CATALYTIC HYDROCARBON REACTIONS OVER SUPPORTED METAL OXIDES

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INTRODUCTION

Oxide catalysis plays a central role in hydrocarbon processing and improvements in catalytic activity or selectivity are of great technological importance because these improvements will translate directly into more efficient utilization of hydrocarbon supplies and lower energy consumption in separation processes. An understanding of the relationships between surface structure and catalytic properties is needed to describe and improve oxide catalysts. Our approach has been to prepare supported oxides that have a specific structure and oxidation state and then employ these structures in reaction studies. Our current research program is focused on studying the fundamental relationships between structure and reactivity for two important reactions that are present in many oxide-catalyzed processes, partial oxidation and carbon-carbon bond formation.

Oxide catalysis can be a complex process with both metal cation and oxygen anions participating in the chemical reactions. Examples of this are found in selective oxidation of olefins [1-18], alkanes [17-30] and alcohols [31-37], CO hydrogenation to iso-olefins [38-40], and selective reduction of nitric oxides [41-43]. From an energy perspective carbon-carbon bond formation is particularly relevant to CO hydrogenation in isosynthesis [38]. Hydrogenolysis and hydrogenation form the basis for heteroatom removal in fuels processing [44-50]. Understanding the catalysis of these processes (and others) requires isolating reaction steps in the overall cycle and determining how structure and composition influence the individual reaction steps. Specially designed oxides, such as we use, permit one to study some of the steps in oxidation, carbon-carbon coupling and heteroatom removal catalysis.

During the course of our studies we have: 1) developed methods to form and stabilize various Mo and W oxide structures on silica; 2) studied C-H abstraction reactions over the fully oxidized cations; 3) studied C-C bond coupling by methathesis and reductive coupling of aldehydes and ketones over reduced cation structures; and 4) initiated a study of hydrogenation and hydrogenolysis over reduced cation structures.

SUMMARY OF PAST EFFORT

The objectives for the current research grant follow. We have made significant progress on each specific objective.

This research program is directed toward developing a fundamental understanding of how catalyst composition, redox properties, and structure control the catalytic properties of metal oxides. Oxide systems that permit examination of the role of metal oxide cations separately and in pairwise combinations will be used. Organometallic molybdenum and tungsten complexes will be used to prepare supported-oxides, on silica, alumina, titania, and zirconia, consisting of metal-metal dimers, isolated cations, and oxygen-bridged cation clusters. These structures will be used as mixed oxide catalysts. The oxidation state of the supported oxides can be controlled. Since we can control the structure and oxidation state, we will be able to explore role of each in oxidation and carbon-carbon coupling reactions.

Olefin and alkane oxidation will be used to study the catalytic properties of fully oxidized cations. Olefin metathesis will be used to study carbon-carbon coupling catalysis over cations in lower oxidation states. Carbonyl coupling reactions will be studied over dimer systems to determine if this carbon-carbon coupling reaction is structure sensitive and how it is related to the cation environment.

Specific objectives include:

- *Determine if the $Cp_2MM(CO)_4$ ($M=Mo, W$) complexes lead to dimers on the surface of silica and the other supports.*

• Study the carbonyl coupling reaction under stoichiometric and catalytic conditions and determine the factors that control the activity of the supported dimers for this reaction.

• Subject the monometallic and bimetallic systems, with similar structures, to the same reactions to determine how the oxidizing ability of the cations alone, and in pairwise combinations, and how the different oxygen ligands of the oxide affect selectivity and activity in oxidation reactions.

• To the extent that uniform oxidation states can be realized for the supported cations through photoreduction and complex decomposition, determine the effects of oxidation state on the initial activity and selectivity of cations in carbon-carbon coupling reactions.

