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ENERGY CONVERSION AND UTILIZATION TECHNOLOGIES PROGRAM

Heterogeneous Catalysis
Modeling Program Concept

G E. Voecks

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ABSTRACT

Insufficient theoretical definition of heterogeneous catalysts is the major difficulty confronting industrial suppliers who seek catalyst systems which are more active, selective, and stable than those currently available. In contrast, progress has been made in "tailoring" homogeneous catalysts to specific reactions because more is known about the reaction intermediates promoted and/or stabilized by these catalysts during the course of reaction. However, modeling heterogeneous catalysts on a microscopic scale requires compiling and verifying complex information on reaction intermediates and pathways. This can be achieved by adapting homogeneous catalyzed reaction intermediate species, applying theoretical quantum chemistry and computer technology, and developing a better understanding of heterogeneous catalyst system environments. Such a total effort is beyond the scope of non-unified universities' research and must also involve an understanding of catalyst preparation and practical experience peculiar only to industry. Research in microscopic reaction modeling is now at a stage where computer modeling, supported by physical experimental verification, could provide information about the dynamics of the reactions that will lead to designing supported catalysts with improved selectivity and stability. Industrial users agree that efforts to find catalysts which will reduce energy consumption and meet the requirements of various future feedstocks must be accelerated as conventional fuels become increasingly scarce and expensive to use.

CONTENTS

SECTION I

INTRODUCTION

A catalyst is a chemical species which, upon entering into a chemical reaction, reduces the energy required for reaction initiation (activation energy) and directs the pathway or mechanism by which the reaction proceeds to give selective products. The ability of catalysts to reduce "activation energy" has led to their application in virtually every commercial petrochemical process, ranging from the production of hydrogen for reactant feedstock to the synthesis of ammonia, polymers (and their building blocks), and fuels. The use of catalysts results in energy savings in both feedstock requirements and process plant operation. Historically, these catalysts have been primarily heterogeneous (i.e., supported on solid materials) because of simplifications in reactor design, with only limited use of homogeneous (i.e., dissolved within reactants) catalysts. The modifications made through the years have been slight and based mainly on necessary adaptations for the particular feedstock available, i.e., petroleum and natural gas. But advancements have been limited by the lack of a understanding of the catalyst function and gas/surface interactions. As feedstocks continue to change due to dwindling oil and gas reserves, industry will be forced to use those derived from coal, shale, and even waste by-products. Hence future feedstock flexibility and economy are dependent upon the development and enhancement of catalysts.

Some improvements in commercial catalysts have recently been made. Industry has developed new supports that are less inhibiting to the catalyst and more stable under reaction conditions. Also, new preparation techniques have been developed based upon a better understanding of catalyst/support interaction. These advances provide a large experimental data base, which is proprietary to a great extent. Advances in surface science have also resulted in better characterization of the supported catalyst under controlled conditions. Academic grants from National Science Foundation (NSF) and Department of Energy/Basic Energy Science (DOE/BES) have supported surface science exploration and fundamental theoretical studies of the chemistry involved in transition metal catalysts to provide better microscopic detail of the sequence of reaction steps under controlled conditions.

While new information and scientific advancements have resulted in a better fundamental understanding of catalysis and more stable industrial catalysts, the key element -- specific catalyst system design for a given process based on the total catalyst system characteristics and behavior -- is lacking. The ability to design a specific catalyst for a particular reaction system is essential in order to enhance the catalyst activity and specificity that will be required to deal with future changing feedstocks and the demand for higher efficiency. This requires detailed understanding of the role of the heterogeneous catalyst "system"; i.e., the supported catalyst, the support, and the gas/solid interaction.

In order to take advantage of what has been learned in basic chemical research under NSF, Petroleum Research Foundation (PRF), DOE/BES, and other

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auspices, as well as the industrial expertise in actually making and using catalysts, a "middle ground," i.e. design phase must be firmly established. Catalyst modeling or designing would combine information and expertise generated in both academia and industry and would take advantage of other recently developed tools, including computers, and atomic/molecular approaches to chemical modeling.

Modeling of catalysts is an immense undertaking at first glance. Initially it depends upon fundamental research from which to draw information on the atomic-level interactions of the catalyst and reactants. It also would necessarily include an investigation into the effects of the support and feedstock on the catalyst and reactants. Typically, industry does not become involved in catalysis at this theoretical level because the risk is high and the payoff is long-term. Because of the broad areas of expertise and knowledge that a modeling endeavor would cover and the wide-ranging impact this effort would have, federal support and participation are necessary. Combining research information from academic efforts with the industrial experience in catalyst formulation is needed to develop, through computer modeling, a more realistic and accurate description of catalyst behavior in chemical reactions. The modeling of catalysts would involve the use of computers to treat the catalyst and its environment as though it were functioning under industrial operating conditions by introducing basic electronic perturbations that would simulate what has been observed in fundamental research. Derived theoretical operation of the catalyst would be compared to actual catalyst performance and characterization, thereby creating an interactive development of the model with the catalyst system function.

Heterogeneous catalysis, although considered a mature technology, is immature in many respects because the desired catalyst performance, i.e. activity and selectivity, is not achieved commercially without overdesign in catalyst type and amount and commonly suffers from limited durability. To date, research in the area has taken two directions -- a basic search pursued by academia for the atomic-level parameters that control a given reaction and a practical search by industry for the factors that meet the formulation, preparation, stabilization, and lifetime demands of catalysts. The ultimate goal has yet to be achieved of designing a catalyst to give ideal product yield and specificity from specific reactants at nearly ideal operating conditions (i.e., temperature, pressure, residence time). This failure to achieve more nearly ideal catalyst design specifications results from the lack of assemblage of the necessary information which would accurately describe (1) what occurs at the catalyst site and (2) what is necessary in catalyst preparation to generate the proper operational environment and control.

