC/MC[d]	4,4'-/2,4'-[e]
					MCDPM			DCDPM						
					A	B	C	D	E	F	G	H		
K-L	6.82	>98	67.4	160.9	3.2	1.1	53.9	1.1	0.3	37.6	0.1	0.1	0.2	6.9
K-L (0.05)[e]	7.43	>98	66.2	156.3	3.1	0.8	53.4	1.1	0.1	7.4	0.1	0.2	0.2	6.5
K-L (0.1)[e]	8.02	>98	60.2	143.7	3.3	0.7	47.4	1.1	0.3	6.8	0.3	0.3	0.2	6.2
K-L (0.3)[e]	8.63	>98	55.2	134.0	3.2	0.6	44.7	0.8	0.2	5.0	0.3	0.4	0.1	6.3
K-L (0.5)[e]	8.73	>98	46.1	110.1	2.8	0.5	38.0	0.6	0.2	3.3	0.3	0.4	0.1	5.5
K-L (0.7)[e]	9.01	>98	44.1	105.0	2.3	0.5	37.2	0.5	0.1	2.6	0.4	0.5	0.1	5.2

[a] Reaction conditions: Catalyst = 50.5 g/mol of DPM; DPM = 0.006 mol; SO_2Cl_2 = 0.012 mol; 1,2-dichloroethane = 2 ml; Reaction temperature = 333 K; Reaction time = 0.083 h.
[b,c,d,e] See the footnotes to Table 3.10.
[e] Values in parentheses correspond to the molarity of HCl solution taken for K-L treatmemt.

As can be seen from the results, the conversion of DPM decreases from 67.4 wt.% to 44.1 wt.% after 0.083 h (5 min) of reaction time, when the SiO_2/Al_2O_3 ratio of zeolite K-L is increased from 6.82 to 9.01, respectively. The DCDPM/MCDPM and 4,4'-DCDPM/2,4'-DCDPM ratios decrease with an increase in the framework SiO_2/Al_2O_3 ratio of zeolite K-L. The higher catalytic activity of fresh zeolite K-L compared to the treated zeolite K-L may be due to the lower SiO_2/Al_2O_3 ratio thus giving higher concentration of aluminium which in turn gives higher number of basic sites for the reaction. The low activity of 0.7 M HCl treated zeolite K-L may be attributed to a combined effect of higher SiO_2/Al_2O_3 ratio and lower crystallinity of zeolite K-L. Thus, higher numbers of basic sites as well as good crystallinity of zeolite K-L are the most important factors for the liquid phase chlorination of DPM.

3.1.3.3.8. Influence of DPM/SO_2Cl_2 molar ratio

The conversion of DPM, product yields, DCDPM/MCDPM as well as 4,4'-DCDPM/2,4'-DCDPM ratios obtained at different DPM/SO_2Cl_2 molar ratios are demonstrated in Table 3.13.

Table 3.13. Influence of DPM/SO_2Cl_2 molar ratio[a]

DPM/ SO_2Cl_2 Molar ratio	DPM Conv (wt %)	Conv Rate[b] mmol $g^{-1}h^{-1}$	Product yields, (wt.%)[c]								DC/ MC[d] ratio	4,4'/ 2,4'-[e] ratio
			MCDPM			DCDPM						
			A	B	C	D	E	F	G	H		
0.33	73.3	175.0	3.1	2.1	55.2	1.5	0.3	10.5	0.1	0.5	0.2	7.0
0.5	67.4	160.9	3.2	1.1	53.9	1.1	0.3	7.6	0.1	0.1	0.2	6.9
1.0	43.4	103.6	2.3	0.8	36.7	0.5	-	2.9	-	0.2	0.2	5.8
2.0	23.7	56.6	2.8	1.2	19.7	-	-	-	-	-	-	-
3.0	17.3	41.3	0.6	0.2	16.5	-	-	-	-	-	-	-
5.0	17.2	41.1	-	-	17.2	-	-	-	-	-	-	-

[a] Reaction conditions: Catalyst = 50.5 g/mol of DPM; DPM = 0.006 mol; 1,2-dichloroethane = 2 ml; Reaction temperature = 333 K; Reaction time = 0.083 h.
[b,c,d,e] See the footnotes to Table 3.10.

The conversion of DPM and the rate of DPM conversion decrease from 73.3 to 17.2 wt.%, and 175.0 to 41.1 (mmol$g^{-1}h^{-1}$), respectively, when the DPM/SO_2Cl_2 molar ratio is increased from 0.33 to 5, after 0.083 h (5 min) of reaction time. The higher molar ratios of DPM/SO_2Cl_2 (DPM/SO_2Cl_2 = 2,3 and 5) give only the formation of MCDPM with a lower conversion of DPM. The DCDPM starts appearing at the DPM/SO_2Cl_2 molar ratio of 1. Thus, 2.9 wt.% 4,4’-DCDPM is obtained at a DPM/SO_2Cl_2 molar ratio of 1 which is increased to 10.5 wt.% at a DPM/SO_2Cl_2 molar ratio of 0.33 and at 0.083 h (5 min) reaction time.

3.1.3.3.9. Recycle of the zeolite K-L

Table 3.14. gives the results of a catalyst recycling experiment using zeolite K-L in the chlorination of DPM at 333 K. After the completion of each reaction, the zeolite K-L was separated from the reaction mixture by filtration, washed with acetone and calcined in air at 773 K for 12 h. It is then characterized for the chemical composition and crystallinity. All the data refers to the calcined samples.

Table 3.14. Recycle of the catalyst K-L[a]

Run	SiO_2/ Al_2O ratio	Deg. K^+-in K-L	DPM conv (wt. %)	Conv rate[b] mmol $g^{-1}h^{-}$	Product yields (wt.%)								DC / MC[d]	4,4’- / 2,4’-[e]	K-L Crys tnty %
					MCDPM			DCDPM							
					A	B	C	D	E	F	G	H			
0	6.8	98.6	67.4	160.9	3.2	1.1	53.9	1.1	0.3	7.6	0.1	0.1	0.2	6.9	100
I	7.0	96.7	43.8	104.6	7.9	2.7	29.2	1.6	0.1	1.5	0.2	0.6	0.1	0.9	69

[a] Reaction conditions: Catalyst) = 50.5 g/mol of DPM; DPM = 0.006 mol; SO_2Cl_2 = 0.012 mol; 1,2-dichloroethane = 2 ml; Reaction temperature = 333 K; Reaction time = 0.083 h.

[b,c,d,e] See the footnotes to Table 3.10.

The aluminium and potassium content as well as crystallinity of K-L samples has been found to decrease after the first recycle. It has been observed that the activity of zeolie K-L is decreased in the first recycle with a drastic decrease in the 4,4’-DCDPM/2,4’-DCDPM ratio from 6.9 to 0.9, respectively, after 0.083 h (5 min) of reaction time. The sulfur dioxide and hydrochloric acid evolve continuously during the reaction, which affects the catalyst activity. In addition, the HCl formed in the reaction extracts aluminium and to some extent potassium from the framework positions of zeolite K-L.

Such type of extractions and the decrease in the crystallinity of zeolite K-L attribute to the decrease in the catalytic activity of zeolite K-L in the chlorination of DPM.

3.1.3.4. Conclusions

4,4'-DCDPM is formed selectively over zeolite K-L in the liquid phase chlorination of DPM with sulfuryl chloride as the chlorinating agent under mild reaction conditions. Other zeolite catalysts as well as the conventional Lewis acid catalyst, $AlCl_3$, are less selective compared to zeolite K-L. The yield of 4,4'-DCDPM increases with the duration of the run, catalyst (K-L) concentration, reaction temperature and concentration of the chlorinating agent (SO_2Cl_2). In all these cases, the 4,4'-DCDPM is obtained at the expense of the 4-CDPM, thus reducing the yield of MCDPM. 1,2-dichloroethane is found to be the best solvent and gives the highest selectivity for 4,4'-DCDPM (4,4'-DCDPM/2,4'-DCDPM isomer ratio = 9.7) at 353 K after 1 h. The increase in the SiO_2/Al_2O_3 molar ratio of zeolite K-L (by HCl treatment) progressively decreases the activity as well as the selectivity of the catalyst. On recycling, the conversion of DPM and 4,4'-DCDPM/2,4'-DCDPM isomer ratio decreases due to the extraction of small amount of aluminium and potassium (by HCl produced in the reaction) as well as the decrease in the crystallinity of zeolite K-L.

3.1.4. Reasons for higher selectivity in the chlorination of aromatics over zeolite K-L

The results obtained in highly selective chlorination reactions of benzyl chloride, cumene and diphenylmethane over zeolite K-L demonstrate that the conventional concept of geometry related shape-selectivity couldn't be related alone to explain the role of zeolite K-L in enhancing the para-selectivity. It is seen that zeolites of similar pore diameter but different structural types behave in different ways[8,12]. In addition, Wortel et al.[23] (in the bromination of halobenzenes), Botta et al.[8] (in the chlorination of biphenyl) and Singh et al.[14] (in the chlorination of toluene) suggested that factors such as size, charge and position of the cations and the electrostatic forces produced by them in the zeolite channels direct the substitution to get higher selectivity for para-products. It is also observed by Van Dijk et al.[4] that highly selective para-substitution in the halogenation of aromatics over zeolite catalysts may be attributed to a specific orientation of the substrate in the cavities of the zeolites resulting in the steric hindrance at the ortho-position and activation of the para-position by the electrostatic influences in the zeolite crystal. The combined effect of all these factors may be responsible for the selective formation of the para-products in the chlorination of above aromatics over zeolite K-L.

An increase in the isomer ratio is observed in the presence of 1,2-dichloroethane (EDC) at its reflux temperature (353 K) in case of the chlorination of all the above aromatics viz., benzyl chloride, cumene and diphenylmethane over zeolite K-L. The reasons for this higher selectivity may be summarized as: presumably, the higher dielectric constant of EDC (ionic medium) favours the easy formation of electrophile (Cl^+)[47] thus preventing the formation of radical ($Cl^\cdot$), which enhances the side-chain chlorination of the aromatic substrate[6]. The higher 4-/2- or 4,4'-/2,4'- isomer ratios observed in EDC in the chlorination of benzyl chloride, cumene or diphenylmethane at 353 K over zeolite K-L may be attributed to the higher polarity of EDC. In addition, it is also suggested[8,9] that solvents may influence the activation of the reactants or may affect the diffusion and transport processes in the zeolite channels, which may enhance the formation of the para-products.

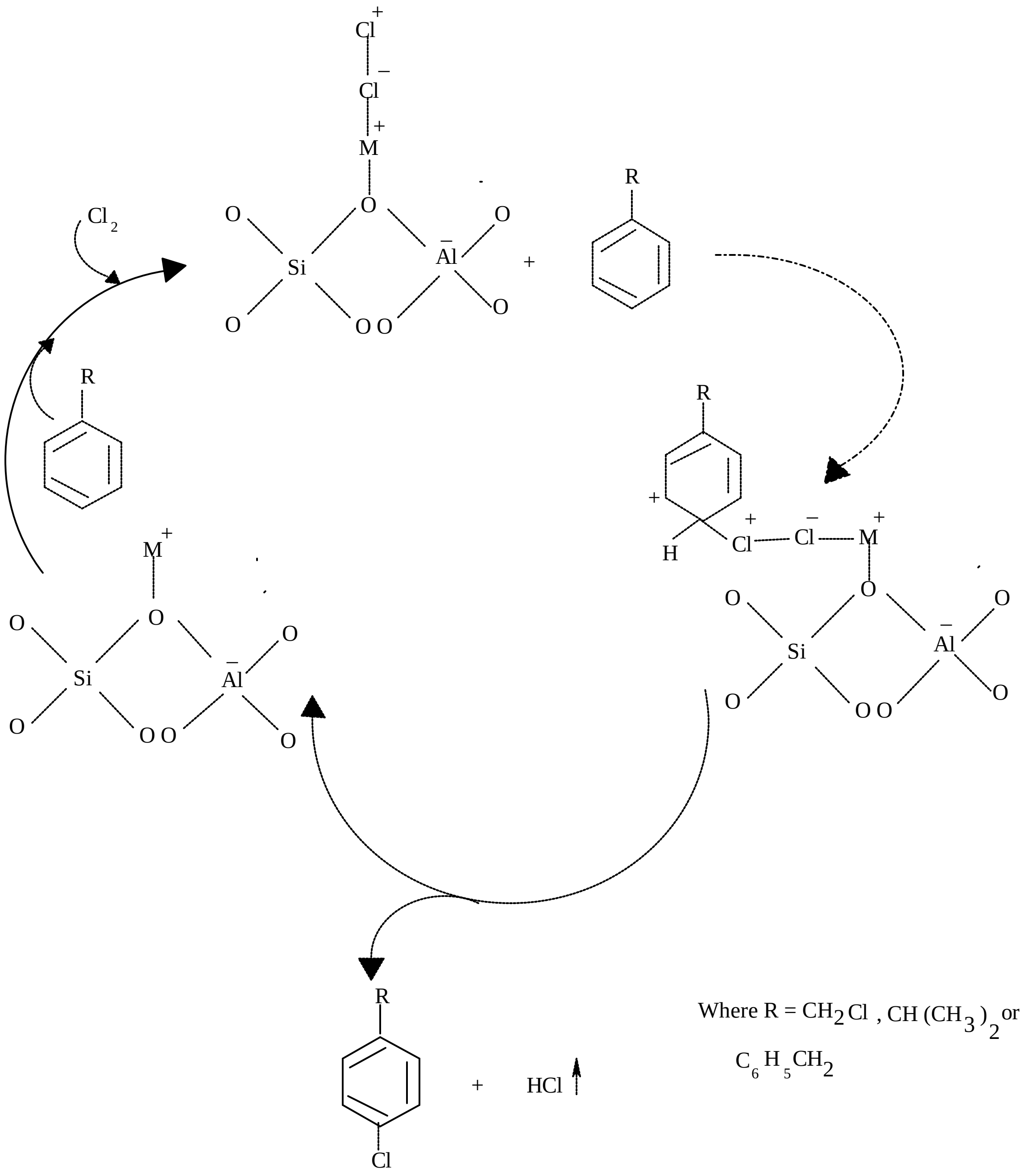
3.1.5. Mechanism for the zeolite catalyzed chlorination of aromatics

In the plausible mechanism[44-46] Cl_2 molecule is dissociated (eq. 2) heterolytically into an electrophile (Cl^+) over zeolite catalysts which then takes part in the electrophilic substitution process (Figure 3.14) resulting in the formation of ring chlorinated products[6,15]. The side-chain such as the a-chlorination of aromatics takes place by radical mechanism[6,24].

In case of sulfuryl chloride as the chlorinating agent, it (SO_2Cl_2) is first decomposed thermally to sulfur dioxide and molecular chlorine (eq. 1). The latter in the presence of zeolite catalysts cleaves heterolytically or is polarized and the positive halogen (Cl^+) serves as the electrophile for the aromatic substitution (eq. 2). The dichloro-aromatics are obtained by the consecutive reaction of the monochloro-compounds.

$$SO_2Cl_2 \dashrightarrow SO_2 + Cl_2 \quad \text{-----------------------} \quad (\text{eq. } 1)$$

$$Cl_2 \longrightarrow Cl^+ + Cl^- \quad \text{-----------------------------} \quad (\text{eq. . } 2)$$



Where R = CH_2Cl , $CH(CH_3)_2$ or $C_6H_5CH_2$

Figure 3.14. Mechanism for chlorination of aromatics over zeolites.

3.2. Bromination

Bromination processes are of importance not only for preparing specific desired end products (e.g. bromine-containing flame retardants), but also as a means of preparing reactive intermediate[48]. Conventionally, the ring bromination of aromatics with N-bromosuccinimide (NBS) or liquid bromine (Br_2) is catalyzed by Lewis acids such as chlorides of aluminium, zinc and iron[49]. Lambert et al.[50] reported on the bromination of benzene and toluene using the NBS-H_2SO_4-H_2O system. However, these methods are unsuitable for the industrial bromination of aromatic compounds owing to the need for stoichiometric amount of the catalyst, formation of polybrominated products and difficulty of separation of catalyst from the final product. During the last decade, there has been an increasing demand for the solid catalysts due to important advantages over soluble mineral acids and metal halides. In addition, the bromination of aromatics mediated by silica gel has been reported[51-54]. Zeolites are well-known materials widely used in petrochemical industries[1,2]. More recently, zeolite catalyzed chlorination of aromatic compounds has attracted considerable attention owing to their simplicity and shape-selectivity[11-20]. However, the use of zeolite as catalyst in the bromination of aromatics has been limited[23,55-61]. Thus, the aim of the present study is to carry out liquid phase selective bromination of ethyl benzene over zeolite catalysts for the synthesis of industrially important para-compounds.

