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MO₆S₈-BASED SINGLE-METAL-ATOM CATALYSTS FOR METHANOL SYNTHESIS FROM STEAM REFORMING OF METHANE

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MO₆S₈-BASED SINGLE-METAL-ATOM CATALYSTS FOR METHANOL
SYNTHESIS FROM STEAM REFORMING OF METHANE

By

Haotian Zhang

A DISSERTATION

Submitted in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

In Materials Science and Engineering

MICHIGAN TECHNOLOGICAL UNIVERSITY

2020

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This dissertation has been approved in partial fulfillment of the requirements for the
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Preface

Methanol synthesis from methane is a promising approach to effectively utilize the surging amount of methane (CH_4) worldwide. However, the industrial methanol synthesis from methane via a two-step process, namely, the production of syngas from steam reforming of methane (SRM) and the follow-up synthesis of methanol from syngas, is energy-intensive and requires large centralized plants. As an alternative method, direct conversion of methane to methanol (DMTM) at a relative low temperature is more desirable for its energy efficiency. Especially, with water as the oxidant, a high selectivity to methanol could be achieved. Nevertheless, the CH_4 conversion still needs to be improved with more advanced catalysts in order to meet the industrial requirement. This motivates us to explore a potential catalyst, namely, single atom (K, Ti, Co, Fe, Ni, Cu, Rh) doped Mo_6S_8 , for direct methanol synthesis from methane with water, i.e. direct SRM to methanol.

Our work focuses on: (1) Confirming the stability of Mo_6S_8 -based catalysts during the reaction process of direct SRM to methanol; (2) Investigating the catalytic behaviors of the different Mo_6S_8 -based catalysts for CH_4 and H_2O adsorption and dissociation; (3) Estimating the most possible reaction pathways of SRM to methanol on the various Mo_6S_8 -based catalysts and finding out the most promising catalyst for this specific reaction.

My PhD research work was supervised by Prof. Yun Hang Hu at Michigan Technological University from 2016 to 2020. This dissertation is based on one publication. I performed all the experiments and data analysis with the guidance of Prof. Yun Hang Hu. Dr. Ping

Liu helped me with the design of the M-Mo₆S₈ clusters. This work would not be possible without the guidance, encouragement and support from Prof. Hu.

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This dissertation is dedicated to all the people who have encouraged, supported, and helped me.

List of Abbreviations

Abbreviations	Full name
BET	Brunauer–Emmett–Teller
DBD	dielectric-barrier discharge
DFT	density functional theory
DMFC	direct methanol fuel cell
DMTM	direct conversion of methane to methanol
DRM	dry reforming of methane
DSS	daily start-up and shut-down
E_a	energy barrier
GGA	generalized gradient approximation
HAP	hydroxyapatite
LDA	local density approximation
MOFs	metal-organic frameworks
NEB	nudged elastic band

NP	nano particle
PAW	projector-augmented wave
PBE	Perdew-Burke-Ernzerhof
PDOS	partial density of states
POX	partial oxidation of methane
PW91	Perdew-Wang
RMM-DIIS	residual minimization scheme, direct inversion in the iterative subspace
RWGS	reverse water-gas shift reaction
S/C	steam/carbon
SACs	single metal atom catalysts
SEM	scanning electron microscope
SMSIs	strong metal-support interactions
SRM	steams reforming of methane
TEM	transmission electron microscopy

TS	transition states
VASP	Vienna Ab initio Simulation Package
WGS	water-gas shift reaction
XPS	X-ray photoelectron spectroscopy
YSZ	yttria-stabilized zirconia

Abstract

The surge of methane as the major component of natural gas and a dominant greenhouse gas calls for the development of efficient strategy to convert it into valuable liquid chemicals such as methanol. However, the current industrial method for methanol synthesis, which consists of the steam reforming of methane (SRM) to syngas and the followed reaction of syngas to methanol, is rather energy-intensive. Direct conversion of methane into methanol (DMTM) is highly desirable in terms of energy efficiency and economy. DMTM with water as oxidant, i.e. SRM to methanol, is a promising solution but the development highly efficient and selective catalyst remains a critical challenge. Mo_6S_8 -based catalysts have shown possible potential for this reaction process. In this thesis, for the first time, the feasibility of using Mo_6S_8 cluster and a series of single metal atom (K, Ti, Co, Fe, Ni, Cu, Rh) doped Mo_6S_8 as catalysts for SRM to methanol were evaluated via DFT calculation.

Chapter 4 provided the structure of Mo_6S_8 and $\text{M-Mo}_6\text{S}_8$ ($\text{M}=\text{K}, \text{Ti}, \text{Co}, \text{Fe}, \text{Ni}, \text{Cu}, \text{Rh}$) clusters and confirmed that they were stable under the reaction condition of SRM.

The catalytic behaviors of Mo_6S_8 and $\text{M-Mo}_6\text{S}_8$ clusters toward CH_4 adsorption and dissociation were evaluated in chapter 5. All metal dopants, except K and Rh, showed enhanced CH_4 adsorption compared to bare Mo_6S_8 via the ensemble effect (the direct participation of M in binding), while CH_4 adsorption was weakened on K- and Rh- Mo_6S_8 due to the ligand effect (the modification of the electronic structure of $\text{M}^{\delta+}$ and $\text{Mo}^{\delta+}$).

Meanwhile, the doping of Co, Fe, Ti, Ni, and K accelerated the first hydrogen abstraction of CH₄ while all the metals suppressed the further dissociation of *CH₃, suggesting their great potential for selective CH₃OH synthesis and high coking resistance.

In chapter 6, the catalytic behaviors of Mo₆S₈ and M-Mo₆S₈ clusters toward H₂O adsorption and dissociation were evaluated. H₂O adsorption was enhanced by all metal dopants except Rh. The ensemble effect was dominating in enhancing the H₂O adsorption. Compared to the bare Mo₆S₈ cluster, the first hydrogen abstraction was enhanced by all the single metal atom dopants, whereas the second abstraction was mostly suppressed except Ti and Fe. Furthermore, since H₂O possessed stronger adsorption than CH₄ on the same active site, the initial step for CH₃OH synthesis via SRM was considered to be the dissociation of *H₂O to *OH and/or *O species.

Based on the results obtained in the above chapters, in chapter 7, the reaction pathways of SRM to methanol on Mo₆S₈ and M-Mo₆S₈ were set up and the energy barrier for each elementary step was calculated. Methanol synthesis was hindered on bare Mo₆S₈ cluster due to the high energy barrier for C-O bond association. All M-Mo₆S₈ showed enhanced activity for CH₃OH synthesis via SRM. The promoting effect of Fe was the most significant, which was followed by Ni, Co, Rh, Cu, K, and Ti in a decreasing order. The ensemble effect and confinement effect as well as the d states of M atom near Fermi level facilitated the reaction, especially in promoting the C-O bond association between *CH₃ and *OH.

Keywords: Single-atom catalyst; Steam reforming; CH₄ activation; Methanol synthesis; Modified molybdenum sulfide; Iron; DFT

1 Introduction

Methane (CH₄) is the primary component of natural gas and a potent greenhouse gas. The surge of natural gas in recent years has urged the development of efficient technologies for the conversion CH₄ into more valuable and environmental-friendly chemicals.¹ Considering the difficulty in long-distance transportation of natural gas, transformation of methane into more transportable liquid fuels is the most promising solution to this issue.² However, the most widely used process currently for the utilization of methane is the streaming reforming of methane into hydrogen and syngas.

1.1 Catalysts for Steam Reforming of Methane

Stearns reforming of methane is the predominant industrial process for hydrogen and syngas manufacturing.^{3, 4} It involves the endothermic reaction (Eq.1-1) between water steam (H₂O) and methane (CH₄) at a high temperature (typically 1023-1223 K) and a wide range of pressure (typically 14-20 atm).⁵ During the process, the water-gas shift reaction (WGS, Eq.1-2) could take place at the meantime, which could further enhance the production of H₂.

The first process for the conversion of hydrocarbon into hydrogen in the presence of water steam was reported by Tessie du Motay and Marechal in 1868.⁶ In 1930, the first industrial application of SRM was implemented.⁶ Till now, SRM remains an important topic in scientific field (Figure 1.1). Developing more efficient and more cost-effective SRM technology is a long-term project. Along the years' research on SRM, a series of catalysts have been explored. Among them, Ni/Al₂O₃ is the most widely employed due to its low cost and high activity.⁷⁻¹⁰ However, coking formation and sintering of Ni particles are two main challenges for the commercial Ni catalysts. Thereby, a majority part of research efforts in this area have been focused on improving the coking and sintering resistance of Ni catalysts.¹¹⁻¹⁴ Besides the Ni-based catalysts, other catalysts, such as noble metals (Rh, Ru, Pt etc.) and other transition metals (Co, Cu, Mo etc.) based catalysts have been explored for SRM all through the years as well.

Figure 1.1. Publications on SRM in the past decade.

1.1.1 Essential Issues for SRM Catalysts

An ideal SRM catalyst should possess both a high activity and a long-term stability. While both aspects are related to the chemical natures and textural properties (morphology, surface area, pore structure etc.) of the catalysts,^{10, 15, 16} two major issues, i.e. coking and sintering, lead to the deactivation (i.e. a poor stability) of a catalyst during the SRM process.³

Sintering is the growing of metal particles. It is a complex process influenced by many factors such as temperature, chemical environment, catalyst composition and structure, and support morphology. Temperature and atmosphere are the two most important factors.¹⁰ For instance, a higher temperature results in obviously a higher sintering rate. Water steam atmosphere can accelerate the sintering as well. Two mechanisms are proposed to describe the sintering: (1) atom migration (Ostwald ripening) and (2) crystallite migration and coalescence. Ostwald ripening mechanism involves the metal atom emitting from one particle to another, while the coalescence process refers to the crystallites themselves move over the support and collide to form larger particles. The driving force for sintering is the difference in the surface energies before and after sintering. Sintering leads to the reduction of metal surface area, thus resulting in the decreased activity.³ Sintering can be effectively suppressed by enhancing the metal-support interaction. For example, the addition of Ir or Rh can mitigate the sintering of Ni by forming Ni-Ir and Ni-Rh alloys during the aging process, respectively.¹⁷ The application of MgAl_2O_4 support for Rh-based catalyst leads to the formation of Rh-O bonds which is the originate of strong metal-support interaction.¹⁸

The modification of structural properties, such as the mesoporous structure, can also prevent the sintering.¹⁹

Coking is a collective description of the carbonaceous deposits originated from dissociation of hydrocarbons on the surface of catalysts. There are three major types of coking, i.e. atomic carbon (C_α), polymerized carbon (C_β) and encapsulating carbon (gum). The C_α species are highly reactive. It can be converted into C_β by rearrangement and polymerization. C_β may be gasified or dissolved in the Ni crystallite. However, these dissolved C_β can diffuse through the nickel to nucleate and precipitate at the rear of crystallite, forming carbon whisker, which can lift nickel crystallite from the support and finally result in fragmentation.^{20, 21} The encapsulating carbon is generated during the reforming of heavy hydrocarbon feeds with a high content of aromatic compounds. This kind of carbon consists of a thin CH_x film or a few layers of graphite covering the Ni particle, leading to the loss of activity. Various strategies can be employed to reduce coking are various. The employment of promoter like alkali metal²², noble metal²³, and rare earth metal²⁴ can reduce coke formation. Application of well-defined support, such as perovskite²⁵ and spinels¹⁹, can reduce the carbon formation as well.

1.1.2 The Development of Ni-based Catalyst

Ni based catalyst is the most commonly used catalyst in the industry, due to its low cost and moderate activity. All through the years, efforts from both scientific and industrial

areas focus on improving the resistance of Ni-based catalysts to carbon deposition and sintering. Three major approaches have been attempted to stabilize Ni-based catalysts, i.e. (1) adding promoters, (2) applying different support materials, and (3) tuning the structure of unsupported Ni catalyst.

(1) Promoters for Ni-based catalysts

Various species have been explored as promoters for Ni based catalysts, including noble metals, coinage metals, redox metal oxides, non-metals, and so forth. While some of them promote both the activity and stability of Ni catalyst, some may enhance the activity at a certain sacrifice of the activity.

a) Promoters based on metal-metal interaction

A series of metals function as promoter for Ni catalysts in SRM by forming metal alloys with Ni, including noble metals like Ru, Rh, Ir, and Pt, coinage metals (i.e. Au, Ag, Cu) as well as K and Co etc.

Ru was found effective in promoting the self-reducibility of Ni/MgAl₂O₄ catalyst during the SRM process, which means that a pre-reduction in H₂ was not needed for the catalysts.²⁶ This promotion could be realized just in the presence of a trace amount of Ru (0.05 wt%). The self-activation of Ru-Ni/MgAl₂O₄ catalysts was due to the reduction of NiO by hydrogen spillover on Ru during the reaction. According to density functional theory

(DFT) calculation, alloying Ni with Ru was more effective in reducing carbon deposition than alloying Ni with Rh.²⁷ However, under a high temperature, the interaction between Ru and Ni became inferior. Morales-Cano et al. suggested that compared to Rh and Ir, the formation of Ru-Ni was energetically unfavorable due to its lower miscibility in Ni and poorer sintering resistance under an aging condition of 800 °C.¹⁷ Rh and Ir could enhance both the activity and sintering resistance of Ni/Al₂O₃ by forming Rh-Ni and Ir-Ni alloy, respectively. Before sintering, the activity of Ru promoted Ni/Al₂O₃ was comparable to the sample promoted by Rh and superior to that promoted by Ir (Figure 1.2A). But after aging the samples at 800 °C, while Rh-Ni/Al₂O₃ showed 6-time higher activity than Ni/Al₂O₃, the Ru-Ni/Al₂O₃ only promoted the activity of Ni catalyst by 4 times and the activity was inferior to that of Ru/Al₂O₃ (Figure 1.2B).

Similarly, a small loading (0.078 wt%) of Pt in nickel-based catalysts could significantly improve their oxidation resistance, thus achieving a stable SRM reactivity at 700 °C.²⁸⁻³⁰ For a plate-type anodic-alumina-supported 17.9 wt% Ni catalyst, which deactivated quickly in daily start-up and shut-down (DSS) SRM at 700 °C, 0.05 wt% Ru or Pt doping allowed the catalyst to exhibit self-activation, self-regeneration, and self-redispersion.³¹ And the Pt-Ni catalyst showed better stability than Ru-Ni in 3000-h continual and 500-time DSS. Moreover, core-shell structure Ni@Pt could significantly suppress the carbon formation and double the activity.³² The modified electron structure of Ni by Pt provided a down-shifted d-band which could accelerate the C-O bond association between *OH and *CH_x species, thus enhancing the coking resistance. In addition, it was suggested that CH₄ activation was the rate-determining step for the reaction on Ni (111), Pt (111), and Ni@Pt.

While *OH-assisted CH₄ activation was preferred on Ni@Pt, direct dissociation of CH₄ was energetically favorable on Ni (111) surface.

For coinage metals (i.e. Au, Ag, Cu), while the selectivity and stability of CO could be enhanced after the introduction of Cu to the commercial Ni/Al₂O₃,³³ Ag and Au enhance the stability of Ni-based catalysts at a minor sacrifice of the initial CH₄ conversion. In specific, 0.3 wt% Ag doped Ni/Al₂O₃ showed a high resistance to coke deposition, attributed to the altered electronic and geometric structure of superficial Ni by Ag.^{23, 34} However, since Ag selectively substituted the more active Ni sites, the activation energy for CH₄ was increased on the Ag covered Ni, resulting in an reduced activity.^{34, 35} Analogous to Ag, Au could be preferentially alloyed with Ni with a low-coordination number and block the active Ni sites.³⁶ Theoretical studies on the effect of Au, Ag, and Cu dopants in Ni catalysts on the major processes in SRM revealed that the metal dopants had a little influence on the two-step dissociation of *H₂O and the dehydrogenation of *CHO was kinetically favorable on all alloy surfaces.³⁷ However, except for the Ni-Cu alloy, both the Ni-Au and Ni-Ag alloys showed higher energy barrier than Ni for the oxidation of *CH to *CHO, indicating their inferior activity.³⁷

Similar to Au and Ag, Co and K improved the coke resistance of Ni/Al₂O₃ catalyst for SRM with a moderate decrease in the initial catalytic activity.^{22, 38} The CH₄ conversion kept at ~95% for 180 h over 7% Co in Ni-Co/Al₂O₃ bimetallic catalyst. However, the low-coordinated active Ni sites could be partially blocked by Co atoms, leading to decreased activity with increasing Co content. K enhanced the coking resistance of Ni in SRM via

the increased barriers of C-H cleavage in the last two steps of CH₄ dissociation.³⁹ The coking initial temperature was raised by 200 °C in the presence of 4 wt% K. But the activity of the K promoted Ni catalyst was only 17% of the undoped Ni/Al₂O₃.²² Nevertheless, the employment of appropriate transition metals with the alkali metal could bring excellent performance improvement. The co-addition of K and Ti species obviously improved the SRM activity of Ni/Al₂O₃ catalyst.⁴⁰ The sample with 11 wt% of K₂Ti_xO_y was optimal, showing a high coking resistance with neglectable activity decrease (Figure 1.2C).

Figure 1.2. Catalytic activity measured of (A) reduced and (B) aged noble-metal-promoted catalysts¹⁷; (C) Change in activity of Ni/K₂Ti_xO_y-Al₂O₃ catalysts and reference catalysts with time-on-stream⁴⁰; (D) Scheme structure of Nb-promoted Ni/Al₂O₃.⁴¹

Alkaline earth metals (Mg and Ca) were effective promoters to improve stability of Ni based catalysts, attributed to the increase of the steam-carbon reaction, the neutralization of the acidity of the support, and their interaction with Ni metal (delusion in Ni). The addition of Mg and Ca to Ni/ α -Al₂O₃ increased the CH₄ conversion from ~10% on Ni-based catalysts to 20%.⁴²

b) Redox metal oxide promoters

Redox metal oxides, such as MoO_x, CeO₂, La₂O₃, Nb₂O₅ etc., could help to stabilize the Ni particles against sintering at high temperatures.^{41, 43-47} Probably due to the synergistic effect between Mo and Ni and increased the electron density of the catalytic site, the catalytic activity and stability was dramatically enhanced after the addition of Mo in Ni catalysts.⁴³ Especially at a low steam/carbon (S/C) ratio of 2.0, only the 0.05 wt% Mo promoted catalyst remained stable throughout the 500-min test.

Both the methane conversion and stability of a Ni/Al₂O₃ (7% wt. Ni) catalyst were improved by the addition of CeO₂ (6% wt.) and La₂O₃ (6% wt.), respectively.⁴⁶ Besides, the CO₂ content in the resultant synthesis gas was considerably decreased in the presence of Ni-CeO₂-Al₂O₃/cordierite catalysts, which might be attributed to suppression of the WGS reaction.⁴⁸ For Ni/Al₂O₃ with different Ni loading amount, the optimal amount of

CeO₂ promoter could vary. For 13 wt% Ni/Al₂O₃, 1.02 wt% Ce showed the best promotion effect, achieving 75% CH₄ conversion at the S/C ratio of 2.7 in 300 h.¹⁶

Niobia promoter improved the SRM performance of Ni/Al₂O₃ catalyst by suppressing the formation of coking on the catalyst via the strong interaction between metal and support (Figure 1.2D).⁴¹ With 5 wt% Nb loading, the CH₄ conversion on Ni/Al₂O₃ reached 98%, which was 10.4% higher than that of the undoped sample. However, when the Nb content reached 20 wt%, the aggregation of Ni was severe and the catalytic activity was reduced.