Over the past several years, basic research has been funded at universities to determine how heterogeneous and homogeneous catalysts operate. Progress has been made in both areas, but more so with homogeneous catalysis primarily because a highly controlled catalyst environment can be maintained which permits reaction sequences to be followed with great accuracy. Heterogeneous catalysis has received a great deal of attention because of its broad application in industry. More information on surface reactions has been gathered over the past ten years as a result of new developments in surface science instrumentation (ESCA, Auger, LEED, STEM,

EXAFS). However, the atomic-level description of the electronic interactions which are responsible for the bond breaking and forming that result in the observed products and catalyst activity is still not available. Similarly, there is still no method for formulating and preparing a catalyst for a specific activity to achieve the most energy-efficient process; despite advances which industry has made over the past 15 years, the technical knowledge required to move ahead into precise catalyst design is immense.

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SECTION II

APPROACH

The development of microscopic reaction models on computers would be the first step in a model-based design process. The development of such a model for a catalyst system would serve as a bridge between microscopic mechanistic research (experimental and theoretical) and in vitro reaction models. The microscopic reaction model would describe the <u>dynamics</u> of the various chemical processes that are involved when specific molecules react with the catalyst surface and with each other. The surface would be defined theoretically to provide a variable distribution of surface sites, including both the catalyst surface and the support. The catalyst surface may initially be defined as an atom, but, depending on the system, may vary from monatomic species to crystalline particles with accompanying variations in crystal face composition. Within the constraints of the above distribution, a unit cell of up to 1000 catalyst surface atoms may be constructed (with periodicity leading to an infinite surface).

The interactive forces on the various molecules and catalyst intermediates during a reaction can be calculated from the electronic wave functions of an interactive system. Theoretical calculations of potential surfaces for prototype systems (a particular absorbate interacting with a particular surface site or two absorbates interacting with each other), when reduced, could result in two-body force fields for rapid computation of the forces on various molecules and fragments as they impinge upon, exchange energy with, and react with a surface. (The information for these fundamental interactions would come mainly from theoretical calculations of potential surfaces.) Force fields are often used for empirical calculations of geometries and energetics for hydrocarbons. However, the parameters in these methods are based on equilibrium structures, whereas the chemistry is dominated by regions near transition states for the various reactions. Consequently, these parameters cannot be used to consider breaking and forming covalent bonds such as in those cases that are essential to advance microscopic reaction modeling to a useful stage. In addition, for the systems of interest to catalysis, not enough experimental data are available to determine the force fields which are basic to this model. An alternative approach is to first determine directly from ab initio calculations the nonbonded interactions that are responsible for steric interactions determining the conformations of molecules. Then, the directed valence bond terms obtained from a combination of theoretical and experimental data would be added to these calculations. (Theory would provide the overall shape; experiment would provide additional information on the exact bond energy and vibrational frequency, where available.)

Initially, the dynamics would be considered by classical trajectories using critical point-sampling techniques. For a practical microscopic model, the incorporation of wavepacket methods would be beneficial to allow the consideration of groups of trajectories at a time. At any one instant, only surface atoms interacting most strongly with the adsorbates and reactant modes would be considered in the dynamics. Energy transfer to and from the other

atoms would be described by modifications (simplification) of the Langevin or response function formalisms.

Initial work would concentrate on developing the various techniques (e.g., force fields, dynamics) required in a practical microscopic reaction model. Subsequently, this model would be used to examine the processes for reactions about which mechanistic data is available. In the second phase, it would be critical to use a graphics system to monitor the progress of the various intermediate steps throughout a reaction.

In order to develop microscopic reaction modeling, a catalyst system should be chosen that can be handled computationally as described above but which also can be experimentally tested. The modifications to the catalyst system would be treated realistically in the model and measured in supporting experiments. The experimental information would be interpreted and translated into accurate theoretical models for use in the characterization of catalysts. The key element of this approach would be to develop initial theoretical models that are based on measured experimental details from relatively well-understood homogeneous reaction systems.

SECTION III

TECHNICAL PROGRAM DESCRIPTION

Early efforts in a catalyst modeling program would deal with the development of computer models that could theoretically describe homogeneous catalyst systems and subsequently be modeled and tested for heterogeneous catalysis. The catalysts systems chosen for modeling would be atomic in nature and supported in the same manner as a typical heterogeneous catalyst. Specific catalysts and reactions would be selected for this initial modeling effort with focus upon: (1) the model approach, (2) the catalyst to be used as a model, (3) the reaction to be modeled, and (4) the support and interaction necessary.

An example of modeling development is presented below with a description of work being conducted by Dr. W. Goddard of Caltech. His work illustrates how microscopic modeling can provide a basis for understanding and predicting catalyst behavior.