3.2.1. Selective bromination of ethyl benzene to 4-bromoethylbenzene

3.2.1.1. Introduction

Ring brominated alkyl benzenes are useful as intermediates for fungicides, insecticides and fire-retardants[62]. Conventionally, the ring bromination of aromatics is catalyzed by homogeneous Lewis acids such as $AlCl_3$, $FeCl_3$ or $ZnCl_2$[49]. The nuclear bromination of ethyl benzene (EB) has been achieved in the presence of silicic acid with bromine as the halogenating agent[62]. Furthermore, brominated ethyl benzenes have been obtained with $GaBr_3$ as a catalyst in the presence of CCl_4[63]. But this method mostly gives polybrominated ethyl benzenes. In another method, monobromination of ethyl benzene was carried out with NaBr or KBr in the presence of NaOCl in acidic medium containing aq. HCl or aq. H_2SO_4[64]. In addition, Swamy et al, have reported[65] N-N'-trimethylenebis [2-aminobenzamide] and lanthanide chlorides to catalyze the bromination of arenes by bromine stereospecifically. But these reported methods are not suitable industrially and thus the need is to brominate ethyl benzene selectively, to 4-bromoethyl benzene, (4-BrEB) in presence of zeolite catalysts. A couple of reactions with N-bromosuccinimide (NBS) as the brominating agent have also been reported. The influence of various catalysts, catalyst concentration, reaction temperature, EB:Br_2 molar ratio as well as the recycle of zeolite K-L has been examined on the conversion of EB and product yields (wt.%), rate of EB conversion (mmolg^{-1}h^{-1}), and the selectivity for 4-bromoethyl benzene (4-BrEB/2-BrEB isomer ratio) using zeolite K-L in the bromination of ethyl benzene with liquid bromine. The results obtained over zeolite K-L (with bromine) and with zeolite H-beta (with NBS) are compared with those obtained over the conventional catalysts, $FeCl_3$ or H_2SO_4, respectively.

3.2.1.2. Experimental

The synthesis of various catalysts, their modification and characterization are carried out as described in Chapter 2. Some physico-chemical properties of the zeolites used in this study are presented in Tables 2.2 and 2.3.

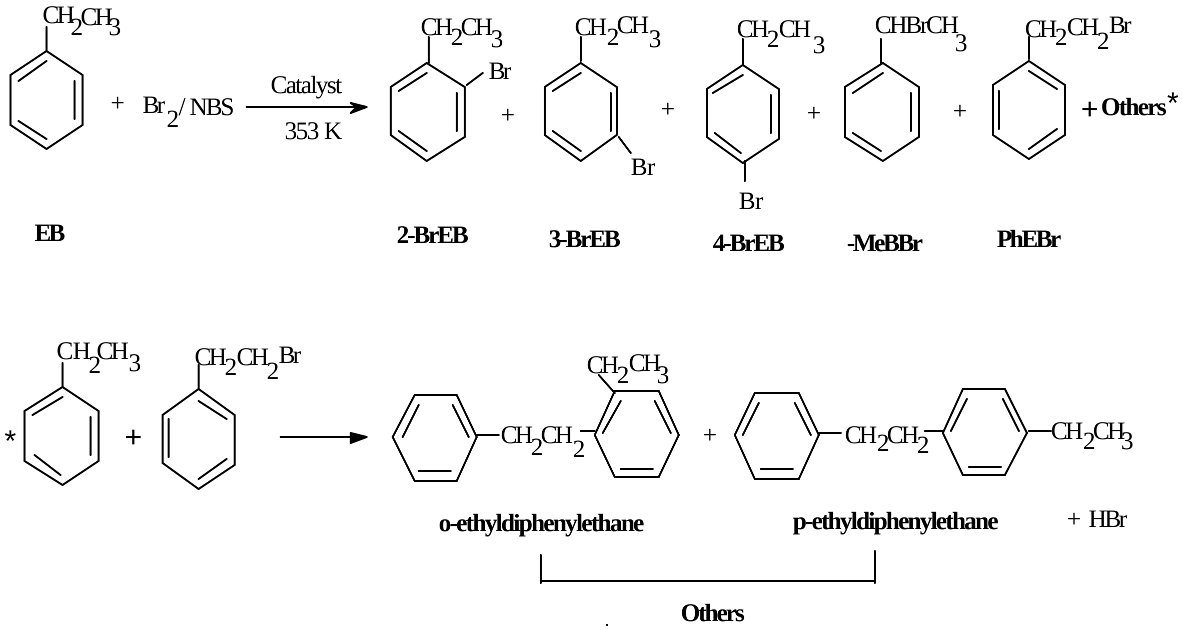
In a typical batch reaction a sample of activated catalyst (0.75 g), EB (0.047 moles), and liquid bromine or NBS (0.0094 moles) were taken in a mechanically stirred, closed, 50 ml glass reactor fitted with a reflux condenser, a thermometer and a septum for withdrawing the samples. The batch reactor was placed in a thermostat at the required reaction temperature. The samples were taken periodically, neutralized by $NaHCO_3$ and analyzed by Gas-chromatograph (HP GC 6890). Product identification was done with reference to standard samples and GCMS (Shimadzu, QP 2000A).

Conversion is defined as the percentage of EB transformed. The rate of EB conversion ($mmolg^{-1}h^{-1}$) is calculated as the amount of EB (mmol) converted per hour per gram of the catalyst. The yield percentage of product represents the amount of the product calculated from selectivity multiplied by the conversion and divided by 100.

3.2.1.3. Results and Discussion

3.2.1.3.1. Influence of various catalysts

The bromination of ethyl benzene (EB) with liquid bromine over various catalysts, without any catalyst and the conventional Lewis acid catalyst, $FeCl_3$, is presented in Table 3.15. The Bromination of EB over H-beta and H_2SO_4 with N-bromosuccinimide (NBS) is also carried out under identical reaction conditions, and the results also are listed in Table 3.15. The reaction produces a mixture of 2-bromoethylbenzene (2-BrEB) and 4-bromoethylbenzene (4-BrEB) as the main reaction products and the side chain brominated products, α-methylbenzyl bromide (α-MeBBr) and phenylethyl bromide (PhEBr) as the side-chain products. In addition, o- and p-ethyldiphenylethane (others) are also obtained over all catalysts (scheme 3.5). The consecutive products (polybrominated products) are not observed may be because of lower reaction temperature and higher $EB:Br_2$ (5:1) or EB:NBS (5:1) molar ratio. The formation of 2-BrEB and 4-BrEB takes palce by parallel reactions[16,4], whereas the firmation of side-chain brominated products such as α-MeBBr and PhEBr takes place by the radical mechanism[6,7,66]. Further, PhEBr reacts with ethylbenzene resulting in the formation of o-ethyldiphenylethane and p-ethyldiphenylethane (Scheme 3.5).



Scheme 3.5

Among the zeolite catalysts studied, zeolite K-L and zeolite H-beta gave comparable selectivity (4-BrB/2-BrEB = 2.3) whereas a very high amount of others are observed over H-beta (10.6 wt. %) compared to K-L (2.2 wt. %). The higher amount of others over zeolite H-beta may be attributed to its strong acidity. Zeolites K-ZSM-5 and H.K-L are active catalysts for the nuclear brominated products and give less amounts of the side chain products and others. The reaction with zeolite K-X and without any catalyst produces mainly the side-chain products and others in higher yields. The conventional catalyst, $FeCl_3$, is found to be comparable with zeolite K-L in terms of activity and selectivity. However, no side-chain product and trace amount of others are obtained over $FeCl_3$ catalyst.

Zeolite H-beta is found to be superior to the conventional catalyst, H_2SO_4, in terms of selectivity for 4-BrEB when the reaction was carried out with N-bromosuccinimide (NBS) under identical reaction conditions (Table 3.15). Mainly the nuclear brominated products are obtained over H-beta[3,6,7,61] with less amounts of others and side chain products, when NBS was used as the brominating agent.

Table 3.15. Bromination of ethyl benzene[a]

Catalyst	EB conv. (wt.%)	Conv. Rate[b] (mmol $g^{-1}h^{-1}$)	Product yields (wt.%)[c]					4-Br/2-Br ratio[d]
			2-BrEB	4-BrEB	α-MeBBr	PhEBr	Others	
K-X	12.6	15.8	1.9	3.8	2.6	0.1	4.2	2.0
K-mord.	16.2	20.3	2.7	5.3	1.0	-	7.2	2.0
K-ZSM-5	15.2	19.1	4.3	8.9	0.2	0.1	2.1	2.1
K-L	19.5	24.5	5.0	11.3	0.8	0.2	2.2	2.3
H.K-L	11.1	13.9	2.4	4.3	0.1	0.1	3.5	1.8
K-beta	18.0	22.6	1.8	4.0	1.7	-	10.5	2.2
H-beta	17.7	22.2	2.1	4.6	0.4	-	10.6	2.3
$FeCl_3$	20.0	25.1	5.8	13.5	-	-	0.7	2.3
No catalyst	10.9	13.7	1.0	2.0	2.7	-	5.2	2.0
H-beta[e]	8.2	10.3	0.9	4.0	0.2	-	3.3	4.5
H_2SO_4[e]	7.8	9.8	2.3	3.4	0.4	-	1.8	1.5

[a] Reaction conditions: Catalyst = 15.93 g/mol EB ; Ethyl benzene () = 0.047 mol; Liq. Br_2 = 0.0094 mol ; Reaction temperature = 353 K; Reaction time = 0.5 h.

[b] Rate of EB conversion is expressed as the millimoles of EB converted per hour per g of catalyst.

[c] 2-BrEB = 2-bromoethyl benzene; 3-BrEB = 3-bromoethyl benzene; 4-BrEB = 4-bromoethyl benzene; α-MeBBr = α-methyl benzyl bromide; PhEBr = Phenylethyl bromide; Others = o-ethyldiphenylethane and p- ethyldiphenylethane.

[d] Isomer ratio of 4-bromoethyl benzene to 2-bromoethyl benzene.

[e] Bromination with N-bromosuccinimide (NBS); Reaction conditions: Catalyst = 15.93 g/mol EB; Ethyl benzene = 0.047 mol ; NBS = 0.0094 mol; Reaction temperature = 353 K; Reaction time (h) = 2.

3.2.1.3.2. Influence of catalyst concentration

The effect of concentration of zeolite K-L on the conversion of EB, product yields and selectivity for 4-BrEB (4-BrEB/2-BrEB isomer ratio) in the bromination of EB with liquid Br_2 is presented in Fig. 3.15.

The catalyst amount was changed every time by keeping the moles of EB constant in the reaction mixture under identical reaction conditions.

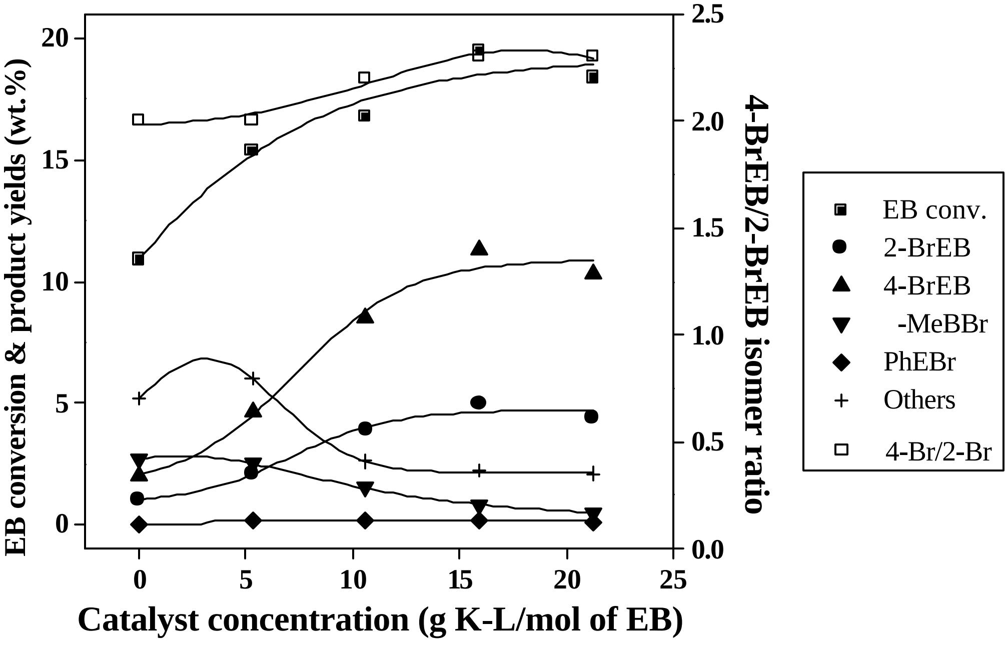


Figure 3..15. **Effect of catalyst (K-L) concentration on the conversion of EB (wt.%), product yields (wt.%) and 4-BrEB/2-BrEB isomer ratio. Reaction conditions: See footnotes to Table 3.15.**

When the catalyst concentration was increased from 0 to 15.9 g/mol of EB, the conversion of EB increased from 10.9 to 18.5 wt.%, respectively, beyond which it leveled off. This increase in the EB conversion is mainly because of significant increase in the yield of 4-BrEB with increase in the catalyst concentration. Furthermore, the yields of side chain products as well as others are found to be reduced on increasing the catalyst concentration. The selectivity shows a marginal increase with an increase in the catalyst concentration. Thus, zeolite K-L mainly gives the nuclear brominated ethyl benzenes with liquid Br_2.

3.2.1.3.3. Influence of reaction temperature

Figure 3.16. represents the effect of reaction temperature on the conversion of EB, product yields and selectivity for 4-BrEB (4-BrEB/2-BrEB isomer ratio) in the bromination of EB with liquid Br_2.

The conversion of EB and the rate of EB conversion increased from 12.1 to 20.0 wt.% and 15.2 to 25.1 mmolg^{-1}h^{-1}, respectively, as the reaction temperature is increased from 313 to 373 K. The increase in the EB conversion is associated with increased yields of the nuclear brominated products. The concentration of the side chain products as well as the selectivity remains almost constant with increase in the reaction temperature. The yields of others, however, increase with an increase in the reaction temperature.

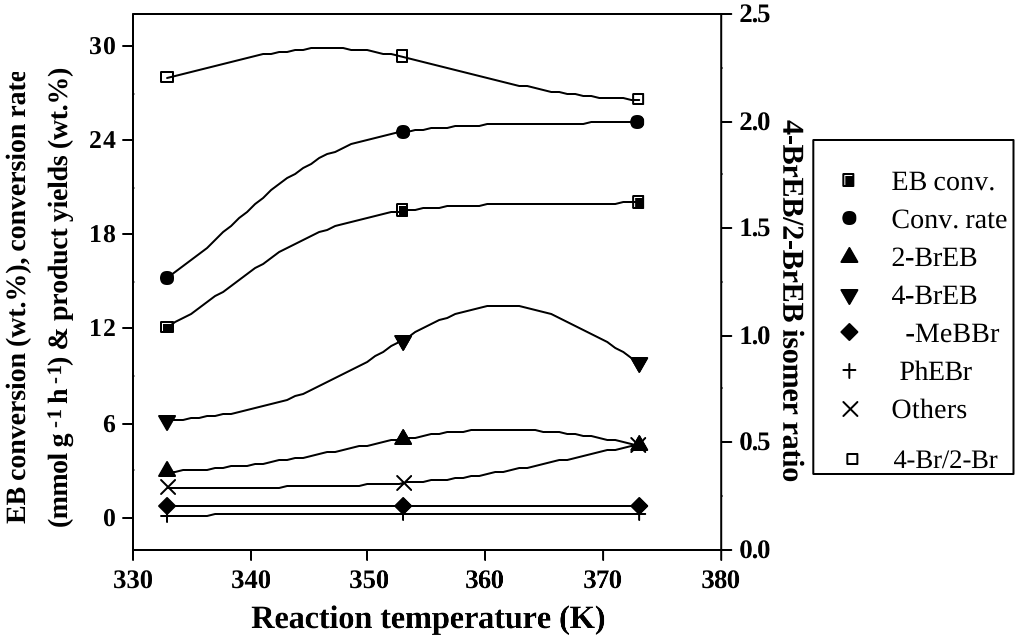


Figure 3.16. **Effect of reaction temperature on the conversion of EB (wt.%), rate of EB conversion (mmolg^{-1}h^{-1}), product yields (wt.%) and 4-BrEB/2 -BrEB isomer ratio. Reaction conditions: See footnotes to Table 3.15.**

3.2.1.3.4. Influence of EB:Br$_2$ molar ratio

The EB:Br$_2$ molar ratio was changed by keeping the amount of EB constant. The conversion of EB and the rate of EB conversion decreased from 80.7 to 12.2 wt.% and 101.3 to 15.3 mmolg^{-1}h^{-1} as the EB:Br$_2$ molar ratio was increased from 1 to 7, respectively. The isomer ratio, however, remains almost constant. (Fig. 3.17).

