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MODEL CATALYTIC OXIDATION STUDIES USING
SUPPORTED MONOMETALLIC AND HETEROBIMETALLIC OXIDES

Progress Report

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INTRODUCTION

This research program is directed toward a more fundamental understanding of the effects of catalyst composition and structure on the catalytic properties of metal oxides. Metal oxide catalysts play an important role in many reactions bearing on the chemical aspects of energy processes. Metal oxides are the catalysts for water-gas shift reactions, methanol and higher alcohol synthesis, isosynthesis, selective catalytic reduction of nitric oxides, and oxidation of hydrocarbons. A key limitation to developing insight into how oxides function in catalytic reactions is in not having precise information of the surface composition under reaction conditions. To address this problem we have prepared oxide systems that can be used to study cation-cation effects and the role of bridging (-O-) and/or terminal (=O) surface oxygen anion ligands in a systematic fashion. Since many oxide catalyst systems involve mixtures of oxides, we selected a model system that would permit us to examine the role of each cation separately and in pairwise combinations. Organometallic molybdenum and tungsten complexes were proposed for use, to prepare model systems consisting of isolated monomeric cations, isolated monometallic dimers and isolated bimetallic dimers supported on silica and alumina. The monometallic and bimetallic dimers were to be used as models of more complex mixed-oxide catalysts. Our current program was to develop the systems and use them in model oxidation reactions.

SUMMARY OF PAST EFFORT

Our research program has been directed at two thrust areas. The first is to prepare and characterize supported oxide systems that permit one to explore the relationships between structure and catalytic properties. A variety of systems have been prepared by exchanging allyl or cyclopentadienyl ligands of organometallic complexes with the support hydroxyl groups. Most of the work has focussed on Mo, W, and Cr on silica. This research is also investigating the exchange processes and the transformation of the complex into the supported oxide. Infrared spectroscopy is used to follow the attachment process and Raman spectroscopy is the principal probe for characterizing the fully-oxidized cations. The second thrust area is devoted to studying the properties of the oxides and catalytic reactions over the oxides. We are focusing on photoreduction as a means of producing cations with the same oxidation state to form coordinatively unsaturated catalyst sites for carbon-carbon coupling reactions, such as olefin metathesis. We also explored the relationships between activity and selectivity in methanol oxidation, and in isopropanol oxidation and dehydration over fully-oxidized cations that are present as isolated cations, in two dimensional ensembles, or in crystallites.

Our research approach to preparing metal oxides was motivated by the publications of Iwasawa [1-5], Yermakov [6], Candlin and Thomas [7], and Che [8-10]. They had used preparations that involve the exchange of surface hydroxyl groups

with one or more of the ligands of the metal oxide precursor. When these authors compared their catalysts over silica against those prepared with ammonium heptamolybdate (AHM; $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$) they consistently found improved catalytic performance that was associated with higher dispersion and unique molybdate structures. Che's preparation involved MoCl_5 . Yermakov used $\text{Mo}(\eta^3\text{-C}_3\text{H}_5)_4$ while Candlin and Thomas, and Iwasawa used $\text{Mo}(\eta^3\text{-C}_3\text{H}_5)_4$ and $\text{Mo}_2(\eta^3\text{-C}_3\text{H}_5)_4$. Most of their work was conducted at low metal loadings (less than 1.5 wt% Mo) and they all reached the conclusion that the fully-oxidized Mo was present as the tetrahedrally-coordinated moiety $(\text{-SiO})_2\text{Mo}^{6+}\text{O}_2$ containing two oxo oxygens (Mo=O). The model developed by Iwasawa [1] envisages isolated or paired bidentate MoO_4 tetrahedra or tetrahedral dimers joined by bridging oxygen, depending on the silica support and precursors. These bidentate, tetrahedral structures were reported to be stable under repeated oxidation and reduction cycles. Similar claims (paired bidentate tetrahedra or tetrahedral dimers) were made by Iwasawa over alumina [1]. On the basis of these studies, we proposed to prepare and study isolated cations, cation pairs and cation dimers of Mo and W in catalytic reactions such as methanol oxidation and alkane and olefin oxidation. We were particularly interested in the role of oxo oxygens and bridging oxygens (Mo-O-Mo) in catalytic reactions, the synergism between cations of different redox characteristics such as Mo and W in hydrocarbon oxidation, and how structure (isolated cations versus small crystallites) affected catalytic properties.

We have used Raman spectroscopy, UV diffuse reflectance spectroscopy, photoluminescence spectroscopy, EXAFS, and IR spectroscopy to characterize the structures that formed from the various preparations following heating in ambient (hydrated) or anhydrous conditions. Raman spectroscopy (in collaboration with Professor I. E. Wachs) has become our primary characterization tool; many of the other tools were used to compare our results and conclusions against the information available in the literature. EXAFS was performed (in collaboration with Iwasawa) to determine if the structures we observed were similar to the structures observed by Iwasawa [1]. Structures have not yet been computed by Iwasawa; however, the raw data suggest that, when hydrated, the structures are equivalent over the same support for different precursors.