Several workers have shown experimentally that high oxidation state group VI systems (e.g., WCl_6) can catalyze metathesis of alkenes[1,2,3] under proper conditions. The mechanism of metathesis involves a metal carbene as the active catalyst and involves formation of a metallacycle intermediate,[3,4] illustrated here with labeled carbons;

$$ (1) $$
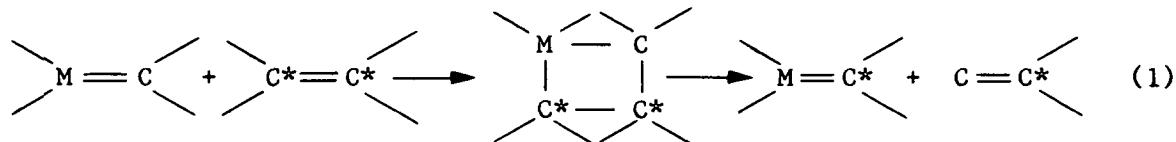
However, from thermodynamic calculations of gas phase species, the formation of the metallacycle intermediate is not favored for normal Cr(VI) and Mo(VI) carbenes,[5]

$$ \Delta G_{300} = +25 \text{ kcal mol}^{-1} \quad (2) $$

$$ \Delta G_{300} = +15 \text{ kcal mol}^{-1} \quad (3) $$
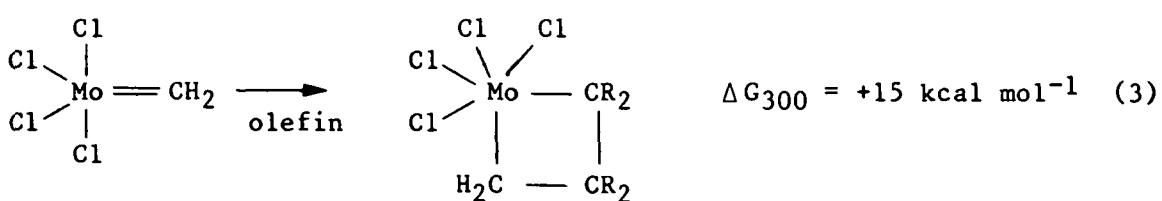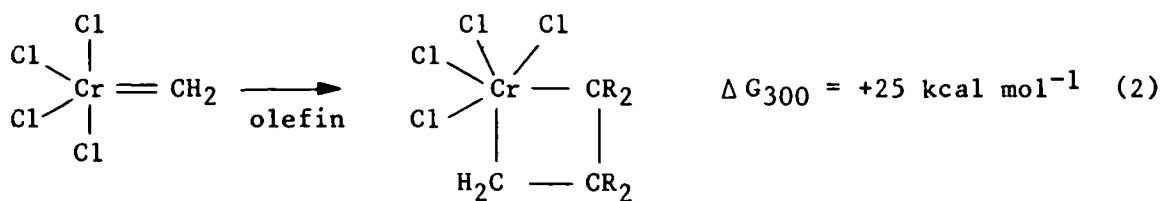
On the other hand, in related Cr(VI) and Mo(VI) systems, carbene species also containing a double-bonded metal-oxygen (metal-oxo) bond are thermodynamically favored to go through the facile formation of metallacycle butane intermediates (without side reactions involving metallacycle oxetane intermediates),

$$
\begin{array}{c}
\text{Cl} \diagdown \quad \diagup \text{O} \\
\quad \text{Cr} \\
\text{Cl} \diagup \quad \diagdown \text{CH}_2
\end{array}
\xrightarrow{\text{olefin}}
\begin{array}{c}
\quad\quad \text{O} \\
\quad\quad \| \\
\text{Cl} \diagdown \quad \\
\quad \text{Cr}\!-\!\!-\!\text{CR}_2 \\
\text{Cl} \diagup \quad | \quad\quad | \\
\text{H}_2\text{C}\!-\!\!-\!\text{CR}_2
\end{array}
\quad (4b)
\qquad \Delta G_{300} = -20 \text{ kcal mol}^{-1} \quad (4)
$$

(4a)

$$
\xrightarrow{\text{olefin}}
\begin{array}{c}
\text{R}_2\text{C}\!-\!\!-\!\text{CR}_2 \\
\quad | \quad\quad | \\
\text{Cl} \diagdown \quad \\
\quad \text{Cr}\!-\!\!-\!\text{O} \\
\text{Cl} \diagup \quad \| \\
\quad\quad \text{CH}_2
\end{array}
\quad (5)
\qquad \Delta G_{300} = +12 \text{ kcal mol}^{-1} \quad (5)
$$

$$
\begin{array}{c}
\text{Cl} \diagdown \quad \diagup \text{O} \\
\quad \text{Mo} \\
\text{Cl} \diagup \quad \diagdown \text{CH}_2
\end{array}
\xrightarrow{\text{olefin}}
\begin{array}{c}
\quad\quad \text{O} \\
\quad\quad \| \\
\text{Cl} \diagdown \quad \\
\quad \text{Mo}\!-\!\!-\!\text{CR}_2 \\
\text{Cl} \diagup \quad | \quad\quad | \\
\text{H}_2\text{C}\!-\!\!-\!\text{CR}_2
\end{array}
\quad (6b)
\qquad \Delta G_{300} = -24 \text{ kcal mol}^{-1} \quad (6)
$$