One of our goals was to prepare and explore the catalytic properties of reduced metal cations. Reduced metal cation catalysts have been used in a variety of reactions including methathesis [51-55], isomerization [56], and polymerization [57]. Reduced metal cations supported on metal oxides are usually formed from fully oxidized samples by thermal reduction or photoreduction. Thermal reduction in hydrogen typically leads to cations with a range of oxidation states [58-62]. We have explored preparation and reduction methods that lead to cations in discrete oxidation states and with uniform composition. We published two papers that document the use of $M_2(CO)_n Cp_2$ ($M_2 = MoMo, WW, MoW$; $Cp = C_5H_5$; $n = 4, 6$) complexes to attach metal dimers on silica that feature a metal-metal bond for cations in the 4+ oxidation state [63,64]. Since surface structures with dimeric metal centers are potentially different catalytically from those containing only isolated metal centers, we were motivated to investigate the properties of the surface species from $Cp_2 M_2(CO)_n$. We also studied photoreduction as a means to generate isolated, reduced cations [65-67].

The attachment process, during which the Cp ligands undergo an exchange reaction with the support hydroxyl groups to form cyclopentadiene and M-O-Si bonds, and the carbonyl ligand desorption process, during which the cations are oxidized from the 1+ to the 4+ oxidation state, have been characterized. We used infrared (IR) spectroscopy to follow the attachment and carbonyl ligand removal process [63]. The bridging carbonyl stretching modes for the dicarbonyl dimers are retained after the Cp ligands have reacted with silica hydroxyl groups revealing that the dimer character of the complex is retained. The carbonyl ligands desorb by 500 K; the IR carbonyl modes simply attenuate and no intermediate structures are discernible. We have also collaborated with B. C. Gates on extended X-ray absorption fine structure (EXAFS) spectroscopy studies of W both before and after removal of the carbonyl ligands. The EXAFS studies are ongoing and we do not yet know the structures before ligand removal. Figure 1 presents top and side views of how the $W_2(CO)_4$ dimer could be bound to the silica surface. The silica surface is modeled as a β -cristobalite (111) surface [68-70]. The dimer sits away from the surface and we were able to accommodate it on the surface without changing any bond lengths or bond angles in the cristobalite surface. We are currently using the $M_2(CO)_4$ and $M_2(CO)_6$ dimers in hydrodesulfurization studies (see below).

Following attachment and carbonyl ligand removal from cyclopentadienyltungsten dicarbonyl dimer, $W_2(CO)_4 Cp_2$, the EXAFS data showed that there were W-O bonds with lengths of 1.96 Å and 2.26 Å, and are consistent with W-W interactions at an average length of 2.96 Å. Figure 2 presents a side and top view of how the W dimer structure could be bound to the silica surface. We looked for locations where the tungsten dimers could be situated that would satisfy the 4+ oxidation state and the bond lengths determined by EXAFS. In order to include four W-O bonds, it was necessary to allow tungsten to bond to some subsurface oxygen atoms with oxygen to silicon bonding being lost in the process. In order to satisfy the bond length determined by EXAFS, it was necessary to assume that some tungsten-bound oxygen atoms were shifted slightly

Geometry of Attached Metal Dimer

Figure 1. Diagram of attached tungsten-carbonyl dimer. (Carbonyl ligands not shown.)

Model Silica Surface

Attached Tungsten Dimer

Figure 2. Diagram of model silica surface and attached tungsten dimer.

from the β -cristobalite geometry. The result shows a tungsten dimer that is located in the surface layer, not atop the surface.

We also performed an extensive series of reductive carbonyl coupling experiments over the MoMo, WW and MoW dimers. We were interested in determining if reductive carbonyl coupling could be used to probe the presence of metal dimers, if the coupling reaction proceeded by a μ -alkylidene intermediate, and if the reaction could be made catalytic. The key findings have been communicated [64]. We find acetaldehyde and acetone will reductively couple to produce *cis*- and *trans*-2-butenes and 2,3-dimethyl-2-butene, respectively. The results of our study establish the value of this molecular probe for dimer structures.

Diolates formed as intermediate products during the coupling reaction.

