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The Nature of Molybdenum Oxide Species Mounted on Alumina: An Oligomer Model

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A model for the structure of the molybdenum species mounted on alumina is developed on the basis of the following considerations. (1) The alumina surface hydroxyl groups remaining after thermal depopulation are found largely in rows. (2) Molybdate species react with the support hydroxyl groups. (3) Molybdate species undergo oligomerization on the alumina support. The structure developed using these criteria has the molybdenum species attached in rows to the support with μ-oxo linkages between adjacent molybdenum atoms along these rows. This requires each alumina surface oxygen atom in these rows to carry one molybdenum atom. The average interatomic molybdenum to molybdenum separation along these surface-attached polymer chains is therefore equal to the ionic diameter of the alumina oxygen atoms (viz., approx. 2.8 Å). On reduction of the molybdenum atoms in these rows, metal–metal bond formation is proposed to occur. On the (111)-face of the alumina steric and charge considerations suggest that in the formation of the polymer chain, one oxygen atom per two molybdenum(VI) atoms is placed in the support in a vacancy formed during partial dehydration of the surface alumina layer. This oxygen is difficult to remove either by reduction or sulfidation. "Fixed" hydrogen, formed on reduction of the catalyst with hydrogen, is associated with isolated relatively immobile μ-OH groups. Catalytic hydrodesulfurization activity is ascribed to dimer species and the utility of alumina as a catalyst support is thought to reside in its ability to promote both the oligomerization and the dispersion of the molybdenum species over the support.

INTRODUCTION

There is still confusion surrounding the nature of the catalyst based on molybdenum oxide supported on alumina (MoO_3/Al_2O_3) (*1*). Interest in these catalysts stems from their hydrodesulfurization (HDS) and hydrogenation activity and from their promotion of other reactions such as the metathesis of olefins. In this communication the structure of the alumina-supported molybdenum oxide catalyst is discussed and related to some of the physicochemical properties of the catalyst described in the literature. The model elaborated is considered in terms of the observed behavior of "molybdena" on alumina; i.e., "molecularly dispersed" type catalysts and not bulk molybdena. Since, in the model developed the supported catalyst species cannot be described as MoO_3, the term *molyoxide* is used for one-dimensional, oligomeric, molybdenum species bonded only by inorganic oxygen atoms or hydroxyl groups. Molyoxide must therefore contain at least two molybdenum atoms. *Molyoxide on alumina* then indicates that molyoxide is bonded to the alumina surface by μ-oxo groups.

DISCUSSION

1. ALUMINA DEHYDRATION

The interaction of molybdenum species with an alumina surface occurs through the alumina hydroxyl groups remaining on the surface after partial dehydration. Of importance when considering alumina surface dehydration is the abundance of the *various* hydroxyl groups on the alumina surface and also their distribution (*2*).

For η-Al_2O_3, it has generally been assumed that the (111)-face is preferentially exposed, and this face may bear five types of hydroxyl groups which is in accord with the observation of five hydroxyl vibrations in the infrared (*2*). The more acidic of these

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hydroxyl groups are thought to provide the proton in the surface dehydration reactions (*2*), while the basicity of others favored their removal as hydroxyl ions. According to Knözinger and Ratnasamy (*2*), on faces bearing more than one type of hydroxyl group, dehydration, especially at low temperatures, will proceed by the condensation of neighboring dissimilar groups. An interesting situation was postulated (*2*) to arise on the A- and B- layers of the (111)-face. After 50% dehydration, under ideal behavior, only one type of hydroxyl group would remain on these layers and these hydroxyls would be arranged in parallel rows (*2*). While deviation from this behavior was considered to disturb this arrangement of surface hydroxyl groups (*2*), it is important to recognize that *rows* of hydroxyl groups were predicted by Knözinger and Ratnasamy to remain on the alumina (111)-face after partial dehydration.

When the hydroxyl groups on an exposed face are all identical, as for example on the (100)-face, dehydration was taken to be random (*2, 3*). The surface dehydration model of Peri (*3*) for the (100)-face of alumina assumes a statistical removal of hydroxyl groups with the restriction that surface oxygens or vacancies will not be formed on adjacent sites. Peri's calculations indicate that the alumina surface at a 2/3 dehydration stage consists largely of *rows* of hydroxyl groups, albeit not necessarily with extended straight runs, between zones containing mainly isolated hydroxyl groups.

On the (110)-face of the alumina, the hydroxide ion packing is least dense and the terminal layer of this face, in the fully hydrated form, has rows of hydroxyl groups separated from each other. We suggest that after partial dehydration *rows* of hydroxyl groups of random length will also remain on this face.

Thus, on all exposed faces of partially dehydrated η- or γ-alumina, isolated hydroxyl groups, pairs of hydroxyl groups, and also rows of hydroxyl groups of variable lengths, will be found. It is argued below that the importance of alumina as a support for molybdenum-based HDS catalysts lies in these rows of hydroxyl groups which are encompassed by areas (or rows) depleted in hydroxyl groups. An alumina face (or part thereof) that dehydroxylates so that it holds only isolated hydroxyl groups or isolated pairs of hydroxyl groups, is therefore not of importance as a catalyst support area. In this respect one may note that on the surface of partially dehydrated silica, the hydroxyl groups are found nearly exclusively in pairs (*4*).

The consequence of having rows of hydroxyl groups on the surface of the alumina on the mounting of the molybdate species will now be considered. In developing our model for the species mounted on the alumina we utilize, for the most part (arbitrarily), the (111)-face of the alumina.