(6a)

$$
\xrightarrow{\text{olefin}}
\begin{array}{c}
\text{R}_2\text{C}\!-\!\!-\!\text{CR}_2 \\
\quad | \quad\quad | \\
\text{Cl} \diagdown \quad \\
\quad \text{Mo}\!-\!\!-\!\text{O} \\
\text{Cl} \diagup \quad \| \\
\quad\quad \text{CH}_2
\end{array}
\quad (7)
\qquad \Delta G_{300} = +2 \text{ kcal mol}^{-1} \quad (7)
$$
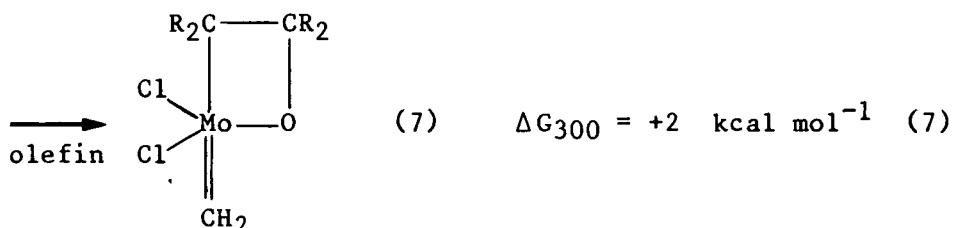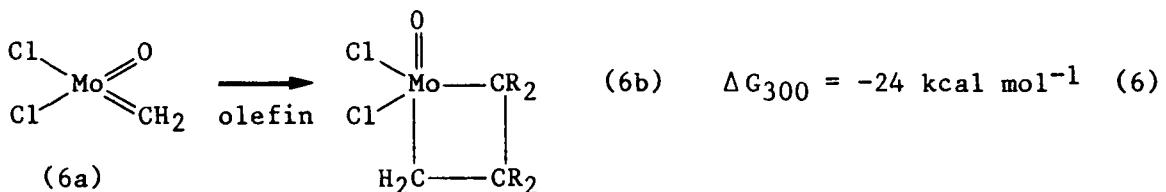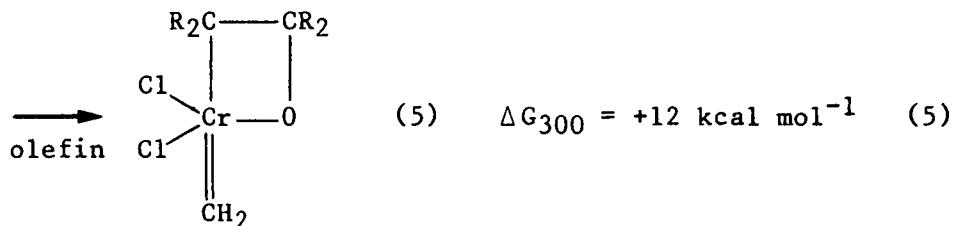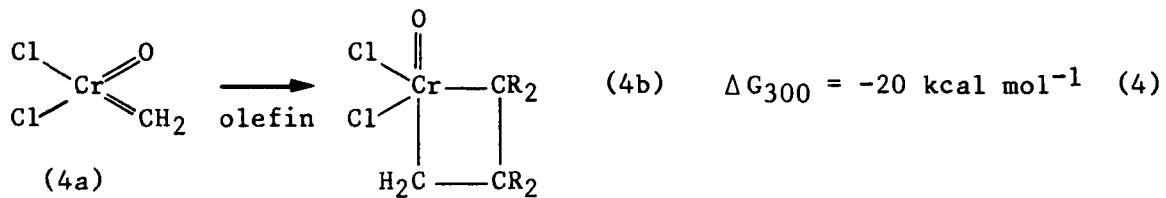
Thus, the presence of a metal-oxo bond drives the preferential formation of the metathesis intermediate, metallacycle butane. The origin of this remarkable difference [(2) to (4) or (3) to (6)] has to do with the character

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of metal-oxo bonds and the change in the electronic environment of the metal, which is a function of the other ligands surrounding it. For species such as

$$\begin{array}{ccc}
\text{Cl}\diagdown \overset{\displaystyle \overset{\text{Cl}}{|}}{\underset{\displaystyle \underset{\text{Cl}}{|}}{\text{Mo}}} \diagup \text{Cl} \!=\! \text{O} & \quad \text{or} \quad & \text{Cl}\diagdown \overset{\displaystyle \overset{\text{Cl}}{|}}{\text{M}} \!=\! \text{O}
\end{array} \tag{8}$$
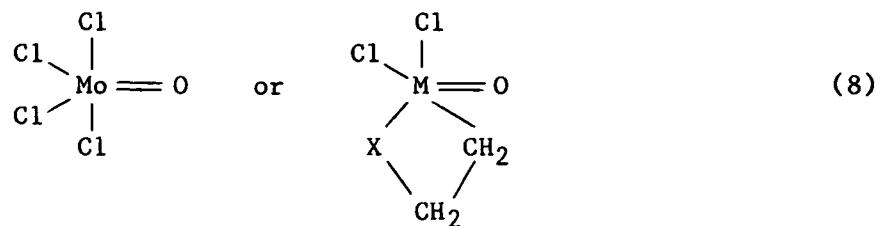
(where M = Cr or Mo and X = O or CH_2), the metal-oxo bond forms an effective triple bond much like that in gaseous CO whereas in species such as

$$\begin{array}{ccc}
\text{Cl}\diagdown \overset{\diagup \text{O}}{\underset{\diagdown CH_2}{\text{M}}} & \quad \text{or} \quad & \text{Cl}\diagdown \overset{\diagup \text{O}}{\underset{\diagdown \text{O}}{\text{Mo}}}
\end{array} \tag{9}$$
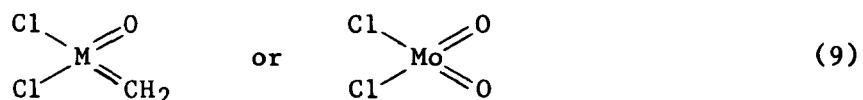
the metal-oxo bond is a double bond much like that in CO_2 or ketones. From calculations of the metal-oxo bond energy of Cl_4MO and Cl_2MO_2, it appears that the M≡O triple bond (8) in the former is 31 kcal stronger than the M=O double bond (9) in the latter when M is Cr, and 23 kcal stronger when M is Mo. Thus, the formation of the metallacycle intermediates (4b) and (6b) is stabilized by ~30 kcal and, by changing the ligands and subsequently the electronic configuration of the intermediate species, an exothermic reaction [(4) or (6)] rather than an endothermic one [(2) or (3)] results.