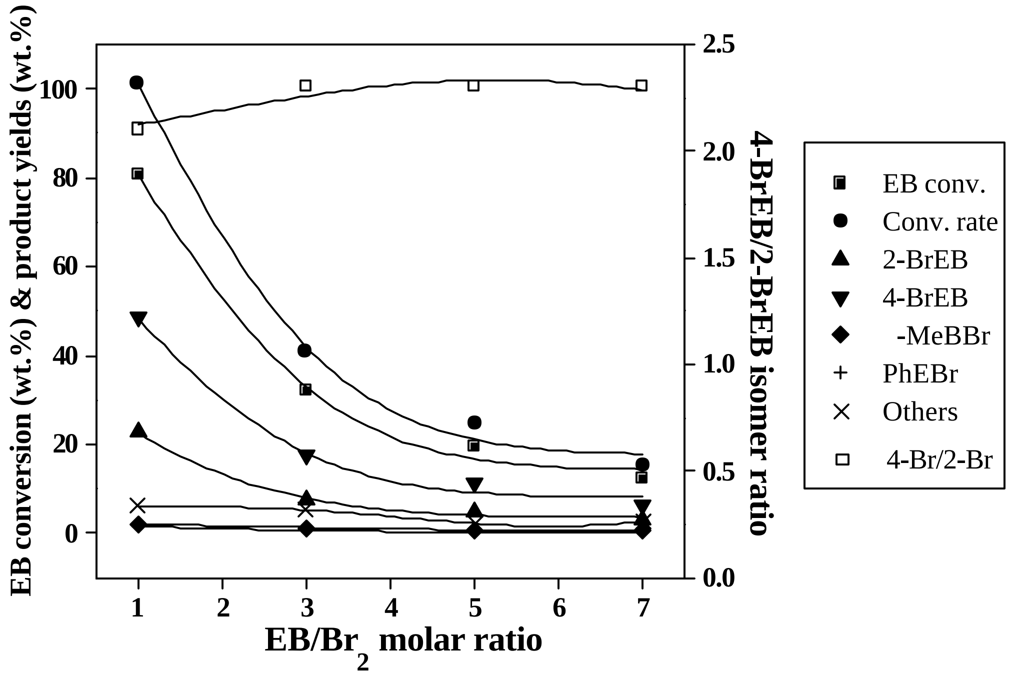


Figure 3.17. Effect of EB:Br$_2$ molar ratio on the EB (wt.%), product yields (wt.%) and 4-BrEB/2-BrEB isomer ratio.
Reaction conditions: See footnotes to Table 3.15.

3.2.1.3.5. Recycle of zeolite K-L

Zeolite K-L was recycled two times in the bromination of EB with liquid Br$_2$ under identical reaction conditions (Table 3.16.). The catalyst was separated from the reaction mixture after the completion of the reaction, washed with acetone, dried and heated at 773 K in air for 12 h and then characterized by XRD and chemical analysis after each run. It is clear from Table 3.16, that there is a decrease in the conversion of EB as well as the isomer ratio of 4-BrEB/2-BrEB after each run. Also, the yields of the side chain products as well as others are increased considerably after each recycle. This deactivation of the catalyst after recycling may be attributed to the reduced crystallinity of the catalyst as well as extraction of some amount of K and Al from the zeolite by the HBr liberated during the reaction.

Table 3.16. Recycle of zeolite K-L[a]

Run	SiO_2/Al_2O_3 ratio	K^+ deg in K-L	EB Conv (wt.%)	Conv rate[b] (mmol $g^{-1}h^{-1}$)	Product yields (wt.%)[c]					4-Br/2-Br[d] ratio	K-L Crystnty (%)
					2-Br EB	4-Br EB	α-Me BBr	Ph EBr	Others		
0	6.8	98.6	19.5	24.5	5.0	11.3	0.8	0.2	2.2	2.3	100
I	7.1	96.5	13.3	16.7	2.1	4.1	1.5	0.2	5.5	1.9	n.d.[e]
II	8.0	94.1	9.8	3.1	1.2	1.8	1.7	0.3	4.8	1.5	Amp.

[a,b,c,d] See the footnotes to Table 3.15.
[e] Amorphous.

3.2.1.4. Mechanism

Mechanistically, it is believed[24,66,78-81] that bromination of ethyl benzene proceeds by the generation of an electrophile (Br^+) which is produced by the heterolytic cleavage of Br_2/NBS by the catalyst. Thus, the generated Br^+ attacks the benzene ring resulting in the formation of brominated nuclear products. The side-chain or α-bromination of aromatics takes place by radical mechanism.

3.2.1.5. Conclusions

Zeolite K-L is found to be comparable in activity and selectivity to the conventional Lewis acid catalyst, $FeCl_3$ in the liquid phase bromination of EB with liquid Br_2. Zeolites K-beta, K-mordenite and H-beta give higher yield of others with Br_2, whereas, zeolite K-X and the reaction without any catalyst mainly gives the side chain product, α-methylbenzyl bromide. Zeolite H-beta is found to be superior to the conventional catalyst, H_2SO_4 in the liquid phase bromination of EB with NBS, giving less amounts of the side chain products and others compared to those with liquid Br_2. Increase in the catalyst K-L concentration as well as reaction temperature favours the formation of 4-BrEB with a decrease in the side chain products as well as others with liquid Br_2. An increase in the EB:Br_2 molar ratio decreases the EB conversion and product yields keeping the selectivity almost constant. The catalyst K-L was recycled two times with a decrease in the EB conversion and selectivity for 4-BrEB after each run because of the reduced crystallinity of K-L as well as the extraction of small amounts of K and Al from the zeolite after each cycle. The plausible mechanism involves an aromatic electrophilic substitution by an electrophile (Br^+) generated by the polarization of Br_2 or NBS by the catalyst.

3.3. Iodination

3.3.1. Selective iodination of chlorobenzene to 4-iodochlorobenzene.

3.3.1.1. Introduction

Iodoaromatic compounds are important in metabolism and radio labeling studies. Thyroid hormones, amphetamines and cortico-steriods have been investigated using radio-iodine derivatives[67]. Direct chlorination and bromination of aromatic compounds are well known. However, the direct and selective iodination of aromatic compounds with molecular iodine is much more difficult owing to lower electrophilic strength of iodine molecule. Conventionally, the iodination of chlorobenzene (CB) has been achieved with ICl or a Cl-I mixture in the presence of homogeneous catalysts such as $MoCl_5$, $FeCl_3$ and/or lanthanide chlorides with a p-/o- ratio of 5.5[68]. Furthermore, in the presence of aq. CF_3COOH, the iodination of chlorobenzene has been carried out with alkali or ammonium meta halides with nitrate promoters[69]. Direct iodination of chlorobenzene in HOAc containing H_2SO_4 and HNO_3 gave 65% yield of para-iodochlorobenzene after 35.5 min at 384 K[70]. The use of mineral acids and metal halides in the iodination reactions poses some major problems like the difficulty of separation of the catalyst from the final reaction mixture, requirement of stoichiometric amount of the catalyst, lower para-selectivity and hazardous reaction conditions. ICl, without involving a Friedel-Crafts catalyst has also been used as an iodinating agent, but its applicability so far is limited because the reaction is not para-selective[71-75]. The direct iodination of chlorobenzene has also been reported with IF made in situ from the corresponding elements without a Friedel-Crafts catalyst[67], but again with a lower selectivity. Recently, zeolite catalysts have been found to catalyze the selective chlorination[7-20] and bromination [23,58,61] of a variety of aromatic substrates. However, only a few reports are available on the selective iodination of aromatics over zeolites[76]. Furthermore, the reports regarding the use of zeolite catalyst in selective liquid phase iodination of chlorobenzene with ICl are scarce. In one method[77], the vapour phase iodination of chlorobenzene at 300^0 C is carried out with air and I in the presence of Na-X zeolite. Therefore, the aim of the present work is to achieve the formation of para-iodochlorobenzene (p-ICB) in high selectivity with ICl in presence of zeolite catalysts under mild reaction conditions. Thus, the present work reports liquid phase iodination of chlorobenzene selectively to para-iodochlorobenzene with ICl in the presence of zeolite catalysts. The results obtained over the zeolite catalysts are compared with those over the conventional homogeneous catalysts. The influence of various parameters such as catalyst concentration, reaction temperature, reaction time, chlorobenzene to ICl molar ratio and recycle of the catalyst has also been studied.

3.3.1.2. Experimental

The zeolites used, their synthesis and physico-chemical characterization have already been reported in Chapter 2. Table 2.3. lists some of their important properties. The zeolite samples were activated in air at 473 K for 2 h, prior to the reaction.

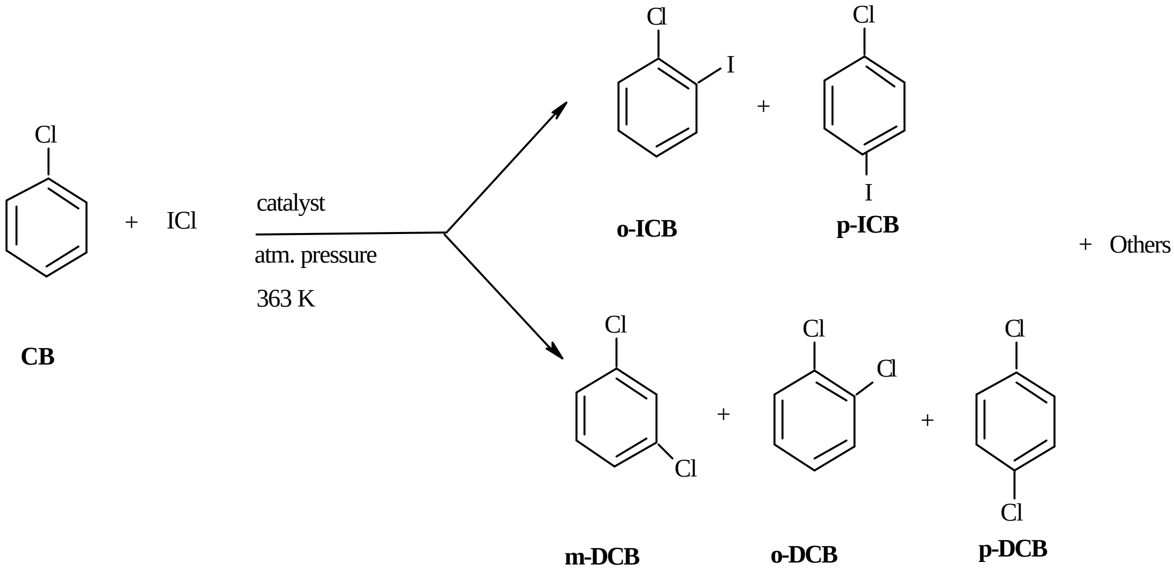
In a typical reaction procedure, 5 g (0.04 mol) of chlorobenzene, 1.44 g (0.0088 mol) of ICl and 0.5 g activated catalyst were mixed in a small round bottom glass flask, fitted with a condenser and a rubber septum for withdrawing the samples. The flask was heated at the required reaction temperature (363 K) with continuous stirring. The product was collected periodically and analyzed by gas-chromatograph (HP 6890) equipped with a FID detector and a Capillary column (50m x 200μm x 0.33 μm) with phenyl methoxy silicone gum. The authentic samples as well as the GCMS (Shimadzu, QP 2000 A) analyses confirmed the products of the reaction.

The conversion of CB is calculated as the amount of CB transformed whereas the rate of CB conversion is the millimoles of CB converted per g of catalyst per hour. The product yields are calculated as the selectivity for a particular product multiplied by the conversion.

3.3.1.3. Results and discussion

3.3.1.3.1 Influence of various catalysts

Table 3.17. lists the results obtained in the liquid phase iodination of CB with ICl over various catalysts at 363 K under atmospheric pressure after 5 min of reaction time. In all the reactions, the iodiantion of CB is accompanied by simultaneous chlorination[71-75], the extent of which depends upon the type of the catalyst used. The reaction produces a mixture of para-iodochlorobenzene (p-ICB), orhto- iodochlorobenzene (o-ICB), meta-dichlorobenzene (m-DCB), para-dichlorobenzene (p-DCB), ortho-dichlorobenzene (o-DCB), along with trace amount of polyhalogenated products (others), as shown in Scheme 3.6.



Scheme 3.6

It is clear from the results that the selectivity for p-ICB (p-ICB/o-ICB isomer ratio) as well as the extent of iodination (ICB/DCB ratio) depend strongly upon the type of the catalyst used in the reaction. Zeolites H-Y and RE (70.6)Y are highly active and selective and the rate of CB conversion and the selectivity (p-ICB/o-ICB isomer ratio) over these catalysts is found to be 128.8 and 135.5 mmolg^{-1}h^{-1} and 13.4 and 13.8, respectively, after 5 min of reaction time. Zeolite RE-Y is, however, more superior to H-Y in that it gives higher yield of iodinated products (ICB) than the chlorinated products (DCB) (ICB/DCB = 2.7). Zeolite H-beta is found to be selective (p-ICB/o-ICB = 11.5) but is less active and gives lower yields of iodinated products compared to H-Y and RE-Y. Other zeolite catalysts (H-ZSM-5 and H-mordenite) as well as SiO_2 are neither active nor selective. The conventional catalyst, H_2SO_4, is moderately active but poorly selective. The reaction without any catalyst gives the lowest selectivity to p-ICB. The lower conversion of CB in the absence of any catalyst may be attributed to the presence of unreactive ICl_2 (or $HICl_2$) species in the reaction mixture produced by the combination of iodine monochloride and liberated hydrogen chloride during the course of the reaction (eq. 4 of scheme 3.7)[71-75].

Table 3.17. Iodination of chlorobenzene (CB) [a]

Catalyst	CB Conv (wt. %)	Conv. Rate[b] (mmol g^{-1}h^{-1})	Product yields (wt.%)[c]						p-ICB/ o-ICB[d]	ICB/ DCB[e]
			DCB			ICB				
			m-DCB	p-DCB	o-DCB	p-ICB	o-ICB	Others		
H-beta	6.9	76.6	0.1	3.0	1.3	2.3	0.2	0.03	11.5	0.6
H-Y	11.6	128.8	0.1	3.0	1.4	6.7	0.5	-	13.4	1.3
H-ZSM-5	5.7	63.3	0.04	2.9	1.2	1.1	0.2	0.1	7.1	0.3
H-mord.	4.9	54.4	0.1	2.7	1.1	0.8	0.2	-	5.2	0.3
RE (70.6)Y	12.2	135.5	-	2.3	1.0	8.3	0.6	-	13.8	2.7
SiO_2	4.5	50.7	0.1	2.4	1.0	0.8	0.1	0.1	6.4	0.3
H_2SO_4	7.8	86.6	0.1	3.5	1.4	2.4	0.6	0.1	4.1	0.6
None	8.3	92.2	0.1	4.4	1.9	1.5	0.4	-	4.3	0.3

[a] Reaction conditions: Catalyst = 11.25 g/mol CB; CB = 0.04 mol; ICl = 0.008 mol; Reaction temperature = 363 K; Reaction time = 0.08 h.

[b] Conversion rate is expressed as the mmol of CB converted per g of catalyst per hour.

c DCB = dichlorobenzenes; ICB = iodochlorobenzenes.
m-DCB = meta-dichlorobenzene; p-DCB = para-dichlorobenzene; o-DCB = o- dichlorobenzene; p-ICB = para-iodochlorobenzene; o-ICB = orhto-iodochlorobenzene; Others = Polyhalogenated products.

