

Theoretical Studies of Methane Partial Oxidation to Methanol Catalyzed by Metal- Exchanged Zeolites

ムハマド, ハリス マヒュディン

<https://hdl.handle.net/2324/1931878>

出版情報：九州大学, 2017, 博士（工学）, 課程博士
バージョン：
権利関係：やむを得ない事由により本文ファイル非公開（3）

氏 名 : Muhammad Haris Mahyuddin
Name

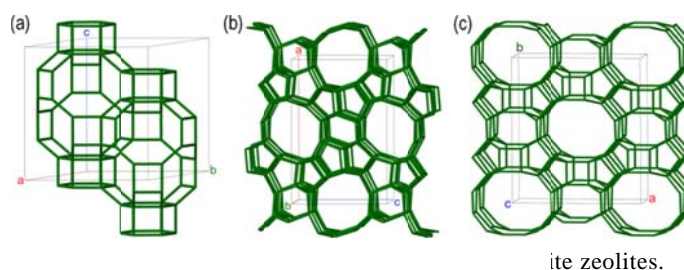
論 文 名 : Theoretical Studies of Methane Partial Oxidation to Methanol Catalyzed by
Title
Metal-Exchanged Zeolites
(金属ゼオライト触媒によるメタノールへのメタン部分酸化に関する研究)

区 分 : Kou (甲)
Category

論 文 内 容 の 要 旨 Thesis Summary

The depletion of fossil energy sources, primarily oil and coal, has driven the utilization of abundant natural gas as a transitional solution toward sustainable energy sources although gas is difficult to transport. To overcome this difficulty, methane, the major component of natural gas, should be converted to liquid forms such as methanol. While the existing technology for such a gas-to-liquid process involves a two-step process including the expensive synthetic gas production, methane can actually be converted in a more efficient and cheaper way through a direct catalytic reaction called partial oxidation or hydroxylation. However, this direct conversion strategy requires a highly reactive catalyst that can easily cleave the strong C–H bond of methane at low temperatures. Among all solid catalysts suitable for this reaction, metal-exchanged zeolites (microporous aluminosilicate anions exchanged for metal cations) are the ones that can achieve activity and selectivity as high as those of the enzymatic catalysts, i.e. methane monooxygenase (MMO). The pioneering works of methane partial oxidation by metal-exchanged zeolites showed that iron- and copper-containing ZSM-5 zeolites oxidize methane at temperatures as low as 25 and 125 °C, respectively. Although the actual active site structures of those catalysts are still unclear and debated, recent experimental studies proposed $[\text{FeO}]^{2+}$ and $[\text{Cu}_2(\mu\text{-O})]^{2+}$ cations as the most likely active species responsible for such facile reactions.

In this thesis, I employed density functional theory (DFT) to calculate reaction energy diagrams of methane partial oxidation over different structures of active sites hosted inside various types of zeolite frameworks (see Figures 1 and 2). The main results of this



thesis are divided into four chapters: Chapter 3~6. In Chapter 3, I compare the reactivity of different 3d metal cations $[\text{MO}]^+$ ($\text{M} = \text{Fe}, \text{Co}, \text{Ni}, \text{and Cu}$) in the absence and presence of ZSM-5 zeolite as a host. It is found that $[\text{CuO}]^+$ -ZSM-5 has the highest reactivity toward methane and zeolite pores confine methane in

such a way that they reduce the methane's C–H bond activation energy. In Chapter 4, I compare two isoelectronic systems of $[\text{FeO}]^{2+}\text{-Z}$ and $[\text{MnO}]^+\text{-Z}$ ($\text{Z} = \text{ZSM-5}$ and SSZ-39 zeolites) reacted with methane to produce methanol. It is found that metal coordination number and the energy gap between the acceptor (metal active site) and donor (CH_4) orbitals are crucial for determining the reactivity and reaction mechanism. In Chapter 5, I compare the reactivity of $[\text{Cu}_2(\mu\text{-O})]^{2+}$ species in different zeolite frameworks, namely the small-pore SSZ-13, SSZ-16, and SSZ-39 zeolites as well as the medium-pore ZSM-5 zeolite, as these Cu-zeolites were experimentally found to yield different amount of methanol from methane. It is found that $[\text{Cu}_2(\mu\text{-O})]^{2+}$ hosted in the small-pore zeolites oxidize methane with lower activation energy than that hosted in the medium-pore zeolite does. This is mainly due to the difference in $\angle\text{CuOCu}$ angle, which affects the energy gap between the acceptor and donor orbitals, while the zeolite confinement effects (i.e. reduction of methane's C–H bond activation energy) exerted by these distinct zeolites are found to be similar. In Chapter 6, I extend the work in Chapter 5 to $[\text{Cu}_2(\mu\text{-O})]^{2+}$ in large-pore Mordenite and Omega zeolites and investigate the role of water molecule in reducing methanol desorption energy. Moreover, I examine the distinct catalytic ability of an alternative active site structure $[\text{Cu}_3(\mu\text{-O})_3]^{2+}$ in oxidizing methane. It is found that a water molecule reduces the high methanol desorption energy to half and one of the three bridging O atoms in $[\text{Cu}_3(\mu\text{-O})_3]^{2+}\text{-Z}$, which has the highest spin density, is about 6 kcal/mol more reactive than the other two bridging O atoms.

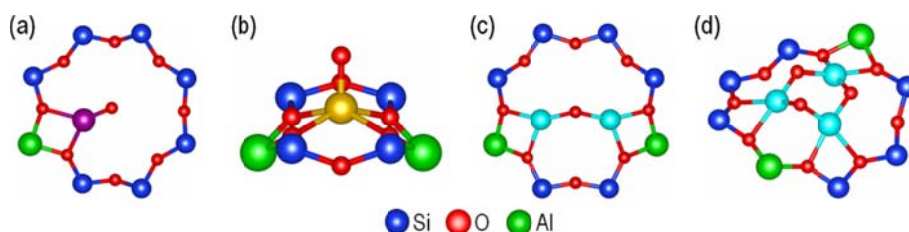


Figure 2. Aluminum atoms in zeolites provide a negative charge exchangeable for metal cation. (a) $[\text{MnO}]^+$, (b) $[\text{FeO}]^{2+}$, (c) $[\text{Cu}_2(\mu\text{-O})]^{2+}$, and (d) $[\text{Cu}_3(\mu\text{-O})_3]^{2+}$ hosted on different rings of zeolites.

This thesis provides clear explanations of how the essentially same Cu-zeolite catalysts (with different pore sizes of zeolites) yield different amounts of methanol, as reported in many experimental works. It also elaborates and confirms that the spin density of the oxo atom, the confinement of methane by zeolite pores, and the energy gap between the acceptor (metal active site) and donor (CH_4) orbitals are crucial for determining the active sites' reactivity toward methane. As the actual active sites' structure of metal-exchanged zeolites is still argued, excellent agreements between the measured and computed C–H bond activation energies reported in this thesis can hopefully provide a useful guidance for the future development of methane partial oxidation by metal-exchanged zeolites.