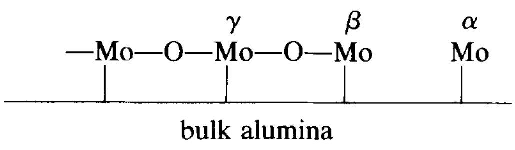
2. MOUNTING OF MOLYBDATES

Solutions used for mounting molybdenum species onto an alumina support are usually prepared from ammonium paramolybdate. In the paramolybdate–alumina system, three processes are considered to occur in competition and these are depolymerization of the paramolybdate anion, repolymerization of molybdate species in solution and on the support, and attachment of the molybdenum species to the support. The interaction of the molybdenum species with alumina is known to be a reversible process as these mounted species, even when calcined onto alumina, can be removed by washing with water, or better, a dilute ammonia solution (*5–7*). The unravelling of the paramolybdate anion to form monomer species (MoO_4^{2-}) is also an equilibrium process, sensitive to solution pH (*8*). It is assumed that all these reactions, involved in preparing supported catalyst, approach equilibrium.

Because of the acidity of the molybdate solution used for mounting the catalyst, some authors (*9–11*) have suggested that polymer species, such as the paramolybdate ion, are bound to be present and are also capable of bonding to the support. Surface-attached paramolybdate ions are, in our view, subject to depolymerization processes, similar to those in solution, and therefore will not be found in significant quantities on the catalyst surface except at very high catalyst loadings ([Mo] ≫ [alumina OH]) or under more highly acidic conditions. It will be seen later that in the absence of added acid under equilibrium loading conditions, when the molybdenum atom concentration does not exceed the alumina hydroxyl group concentration, the protons required for polymerization of the molybdenum species on the support and for attachment to the support (to form surface-attached molyoxide species), *tend* to balance the number of protons released through paramolybdate depolymerization.

2.a. Oligomerization of Molybdate Species on the Support

It has been shown that the molybdate–alumina interaction involves the hydroxyl groups on the alumina (*7*, *12–15*) and a significant proportion of these hydroxyl groups, remaining on the partially dehydroxylated alumina surface, are in rows. It is most important to recognize these hydroxyl group rows as multidentate ligands. As a consequence the molybdate ions will preferentially oligomerize along these rows due to the higher stability toward dissociation and removal from the support of the surface-attached *oligomer* than that of the *single* molybdate ions on the support. To remove a molybdate unit from such a polymer chain requires the simultaneous rupture of at *least* one Mo–O–Mo (μ-oxo) bond and of the bond attaching the molybdenum atom to the alumina. Desorption of the isolated molybdate species on the alumina from the surface only requires the breaking of the support interaction. The concept here is that the ease of desorption of the molybdenum species varies in the order $\alpha > \beta > \gamma$.[1] Thus, the tendency will be for the α-molybdate to desorb reversibly from the surface until it has an opportunity to add to the end of the β-species where it may contribute to chain growth. That is, the molybdate groups will arrange themselves in chains on the rows of alumina hydroxyl groups even in the presence of excess surface hydroxyl groups, and therefore chain configurations of molybdates dominate on the surface of the alumina.


$$\mathrm{-Mo-O-\overset{\gamma}{Mo}-O-\overset{\beta}{Mo}\qquad\overset{\alpha}{Mo}}$$

Because chain-terminating species (type β) are more labile than the γ-chain links, short chains may desorb, one molybdate at a time with the end effect to maximize the placement of molybdenum species in like (type γ) environments at medium catalyst surface cover. Only at high molybdenum concentrations would significant numbers of short rows and isolated surface hydroxyl groups be occupied. In this respect the work of Iannibello and Mitchell (*12*) is interesting as they found that all the molybdate in excess of about 8–9 wt% (as MoO_3), mounted on γ-alumina by equilibrium adsorption, could be washed off with distilled water. The molybdenum species remaining are considered bound to the alumina in polymer chains.

This scheme of mounting molybdenum oxide species can be disturbed by factors which alter the relationships between polymerization, depolymerization, and surface interaction. The introduction of bases into the ammonium paramolybdate–alumina system would constitute such a perturbation. This has been done by either raising the pH of the solution directly (*6*, *10*, *11*) or by impregnating alumina with sodium ions (*16*) prior to treatment with paramolybdate species. Under these conditions polymerization of molybdates is hindered and because of the lability of the μ-oxo bonds under basic conditions, mounting of molybdenum species from such solutions (under equilibrium conditions) leads to cat-

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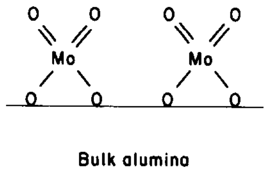
[1] A more detailed view of this may be obtained by inspection of Structures (**I**) and (**III**).

alysts with low molybdenum content (*6*). The molybdate species laid down on the surface under mildly basic conditions would be of the type Structure **(I)**.

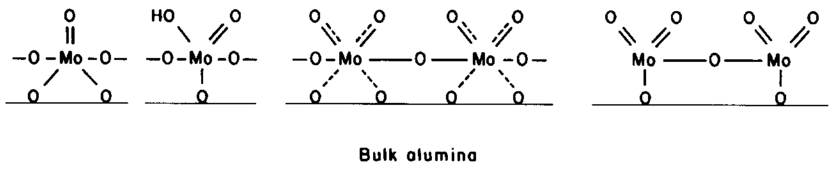


(I)

The concentration of **(I)** on alumina surfaces, generally correlated with spectroscopic data associated with tetrahedral molybdate species (*7, 9–14, 17*), is high at low catalyst loading (*7, 12, 14, 17*). This is comprehensible if the rate of migration of the molybdate ions, present in low concentration, to centers of chain growth (type β molybdenum species), is hindered by their repeated reattachment to the support. If the migration of molybdate species on the surface occurs preferentially along the rows of alumina surface hydroxyl groups, polymerization of the molybdate ions (at low molybdate ion concentration) will be more probable on the longer rows of hydroxyl groups. It may also be noted that the formation of these monomer molybdate species of Structure **(I)** from the paramolybdate anion, depletes the solution proton concentration.

