

## Multi-Scale Theoretical/Computational Approach to Heterogeneous Catalysis

(National Institute for Materials Science (NIMS))

○ Atsushi Ishikawa

**Keywords:** Density functional theory, microkinetics, chemical kinetics, reaction mechanism

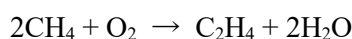
### 1. Introduction

The oxidative coupling of methane (OCM) has long been studied to provide an efficient way to convert natural gas into high-value chemicals. For the full understanding of its reaction mechanism, the multi-scale theoretical simulation was conducted; the method is based on the density functional theory (DFT), microkinetics, and chemical reactor modeling. Our purpose is to predict the activity (the reactant conversion) and the product selectivity, from atomic or molecular level simulations.[1]

In addition to the above topic, our recent approach that combines the machine-learning with DFT-based microkinetics focusing on the  $\text{NH}_3$  synthesis is also introduced.[2]

### 2. Theoretical method

We investigated the OCM reaction

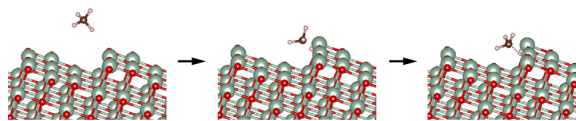


catalyzed by MgO, first found by Lansford *et al.*[3] We modeled the active site as the stepped MgO surface, based on previously reported experimental results and our theoretical works.[4, 5] The reaction model includes 109 gas-phase and 61 surface reactions. Using DFT, reaction energy ( $\Delta E$ ) was calculated, and activation barrier ( $E_a$ ) were estimated from  $\Delta E$  values using the linear free energy relationship. For the DFT calculation, VASP 5.4 program package was used. From  $\Delta E$  and  $E_a$  values, we evaluate the reaction rate constants and constructed reaction rate equations. Reaction rate equations were solved numerically using MATLAB software. The reactant conversion and product selectivity were evaluated from composition of the inlet and outlet gas.

### 3. Results and discussion

In Figure 1, the transition state (TS) of the H-abstraction from  $\text{CH}_4$  obtained from the DFT calculation is shown. The preliminary microkinetic analysis show that this process has the largest contribution to the reactant conversion. The calculated  $E_a$  value is 96.5 kJ/mol, which is reasonable agreement with experimental range.

From this  $E_a$  value other elementary reactions, the kinetic parameters are obtained and the microkinetic and reactor analysis are performed. In Figure 2, the change of the molar



**Figure 1.** Optimized structures of the  $\text{CH}_4$  activation at the stepped MgO. The left, middle, and right correspond to the reactant, TS, and product states.

fraction with reaction time is shown. The reactant i.e.  $\text{CH}_4$  and  $\text{O}_2$  decreases as the reaction proceeds, while  $\text{C}_2\text{H}_6$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}$  and  $\text{CO}_2$  are generated.

In Figure 3, the  $\text{CH}_4$  conversion and composition of C-containing compounds were shown. With the increase of temperature, the  $\text{CH}_4$  conversion becomes higher but  $\text{C}_2$  compounds decreases, which agrees with experimental tendency. Thus, our multi-scale simulation correctly reproduces the activity and selectivity tendency of the OCM catalyst.

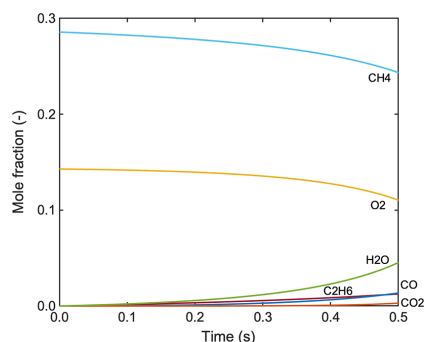
#### 4. Conclusions

We theoretically investigated the OCM over  $\text{MgO}$ , with the DFT calculation, microkinetics, and chemical reactor simulations to evaluate the reactant conversion and product selectivity. What is unique in this study is that both gas-phase and surface-mediated reactions were included, and the kinetic and thermodynamic properties of 170 elementary reactions were all calculated by DFT. Our simulation have found that;

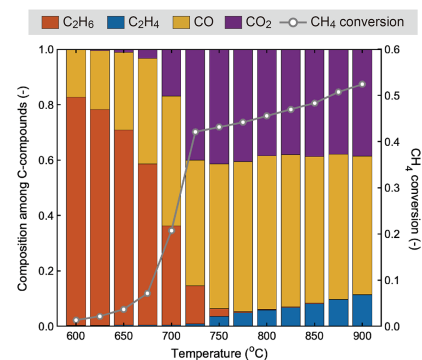
- 1)  $\text{CH}_3$  formation from  $\text{CH}_4$  is highly endothermic in the gas phase ( $\Delta E = 4.73$  eV), while  $\Delta E$  decreases to 0.33 eV when  $\text{CH}_4$  activation occurs on the stepped  $\text{MgO}$ .
- 2) The mole fraction change along the reaction shows that the  $\text{C}_2$  compounds are formed first but  $\text{CO}_x$  ( $x = 1, 2$ ) are formed later, indicating the overoxidation of  $\text{C}_2$  compounds.
- 3) The effects on  $\text{CH}_4$  conversion and  $\text{C}_2$  selectivity from the temperature and  $P_{\text{CH}_4} : P_{\text{O}_2}$  are observed. The  $\text{CH}_4$  conversion increases with temperature, while the  $\text{C}_2$  selectivity becomes lower. A similar but more moderate dependency was observed for  $P_{\text{CH}_4} : P_{\text{O}_2}$ . These trends agree well with experimental reports.

Our study strongly suggests that DFT-based microkinetics is a strong approach to analyze the catalysis from the atomic or molecule scale resolution.

- 1) A. Ishikawa and Y. Tateyama, *ACS Catal.*, **2021**, 11, 2691–2700; 2) A. Ishikawa, *submitted*;
- 3) T. Ito, J. H. Lunsford et al., *J. Am. Chem. Soc.*, **1985**, 107, 5062; 4) A. Ishikawa and Y. Tateyama, *J. Phys. Chem. C*, **2020**, 124, 6054–6062.; 5) A. Ishikawa and Y. Tateyama, *Catal. Lett.*, **2021**, 151, 627–633



**Figure 2.** Mole fraction along the reaction time (s) calculated by the reactor simulation.



**Figure 3.** Dependence of the composition of C-containing species (left axis) and  $\text{CH}_4$  conversion (right axis) on reaction temperature (in  $^{\circ}\text{C}$ ).