We studied Mo on silica, alumina, and magnesia prepared from AHM, $\text{Mo}(\eta^3\text{-C}_3\text{H}_5)_4$, $\text{Mo}_2(\eta^3\text{-C}_3\text{H}_5)_4$, MoCl_5 , and $\text{H}_2(\text{MoO}_3\text{C}_2\text{O}_4)\cdot 2\text{H}_2\text{O}$ to establish a reference case and refine techniques before starting to work on heterobimetallic systems. A complete discussion of the Raman and UV diffuse reflectance work over silica and alumina can be found in References [11] and [12]; a manuscript describing the results over magnesia is in preparation. We never detected the structures claimed by the authors listed above and since our results were unexpected, we spent a considerable amount of time trying to sort out what controls the structure of supported Mo^{6+} .

We specifically examined weight loadings reported by Iwasawa and Che, we obtained samples of their supports, and even analyzed some of their catalysts. When all preparations are examined as a set and subjected to a consistent form of analysis, a different interpretation emerges [11,12]. This insight forced us to reexamine what was possible vis-à-vis preparation of the unique structures mentioned above to probe cation-cation and oxygen ligand effects in catalysis.

Our work with Mo has shown that the final dispersed molybdate structure is independent of the precursor. X-ray amorphous molybdate species and crystalline compounds form over the supports. Two types of crystalline compounds were detected, MoO_3 crystallites and compounds, such as CaMoO_4 and MgMoO_4 , that formed between Mo and the Ca impurity on silica or the Mg support cations. Different X-ray amorphous molybdate species form; their structure is understood over silica and alumina but questions remain for magnesia. Support and loading are the key variables in determining the molybdate structure. Precursor and method of preparation do control the formation of MoO_3 crystallites; however, these were not catalytic in the reactions we studied. The aqueous routes over silica appeared to lead to crystallites of MoO_3 at loadings as low as 0.4 wt% Mo. The recent paper by Desikan et al. [13] provides evidence for crystallite formation from AHM at 0.2 wt% Mo. Over alumina, MoO_3 crystallites were observed at 13.3 wt% Mo. We have been able to reach 6.4 wt% Mo (1.3 Mo/nm²) over silica, by using the organometallic precursor $\text{Mo}_2(\eta^3\text{-C}_3\text{H}_5)_4$, without crystallite formation.

The dispersed molybdate structure changes with the environment, hydrated or dehydrated, and with the Mo loading. We have shown that the hydrated structures are analogous to the Mo^{6+} structures that form in aqueous solutions. This insight permits one to predict a structure knowing the Mo concentration and the local surface charge. In the case of aqueous Mo^{6+} , above *ca.* pH 7 MoO_4^{2-} (T_d) predominates, below pH 6.8 the $\text{Mo}_7\text{O}_{24}^{6-}$ (O_h) polyanion forms, and below *ca.* pH 2.2 $\text{Mo}_8\text{O}_{26}^{4-}$ (O_h) forms [14-17]. Both MoO_4^{2-} and $\text{Mo}_7\text{O}_{24}^{6-}$ are present between pH 5 and 6.8. We have measured the point of surface charge (PZSC) for Mo^{6+} , W^{6+} , and Nb^{5+} on the various supports. The results over silica and alumina are presented in Figure 1. Consistent with the PZSC data and the Raman absorbance for aqueous Mo^{6+} , we find that over SiO_2 , at all loadings, a polymolybdate $\text{Mo}_7\text{O}_{24}^{6-}$ (O_h) structure forms. (⁹⁵Mo NMR analysis of a 6.4 wt% Mo/ SiO_2 sample prepared from $\text{Mo}_2(\eta^3\text{-C}_3\text{H}_5)_4$ have been performed in collaboration with Professor G. L. Haller; when analyzed in the ambient state (i.e. hydrated) the spectrum is a perfect match to an aqueous solution of $\text{Mo}_7\text{O}_{24}^{6-}$ [18].) Over Al_2O_3 , at the lowest loadings (<1 Mo/nm²), where the PZSC is above 7, the MoO_4^{2-} (T_d) structure forms, and as the loading is increased the polymolybdate $\text{Mo}_7\text{O}_{24}^{6-}$ (O_h) structure begins to form. MoO_3 crystallite formation occurs at 13.3% Mo (5-6 Mo/nm²) and, as seen from Figure 1, the PZSC begins to show asymptotic behavior well before the monolayer limit

P.Z.S.C. OF VARIOUS CATALYSTS AQUEOUS PREPARATION

Wt % METAL

FIGURE 1

(13.3% Mo) has been reached. (Similar correlations between structure changes, monolayer limits and the PZSC were observed for W and Nb and will be communicated in a manuscript that is in preparation.) The significance of our work is that Mo^{6+} in the ambient state is solvated by the water that has adsorbed on the support, and Mo^{6+} can have no memory of how it was made.