2.b. Structure of the Mounted Molybdenum Species

The Structure **(I)** above is one of many that have been proposed for the molybdenum species on the surface of alumina. Others (*18–21*) are shown in Structures **(IIa–d)**.



(IIa) (IIb) (IIc) (IId)

More detailed surface models for MoO_3/Al_2O_3 have been discussed by Schuit and Gates (*22*), Sonnemans and Mars (*6*), Hall and co-workers (*23, 24*), and Massoth (*25*). Schuit and Gates (*22*) considered the catalyst to be a two-dimensional monolayer on the (110)-plane of the alumina. Sonnemans and Mars (*6*) in their model of the catalyst surface, also stipulated that the molybdenum species are incorporated as a monolayer on the alumina surface in a way that continues the structure of the alumina crystal. Since Al–O–Al bonds occur in alumina, it follows from the epitaxial monolayer model that some alumina faces will carry molybdenum atoms also oxo-bridged to neighboring molybdenum atoms. Massoth (*25*) viewed the MoO_3/Al_2O_3 catalyst surface structure in terms of one-dimensional "chains" of MoO_2 with the third oxygen atom of the MoO_3 entities occupying a vacancy, beneath the molybdenum atoms, in the underlying alumina layer. No interaction between MoO_3 species was indicated.

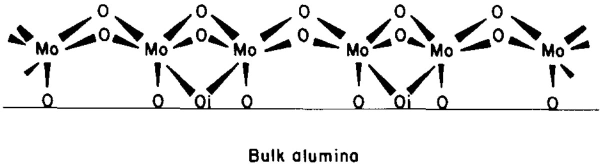
2.b.1. Molybdenum–molybdenum separations. The polymerization of molybdate ions on the support requires that the molybdenum atoms must be bridged by oxygen atoms to both neighboring molybdenum atoms and also to the aluminum atoms of the support. The separation of the hydroxyl group oxygen atoms in the *isolated rows* of hydroxyl groups on the alumina surface then restricts the structures possible for the mounted species. Taking 2.8 Å for the diameter of the alumina surface oxygen atoms it is clear that polymers of Structure **(I)**, that is, Structures **(IIa)** and **(IIc)**, cannot represent the surface molybdenum species. In these structures (based on molybdate species bonded through *two* oxygen atoms to the support), the molybdenum atom separation is 5.6 Å which is too long for a Mo–O–Mo bond (*26*).

Therefore, the only polymeric structures which can form along *isolated rows* of hydroxyl groups are those in which each molybdenum atom is bound to just one alumina oxygen atom, so that all oxygen atoms, from the hydroxyl group row involved in molyoxide formation, carry one molybdenum atom. In this respect it is interesting that Millman *et al.* (*15*), from an infrared spectral study of alumina hydroxyl groups, suggested that the ratio of molybdenum atoms mounted on the alumina, from a paramolybdate anion-containing solution, to the number of alumina hydroxyl groups eliminated, may be as low as one. While they proposed therefore that paramolybdate ions can also become bound to the surface, our model for molyoxide formation requires that the number of alumina OH groups removed equals the number of molybdenum atoms mounted. On partially dehydroxylated alumina containing isolated rows of hydroxyl groups, only through the formation of species based on Structure **(I)** can the ratio of the number of hydroxyl groups replaced to molybdenum atoms mounted be lifted above 1. This, as indicated above, occurs during the initial addition (i.e., low metal ion concentration) of molybdate ions to the support.

The alumina oxygen diameter therefore, in large measure, determines the molybdenum atom separations which fall within the domain where metal–metal bonding occurs (*27*). Not all interatomic molybdenum distances need necessarily be equal and indeed later it is postulated that dimeric interactions do occur between adjacent, lower valent, molybdenum atom pairs. Short interatomic molybdenum distances with nonlinear μ-oxo bridges as required by the considerations above are fundamental in describing some of the properties of the molybdenum species on alumina. Indeed even their catalytic properties may well stem from these short intermetallic separations.

The close association of the molybdate species on alumina, may encourage hydroxyl groups on neighboring molybdenum atoms to preferentially cocondense rather than interact with molybdate species in solution, to maximize the dispersion of the molybdenum atoms on the support.

2.b.2. The molyoxide structure. The completely dehydrated molyoxide species formed on condensation on the (111)-face of the alumina, can be represented by Structure **(III)**,



(III)

where the O_i oxygen atoms (interstitial oxygen atoms) are located in the surface alumina layer *in a vacancy formed during alumina dehydration.* It should be noted that for clarity not all the interactions between the molybdenum atoms and the support oxygen atoms are shown in Structure **(III)** (and in others given later describing molyoxide on alumina). Only those Mo–O bonds required to satisfy the valence state of the molybdenum atoms have been included.