Two possible mechanisms are suggested, one that involves ketyl radicals and the second that involves carbonyl dianions [71-73]. We did not study the mechanism. Infrared bands were observed at 2929, 2925, and 2859 cm^{-1} that correspond to $\nu_{\text{asy}}\text{CH}_3$, νCH , and $\nu_{\text{sy}}\text{CH}_3$, respectively for the 2,3-butane diolate formed from acetaldehyde. The hydrogens on the methyl groups for the acetone reductive coupling intermediate, 2,3-dimethyl-2,3-butanediolate, were not equivalent, resulting in the appearance of three C-H stretching frequencies at 2977, 2939, and 2891 cm^{-1} that are assigned to A'_{asy} , A'' , and A'_{sy} of CH_3 , respectively.

We had hoped the coupling would proceed by the μ -alkylidene complex route Chisholm and coworkers [74-76] found over ditungsten(IV) hexalkoxides.

Were such an intermediate formed on our supported systems, we would have used them to study reactions and infrared modes of different μ -alkylidene structures because of the relevance alkylidenes have as intermediates in Fischer-Tropsch synthesis [77].

The reductive coupling reaction over the dimer structure is stoichiometric; the metal center is oxidized to the 6+ oxidation state while the aldehyde/ketone is reduced. Oxidation destroys the metal-metal bond and the template for the coupling reaction. This oxidation process is irreversible and it is not possible to reform the metal-metal bond during subsequent reduction. Reductive carbonyl coupling requires a site that is able to release four electrons, i.e., change four oxidation states. The Mo(IV) or W(IV) dimer template satisfies this criteria. We were also able to show that isolated Mo(II) would serve as a reaction center for the coupling reaction [64]. Knowing this we set about to determine if the coupling reaction could be made catalytic over a supported oxide that was more reducible than Mo or W. Photoreduction studies with CO over Cr(VI) revealed that Cr(II) could be formed readily by either photoreduction or by thermal reduction in CO at 450 $^{\circ}\text{C}$. This high temperature is ideally suited to the temperature we used to form the butenes during coupling over Mo or W. We examined the production of butenes during continuous delivery of

acetaldehyde over prereduced and fully oxidized chromia on silica, and over fully oxidized chromia in the presence of CO and in the presence of CO and ultraviolet light illumination. We also tried to couple benzaldehyde to stilbene in a catalytic cycle using heat and CO, or UV light and CO to regenerate the active center. There is no clear evidence that the reaction is catalytic or could be made catalytic over silica-supported metal oxides.

We continued and completed our study of methods to prepare cations in discrete oxidation states and with known structures by studying the photoreduction of W(VI) and Cr(VI) on silica [66,67]. We had studied the photoreduction of Mo earlier [65]. Our studies reveal both similarities and differences for these three cations when photoreducing them at room temperature in ~760 Torr of CO using a 100-W mercury arc lamp. Each cation forms multiple carbonyl structures that we assigned by using ^{13}C and ^{18}O labeled CO. Figure 3 summarizes the results. In some cases these carbonyl structures coexist on the surface, which complicates the assignment of bands and illustrates that simple band position is a poor diagnostic of oxidation state over metal oxides. Mo and W are photoreduced to the 4+ oxidation state. Cr is photoreduced to the 2+ oxidation state. The rates of reduction varied considerably, with the relative rates being 1, 0.1, and 0.02 sites reduced/time for Cr(VI), Mo(VI), and W(VI), respectively. A meridional tricarbonyl formed with each cation and each can be accommodated on the β -cristobalite surface.

