

COMPUTERISED



**SYNTHESIS, CHARACTERIZATION AND CATALYTIC
PROPERTIES OF MEDIUM AND LARGE PORE TIN-
CONTAINING MOLECULAR SIEVES**

**A THESIS
SUBMITTED TO THE
UNIVERSITY OF PUNE
FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
(IN CHEMISTRY)**

by

NAWAL KISHOR MAL

**CATALYSIS DIVISION
NATIONAL CHEMICAL LABORATORY
PUNE-411008, INDIA.**

JANUARY 1997

CHAPTER 6

SUMMARY

6 SUMMARY

The titanium silicalite (TS-1, where Ti is in the framework of MFI structure) invented in the 1980s by Enichem has been one of the landmarks in the area of the catalysis. As against the well-known acid catalysis of aluminosilicates i.e., zeolites, shape-selective oxidation by titanosilicalites has opened up a major avenue for the synthesis of a number of chemical intermediates and fine chemicals. Following TS-1, a number of other metallosilicate molecular sieves having V, Cr, Ge, Sn, etc, both in medium pore and large pore structures have been synthesized and explored for different catalytic applications. Stannosilicates have been one set of such metallosilicates, which have been prepared both by post-synthesis treatment of several zeolites or by hydrothermal synthesis. Eventhough several documents, mostly available in the patent literature deal with claims of successful synthesis and incorporation of Sn ions in the framework of different zeolite structures, these have not been substantiated. Particularly, the extent to which bigger Sn^{4+} ions could substitute Si^{4+} in medium and large pore silicalites, the location of Sn^{4+} ions in the zeolite structure and their environment have not been studied in detail. This thesis is an attempt to answer some of these questions. The main objective of this thesis, hence, was to systematically study different methods of hydrothermal synthesis, of Al free- Sn-silicates with MFI and other structures, follow the course of crystallization from the gel applying some instrumental techniques, like liquid ^{29}Si NMR, XRD etc, check the purity of the resulting materials which after calcination, could be characterized thoroughly. The application of these Sn-silicalite molecular sieves in selective oxidation of organic substrates, using H_2O_2 as oxidant and in the weak-acid catalyzed reaction has been presented.

Among four different methods used for the synthesis of Sn-silicalite-1 (MFI structure) molecular sieves, the method in which a source of tin was added to tetraethyl orthosilicate (TEOS) followed by the addition of tetrapropylammonium hydroxide (TPAOH) was found to be the best. ^{29}Si liquid NMR studies show that stannic chloride is hydrolysed and oligomerized from the mixture of SnCl_4 and TEOS by addition of TPAOH into Q^2 and Q^3 units. Tin is probably incorporated into the silicate species during oligomerization (SnO_2 is not precipitated in the solution). For the hydrothermal synthesis of Sn-sil-1 the optimum conditions have been found to be as follows: $\text{SiO}_2/\text{SnO}_2 = 33$, $\text{TPAOH}/\text{SiO}_2 = 0.45$, $\text{H}_2\text{O}/\text{SiO}_2 = 35$ temperature = 433 K, duration = 2 days.

The Sn-sil-1 samples used in this study are microporous (sorption studies), well-defined and crystalline (X-ray and SEM) materials. During the hydrothermal synthesis, the interaction

between Si-OH and Sn-OH monomers leads to the formation of Si-O-Sn linkage (FTIR

spectrum). The oxidation state of tin is 4+ both on the surface and in the bulk (XPS). A part of tin is probably in the edge-sharing or corner-sharing positions of the silicalite-1 structure (XRD, unit cell expansion with tin content). The Sn⁴⁺ ions which may be close to the defect silanol groups are octahedrally coordinated (¹¹⁹Sn MAS NMR). A part of Sn⁴⁺ ions (20 %) are probably in the tetrahedral coordination in MFI structure (XRD, ¹¹⁹Sn static NMR). However, large cations like Sn⁴⁺ (compared to Si⁴⁺) have a tendency to expand their coordination sphere to a five or six-fold, on interaction with one more ligands (UV-Vis.). Sn⁴⁺ ions form tin-peroxide radical on interaction with H₂O₂ and H₂O (EPR spectrum).