Aside from the homogeneous catalysis experiments, the principle concerning stabilization of reaction intermediates by spectator oxo bonds discovered in the studies on gas phase metathesis catalysts applies also to surface reactions on transition metal oxides. Consequently, some aspects of the chemistry on molybdate surfaces have been examined. These catalysts are used commercially for selective oxidations, e.g.,

$$H_2C \!=\! \text{CH} \diagup^{CH_3} + 1/2 \ O_2 \longrightarrow H_2C \!=\! \text{CH} \diagup^{HC \,=\, O} + H_2O \tag{10}$$

and ammoxidations, e.g.,

$$H_2C \!=\! \text{CH} \diagup^{CH_3} + NH_3 + \frac{3}{2} O_2 \longrightarrow H_2C \!=\! \text{CH} \diagup^{\overset{N}{\underset{}{\|\|}}_{C}} + 3H_2O \tag{11}$$
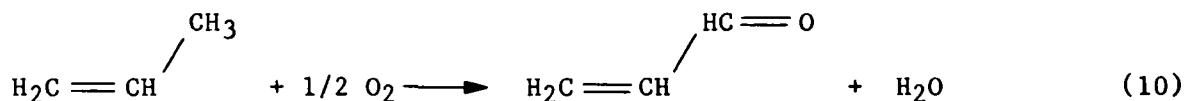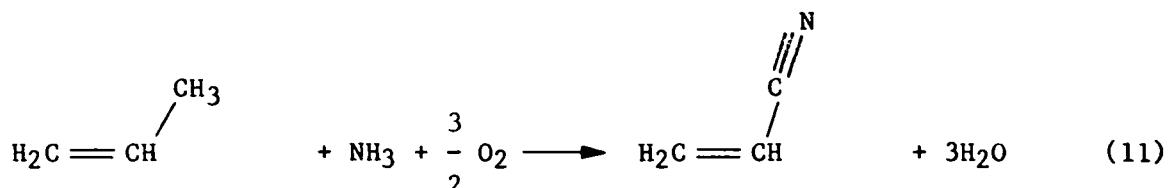
and also for metathesis,

$$2 = * \rightleftharpoons = + * = *$$ (12)

and polymerization of olefins. Thus, with detailed knowledge of the reaction mechanisms, some suggestions could be made on the preparation and operation of these catalysts that might improve the selectivity and rates for commercial processes.

There is considerable evidence that the dominant surface species of molybdate catalysts involve Mo^{6+} centers of the form

$$
\begin{array}{c}
O \diagdown \quad \diagup O \\
Mo \\
O \diagup \quad \diagdown O \\
| \qquad |
\end{array}
$$ (13)

with only a monolayer of Mo sites on the supported catalyst.[6] The bismuth molybdate catalysts have one surface Bi per surface Mo,[7] perhaps connected through an oxide bridge. In selective oxidations (10) and ammoxidations (11), the surface is first reduced (e.g., with H_2 or CO), leading to large concentrations (10 to 30%) of new surfaces species that may have the form[8]

$$
\begin{array}{c}
O \diagdown \quad OH \\
Mo \\
O \diagup \quad \diagdown O \\
| \qquad |
\end{array}
$$ (14)
$$
\begin{array}{c}
O \\
\| \\
Mo \\
O \diagup \quad \diagdown O \\
| \qquad |
\end{array}
$$ (15)
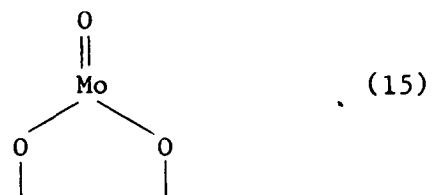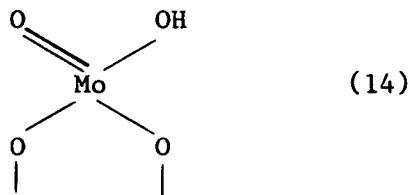
However, as is known from poisoning studies, only a small fraction of the surface (<1%) is catalytically active and the form of this active site is unknown.[9]

In the selective oxidation of propylene (10), it has been established that the initial step (the rate-determining step in some systems) is β-hydrogen abstraction to yield a symmetric π-allyl chemisorbed at the surface.[10-12] Subsequent steps involve transfer of a <u>lattice</u> oxygen[11,13] and dehydrogenation (order not established) to yield acrolein. Reoxidation by O_2 to replenish the lattice oxygen appears to be independent of the reduction site.[11]

Hall and coworkers have shown that addition of cyclopropane to the reduced catalyst leads to four reactions: metathesis, polymerization, hydrogenation, and isotope exchange; and poisoning studies indicate that these reactions involve at least two separate pathways.