CaZrO₃ perovskite oxide has been applied as promoter to enhance the catalytic performance of Ni/ α -Al₂O₃ as well.⁴⁹ The size and amount of CaZrO₃ affected not only the dispersion of Ni, but also the interaction between Ni and Al₂O₃ and the number of oxygen vacancies, which could facilitate the steam adsorption-dissociation. 15 wt% CaZrO₃ promoted Ni/ α -Al₂O₃ attained the optimal CH₄ conversion (67%) and H₂ yield at 700 °C and S/C ratio of 1.0.

c) Non-metal promoters

Boron is the only non-metal promoter that has been explored.⁵⁰ It could enhance both the activity and the stability of Ni-based catalysts by assisting in preventing coke formation. The unpromoted catalyst could only convert 55% CH₄ at the beginning and lost 21% of its initial activity after 10-h SRM reaction. After 1 wt% B doping, the CH₄ conversion was increased to ~61% at the beginning and retained at ~56% after 10 h. However, theoretical

computation revealed that B atom could block all the step sites of Ni first and then occupy the octahedral sites just below the surface. Excessive addition of B atom could reduce the activity of Ni catalysts.

(2) Supports for Ni-based catalysts

Except for the most widely used Al_2O_3 support, various other oxide supports have attracted researcher's attention in the past decade, including MgO , SiO_2 , ZrO_2 , La_2O_3 , Pyrochlore, and Perovskite etc. Different supports lead to different textual properties (surface area, porosity, heat transfer, etc.) and varied interactions with Ni species. Strong metal-support interactions (SMSIs) can increase the dispersion of Ni species and thus are important for a high SRM activity. Some supports can provide highly mobile oxygen or oxygen vacancies which can accelerate the reaction. Advanced preparation methods could result in improved textual properties such as increased surface area and porosity, which could enhance the SMSIs and lead to an advanced SRM performance.

a) MgO -based substrates

MgO -based materials were extensively studied as the support for Ni-based SRM catalyst. Small and well-dispersed Ni metallic particles on a highly stable $\text{Ni}_{0.03}\text{Mg}_{0.97}\text{O}$ solid solution support attained 90% CH_4 conversion at a low S/C ratio of 1.0 and kept stable for

70 h with a high coke resistance.⁵¹ The metallic Ni particles which homogeneously distributed on the surface of the parent $\text{Ni}_{0.4}\text{Mg}_{0.6}\text{O}$ solid solution supports (Figure 1.3A) could completely convert CH_4 for 1000 h without deactivation.⁵²

With the cooperation of MgO and Al_2O_3 , MgAl_2O_4 spinel was another popular support for Ni catalyst for SRM.⁵³ The Ni/Mg-Al-O catalyst prepared from Mg-Al hydrotalcite precursors allowed the formation highly dispersed Ni particles (with a size smaller than 15 nm after reduction at 1073 K) on its surface, leading to a high activity and stability (100% CH_4 conversion at 1073 K with S/C ratio of 2.0 for 600 h).⁵⁴ By using block copolymer as the template, a Ni-Mg-Al oxides with high surface area and ordered mesopores was synthesized.¹⁹ The mesoporous structure contributed 20% more surface area and pore structure was stable under the reaction condition. The porous structure prevented the metallic Ni from sintering and Ni particles kept a size of 3-5 nm after reaction. Meanwhile, the presence of MgAl_2O_4 spinel phase reduced the coke formation. Accordingly, the mesoporous Ni-Mg-Al oxides exhibited ~70% CH_4 conversion at S/C ratio of 1.0 and temperature of 750 °C for 10 h, while the unmodified Ni/MgO- Al_2O_3 only converted ~57% CH_4 and deactivated soon under the same condition. In addition, 3D engineering method was employed to place Ni atoms inside the nanoribbon of hydrotalcite-derived mixed oxides.⁵⁵ The tri-compound Ni-Mg-Al catalysts were efficient for SRM at a wide range of S/C ratio from 1.0 to 4.0. As the S/C ratio was as high as 4.0, the 100% conversion of CH_4 could be realized at a low temperature of 823 K. Furthermore, Ni-based Mg-Al oxides catalysts in other stoichiometric ratio have also been explored, such as $\text{Ni}_{0.5}\text{Mg}_{2.5}\text{AlO}_9$. At

a very short residence time of 20 ms, the $\text{Ni}_{0.5}\text{Mg}_{2.5}\text{AlO}_9$ catalysts showed higher activity and stability compared to $\text{Ni}/\text{ZrO}_2/\text{Al}_2\text{O}_3$ and $\text{Ni}/\text{La-Ca}/\text{Al}_2\text{O}_3$.⁵⁶

Figure 1.3. (A) SEM images of reduced NiO-MgO catalyst samples⁵²; (B) Schematic representation of carbon deposition during SRM reaction over Ni/SiO₂-C (left) and Ni/SiO₂-DBD (right) catalysts⁵⁷; (C) Long-term stability tests of Ni/Y₂B₂O₇ (B = Ti, Sn, Zr, or Ce) catalysts at 750 °C for methane steam reforming⁵⁸; (D) The structure of Ni honeycomb.⁵⁹

b) SiO₂ supports

Ni catalysts on silica supports was another important kind of potential candidate for efficient SRM. Coke resistance of Ni/SiO₂ catalyst could be enhanced by dielectric-barrier discharge (DBD) treatment at a wide range of S/C ratios.^{57, 60} This Plasma treatment during

preparation process resulted in a high Ni dispersion and small Ni particle size. The smaller Ni particles formed a smaller angle with graphene embryo and significantly prohibited coking (Figure 1.3B). The stability of Ni/SiO₂ catalyst was improved by using polymer-assisted method for preparation.⁶¹ With chelation introduced by polymer, smaller Ni particle size could be reached after calcination. Incipient wetness impregnation method provided 45.5 nm Ni particles on Si-AE support after reduction while polymer-assisted method could generate 8.7 nm Ni particles on the same support. Though the sample prepared by the polymer-assisted method showed a weak interaction between NiO and the support, it showed higher and more stable CH₄ conversion and H₂ yield in 40 h with little carbon deposition. In fact, the coking resistance and catalytic activity were both intimately affected by the Ni particle size. A recent study with Ni particles on SiO₂ in a size range from 1.2 to 6.0 nm suggested that carbon whisker formation was maximum with Ni at 4.5 nm and the maximum activity was achieved on 2-3 nm Ni.⁶² Pradhan and co-workers prepared an alumina supported nano-NiO/SiO₂ catalyst with high activity and selectivity.⁶³ The highest CH₄ conversion was achieved at 700 °C while it decreased beyond this temperature due to coke formation.

Core/shell structure of Ni@SiO₂ with Ni nanoparticle as the core and SiO₂ layer as shell has received increasing attention in these years. The SiO₂ shell was believed to provide physical protection to Ni nanoparticles, avoiding the contact and aggregation of the Ni particles. Compared with other silica-supported, Ni@SiO₂ exhibited a higher CH₄ conversion rate with low Ni loading and at low S/C ratio. For instance, a Ni@SiO₂ catalyst consisted of a 10-15 nm Ni nanoparticle as the core and SiO₂ shell with diameter of 30 nm

achieved 83% CH₄ conversion at 1073 K under a S/C ratio of 1.0.⁶⁴ Similarly, a Ni@SiO₂ catalyst synthesized by a deposition-precipitation method exhibited a high methane conversion of 85% at 1023 K.⁶⁵ When synthesizing Ni/Al₂O₃-Sil-1 core-shell catalysts, Zhang et al. found that the formation of the inactive NiAl₂O₄ spinel phase should be prevented. With Ni depositing on a preformed Al₂O₃-Sil-1 core-shell beads, the SRM activity was improved by 10% and rather stable even exposed to alkali vapor compared to Ni/Al₂O₃ in Sil-1 shell.⁶⁶

SBA-15 is a typical type of mesoporous silica and an ideal support for Ni based catalysts. The optimum loading of Ni on SBA-15 was found to be 10 wt%, for instance, 1 wt% Ce/10 wt% Ni/SBA-15 achieved 92-99% methane conversion with a high H₂/CO ratio and was highly resistant to carbon deposition under a S/C ratio of 1.0-2.0 at atmospheric pressure and 1073 K.⁶⁷ The addition of Ce_xZr_{1-x}O₂ in 10 wt%Ni/10 wt%Ce_xZr_{1-x}O₂/SBA-15 could further promote dispersion of the nickel species, which exhibited a CH₄ conversion of ~94% at 923 K and an excellent stability in 740 h.²⁴

c) ZrO₂ supports

ZrO₂-based material was an important type of support for Ni-based catalysts as well. With a uniform dispersion of Ni particles on ZrO₂, the CH₄ conversion on Ni/ZrO₂ was ~88% at the beginning, slight decreased to ~86% after 50 h and then maintained at this level for another 200 h.⁶⁸ The high activity was attributed to the high percentage metal-oxide

boundary in the nanocomposite. Tuning the morphology of the ZrO₂ substrate was effective for promoting the catalytic activity of Ni/ZrO₂ catalysts. A unique hollow shell structure of ZrO₂ was obtained by Lim et al.⁶⁹ Metallic Ni particle with particle size of 8.9 nm could be uniformly dispersed on ZrO₂ hollow shells with suppressed aggregation. Besides, the large amount of micropores on the shell allowed efficient gaseous exchange. Resultantly, on this specially structured catalyst, 93% CH₄ could be converted at 973 K with S/C ratio of 2.5 with slight deactivation in 20 h. Similarly, the rich porosity and appropriate pore sizes of Ni/yolk-ZrO₂ catalyst contributed greatly to its high activity.⁷⁰ However, compared with other support (MgO, MgO-Al₂O₃, and SiO₂), ZrO₂ was not advantageous. The activity of Ni/ZrO₂ at low S/C ratio was comparable with Si-based and Mg-Al-based catalyst, while at high S/C ratio, the activity of Ni/ZrO₂ was lower.

Ce could promote the activity of Ni/ZrO₂ catalyst since CeO₂-ZrO₂ had an excellent oxygen storage/release capacity.⁷¹ The interaction between Ni and Ce-ZrO₂ support could improve the reducibility of Ni and Ce.⁷² Accordingly, the oxygen mobility was enhanced, which in turn promoted the coking resistance of the catalyst. 15 wt% Ni/Ce-ZrO₂ exhibited a CH₄ conversion of 97% at 750 °C and S/C ratio of 3.0.⁷³ Ce-ZrO₂ support could be optimized by changing the Ce:Zr ratio.⁷⁴ The CH₄ conversion reached 97% when Ce:Zr equal to 1, and decreased to ~71% when Ce:Zr equal to 5 which was even lower than pure ZrO₂ support. The particle size of Ni was also essential. Strong interaction could form between small-size (5-10 nm) NiO particles and CeZrO₂ support, leading to fast and easy oxygen transfer to and from NiO/Ni⁰ active phases. Thus, 250-h stable SMR could be realized at a S/C ratio of 2.0 on this catalyst.⁷⁵

An additional protection shell for the Ni/Ce-ZrO₂ catalysts could further increase its activity. H- β zeolite membrane encapsulated 1.6%Ni/1.2%Mg/Ce_{0.6}Zr_{0.4}O₂ prepared by a physical coating method showed 2-3-factor enhancement in CH₄ conversion compared to the catalyst without a zeolite shell.⁷⁶ Both the confined reaction effects (increase residence time within pores) and the promotion effect of Al³⁺ in the zeolite shell to the active sites contributed to the promotion.

In addition, yttria-stabilized zirconia (YSZ) has been employed as the support for Ni-based catalyst. Using the sucrose-concentrated H₂SO₄ dehydration reaction, Wu et al. prepared flake-shaped NiO-YSZ particles, which outperformed the mixed commercial NiO-YSZ.⁷⁷ However, it was found that the strong interaction between NiO and the substrate hampered the reduction of NiO.⁷⁸ Further decoration of Ru could accelerate the reduction of NiO by H₂. The addition of 1.3 wt% Ru into 10 wt% Pr_{0.15}La_{0.15}Ce_{0.35}Zr_{0.35}O₂/NiO+YSZ showed a high CH₄ conversion of ~65% at 800 °C. Coking was prevented due to the high oxygen mobility in the oxides. Hong and co-workers promoted the Ni/YSZ catalyst by Pd addition.⁷⁹ Pd-Ni/YSZ reached a high CH₄ conversion of 94.6% at 650 °C. However, the CO selectivity is relatively low due to the promoted WGS by Pd.

d) Other metal oxide substrates

Due to their rich chemical properties, renowned complex oxides with fixed stoichiometric ratios, such as Pyrochlore ($A_2B_2O_7$)^{58, 80-82} and Perovskite (ABO_3) as well as some other complex metal oxides have been widely studied as catalyst supports for SRM.

$La_2Sn_2O_7$ and $La_2Zr_2O_7$, as supports, could significantly improve the stability of Ni-based catalyst despite of a low CH_4 conversion and H_2 yield at the beginning.^{58, 80-82} While Ni/ γ - Al_2O_3 lost ~15% of its CH_4 conversion after 80 h, $La_2Zr_2O_7$ supported catalyst showed increasing CH_4 conversion during a long-term running (250 h) and finally reached CH_4 conversion of ~95%. $La_2O_2CO_3$ in Ni/ $La_2Zr_2O_7$ was found responsible for removing carbon deposition. Ni/ $Y_2Zr_2O_7$ showed even better performance with the complete conversion of CH_4 at 800 °C for more than 200 h without any carbon deposition. The high activity was mainly attributed to the smaller Ni particle size than Ni/ $La_2Zr_2O_7$ and the stronger SMSIs between Ni and Y.

Different metal elements (Ti, Sn, Zr, and Ce) were investigated as the alternation for Zr to improve Ni/ $Y_2Zr_2O_7$. Sn and Ce exhibited the lowest activity due to the large Ni particle size and severe sintering. Ti was a better choice due to its best dispersion of Ni species with mild sintering and the largest number of oxygen vacancies. Both CH_4 conversion and H_2 yields followed the order of Ti > Ce > Zr > Sn (Figure 1.3C). Furthermore, based on $A_2Ti_2O_7$, the replacement of A site was investigated among La, Pr, Sm, and Y. The Y contained substrate allowed the formation of Ni particles with the smallest size and the largest surface area. As a result, the highest CH_4 conversion and H_2 yield with lowest H_2/CO ratio was obtained on $Y_2Ti_2O_7$.

Perovskite support was investigated as the support for Ni catalyst for SRM due to their high coking resistance. Surface oxygen in perovskite could take part in the reaction, promoting the carbon resistance.²⁵ Ni/ NaCeTi₂O₆ (Ni/NCT) catalyst showed a high activity with CH₄ conversion of ~95% at 973 K without deactivation for 24 h.⁸³ Two complex Ni/perovskite catalysts were evaluated by Penner and co-workers. By forming hollow shells on La_{0.6}Sr_{0.4}FeO_{3-δ} (LSF) and SrTi_{0.7}Fe_{0.3}O_{3-δ} (STF) substrates, the Ni particles were free from sintering during the reduction process.⁸⁴ Ni/LaFeO₃ showed CH₄ conversion of ~80% and H₂ yield of ~70% at 800 °C at S/C ratio of 2.0.⁸⁵ Further plasma treatment could slightly enhance the CH₄ conversion to ~83% and H₂ yield to ~78% under the same condition. Strong interaction between Ni and La on NiLaO₃ perovskite could prevent the sintering of Ni as well.⁹² With a high degree of SMSIs, Ni/La₂TiO₅, which was derived from ordered double perovskite La₂NiTiO₆, reached a CH₄ conversion of 95% at 950 °C and maintained it for 24 h.⁷

Other complex oxide substrates have also been explored. For instance, a complex Ce_{0.65}Hf_{0.25}M_{0.1}O_{2-δ} (CH-M, M = Tb, Sm, Nd, Pr, and La) solid solution was developed as the support for catalytic SRM.⁸⁶ The introduction of Pr, Tb, and La increased the amount of oxygen vacancies and facilitated the coke resistance. Ni/CH-Pr was the best among the studied catalysts with CH₄ conversion of 85% and long-term stability for 30 h. Analogously, Ni catalysts on (Ce_{0.75}/1.025Zr_{0.25}/1.025-Pr_{0.025}/1.025)O_{2-y} (Ni-CZP), which was a mixture of a Pr-rich λ phase and a Ce-rich cubic phase, demonstrated much better catalytic performance than that of Ni catalysts supported on (Ce_{0.75}Zr_{0.25})O_{2-y} (Ni-CZ), due to the

strained but coherent oxygen-vacancy-rich interface between the λ phase and the cubic phase.⁸⁷

(3) Unsupported Ni catalysts

Via elaborate synthesis control, unsupported Ni catalysts with specific structures could exhibited an outstanding performance in SRM as well.

By thermal decomposition of Nickel tetra carbonyl, pure nickel powder with an open filamentary structure and irregular spiky surface was prepared.⁸⁸ Catalyst performance was tested at various S/C ratio. At the S/C ratio of 2.0, H₂ production began at 325 °C and increased with the increasing temperature until 500 °C. The CO and CO₂ production began at approximately 325 °C and reached highest at 700 °C. CH₄ conversion was beyond 95% for 100 h, indicating its good activity and stability. SEM images confirmed the sintering during reaction at 700°C, however, the performance was not impacted. At 700 °C, CH₄ conversion and H₂ production decreased with the decreasing S/C ratio sharply, for instance, CH₄ conversion was ~75%, ~40%, and ~30% at the S/C ratio of 1.0, 0.7, and 0.5, respectively, which was due to the kinetic factors. Carbon deposition was rare on the catalyst surface based on the XPS and TEM analysis. Thus, the unsupported Ni catalyst, with high coke resistance, presented high activity and stability toward SRM.

Honeycomb structured Ni has attracted a number of attention in the past few years (Figure 1.3D).^{59, 89, 90} Compared with commercial catalysts, BET surface area of the honeycomb-

Ni catalyst was nearly 30 times larger which was an important reason for its higher activity. The selectivity to CO of honeycomb-type catalyst was a little bit lower than commercial Ni-based catalyst, however, the activity was 3 times higher. Due to the increasing geometric surface area, the CH₄ conversion on high-cell-density catalyst was 25-40% higher than that on the low-cell-density one at low temperature range (873-1023 K), 50-70% higher in medium temperature range (1023-1123 K), and 25-40% higher in high temperature range (>1123 K). The high coke resistance of honeycomb catalyst might be due to the flat Ni (001) surface which was a less suitable nucleation site for carbon deposition. However, the activity of honeycomb catalyst decreased in the first several hours due to the oxidation of surface Ni in the reaction. More lately, a Ni coil catalyst with a high geometric surface area per catalyst volume (88.1 cm²/cm³) was synthesized by Hirano et al.⁹¹ This catalyst achieved 94 % CH₄ conversion, 77.6 % H₂ production and 91.1 % CO selectivity at 1073 K under a S/C ratio of 1.24, which could be hardly realized on the Ni honeycomb catalyst that showed a geometric specific surface area of 59.4 cm²/cm³.