[d] isomer ratio of para-iodochlorobenzene/ortho-iodochlorobenzene.

[e] ratio of iodochlorobenzenes/dichlorobenzenes.

Table 3.17. shows that the selectivity for p-ICB not only depends upon the pore structure of the zeolite but probably on the acid strength of the catalyst, electrostatic forces produced in the zeolite channels and the restricted orientation of the adsorbed molecule in the pores of the zeolite[7,8,14-17,23,58]. Thus, zeolite RE-Y is found to be the most active and selective catalyst in the iodination of chlorobenzene to p-iodochlorobenzene with ICl.

3.3.1.3.2. Duration of run using various catalysts

The influence of reaction time on the conversion of CB over various catalysts at 363 K under atmospheric pressure is illustrated in Fig. 3.18.

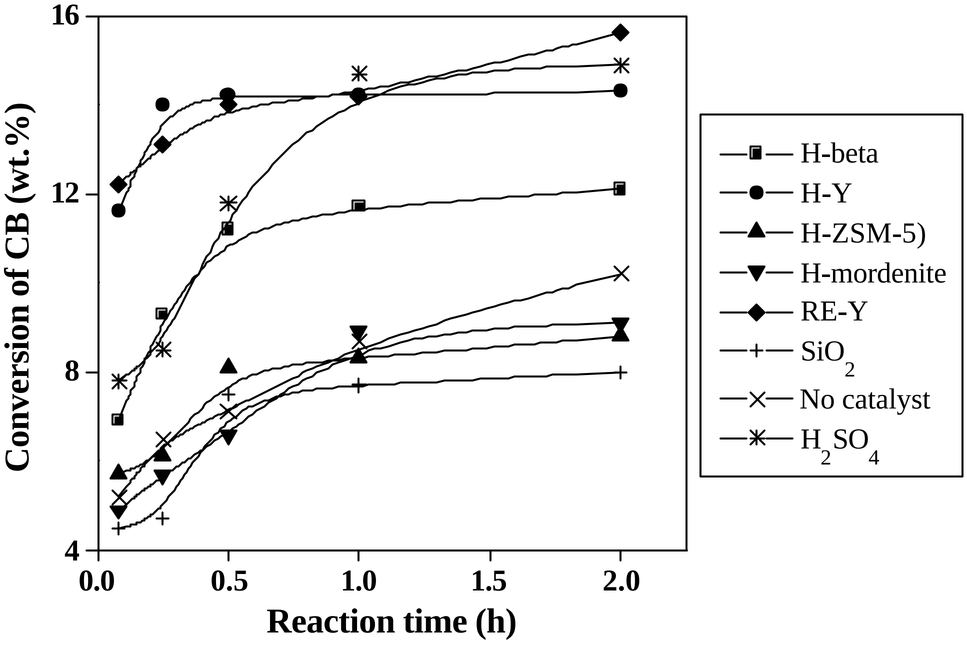


Figure 3.19. Iodination of chlorobenzene with ICl: Effect of reaction time on the performance of various catalysts. Reaction conditions: See the footnotes to Table 3.17.

Increasing the reaction time increased the conversion of CB over all the catalysts. However, in case of zeolites H-Y and RE-Y, the reaction is very fast and a higher conversion of CB is observed in the initial 0.083 h of reaction time showing that zeolites

H-Y and RE-Y are the most reactive catalysts in the iodination of CB. In case of other catalysts the conversion increased slowly with time. Zeolite H-beta and the conventional catalyst, H_2SO_4 are found to be less active initially compared to H-Y or RE-Y, but the conversion increased gradually with time. Zeolites H-ZSM-5, H-mordenite and SiO_2 are less active.

3.3.1.3.3 Duration of run with H-beta and RE-Y

The performance of zeolites H-beta and RE-Y at 363 K in terms of CB conversion, product yields, ICB/DCB ratio and p-ICB/o-ICB ratio as a function of time on stream is presented in Fig. 3.20.

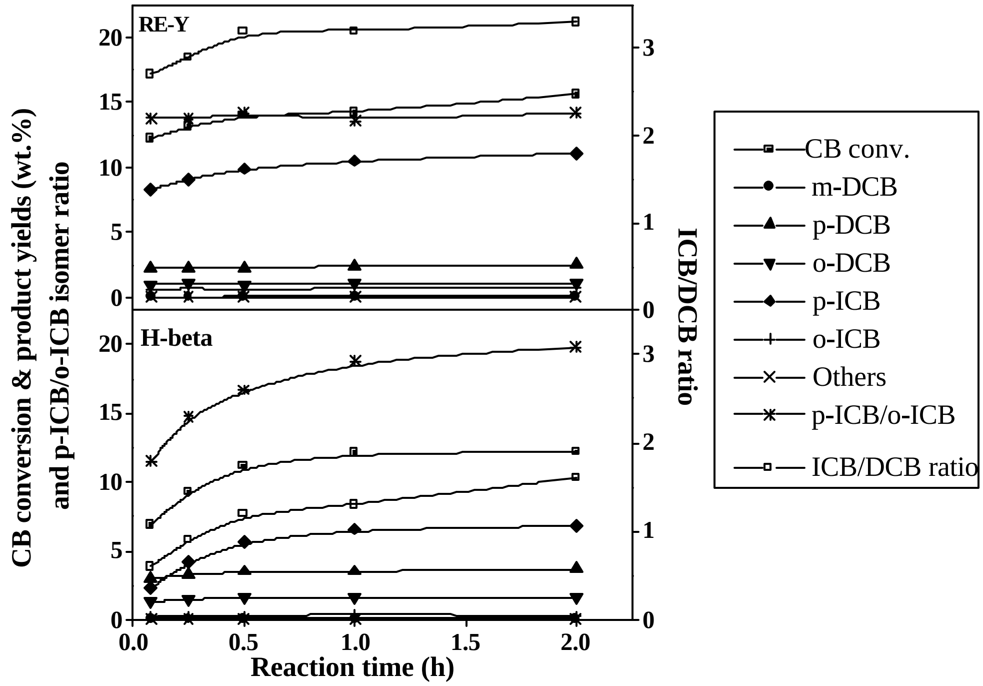


Figure 3.20. Effect of reaction time on the conversion of CB and product yields (wt.%), p-ICB/o-ICB isomer ratio and ICB/PCB ratio over zeolites RE-Y and H-beta. Reaction conditions: See footnotes to Table 3.17.

The conversion of CB as well as the product yields increase with reaction time in case of both the catalysts. As seen in Fig. 3.20, zeolite H-beta is less active initially, but the conversion increases gradually with time. Also the extent of iodination (ICB/DCB ratio) is found to be less in case of H-beta and gives lower yields of iodinated products. The yield of p-ICB, however, increases with time, thus increasing the p-ICB/o-ICB ratio.

Zeolite RE-Y (Fig. 3.20) is highly active catalyst and almost maximum conversion of CB is achieved in the initial 5 min (0.08 h) only without giving any noticeable change as the reaction is proceeds. The yields of iodinated products are far higher than that of the chlorinated products in case of zeolite RE-Y, thus giving higher ICB/DCB ratio. The selectivity for p-ICB (p-ICB/o-ICB ratio) is higher than that for zeolite H-beta and remains almost constant throughout the reaction.

3.3.1.3.4. Influence of catalyst concentration

The effect of different catalyst concentration for the zeolites H-beta and RE-Y on the conversion of CB, product yields, ICB/DCB ratio and p-ICB/o-ICB ratio is illustrated in Fig. 3.21.

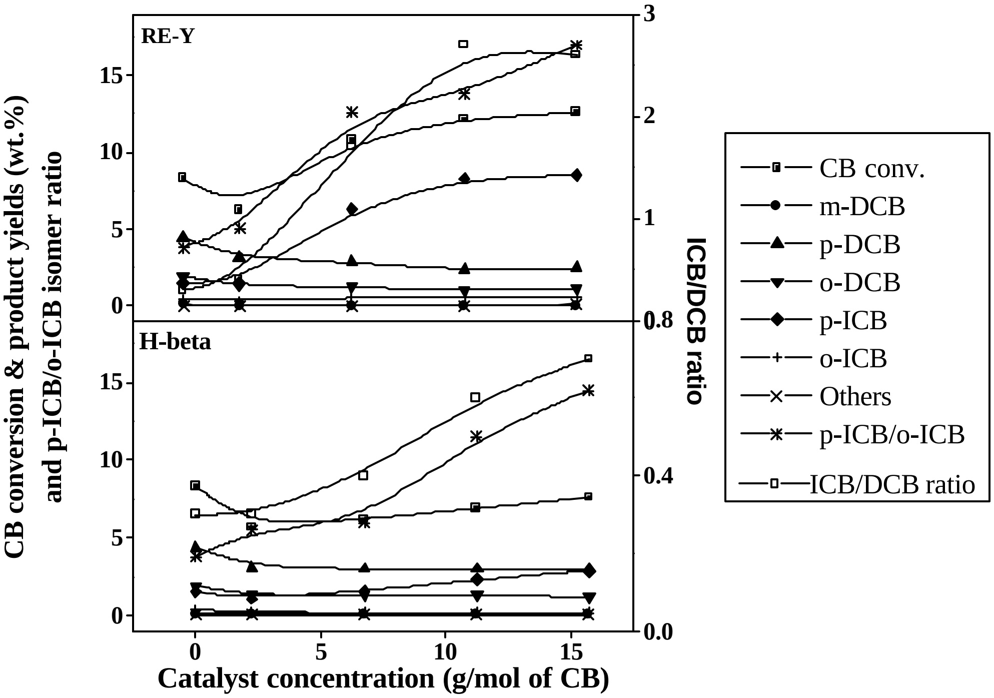


Figure 3.21. Effect of catalyst concentration on the conversion of CB and product yields (wt.%), p-ICB/o-ICB isomer ratio & ICB/DCB ratio. Reaction conditions: See the footnotes to Table 3.17.

An increase in the catalyst concentration of H-beta (Fig. 3.21) does not produce a remarkable change in the conversion of CB. However, the selectivity (p-ICB/O-ICB ratio) as well as the extent of iodination (ICB/DCB ratio) increases from 4.0 to 14.5 and 0.3 to 0.7, respectively, as the catalyst concentration is increased from 0 to 15.75 g/mol of CB.

In case of zeolite RE-Y (Fig. 3.21), the conversion of CB, the selectivity (p-ICB/O-ICB ratio) as well as the extent of iodination (ICB/DCB ratio) increases from 5.2 to 12.6, 0.3 to 2.6 and 4.0 to 17.0, respectively, with an increase in the catalyst concentration from 0 to 15.75 g/mol of CB. Thus, zeolite RE-Y is found to be superior to H-beta in terms of higher CB conversion, higher selectivity to p-ICB and higher yield of iodinated products. The increase in the conversion and selectivity with an increase in the catalyst concentration may be attributed to the increase in the total number of active sites of the catalyst.

3.3.1.3.5. Influence of reaction temperature with zeolite RE-Y

Figure 3.22 illustrates the effect of different reaction temperature on the conversion of CB, rate of CB conversion, product yields, ICB/DCB ratio as well as p-ICB/o-ICB isomer ratio with zeolite RE (70.6)Y.

With an increase in the reaction temperature from 328 to 383 K, the rate of CB conversion increases from 111.1 to 240.6 mmolg^{-1}h^{-1}, respectively, after 5 min of reaction time. There is a remarkable increase in the yield of p-ICB with an increase in the reaction temperature thus giving higher ICB/DCB ratio at higher temperature. The selectivity, however, remains almost constant with increasing the reaction temperature.

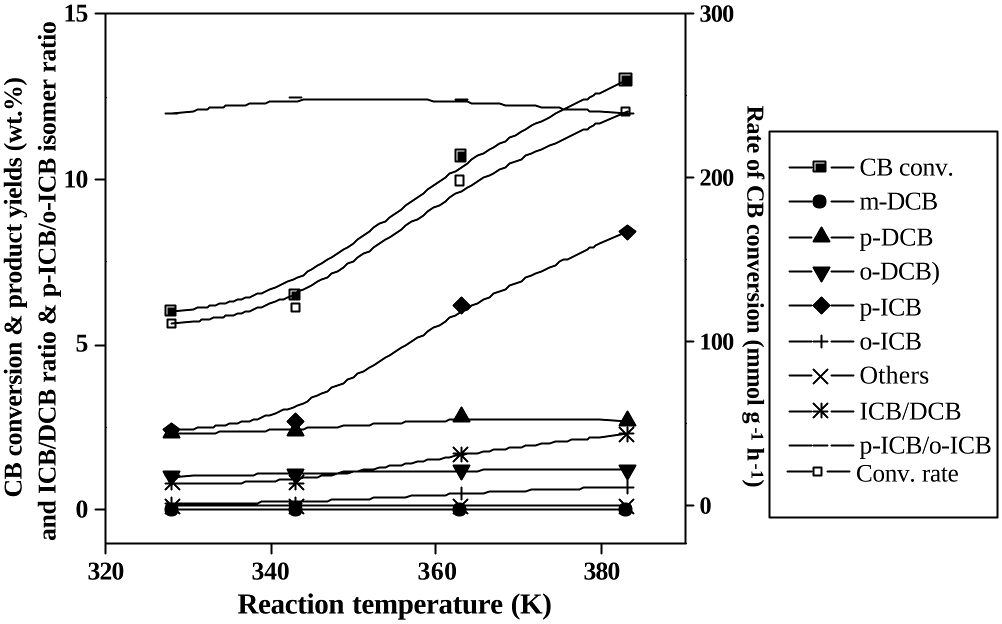


Figure 3.22. **Effect of reaction temperature on the conversion of CB (wt.%), rate of CB conversion (mmolg^{-1}h^{-1}), p-ICB/o-ICB isomer ratio and ICB/DCB ratio over zeolite RE-Y. Reaction conditions: Catalyst = 6.75 g/mol CB; CB = 0.04 mol; ICl = 0.008 mol; Reaction time = 0.083 h.**

3.3.1.3.6. Influence of CB:ICl molar ratio with zeolite RE-Y

The effect of different CB: ICl molar ratio on the conversion of CB, rate of CB conversion, product yields, ICB/DCB ratio as well as p-ICB/o-ICB isomer ratio with zeolite RE (70.6)Y is demonstrated in Table 3.18.

Table 3.18. Influence of CB: ICl molar ratio[a]

CB/ICl Molar Ratio	CB Conv. (wt.%)	Conv. Rate[b] (mmol g^{-1}h^{-1})	Product yields (wt.%)[c]						p-ICB/ o-ICB[d]	ICB/ DCB[e]
			DCB			ICB				
			m-DCB	p-DCB	o-DCB	p-ICB	o-ICB	Others		
1	41.9	775.5	0.5	22.1	9.5	8.8	1.3	0.2	6.8	0.24
3	16.1	298.0	0.1	4.8	2.1	8.2	0.8	0.1	10.3	1.3
5	10.7	198.1	0.01	2.8	1.2	6.2	0.5	-	12.4	1.7
7	8.4	155.5	0.02	1.6	0.7	5.6	0.4	0.02	14.4	2.6

[a] Reaction conditions: Catalyst = 6.75 g/mol CB; CB = 0.04 mol; Reaction temperature = 363 K; Reaction time = 0.08 h.

[b,c,d,e] = See footnotes to Table 3.19.

As the CB: ICl molar ratio is increased from 1 to 7 (reduced concentration of ICl), the conversion of CB decreased from 41.9 to 8.4 wt.%, respectively. The ICB/DCB ratio as well as p-ICB/o-ICB isomer ratio, however, increases with an increase in the CB: ICl molar ratio. Thus, the reaction becomes more selective to iodochlorobenzenes, particularly to para-iodochlorobenzene, when a higher molar ratio of CB: ICl is taken.

3.3.1.3.7. Recycle of zeolite RE-Y

Table 3.19. presents the results obtained in the recycle of zeolite RE-Y at 363 K after 5 min of reaction time.

