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CATALYTIC HYDROCARBON REACTIONS OVER SUPPORTED METALS

Progress Report

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INTRODUCTION

This research program is directed toward developing a fundamental understanding of how catalyst composition, redox ability, and structure control the catalytic properties of metal oxides. Molybdenum and tungsten oxide systems that permit examination of the role of metal oxide cations separately and in pairwise combinations are being developed. The research involves characterization of the organometallic deposition process used to prepare the catalysts, characterization of the resulting oxides using spectroscopic techniques, studies of the catalytic properties of the fully oxidized cations in oxidation reactions, studies of the photoreduction of the oxides to lower oxidation states, and studies of the catalytic properties of coordinatively unsaturated sites resulting either from photoreduction or precursor decomposition in olefin metathesis and reductive aldehyde coupling reactions.

RESEARCH HIGHLIGHTS

During the past year we have completed our characterization of the factors that control the structure of fully oxidized W and Mo on silica and have established that support hydroxyl groups play a central role in dispersing and attaching cations to the support oxide. Our work with the $M_2(CO)_4Cp_2$ ($M_2=MoMo, WW, MoW$) system has been very encouraging and continues to support the notion that it may be possible to control the structure of adsorbed catalysts (in this case generate metal dimers) by use of organometallic precursors. Finally, we are developing the techniques necessary to employ XPS as a means to characterize the attachment process and the oxidation state of the cations after various thermal and photolytic reduction steps.

SUMMARY THE EFFORT

The abstracts are listed below for the papers that appeared in print or are in press.

R. D. Roark, S. D. Kohler, and J. G. Ekerdt, Role of Silanol Groups in Dispersing Mo(VI) on Silica, *Catal. Lett.* 16 (1992) 71.

Infrared spectroscopy was used to follow the intensity of the isolated silanol stretching mode during the reversible transformation of supported molybdenum between the hydrated, polymolybdate structure and the dehydrated, isolated Mo^{6+} structure. The isolated silanol absorbance intensity was attenuated upon dehydration and spreading of Mo^{6+} . The Si-OH (or Si-OD) silanol band was regenerated by rehydration with H_2O (or D_2O). A model for spreading is proposed in which the surface silanol groups are the sites for attachment of the isolated Mo^{6+} cation.

R. D. Roark, S. D. Kohler, J. G. Ekerdt, D. S. Kim, and I. E. Wachs, Monolayer Dispersion of Molybdenum on Silica, *Catal. Lett.* 16 (1992) 77.

Laser Raman spectroscopy was used to characterize the hydrated and dehydrated states of surface-supported Mo^{6+} on Davison 952 silica gel. Silica-supported Mo samples were prepared from $Mo_2(\eta^3-C_3H_5)_4$ and $(\eta^5-C_5H_5)_2Mo_2(CO)_4$. Metal loadings of 5.1-7.8 wt % Mo were studied. Crystallites of MoO_3 were not observed at these high loadings. An upper limit for dispersing dehydrated, isolated Mo^{6+} was found at about 1 Mo atom/nm², which corresponds to the isolated silanol density of silica.

S. D. Kohler, J. G. Ekerdt, D. S. Kim, and I. E. Wachs, Relationship Structure and Point of Zero Surface Charge for Molybdenum and Tungsten Oxides Supported on Alumina, *Catal. Lett.* 16 (1992) 231.

Laser Raman spectroscopy was used to characterize alumina-supported molybdenum and tungsten oxides at loading ranging from 0.5 to 15 wt % Mo and 0.5 to 30 wt % W. The structure of calcined $\text{Mo}^{6+}/\text{Al}_2\text{O}_3$ and $\text{W}^{6+}/\text{Al}_2\text{O}_3$ was governed by the point of zero surface charge of each system, with the point of zero surface charge being dependent on metal loading. The structures formed by the molybdenum and tungsten overlayers at the sample point of zero surface charge were found to be analogous to the structures formed by molybdenum and tungsten oxyanions in aqueous solution at a solution pH equal to the sample point of zero surface charge.

C. C. Williams and J. G. Ekerdt, The Absence of Molybdenum Precursor Effects for Methanol Oxidation over Molybdenum Oxide Supported on Silica, *J. Catal.* 141 (1993) xxx.

The partial oxidation of methanol to formaldehyde and methyl formate has been studied at low conversion over Mo/SiO_2 . Catalysts up to 1.1 wt% Mo were prepared from MoCl_5 , $\text{Mo}_2(\eta^3\text{-C}_3\text{H}_5)_4$, and $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$. Fumed silica (Cab-O-Sil EH-5), silica gel (Davison 952 and Rhone-Poulenc XOA-400) and Davison 952 silica, washed in acid to remove calcium, were used as supports. Iron-doped Cab-O-Sil was also used. Over identical supports, the activity and selectivity of methanol oxidation was similar for samples prepared from all precursors, although some slight differences were observed. More significant differences were observed, however, when the impurity levels were changed by acid-washing, iron-doping, and using different types of silica. The results suggest that impurities on the silica support, rather than the method of preparation or precursor, have a greater influence on methanol oxidation selectivity for loadings less than 1.1 wt% Mo metal.