1.1.3 Noble Metal Catalysts

Noble metal catalysts (Rh, Ru, Pt, Pd and Ir) are ideal catalysts for SRM. They showed higher catalytic activity and stability than Ni catalysts. For instance, Ru/Al₂O₃ and Ru/MgO exhibited higher CH₄ conversion than Ni/Al₂O₃ (72% vs. 17.8%) and Ni/MgO (99% vs. 90%), respectively, at 750 °C.⁹² However, their application was limited by their high cost. Despite their superior performance, they still suffer from aggregation and carbon

deposition. Thereby, a number of research efforts are still being paid to optimize the SRM performance of noble metal catalysts while decreasing their loading amount.

(1) Ru-based catalysts

The activity and stability of Ru/Al₂O₃ catalyst have been improved by tuning the structure and chemical composition of substrate. Al₂O₃@Al core-shell structure consisting an Al metal core with high surface area Al₂O₃ shell was employed as the support for Ru.⁹³ The Al₂O₃@Al particle would aggregate during synthesis process, forming a secondary structure which was advantageous for heat transfer and higher dispersion of Ru. Accordingly, the Ru/Al₂O₃@Al exhibited higher activity than Ru/Al₂O₃ and no deactivation was observed during 40 h reaction. With La element forming a thin, homogeneous, and amorphous surface La₂O₃ layer on Al₂O₃, the Ru species in Ru/La-Al₂O₃ were detected as RuO₂, indicating an enhanced mater-substrate interaction.⁹⁴ By coated on monolith support, nearly complete CH₄ conversion (97.3%) and 78.3% H₂ yield could be realized at 800 °C on Ru/La-Al₂O₃. With Ni₆Al as the support and a small Ru loading amount (0.5 wt%), RuO₂ particles was formed and dispersed uniformly on the support surface.⁹⁵ A synergistic effect between Ru and Ni could be formed and contribute to a high SRM activity. Ru/Co_{6-x}Mg_xAl₂ catalyst exhibited outstanding activity in SRM with a complete CH₄ conversion at 700 °C.⁹⁶ However, increasing Mg content led to an increased RuO₂ particle size due to agglomeration on Mg-rich support. As a result, CH₄ conversion and H₂ yield increased with the decreasing of Mg content at low temperatures (Figure

1.4A). The Ru/Co₆Al₂ exhibited the best activity and an excellent stability (Figure 1.4 B and C).

Figure 1.4. CH₄ conversion on Ru/Co_{6-x}Mg_xAl₂ with different Mg content (A); Stability of Ru/Co₆Al₂ catalyst as a function of cycled times (B) and time (C).⁹⁶

Despite of the negative effect of MgO in the composite oxides,⁹⁵⁻⁹⁷ both MgO and Nb₂O₅ supported Ru catalyst showed appreciable performance for SRM.⁹⁸ MgO supported Ru achieved CH₄ conversion higher than 99%, 62% CO₂ selectivity, and H₂ concentration of 78% in the outlet at 750 °C, while Nb₂O₅ support led to complete CH₄ conversion, 71% CO₂ selectivity, and 78% H₂ in outlet at the same temperature. The electron transfer from support to Ru metal particles might be the reasons for high catalytic performance on Ru/MgO. The better catalytic performance of Ru/Nb₂O₅ could be attributed to two reasons: Nb⁵⁺ ion on the surface could interact with Ru and phase transfer of Nb₂O₅ from amorphous to tetragonal after the SRM reaction.

(2) Rh-based catalysts

Rh was one of the most active catalyst for CH₄ adsorption, activation and desorption and thus a potential catalyst for SRM. Onset for SRM on Rh/Al₂O₃ was slightly higher than 700 °C.⁹⁹ CH₄ conversion on Rh/Al₂O₃ reached ~78% at ~875 °C with CO selectivity of ~70%, which was comparable with Ru. With higher metal content and reaction temperature, CH₄ conversion on Rh was slightly higher than Ru (78% vs. 72%) at a low S/C ratio of 1.77. Comparing the SRM activity of catalysts with Ru, Rh, and Pt deposited over CeO₂ and Al₂O₃ carriers, 1.5% Rh/CeO₂ showed the highest conversion of methane.¹⁰⁰

Textual properties of support could influence the activity via not only the SMSIs but also the structural optimization of metal particle. Rh particles were distributed within a narrow range of 1-3 nm on Al₂O₃ synthesized flame spray pyrolysis (FAI), whereas the Rh particles size ranged from 2 to 7 nm on Al particle suspension (SAI).¹⁰¹ With Rh content lower than 1 wt%, Rh/SAI showed higher CH₄ conversion while Rh/FAI exhibited higher activity at 5 wt% Rh loading (69% vs. 65%). Hydroxyapatite (HAP) supported Rh (1 wt%) showed the highest CH₄ conversion of 77% at 923 K without deactivation for 30 h.¹⁰² Atomically dispersed Rh catalyst on Al₂O₃ was designed for SRM.¹⁰³ However, promoters were required to avoid the aggregation of Rh during SRM at 1033 K. Sm₂O₃ and CeO₂ in Rh/xSm₂O₃-yCeO₂-Al₂O₃ catalyst could effectively improve the reaction rate per surface Rh and stabilize the structure of Rh particles.¹⁰⁴ With the addition of CeO₂ promoters, the formation and stabilization of atomically dispersed Rh metal species could be enhanced due to the SMSI, namely, the metal-O-Ce bonds.^{103, 105, 106} Besides, carbon deposition was removed by the active oxygen in CeO₂.

Rh/MgAl₂O₄ showed a CH₄ conversion of ~41% at 1123 K.¹⁸ Both the carbon deposition and metal sintering were rare on Rh/MgAl₂O₄. Theoretical results suggested the Rh-O bonds were the primary form of metal-support interaction in Rh/MgAl₂O₄, which could modify the electronic structure of Rh and limit its sintering. Also, dissociative adsorption of H₂O was enhanced at interface which facilitated the SRM. Rh could be highly dispersed on Sr-substituted hexaaluminate surface. Sr-substituted hexaaluminate was stable under high-temperature conditions without surface area loss and could prevent Rh particles from sintering.¹⁰⁷ This catalyst could convert 45% of CH₄ and show 69% H₂ selectivity at 740 °C.

(4) Pt-based catalysts

The performance of Pt/Al₂O₃ has been promoted by CeO₂, La₂O₃ and MgO. The CH₄ conversion on the Pt-NPs/CeO₂-Al₂O₃ with 3 nm Pt particle size was twice that on Pt-NPs/Al₂O₃ catalyst with similar Pt-NP sizes.¹⁰⁸ Bueno and co-workers studied Pt/La₂O₃-Al₂O₃ catalysts for SRM.^{109, 110} The addition of 12 wt% La₂O₃ led to the highest activity toward SRM. La₂O₃ could decrease the particle size of Pt, however, it could block active Pt sites as well. Also, La₂O₃ could narrow the electron density distribution on Pt sites and the formed LaPtO_x-like species could increase the CH₄ accessibility by promoting the removal of carbon deposition, indicating that SMSIs between Pt and La₂O₃ played an important role in promoting Pt/La₂O₃-Al₂O₃. The same group further promoted Pt/La₂O₃-Al₂O₃ by adding CeO₂.¹¹¹ The addition of CeO₂ introduced Ce⁴⁺/Ce³⁺ redox couple which

could cooperate with $\text{Pt}^{\delta+}/\text{Pt}^0$ couple for enhanced activity and stability. Although the introduction of Ce decreased the dispersion of Pt, the resulted high capacity for carbon cleaning via the high oxygen mobility compensated it. Another report for Pt/CeO₂ catalysts stated that CH₄ conversion showed a positive correlation with Pt content and 10 wt% Pt exhibited the highest CH₄ conversion of 71.4%. After 6 h running, the conversion rate only slightly dropped to 69.7%, indicating its high stability.¹¹² Furthermore, with a small amount of MgO (Al/Mg = 5) present in Pt/Al₂O₃, the CH₄ conversion and H₂ production could be obviously enhanced, even though an excessive loading of MgO (Al/Mg < 5) brought an negative effect to the SRM performance of Pt/Al₂O₃.¹¹³

1.1.4 Other Transition Metal Catalysts

Transition metal catalysts (Co, Cu, and Mo) are ideal candidate catalysts for SRM. Compared with Ni-based catalysts, they showed higher catalytic activity. For instance, MoC₂/Al₂O₃ exhibited significantly higher CH₄ conversion (95%) than Ni/Al₂O₃ (17.8%), even at a lower reaction temperature (700 °C vs. 750 °C).¹¹⁴ Despite their super performance, they still suffered from low reducibility,¹¹⁵ easy deactivation (due to the oxidation of metallic species),¹¹⁶ carbon deposition,^{180, 181} and high-temperature induced aggregation.^{116, 115, 117}

(1) Co-based catalysts

Co-based catalysts exhibited promising performance toward SRM. However, the deactivation due to oxidation of metallic Co by H₂O was a critical disadvantage which could be suppressed by the addition of the noble metals on the Co/Al₂O₃ catalyst that ensured a more stable metallic state of Co and made the catalyst less susceptible to deactivation during SRM. The presence of Pd, Pt, Ru, and Ir markedly reduced the reduction temperature of both Co₃O₄ and Co surface species via the hydrogen spillover effect.¹¹⁵ 0.3 wt% Pt, Pd, and Ir could enhance CH₄ conversion from ~7% on unpromoted catalysts to 50-60% at 973 K and S/C ratio of 4.0 with Pt presenting the highest CH₄ conversion, H₂ production and stability. The doping of non-noble transition metals could, to a certain extent, improve the activity of Co catalysts as well. The Co/Mg/Al catalyst promoted by La and Ce reached 85% CH₄ conversion at 973 K and S/C ratio of 2.0.^{118, 119} At a lower S/C ratio of 0.5, unpromoted catalyst suffered from severe coke formation, whereas the La and Ce promoted catalysts were highly resistant to carbon deposition. However, a certain deactivation was still observed for the oxidation of Co. Promisingly, with the co-existence of Zr, La and Pt with Co, Co-Pt-Zr-La/Al₂O₃ catalysts could achieve a nearly complete CH₄ conversion (99.3%) at 750 °C and S/C ratio of 1.25 without any sintering or carbon deposition.¹¹⁶

(2) Cu-based catalyst

Cu/Co₆Al₂ catalyst exhibited promising performance for SRM.¹¹⁷ 5 wt% Cu/Co₆Al₂ could nearly completely convert CH₄ at 700 °C (S/C ratio: 3.0) without coke formation. However,

increasing Cu content led to deactivation due to the agglomeration of copper oxide. Yet, high Cu content resulted in higher selectivity to CO due to the enhanced reverse-WGS (RWGS).

(3) Mo-based catalyst

Mo was not only a good promoter for Ni-based catalyst⁴³, but also active for SRM. Al₂O₃ supported Mo₂C exhibited promising activity with ~95% CH₄ conversion rate and H₂ selectivity of ~70% at 700 °C and S/C ratio of 4.0.¹¹⁴ However, unsupported Mo₂C showed a lower CH₄ conversion of ~40% and H₂ selectivity of ~35%. Such difference was probably due to the phase transfer from β -Mo₂C in unsupported Mo₂C to α -Mo₂C in Al₂O₃ supported one.

1.1.5 Summary

Steam reforming of methane is an important industrial process. The promotion of catalysts for SRM is a long-term research topic. Various methods have been applied to improve the activity and/or stability of the practically applied Ni-based catalyst, including the addition of promoter, the employment of supports, and the modification of morphology (honeycomb structure) of unsupported Ni catalyst. Rh, Ce, Co, Nb, K-Ti, have been proven excellent promoters. MgO, MgO-Al₂O₃, and CeO₂ were suggested to be promising supports for Ni-based catalyst. Besides Ni, catalysts based on noble metals (Ru, Rh, Pd, and Pt) and other non-noble transition metals (Co, Cu, Mo etc.) catalysts have been explored. However, they are either high in cost or showed limited performance.

Moreover, more valuable products such as methanol other than hydrogen and syngas are desired from the direct SRM process to reduce synthetic energy consumption. However, none of the developed catalysts have shown such a capability. New catalytic systems for novel SRM processes with value-added chemicals as products need to be explored to boom the development of SRM technology.

1.2 Methane to Methanol Conversion

Methanol (CH₃OH) is a useful chemical for energy storage and transportation (Figure 1.5). It can be mixed with commercial gasoline up to 15% without modification of vehicle

engines. This mixture results in lower exhaust temperature, lower emission, and improved economy and performance. Other than blended with gasoline, methanol is also ideal for fuel cells.¹²⁰ Methanol can be used in the direct methanol fuel cell (DMFC) where methanol is directly oxidized by air to produce electricity. This greatly simplifies the fuel-cell technology and makes it available to a wide scope of applications: providing power to small gadgets like cell phones and computers, or to large facilities like motor scooters and cars.¹²¹ Besides energy application, methanol has long been used in consumer products as windshield washer fluids, deicing fluids, antifreezes, and fuels for camping and outdoor activities.¹²² Also, CH_3OH is a useful building block for obtaining more complex chemical compounds, such as acetic acid, dimethyl ether, methylamine, etc..¹²³ Moreover, the transportation of methanol is convenient. It is easily stored in conventional fuel tanks and can be transported via land transportation by tank cars and trucks and via marine transportation by tankers; besides, pipelines for oil and chemicals are both available for methanol transportation.

Figure 1.5. Source, transport, and possible application of methanol.¹²⁰

In industry, the synthesis of methanol is based on a two-step process, namely, the production of syngas from SRM and the synthesis of methanol from the syngas. However, this process is energy-intensive which requires large centralized plants that are poorly compatible with the distribution of methane reserves.¹²⁴ Direct conversion of methane to methanol (DMTM), which can be carried out at a relatively low temperature, is more energy-efficient.^{125, 126}

Partial oxidation of methane (POX) processes with O₂ as oxidant were widely investigated for DMTM. Cu-containing zeolites were the most effective catalysts currently for selective POX to methanol.¹²⁷ Bokhoven and co-workers proposed that zeolite structure was one of the most important factors for catalytic performance.¹²⁸ 8-memberance ring pore structure

was preferable due to the confinement effect between CH₄ and Cu-oxo active site. Also, highly dispersion of Cu²⁺ ions on zeolite, which could be controlled by the Si/Al ratio of zeolite and the preparation methods, was essential.^{129, 130} Cu-O-Cu group was regarded as the active site on Cu-exchanged mordenite catalyst while [CuOH]⁺ was considered as the active site for 8-memberance Cu-exchanged zeolites.^{131, 132} C-H bond cleavage/activation was the rate-determining step for methanol synthesis. Besides Cu, other metals like Pd,^{133, 134} Au,^{135, 136} Co^{137, 138} and Fe¹³⁹ are also studied as the potential catalysts for oxidation of methane into methanol.

However, oxygen-driven POX process suffers from a low methane conversion efficiency and a moderate methanol selectivity, due to the limited capability of the catalysts for methane activation and the over oxidation of methanol into HCHO and/or even CO₂ under the reaction conditions.^{123, 140} Compared to oxygen, water/steam is a milder oxidant that could lead to a higher selectivity to methanol but it has received less attention. In 2017, a high methanol selectivity (~97%) has been achieved on a copper-containing zeolite by Sushkevich et al. with water as the oxidizing agent. Although the process is stepwise, namely, methane was first oxidized to methoxy intermediates by copper (II) in the zeolite and then water was added to reoxidize copper and release methanol and hydrogen, it indicated the great advantage of water in promoting the selectivity to methanol.¹⁴¹ Later, Park et al. reported that continuous methanol synthesis at a rate comparable to the stepwise process by co-feeding methane and steam.¹⁴² Nonetheless, methane conversion to methanol with water as oxidant, i.e. the steam reforming of methane to methanol, on Cu-based zeolite catalysts exhibited relatively low methane conversion efficiencies. It is imperative to

development alternative catalysts that could achieve both a high activity and a high selectivity for SRM to methanol.¹⁴³

1.3 Single Atom Catalysts (SACs)

Recently, single-atom catalysts have drawn considerable attention. To make use of each metal atom, metal nanoparticles are downsized to well-defined, atomically distributed metal active centers, that is, SACs, which is the ultimate goal of fine dispersion.¹⁴⁴⁻¹⁴⁷ Zhang, Li, Liu and co-workers first demonstrated experimentally that Pt single atoms dispersed on the FeO_x surface could promote CO oxidation and preferential oxidation of CO in H₂.¹⁴⁴ With a low Pt loading (0.17 wt%), the reaction rate on SACs at 300 K was almost tripled compared to that obtained with a 2.5 wt % Pt loading. The highly efficient utilization of noble metal led to both a great performance and a low price. The use of SACs has improved numerous catalytic processes such as benzene combustion,¹⁴⁸ NO reduction,¹⁴⁹ CO₂ hydrogenation,^{150, 151} dry reforming of methane (DRM),¹⁵² water-gas shift (WGS),^{153, 154} reverse water-gas shift (RWGS),¹⁵⁵ organic chemical reactions,¹⁵⁶ CO oxidation, etc. However, limited attention has been paid on the catalytic performance of SACs for direct methanol synthesis from methane with water as oxidant.

1.4 Molybdenum Sulfide Cluster (Mo₆S₈)

Mo₆S₈ cluster is the building block of sulfide chevreton phase (M_xMo₆S₈). It has been coordinated with various metals to show promising catalytic performance in a wide range of reactions. The cracking of methyl tert-butyl ether to isobutene could be catalyzed on Cu_xMo₆S_{8-δ}.¹⁵⁷ The mixture of H₂S/CH₃OH could be catalytically converted into CH₃SH on a series of ternary M^{x+}_n(Mo₆S₈)S^x_{n/2} cluster (M= La, Ho, Sn, Pt, Na).¹⁵⁸⁻¹⁶¹ Rh-, Pd-, Pt-, and Ag-Mo₆S₈ were reported as an effective catalyst for RWGS theoretically.^{162, 163}

M-Mo₆S₈ with different coordination metals could show distinct catalytic behaviors. For example, Ni single atom supported on Mo₆S₈ (Ni-SA/Mo₆S₈) was promising for ethanol formation from CO with an extremely high activity and selectivity.¹⁶⁴ C-C bond association between *CH₃ and *CH₃O group was endothermic and required a barrier of ~0.13 eV on bare Mo₆S₈ cluster, whereas the process was barrier-less and exothermic on Ni-Mo₆S₈. In contrast, Co in Co-Mo₆S₈, could directly participate in ethanol steam reforming reaction, helping to break C-C bond.¹⁶⁵ Noble metals (Rh and Ir) doped Mo₆S₈ also showed potential for ethanol reforming but via slightly different reaction pathways.¹⁶⁶ On Rh-Mo₆S₈, the decomposition started with O-H bond scission and followed by dehydrogenation to *CHCO intermediate, which would dissociate to *CH and *CO. The most likely final products were CH₄ and CO₂. On Ir-Mo₆S₈, ethanol decomposition also started with O-H bond cleavage but the following dehydrogenation processed only on α-H to *CH₃CO which would dissociate to *CH₃ and *CO. On Pt-Mo₆S₈, C-C bond scission was via the dissociation of *CH₃CHO to *CHO and *CH₃ which led to *CO and *CH₄, respectively.¹⁶⁷

Essentially, in the synthetic reaction with CO₂ and H₂, the unique structure of Mo₆S₈ could prevent the cleavage of the C-O bond in H_xCO intermediates and lead to the high selectivity toward methanol along with a high activity and strong resistance to sulfur and coke.¹⁶⁸ The single-atom metal dopant in M-Mo₆S₈ could play an important role in varying the number of carbon atoms in the alcohol product. Specifically, CH₃OH remained the major product with single K atom on Mo₆S₈, while the selectivity was changed to C₂H₅OH if Ni and Pd atoms were present.¹⁶⁹⁻¹⁷²

In this light, provided with proper metal coordinators, the Mo₆S₈-based catalysts, especially, single atom doped Mo₆S₈, could be potential catalysts for CH₃OH synthesis from CH₄ and H₂O as well. However, to the best of our knowledge, up to now, this reaction on Mo₆S₈-based catalysts has not been investigated yet. Accordingly, exploring the potential of M-Mo₆S₈ for SRM to methanol would not only be scientifically interesting, but also important to the development of SRM industry.