The substitution of Sn⁴⁺ in the MFI structure in place of Si⁴⁺ leads to interesting catalytic properties in both oxidation reactions in presence of aqueous H₂O₂ and acid-catalyzed reactions. In the hydroxylation of phenol, the ortho to para product ratio of 1.6 under optimum conditions suggest that isolated Sn⁴⁺ ions which are uniformly distributed on the external surface as well as within the channels are the active centers. Among the different solvents, water is found to be more efficient. The isolated Sn⁴⁺ centers in Td configuration tend to coordinate strongly with solvent molecules and probably reduce the rate of solvolysis of the (Si-O-Sn) units and hence the formation of peroxo intermediate with H₂O₂ (EPR observation). Like the vanadium silicalite-1, Sn-sil-1 activates both primary and secondary carbons in the oxidation of ethylbenzene (side chain) and n-hexane in presence of aqueous H₂O₂. Peroxo radical intermediate is probably capable of the side chain oxidation of aromatic substrate and oxyfunctionalization of primary carbon atom in the ethylbenzene oxidation. TS-1 activates only the secondary carbon atom and the reaction follows mainly an ionic mechanism. The hydroxylation of phenol over silylated Sn-sil-1 yields catechol to hydroquinone product ratio equal to 1.0, which is due to coverage of well dispersed Sn-enriched surface of the catalyst.

The weak acidity associated with Sn-sil-1 is responsible for the dehydration of cyclohexanol and isomers of butanol. The low conversion in the isomerization of m-xylene over Sn-sil-1 at 623 K (conv. = 0.80 %) indicates that very weak acidity is associated with Sn in Sn-sil-1. In the reforming of n-hexane over Pt-Sn-silicalite-1 molecular sieve, toluene is the major aromatic product and this suggests that the aromatization proceeds via hydrogenolysis, dehydrogenation to C₂ - C₄ olefins followed by oligomerization inside the intermediates. The incorporation of Pt during the synthesis of the stannosilicate (Sn-sil-1) yields a more active catalyst than when Pt is loaded by impregnation of Sn-sil-1. The Pt-Sn-sil-1 catalyst showed good activity and stability at atmospheric pressure.

Hydrothermal syntheses of medium pore Sn-sil-2 (MEL structure) and Sn-ZSM-48 leads to microporous, thermally stable and catalytically active materials in the oxidation of phenol and

toluene in presence of aqueous H_2O_2 . Probably 20 % of tin is substituted into the framework of silicalite-2 and ZSM-48 structures. We have also hydrothermally synthesized Al free- Sn-ZSM-12 (MTW structure) and Al free- Sn-beta (BEA structure). The hydrothermally synthesized Al free- Sn-beta and Sn-beta are distinguished by the acidic and oxidation properties, in the acetylation of 1,3,5- trimethylbenzene (1,3,5 TMB) with acetyl chloride and in the oxidation of m-cresol and 1,3,5- TMB with aqueous H_2O_2 , respectively. Finally a comparison of the oxidation of various organic substrates such as phenol, toluene, meta- cresol, meta-xylene, naphthalene and 2- methyl naphthalene was carried out over medium pore (Sn-sil-1 and Sn-sil-2) and large pore (Sn-ZSM-12) tin- containing molecular sieves. The results show that conversion of relatively smaller molecules such as phenol and toluene is more over medium pore, while the conversion of large molecules such as naphthalene and 2-methyl naphthalene is predominant over large pore Sn-ZSM-12, which indicates certain reactant shape selectivity.