10

Based on studies of homogeneous metathesis reactions, the active site for metathesis on the molybdate surface may be the oxo-carbene

$$
\begin{array}{c}
O \diagdown \quad \diagup C - \\
\diagdown\!=\!\diagup \\
Mo \\
\diagup \quad \diagdown \\
O \qquad O \\
| \qquad |
\end{array}
\qquad (16)
$$

This oxo-carbene may be formed on the oxidized surface by activation of the dioxo system using an olefin

$$
H_2C = CHR +
\begin{array}{c}
O \quad O \\
\diagdown\!\diagup \\
Mo \\
\diagup\diagdown \\
O \quad O \\
| \quad |
\end{array}
\longrightarrow
\begin{array}{c}
H_2C - CHR \\
O \;\; | \qquad | \\
\diagdown\; | \\
Mo - O \\
\diagup\diagdown \\
O \quad O \\
| \quad |
\end{array}
\longrightarrow
\begin{array}{c}
O = CHR \\
+ \\
O \qquad CH_2 \\
\diagdown\!\diagup \\
Mo \\
\diagup\diagdown \\
O \quad O \\
| \quad |
\end{array}
\qquad (17)
$$
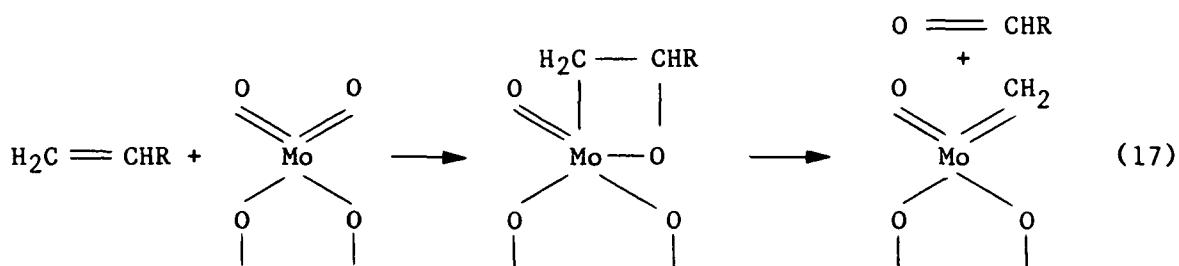
Pathways such as (17) have not been previously proposed, but there already are some experiments consistent with this process. For example, using

$$
D_2C = CH \diagup CH_3
\qquad (18)
$$

Portefaix, et al.,[14] find O=CHR with little contamination of D, and they show that this involves a route different from the one involved in acrolein formations. In this system the oxo-carbene in (17) would promote metathesis but without D exchange.

$$
\begin{array}{c}
D^2C = CHR \\
+ \\
O \qquad CH_2 \\
\diagdown\!\diagup \\
Mo \\
\diagup\diagdown \\
O \quad O \\
| \quad |
\end{array}
\longrightarrow
\begin{array}{c}
D_2C - CHR \\
O \;\; | \qquad | \\
\diagdown\; | \\
Mo - CH_2 \\
\diagup\diagdown \\
O \quad O \\
| \quad |
\end{array}
\longrightarrow
D_2C = CHR \text{ or } H_2C = CHR
\qquad (19)
$$
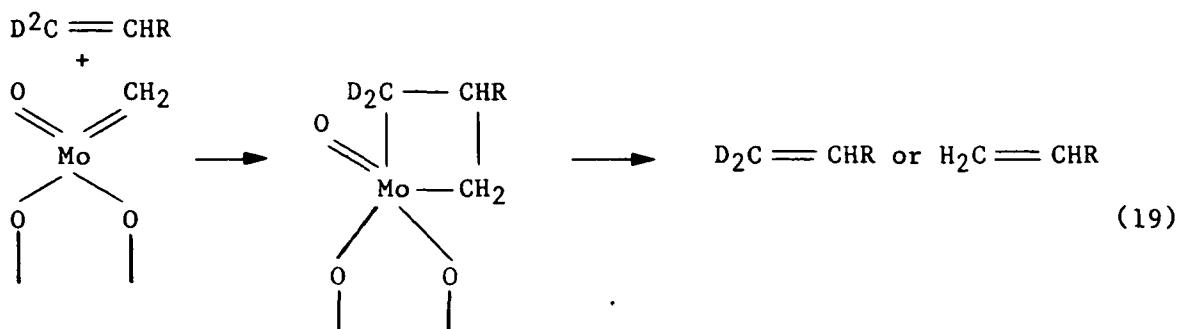
Experimental tests of this hypothesis (17) could be investigated as one part of a program to characterize the catalyst responsible for conversion with theoretical models.

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The metathesis mechanism requires additional detailed knowledge of the chemistry likely to occur for various postulated surface complexes. Current ideas of binding and reaction steps (based on considerable experimental data) would allow the design of a sequence of plausible surface catalyst configurations. Using such surface catalyst configurations, it should be possible to use theoretical methods to establish the likely reactions and important intermediates. In addition, predictions of various measured parameters should allow experimental tests for certain surface species [e.g., vibrational frequencies, chemical shifts of the core levels (from XPS)]. With specific information about the reaction steps, experimental tests (isotope exchange, poisoning, reactant competition) would be conducted to identify the mechanisms operating in supported catalysts. With such understanding of the microscopic basis for the mechanisms, design of improved catalysts would begin to become possible.

In order to design catalysts based on theoretical models, the preparation of catalysts and their characterization must be integrally included. The successful interaction of modeling and experimental work is dependent upon carefully prepared, fully defined catalysts. Iterations between carefully executed experimental preparative procedures followed by a complete and accurate description and characterization of the catalysts before, during, and after reaction will help determine the effect of catalyst preparation on performance and model description. Close cooperative efforts between academia and industry must be developed to establish this link in a program effort.