We explored photoreduction as a way to prepare isolated W and Mo in the 4+ oxidation state and compare their catalytic properties against the dimers that also featured metals in the 4+ oxidation state. Propylene metathesis was run over silica-supported molybdenum and tungsten oxide catalysts to determine the dependence of oxidation state and coordinative structure upon catalytic activity. The oxidation state of the supported metal cation had the largest effect with Mo(IV) being the most active. There exists an extensive literature on methathesis over Mo and our work agrees with the findings of Kazansky [55]. We did find that there was a direct correlation between the amount of W(VI) photoreduced to W(IV) and the metathesis activity [78]. We were most interested in determining if the dimer structure altered the activity or selectivity for the metathesis reaction for that observed over the isolated 4+ structures. No dependence of the catalytic activity upon coordinative structure was found.

Our final studies involved characterizing the structure of W(VI)/SiO₂ using Raman spectroscopy. These results were recently communicated [79]. The studies with W parallel our previous work with Mo. The preparation method exerts a strong influence on dispersion of the surface tungsten oxide species on SiO₂. Supported W(VI) contains crystallites of WO₃ when aqueous preparation methods [(NH₄)₆H₂W₁₂O₄₀] are used and it does not contain crystallites when nonaqueous methods [W(η^3 -C₃H₅)₄] are used. The surface tungsten oxide species under ambient conditions possess polytungstate clusters, W₁₂O₄₂¹²⁻, on the silica support. Upon dehydration at elevated temperatures the hydrated polytungstate clusters decompose and interact with the silica support forming isolated, octahedrally coordinated tungsten oxide species. These tungsten preparations were used in oxidation studies (see below).

To date the key contributions of our work have been the development of means to disperse and stabilize Mo and W cations on silica at high loadings without crystallite formation [79-81], an explanation of factors that control and supported Mo and W structures [80,82], a detailed exploration of photoreduction of the Group VIa cations (Cr, Mo, and W) and assignment of their carbonyl bands to various reduced structures [65-67], and attachment and characterization of dimers that feature metal-metal bonds [63,64].

Figure 3

CURRENT PROJECTS

One of the objectives of the current program was to study olefin oxidation over Mo(VI) and W(VI) oxides supported on various supports. We are particularly interested in the role of oxo oxygens ($M=O$) and bridging oxygens ($M-O-M'$; $M=Mo, W$; $M'=M, Si, Al, Ti, Zr$) in catalytic reactions, and the synergism between cations with different redox characteristics such as Mo and W in hydrocarbon oxidation. Depending on the support and loading, it is possible to prepare supported oxides that consist of one or more of the following structures: isolated cations, $M-O-M$ ($M=Mo$ or W) bridged cluster structures, and crystallites [83-87]. Silica and alumina do not have labile support oxygen, whereas titania and zirconia have labile support oxygen thereby permitting a study of support-oxygen lability in olefin oxidation. This concept of support-oxygen lability can be found in a study of methanol oxidation over vanadia and molybdena supported a variety of supports, where the structures are documented on each support and the oxidation activity was found to increase with increasing reducibility of V or Mo the support [32-34,37,88]. Ono et al. [89] have also seen ethanol oxidation activity to increase for molybdena supported on various supports; however, different molybdena structures and crystallites were present simultaneously and their interpretation is incomplete. Some authors have suggested $M=O$ can be influenced by the support [89a,89b] and this could be a contributing factor to the different activities. Kim et al. find no effect of the $M=O$ bond and suggest cation reducibility is most important [32]. The role of $M-O-M'$ bonds in oxidation catalysis is unclear at present.

We are studying oxidative dehydrogenation of 1-butene to butadiene and 1-butene isomerization to *cis*-2- and *trans*-2-butene. Preliminary experiments with butane oxidation revealed that the activity of Mo and W was too low for this reaction in comparison to the activity of the supports. Alumina, zirconia and titania supports are more active than preparations containing low Mo or W loadings and cannot be used to explore the effect of support oxygen in the oxidation reaction. This likely stems from the ability of these supports to act as Bronsted acids and provide an additional oxidation channel to the olefins. Our studies of oxidation and isomerization are ongoing and their analysis is incomplete. The studies over silica reveal that the redox properties of the cation play the dominant role in oxidation activity but not in isomerization reactions.