LIST OF PUBLICATIONS

1. Synthesis and characterization of crystalline tin silicate molecular sieve with MFI structure.
N.K. Mai, S. Ganapathy, V. Ramaswamy and A.V. Ramaswamy.
J. Chem. Soc., Chem. Commun., 1933 (1994).
2. Synthesis of tin silicate molecular sieves with MEL structure and their catalytic activity in oxidation reactions.
N.K. Mai, V. Ramaswamy, S. Ganapathy and A.V. Ramaswamy.
Appl Catal, A General, 125, 233 (1995).
3. Sn-ZSM-12, a new large pore MTW type tin silicate molecular sieves: Synthesis, characterization and catalytic properties in oxidation reactions.
N.K. Mai, A. Bhaumik, R. Kumar and A.V. Ramaswamy.
Catal Lett. **33**, 387 (1995).
4. Synthesis of Al-free Sn-containing molecular sieves of MFI, MEL and MTW types and their catalytic activity in oxidation reactions.
N.K. Mai, A Bhaumik, V. Ramaswamy, A.A. Belhekar and A.V. Ramaswamy.
Stud Surf. Sci. Catal, **94**, 317 (1995).
5. Characterization and catalytic activity of medium pore Tin-silicate molecular sieves.
N. K. Mai, V. Ramaswamy and A.V. Ramaswamy.
Catalysis: Modern Trends, (Eds. N.M.Gupta and D.K. Chakrabarty), Narosa Publishing House, New Delhi, p. 173 (1995).
6. Synthesis, characterization and catalytic properties of alumino-, titano- and tin- silicates with MFI structure.
N.K. Mai, B. Rakshe, V. Ramaswamy and A.V. Ramaswamy.
13th National workshop on Catalysis, 20-22, Dec 1995, Bhavnagar.
7. Hydroxylation of phenol over Sn-silicalite molecular sieves: Solvent effects.
N.K. Mai and A.V. Ramaswamy.
J. Mol. Catal A: Chemical, 105, 149 (1996).
8. Oxidation of ethylbenzene over Ti, V- and Sn- containing silicalites with MFI structure.
N.K. Mai and A.V. Ramaswamy.
Appl. Catal A.General, 143, 75 (1996).
9. Synthesis and characterization of tin- containing ZSM-48 type molecular sieves using different templates.
N.K. Mai, V. Ramaswamy, B. Rakshe and A.V. Ramaswamy.
Stud Surf. Sci. Catal, 1996 (in press).

10. ^{29}Si Liquid NMR studies of Sn-silicite-1 molecular sieves during synthesis.
N.K. Mai, V. Ramaswamy and A.V. Ramaswamy
14th National Symposium on Catalysis, Deharadun, Accepted for oral presentation between 2-4th April 1997.
11. Synthesis, Characterization and Catalytic properties of large pore tin-beta and Si-free tin-beta molecular sieves.
N.K. Mai, A.V. Ramaswamy.
J. Chem. Soc., Chem. Commun., (in press, 1996)
12. An in situ ^{119}Sn -Mössbauer spectroscopic study on MFI, MEL and MTW tin-silicates.
K. Lazar and A.M. Szeleczky. Institute of Isotopes, Budapest, P.O.B. 77, H-15325, Hungary.
N.K. **Mai** and A.V. Ramaswamy. National Chemical Laboratory, Pune 411 008, India. *Catal. Zetf.*, (Submitted, 1996)
13. Sn-MFI: Synthesis methods, ^{29}Si Liquid and Solid MAS-NMR, ^{119}Sn Static and MAS-NMR.
N.K. Mai, V. Ramaswamy and A.V. Ramaswamy.
Zeolites (Submitted, 1996)
14. Reforming of n-hexane over pt-tin silicate molecular sieves.
N.K. Mai, S. Sivasanker and A.V. Ramaswamy.
Appl Catal., (Submitted, 1996).
15. Silylation of metallo-silicates with MFI structure and catalytic properties in the hydroxylation of phenol.
N.K. **Mai** and A.V. Ramaswamy
Catal. Lett., (to be submitted)

PATENTS

1. An improved Process for the preparation of Tin containing crystalline molecular sieves.
N.K. Mai, V. Ramaswamy and A.V. Ramaswamy.
PatApp.No. 1189/DEL/94
2. An improved Process for the preparation of Tin containing crystalline molecular sieves MEL types
N.K. Mai, V. Ramaswamy and A.V. Ramaswamy.
PatApp.No. 1191/DEL/94
3. An Improved Process for the preparation of tin-containing large-pore crystalline molecular sieves.
N.K. **Mai**, V. Ramaswamy and A.V. Ramaswamy
Indian patent (to be submitted)
4. Improved process for the reforming of n-hexane over pt-tin silicate molecular sieves.
N.K. Mai, S. Sivasanker and A.V. Ramaswamy
Indian patent (in preparation, 1996)