While the catalysts and models described so far are single, transition metals, these are not the only catalysts to be considered. Preparation of supported single metal atoms or small clusters and metal atom clusters which have metallic characteristics would also be required. Study of both catalyst systems would provide valuable information regarding the role of external catalyst ligands that include (1) unsupported, non-metals such as halides, phosphines, carbonyls, organic fragments, and others; (2) supported metal oxides; and (3) single metals as well as combinations of metals (alloys).

An increasing body of evidence (both experimental and theoretical) points to the modification of collective electronic properties and catalytic behavior when the number of metal atoms in the supported metal cluster decreases into an extremely small size range (diameter < 20 Å).[15] These observations are important when one considers that the major way of maximizing catalyst activity is through the high dispersion of the metal in the form of small metal particles on a support. As the dispersion approaches 1, the number of surface metal atoms approaches the total number of metal atoms present corresponding to the maximum number of catalytic sites. Theoretical calculations, however, indicate that as the metal cluster becomes very small, the electronic properties change dramatically when the band structure of the bulk metal is lost, and the particle attains a pseudo-molecular electronic configuration en route to the atomic state. Considerable controversy exists at present concerning the nuclearity necessary for the onset of a d-band.[16]

Experimental evidence has also been obtained for a drastic modification of the catalytic properties of very small metal particles attached to oxides. Indeed, it has been reported that ~5Å Rh clusters, when supported on silica,

are catalytically inactive and require a preactivation step, apparently involving aggregation, prior to becoming active for arene hydrogenation.[17] Although this behavior may be explained by unfavorable electronic factors giving rise to, for example, associative adsorption rather than dissociative adsorption, it also may be due to the small clusters presenting different crystal faces to the incoming molecules. For example, a 13-atom particle ($\sim$7-Å diameter) exists in an icosahedral arrangement as its most stable form, resulting in only triangular <111> faces occurring, compared with both <100> and <111> faces for the bulk metal. Alternatively, the different activity may be associated with the existence of interstitial carbides or hydrides. Examples of transition metal cluster complexes containing reactive carbidic carbon atoms[18] or hydrides[19] have been established. Without experimental data concerning the electronic properties of these oxide-attached small metal clusters and how they may be affected by interactions with the support (the support effect), this interface region between the atomic and bulk-like metal behavior remains obscure.

Currently, attempts to prepare and isolate oxide-supported small metal clusters (<10 Å) through reproducible means have enjoyed only limited success. Conventional techniques can be divided into salt impregnation and ion-exchange. The former procedure consists of permeation of an oxide support by an aqueous solution of a metal salt (or salts), followed by drying and reduction (usually by hydrogen at high temperature), resulting in aggregation or sintering to produce a metal cluster attached to the support. Ion exchange makes use of the presence of hydroxyl groups on the surface of the silica which can be "ammoniated;" the ammonium ions produced are then exchanged with the desired metal ion(s), as shown below:

$$
\begin{array}{ccccccc}
 & & \overset{+}{NH_4} & \overset{+}{NH_4} & & M^{2+} & \\
OH & OH & O^- & O^- & {}^-O & O^- & (20)\\
| & | \quad NH_3 & | & | \quad M^{2+} & | & | & \\
Si & Si \longrightarrow & Si & Si \longrightarrow & Si & Si & \\
\end{array}
$$
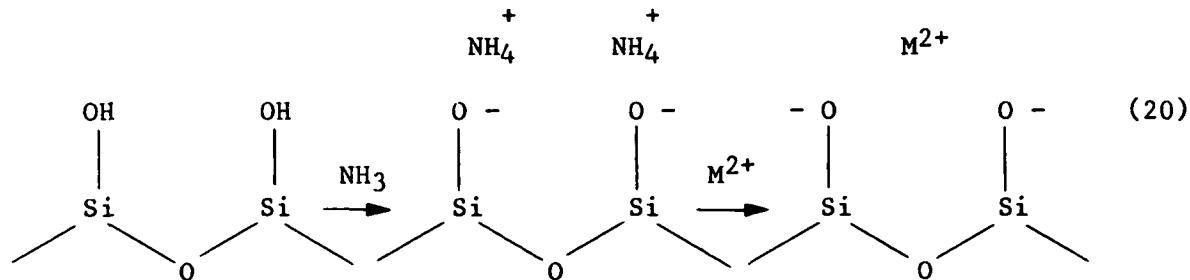
Reduction to the metal atom is followed by aggregation or sintering to generate the silica-supported metal cluster.

Both methods exhibit advantages in ease of preparation and extension of the route to bimetallic or "alloy" catalysts[20], an area of particular interest at present. However, less desirable factors are the relatively large distribution of particle sizes produced, typically 30 to 50 Å, with an average particle size in the range of 20 to 40 Å, depending on the system under study.[4] Through carefully controlled experimental conditions, such as pretreatment of the support or the temperature of reduction, narrower ranges can in some cases be obtained.[4] However, neither method is suited for preparation of very small metal particles (<10 Å).

An equally intriguing route to the desired small, well-defined metal particles is via a preformed transition metal cluster complex deposited onto the surface of the oxide,[21] followed by removal of the stabilizing ligands, allowing extrusion of the metal core. This method has the unique advantage of producing heteronuclear bimetallics of precisely known stoichiometry. However, as yet, its limitation is associated with a degree of aggregation occurring during ligand removal. Careful pretreatment procedures and ligand removal steps will be necessary to achieve the smallest regimes.

