

Theoretical investigation on the methane activation in ion-exchanged MFI zeolite toward direct methane conversion

Kaoru Yamazaki^{1*}, Nobuki Ozawa¹, and Momoji Kubo¹

¹Institute for Materials Research, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan

*Corresponding author, e-mail kaoru.yamazaki@imr.tohoku.ac.jp, fax +81-22-215-2840

We theoretically investigated the diffusion methane coupling (DMC) reaction to ethane in MO/[M']-MFI (M, M' = Al, Ga, In) at the PM7 level of theory. We found that the relative energy of dissociative adsorption ΔE_{DA} is proportional to the energy level of MFIs' lowest unoccupied molecular orbital (LUMO) E_{LUMO} which is localized on the reaction center MO^+ . Tuning the interaction between the highest occupied molecular orbital of methane and the LUMO of MFI should enhance the DMC reaction.

1. Introduction

Methane activation is believed to be a key reaction for the direct conversion of methane contained in natural gas into variable chemicals. This reaction requires very efficient catalysis and many experimentalists and theoreticians try to find productive ones. [1] Ion-exchanged MFI zeolite is a prominent candidate of the methane conversion catalyst. Mahyuddin *et al.* theoretically suggested that the ion-exchange of the MFI zeolite to transition metal cations can realize the efficient direct conversion from methane into methanol by means of density functional theory [2,3]. In this study, we theoretically investigated the dissociative adsorption of methane to the ion-exchanged MO/[M']-MFI (M, M' = Al, Ga, In) and subsequent diffusion methane coupling (DMC) into ethane.

2. Computational methods

We used double unit cell model of MO/[M']-MFI with 580 atoms shown in Figure 1. The Si atoms at the T12 sites were replaced by M' atoms by isomorphous replacement and the reaction center MO^+ were introduced on the oxygens next to T12 site by ion-exchange. We optimized the geometries of the reactant, product, and intermediates at the PM7 level of semi-empirical molecular orbital theory [4] under periodic boundary condition. The transition states were optimized by the climbing-image nudged elastic band method [5].

3. Result and discussions

We found that the DMC reaction with GaO/[Al]-MFI is exothermic reaction as shown in Figure 2. Methane rapidly undergoes dissociative adsorption since the activation barrier for this step is only 3 kcal/mol for two methane molecules. This also indicates that the rate-determining step will be either the desorption from Ga^{3+} or diffusion of methyl radicals and that the stability of the dissociative adsorption state is a key to control

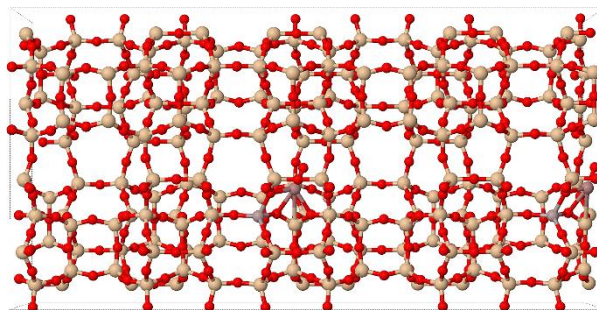


Figure 1: Double unit cell model of GaO/[Al]-MFI (580 atoms) used in this study.

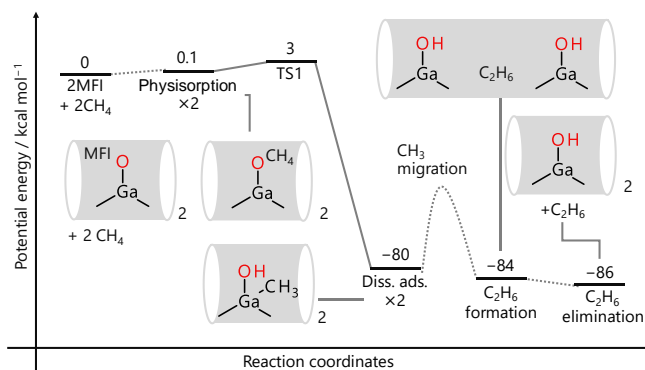


Figure 2: Schematic potential energy profile of the DMC reaction catalyzed by GaO/[Al]-MFI. Result at the PM7 level of theory.

the reaction barriers.

We thus try to control the stability of the dissociative adsorption state by substituting the reaction center MO^+ and the metal atoms at the T12 sites M' by M , $\text{M}' = \text{Al, Ga, In}$. We found that the relative energy of dissociative adsorption ΔE_{DA} is proportional to the energy level of MFIs' lowest unoccupied molecular orbital (LUMO) E_{LUMO} which is localized on the reaction center MO^+ (Figure 3). The methane coupling step for $\text{GaO}[\text{Al}]\text{-MFI}$ whose LUMO was located relatively high energy region ($E_{\text{LUMO}} = -0.44 \text{ eV}$), was exothermic but those for the other MFIs ($E_{\text{LUMO}} < -1.0 \text{ eV}$) were endothermic due to over binding of methyl radical on the MO^+ .

4. Conclusions

In summary, we investigated the DMC reaction to ethane catalyzed by $\text{MO}[\text{M}']\text{-MFI}$ ($\text{M, M}' = \text{Al, Ga, In}$) at the PM7 level of semi-empirical molecular orbital theory. We found that the DMC reaction with $\text{GaO}[\text{Al}]\text{-MFI}$ is exothermic reaction and its rate-determining step will be either the desorption from Ga^{3+} or diffusion of methyl radicals. The relative energy of dissociative adsorption ΔE_{DA} is proportional to the energy level of MFIs' lowest unoccupied molecular orbital (LUMO) E_{LUMO} which is localized on the reaction center MO^+ . Tuning the interaction between the highest occupied molecular orbital of methane and the LUMO of MFI should enable to control reactivity on the dissociative adsorption of methane and DMC reaction.

References

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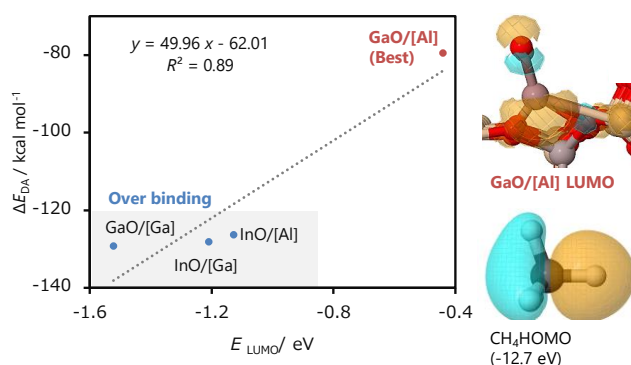


Figure 3: Correlation between the relative potential energy of dissociative adsorption ΔE_{DA} and the energy level of lowest unoccupied molecular orbital (LUMO) E_{LUMO} of MFIs $\text{MO}[\text{M}']\text{-MFI}$. Result at the PM7 level of theory.