325d Dynamic Electronic and Molecular States of Surface Mo Species in Mo/Hzsm5 Catalyst: in Situ Uv Raman and Uv-Vis Drs Spectroscopy Studies during Ch4 Aromatization

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Introduction The non–oxidative aromatization of methane remains a potential route to convert natural gas to both aromatics and hydrogen. Mo/HZSM5 was extensively investigated for this application because of its high activity/selectivity to benzene at 973 K. Recently, Iglesia et al. proposed that unique Mo2O52+ dimeric dioxo species form in supported Mo/HZSM5 during preparation that are converted to MoCx species, while regenerating the bridging hydroxyls, during CH4 aromatization. The objective of this investiagtion is to characterize the various Mo species present in the supported Mo/HZSM5 catalyst as a function of synthesis and reaction conditions to be able to establish electronic/molecular structure-activity/selectivity relationships on a molecular level. Both in situ UV Raman and UV-Vis DRS characterization studies were performed under all the different catalytic reaction conditions to obtain the desired molecular level electronic and molecular structural insights.

Experimental The 2% Mo/HZSM5 catalysts were prepared by incipient wetness impregnation of commercial HZSM5 with different SiO2/Al2O3 ratios (30, 50, 80 and 280) with an aqueous solution of (NH4)6[Mo7O24].4H2O followed by drying at room temperature. After drying, the samples were calcined in air at 773K for 6h. The UV-Vis spectra were recorded between 200- 800 nm on an UV-Vis NIR spectrometer (Varian Cary 5E) that was equipped with an integrating sphere (Harrick) using HZSM5 as reference. UV Raman spectra were collected in the range of 300-3000 cm-1 on a Jobin Yvon LabRam HR/notch filter/CCD system with UV laser excitation (325 nm). The scattered light was directed into a spectrometer with a notch filter UV sensitive CCD detector (Jobin Yvon CCD 3000V). A high temperature Linkam cell (TMS 1500) was used to control the reaction temperature and the reaction conditions.

Results and Discussion The UV-Vis DRS absorption edge energy (Eg) values of reference bulk molybdates (possessing MoO4 or MoO6 coordinated monomers and dimers, linear chains of alternating MoO4/MoO6 units, [Mo7O24]6- and [Mo8O26]4- clusters composed of MoO6 units, MoO5 units in XMo12O40 Keggin/Anderson clusters (where X=Al, Si, P) and infinite 3D coordinated MoO6 structures in alpha-MoO3) were determined to establish a correlation between the MoOx band gap and the domain size of the MoOx species. The MoOx band gap was found to be independent of the nearest neighbor cations (Al, Fe, Mg, K, Na, Co Ni, etc.) and only dependent on the local Mo(VI) domain size. For the bulk Mo(VI) compounds, Eg varies inversely to the number of nearest bridging Mo-O-Mo bonds. This fundamental relationship was applied to determine the local Mo (VI) domain size for different catalytic samples and reaction environments. The edge energies of 2% Mo/HZSM5 catalysts under dehydrated conditions were found to increase with the Si/Al ratios, which indicate that the supported MoOx species were present as isolated MoOx species on the HZSM5 supports. These results are consistent with the absence of bridging Mo-O-Mo bands in the 500-750 cm-1 range of the UV Raman spectra. Thus, dimeric dioxo (Mo2O5)2+ species were not found to be present on the HZSM5 support and, consequently, the resulting catalytic activity and selectivity are only due to the presence of isolated surface MoO4 species in the HZSM5 support. Two kinds of surface MoO4 species were detected in 2% MoOx/ZSM5 catalysts with various SiO2/Al2O3 ratios, which are interacting with Al and Si atoms respectively. Furthermore, the appearance of crystalline Al2(MoO3)4 is detected by UV Raman during high calcination temperature and HZSM5 possessing high Si/Al ratios. Thus, the strong interaction of Mo-Al atoms can extract the Al atoms from zeolite framework, which is consistent with previous solid state Al MAS-NMR studies.

In situ UV Raman of 2% Mo/ HZSM5, the HZSM5 support, 2% MoO2/Al2O3 and 2% MoO3/Al2O3, as well as 2% MoO3/10%Al2O3/SiO2 during methane aromatization were investigated from room temperature to 700 C. The absence of carbon deposits on HZSM5 and 2% MoOx/SiO2 indicates that the acidic active sites present in HZSM5 and the MoOx-Si species can't activate methane C-H bond, and that CH4 activation is ONLY achieved in the presence of surface MoOx-Al species, which suggest that MoOx- Al is the catalytic active site for CH4 aromatization reaction to benzene.