We have also examined the Raman spectra of samples in the dehydrated state (*in situ* Raman). Our study of 6.4 wt% Mo prepared from $\text{Mo}_2(\eta^3\text{-C}_3\text{H}_5)_4$ was the first to show that Mo^{6+} spreads on silica to form an isolated cation. We were able to observe this spreading because the allylic preparation route avoided crystallite formation and all of the Mo was present as polymolybdate before dehydration. We were unable to assign a structure because there was no independent measure of the symmetry. We attempted to observe the $\text{Mo}=\text{O}$ stretch with IR to determine if the $\text{Mo}=\text{O}$ Raman and IR stretches were coincident or differed. A coincident stretch would mean octahedral Mo symmetry. Unfortunately, the vibrational lattice modes of silica (and their overtones) obscured the IR modes for $\text{Mo}=\text{O}$. In a publication subsequent to ours, de Boer et al. also report spreading of Mo^{6+} on silica [19]. They employed Raman, EXAFS and EXANES and were also unable to identify the symmetry and structure of the isolated Mo^{6+} ; they do suggest, by analogy to inorganic molybdenum compounds, that the isolated cation is octahedral MoO_6 .

The *in situ* Raman spreading results are significant in several respects. It is the first example of silica functioning like other supports in dispersing cations when the water of hydration is removed. This means 1) that only isolated Mo^{6+} is present under reaction conditions when preparations are employed that avoid crystallites and 2) that both MoO_3 crystallites and isolated Mo^{6+} are present when the preparation leads to crystallites, such as occurs with AHM. Since silica is catalytically inert in acid, dehydration, and selective oxidation reactions, is resistant to reduction, and retains its textural properties during high temperature processing, our results may lead to the development of catalytic processes that require high active component dispersion and chemical inertness. We are currently studying the generality of our results with Mo by using organometallic precursors for W, Zr, Nb, and Cr.

We have tested the factors that limit the amount of a cation that can be dispersed on silica. Once it became apparent that we could avoid crystallites using the allylic preparation, we attempted to push the loading to higher limits than had been explored by Iwasawa. The 6.4 wt% sample [11] corresponds to 1.3 Mo/nm^2 . Morrow and McFarlan [20] have reported that hydroxylated aerosil and precipitated silicas contain about 1.1 isolated silanols/ nm^2 . Iwasawa has published hydroxyl density as a function of thermal treatment over a variety of oxides [1]; 1.5-1.6 OH/nm^2 remain on silica following treatment at 550 °C. (Alumina has about twice the hydroxyl density of silica at 550 °C and it can disperse 5-6 Mo/nm^2 before MoO_3

crystallites are seen [12].) Figures 2 and 3 present the hydrated and dehydrated Raman spectra for samples ranging from 5.1-7.8 wt% Mo we prepared from $\text{Mo}_2(\eta^3\text{-C}_3\text{H}_5)_4$ and $\text{Cp}_2\text{Mo}_2(\text{CO})_4$. The Raman band at $945\text{-}950\text{ cm}^{-1}$ in Figure 2 is indicative of the Mo_7 -polymolybdate [11], and the Raman band at *ca.* 988 cm^{-1} in Figure 3 is associated with the isolated Mo^{6+} cation [11,19]. Crystallites were not observed following the initial preparation all of the way up to 7.8 wt% Mo. Above 6.4 wt% not all of the polymolybdate could be dispersed as evidenced by the bands at $966\text{-}970$ and 285 cm^{-1} in these dehydrated spectra. In a parallel study we examined the change in the absorbance intensity of the isolated Si-OH groups using IR spectroscopy. These results, shown in Figure 4, illustrate that not all of the OH groups are consumed for 6.4 wt% Mo. The results in Figures 2-4 demonstrate that the isolated OH groups are involved in the process of dispersing and anchoring the Mo^{6+} cations on the silica surface. A manuscript describing the results represented in Figures 2-4 is currently in preparation [21].

In a separate study we have been able to show that the hydroxyl groups are consumed and that H gets displaced during the dispersion process. We wanted to know if Si-OH groups were intact after dispersion and if the O-H stretch was not observed because Si-OH was somehow involved in anchoring the Mo^{6+} cation. Figures 5 and 6 present IR spectra of the hydroxyl region following the reversible transformation of the Mo^{6+} cations between the polymolybdate and isolated structures. When H_2O was used to rehydrate the dispersed Mo^{6+} , the Si-OH stretch was observed to return at 3742 cm^{-1} . However, when D_2O was used to rehydrate the dispersed Mo^{6+} cations, Si-OD bands were seen and the Si-OH bands did not return. These data demonstrate that the O-H bond is somehow broken during dispersion and the Mo^{6+} cation is tethered to the silica through the Si-O site. Dispersion is not related to defect sites; it is related to Si-OH sites. A manuscript describing this is currently in preparation [21a].