Table 3.19. Recycle of zeolite RE (70.6)Y[a]

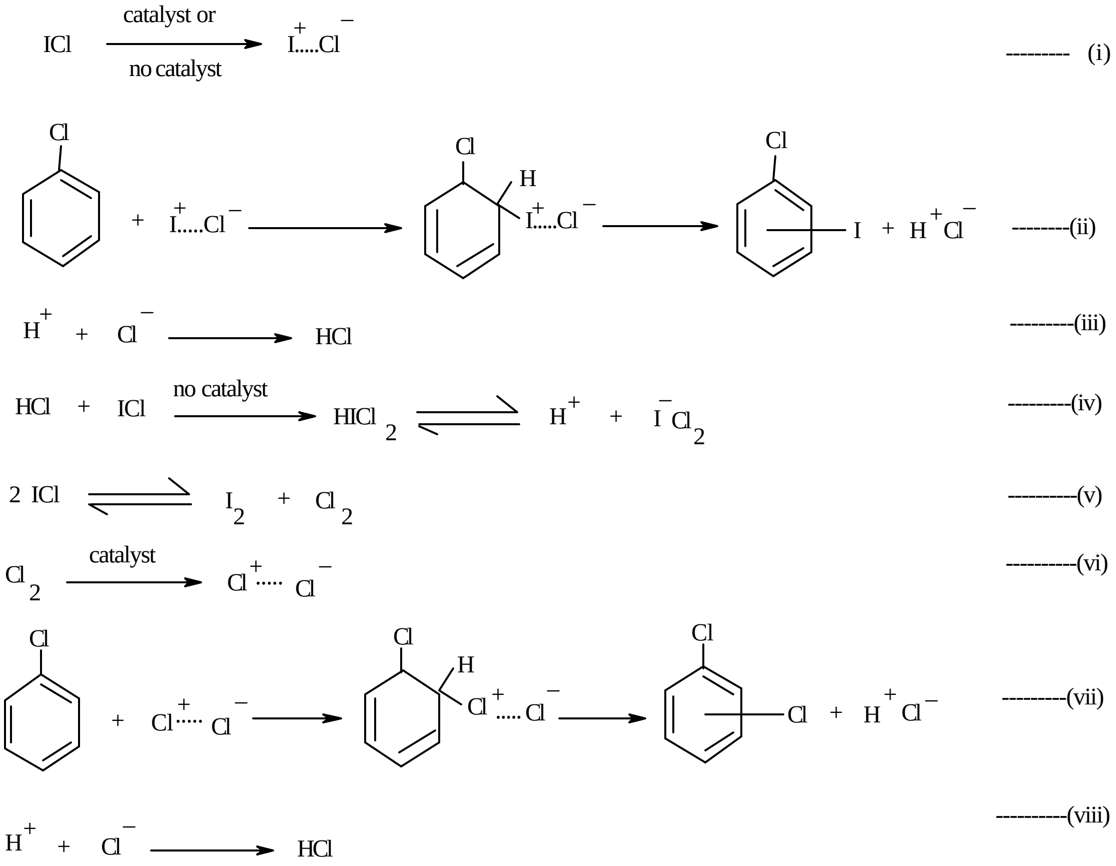
Run	CB conv (wt.%)	Product yields (wt.%)[c]						p-/o-ICB[d]	ICB/DCB[e] ratio	% Crystallinity
		DCB			ICB					
		m-DCB	p-DCB	o-DCB	p-ICB	o-ICB	Others			
0	10.8	0.03	2.8	1.2	6.3	0.5	0.01	12.6	1.7	100
I	5.9	0.02	2.7	1.2	1.8	0.2	0.1	8.2	0.5	-
II	5.5	0.02	2.6	1.1	1.5	0.3	0.03	5.0	0.5	17

[a,c,d,e] See footnotes to Table 3.17.

The catalyst is recycled two times with a progressive decline in its activity. The used catalyst is activated each time at 773 K in air and characterized for its chemical composition and crystallinity. From fresh to the second recycle, the conversion of CB decreases with a decrease in the yield of iodinated products (ICB/DCB ratio) as well as the selectivity (p-ICB/o-ICB isomer ratio) after each run. The decrease in the catalytic activity with recycling may be attributed to the reduced crystallinity of the catalyst. The deactivation of the catalyst is caused, probably, due to the HCl liberated during the course of the reaction.

3.3.1.4. Mechanism

The formation of iodochlorobenzenes (ICB) as well as little amount of dichlorobenzenes (DCB) takes place by an electrophilic aromatic substitution mechanism (Scheme 3.6)[71-75]. The ionization of ICl molecule gives rise to an electrophile (I^+) (eq. 1) which then attacks the aromatic ring of CB giving rise to the iodochlorobenzenes (eq. 2-3). Similarly, it is believed that the chlorination of CB also proceeds by electrophilic substitution. The fact that ICl molecule dissociates into elements (I_2 + Cl_2) to a little extent (eq. 5), suggests that zeolite catalyst or other ICl molecule (Lewis acid) polarize the Cl_2 molecule into an electrophile (Cl^+) which then reacts with the aromatic ring resulting in the formation of dichlorobenzenes (DCB) (eq. 6-8)[71-75].



Scheme 3.6.

3.3.1.5. Conclusions

Zeolite RE-Y catalyzes the liquid phase iodination of chlorobenzene selectively to p-iodochlorobenzene with ICl as the iodinating agent under mild reaction conditions and is found to be superior over the other zeolite catalysts as well as the conventional catalyst, H_2SO_4. Zeolite H-Y is also an active and selective catalyst, but gives lower ICB/DCB ratio compared to RE-Y. Zeolite H-beta is a selective catalyst, but gives lower yields of iodochlorobenzenes (lower ICB/DCB ratio) than those with H-Y or RE-Y. However, the yields of iodochlorobenzenes increase with the reaction time and catalyst concentration. Also, with zeolite RE-Y, increase in the duration of run, catalyst concentration and reaction temperature increases the conversion of CB with a substantial increase in the iodochlorobenzene yields. An increase in the CB:ICl molar ratio decreases the CB conversion, but the selectivity (p-ICB/o-ICB isomer ratio) is increased also increasing the ICB/DCB ratio. Zeolite RE-Y is recycled two times with a progressive decrease in the conversion of CB and the selectivity for p-ICB because of decreased crystallinity of the catalyst. The reaction pathway involves an electrophilic aromatic substitution mechanism giving iodochlorobenzenes as well as dichlorobenzenes by the formation of respective electrophiles (I^+/Cl^+) from ICl by the catalyst.

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Isomerization

4. Isomerization of o-chlorotoluene to m-chlorotoluene

4.1. Introduction

Chlorotoluenes are important intermediates in the synthesis of pharmaceuticals and agricultural chemicals and are produced by the liquid phase chlorination of toluene in the presence of Lewis acid catalysts[1] or zeolite catalysts[2] in which o- and p-isomers are produced together owing to the directing effect of the methyl group. Accordingly, when m-chlorotoluene (MCT) is required in large amounts, it is desirable to isomerize o-chlorotoluene (OCT) or p-chlorotoluene (PCT) to MCT. In addition, the isomerization of OCT to PCT is also important because the para-isomer is especially useful as a raw material for pesticides, peroxides, dyes, pharmaceuticals etc[3].

Conventionally, MCT is prepared by the liquid phase rearrangement reactions of OCT or PCT by heating with homogeneous Lewis acid catalysts like $AlCl_3$ and $FeCl_3$ or with H_2SO_4[4,5]. The isomerization of OCT is also known to occur with water-promoted Al_2Cl_6[6] or with strong acid catalyst HF-BF_3[7]. However, these catalysts are unstable, very difficult to recover and highly corrosive. In order to overcome the difficulties of the homogeneous system, the development and utilization of a solid catalyst is important. In the pioneering work of Venuto and Landis[8], it was demonstrated that solid acids in many catalytic reactions could replace liquid acids. In addition, Singh et al have shown the use of solid catalysts in selective halogenation reactions of aromatics[9,10]. In this shift from homogeneous catalysts to heterogeneous ones, zeolites play a major role because of their acidity, shape selectivity and regenerability[11].

With regard to the functionalized aromatics, most of the relevant work is reported in the patent literature dealing with the isomerization of cresols[12], halotoluenes[13-16] and dihalobenzenes[17,18] on zeolites. Different zeolites including faujasites, mordenites and pentasil type zeolites were claimed to be the active catalysts. Among these, zeolite H-ZSM-5 has been a popular catalyst for the isomerization of substituted toluene[19]. It has strong acid sites and its intermediate sized pores resist the coke formation better than the large pore faujasites. The three-dimensional pore structure is more resistant to blockage than the one-dimensional structure of mordenites.

The vapour phase isomerization of OCT under a pressure of 20 kg/cm^2 has been reported in Japanese and European patents[21,22]. In addition, Okazaki and Jouhouji[20] have used chlorotrifluoromethane treated H-mordenite catalyst for the vapour phase isomerization of OCT. However, details concerning the stability and regenerability of the catalyst as a function of time on stream are scarce. In view of this, the present investigation deals with the vapour phase isomerization of OCT under atmospheric pressure over zeolite catalysts. The paper discusses the influence of various zeolites, Si/Al ratio of H-ZSM-5, WHSV (h^{-1}), partial Na-exchange in H-ZSM-5, reaction temperature, different diluents, time on stream and regeneration of the H-ZSM-5 catalyst on the conversion of OCT, product distribution, disproportionation (I/D ratio) and deactivation of the catalyst in the isomerization of OCT.

4.2. Experimental

(a) *Catalyst preparation and characterization*

The zeolites used, their synthesis, modification and physico-chemical characterization including acidity measurement have already been reported in Chapter 2. Some important properties of these zeolites are listed in Table 2.3.

The modified forms of H-ZSM-5, such as H.Na (28.9) ZSM-5 and H.Na (34.1) ZSM-5 (28.9 and 34.1 are the values of the percent of Na^+ exchanged in H-ZSM-5), were prepared by the exchange of fresh H-ZSM-5 catalyst with 0.1 M and 1 M $NaNO_3$ solution, respectively, for 8 h at 353 K, followed by washing with deionized water and heating at 423 K for 2 h.

The protonic form of H-ZSM-5 was shaped into extrudates using hydrated alumina as a binder, with a H-ZSM-5: Al_2O_3 wt. ratio of 65:35, in the presence of 3 % acetic acid solution. The machine-made extrudates were dried and then calcined in air at 500^0 C overnight. The extrudates were broken into uniform 0.2-0.2 mm pieces and used in the isomerization of OCT.

(b) ***Catalytic reaction experiment***

The vapour phase isomerization of OCT was carried out in a fixed bed reactor with a continuous flow system under atmospheric pressure in the temperature range of 520 to 585 K. The experimental set up as well as the product analysis is done according to the procedure given in Chapter 2, Section 2.2.2.7.

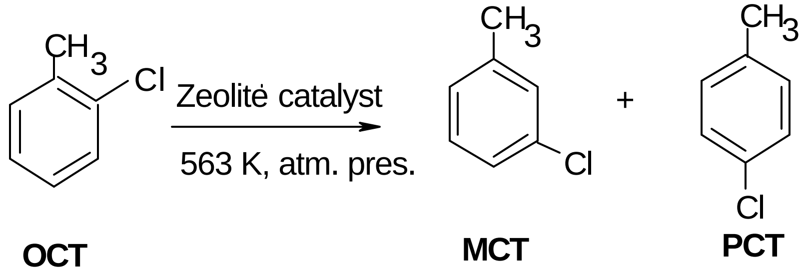
The conversion of OCT is calculated as the amount of OCT transformed. The product yields are calculated as the selectivity for a particular product multiplied by the conversion. The I/D ratio is the ratio of the summation of the isomerization products to the summation of the disproportionation products.

4.3. Results and Discussion

4.3.1. Influence of various catalysts

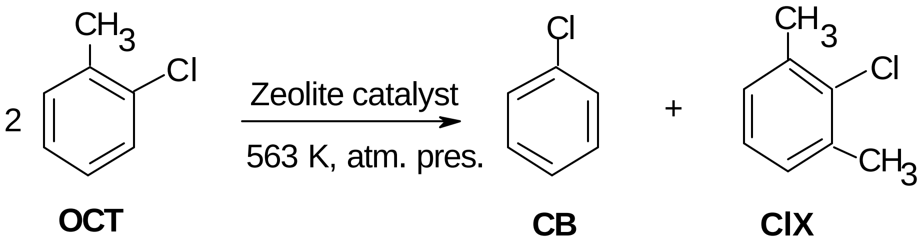
Table 4.1 compares the results obtained in the vapour phase isomerization of OCT over zeolites H-ZSM-5, H-mordenite, H-beta and H-RE(70.6)Y at 563 K under atmospheric pressure with a WHSV (h^{-1}) of 1.

The reaction produces mainly a mixture of m-chlorotoluene (MCT) and p-chlorotoluene (PCT) by the consecutive reaction pathway (eq.1) as the isomerization products (I) whereas small amounts of chlorobenzene (CB) and chloroxylenes (ClX) are detected as the disproportionation products (D) (eq.2). Trace amount (≅1%) of toluene (Tol) is also obtained due to the dechlorination of OCT (eq.3).



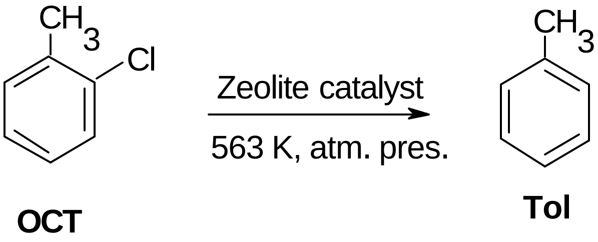
--------- (eq. 1)

Isomerization



---------- (eq. 2)

Disproportionation



--------- (eq. 3)

Dechlorination

As can be seen from Table 4.1, zeolite H-ZSM-5 exhibits higher catalytic activity compared to the other zeolite catalysts. The I/D ratio obtained over H-ZSM-5 is much higher than those for the other zeolites. This may be attributed to a higher concentration of strong acid sites for H-ZSM-5 than the other zeolites (Table 2.3). In addition, the H-ZSM-5 channel system has spatial constraints on the disproportionation reaction. This has been shown earlier by others[28,29] for the xylene isomerization/disproportionation reaction. The results obtained here for the chlorotoluene system are thus in agreement with the xylene isomerization reaction.

Table 4.1. Isomerization of OCT over various catalysts[a]

Catalyst	Conv. of OCT (wt.%)	Product yields (wt.%)					I/D ratio	MCT/ PCT ratio
		Tol	CB	ClX	MCT	PCT		
H-ZSM-5	50.8	1.1	3.2	2.9	32.2	11.4	7.1	2.8
H-beta	10.1	1.2	1.9	3.2	2.8	1.0	0.7	2.8
H-Mord.	11.3	0.8	2.5	3.6	3.6	0.8	0.7	4.5
H-RE (70.6)Y	2.6	0.5	0.8	1.0	0.2	01	0.2	2.0

[a] Reaction conditions: Catalyst = 2 g; Temperature = 563 K; OCT feed rate = 2 ml/h; Reaction time = 2 h.

The influence of time-on-stream (up to 6 h) on the conversion of OCT over these catalysts under identical reaction conditions is shown in Figure 4.1. It is clear from the catalyst comparison that while all the catalysts tested undergo significant aging under the reaction conditions, H-beta, H-mordenite and H-RE-Y age much more rapidly compared to zeolite H-ZSM-5 which retains almost 68 % of its initial activity after 6 h of reaction time. This is because of the shape selective, three-dimensional, peculiar medium pore structure of H-ZSM-5 which significantly inhibits the coke formation, thus reducing the deactivation.

Since H-ZSM-5 (without binder) is found to be superior in the isomerization of OCT, the further study of this reaction is carried out over H-ZSM-5 catalyst. Unless otherwise stated, the same catalyst H-ZSM-5 (SiO_2/Al_2O_3 = 41) diluted with 35 % Al_2O_3 as a binder, in the form of extrudates is used in the reactions.

