

Selective Oxidation of Methane over Metallozeolite Catalysts: DFT Analysis of the Reaction Mechanism

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Selective oxidation of methane to methanol by molecular oxygen or air is fundamentally important in energy storage and transport, the production of platform chemical, and the mitigation of greenhouse gas emissions.

In the field of e-fuels, oxidation of methane to methanol is the key reaction in the reaction chain from carbon dioxide and hydrogen to methane to methanol to olefins. Transformation of methane to methanol can represent an environmentally friendlier equivalent of its liquefaction. Small technology units for oxidation of methane are crucial for the utilization of flare gases or transport of biogas from remote sources. Current available method of the conversion of methane to methanol represents two-step process of syngas production and its conversion to methanol or hydrocarbons by Fischer-Tropsch process. High pressure and temperature require high investment and operating costs and are economically feasible only producing methanol as a chemical in large facilities.

Newly developed catalytic systems for selective methane oxidation by molecular oxygen necessitate the extraction of methanol by water vapor, and this use of water vapor results in low methanol yields.

More recently, a new type of active sites and a new mechanism for activating of molecular oxygen over them were developed.

This active site is built by two transition metal ions (TMI) capable of the $2^+ \leftrightarrow 4^+$ redox cycle stabilized in extra-framework positions of the aluminosilicate zeolite matrix facing each to other in the distance of ca. 7.5 Å. Cooperation of these two cations embedded in zeolite matrix efficiently splits molecular oxygen into two $[M^{4+}=O^{2-}]^{2+}$ (α -oxygen) species.¹⁻³

Formed α -oxygens are very reactive and oxidize methane to methanol at low temperatures. Moreover, formed methanol is desorbed from TMI also at low temperature and assistance of an effluent for methanol production is not required. All these make binuclear TMI sites highly promising as a base for the development of the compact technology for converting methane to methanol.

However, tuning the reaction system and understanding the mechanism of the complex multi-step reaction (involving oxygen adsorption and splitting, methane

adsorption and oxidation, and product desorption) requires deep understanding of the active site's properties and the reaction mechanism. Surprisingly, the splitting of molecular oxygen or perturbation of the highly stable C-H bond does not represent the critical issue. Critical is the formation of methanol from methane molecule over active site formed by two enormously reactive α -oxygen. DFT calculations show that methoxyl group bounded to one Fe^{2+} ion and FeOH represent oxidation products. The cooperation of several molecules (methane, oxygen, water) is a key factor in forming methanol molecule instead of highly stable methoxyl species.

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