As stated above our work has two thrusts 1) synthesis and characterization and 2) study of the catalytic properties of the supported cations. We have investigated the photoreduction and reoxidation of Mo/SiO_2 to probe the structure of the supported Mo and, as we will described later, to form cations of one oxidation state that are coordinatively unsaturated so we can study catalytic reactions as a function of oxidation state. The photoreduction work with CO over Mo/SiO_2 has been submitted for publication in two manuscripts, one assigning the structures and the second discussion oxidation-reduction studies and how the various carbonyls form [22,23]. We have also investigated the catalytic activity of Mo in methanol oxidation and isopropanol dehydration and oxidation.

The molybdenum carbonyl species formed by thermal [24-26] and photochemical [27-32] reduction have been studied principally to characterize supported molybdenum oxide catalyst systems. The CO stretching frequency can

Figure 2 Raman spectra of $\text{Mo}^{6+}/\text{SiO}_2$ under ambient conditions: a) 7.8% $\text{Mo}^{6+}/\text{SiO}_2$ prepared from $\text{Mo}_2(\text{allyl})_4$, b) 6.7% $\text{Mo}^{6+}/\text{SiO}_2$ from $\text{Mo}_2(\text{allyl})_4$, c) 6.4% Mo/SiO_2 from $\text{Mo}_2(\text{allyl})_4$, d) 5.1% $\text{Mo}^{6+}/\text{SiO}_2$ from $\text{Mo}_2(\text{allyl})_4$, e) 5.1% $\text{Mo}^{6+}/\text{SiO}_2$ from $\text{Cp}_2\text{Mo}_2(\text{CO})_4$.

Figure 3 Raman spectra of $\text{Mo}^{6+}/\text{SiO}_2$ under dehydrated conditions: a) 7.8% $\text{Mo}^{6+}/\text{SiO}_2$ prepared from $\text{Mo}_2(\text{allyl})_4$, b) 6.7% $\text{Mo}^{6+}/\text{SiO}_2$ from $\text{Mo}_2(\text{allyl})_4$, c) 6.4% $\text{Mo}^{6+}/\text{SiO}_2$ from $\text{Mo}_2(\text{allyl})_4$, d) 5.1% $\text{Mo}^{6+}/\text{SiO}_2$ from $\text{Mo}_2(\text{allyl})_4$, e) 5.1% $\text{Mo}^{6+}/\text{SiO}_2$ from $\text{Cp}_2\text{Mo}_2(\text{CO})_4$.

SILICA HYDROXYLS WITH MOLYBDENUM LOADING

Figure 4

FTIR spectra of the isolated (3742 cm^{-1}) and adjacent ($3700\text{--}3250\text{ cm}^{-1}$) hydroxyl regions of 6.4 wt. % Mo on SiO_2 . A) Wafer in ambient, hydrated state. B) Wafer was dehydrated in hydrocarbon-free air at 873 K. C) Wafer was rehydrated with H_2O .

FTIR spectra of the isolated (2743 cm^{-1}) and adjacent ($2715\text{--}2200\text{ cm}^{-1}$) (--OD) regions of 6.4 wt. % Mo on SiO_2 . A) Wafer was hydrated with D_2O at 273 K. B) Wafer was dehydrated in hydrocarbon-free air at 873 K.

Figure 6

provide information concerning the oxidation state of the metal cation adsorption site [33,34].

A literature review reveals many contradictory viewpoints concerning the oxidation state and CO ligand structure of photochemically formed molybdenum carbonyl species. Kazansky and coworkers [28,35] determined that UV photoreduction of Mo/SiO₂ in CO leads to selective formation of Mo⁴⁺(CO)_x (x not determined) species. It was assumed that tetrahedrally-coordinated molybdenum cations were the active photoreduction sites. Guglielminotti and Giamello reported the IR spectra of photoformed molybdenum carbonyl species [30]. A molybdenum dicarbonyl was proposed to occur on Mo²⁺. Evacuation led to the formation of a monocarbonyl, which was assigned to a bridging CO group because its frequency (2043 cm⁻¹) was thought to be too low to be a linear carbonyl. A second type of dicarbonyl was proposed and was assigned to an oxidation state of +4 because prolonged photoreduction converted it to the dicarbonyl on Mo²⁺. Gerasimov [27] also reported the two sets of peaks reported by Guglielminotti and Giamello; one set of bands was assigned to two species that were proposed to form on isolated MoO₄ tetrahedra, because they were observed at low Mo loadings, where it was thought that Mo tetrahedra existed [36]. The second set was assigned to the same two species that had formed on polymolybdate chains. Rodrigo et al. [31] assigned the bands they observed to a Mo³⁺(CO)₂ species which could be photoreduced to a Mo²⁺(CO)₂ species; comparison with UVDRS results led to the conclusion that photoreduction occurred on dimeric surface molybdate. Finally, Anpo et al. [29] determined the oxidation state of the photoreduced Mo cations and concluded that the oxidation state of photoreduced samples prepared from AHM was +4 and that the oxidation state for photoreduced samples prepared from Mo(η³-C₃H₅)₄ was +2.