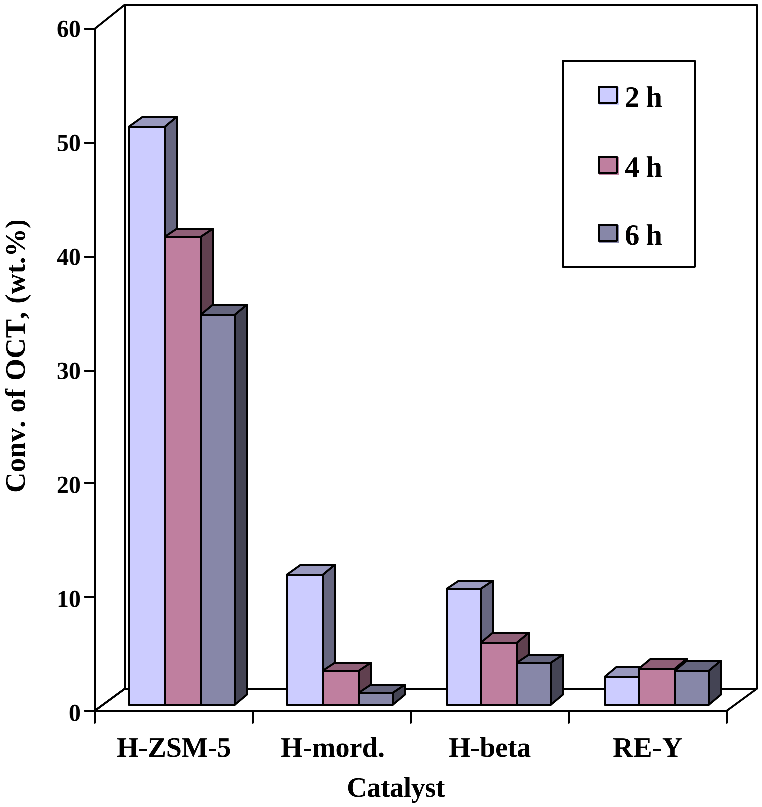


Figure 4.1 **Influence of reaction time on the conversion of OCT over various catalysts. Reaction conditions: See footnotes to Table 4.1.**

4.3.2. Influence of SiO_2/Al_2O_3 molar ratio

Figure 4.2 represents the influence of silica to alumina molar ratio of H-ZSM-5 on the conversion of OCT, product yields, I/D and MCT/PCT ratio in the isomerization of OCT at 583 K under atmospheric pressure at a WHSV (h^{-1}) of 0.8. The conversion of OCT decreased from 58.4 to 25.5 wt.% as the SiO_2/Al_2O_3 molar ratio is increased from 41 to 79, respectively. This shows that as the number of total acid sites increases, a higher conversion of OCT is obtained. On the other hand, the MCT/PCT as well as I/D ratio increases from 2.5 to 3.6 and 4.4 to 11.3 respectively, as the SiO_2/Al_2O_3 molar ratio is increased from 41 to 79. The increase in the I/D and MCT/PCT ratios with increased SiO_2/Al_2O_3 molar ratio may be attributed to the increase in the acid strength of the zeolite.

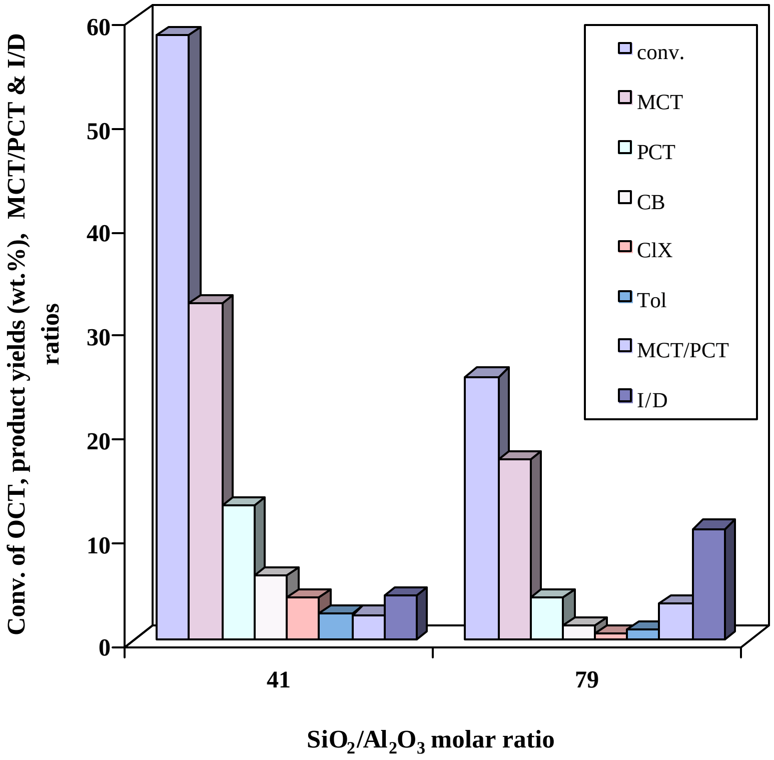


Figure 4.2 **Influence of SiO_2/Al_2O_3 molar ratio of H-ZSM-5 on the conversion of OCT, product yields, I/D and MCT/PCT ratios. Reaction conditions: Catalyst H-ZSM-5 (extrudates) = 3.1 g; Reaction temperature = 583 K; OCT feed rate = 2 ml/h; Reaction time = 2 h.**

4.3.3. Influence of partial Na-exchange in H-ZSM-5

The results obtained by using partially Na-exchanged zeolites H.Na(28.9)ZSM-5 and H.Na(34.1)ZSM-5 in the isomerization of OCT at 563 K under atmospheric pressure with a WHSV (h^{-1}) of 1 are presented in Table 4.2 and compared with the parent zeolite H-ZSM-5. The data shows that the conversion of OCT decreases in the following order: H-ZSM-5 > H.Na(28.9)ZSM-5 > H.Na(34.1)ZSM-5. This may be attributed to the decrease in the number of acid sites of ZSM-5 due to the exchange of Na^+- in H-ZSM-5. The MCT/PCT ratio as well as the I/D ratio, however, increases with decrease in the conversion of OCT (Table 4.2). The reduced acidity of H-ZSM-5 as a result of Na-exchange suppresses the disproportionation of OCT as well as isomerization of MCT to PCT.

Table 4.2. Influence of Na-exchanged H-ZSM-5 on OCT isomerization[a]

Catalyst	Conv. of OCT (wt.%)	Product yields (wt.%)					I/D ratio	MCT/ PCT ratio
		Tol	CB	ClX	MCT	PCT		
H-ZSM-5	50.8	1.1	3.2	2.9	32.2	11.4	7.1	2.8
H.Na(28.9) ZSM-5[e]	27.4	0.3	0.4	0.6	20.4	5.7	26.1	3.6
H.Na(34.1) ZSM-5[e]	22.4	0.2	0.3	0.3	17.8	3.8	36.0	4.7

[a] Reaction conditions : H-ZSM-5 = 2 g; Reaction temperature = 563 K; OCT feed rate = 2 ml/h**.**
[e] the percentage of Na-exchanged in H-ZSM-5 is given in parenthesis.

4.3.4. Influence of reaction temperature

Figure 4.3 represents the influence of the reaction temperature on the conversion of OCT, product yields (wt.%) as well as on the I/D ratio in the isomerization of OCT under atmospheric pressure at a WHSV (h^{-1}) of 0.8.

The conversion of OCT increases from 5.9 wt.% to 58.4 wt.%, when the temperature is raised from 523 to 583 K, respectively, after 2 h of reaction time. It is also clear from Fig. 4.3 that the I/D ratio decreases with the increase in the reaction temperature. Dechlorination also becomes prominent at higher temperature, thus giving higher amount of toluene (2.6 wt.%) at 583 K. The decrease in the I/D ratio with increase in the reaction temperature is due to the formation of chloroxylene (ClX) and chlorobenzene (CB) by the disproportionation of OCT at higher temperature. In addition, higher temperature favours the formation of PCT due to the consecutive reaction scheme and hence the MCT/PCT ratio has been found to decrease from 8.5 to 2.6 in the isomerization of OCT.

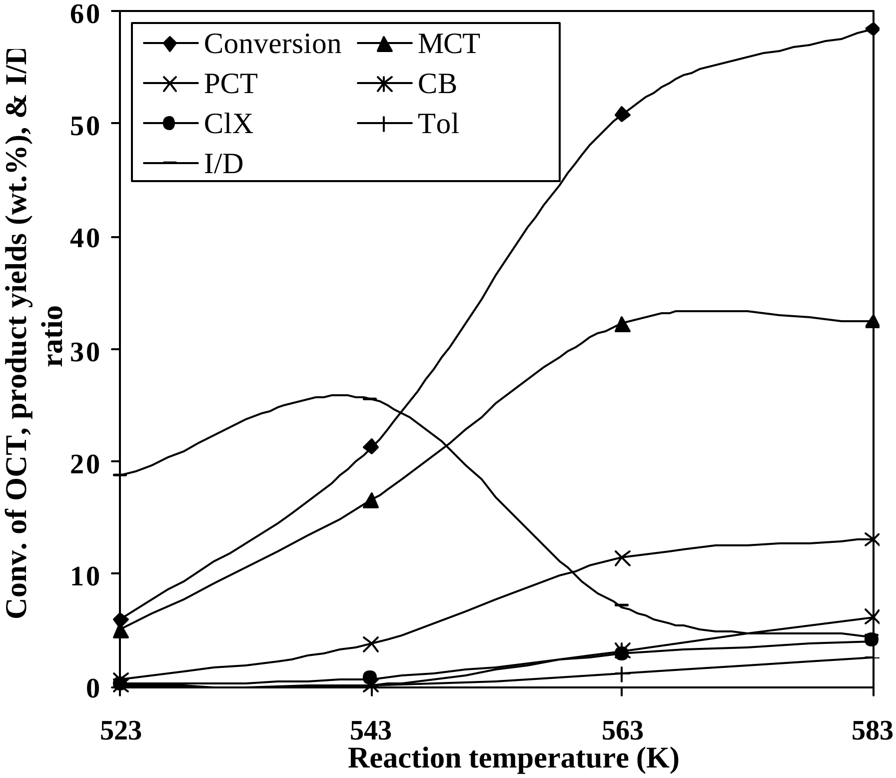


Figure 4.3 **Influence of reaction temperature on the conversion of OCT, product yields, I/D and MCT/PCT ratios. Reaction conditions: Catalyst H-ZSM-5 (extrudates) = 3.1 g; OCT feed rate = 2 ml/h; Reaction time = 2 h.**

The effect of the reaction temperature on the conversion of OCT versus time on stream in the isomerization of OCT is shown in Figure 4.4. The initial conversion of OCT decreases progressively from 2 h to 6 h of reaction time for each reaction temperature due to the deactivation of the H-ZSM-5 catalyst.

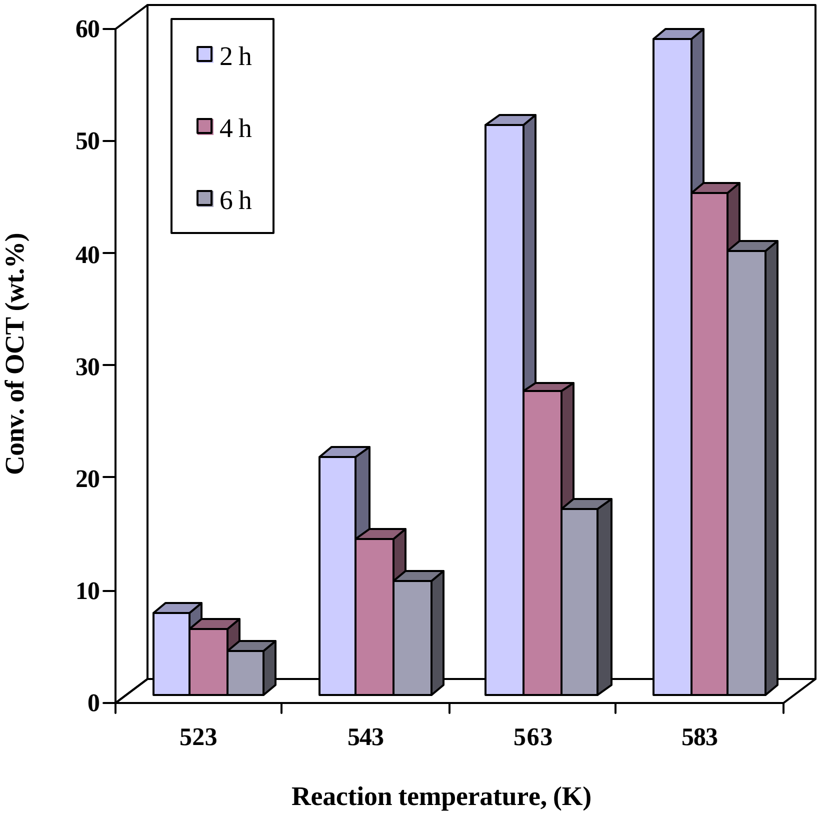


Figure 4.4 **Influence of reaction temperature on the conversion of OCT versus time on stream. Reaction conditions: Same as for Figure 4.3, reaction time = 6 h.**

4.3.5. Influence of diluent

Diluting the OCT feed may reduce the aging of the catalyst. Thus, the influence of different diluents like benzene, toluene, chlorobenzene, o-dichlorobenzene and n-hexane on the isomerization of OCT over zeolite H-ZSM-5 at 563 K, under atmospheric pressure and a WHSV (h^{-1}) of 0.8 is studied and the results are represented in Table 4.3. The OCT/diluent molar ratio in each case is 2.

It is clear from the results that benzene (B) is a good diluent among all other diluents studied and the initial activity of the catalyst is nearly retained after 6 h of the reaction time without any appreciable change in the MCT/PCT and I/D ratios. The diluent may inhibit the coke deposition inside the zeolite pores, thus reducing the deactivation. This is in agreement with the data of Tada et.al[14] where benzene was used as the diluent in the conversion of o-dichlorotoluene on H-ZSM-5 at 338 K.

Table 4.3. Influence of diluent in the isomerization of OCT[a]

Solvent	TOS (h)	OCT Conv. (wt%)	Product yields (wt. %)					I/D *ratio*	MCT/ PCT ratio
			Tol	CB	ClX	MCT	PCT		
C_6H_6	2	52.3	0.9	0.4	0.3	36.5	14.2	72.4	2.6
	6	51.0	0.9	0.4	0.3	35.5	13.9	70.6	2.6
C_6H_5 CH_3	2	51.0	-	1.3	0.7	35.2	13.8	24.5	2.6
	6	42.6	-	1.3	0.6	30.7	10.0	21.4	3.1
C_6H_5 Cl	2	65.9	0.5	-	0.9	45.4	19.1	71.7	2.4
	6	39.0	0.3	-	0.4	27.9	10.4	95.8	2.7
o-$C_6H_4Cl_2$	2	55.7	0.5	0.5	0.4	38.0	16.3	60.3	2.3
	6	40.6	0.4	0.6	0.3	28.8	10.5	43.7	2.7
n-C_6H_{14}	2	32.6	1.4	1.0	0.4	21.9	7.9	21.3	2.8
	6	26.5	1.1	0.8	0.4	17.0	7.2	20.2	2.4

[a] Reaction conditions: Catalyst H-ZSM-5 (extrudates) = 3.1 g; Temperature = 563 K; OCT/solvent (molar ratio) = 2:1; feed rate = 2 ml/h.

Table 4.4 represents the influence of different OCT/benzene molar ratio on the conversion of OCT, product yields, I/D and MCT/PCT ratios using H-ZSM-5 as the catalyst in the isomerization of OCT under similar reaction conditions. The conversion of OCT at 2 h and 6 h reaction time in the presence of diluent (OCT/ benzene = 2) and in the absence of any diluent decreases from 52.3 to 51.0 wt.% and 50.8 to 36.3 wt.%, respectively. The best results were obtained with the 2:1 molar ratio of OCT to benzene.

Table 4.4. Influence of OCT/benzene molar ratio[a]

OCT/ B molar ratio	TOS (h)	OCT Conv. (wt%)	Product yields (wt. %)					I/D ratio	MCT/ PCT ratio
			Tol	CB	ClX	MCT	PCT		
2.0	2	52.3	0.9	0.4	0.3	36.5	14.2	72.4	2.6
	6	51.0	0.9	0.4	0.3	35.5	13.9	70.6	2.6
5.0	2	51.8	0.6	0.5	0.4	35.9	14.4	55.9	2.5
	6	47.1	0.5	0.4	0.5	33.9	11.8	50.8	2.9
10.0	2	51.9	0.6	0.5	0.5	35.7	14.6	50.3	2.4
	6	46.5	0.7	0.5	0.4	33.0	11.9	49.9	2.8
No Diluent	2	50.8	1.1	3.2	2.9	32.2	11.4	7.1	2.8
	6	36.3	0.3	0.9	2.9	25.4	6.8	8.5	3.7

[a] Reaction conditions: Catalyst H-ZSM-5 (extrudates) = 3.1 g; Temperature = 563 K; OCT + benzene feed rate = 2 ml/h.