2 Goals and Hypotheses

Based on the background in Chapter 1, the exploration of advanced catalytic materials for the production of value-added products from steam reforming of methane (SRM) is highly desired for the future development of SRM technology. Methanol is a useful chemical for various practical applications and chemical industrial processes. However, the current industrially employed two-step approach for methanol synthesis is energy-intensive. Direct conversion of methane to methanol (DMTM) with water as oxidant, i.e. SRM to methanol, is promising in leading to an energy-efficient synthesis of methanol and an effective utilization of methane. Nevertheless, developing catalysts with both high activity and selectivity for SRM to methanol remains a great challenge. With their distinctive structures and chemical diversities, a carefully designed Mo₆S₈-based catalysts, especially, single atom doped Mo₆S₈, could be promising for methanol synthesis from SRM with high activity, selectivity, and stability, but this has not been explored by researchers yet.

Therefore, our goal is:

To reveal the potential of single metal atom doped Mo₆S₈ clusters (M-Mo₆S₈, M = K, Ti, Co, Fe, Ni, Cu, Rh) as catalysts for SRM to methanol by DFT calculation.

The specific aims to the goal are:

1. To evaluate structure of Mo₆S₈ and M-Mo₆S₈ clusters and their structural stability in the oxidative reaction condition by calculating the binding energy of Mo-S, metal-Mo₆S₈, and Mo-O.
2. To identify the active sites, explore the major dissociation products of CH₄ and H₂O

on Mo_6S_8 and $\text{M-Mo}_6\text{S}_8$ clusters as well as evaluate the coking resistance of Mo_6S_8 and $\text{M-Mo}_6\text{S}_8$ clusters by calculating the adsorption energies of CH_4 and H_2O and energy barrier for each elementary step in the dissociation of CH_4 and H_2O on the various clusters.

3. To build the reaction pathway and confirm the rate-determining step for SRM to methanol on Mo_6S_8 and $\text{M-Mo}_6\text{S}_8$ clusters by calculating the energy barrier for each elementary step along the reaction pathway.

This project is based on these following hypotheses:

Hypothesis 1: Mo_6S_8 and $\text{M-Mo}_6\text{S}_8$ catalysts are stable for CH_3OH synthesis via SRM.

As reported in the previous reports, electron transfer from M to Mo_6S_8 was observed, indicating the strong interaction between M and Mo_6S_8 cluster. Thus, single metal atom could be stably adsorbed on Mo_6S_8 . Based on the previous experimental results, $\text{Cu}_x\text{Mo}_6\text{S}_8$ - δ chevrel phase showed promising stability for methyl tert-butyl ether cracking at 400 °C while LaMo_6S_8 chevrel phase exhibited high stability for hydrodesulfurization at 400 °C. Also, chevrel phase LaMo_6S_8 has been reported stable in the presence of H_2S and CH_3OH at 250 °C. Chevrel phase survived at such high temperature, indicating its promising thermal stability. Thereby, we hypothesize that Mo_6S_8 and $\text{M-Mo}_6\text{S}_8$ would show high stability in the oxidative environment during SRM to CH_3OH .

Hypothesis 2: Co-, Fe-, and Ni- Mo_6S_8 are efficient for CH_4 activation.

Based on the previous theoretical studies for CH_4 dissociation on different metallic surface, the energy barrier for the first hydrogen abstraction on Fe (110) was only 0.69 eV and 0.78

eV on Ni (211) surface, indicating the high activity of Fe and Ni for CH₄ activation. The energy barrier for the first hydrogen abstraction was 0.63 eV on Al₂O₃ supported Ni catalyst and less than 0.5 eV on Fe/ZnO catalyst, indicating that this process could be accelerated by SMSIs. Thus, a high activity in CH₄ activation on Ni- and Fe-Mo₆S₈ is hypothesized. Meanwhile, since Co located nearly Fe and Ni on the periodic table of elements, high activity toward CH₄ activation on Co-Mo₆S₈ is also expected.

Hypothesis 3: Fe- and Co-Mo₆S₈ are efficient for H₂O dissociation.

Based on the previously theoretical studies for H₂O dissociation on Fe and Co metallic surface, the energy barriers for the first and second hydrogen abstraction on Fe (110) were only 0.68 eV and 0.90 eV, respectively, and those on Co were ~0.82 eV and ~1.00 eV, respectively. Thus, our third hypothesis is the high activity toward H₂O activation could be associated with Fe- and Co-Mo₆S₈.

Hypothesis 4: Fe- and Co-Mo₆S₈ are promising for methanol synthesis via SRM.

The dissociation of CH₄ and that of H₂O are important steps for SRM. Since Fe- and Co-Mo₆S₈ can promote the dissociation of both CH₄ and H₂O, we speculate that they could show a good performance in SRM. Furthermore, Fe-based catalysts supported on metal-organic frameworks (MOFs) and zeolites were reported as promising catalysts for methanol synthesis. Thus, Co- and Fe-Mo₆S₈, especially Fe-Mo₆S₈, are expected to be excellent catalysts for SRM to methanol.

3 Computational Methods Applied

Density functional theory (DFT) calculation is one of the most popular computational quantum mechanical modeling approaches used by physics, chemistry, and material scientists. Supported by DFT methodology, fundamental catalysis research has transformed from a trial-and-error mode to a more rational way with solid insights at the molecular level.¹⁷³ The active centers on the catalyst surface, the participating species/molecules, and the energetics of the elementary reaction mechanisms can be well defined via DFT.

In this chapter, started from the development of DFT method, the reason for selecting the current functional to describe the exchange and correlation interaction and the details in my calculation were narrated.

3.1 The Development of Density Functional Theory

The goal of DFT is to approximately solve the non-relativistic and time-independent Schrödinger equation:

$$\hat{H}\Psi_i = E_i\Psi_i \quad (3-1)$$

$\hat{H}$ is the Hamilton operator for a molecular system consisting of M nuclei and N electrons without any external field such as magnetic and electric fields:

$$\hat{H} = -\frac{1}{2}\sum_{i=1}^N \nabla_i^2 - \frac{1}{2}\sum_{A=1}^M \frac{1}{M_A} \nabla_A^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} + \sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}} \quad (3-2)$$

The first two terms represent the kinetic energies of the electrons and nuclei, respectively. The last three terms represent the potential part: the attractive electrostatic interaction between the nuclei and the electrons, the repulsive potential between electrons, and nucleus-nucleus interactions, respectively.

Since the nucleus is much more massive than the electron, it moves much slower than the electron. It is reasonable to assume that the electrons move in the field of a fixed nuclei, which is the famous Born-Oppenheimer or clamped-nuclei approximation.¹⁷⁴ Thus, nuclei's kinetic energy, which is the second term of Eq.3-2, is zero and the nucleus-nucleus interactions can be treated as a constant. Accordingly, Eq.3-2 is simplified into Eq.3-3, where $\hat{H}$ is called electronic Hamiltonian ($\hat{H}_{\text{elec}}$):

$$\hat{H}_{\text{elec}} = -\frac{1}{2}\sum_{i=1}^N \nabla_i^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} = T + V_{\text{Ne}} + V_{\text{ee}} \quad (3-3)$$

Thus, electronic wave function Ψ_{elec} and the electronic energy E_{elec} are the solution of the Schrödinger equation with $\hat{H}_{\text{elec}}$. Specifically, V_{Ne} in Eq.3-3 is often treated as the external potential V_{ext} in DFT. The variation principle states that the energy computed as the expectation value of the Hamilton operator $\hat{H}$ from any guessed wave function Ψ will be an upper bound to the true energy E_0 of the ground state Ψ_0 .¹⁷⁵ Accordingly, it is possible to obtain the ground state wave function by building $\hat{H}$ based on the number of electron N in the system and the external energy V_{ext} .

The first Hohenberg-Kohn theorem¹⁷⁶ states that the external potential $V_{\text{ext}}(\vec{r})$ is a unique functional of electron density $\rho(\vec{r})$. Because the external potential $V_{\text{ext}}(\vec{r})$ determines $\hat{H}$, ground state Ψ_0 is a unique functional of $\rho(\vec{r})$. The ground state energy can be expressed as

$$E_0[\rho_0] = T[\rho_0] + V_{\text{ee}}[\rho_0] + V_{\text{Ne}}[\rho_0] \quad (3-4)$$

, where the first term represents the kinetic part and the last two terms represent the potential energy due to electron-electron interaction and nuclei-electron interaction, respectively. Here, only the $V_{\text{Ne}}[\rho_0]$ term depends on the actual system while the other two terms are irrelevant to the actual system. By gathering the system independent parts as Hohenberg-Kohn function $F_{\text{HK}}[\rho_0]$, ground state energy can be written as

$$E_0[\rho_0] = V_{\text{Ne}}[\rho_0] + F_{\text{HK}}[\rho_0] \quad (3-5)$$

$F_{\text{HK}}[\rho]$ contains the kinetic energy term $T[\rho]$ and the electron-electron interaction term $V_{\text{ee}}[\rho]$. Unfortunately, the analytical solution of both these functionals was unknown. One step further, the classical Coulomb part $J[\rho]$ can be separated from the $V_{\text{ee}}[\rho]$ term:

$$V_{\text{ee}}[\rho] = E_{\text{ncl}}[\rho] + J[\rho] \quad (3-6)$$

$E_{\text{ncl}}[\rho]$ is the non-classical contribution to the electron-electron interaction containing all the effects of self-interaction correction, exchange and Coulomb correlation.

The second Hohenberg-Kohn theorem, which is the variational principle, states that delivers the ground state energy of the system gives the lowest energy if and only if the input density is the true ground state density.

Kohn and Sham defined T_s to represent the exact kinetic energy of the non-interacting reference system with the same electron density as the real,¹⁷⁷

$$T_s = -\frac{1}{2} \sum_i^N \langle \varphi_i | \nabla^2 | \varphi_i \rangle \quad (3-7)$$

Obviously, although sharing the same electron density, the non-interacting kinetic energy is not equal to the true kinetic energy of the interacting system. Thus, Kohn and Sham accounted for that by introducing the following separation of the functional $F_{HK}[\rho]$

$$F_{HK}[\rho] = T_s[\rho] + J[\rho] + E_{xc}[\rho] \quad (3-8)$$

, where E_{xc} , the so-called exchange-correlation energy is defined as

$$E_{xc} \equiv (T[\rho] - T_s[\rho]) + (E_{ee}[\rho] - J[\rho]) = T_c[\rho] + E_{nc}[\rho] \quad (3-9)$$

T_c is residual part of the true kinetic energy which is not covered by T_s . E_{xc} is the functional which contains everything that is unknown. Accordingly, the quality of the density functional approach matters solely the accuracy of the chosen approximation to E_{xc} . Hence, finding more accurate approximation to E_{xc} is the key problem of DFT development.

To make an approximation of E_{xc} , Local Density Approximation (LDA) approach introduced a uniform electron gas and back ground charge. However, the moderate accuracy of LDA is insufficient for chemistry. In the Generalized Gradient Approximation (GGA), not only the local electron density but also the gradient of the density, $\nabla\rho$, was considered,

$$E_{XC}^{GGA}[\rho_\alpha, \rho_\beta] = \int f(\rho_\alpha, \rho_\beta, \nabla\rho_\alpha, \nabla\rho_\beta) d\vec{r} \quad (3-10)$$

GGA functional have overcome the deficiencies of LDA to a considerable extent. In particular, they can provide more accurate results about the energetics of elemental chemical reactions. In practice, E_{XC}^{GGA} can be rewritten as

$$E_{XC}^{GGA} = E_X^{LDA} - \sum_\sigma \int F(s_\sigma) \rho_\sigma^{\frac{4}{3}}(\vec{r}) d\vec{r} \quad (3-11)$$

The realization of function F in Eq.3-11 is the key for the more accurate approximation.

3.2 Computational Methods Used in This Thesis

Among the various computation programs and softwares (e.g. Gaussian, Material Studio, Vienna Ab initio Simulation Package (VASP), etc.), VASP is one of the most widely used programs. In VASP, the projector-augmented wave (PAW) method is applied for a very small size of the basic set, resulting in the fast and reliable computation.¹⁷⁸ The combination of self-consistency cycle and efficient numerical methods (implemented iterative matrix diagonalization schemes, RMM-DISS, and blocked Davidson) lead to efficient, robust and fast scheme for evaluating the self-consistent solution of the Kohn-Sham functional. Meanwhile, the supplied PAW pseudopotentials is generally accurate and enable to eliminate the need for tedious tests. The major drawback for PAW pseudopotentials is the large error when handling f-elements.

Among all the functionals for describing the exchange and correlation energy in VASP, Perdew-Burke-Ernzerhof (PBE)¹⁷⁹ and Perdew-Wang (PW91)¹⁸⁰ are two most widely used functionals. PBE is based on PW91 with improved description of the linear response of the uniform electron gas, corrected behavior under uniform scaling, and a smoother potential.¹⁷⁹

Thereby, in this thesis, for demonstrating the SMSIs in SACs based on Mo₆S₈, DFT method was employed to calculate the binding energy and electronic structure of the single metal atoms on the support. The reaction pathways were proposed by calculating the reaction energy and energy barrier of the intermediate species. Finally, the catalytic rates were estimated with the help of Arrhenius equation. To ensure the accuracy of the calculation results, it is important to employ appropriate functional.

The GGA-PBE¹⁷⁹ was employed as the exchange and correlation functional. By testing the optimization of Mo₆S₈ using PBE and PW91, PBE gave more accurate result with respect to experimental results¹⁸¹ and was in a good agreement with previous work.¹⁸² For instance, as for the optimization of Mo₆S₈, PBE functional gave the Mo-Mo bond length of 2.65 Å while PW91 functional gave 2.64 Å. The experimental value of Mo-Mo bond length was 2.65 Å in Mo₆S₈. Thus, PBE functional was employed to describe the exchange and correlation energy in this work.

Spin-unrestricted DFT calculations for the activation and conversion of CH₄ and H₂O into CH₃OH on a single-metal-atom doped M-Mo₆S₈ cluster were performed with the PAW method using VASP^{183, 184}. The kinetic energy cutoff for a plane wave basis set was 500

eV. Only Γ -points was considered for the calculations. M-Mo₆S₈ clusters were allowed fully relaxed together with the adsorbates. Relaxations of the ion positions were performed using a conjugate gradient algorithm, until the forces on all atoms were less than 0.01 eV/Å and convergence to 1E-5 eV of the total electronic energy. The effect of zero-point energy correction is not include due to its bare influence on the barrier.¹⁶⁹ The calculated adsorption energy was expressed as $E_{\text{ads}} = E(\text{adsorbate/Cluster}) - E(\text{Cluster}) - E(\text{adsorbate})$, where $E(\text{adsorbate/Cluster})$, $E(\text{Cluster})$, and $E(\text{adsorbate})$ represent the total energies of Mo₆S₈ interacted with the adsorbate, Mo₆S₈ cluster in gas phase and the adsorbate in gas phase, respectively. The transition states were located by NEB method.¹⁸⁵⁻

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4 Geometry and Stability of Single-Metal-Atom Doped

Mo₆S₈

4.1 Introduction

A high stability of the catalyst is important for a promising catalytic performance. Strong Mo-S chemical bonds and strong metal-support interactions (SMSIs) are required for single-metal-atom doped Mo₆S₈ to survive under the reaction conditions. Strong Mo-S bond can guarantee the intact structure of Mo₆S₈ cluster, while SMSIs allow a stable adsorption of the single metal atom on Mo₆S₈ cluster. For evaluating the potential of M-Mo₆S₈ (M=K, Ti, Co, Fe, Ni, Cu, Rh) for steam reforming of methane (SRM) to methanol, the preliminary step is to ensure the stability of these structure under the SRM reaction conditions.

Mo₆S₈-based materials have been experimentally tested as the catalysts for CH₃SH synthesis from H₂S and CH₃OH,¹⁵⁸ hydrodesulfurization,¹⁶¹ and methyl tert-butyl ether cracking,¹⁵⁷ suggesting their high thermal stability at temperatures over 400 °C. Besides, the high stability of Mo₆S₈-based catalyst for methanol synthesis via CO₂ hydrogenation has been revealed.^{169, 182} However, these reaction are all taking place at an atmosphere in the absent of water. During SRM to methanol, the oxidation of catalyst by water steam via the substitution of S atom into O atom are likely to occur and lead to deactivation of the catalyst. The stability of Mo₆S₈-based catalysts in an oxidative environment with the presence of H₂O remains to be investigated.

Partial density of states (PDOS) described the electronic structure of catalysts. The d-band shifting of Mo atom due to the single metal atom doping indicated the electron transfer between Mo and M atoms.¹⁶⁵ Meanwhile, the d states near Fermi level could explain the reactivity of catalysts, which is the d-band center theory.¹⁹¹ However, the PDOS of K-, Ti-, Fe-, Ni-, and Cu-Mo₆S₈ clusters have not been reported and analyzed.

Thereby, in this section, the stability and geometry of M-Mo₆S₈ (M= K, Ti, Co, Fe, Ni, Cu, Rh) will be evaluated by calculating the length and strength of the Mo-S covalent bonds and the M-S bonds in the M-Mo₆S₈ clusters. Besides, the stability of Mo₆S₈ cluster under steam-rich atmosphere will be discussed by calculating the reaction energy of one S atom substitution by one O atom. Meanwhile, the SMSIs will be discussed based on the electronic structures of the single metal atoms and their neighboring Mo atoms.

4.2 Results and Discussion

4.2.1 Geometry and stability of Mo_6S_8 cluster in $\text{M-Mo}_6\text{S}_8$

Figure 4.1. Optimized $\text{M-Mo}_6\text{S}_8$ structure. (a) M atom anchored at S-Mo-Mo-S 4-fold site; (b) M atom anchored at S-S 2-fold site. (Mo: small purple, S: yellow, M: big purple or dark blue.)