We also observed sets of bands to form and change in response to the extent of photoreduction and CO pressure [22,23]. We worked at 298-193 K and examined the carbonyl modes at pressures from 1 atm to vacuum. By working at 1 atm, a pressure much higher than previous researchers had worked, we were able to observe a new IR mode (at 2181 cm⁻¹) and once it was determined that this band and two others (that other researchers had also seen) acted in parallel we conducted a series of isotopic substitution experiments using ¹²C¹⁶O, ¹³C¹⁶O, and ¹³C¹⁸O. The IR bands were analyzed by assuming non-mechanical coupling between the CO groups [37]; frequencies and positions of prospective molybdenum carbonyl species were calculated with the standard GF matrix approach [38-41]. We also performed desorption studies and characterized the oxidation state by observing CO₂ formed during reduction and monitoring O₂ required in reoxidation.

The two schemes presented in Figure 7 illustrate the structures we observed; the key results are summarized below. 1) Photoreduction of silica-supported molybdenum oxide leads first to the formation of *mer*-Mo⁴⁺(CO)₃. This species is

Photoreduction

Room Temperature Transformations

Figure 7

identified through its stoichiometry of formation, through the intensity and position of its three IR bands at 2180, 2141, and 2108 cm^{-1} and their changes upon partial isotopic substitution with $^{13}\text{C}^{16}\text{O}$ and $^{13}\text{C}^{18}\text{O}$, and through its temperature programmed desorption (TPDE) pattern. 2) $\text{Mo}^{4+}(\text{CO})_2$ is formed from *mer*- $\text{Mo}^{4+}(\text{CO})_3$ upon prolonged photoreduction or evacuation of CO below 60 Torr. $\text{Mo}^{4+}(\text{CO})_2$ is characterized by its IR bands at 2128 and 2080 cm^{-1} . Although the interdipole angle between the two CO groups is nearly that of a perfect tetrahedron, this species is formed by photoreduction of the same Mo^{6+} sites that lead to $\text{Mo}(\text{CO})_3$. 3) Linear $\text{Mo}(\text{CO})$, characterized by a single band at 2145 cm^{-1} , is formed by continued evacuation of $\text{Mo}^{4+}(\text{CO})_2$ or heating $\text{Mo}^{4+}(\text{CO})_3$ in an inert purge. 4) Extreme photoreduction of $\text{Mo}^{6+}/\text{SiO}_2$ leads to the formation of physisorbed and chemisorbed $\text{Mo}(\text{CO})_6$. 5) $\text{Mo}(\text{CO})_3$ can be converted to $\text{Mo}(\text{CO})_2$ by room-temperature evacuation or extended photoreduction. $\text{Mo}(\text{CO})_3$ decomposed into $\text{Mo}(\text{CO})$ during TPDE. 6) $\text{Mo}(\text{CO})_2$ can be converted to $\text{Mo}(\text{CO})$ by room temperature evacuation and to $\text{Mo}(\text{CO})_6$ by extended photoreduction. $\text{Mo}(\text{CO})_2$ decomposes into $\text{Mo}(\text{CO})$ during TPDE. 7) The same photoreduction mechanism occurs on samples prepared from all precursors studied.

Our work has identified a new and different carbonyl of Mo, the tricarbonyl. We were also able to explain some of the conflicting interpretations that had been published once it was realized that the third weak band contributed to a species that had been assigned to a dicarbonyl on special sites or to a different Mo oxidation state. We were also able to better verify the oxidation state of carbonyl formed under conditions that prevent reduction to the hexacarbonyl. The results will permit us to reduce Mo^{6+} to Mo^{4+} , and then desorb the carbonyl ligands so we can assess the role of oxidation state in catalytic reactions.

Our characterization studies had shown all of the precursors to give the same molybdate structures on silica. Methanol oxidation has been found to be a structure sensitive reaction over unsupported MoO_3 [42,43]. Che and coworkers have proposed methanol oxidation also exhibits structure sensitivity for surface molybdate species formed on silica [44,45]. Isolated molybdate formed from MoCl_5 was argued to have a different oxidation selectivity than the poorly dispersed, "clustered-molybdate" formed from AHM. We studied methanol oxidation (before we had a complete picture of the structures formed on silica) to determine if we formed the unique structures proposed by Iwasawa and Che. The methanol study has been submitted for publication [46]. We examined catalysts containing up to 1.1 wt% Mo from a variety of precursors and over a variety of supports. Over identical supports, the activity and selectivity of methanol oxidation were similar for samples prepared from all precursors, although some slight differences were observed. More significant differences were observed, however, when the impurity levels of the silica were changed by doping with iron or by acid-washing to remove impurities. Our results suggest that impurities on the silica 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. Our results also showed that since Mo supported on silica is such a poor catalyst for methanol oxidation, subtle differences in the systems, such as impurity differences for various silicas, can lead to conflicting interpretations of essentially the same experimental data.