The molybdenum atoms in Structure **(III)** have an oxidation state +6 and therefore even though interatomic molybdenum separations are within those required for metal–metal bonding, none can occur unless ligand electrons can delocalize into metal–metal bonding orbitals. Brown *et al.* (*28*) have, from molecular orbital calculations, shown that this can occur and calculated a metal–metal bond order of 0.38 for a hypothetical Mo(VI) species in which the Mo–Mo separation was 2.569 Å. Interactions of this type may aid polymerization of molybdates during catalyst mounting by stabilizing Structure **(III)**.

The placement of the molybdenum species in polymer chains, according to this model, restricts the number of surface oxygen atoms that can bond to the molybdenum atoms. This restriction, of greatest significance when the molybdenum atoms are in their highest (+6) oxidation state, would limit the number of hydroxyl groups that can be carried by the molyoxide. In our view, as mentioned above, the short intermolybdenum atom separations in molyoxide would also facilitate the cocondensation of neighboring nonbridging hydroxyl groups. In the structure proposed for molyoxide, the molybdenum atoms are therefore shown bonded only to oxo groups. This oxo structure, which may form either during mounting or calcining of the catalyst, concurs with the finding (*25*) that the oxidic catalyst does not hold many exchangeable protons. Hydroxyl groups on molyoxide are thus considered to be located primarily on chain-terminating molybdenum atoms.

We suggest that species based on Structure **(III)**, i.e., $Mo_2(\mu\text{-}O)_5(OAl)_2$ can best be accommodated on the (111)-face of the alumina surface in the fashion described above. The Structure **(III)**, placed on the 50% dehydrated (according to Knözinger) (111)-face of the alumina, forms a surface monolayer. Molyoxide species in which a terminal oxo group resides on each molybdenum atom (repeating unit is $Mo_2O_2(\mu\text{-}O)_3(OAl)_2$) can also most favorably be accommodated spacially on this alumina surface if one of the μ-oxo groups fits into the alumina surface (i.e., is a $\mu\text{-}O_i$ group). Otherwise five molyoxide oxygen atoms must fit on an area equivalent to four alumina surface oxygen atoms. Following the work of Brown *et al.* (*28*) on species containing Mo=O bonds, some bonding interactions between adjacent molybdenum atoms along the molyoxide chain through these terminal oxo groups, (i.e., Mo=O--Mo) may occur, reducing the dissimilarity between this structure and Structure **(III)**. Structure **(III)**, containing only μ-oxo ligands, is therefore taken as the basic molyoxide species formed on calcination of MoO_3/Al_2O_3 catalysts.

Although Structure **(III)** refers to species mounted on the (111)-face of alumina, it is thought that species on other faces are closely related. For instance on the (100)-face, which is subject to dehydration according to Peri (*3*), we view the mounted molyoxide as Structure **(III)** in which the Mo–O–Al oxygen atoms may also bridge adjacent molybdenum atoms along the molyoxide chain. On the (110)-face (γ-alumina) the $\mu\text{-}O_i$ groups do not fit completely into the alumina surface layer. However, one may suggest that along the isolated molyoxide rows, the calcined catalyst species will be as in Structure **(III)**, but for the more exposed $\mu\text{-}O_i$ oxygen atoms, which are placed in the "valleys" running alongside the rows of oxygen atoms bonding the molybdenum atoms to the alumina surface. These "valleys" arise on the alumina (110)-face because the rows of hydroxyl groups on the hydrated surface do not abut.

The rows of hydroxyl groups on partially dehydroxylated alumina will be of random lengths. If short gaps (one or two missing hydroxyl groups) occur in the rows of alumina hydroxyl groups, these gaps can, conceivably, be spanned, especially at higher catalyst loadings, by molybdate species which are not attached to the alumina surface. On calcination of the catalysts, if rearrangement of these "fly-over" species eventuates so that they also become attached to the alumina surface, longer polymers of molyoxide are obtained. This places more molybdate species in identical environments.

Inspection of Structure **(III)** shows that there are three types of μ-oxo groups and as the exposure of these μ-oxo groups to incoming reactants (e.g., H_2, H_2S) differs, so will their reactivity. The molyoxide end groups, which have been omitted for the sake of clarity from the structures of molyoxide illustrated in this communication, are taken to bear terminal-oxo and/or hydroxyl groups.

One further point which follows from this model, is that in ligand → metal charge transfer transitions, the metal acceptor orbitals will most probably be molecular orbitals formed by Mo–Mo orbital overlap.