The Mo_6S_8 cluster consists of a Mo_6 octahedral core situated inside an almost regular cubic cage of 8 S atoms (Figure 4.1). The bond length of Mo-S and Mo-Mo bonds in our calculations were 2.46 Å and 2.65 Å, respectively, which were in a good agreement with that in previous work¹⁸² and the experimental value¹⁸¹, indicating that our calculation results were reliable. Compared with Mo-S and Mo-Mo bonds in MoS_2 , the Mo-S bond in Mo_6S_8 was 0.09 Å longer whereas the Mo-Mo bond was 0.55 Å shorter. This unique structure led to less active Mo site than that in MoS_2 but more active S site.¹⁸²

Each S atom tightly combined with three Mo atoms with a binding energy of 5.90 eV. This strong interaction could prevent the decomposition of the Mo_6S_8 cluster in the reaction environment. Also, the oxidation of the Mo_6S_8 cluster was energetically unfavorable. The replacement of the S atom by the O atom was extremely endothermic with a reaction energy

of 4.06 eV, indicating that the Mo₆S₈ cluster is likely to survive under an oxidizing environment.

4.2.2 The SMSIs between M and Mo₆S₈

Table 4.1. Binding energy (eV) and bond length of M-S bond of single-metal-atom over Mo₆S₈ cluster.

Metal	K	Ti	Fe	Co	Ni	Cu	Rh
M-S bond length (Å)	3.04	2.27	2.17	2.13	2.15	2.18	2.37
Binding Energy (eV)	-2.71	-5.24	-3.77	-3.57	-3.69	-2.55	-4.33

According to our DFT calculation results, the singly-doped Ti, Fe, Co, Ni, Cu, Rh could be well stabilized at the S-Mo-Mo-S 4-fold sites at the edge of Mo₆S₈ cluster (Figure 4.1a), whereas K preferred adsorbing at the S-S 2-fold site (Figure 4.1b). These were in a good agreement with the previous studies.^{162-164, 169} The bond length of transition metals (Ti, Fe, Co, Ni, Cu) were around 2.10 Å, while that of Ti-S was slightly longer probably due to the larger atom radius of Ti atom. Rh-S bond even possessed a longer length than Ti-S bond because of its much larger atom radius. The alkali metal, K, lost one electron and forms K⁺ on its interaction with Mo₆S₈. Accordingly, K-S bond was significantly longer than other M-S bonds due to the electrostatic repulsion between K⁺ cation and Mo^{δ+}.

The binding energy of M and Mo₆S₈ followed the order: Ti > Rh > Fe > Ni > Co > K > Cu (Table 4.1), which was in a good agreement with the previous studies.¹⁶⁹ The interaction between early transition metal, Ti, and Mo₆S₈ cluster was the strongest ($E_{\text{ads}} = -5.24$ eV),

while Cu had the weakest interaction ($E_{\text{ads}} = -2.55$ eV). Even the corresponding interaction of K^+ on the 2-fold S-S site was slightly stronger ($E_{\text{ads}} = -2.71$ eV) than that of $\text{Cu-Mo}_6\text{S}_8$.¹⁶⁹ More importantly, although the M- Mo_6S_8 interaction was strong, the Mo_6 octahedral core remained mostly intact with only a slight structural distortion.

Figure 4.2. Partial density of states (PDOS) of Mo_6S_8 and metal modified M- Mo_6S_8 (M = K, Ti, Fe, Co, Ni, Cu, and Rh) cluster.

As shown in Figure 4.2, partial density of states for single metal atoms M and neighboring Mo atom were calculated to reveal the electronic structure of M-Mo₆S₈. The oxidation of the M atoms and the reduction of the neighboring Mo atom were proposed based on the emergence of new Mo 4d intermediate states at the Fermi level as well as the down shifted d band of Mo atom beyond the Fermi level. These Mo 4d states were weakest on Rh-Mo₆S₈, indicating the least electron transfer from Rh to Mo₆S₈. As for the case of K atom, the Mo 4d states were strongest among all the studied cases, indicating the most intensive electron transfer from K to Mo₆S₈.

The d states near Fermi level, which were contributed by the single metal atoms M and neighboring Mo atom, were potential for the activation of CH₄ and H₂O. However, since the s electron of K contributed nothing near the Fermi level due to the formation of K⁺ ion on Mo₆S₈, the activation of CH₄ and H₂O might be not likely to occur on K site. The strong d states of Ti, Fe, Co, Ni, Cu, and Rh near Fermi level indicated that the activation of CH₄ and H₂O prone to take place on the M sites, i.e. these single metal atoms. As the Mo atom contributed to the d states near Fermi level as well, it was possible for the Mo sites to participate in the activation of CH₄ and H₂O. Accordingly, the most likely CH₄ and H₂O adsorption sites on M-Mo₆S₈ (M= Ti, Fe, Co, Ni, Cu, and Rh) were the M top site or the M-Mo bridge site. The co-participation of single metal atoms M and neighboring Mo atom could accelerate the CH₄ and H₂O activation. But on K-Mo₆S₈, the Mo top site might be the most likely activation site for CH₄ and H₂O.

Detailed catalytic behaviors of M-Mo₆S₈ would be discussed in the following chapters, including the CH₄ adsorption and dissociation, H₂O adsorption and dissociation, and finally the optimized reaction pathway for methanol synthesis via SRM.

4.3 Conclusion

The geometry of Mo₆S₈ cluster was described by calculating the bond length of Mo-S and Mo-Mo. Our computation results were in a good agreement with the previous theoretical reports and experimental results, indicating the reliability of our computation method. Strong Mo-S binding and M-S interaction indicated the high stability of M-Mo₆S₈. The extremely endothermic S substitution by O confirmed the difficult oxidation of M-Mo₆S₈, which further demonstrated the high stability of M-Mo₆S₈ under the reaction condition.

All the studied single metal atoms prefer to be adsorbed on Mo-S-S-Mo 4-fold site, except K which turned to K⁺ and adsorbed on S-S site. The SMSIs were described by the strong M-S binding and the electron transfer from the M atoms to their neighboring Mo atoms. Based on the PDOS results, the critical d states near Fermi level, which is important for CH₄ and H₂O activation, were mainly contributed by single metal atoms M (except K) and partially contributed by Mo atom, indicating that the active site for CH₄ and H₂O might be the M top site or the M-Mo bridge site. However, on K-Mo₆S₈, K might not directly participate in the reaction of CH₄ and H₂O activation and the final CH₃OH synthesis.

5 CH₄ Adsorption and Dissociation on M-Mo₆S₈

5.1 Introduction

The adsorption and dissociation of CH₄ were slow steps in CH₄ reforming process due to the robust C-H bonds in CH₄ molecule and the weak interactions between CH₄ and most catalysts.^{192, 193} An ideal catalyst for SRM to methanol should show high activity for CH₄ activation while suppressing the formation of carbon deposition from the complete dissociation of CH₄. Via DFT calculation, the adsorption energy of CH₄ and energy barrier for each elementary step of CH₄ dissociation on a catalyst surface can be obtained. Based on these data, one can estimate the most stable CH₄ adsorption site and the major product of CH₄ dissociation on the catalyst, as well as the coking resistance of the catalyst. More importantly, these information is necessary for deducing the reaction pathway of SRM to CH₃OH on a certain catalyst.

CH₄ dissociation on various catalysts has been studied theoretically. For example, Wang and co-workers studied the CH₄ dissociation on Ni/Al₂O₃ and K-promoted Ni/Al₂O₃ catalysts using a Ni₄ cluster as the model.³⁹ CH₄ weakly binded on Ni through C atom with an adsorption energy of -0.18 eV. The addition of K weakened the adsorption by 0.04 eV. Nevertheless, K promoted the first two steps CH₄ dissociation, namely, *CH₄ to *CH₃ and *CH₃ to *CH₂ and suppressed the last two steps dissociation, namely, *CH₂ to *CH and *CH to *C, indicating the coking resistance of the catalyst could be promoted by the introduction of K. As for the CH₄ dissociation on metallic Ni, Ni (211) surface was most

active while Ni (111) was most inert.¹⁹⁴ The interaction between CH₄ and metallic Co was weak (~0.05 eV).¹⁹³ The first hydrogen abstraction on metallic Co was moderate with energy barrier of 1.25 eV on Co (111) and (110) surface and 1.02 eV on Co (100). The further dissociation of *CH₃ was faster than the first step. On Fe (100) surface, the CH₄ adsorption was even weaker (-0.04 eV).¹⁹⁵ However, the first hydrogen abstraction (energy barrier, 0.69 eV) on Fe (100) was faster than that on Co and comparable with that on Ni/Al₂O₃. The further dissociation was easier than the first hydrogen abstraction, indicating the high activity and likely coking on Fe (110) surface. The interaction between Fe and ZnO could promote the first hydrogen abstraction by 0.39 eV, indicating that the SMSIs played an important role in enhancing the CH₄ dissociation. Rh (111) was more active than Fe (110) toward CH₄ dissociation (energy barrier, 0.60 eV) whereas the final dissociation to carbon was slow (energy barrier, 1.08 eV), indicating the high coking resistance on Rh.¹⁹² Cu (111) was inert for the first hydrogen abstraction of CH₄ (energy barrier, 1.57 eV).¹⁹⁶

However, CH₄ adsorption and dissociation on single atom (K, Ti, Co, Fe, Ni, Cu, Rh) doped Mo₆S₈ cluster have not been explored yet. In this section, the adsorption site of CH₄ on these M-Mo₆S₈ structures will be confirmed by comparing the adsorption energy of CH₄ on the different sites of M-Mo₆S₈. The geometries and energy barriers of the elementary steps for CH₄ dissociation will be calculated as well to determine the most possible product of CH₄ dissociation on the different clusters as well as the coking resistant of the catalysts.

5.2 Results and Discussion

5.2.1 CH₄ Adsorption

The adsorption and activation of CH₄ is an important step for SRM reaction. The activated CH₄ adsorption had positive influence on the following first H abstraction process.

Table 5.1. Adsorption energy (eV) of molecule CH₄ on bare cluster and metal modified clusters.

Site	Mo ₆ S ₈	K-Mo ₆ S ₈	Ti-Mo ₆ S ₈	Fe-Mo ₆ S ₈	Co-Mo ₆ S ₈	Ni-Mo ₆ S ₈	Cu-Mo ₆ S ₈	Rh-Mo ₆ S ₈
Mo	-0.30	-0.17	-0.21	-0.10	-0.15	-0.13	-0.18	-0.12
Metal		-0.11	-0.46	-0.36	-0.48	-0.53	-0.38	-0.05

CH₄ adsorption on bare Mo₆S₈ was preferred on the Mo top site (Figure 5.1) with an adsorption energy of -0.30 eV. The distance between Mo and C was 2.80 Å, which was consistent with the previous report.¹⁵⁹ The two C-H bonds that pointed to the Mo atom were slightly elongated from 1.09 Å to 1.10 Å due to the interaction between the H and Mo atoms, indicating the activated adsorption process. Compared with CH₄ adsorption on MoS₂ surface, the adsorption energy of CH₄ on Mo₆S₈ was close to that on pristine MoS₂ (-0.32 eV) and Mo-vacancy (-0.31 eV), however, weaker than that on S-vacancy (-0.41 eV) and divacancy (-0.46 eV).¹⁹⁷

Single-atom doping did not affect the bonding motif via H of CH₄, which was previously proposed as the precursor for CH₄ activation, while it varied the interaction with CH₄ via

either the ligand effect (the modification of the electronic structure of $M^{\delta+}$ and $Mo^{\delta+}$) or the ensemble effect (the direct participation of M in binding). After the loading of different atomic metals, the adsorption sites and energy of CH_4 on the cluster were varied (Table 5.1). The M top site was the preferred adsorption site for CH_4 on Ni-, Co-, Ti-, Fe-, Cu-, and Ti- Mo_6S_8 , while Mo top site was more favorable on K- and Rh- Mo_6S_8 . Among all the involved metal doping, the adsorption energies followed the decreasing order: Ni- Mo_6S_8 (-0.53 eV) > Co- Mo_6S_8 (-0.48 eV) > Ti- Mo_6S_8 (-0.46 eV) > Fe- (-0.36 eV), Cu- Mo_6S_8 (-0.38 eV) > Mo_6S_8 (-0.30 eV) > K- Mo_6S_8 (-0.17 eV) > Rh- Mo_6S_8 . (-0.12 eV).

To find out the reason for the different adsorption behaviors of CH_4 on the various atomic metal doped Mo_6S_8 clusters, the CH_4 adsorption geometries on the various M- Mo_6S_8 are demonstrated in Figure 5.1. For Ni- Mo_6S_8 , the strong interaction between Ni atom and CH_4 elongated the two C-H bonds pointed to Ni atom to 1.13 and 1.12 Å, respectively, from 1.09 Å in free CH_4 molecule, indicating the activated adsorption of CH_4 on Ni- Mo_6S_8 . Similar elongation was observed on Co- Mo_6S_8 , where the two C-H bonds pointed to Co atom were elongated to 1.14 and 1.11 Å, respectively. However, on Fe- and Cu- Mo_6S_8 , although sharing the same CH_4 adsorption configuration, the C-H bonds were only elongated to 1.11 Å because of the relative weak interactions between CH_4 and Fe- and Cu- Mo_6S_8 . But the interactions were still more intense than that on Mo_6S_8 . On Ti- Mo_6S_8 , the configuration of CH_4 adsorption was slightly different. Three C-H bonds pointed to Ti rather than two in the case of Ni and Co. As a result, the elongation of C-H bonds on Ti- Mo_6S_8 was negligible. As for the cases of K- and Rh- Mo_6S_8 , due to the weak adsorption and metal- CH_4 interaction, C-H bonds elongation was negligible.

Based on the above calculation results, it could be deduced that the interaction of Mo₆S₈ with CH₄ could be altered on different M-Mo₆S₈ by the ligand effect and the ensemble effect. With regard to the ligand effect, the CH₄-Mo interaction on Mo₆S₈ could be weakened by the doped single-metal atoms (M = K, Ti, Fe, Co, Ni, Cu, Rh, Table 5.1) via the electrostatic repulsion between H⁺ of CH₄ and the doped single M^{δ+}. Such repulsion was particularly significant with the fully oxidized K⁺ in K-Mo₆S₈. This is an important reason why the Mo top site of K-Mo₆S₈ is more stable site for CH₄ than the K⁺ site.

The ionic forms of the metals are active enough to stabilize CH₄ and the M exhibited a stronger interaction with CH₄ than the Mo top site. According to the CH₄ adsorption energy on the different atomic site, the ensemble effect of the different metal atoms followed the decreasing order: Ni > Co > Ti > Cu > Fe. The most promotion was shown on the atomic Ni with the CH₄ adsorption energy increases from -0.30 eV for Mo₆S₈ to -0.53 eV for Ni-Mo₆S₈. But the enhancement in the adsorption of CH₄ on Cu (-0.38 eV) and Fe (-0.36 eV) was rather limited.

Rh is the only 4d metal dopant considered in our study. Compared to the 3d metal dopants, Rh is the least oxidized. However, with the lower-lying d-band (Figure 4.2), the doped single Rh atom is not active enough to adsorb CH₄ according to the d-band theory,¹⁹⁸ and the molecule still prefer to adsorb on the Mo top site as in the cases on K-Mo₆S₈ and Mo₆S₈.

Figure 5.1. Geometries of the reaction intermediates and transition states (TS) involved in CH_4 dissociation on single metal-atom modified Mo_6S_8 clusters (Mo: small purple; S: yellow; C: brown; H: white; metal: K: big purple; Ti: light blue; Fe: wine; Co: dark blue; Ni: green; Cu: orange; and Rh: grey).

The interaction between Mo₆S₈ and metal atom also influence the CH₄ adsorption. CH₄ adsorption on metallic surface was extremely weak while the interaction between the single metal atoms and Mo₆S₈ support could significantly enhance the adsorption. CH₄ adsorption on Ni-Mo₆S₈ was much stronger than that on pure Ni surface and Ni/Al₂O₃.^{39, 199} Meanwhile, CH₄ adsorption on Ni was sensitive to the size of the Ni species, namely, the smaller the Ni species were, the stronger the CH₄ adsorption was.²⁰⁰ Based on these report, the strong CH₄ adsorption might be due to the synergy of the size effect of Ni species and the interaction between Ni and Mo₆S₈ cluster. Analogously, CH₄ adsorption on Co (111) surface (-0.06 eV), Co (110) surface (-0.04 eV), and Co (100) surface (-0.06 eV) was significantly weaker than that on Co-Mo₆S₈, probably due to the interaction between Co and Mo₆S₈.¹⁹³ Cases on Fe and Cu were similar as well. CH₄ adsorption energies on Fe (100) surface (-0.02 eV), Fe (110) surface (-0.03 eV) and Cu (111) (-0.01 eV) were almost negligible, suggesting the interaction between Fe/Cu and Mo₆S₈ obviously influenced the catalytic behavior of Fe.^{195, 196}

5.2.2 *CH₄ Dissociation

Figure 5.2. Optimal Potential Energy Diagrams for methane dissociation on Bare, K-, Ti- and Fe-Mo₆S₈ cluster (top) and Co-, Ni-, Cu- and Rh-Mo₆S₈ cluster (down). Arrows points to the step with highest barrier.

The CH₄ dissociations on all studied clusters were highly endothermic processes (Figure 5.2). The bare Mo₆S₈ cluster displays the higher endothermicity than M-Mo₆S₈ clusters, where the energy was uphill all the way going from *CH₄ (-0.30 eV) to *C (3.68 eV). The hydrogen abstraction proceeded at the Mo-S bridge sites (Figure 5.1). The first C-H bond cleavage (*CH₄ + * → *CH₃ + *H) corresponded to an energy barrier (E_a) of 1.45 eV (Figure 5.2). During the dissociation, the S atom helped to facilitate the C-H bond cleavage via the stabilization of the dissociated *H atom (Figure 5.1), which was also observed previously for hydrogenation reactions.^{162-164, 169} Here, we noted that the effect of co-adsorption of *H on the energetics was not included in the potential energy diagram. In agreement with our previous studies on Mo₆S₈ and doped-Mo₆S₈,^{169, 182} the present calculation showed that *H prefers to the S site via the strong S-H bond and did not compete with the other intermediates for the active sites (Mo or M). In addition, the binding energy did not vary significantly on co-adsorption with other intermediates (<0.2 eV) and the shifted in energy in the potential energy diagram by including co-adsorbed *H remained mostly the same. In addition, the high mobility of *H under the methane activation conditions likely enabled the facile recombination of two *H and desorption.

The single-metal-atom dopants displayed more significant effect on the hydrogen abstraction of CH₄ as compared to the molecular adsorption. For the first hydrogen abstraction, the corresponding E_a decreased in the order: Co-Mo₆S₈ (E_a = 0.58 eV) > Fe-Mo₆S₈ (E_a = 0.71 eV) > Ti-Mo₆S₈ (E_a = 0.83 eV) > Ni-Mo₆S₈ (E_a = 1.07 eV) > K-Mo₆S₈ (E_a = 1.33 eV) > Mo₆S₈ (E_a = 1.45 eV) > Rh-Mo₆S₈ (E_a = 1.51 eV) > Cu-Mo₆S₈ (E_a = 1.72 eV).