We also examined isopropanol oxidation to acetone and dehydration to propylene as a way to test the differences in oxidative and acid catalyzed reactions. We examined isopropanol conversion over catalysts made from $\text{Cp}_2\text{Mo}_2(\text{CO})_4$, $\text{Mo}_2(\eta^3\text{-C}_3\text{H}_5)_4$, AHM, $\text{Cp}_2\text{MoW}(\text{CO})_4$, $\text{Cp}_2\text{W}_2(\text{CO})_4$, and $(\text{NH}_4)_6\text{H}_2\text{W}_{12}\text{O}_{24}$. The catalysts made from the organometallic precursors had isolated cations present before reaction, and the catalysts made via AHM and $(\text{NH}_4)_6\text{H}_2\text{W}_{12}\text{O}_{24}$ had both isolated cation and crystallites. We selected the isopropanol reaction because silica has no Lewis acidity and therefore we would be measuring the inherent properties of the supported cations. There were no discernable trends in activity or selectivity that could be associated with dispersed cations versus crystallites of W or Mo. There does not appear to be a difference in the selectivity between oxidation and dehydration for the aqueous and organometallic preparations. This is reasonable since the isolated cations should exist along with crystallites over the samples prepared from aqueous compounds. We suspect the crystallites to be inactive and the isolated structures to dominate the catalysis. The overall activity is greater for the catalysts made with organometallic complexes; this is also consistent with more of the supported cation being present in the dispersed form.

CURRENT PROJECTS

One of the objectives of the current program was to synthesize and fix Mo_2 , W_2 and MoW dimer complexes to the surface of silica. We had originally thought it would be possible, on the basis of Iwasawa's work [1], to attach dimers on the surface and keep them as a dimer or cation pair throughout the repeated oxidation/reduction cycles. We now know that, once oxidized and exposed to ambient, the dispersed cations become solvated by adsorbed water and coalesce into polyanions on silica and alumina. The question remaining to be answered, and one which we are currently addressing, is what happens to a dimer system without exposure to ambient and what happens if the cations are not fully oxidized. Our preliminary results are very intriguing and suggest several areas for future work.

To study the attachment process and properties of dimer systems we are using the complexes $\text{Cp}_2\text{Mo}_2(\text{CO})_4$, $\text{Cp}_2\text{W}_2(\text{CO})_4$, and $\text{Cp}_2\text{WMo}(\text{CO})_4$ that have been reported by Curtis et al. [47]. Using a specially designed IR cell, we introduce a benzene- D_6 solution of the complex, dip self-supporting silica wafers in the benzene solution, pump away the solvent, and follow the surface hydroxyl groups, the cyclopentadienyl (Cp) ligand of the complex and the CO ligands of the complex as a

function of time and temperature. Zecchina et al. [48] have followed the interaction of chromocene, $\text{Cr}(\text{Cp})_2$, with silica using IR and they report retention of the Cp- ring by the attached Cr. We find that the Cp- ligand of our complexes (with ν_{CH} at 3107 cm^{-1}) to be absent following attachment to the surface. As expected the silanol group absorbance intensity is also attenuated after attachment and removal of benzene solvent. Figures 8-10 present spectra of the dimer complexes in solution, the carbonyl region after attachment, and the carbonyl region during heating the Mo_2 -carbonyl structure. In all cases the carbonyl region is slightly different for the surface bound compounds than the solution complexes. Spectrum 9B is not a simple composite of 9A and 9C. We suspect that, throughout the attachment and heating process, the complexes remain in close proximity and may even retain dimer character since the carbonyl modes appear to attenuate in parallel with heating. It has not been possible to repopulate the adsorbed cations with CO at room temperature, after complete removal of the carbonyl ligands. We will attempt to repopulate the carbonyl ligands at elevated temperatures, since repopulation will be helpful in characterizing the oxidation state and structure that forms after the initial removal of carbonyl ligands. We are continuing to study the attachment, decomposition and ligand desorption processes. The oxidation state of the complex following attachment and ligand removal will be determined. The metals are each 1+ in the dimer complex. If, after attachment and carbonyl ligand removal the metals are tethered to the surface as $(\text{SiO})_2\text{-M}$, then the oxidation state should be 2+.