The problem of uncontrolled metal aggregation has been encountered in existing approaches to the synthesis of oxide-attached metal clusters by metal atom techniques. This method, devised by Klabunde,[22] involves the co-deposition of the metal vapor with weakly stabilizing organic molecules such as alkanes, toluene, or tetrahydrofuran matrix in the presence of the oxide support, which allows the atoms to aggregate and be deposited on the oxide surface. However, warming from 77° K, tends to produce larger crystallities in the range of 30 to 80 Å for nickel on alumina.

Having considered the problem of producing highly dispersed metals, it may be noted that, for very small metal particles, the required information often is outside the range of sensitivity of normal surface techniques such as electron microscopy or chemisorption . Although high accelerating voltages have led to electron microscopes with resolution of the order of 2 Å, in general the limitation of resolution of a conventional electron microscope is of the order of 10 Å. However, objective imaging has been claimed as a way of observing individual Rh atoms in a supported particle.[23] Thus, electron microscopy is at its lower limit of accuracy for the desired cluster sizes (<10 A), although information regarding rafts versus 3-D particles can be obtained. In recent years there has been an increase in interest relating to EXAFS, which is ideal for obtaining local information for an environment up to 10 Å. Whyman and coworkers[24] have shown that highly dispersed ruthenium (<20 Å) reveals different coordination shells, as determined by the metal-metal vectors in the small-size regime. This indicates that important information regarding small metal clusters may be probed by using this local environment method. Use of secondary ion mass spectrometry (SIMS) for supported metal particles should produce information concerning metal-support interactions, although such studies are presently at an early stage.

Reflectance vibrational spectroscopies have proven valuable for determining information (in particular regarding the molecular integrity) of transition metal cluster carbonyl complexes supported on oxides, via the $\upsilon(CO)$ region. However, extrusion of the metal cone to yield a "real" supported catalyst removes the handle in the form of the CO stretch. Primet and co-workers[25] have viewed the adsorption of NO on such a bare Pt cluster and demonstrated a size dependence on the strength of interaction of the NO as measured by $\upsilon(NO)$ vibrations, indicating that changes in the electronic factors may be revealed by such a method. Probably the greatest successes will emerge from Raman spectroscopy since metal-metal bonds are in general highly polarized, giving rise to well-defined bands in the 100 to 350 cm^{-1} range. In addition, resonance enhancement due to coupling with the electronic component often results in very strong bands, overcoming the problem of sensitivity inherent in most vibrational studies. This technique has been

valuable in the study of small metal cluster species, V_2, Mo_2, Mo_3. In the future, use of FTIR techniques in the far-infrared, when coupled with vacuum sample cavities, also appears feasible to elucidate support effects.

Spectroscopic studies of adsorbed molecules on metal surfaces have been shown to provide detailed physicochemical information important for the understanding of metal surface interactions. Vibrational spectroscopy in particular has been widely exploited for the detection of chemical species on clean, well-defined, metal surfaces.[26,27] Electronic spectroscopic methodologies have been developed more slowly but with notable successes.

Drexhage and coworkers[28] have employed the fatty-acid monolayer techniques to Kuhn and coworkers[29] to assemble fluorescent dye molecules at fixed distances from metal surfaces. The unique oscillatory pattern of the dye fluorescence lifetime with distances from the surface between fifty and several thousand angstroms was explained by the single-crystal metal surface acting as a mirror for the electric field of the emitter. The observed lifetime oscillations resulted from interference between the reflected and initial waves. More recently, Campion and coworkers[30] found efficient electronic energy transfer from pyrazine to a Ni <III> surface at distances less than 50 Å. The observed cubic distance dependence is in agreement with the classical image dipole theory developed by Chance.[31] However, this process requires a well-defined, single-crystal metal surface. On the other hand, Rosetti and Brus[32] claim that classical electromagnetic theory agrees well with the results for energy transfer from pyrazine to a silver surface exclusively at longer distance (<125 Å). There is evidence of slower transfer rates at the shorter distances.

Concern has been expressed about the applicability of the above type of studies on well-defined metal surfaces for understanding the electronic character of metal clusters dispersed on supports (which is the nature of many real catalyst systems). In particular, the possibility of metal-support interaction as well as uncertainty in connection with the size domain for changeover from bulk to atomic metal properties are complications in relating spectroscopic studies on clean metal surfaces to real catalyst systems. Even calculations on unsupported small metal clusters do not unequivocally reveal the critical size region for changeover from bulk to atomic metal properties. The conclusion derived from X-α calculations that clusters above ten metal atoms will have bulk metal properties was recently challenged by the results of ab initio-SCF calculations.[33] The possible importance of metal cluster-support charge transfer interaction has been noted by Basset[1] and Baetzold[34] for clusters with fewer than ten atoms. Thus, direct experimental data is needed to probe the character of the small metal clusters on supports.

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SECTION IV

CONCLUSIONS

The work of Dr. Goddard of Caltech and others has helped to clarify basic principles associated with reaction mechanisms through the characterization of metallacycle reaction intermediates. However, detailed characterization in the modifications of catalysts is needed to achieve the collective electronic properties required for controlled reactions. Research in microscopic reaction modeling has reached a stage where a computer modeling effort that is supported by physical experimental verification could provide information about the dynamics of the reaction and thus lead to design of supported catalysts with improved selectivity and stability. Industrial catalyst users agree that efforts to find catalysts that will reduce their use of energy and meet the requirements of changing feedstocks must be accelerated to compete with fuel scarcities and rising costs.

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SECTION V

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