

Nature of the active sites confined in Mo/ZSM-5 zeolite for methane dehydroaromatization reaction

Guanna Li,^{a,b,*} Ina Vollmer,^a Nikolay Kosinov,^b Ágnes Szécsényi,^{a,b} Evgeny Pidko,^b Jorge Gascon^a

^a*Catalysis Engineering, Department of Chemical Engineering, Delft University of Technology*

^b*Inorganic Systems Engineering, Department of Chemical Engineering, Delft University of Technology*

*Corresponding author: +31 15 2784358, g.li-2@tudelft.nl

Abstract: Valorization of methane to liquid chemicals is of great importance for natural gas transportation and utilization. One promising strategy is on-site non-oxidative conversion to aromatics. Mo/ZSM-5 zeolite is a representative catalyst for this reaction, however, the structure of the active site and the reaction mechanism are still under debate. In this work, we endeavour to address these crucial questions at atomic level by periodic density functional theory studies. It indicates that mononuclear [MoO]²⁺ species is relevant to methane C-H bond activation and CH₃ radical formation, and radical aggregation to aromatics is initiated by cooperation between Mo⁴⁺-oxo and polyaromatic hydrocarbon species.

Keywords: methane dehydroaromatization, Mo/ZSM-5, DFT.

1. Introduction

The abundant reserves of natural gas, especially with the rapid development of shale gas, are a very strong driving force for the development of efficient methane valorization technologies. The new procedures allowing a direct onsite upgrading of methane to shippable liquid chemicals are mandatory for the valorization of small-scale reservoirs and reservoirs in remote locations, where the indirect methane conversion technologies are very energy and capital consuming, and only suitable for large-scale natural gas fields.¹ In this context, direct non-oxidative conversion of methane to aromatics and hydrogen (methane dehydroaromatization, MDA) is a very attractive alternative from both economic and environmental viewpoints. The valuable products of benzene and hydrogen allow a 100% atomic utilization of both carbon and hydrogen sources.

The most active and selective catalyst for MDA reaction is Mo/HZSM-5 zeolite. Mo/HZSM-5 is the most selective zeolite-based MDA catalyst. However, this catalyst suffers from rapid deactivation due to fast coke formation.² Since the molecular structure of the active sites and the reaction mechanism are poorly understood, it is hence very challenging to optimize and rationally design MDA reaction into industrial scale application. Indeed, currently catalyst design is more art than science. Therefore, the aim of this study is to discover and to understand the most relevant structure-reactivity relationships that govern catalytic performance of Mo/HZSM-5 in the MDA reaction by theoretical methods.

2. Computational details

All calculations were carried out in the framework of periodic DFT using the Vienna Ab initio Simulation Package (VASP).³ The generalized gradient approximation (GGA) Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional was used together with the plane-wave approach to describe valence electrons, while the projected augmented wave (PAW) method accounted for the valence-core interactions. Van der Waals (vdW) interactions were considered by using Grimme's DFT-D3(BJ) method as implemented in VASP. The kinetic energy cut-off of the plane wave basis set was set to 500 eV. A Gaussian smearing of the population of partial occupancies with a width of 0.05 eV was used during iterative diagonalization of the Kohn-Sham Hamiltonian. The threshold for energy convergence for each iteration was 10⁻⁵ eV. Geometries were assumed to be converged when forces on each atom were less than 0.05 eV/Å. Spin-polarized calculations were performed throughout this study. The minimum-energy reaction pathways

and the corresponding transition states were determined using the nudged-elastic band method with the improved tangent estimate (CI-NEB) method.

