Supplementary information for Boosting hydrogen production at room temperature by synergizing theory and experimentation

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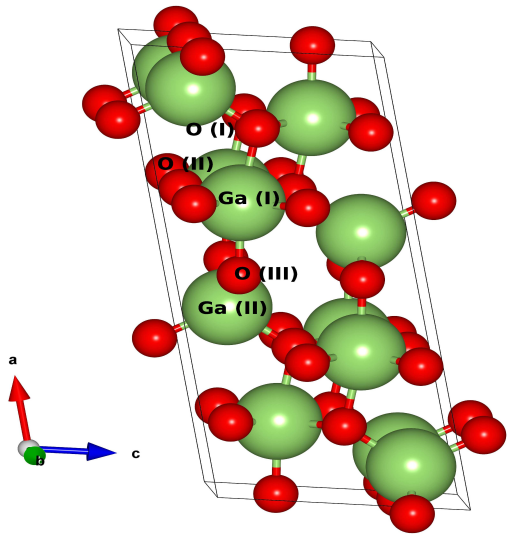

Figure SI-1: Bulk: monoclinic β-Ga_2O_3. There are two types of gallium atoms, Ga(I) and Ga(II), which have octahedral and tetrahedral coordination, respectively. One of the oxygen atoms, O(I), has tetrahedral coordination and is connected to three Ga atoms from the octahedral unit and one from the tetrahedral unit. Another oxygen atom, O(II), is coordinated to three Ga atoms, two of which belong to the octahedral chain and one to the tetrahedral chain. The third oxygen atom, O(III), is coordinated with two tetrahedral Ga atoms and one octahedral Ga atom.

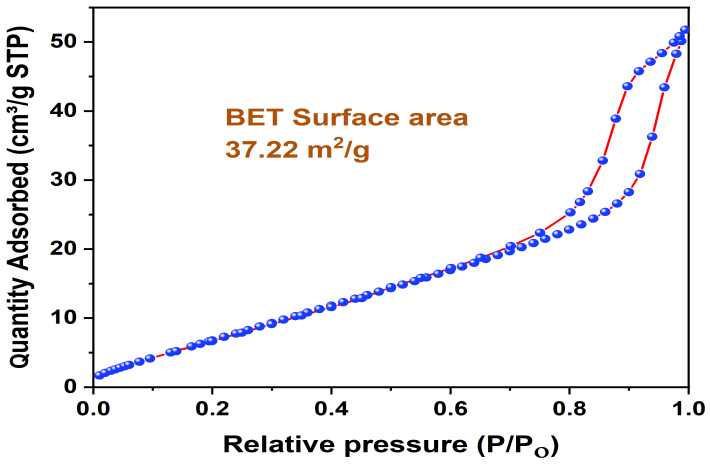

Figure SI-2: (a) BET specific surface area of β-Ga_2O_3. Catalyst exhibit type IV BET isotherm and mesoporous in nature.

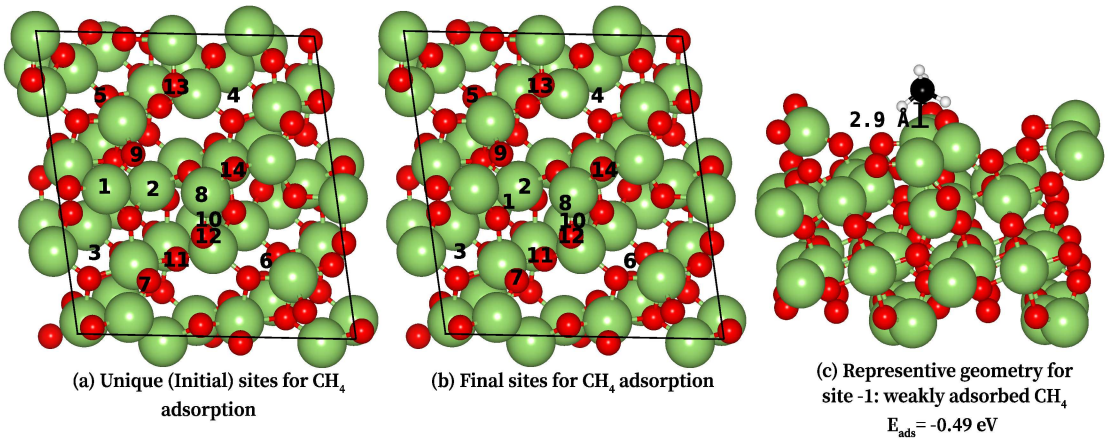

Figure SI-3: (a) Schematic representation of top view bare β-Ga_2O_3 (111) surface with unique (initial) adsorption sites. (b) Final positions after CH_4 adsorption. CH_4 is found to weakly adsorb at site 1 and 2. The C-H bond length for weak adsorption is 1.11 Å which is slightly greater than molecular bond length 1.09 Å. For weak adsorption at site 1, the final position is shifted. At all other sites, CH_4 is physisorbed. The final adsorption positions are the same as that of initial in case of physisorption. (c) Pictorial representation of weakly adsorbed CH_4 (side view).