The oxidation of 1-butene was studied in flow reactor at temperatures ranging from 473 to 773 K and 1 atm of gas (1.6% 1-butene, 1.6% O_2 , balance He). The products of this reaction are *cis*-2- and *trans*-2-butene, 1,3-butadiene, CO and CO_2 . We checked to determine that the reactions were catalytic. Figures 4-6 are representative of the results over the temperature range 443 to 773 K. Figures 4 and 5 present the rate of butadiene formation on a per unit area basis and illustrate several points. Figure 4 demonstrates the background activity of Al_2O_3 , ZrO_2 and TiO_2 , and that the activity over SiO_2 increases with the amount of Mo present. Figure 5 demonstrates that the rate does not increase appreciably beyond the activity of Al_2O_3 until the monolayer Mo limit has been reached beyond which MoO_3 crystallites are also present. MoO_3 crystallites are also present for the 10 wt % Mo/ SiO_2 sample (Figure 4). The turn over number (TON) for butadiene formation is similar for samples containing crystallites on both Al_2O_3 and SiO_2 .

Figure 6 presents the rate of butadiene formation per Mo site. The samples with the "org" designation were prepared by non-aqueous methods, consist of isolated Mo(VI) octahedra and do not contain crystallites of MoO_3 . The 1.72 and 4.21 wt% Mo samples contain MoO_3 crystallites and isolated Mo(VI) octahedra. When compared on a per Mo basis at these low loadings, the isolated cations appear to be slightly more active than the crystallites. At higher loadings, 10 and 15 wt% Mo, the activity per site is comparable to the activity of the lower loading preparations. The lower activity for 15 wt% Mo could be caused by larger crystallite size and thereby reduced utilization of the Mo.

The selectivity changed with loading and preparation method. For example at 650 K the conversion of 1-butene was 18, 22, and 57 % over the 4 wt%-org, 4.2 wt%, and 15 wt% catalysts, respectively. Of the amount converted, 70, 80 and 50 % went to the 2-butene isomers for the 4 wt%-org, 4.2 wt%, and 15 wt% catalysts, respectively, with the balance going to butadiene or CO and CO₂. These results reveal that the crystallites lead to more oxidative dehydrogenation and more complete oxidation of 1-butene. During the course of these studies we noted that at a sufficiently low temperature only isomerization occurred and that lower temperatures were required to reach this condition if large MoO₃ crystallites were present.

To get a better sense of the oxidation/isomerization selectivity we have begun to study the 1-butene/O₂ mixture at much lower temperatures than are shown in Figures 4-6 over W, Mo, and Cr catalysts supported on silica. As might be expected, the temperature for the onset of oxidation decreases with increasing ability of the cation to be reduced. We see CO₂ and butadiene over Cr/SiO₂ at 500 K (and very little isomerization). The onset for oxidation is 575-600 and 625-650 K for Mo and W, respectively. The onset for oxidation over the 15 wt% Mo/SiO₂ sample was 500 K. Quite unexpectedly, the activity for 1-butene isomerization is approximately one order of magnitude higher over W than over Mo on a per site basis.

This last observation is particularly intriguing. The mechanisms for isomerization and oxidation have been reviewed [17,90,91]. Isomerization over the silica supported systems most likely proceeds by hydrogen transfer to form an allylic intermediate. The manner by which this hydrogen transfers and the site to which it transfers is unknown. An adaptation of the general scheme shown by Kung would be

for Mo(VI), during which the metal center is reduced by one oxidation state and the hydrogen transfers as a proton to an oxygen anion. Clearly this is inconsistent with our results since W is more difficult to reduce one would not expect it to have a TON that is almost 10 times greater than Mo. Another pathway for hydrogen abstraction has been proposed. Weber [92] has reasoned that C-H abstraction from the methoxy methyl group involves a transfer to the metal not to the metal-support oxygen bond, and that it is more hydride-like than proton-like in character. We have not yet developed a reason for increased W isomerization activity.

