Investigation of Methane Aromatization over Mo/ZSM-5 Catalysts with DFT Calculations and *Operando* Molecular Spectroscopy

Jie Gao[1], Jih-Mirn Jehng[2, 3], George B. Fitzgerald[4], Israel E. Wachs[2*], Simon G. Podkolzin[1*]

[1]*Department of Chemical Engineering and Materials Science*
Stevens Institute of Technology, Hoboken, New Jersey 07030 USA

[2]*Operando Molecular Spectroscopy & Catalysis Laboratory,*
Department of Chemical Engineering, Lehigh University, Bethlehem, Pennsylvania 18015 USA

[3]*Department of Chemical Engineering,*
National Chung Hsing University, Taichung 402, Taiwan, R.O.C.

[4]*Accelrys,10188 Telesis Court, San Diego, CA 92121 USA*

*iew0@Lehigh.edu; *Simon.Podkolzin@Stevens.edu

Introduction

Methane conversion into valuable aromatic products represents a highly desirable route for conversion of natural gas into liquid fuels or chemical feedstocks. The Mo/ZSM-5 system has been found to catalyze methane dehydroaromatization to benzene [1]. The nature of Mo species present in this catalytic system and their catalytic properties have been the focus of many publications [2]. Contradictory conclusions, however, have appeared in the literature about the nature of molybdenum oxide species after calcination (initial state of the catalyst) and during catalyst operation (reduced state). An *operando* molecular spectroscopic approach, which involves simultaneous catalyst molecular spectroscopic characterization under reaction conditions and online reaction product analysis, was undertaken for the first time in order to elucidate the structure of molybdenum active sites.

Materials and Methods

Mo/ZSM-5 catalysts with variable Si/Al atomic ratios (15-140) and variable Mo loadings (1-5 wt %) were prepared by incipient wetness impregnation with aqueous Mo heptamolybdate. The catalysts were tested for methane activation (flow of 1.5 mol % CH_4 in He) by simultaneously collecting *operando* Raman spectra and online mass spectra of reaction gases. In addition, UV-vis diffuse reflectance spectra of Mo/ZSM-5 were compared to those of multiple Mo reference compounds. Gradient-corrected DFT calculations were performed with the DMol3 code in Materials Studio by Accelrys using the double numerical with polarization (DNP) basis set and the generalized gradient-corrected revised Perdew-Burke-Ernzerhof (GGA RPBE) functional.

Results and Discussion

A linear inverse correlation was established between the UV-vis edge energy and the number of bridging Mo-O-Mo covalent bonds around the central Mo cation for multiple Mo reference compounds [3]. A comparison with this correlation trend demonstrates that Mo in ZSM-5 is present in the form of atomically dispersed Mo oxide species. The absence of sharp Raman bands from crystalline MoO_3 (820 cm^{-1}) or $Al_2(MoO_4)_3$ (1004 and 1026 cm^{-1}) nanoparticles in Figure 1 indicates, in agreement with the UV-vis results, that the dehydrated supported molybdenum oxide phase is 100% dispersed on the ZSM-5 support since any amorphous Mo oxide phases would be crystallized at the elevated pretreatment temperatures. The initial Mo oxide species with the characteristic Raman bands at 975 and 994-997 cm^{-1} transform into Mo carbide species under reaction conditions, but can be fully recovered on catalyst regeneration with gas-phase oxygen, as shown in Figure 1. An analysis of *operando* Raman spectra with DFT calculations suggests Mo preferentially binds to an Al site inside ZSM-5 pores and forms the dioxo $MoO_2(O_2)$ structure in Figure 2 with two terminal Mo=O bonds and two bridging Mo-O-Al bonds. This $MoO_2(O_2)$ structure on a single framework Al was observed for all investigated catalysts (peak at 975 cm^{-1} in Figure 1). For catalysts with a high Al content (Al/Mo > 4), another dioxo $MoO_2(O_2)$ structure was observed where Mo atom is bound simultaneously to 2 framework Al atoms across a zeolite ring (peak at 997 cm^{-1} in Figure 1). For catalysts with a low Al content, dioxo MoO_4 and mono-oxo MoO_5 species were identified on the outer surface of the zeolite. The activity of Mo oxide species bound to Si only was found to be significantly lower than that of Mo oxide bound to Al or Si-Al.

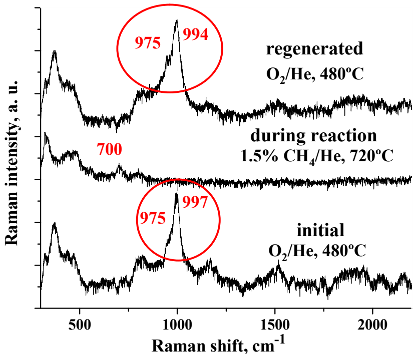

Figure 1. *Operando* Raman spectra (442 nm excitation) for 3 wt % Mo/ZSM (Si/Al=15).

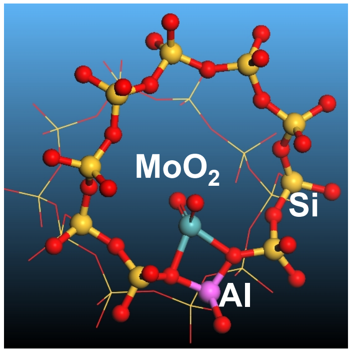

Figure 2. DFT model of *isolated* dioxo $MoO_2(O_2)$ species bound to framework Al in ZSM-5 with ν_s(O=Mo=O) of 975 cm^{-1}.

Significance

The initial structure of the molybdenum active site in Mo/ZSM-5 catalysts for the conversion of methane to benzene has been identified as *isolated* Mo oxide surface species by closely integrating experimental *operando* Raman and UV-vis spectroscopies with DFT calculations. The initial surface Mo oxide species transform into Mo carbide species under reaction conditions, but can be fully recovered on catalyst regeneration with gas-phase oxygen.

References

1. Wang, L., Tao, L., Xie, M., Xu, G., Huang, J. Xu, Y. *Catal. Lett.* 21, 35 (1993).
2. Ismagilov, Z.R., Matus, E.V, Tsikoza, L.T. *Energy Environ. Sci.* 1, 526 (2008).
3. Tian, H., Roberts, C.A., Wachs, I.E. *J. Phys. Chem. C* 114, 14110 (2010).