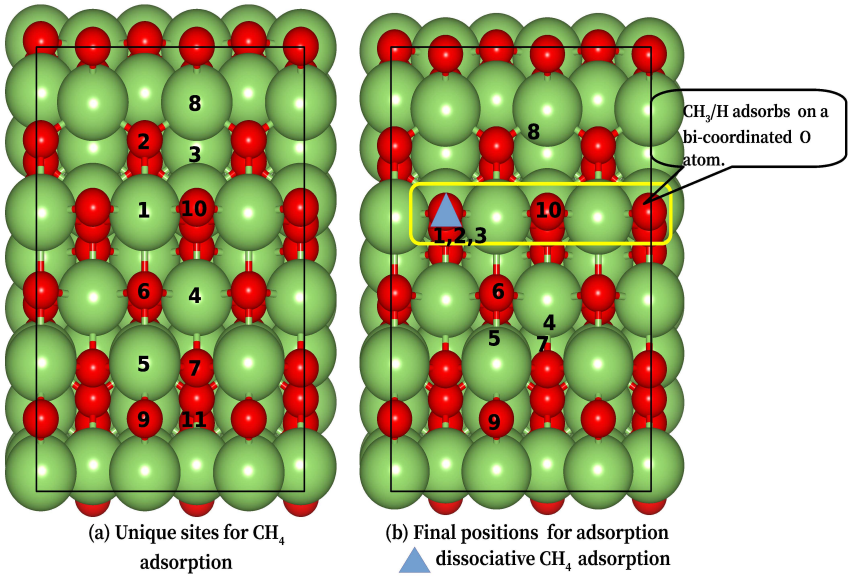

Figure SI-4: Schematic representation of top view of bare β-Ga_2O_3 ($\bar{2}02$). (a) Unique sites scanned for CH_4 adsorption corresponding to initial positions. (b) Final positions after adsorption. The yellow box contains bi-coordinated surface oxygen sites where CH_3/H adsorbs after methane dissociation The triangle corresponds to initial geometry 1,2,3, leading to dissociated CH_4. The final positions for physisorbed CH_4 are slightly shifted compared to initial except for 6 and 9.

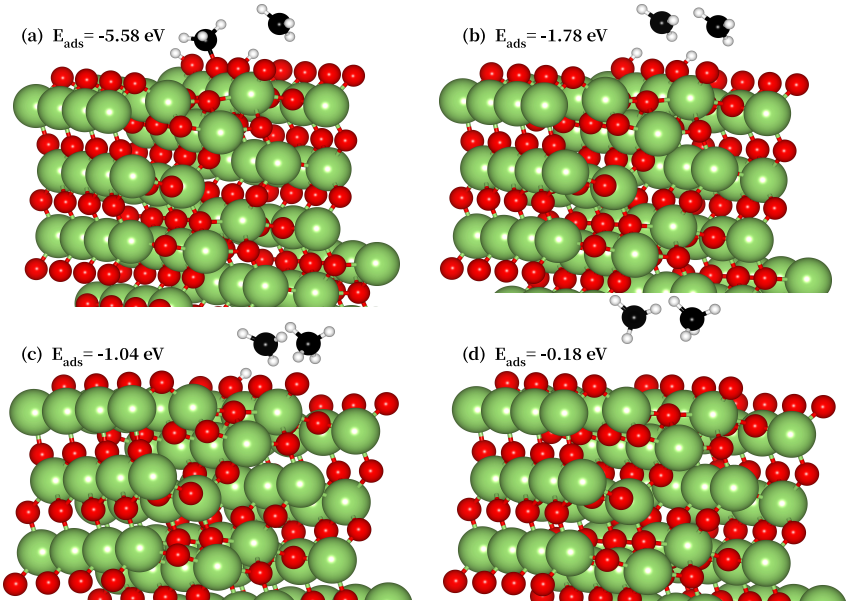

Figure SI-5: co-adsorption of two methane molecules over β-Ga_2O_3 ($\bar{2}02$). Four distinct final geometries are observed. (a) formation of a mixed CH_3O_s* and CH_3*. (b) formation of 2 methyl radicals, (c) formation of 1 methyl radical and physisorption of other molecule, and (d) physisorption of both molecules of methane.