One of the objectives of the research program is to examine the effect of oxidation state on the catalytic properties of supported metals. To accomplish this we proposed to cycle the cations between the fully oxidized state (6+) and lower states (5+, 4+, 3+, 2+) that we would reach by photo or thermal reduction. Hercules' group [49,50] has been involved in speciation of Mo on supports and have discussed the thermal oxidation-reduction of Mo, as determined by XPS, on a variety of supports. Over silica and alumina there is generally a distribution of oxidation states and it has not been possible to take Mo to one oxidation state. This creates problems with data interpretation if one of the oxidation states is present at low levels, yet is many times more catalytically active than the other oxidation states that are present. One way to overcome this is to photoreduce the Mo (or W) with CO; our work with Mo was described in the preceding section. Using Mo^{6+} and CO, one can restrict the reduction to Mo^{4+} and generate a system consisting of Mo^{6+} and Mo^{4+} cations. Over-reduction leads to the formation of $\text{Mo}^0(\text{CO})_6$ that can be seen with IR; most likely some Mo^{2+} is also present along with Mo^{4+} , for 'over-reduced' samples. One possible route to Mo^{2+} involves the complexes. Following complex exchange, the oxidation state of the cations should be 2+ if tethered by two SiO-bonds. The allylic complexes require heating to 550°C to remove the allylic ligands remaining after exchange. The $\text{CpM}_2(\text{CO})_4$ complexes only require 225°C to remove the carbonyl ligands. We are currently testing reactions over Mo^{4+} and W^{4+} that result from photoreduction and over what could be Mo^{2+} and W^{2+} that result from

FTIR spectra of $\text{Cp}_2\text{MM}(\text{CO})_4$ dissolved in perdeuterated benzene where MM - a) W-W, b) Mo-W, c) Mo-Mo.

Figure 8

Figure 9

FTIR spectra of adsorbed Mo carbonyl loss as a function of temperature. The sample was prepared from $\text{Cp}_2\text{Mo}_2(\text{CO})_4$. The SiO_2 wafer was heated for 20 min. at: a) 323 K, b) 373 K, c) 423 K.

attachment and carbonyl ligand desorption.

Two reactions have been studied over reduced oxides, olefin metathesis and carbonyl coupling. Olefin metathesis has been studied by a number of groups over Mo and W [51-62]. Kazansky and co-workers [51] have investigated the oxidation state of the active catalyst and have also explored the role of the precursor on the activity. We selected propylene metathesis as a test reaction because it is generally agreed to occur over reduced cation sites. However, the nature of the active oxidation state remains to be resolved. Representative data are presented in Figure 11, where the amount of ethylene formed increases linearly with the extent of photoreduction. The turnover number (TON), based on Mo^{4+} , is constant at about 0.027 molecules ethylene/(site-sec). These are less than the values reported by Shelimov et al. [51]; where they report TONs of 0.2-0.6 sec^{-1} . We have not resolved the differences in activity yet, but they may be unimportant since this reaction is being used to probe relationships between structure, oxidation state and activity in samples we prepare. We have also measured the activity over several other catalysts and find different activities depending on metal, oxidation state (4+ versus 2+) and composition (W, Mo, or Mo-W). These differences will need to be characterized so that we can associate them with either structure or a component's inherent reactivity, and establish the utility of metathesis as a probe reaction for supported cations.

We have also studied carbonyl coupling catalysis. We were motivated by a report from Barteau's group [63] that showed carbonyl metathesis of aldehydes to olefins ($2\text{RCHO} \rightarrow 2\text{O} + \text{RCH=CHR}$) over a partially reduced TiO_2 surface. Since this is a 4-electron transfer process and they knew Ti^0 was not present, they suggested a pair of cation sites to be involved in the reaction. We have attempted carbonyl coupling over catalysts made from $\text{Cp}_2\text{Mo}_2(\text{CO})_4$ and $\text{Cp}_2\text{W}_2(\text{CO})_4$ and find, at 40 °C, that acetaldehyde undergoes coupling to *cis*-2- and *trans*-2-butenes over the W_2 -based catalysts. The reaction has not, to date, worked over Mo_2 . Carbonyl coupling has been reviewed in the literature [64]; both Mo and W homogeneous complexes have been shown to work. Recent studies by Chisholm [65-67] have shown that the mechanism over W_2 complexes proceeds by a μ -alkylidene intermediate, whereas the mechanism over Ti involves pinacولات. The key issue here is a bridging alkylidene was involved and this could mean dimers are also required on the surface. Our results are very exciting because they suggest one can take specific complexes and extend the structure sensitivity of these systems to similar reactions on surfaces. Clearly more work is needed on this reaction. We have run the reaction several times with the same results but have not conducted all the ancillary experiments needed to establish if any form of low valent W that is deposited/formed by other precursors is active or if the W_2 -complex is the key to coupling activity.