The doping of the single metal-atom of Co, Fe, Ti, and Ni greatly lowered the reaction energy and the corresponding barrier for the first hydrogen abstraction on Mo₆S₈. The ensemble effect played a dominant role in these cases, as demonstrated by the direct participation of doped M^{δ+} in stabilizing *CH₄ and the dissociated *H (Figure 5.1). The higher activity of single-metal-atom M^{δ+} (M = Co, Fe, Ti, Ni) than Mo^{δ+} was associated with the lower oxidation state. The corresponding d states of M^{δ+} located closer to the Fermi level than that of Mo^{δ+} (Figure 4.2), which helped to stabilize the reaction intermediates (*CH₄, *CH₃, and *H), and the transition states via the facilitated electron transfer from the cluster. CH₄ dissociation on Ni-Mo₆S₈ was 0.11 eV faster than that on Ni (111), indicating that the synergy between Ni single atom and Mo₆S₈ enhanced the CH₄ activation.²⁰¹ CH₄ activation was 0.67, 0.66, and 0.44 eV faster on Co-Mo₆S₈ than that on Co (110), (111), and (100) surface, respectively, indicating that the cooperation between Co and Mo₆S₈ was successful for CH₄ activation.¹⁹³

On atomic Fe doped Mo₆S₈, the first hydrogen abstraction was attributed to the activated CH₄ adsorption and d states of Fe atom near Fermi level (Figure 4.2). The first CH₄ abstraction on Fe-Mo₆S₈ was similarly fast with that on Fe (110) surface (E_a = 0.69 eV) but slower than that on Fe/ZnO catalysts (E_a = 0.30 eV).^{202, 203} Here, we noted that the first C-H bond cleavage of *CH₄ at the Fe site of Fe-Mo₆S₈ was lower in E_a by 0.95 eV than that of the Fe-based sMMO catalyst,²⁰⁴ while it was higher by ~0.2 eV than that of Fe-ZSM due to the assistance of the O atom from the confined environment.^{137, 205}

In contrast, the ensemble effect introduced by doping Cu was opposite. The dehydrogenation of $^*\text{CH}_4$ on Cu-Mo₆S₈ corresponds to the highest barrier among all the systems studied. In this case, the doped Cu corresponded to the lower-lying d states than the other dopants (Figure 4.2), which hindered the stabilization of the transition state for C-H bond cleavage, specifically $^*\text{H}$, and thus raised the activation barrier. As a result, the first hydrogen abstraction was suppressed on Cu-Mo₆S₈ by 0.15 eV compared with that on Cu (111) surface.¹⁹⁶

Similarly, the doping of Rh did not help for the first hydrogen abstraction, though the Rh site directly participated in interaction with the dissociated $^*\text{CH}_3$ via the ensemble effect. The corresponding barrier on Rh-Mo₆S₈ was 0.21 eV lower than that of Cu-Mo₆S₈. This was due to the less stable initial state, $^*\text{CH}_4$, introduced by doping Rh than Cu. As a result of these, compared with that on Rh (111) surface, the interaction between Rh and Mo₆S₈ slowed down the CH₄ activation. The first hydrogen abstraction was fast on Rh (111) surface ($E_a = 0.60$ eV) which was 0.91 eV faster than that on Rh-Mo₆S₈.¹⁹²

With one electron transfer, K^+ on Mo₆S₈ did not contribute to the states near the Fermi level, while the donated electron resulted in the reduction of $\text{Mo}^{\delta+}$, which was observed with some of the low empty states of Mo 4d states filled (Figure 4.2). The reduction of Mo was supposed to help the adsorption of CH₄, while the binding on K-Mo₆S₈ was weaker than Mo₆S₈ due to the dominating electrostatic H^+-K^+ repulsion (Table 5.1). Yet, the transition state for the C-H cleavage on K-Mo₆S₈ was energetically comparable to that of Mo₆S₈ (Figure 5.2), as the destabilization of $^*\text{CH}_3$ due to electrostatic repulsion was

compensated by the stabilization of dissociated *H by reduced $Mo^{\delta+}$ at the transition stage (Figure 5.1). As a result, the barrier was slightly lowered.

Interaction between Mo_6S_8 and metal atom exhibited different influence on the activity toward CH_4 activation. The activity of Ni and Co was promoted whereas Rh and Cu was suppressed. However, this interaction had little influence on Fe. The d states of single metal atoms near Fermi level played an important role in CH_4 activation helped to stabilize the dissociation intermediates which could lower the energy barrier of CH_4 dissociation.

5.2.3 *CH_3 Dissociation

On Mo_6S_8 , *CH_3 adsorbed on Mo-S bridge site through C by forming Mo-C (2.74 Å) and S-C (1.86 Å) bonds. C-H bond toward Mo atom was slightly elongated to 1.11 Å due to the interaction between Mo and H atoms which may be the reason for the faster *CH_3 dissociation than that on single-metal-atom doped M- Mo_6S_8 . However, *CH_3 adsorption was confined on M-Mo bridge site through C atom on Ti-, Fe-, Co-, and Ni- Mo_6S_8 where the Mo-C bond was ~ 2.5 Å and C-M bond was 2.17, 2.03, 1.97, and 1.95 Å, respectively. Similar to the case on bare Mo_6S_8 , C-H bond toward Mo was elongated to ~ 1.11 Å while on Ti- Mo_6S_8 , only the C-H pointed to Ti atom was elongated. On Cu- and Rh- Mo_6S_8 , M top site was the most likely adsorption site for *CH_3 with M-C bond length of 1.93 and 2.04 Å, respectively. Only the C-H bond toward Rh atom was slightly elongated to 1.11 Å while on elongation was observed on Cu- Mo_6S_8 .

The single-metal-atom dopants caused the difficulty for the second hydrogen abstraction, where the corresponding barrier increased following the order of Mo₆S₈ ($E_a = 1.07$ eV) < Rh-Mo₆S₈ ($E_a = 1.21$ eV), K-Mo₆S₈ ($E_a = 1.24$ eV) < Co-Mo₆S₈ ($E_a = 1.35$ eV), Ti-Mo₆S₈ ($E_a = 1.33$ eV) < Cu-Mo₆S₈ ($E_a = 1.49$ eV) < Ni-Mo₆S₈ ($E_a = 1.65$ eV) < Fe-Mo₆S₈ ($E_a = 1.83$ eV).

For M = Co, Fe, Ti, Ni, Rh, Cu, the direct participation of the doped single M atom in binding (Figure 5.1) particularly promoted the stability of *CH₃ as compared to Mo₆S₈ (Figure 5.2), which hindered the dissociation. That was, the ensemble effect of single-metal-atom dopants suppressed the *CH₃ dissociation, whereas the ligand effect was rather weak. This suppression indicated that *CH₃ might be the most likely product of *CH₄ dissociation which could take part in the CH₃OH synthesis via the C-O bond association. Thus, although the *CH₃ dissociation was suppressed due to the participation of single metal atoms, this suppression might have positive influence on the CH₃OH synthesis as well as the coking resistance. In the case of K-Mo₆S₈, the H⁺-K⁺ electrostatic repulsion drove the adsorption of *CH₂ away from K⁺ toward the dissociated *H. As a result, the *CH₃ → *CH₂ transition state was destabilized due to lateral repulsion. During this process, K⁺ was not directly involved.

Compared with this elementary step on metallic surface, the interaction between metal atom and Mo₆S₈ suppressed the *CH₃ dissociation, for instance, *CH₃ dissociation was slowed down by 0.79, 1.59, 0.74, 0.13, and 0.35 eV on Ni-, Fe-, Rh-, Cu-, and Co-Mo₆S₈, respectively.^{192, 193, 196, 201, 202} Based on this, it seemed that the interaction between Mo₆S₈

and single metal atoms enhanced the coking resistance with respect to both Mo₆S₈ and metallic surface. Thus, the suppressed *CH₃ dissociation might have positive influence on the catalytic performance of single metal atom doped M-Mo₆S₈ due to the enhanced coking resistance and better selectivity to CH₃OH.

5.2.4 *CH₂ Dissociation

*CH₂ moved to hollow site from Mo-S bridge site on bare Mo₆S₈ cluster, forming two Mo-C (2.41 and 2.28 Å) bonds and S-C (1.74 Å) bond which were significantly shorter than that in *CH₃ adsorption, indicating the stronger interaction. The C-H bond with H atom toward Mo atom was obviously elongated to 1.12 Å. However, although C-H bond was elongated more than that in *CH₃, the cleavage of C-H bond in CH₂ was more difficult than that in *CH₃, which was probably due to the stronger interaction between *CH₂ and Mo₆S₈. Also, different from the case of *CH₃ dissociation, dissociated H atom was solely stabilized by S atom rather than the cooperation of S and Mo. This might be another reason for the higher energy barrier of *CH₂ dissociation.

For Ti, Fe and Cu single atom doped Mo₆S₈, the M-Mo bridge site was the preferred adsorption site for *CH₂. The Mo-C bond on Ti- and Fe-Mo₆S₈ was ~2.35 Å, while much shorter 2.09 Å Mo-C bond was formed on Cu-Mo₆S₈. These Mo-C bonds were shorter than that in *CH₃ adsorption, indicating the stronger interaction between *CH₂ and Mo. The M-C bond was 1.95, 1.80, and 2.06 Å on Ti-, Fe-, and Cu-Mo₆S₈, respectively. The Ti-C and Fe-C bonds were shorter than those in *CH₃ adsorption, whereas the Cu-C bond became longer. This was probably due to the different adsorption site and stronger steric hindrance

between $^*\text{CH}_2$ and Cu. Only the C-H bond toward Mo on Fe-Mo₆S₈ was elongated to 1.12 Å while the rest C-H bonds on Ti-, Fe-, and Cu-Mo₆S₈ stayed unchanged.

M top site was favored on Co-, Ni-, and Rh-Mo₆S₈ with M-C bond of 1.73, 1.75, and 1.85 Å, respectively. All the M-C bonds were shorter than those in CH₃ adsorption, indicating the stronger interactions. However, no C-H bond was elongated indicating that CH₂ was not activated on Co-, Ni-, and Rh-Mo₆S₈.

On K-Mo₆S₈ cluster, the Mo-S bridge site away from K was the most likely site for $^*\text{CH}_2$ adsorption with Mo-C bond of 2.19 Å and S-C bond of 1.86 Å. Interestingly, S-C bond was of the same length of that in $^*\text{CH}_3$ adsorption on bare Mo₆S₈ while the Mo-C bond was much shorter (2.19 Å vs. 2.74 Å).

The barrier for $^*\text{CH}_2$ dissociation to $^*\text{CH}$ increased in the order of Ni-Mo₆S₈ ($E_a = 0.47$ eV) < Fe- ($E_a = 0.69$ eV), Co-Mo₆S₈ ($E_a = 0.69$ eV) < Mo₆S₈ ($E_a = 1.17$ eV), K-Mo₆S₈ ($E_a = 1.18$ eV) < Cu-Mo₆S₈ ($E_a = 1.30$ eV) < Rh-Mo₆S₈ ($E_a = 1.46$ eV) < Ti-Mo₆S₈ ($E_a = 1.77$ eV). Ti-Mo₆S₈ displayed the highest barrier toward $^*\text{CH}_2$ dissociation, while the introduction of the Fe, Co and Ni single-atom could accelerate the process on Mo₆S₈ (Figure 5.2). Again, the ensemble effect made the dominant contribution to the tuned energetics (Figure 5.1). K-Mo₆S₈ was the only exception, where only the ligand effect matters. The $^*\text{CH}_2$ dissociation was obviously faster than $^*\text{CH}_3$ dissociation, indicating that the deep dissociation was likely once $^*\text{CH}_3$ was dissociated. In other words, the dissociation of $^*\text{CH}_3$ could probably lead to carbon deposition on the catalysts.

Comparing this elementary step on M-Mo₆S₈ to that on metallic surface, interesting results could be obtained. *CH₂ dissociation on Ni-Mo₆S₈ was as fast as that on Ni-Mo₆S₈ and Ni (111) surface ($E_a = 0.46$ eV).²⁰¹ *CH₂ dissociation on metallic Co (110) is 0.54 eV slower than that on Co-Mo₆S₈, however, this process was 0.38 and 0.64 eV faster on Co (111) and (100) surface, respectively, with respect to that on Co-Mo₆S₈.¹⁹³ *CH₂ dissociation was 0.36 eV faster on Cu (111) than that on Cu-Mo₆S₈¹⁹⁶ and nearly barrier-less on Rh (111) and Fe (110) surface.^{192, 202} Overall, it seems like that the interaction between M and Mo₆S₈ showed a negative influence on the dissociation of *CH₂.

5.2.5 *CH Dissociation

As for the *CH adsorption, hollow site was the most favorable on all the studied clusters except Ti-Mo₆S₈. On bare Mo₆S₈ two Mo-C bonds were formed with an equal length of 2.09 Å, while the S-C bond was 1.79 Å. Compared with *CH₂ dissociation, the Mo-C bond was significantly shortened, while the S-C bond was elongated by 0.05 Å. Two Mo-C bonds on single metal atom doped M-Mo₆S₈ were ~2.15 and ~2.35 Å long, respectively, while S-C bond was ~1.80 Å except Rh. On Rh-Mo₆S₈, S-C bond was obviously shorter (1.71 Å) than that on other M-Mo₆S₈. *CH group stayed at Ti-Mo bridge site with Mo-C bond of 2.16 Å and Ti-C bond of 1.88 Å. No C-H bond was elongated on all studied clusters, indicating the difficult final dissociation.

The barrier for *CH dissociation to *C increases in the order of Co-Mo₆S₈ ($E_a = 0.99$ eV), Ni-Mo₆S₈ ($E_a = 1.00$ eV) < Fe-Mo₆S₈ ($E_a = 1.14$ eV) < Cu-Mo₆S₈ ($E_a = 1.31$ eV) < K-Mo₆S₈ ($E_a = 1.51$ eV) < Rh-Mo₆S₈ ($E_a = 1.66$ eV) < Ti-Mo₆S₈ ($E_a = 1.82$ eV) < Mo₆S₈ ($E_a = 2.00$ eV). The adsorption of *CH was comparable on the clusters with and without doping, whereas the final dissociation state, *C, could be significantly stabilized on M-Mo₆S₈ (Figure 5.2). *C adsorbed at hollow sites for all clusters, and formed the strong binding with S, Mo, and M atoms (Figure 5.1). The facilitated *CH dissociation was associated with the formation of the strong M-C bond via the ensemble effect (Figure 5.1). In the case of K-Mo₆S₈, the enhancement solely depended on the ligand effect. The reduced Mo^{δ+} by K doping helped to strengthen the Mo-*CH binding as compared to Mo₆S₈, while the weakening due to the H⁺-K⁺ electrostatic repulsion was less significant.

We further compared the *CH dissociation on the M-Mo₆S₈ clusters to those on metallic surfaces. Final dissociation was 0.47 eV slower on Ni (111) than that on Ni-Mo₆S₈ and 0.53 eV slower on Cu (111) surface than on Cu-Mo₆S₈.^{196, 201} This final step was 0.23 eV slower on Co (111) surface but 0.25 and 0.30 eV faster on Co (110) and (100) surface, respectively.¹⁹³ *CH dissociation on Fe-Mo₆S₈ was 0.66 eV slower than that on Fe (110) surface, and that on Rh-Mo₆S₈ 0.58 eV slower than that on Rh (111) surface.^{192, 202} The suppressed dissociations were indicatives of enhanced coking resistance of M-Mo₆S₈ catalysts.

5.3 Conclusion

The doping of single-metal-atom significantly influenced the CH₄ adsorption and dissociation on Mo₆S₈. CH₄ adsorption (on M top site) was enhanced on Ti-, Fe-, Co-, Ni-, and Cu-Mo₆S₈ via the ensemble effect, whereas CH₄ adsorption was weakened on K- and Rh-Mo₆S₈ (on Mo top site) due to the ligand effect. The adsorption energies followed the decreasing order: Ni-Mo₆S₈ (-0.53 eV) > Co-Mo₆S₈ (-0.48 eV) > Ti-Mo₆S₈ (-0.46 eV) > Fe- (-0.36 eV), Cu-Mo₆S₈ (-0.38 eV) > Mo₆S₈ (-0.30 eV) > K-Mo₆S₈ (-0.17 eV) > Rh-Mo₆S₈ (-0.12 eV).

The interaction between M and Mo₆S₈ enhanced *CH₄ activation but suppressed the dissociation of *CH₃. The activation toward the first hydrogen abstraction followed the decreasing order of Co-Mo₆S₈ (E_a = 0.58 eV) > Fe-Mo₆S₈ (E_a = 0.71 eV) > Ti-Mo₆S₈ (E_a = 0.83 eV) > Ni-Mo₆S₈ (E_a = 1.07 eV) > K-Mo₆S₈ (E_a = 1.33 eV) > Mo₆S₈ (E_a = 1.45 eV) > Rh-Mo₆S₈ (E_a = 1.51 eV) > Cu-Mo₆S₈ (E_a = 1.72 eV). Along the *CH₄ dissociation to *C, the step corresponding to the highest barrier varied with the different dopants. For K, Rh, and Ti- Mo₆S₈, the *CH → *C transition remained as the most difficult step as that on Mo₆S₈, while the rate-limiting step was *CH₃ → *CH₂ for Fe, Ni, Co-Mo₆S₈ and *CH₄ → *CH₃ for Cu-Mo₆S₈. According to the highest barrier along the pathway, the Co-Mo₆S₈ was likely the most effective catalyst for CH₄ activation and dissociation, which was followed by Mo₆S₈ > K-Mo₆S₈ > Ni-, Rh-Mo₆S₈ > Ti-Mo₆S₈ > Cu-Mo₆S₈ > Fe-Mo₆S₈ in a decreasing sequence. Furthermore, the suppression of *CH₃ dissociation on Mo₆S₈

introduced by single atoms doping could be beneficial for the direct CH_3OH synthesis and hindered the undesired formation of syngas and cokes.

6 H₂O Adsorption and Dissociation on M-Mo₆S₈

6.1 Introduction

The adsorption and dissociation of H₂O are vital for SRM process in providing *OH or *O species for C-O bond association with *CH_x, which is one of the key steps to the generation of methanol. It is vital to study the adsorption and dissociation of H₂O on the different single atom (K, Ti, Co, Fe, Ni, Cu, Rh) doped Mo₆S₈ clusters as a preliminary work to deduce the reaction pathways of SRM to methanol on these catalysts.

The adsorption and dissociation of H₂O have been widely evaluated on metallic forms of Co, Fe, Ni, Cu and Rh. For metallic Co, the adsorption of H₂O was strongest on Co (110), followed by (100) and (111) surface.²⁰⁶ The first hydrogen abstraction was fast on all the Co surfaces while the second hydrogen abstraction was slowest on Co (100) surface with an energy barrier of 1.10 eV, followed by Co (110) (0.99 eV) and Co (111) (0.89 eV). Fe-O binding (2.40 eV) on Fe (111) was much stronger than Co-O binding. The first hydrogen abstraction of H₂O on Fe (110) with an energy barrier of 0.68 eV was also faster than that on Co as well as the second hydrogen abstraction, indicating the higher activity of Fe (110) for H₂O dissociation.²⁰⁷ Rh (111) was even more active than Fe (110). The first hydrogen abstraction on Rh (111) was 0.02 eV faster than that on Fe (110).²⁰⁸ However, *H₂O and *OH dissociation on Ni (111) surface was 0.28 and 0.13 eV slower than that on Fe (110) surface, respectively.²⁰⁹ The energy barrier for *H₂O dissociation on Cu (111) was higher than 1 eV and the *OH dissociation was even harder with a high energy barrier of 1.51 eV.