3. LOWER VALENT MOLYBDENUM SPECIES ON ALUMINA

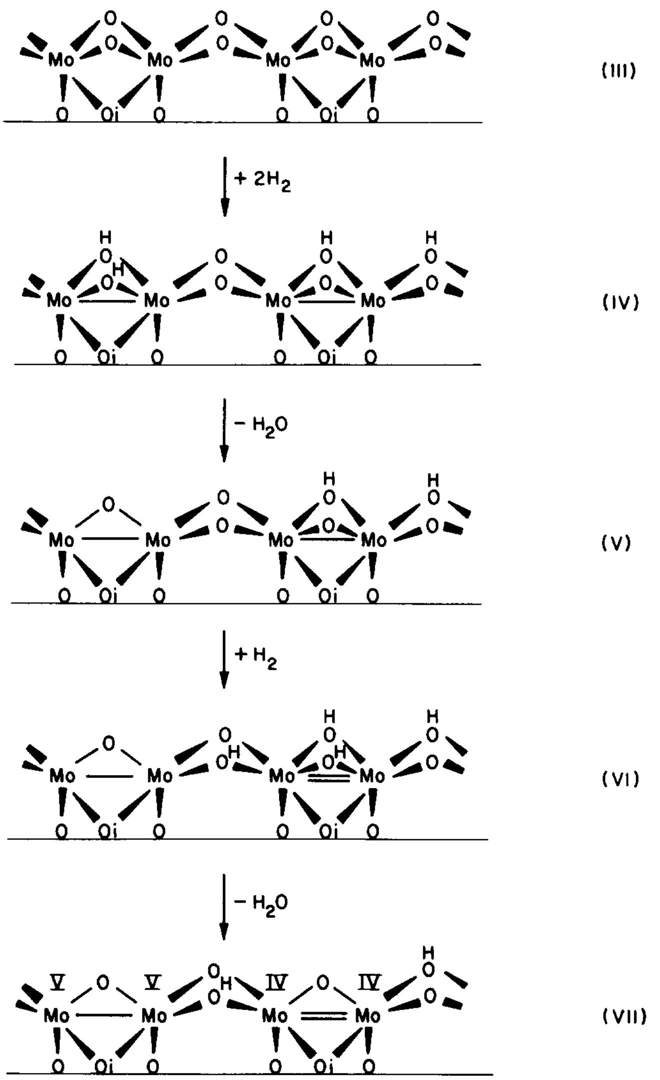
Above we argued that the short interatomic molybdenum separations, inherent in this model of molyoxide, would encourage Mo–Mo bond formation. One may further suggest that the opportunity for metal–metal bond formation in molyoxide would also help facilitate the reduction of the molybdenum atoms in this structure.

3.a. Reduction of the Catalyst

It has been shown that catalysts with low molybdenum content are more difficult to reduce than those in which the molybdenum content exceeds 3 wt% (*18, 29*). This is explicable by recourse to our model for catalyst loading which, in agreement with observation (*14*), indicated that at low loadings more monomeric species (Structure **(I)**) are formed on the alumina surface and these, by analogy with $Al_2(MoO_4)_3$ (*18*), are assumed difficult to reduce. The higher facility toward reduction of molybdenum in molyoxide, suggested above from metal–metal bonding considerations, concurs with findings such as the formation of Mo(V) species on supported catalysts after calcining in air (*16*). It is of interest that Giordano *et al.* (*20*) observed ESR signals only in those catalyst samples (calcined and then outgassed at 500°C in He) with a molybdenum loading exceeding 4 wt%. MoO_3/Al_2O_3 catalysts have also been reduced (and activated toward metathesis reactions) with alkenes such as *cis*-2-butene (*30*) at temperatures of 60°C or below.

3.b. Detection of Mo(V) Species

In the reduction of dimolybdenum centres in which metal–metal bonding can occur, magnetic techniques do not permit observation of more than half the molybdenum atoms as Mo(V). In general, on reduction of molyoxide on alumina with hydrogen, the concentration of Mo(V) species detected by ESR was small (*19, 20, 24, 31, 32*). Results indicating a Mo(V) concentration approaching 50% (or even exceeding this value) are at variance with this molyoxide model. Only in catalysts consisting largely of isolated, noninteracting molybdate species can the Mo(V) concentration exceed 50% and then only if reduction to Mo(IV) is somewhat slower. Seshadri and Petrakis (*31*) found that on heating MoO_3/Al_2O_3 catalysts in hydrogen, the concentration of Mo(V) rapidly increased to a maximum equivalent to about 10% of the molybdenum atoms available. The ESR results of Abdo *et al.* (*32*) suggesting that much of the Mo(V) formed on catalyst reduction was antiferromagnetically coupled, are also in agreement with the molyoxide formulation for the catalyst structure proposed here—as is the finding (*33*) that it was possible to account for the majority of the alumina surface hydroxyl groups on a reduced catalyst (8 wt% Mo) by ^{1}H-NMR. Both the placement of the molybdenum atoms in rows and the Mo–Mo bonding proposed on reduction, ensures that the alumina surface is not uniformly



SCHEME 1. Hydrogenation/dehydration reactions of molyoxide. Reduction of Mo(V) centers to Mo(IV) as seen in the conversion of **(V)** → **(VI)** is considered slower than the formation of the Mo(V) centers and the dehydration reactions. Reduction of **(VII)** continues at the Mo(V) centers until all have been reduced to Mo(IV). The incorporation, as shown, of the O_i atoms into the dimeric metal–metal bonded units has been done arbitrarily. The stereochemistry of the μ-OH groups, formed during reduction, makes hydrogen bonding with adjacent μ-O(H) groups likely.

covered with paramagnetic centers on reduction of the molybdenum species.

3.c. Reduction and Dehydration Reactions

The formation of hydroxyl groups on hydrogenation of MoO_3/Al_2O_3 catalysts has been observed (*18, 23*). The hydrogenation reaction along the molyoxide chain is taken to involve the conversion of μ-oxo linkages to μ-hydroxo ones which, at the elevated reaction temperatures, can be eliminated by subsequent dehydration reactions. A number of possible structures[2] can be written

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[2] For clarity we show the Mo(V) atoms of the dimer units in these reduced molyoxide species to be joined by a single bond and the corresponding Mo(IV) atoms by a double bond.

for partially reduced species bearing hydroxyl groups and several of these are given in Scheme 1.