PHOTOREDUCED CATALYST IS MORE ACTIVE THAN THERMALLY REDUCED

Figure 11. Formation of ethylene over photoreduced and thermally reduced 0.4% Mo / SiO₂. Samples were photoreduced for various times through 6 mm of pyrex filter in 1 atm of flowing CO. Samples were thermally reduced at 350 C in 1 atm of flowing CO. Reduced catalysts were heated in 20 CC/min of He to 400 C to remove carbonyl ligands. Metathesis reaction took place at 40 C.

As part of our study of forming reduced oxidation state cations we have continued to study photoreduction. Figure 12 presents spectra for W and Cr carbonyls formed by photoreduction. Over W, we observe a dimer with an interdipole angle of 102.8° between the carbonyl ligands. We are continuing to examine this system and still need to verify the oxidation state of the W-carbonyl. Our results have shown W to be more difficult to reduce than Mo. The Cr carbonyl ligands were studied because there are conflicting interpretations in the literature about the assignment of these modes [68-71]. We propose that Cr-carbonyl spectrum in Figure 12 is best described by a dicarbonyl with bands at 2203 and 2183 cm^{-1} and a monocarbonyl with a band at 2100 cm^{-1} . We use the C-O stretching constant and the interaction parameter determined for $^{12}\text{C}^{16}\text{O}$ to predict the absorbance positions and intensities for partial substitution, as illustrated in Figure 13. We expect to complete this study shortly.

Publications and Manuscripts

A Raman and Ultraviolet Reflectance Spectroscopic Investigation of Silica-Supported Molybdenum Oxide (C. C. Williams, J. G. Ekerdt, J-M. Jehng, F. D. Hardcastle, A. M. Turek, and I. E. Wachs), *J. Phys. Chem.* **95**, 8781 (1991).

A Raman and Ultraviolet Diffuse Reflectance Spectroscopic Investigation of Alumina-Supported Molybdenum Oxide (C. C. Williams, J. G. Ekerdt, J-M. Jehng, F. D. Hardcastle, and I. W. Wachs), *J. Phys. Chem.* **95**, 8791 (1991).

Infrared Spectroscopic Characterization of Molybdenum Carbonyl Species Formed by Ultraviolet Photoreduction of Mo(VI)/SiO_2 in Carbon Monoxide (C. C. Williams and J. G. Ekerdt), *J. Physical Chemistry* (submitted).

Temperature Programmed Desorption Study and the Transformations of Molybdenum Carbonyl Species Formed by Ultraviolet Photoreduction of Mo(VI)/SiO_2 in Carbon Monoxide (C. C. Williams and J. G. Ekerdt), *J. Physical Chemistry* (submitted).

Methanol Oxidation over Silica-Supported Molybdenum Oxide (C. C. Williams and J. G. Ekerdt), *J. Catalysis* (submitted).

A Laser Raman and UV Diffuse Reflectance Spectroscopic Investigation of Magnesia-Supported Molybdenum Oxide (C. C. Williams, J. G. Ekerdt, I. E. Wachs, J-M. Jehng, and C-K. Chen) (in preparation).

The Role of Hydroxyl Groups in Dispersing Molybdenum on Silica (with S. D. Kohler, and R. D. Roark) (in preparation).

WAVENUMBERS

FTIR spectra of photoformed chromium and tungsten carbonyls. (A) Catalyst wafer was photoreduced for 4 min (2 min per side) through 6 mm of pyrex filter in 760 torr of CO at room temperature. Sample is 0.87% Cr/SiO₂ prepared from Cr (n-C₃H₅)₃ on Davison 952 SiO₂. (B) Catalyst wafer was photoreduced for 30 min (15 min per side) in 760 torr of CO at room temperature. Sample is 1% W/SiO₂ prepared from (NH₄)₆W₁₂O₄₀ on Davison 952 SiO₂.

FTIR spectra of photoformed chromium carbonyls. (A) Catalyst wafer was photoreduced for 20 min (10 min per side) through 6 mm of pyrex filter in 33% $^{13}\text{C}^{16}\text{O}$ and 67% $^{12}\text{C}^{16}\text{O}$ at room temperature. Sample is 0.87% Cr/ SiO_2 prepared from Cr ($n\text{-C}_3\text{H}_5$)₃ on Davison 952 SiO_2 . (B) Predicted spectra based on structure consisting of photoformed $\text{Cr}(\text{CO})_2$ and CrCO . Solid line is based on observed peak widths. Dotted line is idealized spectra.

Figure 13

Monolayer Dispersion of Molybdenum and Tungsten on Silica: An in situ Raman Study (with S. D. Kohler, R. D. Roark, D. S. Kim, and I. E. Wachs) (in preparation).

Relationship Between Structure and Isoelectric Point for Molybdenum, Tungsten, and Niobium on Alumina. (with S. D. Kohler, R. D. Roark, J-M. Jehng, and I. E. Wachs) (in preparation).

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