The abstracts are listed below for the manuscripts under review or in preparation.

C. C. Williams, J. G. Ekerdt, J.-M. Jehng, C.-K. Chen, F. D. Hardcastle, and I. E. Wachs, Characterization of Molybdenum Oxide Magnesia Catalysts, Submitted to the *Journal of Physical Chemistry*

Laser Raman spectroscopy, X-ray photoelectron spectroscopy, ultraviolet-visible diffuse reflectance spectroscopy, X-ray diffraction, and BET surface area analysis were used to characterize magnesia supported Mo^{6+} prepared from $\text{Mo}(\eta^3\text{-C}_3\text{H}_5)_4$, $\text{Mo}_2(\eta^3\text{-C}_3\text{H}_5)_4$, MoCl_5 , and $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$. A well-dispersed and isolated molybdenum oxide species formed from all precursors at weight loadings from 0.3 to 30% Mo. The results suggest a subsurface molybdate species forms. Crystalline forms of molybdenum were also observed. MgMoO_4 and MoO_3 formation occurred on samples containing 10 and 30% Mo, respectively, and was favored by calcination at 700°C . CaMoO_4 was formed at higher loadings on samples prepared by aqueous impregnation with $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$.

S. D. Kohler, M. F. Arendt, and J. G. Ekerdt, An XPS and IR Study of Silica-Supported Chromium Oxide Photoreduction in CO, Manuscript in preparation.

The photoreduction of silica-supported chromium oxide in CO at 300 K was studied using Fourier Transform infrared spectroscopy and X-ray photoelectron spectroscopy (XPS). Chromium metal loadings of 0.5 to 2.0 wt % were investigated. The carbonyl stretching modes were monitored as a function of reduction time using $^{12}\text{C}^{16}\text{O}$, $^{13}\text{C}^{16}\text{O}$, and $^{13}\text{C}^{18}\text{O}$. XPS was used to characterize the oxidation state. The fully oxidized chromium, which was noncrystalline,

had a Cr ($2p_{3/2}$) binding energy (BE) of 578.3 eV that is associated with Cr^{6+} . Photoreduction was not wavelength dependent between 400-200 nm and produced a Cr ($2p_{3/2}$) XPS BE at 577.8 eV that is assigned to Cr^{2+} . The shape of the Cr ($2p_{3/2}$) XPS band for photoreduced chromium oxide suggests the presence of some Cr^{4+} . The C (1s) BE was also observed at 284.9 eV. The spectra for $^{12}\text{C}^{16}\text{O}$ produced three bands, a weak band at 2201 cm^{-1} that is associated with Cr^{4+} -monocarbonyl, a band at 2183 cm^{-1} that is associated with Cr^{2+} -monocarbonyl, and a band at 2098 cm^{-1} that is a monocarbonyl and may be associated with reduced Cr modified by carbon.

R. D. Roark and J. G. Ekerdt, Reductive Acetaldehyde Coupling to 2-Butenes over Silica-Supported Molybdenum(IV) and Tungsten(IV), Manuscript in preparation.

Acetaldehyde was found to couple over silica-supported W(IV) at 150 and 350 °C and over silica-supported Mo(IV) at 350 °C, producing 2-butenes. $\text{Mo}_2(\text{CO})_4\text{Cp}_2$ and $\text{W}_2(\text{CO})_4\text{Cp}_2$ (Cp = cyclopentadienyl) were used to attach the metals to the support at 7.5 wt % for Mo and 5.5 wt % for W. Oxygen titration experiments reveal the metals to be in the 4+ oxidation state following exchange of the Cp ligands with silica hydroxyl groups and heating to 375 °C to remove the carbonyl ligands. Infrared spectra of the adsorbed complexes contain bridging carbonyl modes suggesting cation dimers form that contain metal-metal bonds. The reductive coupling reaction is proposed to proceed through a μ -ethylidene intermediate.

CURRENT WORK

We are also continuing to work on several problems associated with photoreduction and carbonyl coupling over silica-supported Mo and W. Experiments are planned with various carbon and oxygen isotopes to determine the structure of the W-carbonyls formed during photoreduction. XPS experiments will be performed in parallel with the IR studies and with oxygen titration experiments to better characterize the oxidation state of the photoreduced W and Mo cations. It may also be possible to deposit the complexes onto silica wafers in an antechamber on the XP spectrometer and study the oxidation state using XPS. Extensive infrared experiments are planned to follow the evolution of the $\text{M}_2(\text{CO})_4\text{Cp}_2$ carbonyl ligands and to determine if ethylidene forms as a reaction intermediate. We will also investigate the coupling of aldehydes and ketones to determine if cross coupling is possible in a two step process during which the aldehyde is used to generate the μ -alkylidene at a low temperature and the ketone is reacted at a higher temperature to form the olefin coupling product; such a process would further support the presence of a metal dimer with a M-M bond.

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