The assumption that the dehydration reactions accompanying hydrogenation go to completion, at all but very high temperatures, need not hold. By reference to Structure **(VII)** one may indeed predict that dehydration will not, except under forcing conditions, go to completion, because of the formation of isolated relatively inert and immobile μ-hydroxo species. Massoth (*18*) and Hall and Massoth (*23*) have shown that not all hydrogen used in reductions was evolved as water and the hydrogen "irreversibly" held on the partially reduced catalyst was thought to be associated with hydroxyl groups attached to molybdenum atoms. We assign structures of the type **(IV)**, **(V)**, **(VI)**, and **(VII)** to species containing this "irreversible" hydrogen. From this it follows that water elimination should not be correlated too closely with extent of the reduction, especially after the initial hydroxyl group depopulation has occurred, since the immobility of the remaining hydroxyl groups and lack of neighboring ones, will hinder further dehydration of the (already) reduced molyoxide species. Following Hall *et al.* (*24*, *34*), in indicating the extent of reduction of the catalyst, the amount of "irreversible" hydrogen on the catalyst must also be taken into account.

It should be borne in mind that a fraction of the water released on reduction of the alumina supported molyoxide may react with the alumina to produce alumina surface hydroxyl groups which, if not completely removed via dehydration reactions at the reduction reaction temperatures, leads to an increase in the number of hydroxyl groups (i.e., isolated groups) on the alumina surface. In this connection, it has been shown (*35*, *36*) that while water adsorbs onto dried alumina as molecular water at room temperature, on heating above 300°C some of this adsorbed water is converted into alumina surface hydroxyl groups. Fractional hydroxylation of the alumina surface in this way by adsorbed water or water produced during catalyst reduction may be significant when the alumina pores are not efficiently swept with a carrier gas during the heating process. One may also note in passing that since hydroxyl groups are formed on dried alumina from adsorbed water only at elevated temperatures (*35*), the isolated rows of hydroxyl groups on the alumina will retain their integrity in water, enabling the catalyst to be mounted from aqueous molybdate solutions as described earlier.

3.c.1. Mechanism of the initial reduction–dehydration process. The initial hydrogenation reaction of molyoxide is thought to entail the addition of one molecule of hydrogen across two adjacent surface (i.e., capping) μ-oxo groups, converting them to μ-hydroxo groups. There are two possible ways in which this hydrogen addition can occur. It can either add to oxygen atoms spanning the same two molybdenum atoms or to neighboring oxygen atoms along the molyoxide chain (see Structure **(IV)**). The stereochemistry of the μ-OH groups would favor dehydration between hydroxyl groups spanning the same molybdenum atoms. This is shown in Scheme 1, in the conversion of **(IV)** to **(V)**. On the assumption that both modes of hydrogen addition onto the Mo(VI) molyoxide species have equal probability *during the initial reaction period* (see Scheme 1, the formation of **(IV)** from **(III)**), then under conditions at which dehydration can ensue, one molecule of water is released for every two molecules of hydrogen consumed. The resulting relationship between water formed and "irreversible" hydrogen remaining on the molyoxide, *at low extents of reduction*, was observed by Hall and co-workers (*23*, *24*).

The relatively low concentration of isolated Mo(V) species formed during reduction (*24*, *31*, *32*), suggests that dimer Mo(V)–Mo(V) and Mo(IV)–Mo(IV) species are formed in preference to mixed oxidation state dimers. If the reduction proceeds in this way, chains containing mainly Mo(V) and Mo(IV) dimers will be obtained. Structure **(VII)** is an example of such a species and contains one "irreversible" hydrogen for every two molybdenum atoms. If further reduction by H_2 addition converts, in the first instance, only the Mo(V) centers remaining to Mo(IV) centers (i.e., no Mo(III) centers), then on dehydration the ratio of the "irreversible" hydrogen held on the catalyst to the molybdenum atom content of the catalyst is maintained at 1/2. This dehydration scheme is in harmony with the results of Hall and Massoth (*23*) and Hall and Lo Jacono (*24*) who found that the above ratio of "irreversible" hydrogen to catalyst molybdenum atom content, was constant (at a little below 1/2) over a wide dehydration range (0.25–0.6 molecules H_2O/molybdenum atom).

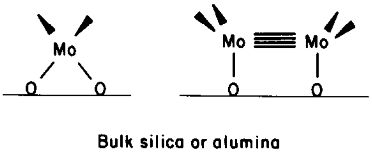
3.d. Catalytic Centers

Inspection of Scheme 1 shows that in mildly reduced catalysts (i.e., mainly Mo(V) species), the chain link molybdenum atoms retain a high coordination number which may inhibit their involvement in low temperature catalysis reactions such as alkene hydrogenation, metathesis, isomerization, and exchange. This property of the molyoxide structure, placing the majority of the molybdenum atoms in like environments (chain link species) and carrying surface (capping) ligands, is in accord with the finding that the above reactions are promoted by a small number of sites on the catalyst (*37, 38*).

The chain-terminating molybdenum atoms are considered to more readily acquire a low oxidation and coordination state, especially on reduction with the more discriminating (larger) reducing agents (e.g., butene), because of their greater accessibility to incoming reagents and the nonbridging ligands they carry may be more facile leaving groups. Recently Rappé and Goddard (*39*) suggested that alkanes and alkenes react with oxo-molybdenum species by addition across a Mo=O bond. Terminal oxo groups can occur on molyoxide on the chain-terminating molybdenum atoms.

3.d.1. Alkene reductions. If the molybdenum end groups on the molyoxide chain impart catalytic reduction behavior to the mildly reduced catalyst, then the more end groups available on the catalyst the greater the number of sites for substrate reduction. The formation of short molyoxide chains on alumina should thus lead to more active reduction catalysts.

