

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

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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.

Experimental

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 % CH₄ in He at atmospheric pressure) by simultaneously collecting *operando* Raman spectra and online mass spectra of reaction gases at 480-760°C. Regeneration was performed in flow of 5 mol % O₂ in He at 480°C. 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. Experimental Raman bands were interpreted based on the vibrational frequencies obtained with DFT models.

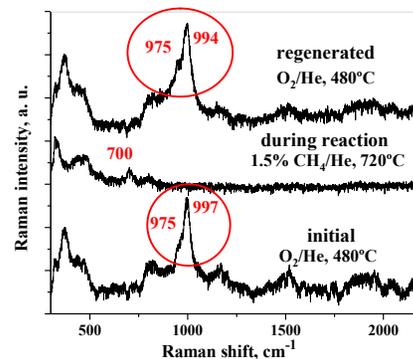


Figure 1. *Operando* Raman spectra (442 nm excitation) for 3 wt % Mo/ZSM-5 (Si/Al=15).

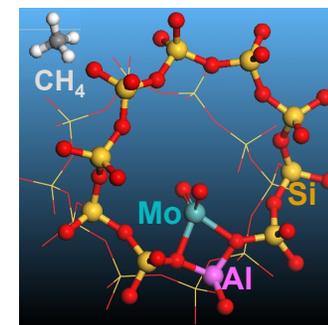


Figure 2. DFT model of *isolated* dioxo MoO₂(O₂) species bound to framework Al in ZSM-5 with $\nu_s(\text{O}=\text{Mo}=\text{O})$ of 975 cm⁻¹.

Results/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 species. The absence of sharp Raman bands from crystalline MoO₃ (820 cm⁻¹) or Al₂(MoO₄)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 crystallize 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 that Mo preferentially binds to a framework Al site and forms the dioxo MoO₂(O₂) structure in Figure 2 with two terminal Mo=O bonds and two bridging Mo-O-Al bonds. This MoO₂(O₂) 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 MoO₂(O₂) 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 MoO₄ and mono-oxo MoO₃ 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.

References.

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