We are continuing to study the isomerization and oxidation reaction. We will also use IR spectroscopy to establish that the allyl forms and to see how the hydroxyl modes change near the temperature where oxidation is observed.

We have initiated a study of hydrogenation reactions over the reduced metal samples. Recall that we can generate isolated cations in the 2+ and 4+ oxidation states and dimers in the 1+ and 4+ oxidation state. The isolated cations and the 4+ oxidation state dimers are coordinatively unsaturated while the 1+ oxidation state dimers have carbonyl ligands to stabilize the structure. We were motivated to study this chemistry because hydrogenation and hydrogenolysis play central roles in hydrogen consumption and selectivity during HDS and HDN catalysis.

The hydrogenation results are summarized below. Briefly, we find that dimers in the 1+ oxidation state are able to convert thiophene into a mixture of C₄ thiols, butenes and butanes, along with an extremely small amount of propylene, propane, ethylene, and dimers in the 4+ oxidation state convert thiophene to n-butane. We have not yet tested for the formation of H₂S and intend to do so. The 1+ oxidation state dimers also convert butanethiol into a mixture of n-butane and

Fig 4. Butadiene formation

Fig 5. Butadiene formation over Mo/Al₂O₃ catalysts

Fig 6. Butadiene formation per mole of Mo
over Mo/SiO₂ catalysts

iso-butane (10:1 n-butane:iso-butane). Infrared studies of the dimer structures indicate that the thiophene will react as long as the carbonyl ligands remain bound to the Mo.

Figure 7 presents the cumulative C₄ hydrocarbon products formed when a 2% thiophene in H₂ mixture flowed continuously at 450 K over a sample prepared from [CpMo(CO)₃]₂. At these conditions the CO ligands will slowly desorb so the decay in production could be related to the loss of carbonyl ligands or it could be due to a change in the oxidation state of the Mo. C₄ thiols were produced at roughly twice the rate as the hydrocarbons. Butanethiol has been identified and other thiols also form. The integrated amount of C₄ hydrocarbons and thiols formed during the experiment shown in Figure 7 correspond to 6 and 13 % of the Mo, respectively. We will determine if the reactions are catalytic. When thiophene and He are passed over the Mo¹⁺ dimer, a similar mixture of C₄ products forms but with a lower percentage of butane.

Figure 8 presents the results of passing thiophene and He over Mo⁴⁺ dimers at 400 K. Interestingly, essentially only n-butane formed. The integrated amount of butane during the 900 min corresponds to 1 % of the Mo present. The results in Figures 7 and 8 clearly show oxidation state has an effect and we will study this further.

These studies will continue during the remainder of the current grant. Several immediate questions we will address include the role of carbonyl ligands (Mo is singly bonded for the hexacarbonyl and triply bonded for the tetracarbonyl) on the rates of conversion, the effect of dimer oxidation state, and the effect of hydrogen pressure on the selectivity to butanes and butenes during thiophene reactions.

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Figure 7. Thiophene over $[Mo(+1)]_2$

Figure 8. Thiophene over Mo(IV)

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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).

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

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Students Supported and Degree Dates

1987 Shiaw C. Tseng (PhD)	Isosynthesis Reactions of CO/H ₂ over Zirconium Dioxide
1989 Ronald G. Silver (PhD)	A Study of Active Sites for Isosynthesis Over Zirconium Dioxide
1990 Nancy B. Jackson (PhD)	CO Hydrogenation over Zirconium-Based Metal Oxides
1990 Clark C. Williams (PhD)	Synthesis, Characterization, and Reactivity of Oxide-Supported Molybdenum Oxide
1993 Ryan D. Roark (PhD)	Synthesis and Characterization of Silica-supported Molybdenum and Tungsten
1993 Steven D. Kohler (PhD)	Characterization of and Reactions over Photoreduced Transition Metal Oxides Supported on Silica