3. Results and discussion

First of all, the stabilities of both mononuclear ($[\text{MoO}_3\text{H}]^+$, $[\text{MoO}_2]^{2+}$) and binuclear ($[\text{Mo}_2\text{O}_5]^{2+}$) Mo-oxo species, which have been proposed to be the active sites for methane dehydroaromatization, confined in different locations in the channels of ZSM-5 zeolite are evaluated. Monovalent cation and bivalent cations are stabilized by one or two $[\text{AlO}_2]^-$ framework units, respectively. DFT results show that, there is no distribution preference in the channel of zeolite for monovalent $[\text{MoO}_3\text{H}]^+$ species. The location only depends on the framework Al distributions. This is reasonable since $[\text{MoO}_3\text{H}]^+$ species only need one charge compensating $[\text{AlO}_2]^-$ nearby. However, the 6-membered ring containing two symmetric Al sites in the intersection of straight and zigzag channels is the most favorable location for stabilize bivalent species of $[\text{MoO}_2]^{2+}$ and $[\text{Mo}_2\text{O}_5]^{2+}$, compared to other locations such as 10-membered ring and double 5-membered ring in the straight channel, or 8-membered ring in the zigzag channel.⁴ Furthermore, the 6-membered ring position is also featured by the spacious void for accommodating aromatic intermediates during the methane dehydroaromatization reaction.

Since the locations of the Mo-oxo species are known, we evaluate the reactivity of these species towards the methane C-H bond activation, which is the first step, and probably the most difficult step, for dehydrogenation reaction to aromatics and hydrogen. The structural evolution of these Mo-oxo active sites to Molybdenum carbides/oxocarbides (induction period) by carburization at the beginning of the methane activation reaction is investigated. The plausible reaction pathways to produce reaction intermediates such as ethylene, ethane, water, and hydrogen are also explored. The results demonstrated that, the C-H bond can be activated and methane is dehydrogenated over $[\text{MoO}_2]^{2+}$ active site to form $[\text{O-Mo-CH}_2]^{2+}$ species and release water, or to form hydrogen, CO, and $[\text{MoO}]^{2+}$. An alternative pathway to $[\text{MoO}]^{2+}$ is to produce ethane and water, which shows the lowest reaction energy profile compared to the others. For the plausible pathways investigated, it is found that mononuclear Molybdenum carbides (such as MoC, or MoC_2) are energetically less stable than $[\text{MoO}]^{2+}$. Therefore, it is proposed that during early induction period, the active site of $[\text{MoO}_2]^{2+}$ is partially reduced into $[\text{MoO}]^{2+}$, and it plays as the true active site for further methane activation to aromatics. The presence of tetravalent Molybdenum $[\text{MoO}]^{2+}$ species is further confirmed by FTIR spectrum and Bader charge analysis. Once $[\text{MoO}]^{2+}$ is formed, it can further activate methane and produce CH_3 radicals. The aggregation of these CH_3 radicals gradually form aromatics by the cooperation effect between partially reduce $[\text{MoO}]^{2+}$ and the polyaromatic carbon species⁵ confined in the zeolitic channels.

4. Conclusions

In this work, the structure, location, and reactivity of molybdenum species confined in ZSM-5 channels are studied in detail by DFT method. It is found that mononuclear molybdenum-oxo species is active for C-H bond activation. It is partially reduced during the induction period to form tetravalent $[\text{MoO}]^{2+}$ species, which is responsible for consecutive methane activation to CH_3 radicals. The so-formed CH_3 radicals further aggregate to produce aromatic products by synergetic effect between $[\text{MoO}]^{2+}$ and the confined polyaromatic carbon species inside ZSM-5 zeolite.

References

1. P. Schwach, X. Pan, X. Bao, Chem. Rev. 117 (2017) 8497-8520.
2. N. Kosinov, F. Coumans, E. Uslamin, F. Kapteijn, E.J.M. Hensen, Angew. Chem. Int. Ed. 55 (2016) 15086-15090.
3. G. Kresse, D. Joubert, Phys. Rev. B 59 (1999) 1758-1775.
4. I. Vollmer, G. Li, I. Yarulina, N. Kosinov, E.J.M. Hensen, K. Houben, D. Mance, M. Baldus, J. Gascon, F. Kapteijn, Catal. Sci. Technol. (2018) 10.1039/C7CY01789H.
5. N. Kosinov, A.S.G. Wijkema, E. Uslamin, R. Rohling, F.J.A.G. Coumans, B. Mezari, A. Parastaev, A.S. Poryvaev, M.V. Fedin, E.A. Pidko, E.J.M. Hensen, Angew. Chem. Int. Ed. (2018) 10.1002/anie.201711098