*H₂O dissociation was also evaluated on other noble metals such as Au, Pt, and Pd, however, none of them was more active than Fe (110) surface.²⁰⁹

H₂O adsorption and activation on K and Ti species have received little attention. Furthermore, as is well-known, substrates could play an important role on the interaction between a metal and an adsorbent (i.e. H₂O molecule herein). With Mo₆S₈ coordinating the different metal species (Co, Fe, Ni, Cu, Rh etc.), the behavior of H₂O on them could vary. In this section, the active site for H₂O adsorption on M-Mo₆S₈ (M= K, Ti, Co, Fe, Ni, Cu, Rh) will be proposed by calculating the adsorption energy of H₂O on the different sites. The roles of both the single metal atoms and the Mo₆S₈ substrates will be investigated by calculating the geometries, the reaction energies, and the energy barrier of each elementary step during H₂O dissociation. Moreover, the competitive adsorption between CH₄ and H₂O on the same site will be discussed based on the adsorption energies of CH₄ and H₂O.

6.2 Results and Discussion

6.2.1 H₂O Adsorption

Table 6.1. Adsorption energy (eV) of molecule H₂O on bare cluster and metal modified clusters.

Site	Mo ₆ S ₈	K-Mo ₆ S ₈	Ti-Mo ₆ S ₈	Fe-Mo ₆ S ₈	Co-Mo ₆ S ₈	Ni-Mo ₆ S ₈	Cu-Mo ₆ S ₈	Rh-Mo ₆ S ₈
Mo	-0.83	-0.88	-0.78	-0.75	-0.79	-0.75	-0.80	-0.80
Metal		-0.52	-1.02	-0.92	-0.99	-0.97	-0.88	-0.79

Mo top site was the favored adsorption site for H₂O on bare Mo₆S₈ cluster ($E_{\text{ads}} = -0.83$ eV, Table 6.1), which was comparable to that of bulk MoS₂.²¹⁰ Mo-O bond was 2.31 Å which is 0.49 Å shorter than Mo-C in CH₄ adsorption. Both the shorter Mo-O bond and stronger binding between H₂O and Mo₆S₈ suggested the stronger H₂O adsorption than CH₄ adsorption. However, the two O-H bonds in H₂O were not elongated, indicating that H₂O molecule was not activated during the adsorption.

On Ti-, Fe-, Co-, Ni-, and Cu-Mo₆S₈, binding energies of H₂O on the M top sites were stronger than those on the Mo top sites. The M-O bond length was 2.21, 2.08, 2.01, 1.99, and 2.02 Å on Ti-, Fe-, Co-, Ni-, and Cu-Mo₆S₈, respectively. No O-H bond was elongated, similar to the case on Mo₆S₈. Compared with H₂O adsorption on Mo₆S₈, H₂O adsorption on Ti-, Fe-, Co-, Ni-, and Cu-Mo₆S₈ was enhanced by 0.05 eV, 0.05 eV, 0.09 eV, 0.14 eV, 0.16 eV, and 0.19 eV, respectively, due to ensemble effect. The direct participation of single metal atom enhanced the adsorption due to the higher lying d states of the doped

$M^{\delta+}$ than $Mo^{\delta+}$ (Figure 4.2), which favored the direct M-O bond formation. Interestingly, compared with Mo_6S_8 , the introduction of Ti, Fe, Co, Ni and Cu atoms all weakened the binding between Mo and O, which was probably due to the less oxidized Mo atom caused by the electron transfer from M to Mo.

In contrast, Mo top site was favored on K- and Rh- Mo_6S_8 . As for K- Mo_6S_8 , the enhancement in *H_2O adsorption on Mo top site was contributed by both ligand and ensemble effects. The ligand effect influenced the Mo-OH₂ interaction via the reduced $Mo^{\delta+}$, while the ensemble effect stabilized *H_2O via the O-K⁺ electrostatic attraction (Figure 6.1). Rh- Mo_6S_8 behaved similarly as bare Mo_6S_8 cluster. The adsorption at the Mo top remained the most stable (ligand effect) with Rh ^{$\delta+$} shifting away from *H_2O . Yet, the adsorption on the Rh site (ensemble effect) was only 0.01 eV less stable than that on that Mo site (Table 6.1).

Compared with H_2O adsorption on metallic Co (110), Fe (110), Ni (111), Cu (111), Rh (111) surfaces, the binding energy of H_2O on the corresponding M- Mo_6S_8 was 0.55, 0.54, 0.68, 0.67, and 0.39 eV higher, respectively.^{206-208, 211} This indicated the positive influence of Mo_6S_8 cluster for the adsorption of H_2O .

Figure 6.1. Geometries of the reaction intermediates and transition states (TS) involved in H_2O dissociation on metal modified cluster and bare cluster. (Mo: small purple, S: yellow, C: brown, H: pink, metal: K-big purple, Ti-light blue, Fe-wine, Co-dark blue, Ni-green, Cu-orange, Rh-grey)

During SRM reaction, H₂O might compete with CH₄ for the same active sites on Mo₆S₈ and M-Mo₆S₈ clusters. For instance, CH₄ and H₂O compete for Mo top site on Mo₆S₈, K-, and Rh-Mo₆S₈ and for M top site on Ti-, Fe-, Co-, Ni-, and Cu-Mo₆S₈. (Table 5.1 and 6.1). Obviously, H₂O adsorption was much stronger than CH₄ adsorption, indicating that H₂O was more likely to occupy the active site. The SRM process was more likely to start with the H₂O dissociation. The generated *OH or *O species at the active sites could become the new active sites for CH₄ to CH₃OH conversion according to the previous studies.^{212, 213}

The competitive adsorption between H₂O and CH₄ initiated the SRM to methanol process. Meanwhile, due to the preferred H₂O adsorption, complete CH₄ dissociation to carbon deposition was less likely, indicating the high coking resistance. However, the oxidation or hydroxylation of single metal atom might be the potential threats for deactivation. By investigated the H₂O dissociation, we could have a deeper understanding of the catalytic behavior of single metal atom doped M-Mo₆S₈ in SRM to methanol process.

6.2.2 *H₂O Dissociation

Figure 6.2. Optimal Potential Energy Diagrams for H₂O dissociation on Bare, K-, Ti- and Fe-Mo₆S₈ cluster (top) and Co-, Ni-, Cu- and Rh-Mo₆S₈ cluster (down). Arrows points to the step with highest barrier.

The $^*\text{H}_2\text{O}$ dissociation on Mo_6S_8 occurred over the Mo-S bridge site, where Mo and S atoms helped to stabilize the dissociated $^*\text{OH}$ and $^*\text{H}$ intermediates, respectively (Figure 6.1). Energetically (Figure 6.2), the first hydrogen abstraction to $^*\text{OH}$ and $^*\text{H}$ was less favorable ($E_a = 1.22$ eV) than that on bulk MoS_2 surface ($E_a = 1.01$ eV).²¹⁰ Here, again, the effect of co-adsorption of $^*\text{H}$ on the energetics was not included in the potential energy diagram due to the same reason in $^*\text{CH}_4$ dissociation. H_2 production via the recombination of two highly mobile $^*\text{H}$ atom was likely.

The formation of M- Mo_6S_8 promoted the $^*\text{H}_2\text{O}$ dissociation to $^*\text{OH}$ with the barrier decreasing in the order of Mo_6S_8 ($E_a = 1.22$ eV) > Ni- Mo_6S_8 ($E_a = 1.10$ eV) > Cu- ($E_a = 1.01$ eV), Rh- Mo_6S_8 ($E_a = 1.03$ eV) > Co- Mo_6S_8 ($E_a = 0.99$ eV) > K- Mo_6S_8 ($E_a = 0.66$ eV) > Ti- Mo_6S_8 ($E_a = 0.45$ eV) > Fe- Mo_6S_8 ($E_a = 0.42$ eV). The promotion was mostly via the ensemble effect, where the dopant enabled the stabilization of the dissociated $^*\text{OH}$ by shifting the adsorption site from the M atop site to the Mo-M bridge site on Fe- and Ni- Mo_6S_8 . Also, confinement effect was obvious on Ti- and Co- Mo_6S_8 where the hydrogen abstraction was confined on M site without the direct assistance from other atoms. The displacement of Cu allowed the assistance from S atom. On Rh- and K- Mo_6S_8 , the dissociation processes were quite similar with that on Mo_6S_8 . Meanwhile, the d states of single metal atom near the Fermi level also helped to stabilize the dissociated $^*\text{OH}$ species.

The Rh- Mo_6S_8 and K- Mo_6S_8 behaved slightly different. For Rh- Mo_6S_8 , the favorable site varied from the Mo top for $^*\text{H}_2\text{O}$ to the Rh top site for $^*\text{OH}$ (Figure 6.1), indicating that ligand effect played the dominated role which decreased the energy barrier by 0.19 eV

compared with that on Mo₆S₈. However, the promotion from K was obvious. In the case of K-Mo₆S₈, the synergy of interaction between K and H₂O and ligand effect due to the one electron transfer from K to Mo₆S₈ together decreased the energy barrier by 0.56 eV despite the similar transition state with that on Mo₆S₈.

Compared with H₂O dissociation on metallic surface, the interaction between M and Mo₆S₈ suppressed this elementary step by 0.16 and 0.37 eV on Co (110) and Rh (111), respectively.^{206, 208} However, H₂O dissociation was accelerated by 0.26 and 0.14 eV on Fe (110) and Ni (111), respectively.^{207, 211} The energy barrier was the same for the case of Cu.²¹¹

6.2.3 *OH Dissociation

*OH group favored the Mo top site on Mo₆S₈ cluster with Mo-O bond of 1.94 Å which was 0.37 Å shorter than that in *H₂O adsorption, indicating the stronger interaction. Again, O-H bond was not activated. The Mo top site was also preferred on K-Mo₆S₈ for *OH adsorption with Mo-O bond of 2.07 Å which was 0.13 Å longer than that in *OH adsorption on Mo₆S₈. However, as shown in Figure 6.2, *OH adsorption was even more stable than that on Mo₆S₈ despite the longer Mo-O bond which might be due to the interaction between K⁺ and *OH. M-Mo bridge site was favored for *OH adsorption on Ti-, Fe-, Co-, Ni-, and Cu-Mo₆S₈. Mo-O bond was ~2.19 Å on Fe-, Co-, Ni-, and Cu-Mo₆S₈ while Mo-O bond was significantly longer on Ti-Mo₆S₈ (2.31 Å). M-O bond was ~1.92 Å on them. Only on

Rh-Mo₆S₈ that *OH adsorbed on M top site with Rh-O bond of 1.91 Å. Again, no O-H bond was activated on M-Mo₆S₈.

A similar motif with *H₂O dissociation was observed on Mo₆S₈ for the *OH dissociation, where the dissociated *O preferred the Mo top site and introduced significant structural distortion of Mo₆S₈ (Figure 6.1). While the second abstraction was greatly facilitated on Mo₆S₈ ($E_a = 1.21$ eV) as compared to that of MoS₂ ($E_a = 1.93$ eV).²¹⁰ This was due to the fact that the unique Mo₆S₈ structure enabled the formation of Mo=O oxo species to promote the stability of the dissociated *O (Figure 6.1). The drawback was, though, the stabilized *OH on the M-Mo₆S₈ clusters hindered the dissociation of *OH to *O. This was the case for M = Ni ($E_a = 1.33$ eV), Co ($E_a = 1.67$ eV), Cu ($E_a = 1.73$ eV), K ($E_a = 1.74$ eV), and Rh ($E_a = 1.80$ eV), where the dissociated *O remained or shifted to the Mo-M bridge site. In contrast, the single Ti ($E_a = 1.03$ eV) and Fe ($E_a = 1.09$ eV) dopants helped to lower the barrier. This was due to the stronger interaction between Fe^{δ+}/Ti^{δ+} and the intermediates (*OH and *O) than the other dopants (Figure 6.2), which resulted in a lower barrier for the dissociation of *H₂O and *OH. We noted, among all the systems studied, the most significant structural distortion was observed for Cu-Mo₆S₈ during the *H₂O dissociation, which broke Cu-S bonds, weakens the interaction between Cu and Mo₆S₈, and resulted in the least stable *O adsorption, yet the Mo₆ octahedral core kept its structure intact.

Compared with *OH dissociation on metallic surface, the interaction between M and Mo₆S₈ suppressed this elementary step by 0.67, 0.19, 0.22, and 0.30 eV on Co (110), Fe (110), Cu (111), and Ni (111), respectively.^{206, 207, 211} Overall, the interaction between M

and Mo_6S_8 enhanced the H_2O adsorption, however, the stepwise dissociation was suppressed.

6.3 Conclusion

H₂O adsorbed in Mo top site on bare Mo₆S₈ which was comparably strong with that on MoS₂. H₂O adsorption was enhanced by metal doping except Rh. Mo top site was the active site on K- and Rh-Mo₆S₈ while M top site was the active site on Ti-, Fe-, Co-, Ni-, and Cu-Mo₆S₈. The adsorption energy followed the decreasing order of Ti-Mo₆S₈ (-1.02 eV) > Co-Mo₆S₈ (-0.99 eV) > Ni-Mo₆S₈ (-0.97 eV) > Fe-Mo₆S₈ (-0.92 eV) > K- and Cu-Mo₆S₈ (-0.88 eV) > Mo₆S₈ (-0.83 eV) > Rh-Mo₆S₈ (-0.80 eV).

Compared to the bare Mo₆S₈ cluster, the first hydrogen abstraction was enhanced by all the single metal atom dopants, whereas the second abstraction was mostly suppressed except Ti and Fe. Ti-Mo₆S₈ showed the highest activity toward *H₂O dissociation in our study.

H₂O won the competitive adsorption with CH₄ because of its stronger binding on the same active site. Coking resistance was promoted due to the suppressed complete dissociation of *CH₄ by the dissociation of *H₂O. The initial step for CH₃OH synthesis via SRM could be the dissociation of *H₂O to generate *OH and/or *O species.

7 Methanol Synthesis via SRM on M-Mo₆S₈

7.1 Introduction

As mentioned in Chapter 1, direct conversion of methane to methanol is particularly desirable for the effective utilization of methane and energy-efficient production of methanol. DMTM with oxygen as oxidant was widely evaluated experimentally, especially on Fe- and Cu-based catalyst.^{126, 214-218} Theoretical studies on oxygen-driven partial oxidation of methane to methanol on Fe- and Cu-based catalysts revealed that the CH₃OH synthesis was via two mechanisms, i.e. (1) M=O oxo group, C-H activation by CH₃ radical intermediate followed by C-O bond association between *OH and CH₃ radical;²¹⁹ or (2) C-H bond activation via HO-M-CH₃ intermediate followed by C-O bond association between *OH and *CH₃ adsorbed on the same metal atom.¹³⁷ However, based on the experimental results, partial oxidation of methane by oxygen suffered from a low selectivity to methanol due to the over oxidation of methanol to HCHO or even CO₂.^{123, 140} Using H₂O as a milder oxidant to realize direct steam reforming of methane to methanol, could lead to more promising selectivity to methanol.^{141, 142} Yet, more advanced catalysts have to be developed to achieve a highly efficient DMTM via SRM that meets the industrial requirements. Particularly designed Mo₆S₈-based materials were theoretically proved to be potential catalysts for alcohol synthesis. It would be scientifically interesting and practically rewarding to study the potential of Mo₆S₈-based materials for methanol synthesis via SRM.¹⁶⁴

Based on our understanding on the catalytic behavior of M-Mo₆S₈ (M= K, Ti, Co, Fe, Ni, Cu, Rh) clusters for CH₄ and H₂O dissociation, the initial step for CH₃OH synthesis via SRM was assumed to be H₂O dissociation. In the chapter, the next key elementary step for building the reaction pathway to methanol, i.e. the C-O bond association, on M-Mo₆S₈ will be investigated. M-OH and M=O oxo groups will be considered as the active site for *OH-assisted or *O-assisted CH₄ dissociation and C-O bond association via CH₃ radical or *CH₃ + *H₂O intermediates. Ensemble effect, namely, the direct participation of single metal atoms M, and the confinement effect, namely, the M enabled the closely packed co-adsorption motif to facilitate the difficult C-O bond association and CH₃OH production, will be taken in to account as well during the calculation. Finally, the full reaction pathways on the different M-Mo₆S₈ will be provided and compared with each other so as to find out the most promising Mo₆S₈ catalyst for direct SRM to methanol.

7.2 Results and Discussion

7.2.1 Methanol Synthesis on Mo₆S₈

Figure 7.1. Optimal potential energy diagram and geometries of intermediates and transition states (TS) for the SRM to CH₃OH synthesis on the Mo₆S₈ cluster. The arrow points to the step with the highest energy barrier (Mo: small purple; S: yellow; C: brown; H: white; and O: red).

The preferential H₂O adsorption and dissociation over CH₄ resulted in the formation of *O on Mo₆S₈, which was more favorable than the formation of *OH (Figure 6.2). On the *O-covered Mo₆S₈ cluster, the formed Mo=O oxo group from *H₂O adsorption was too stable to activate CH₄. As shown in Figure 7.1, the direct CH₄ dissociation to CH₃OH (*O + CH₄

→ *CH₃OH) was highly activated ($E_a = 2.22$ eV). By comparison, *OH-assisted CH₄ dissociation (*OH + CH₄ → *CH₃ + *H₂O) was more favorable ($E_a = 1.20$ eV), yet *OH was not as stable as *O on Mo₆S₈.

Figure 7.2. Structure together with the labeled bond lengths for the initial (left) and transition state (right) involved in the direct CH₄ → CH₃OH conversion over the *O-covered Mo₆S₈. (Mo: small purple, S: yellow, C: brown, H: white, O: red.)

Previously, the Cu, Fe=O oxo groups were proposed as the active sites for direct CH₄ → CH₃OH conversion in metal-organic frameworks (MOFs) and zeolites with structural confinement.^{213, 220, 221} As shown in Figure 7.2, the transition structure for CH₄ → CH₃OH conversion on the Mo=O of Mo₆S₈ was similar to that of Fe=O of zeolite.²¹³ However, the rigid octahedral Mo₆ structure hindered the Mo-O interaction and thus the capability in stabilizing the CH₄ and H-O···CH₃ transition state. As a result, the corresponding initial and transition states showed a longer adsorbate-oxo bond and smaller structural changes in CH₄ (Figure 7.2) as compared to that of Fe=O in zeolite.²¹³ The metal-oxo motif was not necessarily the active sites for CH₄ activation, where the fluxionality of the local structure could be important. The overall reaction was hindered by the CH₄ dissociation to the

CH₃OH at *O site, corresponding to the highest barrier of 2.22 eV along the pathway (Figure 7.1).