In this respect it is interesting to view the work of Iwasawa *et al.* (40) who reacted the monomeric $Mo(allyl)_4$ and dimeric $Mo_2(allyl)_4$ with silica or alumina hydroxyl groups to form surface-attached molybdenum centers of the types shown in Structure **(VIII)**.



(VIII)

Here we have a maximum number of end groups and Iwasawa *et al.* (*40*) have shown that the monomer and dimer species on alumina and the dimeric one on silica are indeed *highly active* reduction catalysts. In our view, after activation (at 870°K in H_2), the catalytic species in all cases are at least dimeric, dimerization of the monomers being possible on alumina but not readily on silica. Dimerization requires the two *monomeric,* surface-attached, molybdenum allyl species to be adjacent and therefore is possible on alumina surfaces which bear rows of hydroxyl groups but not on silica where the hydroxyl groups occur as isolated pairs (*4*).

A consequence of considerations based on *low oxidation state end groups* is that poisoning of the reductive power of mildly reduced and dehydroxylated molyoxide requires the poisoning of coordinatively unsaturated molybdenum end groups only. Hall and co-workers (*37, 41*) found that only two nitric oxide molecules, which dimerized on the catalyst, were required per

40–50 molybdenum atoms to reduce the rate of propene reduction by 99%, without affecting the metathesis (propene → ethene + butene) rate of their catalyst. Lombardo *et al.* (*37*) and others (*29*) have demonstrated that the initial adsorption of NO onto prereduced MoO_3/Al_2O_3 catalyst was strong and irreversible, whereas additional NO adsorption was reversible. This reversible adsorption may reflect weaker interactions on the more sterically hindered Mo(IV) dimer sites along the molyoxide chain. Peri (*29*) deduced, also from NO adsorption studies, that the exposure of molybdenum atoms on reduction of the catalyst was never greater than 8–9% and normally 2–3%.

The alkene reduction activity of the catalyst (under mild conditions) increases with vacancy formation on the catalyst (*34, 37*). Since these sites are completely eliminated on reaction with NO, they are presumably the *most highly reduced and coordinatively unsaturated* (accommodate the dinitrosyl species) sites. Such sites, we conjecture, would most likely be formed on *isolated dimeric molybdenum species.*

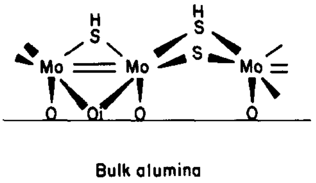
3.d.2. Metathesis and isomerization reactions. While reduced isolated dimeric molybdenum species are presumably also active for the (slower) metathesis reaction, it is, in addition, tempting to assign low temperature metathesis activity to sites on *terminating species on longer molyoxide chains.* Moreover, since NO does not poison the isomerization activity of the catalyst (*37*), isomerization reactions may also proceed on those sites active in metathesis. However, the requirement of an acidic function adjacent to the metal atom for isomerization reactions (*38*), would then suggest that the molyoxide, on mounting, did not completely fill the alumina hydroxyl group row. On this basis isomerization activity of the catalyst could be ascribed to the terminal reduced molybdenum species working in conjunction with the adjacent alumina hydroxyl group. Lombardo *et al.* (*37*) found that the Brønsted acid site involved in the decomposition of cyclopropane was an alumina hydroxyl group not introduced during catalyst reduction.

3.e. "Reversibly" Bound Hydrogen

An interesting property of reduced MoO_3/Al_2O_3 catalysts is their ability to reversibly adsorb hydrogen (*15, 23*). Hall and co-workers (*15, 23, 24, 33, 38*) have suggested that this "reversibly" bound hydrogen on the catalyst, which correlated linearly with the number of vacant coordination sites formed on the catalyst (i.e., water molecules produced on reduction of the catalyst with hydrogen), was heterolytically adsorbed on Mo(IV) sites. Hydrogen desorption studies indicated that for every molecule of hydrogen removed from the catalyst, one hydroxyl group was also eliminated (*15, 33*). These hydroxyl groups were detected in the ^{1}H-NMR (and also ir) spectrum of the reduced catalyst (*15, 33*) and therefore they cannot be (extensively) associated with paramagnetic centres. On the basis of the molyoxide structure for the catalyst, this reversible addition of hydrogen molecules may occur heterolytically across Mo–O bonds pertaining to the Mo(IV) dimer species formed along the molyoxide chains. Then centers containing units such as $Mo_2(\mu\text{-H})(\mu\text{-OH})$ may form. To conform with experimental data (*15, 23, 33*), the elimination of water from these units is less likely than H_2 abstraction, which implies that reduction of these molybdenum atoms to their tervalent state is difficult. A well characterized Mo(IV) compound with the $Mo_2(\mu\text{-H})(\mu\text{-OH})$ center has been described in the literature (*42*).

4. SULFIDATION

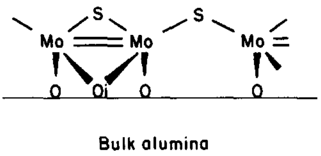
Massoth (*25*) has outlined a mechanism for the sulfidation of MoO_3/Al_2O_3 catalyst which involves proton transfer from unstable (*43*), acidic (*44*) coordinated H_2S molecules to oxo groups to form condensable hydroxyl groups. The surface oxygen atoms of the catalyst are thus rapidly exchanged for sulfur atoms, and in the presence of hydrogen, reduced molybdenum oxysulfide species are formed. A molybdenum oxysulfide segment derived from molyoxide on alumina is shown in Structure **(IX),** where the oxygen atoms remaining are those located within the alumina surface layer.