The influence of diluent (OCT:benzene molar ratio = 2:1) on the conversion of OCT, product yields, I/D and MCT/PCT ratios vs. time on stream (TOS) over H-ZSM-5 in the isomerization of OCT is shown in Figure 4.5 a.

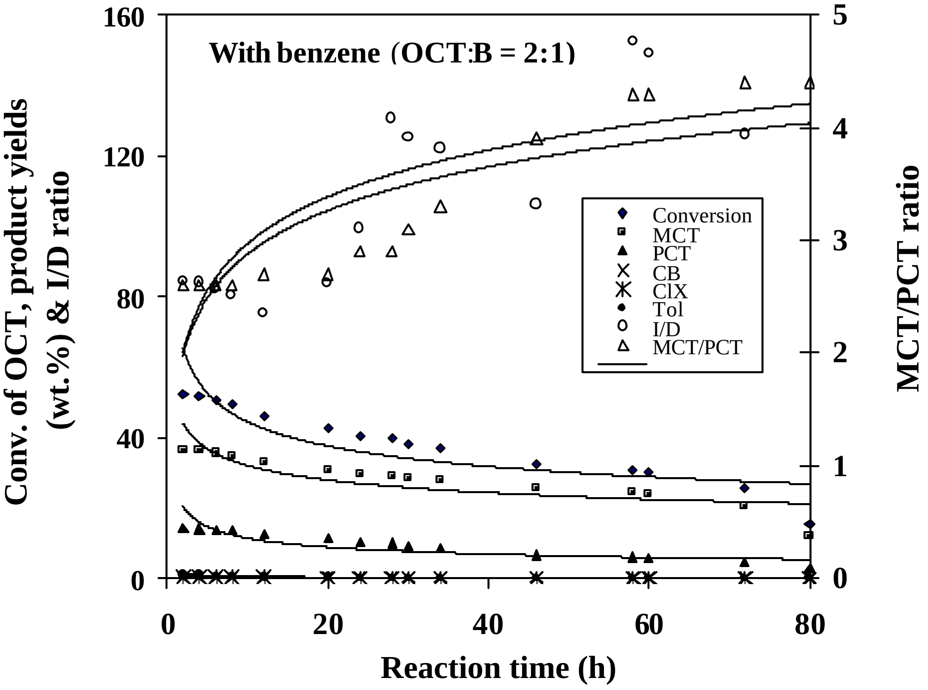


Figure 4.5 a **Influence of diluent (OCT:benzene molar ratio = 2:1) on the conversion of OCT versus time on stream. Reaction conditions: See footnotes to Table 4.3, Reaction time = 80 h.**

The performance of zeolite H-ZSM-5 vs. time on stream in the absence of diluent is given in Fig. 4.5 b.

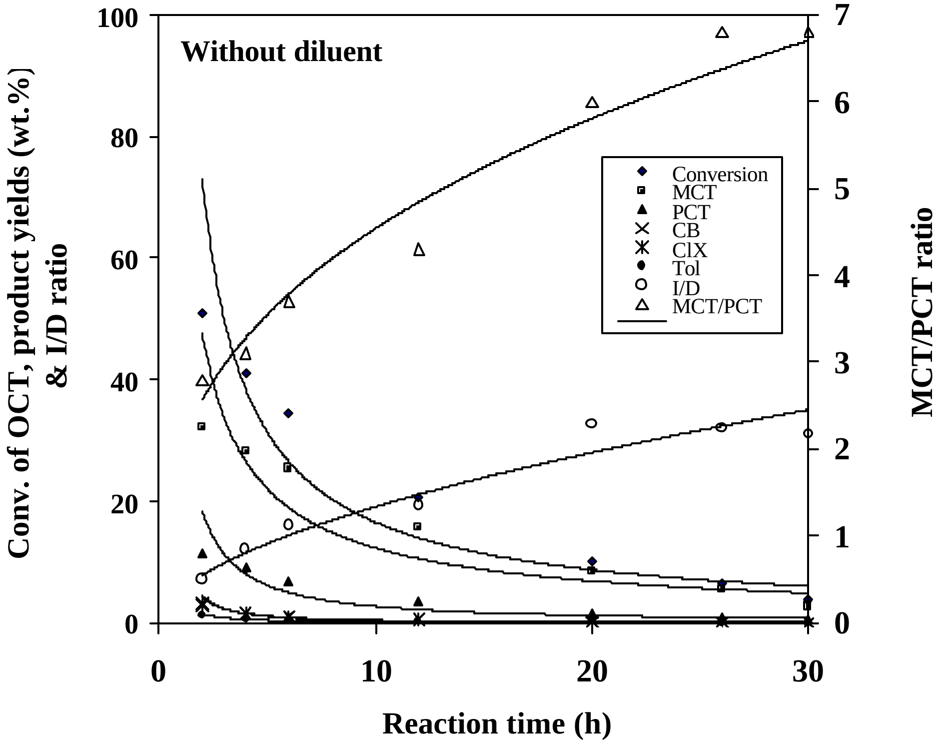


Figure 4.5 b **Conversion of OCT versus time on stream (without diluent). Reaction conditions: See footnotes to Table 4.3, Reaction time = 30 h.**

It is clear that the deactivation of H-ZSM-5 is very fast when no diluent is used and the conversion of OCT decreases from 52 wt.% to 5 wt.% after 30 h on stream. On the other hand, when benzene is used as diluent, the catalyst aging is reduced considerably and almost 50 % of initial activity of the H-ZSM-5 is retained after 80 h of reaction time (Fig. 4.5 a). From Fig. 4.5 a and 4.5 b, it is clear that the I/D ratio in both the cases increases with the decrease in the conversion of OCT versus TOS showing that the disproportionation in very low (≤ 1%) in both the cases. The deactivation of the catalyst is due to the coke deposition inside the pores of the zeolites reducing the access of the reactant molecules to the active sites. Beginning carbonaceous deposits inside the zeolite channels may be washed away in the presence of benzene as diluent, thus giving higher life to the catalyst. In addition, the diluent will reduce the inner OCT concentration and thus will decrease the bimolecular OCT reactions. The MCT/PCT ratio, however, increased with TOS in both cases which may be attributed to the decrease in the conversion level of OCT.

Thus, the deactivation of H-ZSM-5 is reduced substantially when benzene is used as a diluent in the isomerization of OCT at 563 K under atmospheric pressure.

4.3.6. *Influence of WHSV (h^{-1})*

The influence of WHSV (h^{-1}) on the conversion of OCT, product yields, MCT/PCT and I/D ratios is presented in Figure 4.6.

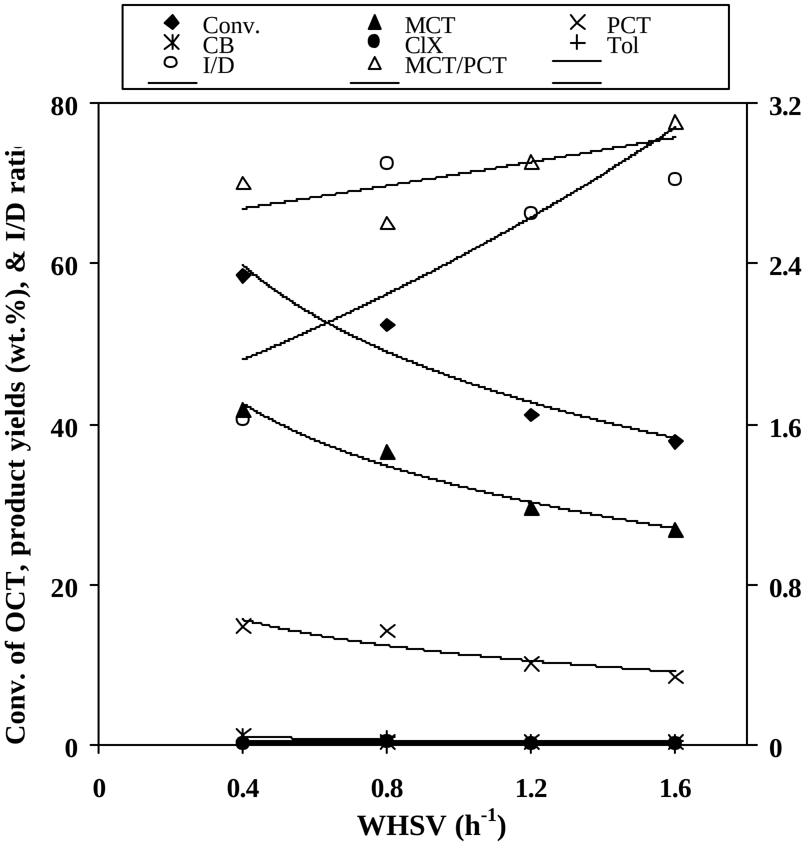


Figure 4.6 **Influence of WHSV (h^{-1}) on the conversion of OCT, product yields, I/D and MCT/PCT ratios. Reaction conditions: See footnotes to Table 4.3.**

The results are obtained at 563 K under atmospheric pressure with an OCT/benzene molar ratio of 2 after 2 h of reaction time. The feed rate is changed each time by keeping the weight of the catalyst constant. The conversion of OCT decreases from 58.4 to 36.5 wt.% when the WHSV (h^{-1}) has increased from 0.4 to 1.6. A marginal increase in the MCT/PCT ratio is observed with the increase in the WHSV. The I/D ratio also increases with an increase in the WHSV (h^{-1}) from 0.4 to 1.6.

Figure 4.7 compares the conversion of OCT versus duration of reaction (up to 6 h) at different WHSV (h^{-1}), under similar reaction conditions as those detailed in Fig. 6. The initial activity of the catalyst is essentially maintained in each case after 6 h of reaction time as shown in Fig. 7. The lower deactivation rate of the catalyst with time on stream may be attributed to the use of benzene as diluent in the isomerization of OCT. .

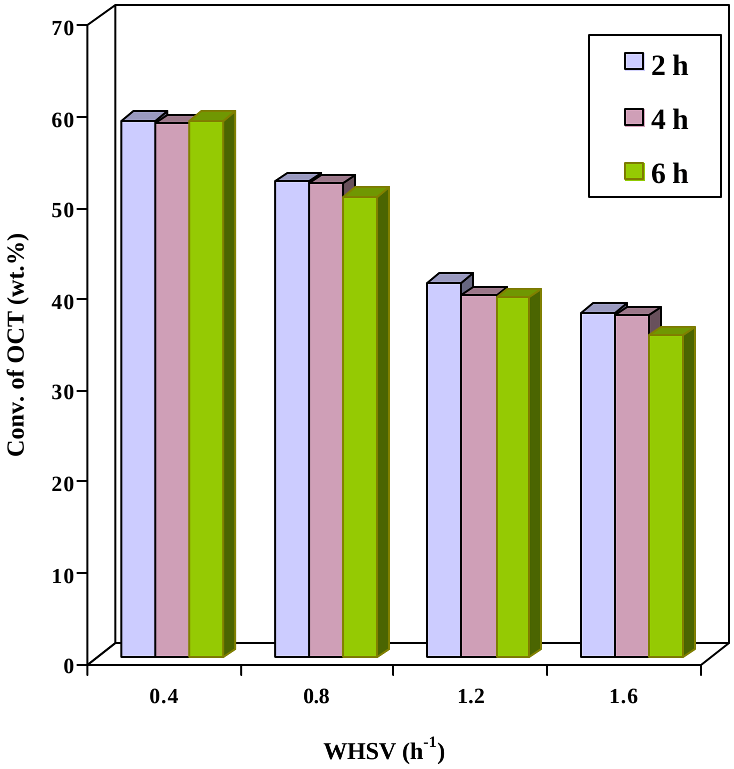


Figure 4.7 **Influence of WHSV (h^{-1}) on the conversion of OCT versus time on stream. Reaction conditions: See footnotes to Table 4.3.**

4.3.7. Catalyst regeneration cycles

Finally, the H-ZSM-5 catalyst was tested in a series of reaction-regeneration cycles. After 72 h on stream, the reactor was flushed with nitrogen and catalyst regeneration was carried out in situ at 773 K for 12 h using air to burn off the coke. The performance of fresh and regenerated catalyst (up to four cycles) is compared in Table 4.5.

Table 4.5. Influence of regeneration of H-ZSM-5[a]

Regeneration cycle	**Conv. of OCT (wt.%)**	**Product yields (wt.%)**					**I/D ratio**	**MCT/ PCT ratio**	**% Crystallinity**
		Tol	**CB**	**ClX**	**MCT**	**PCT**			
Fresh	52.3	0.9	0.4	0.3	36.5	14.2	72.4	2.6	100
I	52.1	0.8	0.6	0.3	36.3	14.1	56.0	2.6	n.d[b]
II	48.6	0.4	0.8	0.6	33.7	13.1	33.4	2.6	n.d[b]
III	46.1	0.8	0.6	0.2	32.9	11.6	55.6	2.8	n.d[b]
IV	42.7	0.6	0.5	0.1	30.5	11.0	69.2	2.8	100

[a] Reaction conditions : Catalyst H-ZSM-5 (extrudates) = 2 g; Reaction temperature = 563 K; OCT + benzene feed rate = 2 ml/h; Reaction time = 2 h.
[b] Not determined.

The results demonstrate that there is a gradual decrease in the conversion of OCT from 52.3 wt.% (for the fresh sample) to 42.7 wt.% after the 4th cycle of the catalyst at 2 h of reaction time. The corresponding MCT/PCT ratio, however, increases from 2.6 to 2.8, respectively.

Figure 4.8 shows the influence of regeneration cycles of H-ZSM-5 on the conversion of OCT versus time on stream under similar reaction conditions up to 72 h. A progressive decrease in the conversion of OCT is observed after each regeneration cycle up to 26 h. However, no substantial change in the conversion of OCT is observed after 26 h time on stream and fresh and fourth time regenerated samples retain activities between 60-52 wt.% in relation to the original activity. The decrease in the conversion of OCT after each regeneration cycle might be attributed to a decreased framework SiO_2/Al_2O_3 molar ratio of H-ZSM-5 after each cycle.

Thus, the zeolite H-ZSM-5 can be used a number of times with regeneration in the isomerization of OCT at 563 K without considerable decay in its activity.