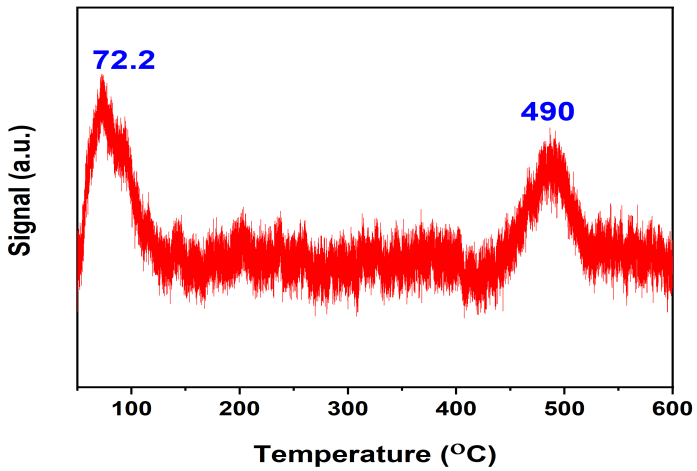

Figure SI-6: CO_2-TPD: The availability of weak and strong basic sites (72.2 and 490 °C) is more preferable for the adsorption of CH_4 over β-Ga_2O_3.

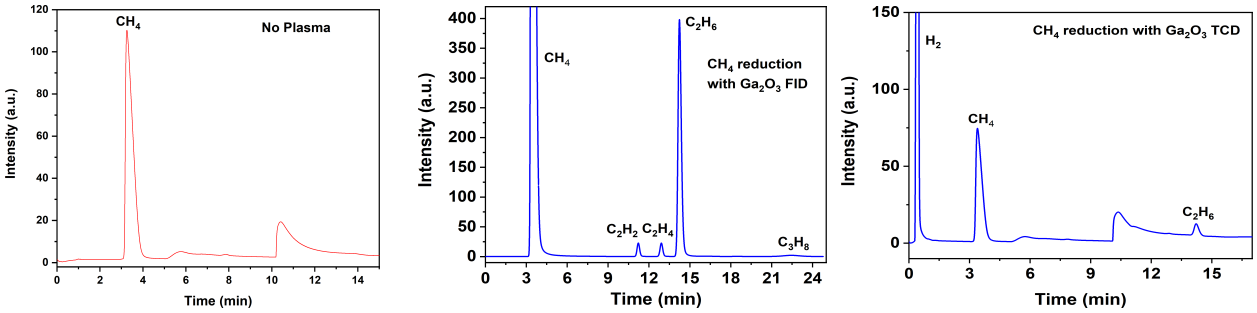

Figure SI-7: Real time gas chromatography results for methane conversion into value added products through NTP using gallium oxide.

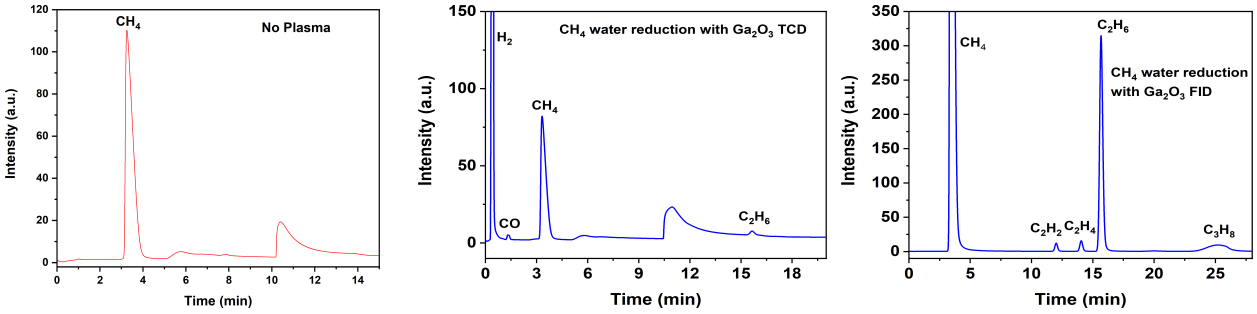

Figure SI-8: Real time gas chromatography results for methane-water conversion into value added products through NTP using gallium oxide.