

Synthesis, Structure, and Catalytic Function of Anchored Metal-Oxo Species within Small-Pore Zeolites

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The challenges of characterizing the structure and function of highly dispersed and non-uniform inorganic structures useful as catalysts has led to a need for synthetic protocols to produce single-site catalysts with uniform structures. The regular channel structure of zeolites and their ability to anchor metal-oxo species at exchange sites make them ideally suited as scaffolds for isolated metal-oxo species and open possibilities for selectivity control via spatial constraints at the nanometer scale. The encapsulation of these active structures leads them to select reactants based on their ability to reach them, to prefer transition states stabilized by outer-sphere modifications induced by zeolite channels and cages, and to allow the preferential diffusion of some of the products and control the extent of their secondary reactions.

Our previous studies have addressed the exchange of high valent metal-oxo species via vapor phase precursors into medium-pore H-ZSM5[1-2]. These materials contain two intersecting ten-membered ring channel structures (~5.5 Å diameter). Here, we report the first demonstrated synthesis of high-valent metal-oxo species into a material containing an eight-membered ring channel system (H-FER). In doing so, we provide potential opportunities for shape selectivity for smaller molecules, for protection of active sites against larger toxic impurities, and for the elucidation of the effects of channel size on the structure of the exchanged species and on their reactivity and selectivity for non-oxidative conversion of methane to higher molecular weight hydrocarbons.

Mo/H-FER (Mo/Al = 0.13-0.93) was prepared by thermal treatment of intimate physical mixtures of MoO₃ and H-FER (Si/Al = 9.55). Thermal treatment of these mixtures in 20%O₂/He led to MoO₃ sublimation, diffusion of Mo₂O₆(g) dimers into channels, and reaction with OH groups to form H₂O. The amount of H₂O evolved during synthesis (measured by mass spectrometry of effluent) corresponds to the titration of 1 H per Mo for Mo/Al_f ratios below 0.5. Treatment with a 5% D₂/Ar mixture up to 673 K led to D₂ reactions with OH; the number of HD and H₂ evolved corresponds to a slightly higher exchange stoichiometry (1.2 H/Mo) than H₂O evolution measurements. These two results taken together with the number of residual OH groups measured from infrared spectra led to an average exchange stoichiometry of 1.1 ± 0.1 protons removed per Mo for Mo/Al below 0.50 (Figure 1). This stoichiometry is consistent with the formation of Mo₂O₅²⁺ dimers, but excludes the possibility of MoO₂²⁺ dimers also interaction with two Al sites (Figure 1 insert), for which a stoichiometry of 2 OH groups per Al would be expected. Statistical studies of the distribution of Al atoms in FER (Si/Al = 11) suggest a maximum loading of ~0.55 Mo/Al for these dimer structures, also consistent with near constant values of ΔH/Mo in materials with Mo/Al ratios above 0.5 (Figure 1).

The structure and oxidation state of Mo-containing species in H-were monitored by X-ray absorption spectroscopy (XAS) during thermal treatments leading to exchange and during CH₄ reactions that lead to the in situ formation of active Mo carbide clusters. Studies of these materials showed that initial spectra before thermal treatment at 973 K corresponded to the crystalline MoO₃ introduced into the physical mixture. The spectra evolved during treatment

into one corresponding to a ditetrahedral structure similar to that for MgMo₂O₇ (Figure 1 insert). Mo atoms retained their +6 oxidation state during synthesis, as indicated by the invariant edge energy evident from these spectra (~20.006 keV). Pre-edge features in the near-edge spectra indicate that Mo coordination changed from distorted octahedral to ditetrahedral during thermal treatment, coincident with H₂O evolution detected by mass spectrometry. Contact with CH₄ streams at ~1000 K during catalytic pyrolysis reaction, led to the removal of oxygen and to the introduction of carbon into Mo-containing species. As in the case of previous studies for H-ZSM5, Mo-oxo dimers formed MoC_x active sites for CH₄ pyrolysis. The removal of oxygen (as CO, CO₂, and H₂O measured by mass spectrometry) coincided with edge energy shifts consistent with reduction and carburization of Mo⁶⁺ and with the detection of catalytic conversion of CH₄ to C₂-C₁₀ hydrocarbons. The amount of oxygen removed was 2.6 ± 0.1 O atoms for samples with Mo/Al_f < 0.5, consistent with the presence of Mo₂O₅²⁺ dimers after thermal treatment. Fine structure analysis of the X-ray absorption spectra are consistent with the initial presence of Mo-oxo dimers and with their conversion to MoC_x clusters ~0.6 nm in diameter during catalytic reactions of methane at 1000 K.

The activation of Mo-oxo species in H-FER (Mo/Al = 0.4) were also examined in the presence of CH₄ and H₂/CH₄ (0.1) mixtures (950 K, 18 kPa CH₄) by time-resolved analysis of the effluent by mass spectrometry. The induction period for Mo/H-FER samples, during which MoC_x species form by stoichiometric reactions of CH₄, was longer than for Mo-oxo species in Mo/H-ZSM5, but trends in H₂, CO, and H₂O evolution rates were similar. At steady-state, hydrocarbon formation rates were about four times lower than on Mo/H-ZSM5. The ethylene to benzene molar ratio in FER samples was 1.1 and 0.67, with and without additional H₂, as compared to 0.57 and 0.14 in H-ZSM5. Naphthalene was not observed on Mo/H-FER. Taken together with the higher ethene/benzene ratio on Mo/H-FER indicates that H-FER channels provide more stringent spatial constraints on the growth of hydrocarbon chains than the larger channels prevalent in H-ZSM5.

Sublimation of VOCl₃ precursors into H-FER led to materials with V/Al ratios of 0.11 and 0.33. Infrared detection of zeolite acidic hydroxyl groups and isotopic exchange of D₂ with OH groups showed that 1.2 ± 0.1 zeolitic protons were replaced by each VOCl₂²⁺ species. These results are consistent with Raman and X-ray absorption spectra, which indicate the predominant presence of VO₂⁺ monomers, as previously found also for VO_x-H-ZSM5 [2].

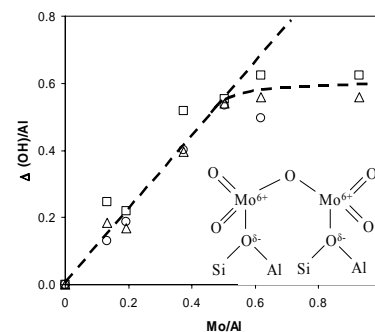


Figure 1. Change in Zeolite OH groups per aluminum plotted against Mo/Al ratio as measured by H₂O evolution (Δ), D₂-OH exchange (□) and infrared spectroscopy (○). The slope of the linear curve (Mo/Al < 0.55) is 1.1 ± 0.1 H/Mo. (insert) Proposed MoO_x structure.

References

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2. Lacheen, H. S.; Iglesia, E. *J. Phys. Chem. B* 110, 5462 (2006).