7.2.2 Methanol Synthesis on Fe-Mo₆S₈

Figure 7.3. Optimal potential energy diagram and geometries intermediates and transition states (TS) for CH₃OH synthesis on the Fe-Mo₆S₈ cluster. The arrow points to the step with the highest energy barrier (Mo: small purple; S: yellow; C: brown; H: white; O: red; and Fe: wine).

On Fe-Mo₆S₈, the dissociated *OH from *H₂O occupied the active Fe sites, which was more favorable than the *O formation (Figure 6.2). The *OH group at the Fe-Mo bridge

site also helped the first C-H bond cleavage of CH₄ via the stabilization of the dissociated *H by the formation of *H₂O at the Mo top site. While the dissociated *CH₃ fragment was strongly adsorbed at the Fe top site (Figure 7.3). The corresponding barrier ($E_a = 0.65$ eV) was only slightly lower than that on bare Fe-Mo₆S₈ ($E_a = 0.71$ eV). Furthermore, the produced *H₂O at the Mo site dissociated to *OH ($E_a = 0.42$ eV), which was much easier than *CH₃ dissociation to *CH₂ ($E_a = 1.83$ eV) and provided the active sites for *CH₃OH formation via the combination with *CH₃. The formation of *CH₃OH via the C-O bond association on Fe-Mo₆S₈ was rate-determining step along the pathway ($E_a = 0.68$ eV). But it was much lower than that on bare Mo₆S₈ due to the promotion of the doped single Fe atom.

We noted that the activation of *CH₄ to *CH₃ was also highly activated on Fe-Mo₆S₈ (TS2, Figure 7.3), which was only 0.03 eV lower in E_a than the most difficult step. Confinement effect and ensemble effect were obvious on Fe-Mo₆S₈. Fe directly participated in the reaction by stabilizing the *CH₃ intermediate while *CH₃ and *OH were closely confined on Fe atom and neighboring Mo atom. Both these effects contributed to the fast C-O bond association on Fe-Mo₆S₈. From the viewpoint of electronic structure, the strong d states of Fe and Mo near the Fermi level contributed to the stabilization of *CH₃ and *OH intermediate. In contrast, the lacking confinement effect in the case of Mo₆S₈ limited the co-adsorption of *O and *CH_x in a neighboring position, and the transition state for C-O bond association involved an unstable CH₃ radical (TS4, Figure 7.1). Thus, a higher barrier and lower activity for CH₃OH production on Mo₆S₈ was observed than that on Fe-Mo₆S₈.

7.2.3 Methanol Synthesis on Co-, Rh-, and Ni-Mo₆S₈

The Co, Rh, or Ni dopants also helped the CH₃OH synthesis. The SRM to CH₃OH over Co-, Rh-, and Ni-Mo₆S₈ clusters followed the same pathway as that on Fe-Mo₆S₈ (Figures 7.4-7.6).

On Ni-Mo₆S₈, *OH-assisted CH₄ dissociation to *CH₃ + *H₂O was active (TS2, Figure 7.4, E_a = 0.38 eV), however, the following *H₂O dissociation was slower (TS3, Figure 7.4, E_a = 1.10 eV). The final C-O bond association between *CH₃ and *OH was promoted by confinement effect and ensemble effect and thus a low energy barrier (TS4, Figure 7.4, E_a = 0.15 eV). The rate-determining step was *H₂O dissociation to *OH, corresponding to the energy barrier of 1.10 eV.

On Co-Mo₆S₈, *OH-assisted CH₄ dissociation (TS2, Figure 7.5, E_a = 1.18eV) was preferred than the formation of CH₃ radical intermediate (E_a = 1.82 eV). Co helped to stabilize *H₂O and *CH₃ by forming Co-C and Co-O bonds which lowered the barrier of *OH-assisted CH₄ dissociation. Meanwhile, *CH₃ and *OH were closely confined on neighboring site. Accordingly, confinement and ensemble effects were dominating. Therefore, C-O bond association between *CH₃ and *OH (TS4, Figure 7.5, E_a = 0.74eV) was faster than *OH-assisted *CH₃ dissociation (E_a = 1.03eV). Thus, CH₃OH formation was strongly preferred. The rate-determining step was *OH-assisted CH₄ dissociation (TS2, Figure 7.5), corresponding to the energy barrier of 1.18 eV. The d states of Co atoms located near fermi level, indicating active Co sites (Figure 4.2). Co atom took part in each step by forming Co-O bonds and Co-C bonds which led to the stabilization of intermediates

and optimized the reaction pathway by lowering the energy barrier for $^*\text{CH}_3$ and $^*\text{OH}$ combination by 0.65 eV with respect to that on bare Mo_6S_8 .

On Rh- Mo_6S_8 , $^*\text{OH}$ -assisted CH_4 dissociation (TS2, Figure 7.6, $E_a = 1.22$ eV) was likely whereas the formation of CH_3 radical intermediate ($E_a = 3.05$ eV) was hindered due to the extremely high energy barrier. C-O bond association between $^*\text{CH}_3$ and $^*\text{OH}$ processed at Rh site with an energy barrier of 0.20 eV (TS4, Figure 7.6). Rh atom optimized the reaction pathway by lowering the barrier of C-O bond association via confinement and ensemble effect, and increasing the stability of reaction intermediates. The rate-determining step is $^*\text{OH}$ -assisted $^*\text{CH}_4$ dissociation (TS2, Figure 7.6), corresponding to the energy barrier of 1.22 eV.

Different from the reaction pathway on Fe- Mo_6S_8 , $^*\text{H}_2\text{O}$ dissociation to $^*\text{OH}$ was the step with the highest barrier on Ni- Mo_6S_8 (TS1, $E_a = 1.10$ eV, Figure 7.4) while it moves to $^*\text{OH}$ -assisted CH_4 dissociation on Co- Mo_6S_8 (TS1, $E_a = 0.99$ eV, Figure 7.5) and Rh- Mo_6S_8 (TS2, $E_a = 1.22$ eV, Figure 7.6). The promotion on the C-O association to $^*\text{CH}_3\text{OH}$, which was demonstrated by the doped single Fe atom (confinement effect and ensemble effect), was also observed for Ni (TS4, $E_a = 0.15$ eV, Figure 7.4), Co (TS4, $E_a = 0.74$ eV, Figure 7.5), and Rh (TS4, $E_a = 0.20$ eV, Figure 7.6).

Figure 7.4. Optimal potential energy diagram and geometries for CH₃OH synthesis on Ni-Mo₆S₈ cluster including reaction intermediates and transition states (TS). The arrow points to the step with the highest energy barrier. (Mo: small purple, S: yellow, C: brown, H: white, O: red, Ni: green).

Figure 7.5. Optimal potential energy diagram and geometries for CH₃OH synthesis on Co-Mo₆S₈ cluster including reaction intermediates and transition states (TS). The arrow points to the step with the highest energy barrier. (Mo: small purple, S: yellow, C: brown, H: white, O: red, Co: dark blue)

Figure 7.6. Optimal potential energy diagram and geometries for CH₃OH synthesis on Rh-Mo₆S₈ cluster including reaction intermediates and transition states (TS). The arrow points to the step with the highest energy barrier. (Mo: small purple, S: yellow, C: brown, H: white, O: red, Rh: grey).

7.2.4 Methanol Synthesis on Ti-, Cu-, and K-Mo₆S₈

The least enhancement in CH₃OH synthesis from the SRM was observed when Ti, Cu, or K atomic atoms were doped on Mo₆S₈. On Ti-, Cu-, or K-Mo₆S₈, the CH₄ was activated via the *O species from H₂O (Figures 7.7-7.9) as that of Mo₆S₈. Although for M = Ti, Cu, K the formation of *OH was more favorable than *O (Figure 6.2), the CH₄ dissociation on *OH to *CH₃ + *H₂O or *CH₃OH + *H was more difficult than the *OH dissociation to *O (1.73 eV vs. 1.82 eV for Cu-Mo₆S₈, 1.74 eV vs. 2.05 eV for K-Mo₆S₈, and 1.03 eV vs. 2.49 eV for Ti-Mo₆S₈). The most difficult step toward the CH₃OH synthesis varied from the *CH₃O hydrogenation to *CH₃OH by doping Ti (TS4, E_a = 1.79 eV, Figure 7.7) to the *O

formation from *OH dissociation by doping Cu (TS2, $E_a = 1.73$ eV, Figure 7.8) and K (TS2, $E_a = 1.74$ eV, Figure 7.9). Besides, other steps were also involved, which corresponded to a barrier slightly lower than the highest, typically involved *CH₄ oxidation by *O to *CH₃O or *CH₃OH (TS3, Figures 7.7-7.9).

Nevertheless, one could see that for Ti-, Cu-, and K-Mo₆S₈, the conversion must overcome several steps with very high energy barriers (>1.70 eV) and thus, a lower activity toward the SRM than Fe-, Co-, and Rh-Mo₆S₈ was observed. Similar to Fe-, Co-, Rh-, and Ni-Mo₆S₈, the site confinement effect to promote the C-O bond association was also observed on the single atom Ti sample (TS3, $E_a = 1.54$ eV, Figure 7.7), while it was not obvious for the less active Cu- (TS3, $E_a = 1.22$ eV, Figure 7.8) and K-Mo₆S₈ (TS3, $E_a = 1.53$ eV, Figure 7.9). On the latter two clusters, the CH₄ approached to the *O site from the gas phase and the C-O bond association occurred via a transition involving an unstable CH₃ radical.

Figure 7.7. Optimal potential energy diagram and geometries for CH₃OH synthesis on Ti-Mo₆S₈ cluster including reaction intermediates and transition states (TS). The arrow points to the step with the highest energy barrier. (Mo: small purple, S: yellow, C: brown, H: white, O: red, Ti: light blue).

Figure 7.8. Optimal potential energy diagram and geometries for CH₃OH synthesis on Cu-Mo₆S₈ cluster including reaction intermediates and transition states (TS). The arrow points to the step with the highest energy barrier. (Mo: small purple, S: yellow, C: brown, H: white, O: red, Cu: orange).

Figure 7.9. Optimal potential energy diagram and geometries for CH₃OH synthesis on K-Mo₆S₈ cluster including reaction intermediates and transition states (TS). The arrow points to the step with the highest energy barrier. (Mo: small purple, S: yellow, C: brown, H: white, O: red, K: big purple).

7.3 Quantitive Study of Activity Toward Methanol Synthesis

To quantify the activity, the CH₃OH synthesis from the SRM on M-Mo₆S₈ clusters was

estimated with respect to Mo₆S₈ via the Arrhenius equation, $e(-\frac{E_a^{\text{Max}} - E_a^{\text{Max, Mo}_6\text{S}_8}}{RT})$, where E_a^{Max}

represented the highest barrier along the optimized reaction pathway and the temperature

T was 525 K in our cases (Figure 7.10). One could clearly see that the Fe was more effective

than the other dopants. The corresponding reaction rate was $\sim 10^{14}$ times faster than that of

Mo₆S₈, which was also higher than the extensively studied FeO⁺-based catalyst.²⁰⁴ Fe-

Mo₆S₈ could be a promising catalyst for CH₃OH synthesis via SRM. As for the relative

reaction rate on Co-, Rh-, and Ni-Mo₆S₈, the enhancement was not as significant as that of Fe by a factor $\sim 10^5$ on Ni-, Co-, and Rh-Mo₆S₈ in terms of the reaction rate while Cu-, Ti-, and K-Mo₆S₈, which were lower than that of Fe by a factor $\sim 10^{10}$.

Figure 7.10. The variation in relative rate for the SRM to CH₃OH over M-Mo₆S₈ clusters with the corresponding *OH adsorption energy.

Overall, the CH₄ → CH₃OH conversion on the Mo₆S₈ and M-Mo₆S₈ clusters via the SRM reaction, specifically the elementary step with the highest barrier and thus the overall rate, was likely to be strongly affected by the binding of *OH or *O from H₂O dissociation. To activate water, *OH should be strongly bound. Once the hydroxylated clusters (Fe-, Co-, Rh-, and Ni-Mo₆S₈) were formed, the activation of CH₄ was likely controlled by the step involving *OH as the reactant. Wherein, *OH could either assist the *CH₄ → *CH₃ dissociation by stabilizing the dissociated *H in the form of water or participating directly to oxidize *CH₃ and forming *CH₃OH via the C-O bond association.

Similarly, for the oxidized Mo₆S₈ and Ti-Mo₆S₈, where the oxidation steps involving *O were always highly activated. For the oxidized Cu- and K-Mo₆S₈ clusters, though, the CH₃OH synthesis could be slowed down by the most difficult *OH dissociation to *O. Thus, the *OH or *O bonding was always involved in the likely rate-determining steps as reactants or products, which could be an effective descriptor to capture the difference in CH₄ → CH₃OH conversion. Indeed, a volcano-like variation between the estimated reaction rate and the *OH adsorption energy was observed (Figure 7.10). A similar trend was also observed when using the *O binding as the descriptor, as the stability of *O and *OH was correlated (Figure 6.2).

A good single-atom promoter to the SRM should provide a moderate *OH binding, being strong enough to allow the adsorption and dissociation of H₂O, but weakly enough to enable the oxidation of CH₄ and facial removal of CH₃OH from the Mo₆S₈ cluster. The dopant like Ti was too active for stabilization of *OH or *O, which hindered the CH₄ oxidation, while the dopant like Cu was too inert, which couldn't catalyze the H₂O dissociation well. The single-metal-Fe dopant was the best among the systems studied. It optimized the reaction pathway via the ensemble effect and confinement effect. Compared to Mo₆S₈, the ensemble effect introduced by the doped single-atom Fe, together with the synergy with the neighboring Mo, enhanced the H₂O and CH₄ dissociation via the formation of Fe-OH and Fe-CH₃ bonds. In addition, the introduced confinement effect enabled the formation of closely packed *CH₃ and *OH over the active single-atom Fe, which enabled the stabilization of the transition state and thus facilitated the difficult C-O

bond association to produce CH_3OH . By contrast, the contribution from the ligand effect was rather small.

7.4 Conclusion

The reaction pathway to CH_3OH was investigated on bare Mo_6S_8 and single metal atom doped $\text{M-Mo}_6\text{S}_8$ ($\text{M} = \text{K}, \text{Ti}, \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}, \text{Rh}$). All doped single-atoms M showed enhancement in CH_3OH synthesis during the methanol synthesis via SRM process. The promoting effect of Fe was the most significant, which was followed by Ni , Co , Rh , Cu , K , Ti in a decreasing sequence. Under the SRM condition, the active Mo or M sites were likely to be occupied by $^*\text{H}_2\text{O}$, which resulted in the formation of oxidized or hydroxylated clusters. The binding of $^*\text{OH}$ was identified as the descriptor for the overall activities. Ensemble effect and confinement effect as well as the strong d states of single metal atom near Fermi level were dominating, especially in promoting the C-O bond association between $^*\text{CH}_3$ and $^*\text{OH}$. The best single-atom dopant, e.g., Fe , could not only facilitate $^*\text{H}_2\text{O}$ dissociation, provide active $^*\text{OH}$ or $^*\text{O}$ species, but also enable the facile association of the $^*\text{CH}_3$ and $^*\text{OH}$ fragments to produce CH_3OH .

8 Summary and Conclusion

In this thesis, the potential of a series of single metal atom (K, Ti, Co, Fe, Ni, Cu, Rh) doped Mo_6S_8 clusters for steam reforming of methane to methanol was evaluated using DFT calculation. In terms of the computational methods, by comparing the Mo_6S_8 optimization results using PBE and PW91 functionals for describing the exchange and correlation energy, PBE functional gave the more accurate results of Mo_6S_8 structure and was thus employed in this work. (Chapter 3)

All the M- Mo_6S_8 (M= K, Ti, Co, Fe, Ni, Cu, Rh) showed a good stability and high resistance to oxidation at the presence of H_2O . Electron transfer between M and Mo atoms were observed from PDOS results. The d states of M and Mo near Fermi level was important for high activity toward CH_4 and H_2O dissociation and CH_3OH synthesis (Chapter 4).

CH_4 adsorption and dissociation on these M- Mo_6S_8 were studied in Chapter 5. The M top site was the preferred adsorption site for CH_4 on Ni-, Co-, Fe-, Cu-, and Ti- Mo_6S_8 , while Mo top site was more favorable on bare Mo_6S_8 , K- and Rh- Mo_6S_8 . The ensemble effect on Co, Ni, Cu, Fe, Ti doped Mo_6S_8 played a dominating role in strengthening the adsorption of CH_4 . In contrast, the ligand effect weakened the CH_4 adsorption on Mo top site of K- and Rh- Mo_6S_8 . The interaction between M and Mo_6S_8 enhanced $^*\text{CH}_4$ activation but suppressed the dissociation of $^*\text{CH}_3$ which could be beneficial for the direct CH_3OH synthesis and hindering the undesired formation syngas and cokes.

For the H₂O adsorption (chapter 6), H₂O shared the same active site with CH₄. Thus, competitive adsorption between H₂O and CH₄ was likely. H₂O won the competitive adsorption with CH₄ because of its stronger binding on the same active site. Coking resistance was promoted due to the suppressed *CH₄ dissociation by the *H₂O dissociation. Compared to bare Mo₆S₈ cluster, the first hydrogen abstraction was enhanced by all the single metal atom dopants, whereas the second abstraction was suppressed except Ti and Fe. Both the M-O and M-OH group could work as the active site for CH₄ activation and C-O bond association. The initial step for CH₃OH synthesis via SRM was the dissociation of *H₂O to generate *OH and/or *O species.

In chapter 7, the reaction pathway to CH₃OH was explored on bare Mo₆S₈ and single metal atom doped M-Mo₆S₈ (M = K, Ti, Fe, Co, Ni, Cu, Rh). All doped single-atoms M showed enhancement in CH₃OH synthesis during the SRM process. The promoting effect of Fe was the most significant, which was followed by Ni, Co Rh, Cu, K, Ti in a decreasing sequence. Methanol synthesis via SRM on Fe-Mo₆S₈ was initiated with H₂O adsorption on Fe atom and *H₂O dissociation to *OH on Fe-Mo bridge site. CH₄ was activated by *OH-assisted CH₄ dissociation to *CH₃ and *H₂O adsorbed on Fe and Mo top site, respectively, follow by *H₂O dissociation to *OH. The C-O bond association between *CH₃ and *OH to target product CH₃OH was confined on neighboring Fe and Mo site. Ensemble effect and confinement effect as well as the strong d states of single metal atom near Fermi level were dominating, especially in promoting the C-O bond association between *CH₃ and *OH. The best single-atom dopant, e.g., Fe, could not only facilitate *H₂O dissociation,

provide active $^*\text{OH}$ or $^*\text{O}$ species, but also enable the facile association of the $^*\text{CH}_3$ and $^*\text{OH}$ fragments to produce CH_3OH .

Co-, Ni-, and Rh- Mo_6S_8 shared the same reaction pathways with Fe- Mo_6S_8 , however, their promotion was less obvious than Fe. On Mo_6S_8 , K-, Ti-, and Cu- Mo_6S_8 , H_2O completely dissociated to $^*\text{O}$, forming Mo=O oxo active site for CH_4 activation. However, the CH_4 activation via $^*\text{CH}_3$ radical intermediate was energetically uphill, indicating the lower activity.

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