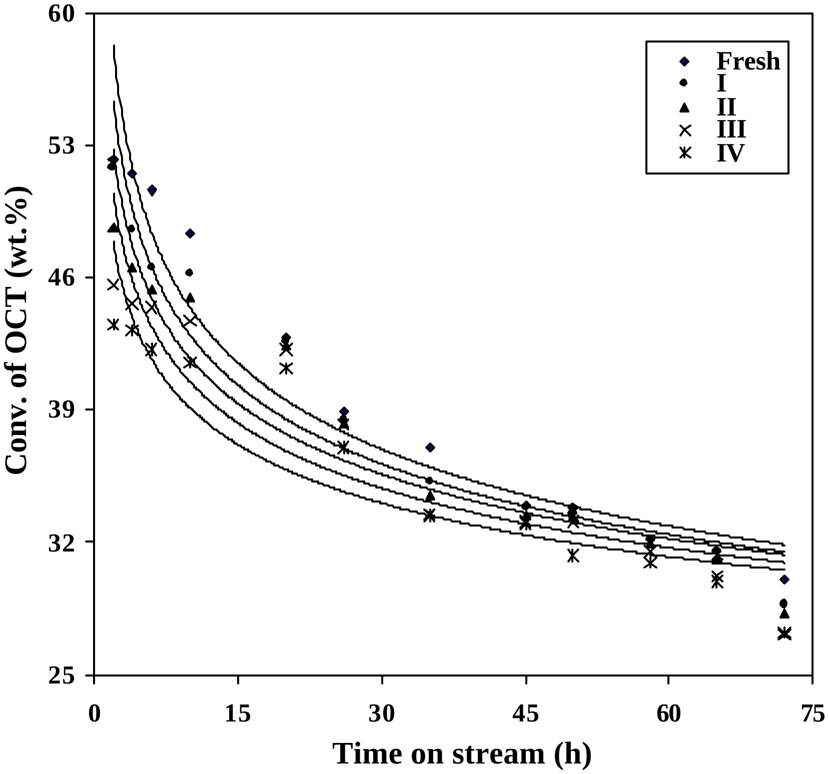
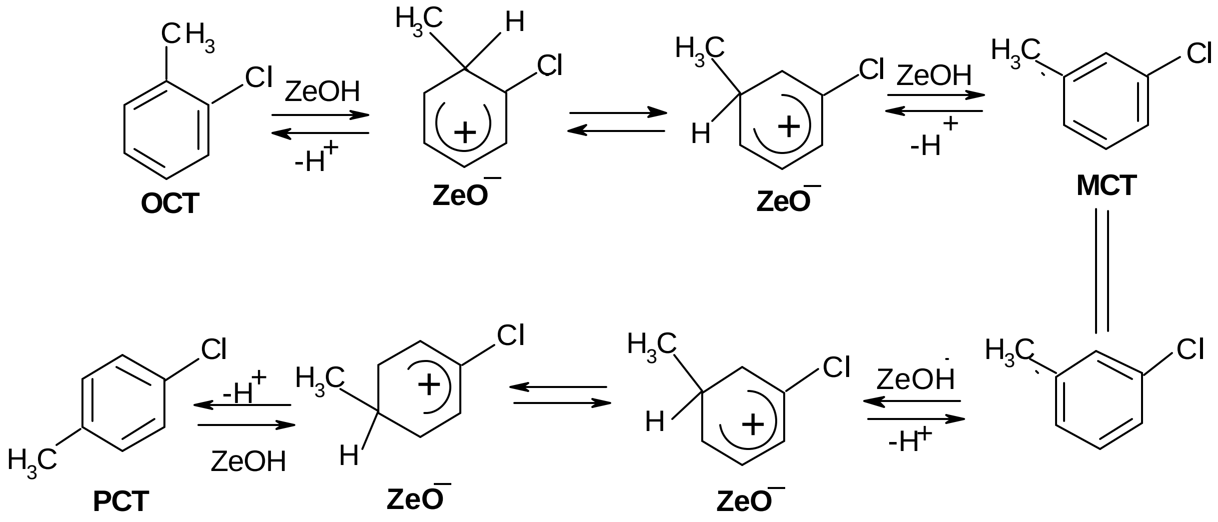


Figure 4.8 **Influence of regeneration cycles of H-ZSM-5 on the conversion of OCT versus time on stream. Reaction conditions: See footnotes to Table 4.5, Reaction time = 72 h.**

4.3.8. Reaction pathway

As in the case of acid-catalyzed, homogeneous isomerisation[6], the same consecutive mechanism of OCT? MCT? PCT is obeyed in the zeolite catalyzed isomerization of OCT involving intramolecular 1,2-methyl shifts. The e^--enriched carbon atom bound to the $-CH_3$ group is first attacked by the proton of the zeolite catalyst and then the isomerization of OCT proceeds by the following reaction pathway (Scheme 4.1).



Scheme 4.1.

The carbon-atom bound to –Cl atom is deactivated and is not attacked by the acid sites of zeolite catalyst. In fact, hardly any toluene is produced by the dechlorination of OCT under the reaction conditions employed in this study.

4.4. Conclusions

The isomerization of OCT was investigated over zeolites H-ZSM-5, H-mordenite, H-beta and H-RE(70.6)Y. Among these, zeolite H-ZSM-5 is found to be highly active in the isomerization of OCT due to higher acid site concentration. In addition, the main factor in case of zeolite H-ZSM-5, is lower aging as a consequence of its peculiar pore system. The deactivation of H-ZSM-5 is reduced substantially by diluting the reactant (OCT) by an inactive component like benzene. Thus, more than 50 % of the initial activity of the zeolite is retained after 72 h of TOS. One of the main findings is higher I/D ratios with reduction in operating severity as brought about by temperature, WHSV, Al content and Na-exchange. The catalyst H-ZSM-5 can be regenerated four times by heating at 773 K in an air flow and reused for the isomerization of OCT with only a little decrease in its activity. In the reaction mechanism, the isomerization of OCT involves a consecutive reaction scheme, OCT? MCT? PCT with an intramolecular 1,2-methyl shift. The selectivity to MCT thus, depends upon the conversion level of OCT over the catalyst.

4.5. References

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The present work reports the synthesis, modification and characterization of synthesized or commercially available zeolite catalysts. The catalytic activity of these zeolite catalysts in the selective halogenation (chlorination, bromination, iodination) as well as isomerization reactions of ortho-chlorotoluene is investigated for producing industrially important products in high selectivity.

The work is presented in five chapters.

A review on the published and patented literature on the use of zeolite catalysts in the synthesis of fine chemicals, particularly in the halogenation and isomerization reactions of aromatics with shape selective characteristics is reported in **Chapter 1**. A brief discussion about zeolites, their classification, synthesis etc is also included in this chapter.

Chapter 2 describes the synthesis, modification and characterization of different zeolites. It contains the hydrothermal synthesis of zeolite K-L, beta and ZSM-5. The modification of various synthesized as well as commercial zeolites into protonic, K^+, RE^{+3} forms is also included here. Characterization of these zeolites with various physico-chemical methods such as chemical analysis, XRD, SEM, surface area measurement as well as acidity measurement using TPD of ammonia is also discussed. In addition the chapter includes procedure for the experimental set up for the evaluation of catalytic activity, product identification and product analysis in different halogenation and isomerization reactions.

Chapter 3 focuses on liquid phase selective halogenation reactions i.e. chlorination of benzyl chloride, cumene and diphenylmethane, bromination of ethyl benzene and iodination of chlorobenzene using zeolite catalysts.

- The liquid phase chlorination of benzyl chloride (BC) has been investigated in the presence of a series of zeolite catalysts at 353 K under atmospheric pressure. A comparative study of these catalysts reveals that zeolite K-L exhibits the higher rate of BC conversion (76.4 mmolg^{-1}h^{-1}), except H(26.1)K-L (98.4 mmolg^{-1}h^{-1}) and higher selectivity for 4-chlorobenzyl chloride (4-ClBC/ 2-ClBC = 3.7) than the other zeolite catalysts. The absence of any catalyst, zeolites K-X and K-Y mainly promote the side chain chlorination of BC to α,α-dichlorotoluene. The effects of reaction time, solvents, catalyst concentration and reaction temperature are also examined. A combination of solvent and reaction temperature not only affect the rate of BC conversion, but also enhance markedly, the isomer ratio of 4-ClBC/ 2-ClBC. 1,2-dichloroethane is the best solvent and the isomer ratio of 4-ClBC/2-ClBC and the rate of BC conversion over zeolite K-L are enhanced from 2.21 to 7.21 and 13.2 to 51.9 mmolg^{-1}h^{-1} (in the presence of solvent), respectively, when the reaction temperature is raised from 313 to 353 K. Further, the use of 1,2-dichloroethane as solvent in the reaction decreases the formation of side chain and consecutive products significantly. As the reaction time and amount of the catalyst in the reaction mixture are increased, an increase in the conversion of benzyl chloride is noticed. The zeolite K-L is recycled three times with a decline in catalytic activity. The probable mechanism involves the formation of an electrophile (Cl^+) from Cl_2 gas over zeolite catalysts which react with BC to form the ring chlorinated products.

- The liquid phase chlorination of cumene has been investigated in the presence of a series of zeolite catalysts and also the conventional catalyst $AlCl_3$ at 333 K under atmospheric pressure with sulfuryl chloride (SO_2Cl_2) as the chlorinating agent. Zeolite

K-L catalyzes the chlorination of cumene selectively to 4-chlorocumene (4-ClCm) and is superior to other zeolite catalysts and $AlCl_3$ in terms of selectivity. Zeolite K-X and the uncatalyzed reaction produce mainly the side-chain chlorinated product, α-chlorocumene (α-ClCm) with much less activity, whereas $AlCl_3$ gives higher amounts of consecutive products. The effect of reaction time, solvent, catalyst (K-L) concentration, cumene/ SO_2Cl_2 ratio, HCl treated K-L and recycle of K-L on the conversion of cumene and selectivity for 4-ClCm have been examined. The activity and selectivity of zeolite K-L depend on the reaction conditions and on the solvent used in the reaction. 1,2-dichloroethane is found to be the best solvent and gives the highest selectivity for 4-ClCm (4-ClCm/2-ClCm = 33.0) at 353 K in the chlorination of cumene with K-L. Further, the use of 1,2-dichloroethane as solvent prevents the formation of the side-chain as well as consecutive products. With an increase in the reaction temperature, the rate of cumene conversion as well as the selectivity for 4-ClCm have been found to increase. Also, increase in the concentration of K-L to 25 g/mole of cumene in the presence of 1,2-dichloroethane gives the highest 4-ClCm/2-ClCm ratio of 38.6 at 353 K. HCl-treated zeolite K-L shows lower activity and selectivity than parent K-L, due to increased SiO_2/Al_2O_3 ratio as well as (to some extent) decreased crystallinity of HCl-treated zeolite K-L. The conversion of cumene is found to increase with a decrease in the cumene/SO_2Cl_2 molar ratio and consequently, in an increase in the concentration of SO_2Cl_2. The catalyst is recycled two times with a progressive decline in its activity. A few reactions of cumene chlorination with molecular chlorine are also studied with zeolite K-L. In this case, a combination of zeolite K-L, chloroacetic acid and 1,2-dichloroethane serves as the best catalyst, giving highly selective para-chlorination of cumene at 353 K under atmospheric pressure. The reaction pathway involves the formation of molecular chlorine by the decomposition of SO_2Cl_2 at the reaction temperature. The catalyst then polarizes the chlorine molecule to the electrophile (Cl^+), which interacts with cumene molecule in an electrophilic substitution reaction, giving ring-chlorinated cumenes.

- The liquid phase chlorination of diphenylmethane (DPM) to 4,4'-dichlorodiphenylmethane (4,4'-DCDPM) is investigated at 333 K, under atmospheric pressure over a number of zeolite catalysts using sulfuryl chloride (SO_2Cl_2) as the chlorinating agent. The results obtained are compared with those over the conventional Lewis acid catalyst, $AlCl_3$ as well as without any catalyst. Zeolite K-L is found to be highly active and selective catalyst for the conversion of DPM to 4,4'-DCDPM. The conversion of DPM, rate of DPM conversion and the selectivity (4,4'-DCDPM/2,4'-DCDPM isomer ratio) over zeolite K-L after 1 h of reaction time is found to be 96.8 wt.%, 19.1 $mmolg^{-1}h^{-1}$) and 7.4, respectively. The conversion of DPM and the product yields increase with duration of the run. Also, the yield of 4,4'-DCDPM increases with a decrease in the 4-chlorodiphenylmethane (4-CDPM) yield with time over zeolite K-L. The influence of solvent, catalyst concentration, reaction temperature, DPM/SO_2Cl_2 molar ratio, recycle of zeolite K-L etc. are also examined. 1,2-dichloroethane is the best solvent and gives the highest selectivity for 4,4'-DCDPM (4,4'-DCDPM/2,4'-DCDPM isomer ratio = 9.7) with zeolite K-L at 353 K after 1 h of reaction time. The formation of 4,4'-DCDPM is favoured by increase in catalyst concentration, reaction temperature and higher concentration of SO_2Cl_2 (lower DPM/ SO_2Cl_2 molar ratio). In all these cases, the yield of 4,4'-DCDPM increases with a decrease in the yield of 4-CDPM which suggests that the formation of 4,4'-DCDPM takes place by the consecutive reaction of 4-CDPM.. Higher SiO_2/Al_2O_3 ratio (obtained by HCl treatment) of zeolite K-L decreases the conversion of DPM. A noticeable decrease in the activity and selectivity of zeolite K-L is observed on recycling; probably due to reduced crystallinity as well as extraction of small amount of Al^+ and K^+ ions by the HCl generated in the reaction. Mechanistically, SO_2Cl_2 is first decomposed into SO_2 and Cl_2; the latter being polarized by the zeolite catalyst to an electrophile (Cl^+) which then attacks the DPM and subsequently produce the monochlorodiphenylmethane (MCDPM). The MCDPM further is attacked by the electrophile (Cl^+) and result in the formation of DCDPM.

- The liquid phase bromination of ethyl benzene (EB) to 4-bromoethyl benzene (4-BrEB) has been investigated at 353 K under atmospheric pressure, using liquid bromine as the brominating agent, over a number of zeolite catalysts and also the conventional Lewis acid catalyst, $FeCl_3$, under mild reaction conditions. In addition, a bromination reaction using N-bromosuccinimide (NBS) as the brominating agent is also carried out using zeolite H-beta as the catalyst and the results are compared with those obtained over the conventional catalyst, H_2SO_4. Zeolite K-L is found to be comparable in activity and selectivity to the conventional Lewis acid catalyst, $FeCl_3$ than the other catalysts, in the nuclear bromination of ethyl benzene. Zeolites H.K-L and K-ZSM-5 also give mostly the nuclear brominated products whereas zeolite K-X and the blank reaction (absence of catalyst) give higher yields of side-chain products and others. Zeolites K-Y, K-beta and K-mordenite are found to give higher amounts of the condensation products (others) giving less amount of the nuclear brominated products in the bromination of ethyl benzene with liquid bromine. In case of bromination with NBS as the brominating agent, zeolite H-beta is found to be superior to the conventional catalyst, H_2SO_4, in giving higher selectivity to 4-BrEB with lower yields of side-chain products as well as others. The selectivity for 4-BrEB is favoured by increase in the catalyst K-L concentration as well as the reaction temperature. An increase in the EB:Br_2 molar ratio decreases the conversion of EB without changing the selectivity. The catalyst K-L is recycled two times with a progressive decrease in the conversion of ethyl benzene and selectivity for 4-BrEB. Presumably, the catalytic bromination of aromatics takes place by the generated electrophile (Br^+) by the heterolytic cleavage of Br_2/NBS which then attacks the aromatic ring giving the nuclear brominated products.

- A new and direct method for the selective liquid phase iodination of chlorobenzene (CB) to para-iodochlorobenzene (p-ICB) with iodine monochloride (ICl) as the iodinating agent has been demonstrated using zeolite catalysts under mild reaction conditions. The conversion of CB, product yields and selectivity for p-ICB mainly depens upon the type of the catalyst used in the reaction and also upon the reaction conditions. Zeolite RE(70.6)Y and H-Y are found to be highly active and selective compared to other zeolite catalysts studied and also the conventional catalysts, H_2SO_4 and SiO_2. Zeolite H-beta is selective but less active and gives higher yields of the chlorinated products (side products) than the iodinated products. An increase in the duration of run, catalyst concentration and reaction temperature increases the yield of p-ICB. The conversion of CB decreases on incresing the molar ratio of CB:ICl. However, the selectivity (p-ICB/o-ICB isomer ratio) as well as the extent of iodiantion (ICB/DCB ratio) increases at higher CB:ICl molar ratio. Zeolite RE-Y is recycled two times with a progressive decrease in the CB conversion as well as selectivity. The probable mechanism for the formation of iodochlorobenzenes (ICB) and some amount of dichlorobenzenes (DCB) involves an electrophilic aromatic substitution of CB by the respective electrophiles (I^+/Cl^+).

Chapter 4 deals with the vapour phase isomerization of o-chlorotoluene (OCT) to m-chlorotoluene (MCT) is carried out at 563 K under atmospheric pressure over various zeolite catalysts viz. H-ZSM-5, H-beta, H-mordenite and H-RE(70.6)Y. Zeolite H-ZSM-5 is found to be highly active as well as selective because of its higher acidity. Furthermore, the medium pore, three-dimensional pore structure of H-ZSM-5 is subject to less deactivation substantially than the other catalysts. In addition, the use of benzene as the diluent reduces the aging of the H-ZSM-5 catalyst thus increasing the activity on time on stream. The conversion of OCT, and the MCT/PCT ratio on zeolite H-ZSM-5 at 563 K is found to be 50.8 (wt.%), and 2.8, respectively, with an isomerization/disproportionation (I/D) ratio of 7.1. The influence of reaction temperature, silica to alumina ratio of H-ZSM-5, space velocity, Na-exchange in H-ZSM-5, time on stream, regeneration of H-ZSM-5, diluent, etc has been investigated in the isomerization of OCT. Conversion of OCT over H-ZSM-5 is favoured by higher temperature, lower space velocity and lower silica to alumina ratio. Increase in the percentage of sodium by Na-exchange in H-ZSM-5 decreases its activity because of reduced acidity. The catalyst H-ZSM-5 is regenerated four times and used for the isomerization reaction with a slight decrease in its activity with each regeneration cycle. Disproportionation and dechlorination is favoured at higher temperature. Generally, the isomerization of OCT over zeolites follows a consecutive reaction scheme OCT? MCT? PCT, thus the selectivity depends essentially upon the conversion level of OCT.