(IX)

In Structure **(IX),** the S/Mo ratio is 1.5 and there is one "fixed" hydrogen per molybdenum atom. Other structures with varying S/Mo or H/Mo ratios can readily be visualized especially under HDS conditions. The presence of SH groups on the surface of the sulfided catalyst has been suggested from D_2 exchange experiments (*25*), but possibly, due to hydrogen bonding, were not detected in an ir study (*45*). The higher extent of sulfidation found for the catalyst on γ-alumina than on η-alumina under more forcing conditions (*25*), may reflect a difference in the ease of substitution between the μ-O_i groups by sulfur. On our model this would arise because the μ-O_i group on the (110)-face (viz., γ-alumina) protrudes above the surface alumina layer, enhancing its availability for substitution. With η-alumina, the μ-O_i group was placed completely into the alumina (111)-face carrying the molyoxide. Replacement of both the μ-O_i groups and the oxygen atoms through which the molybdenum atoms are bound to the support by sulfur would completely disrupt the catalyst structure and presumably lead to the formation of bulk MoS_2.

It has been shown that the species containing an S/Mo ratio of 1 is the most active in the HDS of thiophene (*5*, *46*), and here it is assigned Structure **(X),** derived from **(IX)** by H_2S elimination.



(X)

The molybdenum atoms in this species may be sufficiently coordinatively unsaturated to promote the HDS reaction. If the sulfur atoms, in sulfur poor species such as **(X)** are also fluxional, the exposure of some of the metal atoms to incoming reactants would be enhanced. In the presence of H_2S, the reverse reaction, reforming species such as **(IX)** from **(X)** can presumably occur to again retard catalytic activity. The lined out activity of MoO_3/Al_2O_3 in HDS reactions may in large measure reflect the equilibrium between species such as **(IX)** and **(X).**

While Structure **(IX)** is drawn as having only μ-sulfido or μ-hydrosulfido ligands, the possibility of having μ-persulfido groups between neighboring molybdenum atoms on the catalyst should not be overlooked. Bridging persulfido groups are known in molybdenum chemistry (*47*) and interestingly so is the formation of partial persulfide linkages between sulfur atoms from adjacent ligands (*48*). The reduced spacial requirements of a persulfido group, which may be of importance in sulfur rich compounds such as **(IX),** compared to two sulfido species, may act to enhance the stability of the persulfido group. If persulfido group formation were possible, deprotonation of **(IX)** could occur without affecting the oxidation state of the molybdenum atoms. It is considered that persulfido group formation is in accord with, for example, the known variations in sulfur content of the catalyst. Thus persulfido group formation allows a S/Mo ratio of as high as 2 to be rationalized for the alumina bound molybdenum atoms, keeping the molybdenum atoms in their +4 oxidation state, while a range of other lower ratios can be reached through persulfide group decomposition by, for example, heating in hydrogen.

$$S_2^{2-} + H_2 \rightarrow H_2S + S^{2-}$$

The oxidation ("oxygen effect") of sulfided MoO_3/Al_2O_3 catalysts, observed by Amberg *et al.* (*49*), which improved their HDS activity, especially their initial activity, can also be thought of in terms of decomposition of persulfido groups,

$$S_2^{2-} + O_2 \rightarrow SO_2 + S^{2-}$$

which regenerates the active low sulfur (Structure **(X)**) catalyst species.

5. CONCLUDING REMARKS

It has been shown that the model for molybdenum oxide species on alumina developed here conforms well with the known behavior of the catalyst. Variations between catalysts will always be found if catalyst loading, loading procedure, and surface hydroxyl concentration vary. The model for the loading of the molybdenum species demands that the rows of hydroxyl groups on the alumina surface are preferentially occupied. At very low catalyst loadings, the molybdenum species will, to a large measure be lone, monomeric aluminum molybdates as depicted in Structure **(I)**. On increasing the loading, the molyoxide species will then tend (under equilibrium loading conditions) to grow along the longer hydroxyl group rows and then fill the shorter ones. Finally, bulk molybdate is deposited.

From the picture of the catalyst developed, it is concluded that a primary role of the catalyst support is to ensure that the mounted molybdenum species will polymerize—at least to the dimer stage—which is considered to be fundamental for catalyst activity. The advantageous property for catalyst synthesis assigned here to alumina is that it can both do this and *highly disperse* the molybdenum species from aqueous solutions. In our view, the distribution of hydroxyl groups on partially dehydroxylated surfaces and the strength of the interaction between these surface hydroxyl groups and the molybdate ions, are important considerations in the preparation of active molybdenum-based HDS catalysts.

The model for Mo/Al_2O_3 described, suggests that on alumina there is a critical molybdenum atom loading required before molybdate polymerization and thus catalytic activity for, for example, HDS will manifest itself. On silica, on the other hand, at low loadings the probability of having bulk molybdate type species present is greater than on alumina because of the weaker interaction of the molybdate ions with the silica surface hydroxyl groups. Since these bulk species will, on reductive sulfidation, form crystallites of MoS_2 which are catalytically active in HDS, the activity of the silica supported catalyst should be higher than the alumina supported catalyst containing only species of Structure **(I)**. In parallel with the model developed it is tempting to assign the activity of MoS_2 crystallites in HDS reactions to the exposure of regular arrays of molybdenum and sulfur atoms, similar to that shown in Structure **(X)**—the support being bulk MoS_2, on the MoS_2 crystallite edge faces.

The structure of the cobalt promoted molybdenum catalyst is considered to follow from the structure of molyoxide proposed and a communication on this topic is in preparation.

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