JOURNAL OF CATALYSIS 34, 41–49 (1974)

Studies of Molybdena–Alumina Catalysts

III. Hydrogen Retention by Reduced Catalysts

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Received December 14, 1974

An 8% Mo/γ-Al_2O_3 catalyst was subjected to various reduction-oxidation treatments in a standard vacuum circulation system. From measurements of gas consumed and water generated in the redox cycle, hydrogen retained on the reduced catalyst was calculated. Two types of adsorbed hydrogen were found: (1) reversibly adsorbed (H_R) which is removed by evacuation, and (2) irreversibly retained (H_I) which was not removed by evacuation. The irreversibly retained hydrogen is desorbed as H_2O at elevated temperature rather than as H_2. Its concentration depends upon the state of reduction of the catalyst. At low reduction, two H_I are present per vacancy oxide ion lost; however, as reduction increases, H_I attains a limiting value of about 0.45 H_I/Mo. Oxidation removes H_I in the form of water. It is proposed that H_I is present as an OH group adjacent to a vacancy, the formation requiring a reduction in the valence of the molybdenum cations involved. A model to account for the results is proposed.

INTRODUCTION

A recent proposal by Lipsch and Schuit (*1*) suggests that the source of active hydrogen in the hydrogenolysis of thiophene over molybdena–alumina catalysts resides on oxide anions adjacent to a vacancy in the molybdena layer of the prereduced catalyst. This mechanism involves a concerted action involving breaking of the C–S bonds, attachment of the S to the vacancy and addition of the hydrogen to the hydrocarbon fragment forming butadiene as a product. Gaseous H_2 in the feed stream removes the S via H_2S, reforming the vacancy, and replenishes the neighboring oxide anions with hydrogen. Although the mechanism calls for two H (presumably as OH) per vacancy, there seems to be no *a priori* reason why this stoichiometry should obtain.

Concerning the H-content of a reduced CoMo/Al_2O_3 catalyst, Lipsch and Schuit (*1*) found reversible H_2 chemisorption (activated) and concluded that H–H bond cleavage was involved. Their measurements were not quantitative, and most importantly were made on reduced catalyst *after* desorption at 500°C. We will call this type of adsorbed H_2, reversibly adsorbed H_2 or H_R. Note that they do not take cognizance of any H that may be present on the reduced catalyst after desorption, which we will call irreversibly retained H_2 or H_I. The active OH hydrogen may be either or both of these.

Owens and Amberg (*2*) reported strong reversible adsorption of H_2 on a sulfided CoMo/Al_2O_3 catalyst; this was characterized as adsorbed (moderate desorption rate) and loosely bound (rapid desorption rate). Thiophene hydrogenolysis occurred primarily with the latter. Irreversibly retained H on the sulfided catalyst was not noted.

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From prior studies in this laboratory on the reducibility of Mo/Al_2O_3 catalysts, it was found that considerable evolution of water attended reoxidation of the reduced catalyst (*3*). This was ascribed to chemisorbed hydrogen possibly held as Mo–O–H surface groups. The earlier work was semiquantitative in nature, being based on effluent gas analysis for H_2O and catalyst weight changes. We report here experiments, made with a volumetric system, and designed to separate the two classes of hydrogen (H_R and H_I). The object was to relate one or both types of H_2 to the degree of reduction of the catalyst. Since hydrogenation of adsorbed sulfur compounds must be an essential part of the desulfurization mechanism, such results are a necessary step to a fuller understanding of the mechanism.

EXPERIMENTAL METHODS

The catalyst consisted of 8.1% Mo supported on a Kjetchen CK-300, thermal stabilized pure γ-Al_2O_3. Preparation involved impregnation of the support (20–40 mesh) by an incipient wetting technique, using ammonium paramolybdate solution. This was followed by drying at 120°C for several hours and final air calcination at 540°C for 16 hr. Surface areas and pore volumes for the support and catalyst were, respectively: 192, 185 m^2/g; and 0.50, 0.42 ml/g.

A conventional high vacuum system was used for the volumetric measurements. A quartz reactor was connected to a Pyrex-glass circulating loop containing a glass magnetic circulation pump. A cold trap (liquid N_2 in the reduction step or dry ice in the reoxidation step) in the loop permitted quantitative removal of H_2O generated. Volumetric determination of collected water was made after removal of the H_2 or O_2 from the system. All gases used were of CP grade and were further purified by conventional methods.

About 3 g of catalyst was subjected to an overnight pretreatment in O_2 at the temperature of the experiment in order to remove excess H_2O. After evacuation for 1 hr at temperature, a known amount of H_2 was added to the circulation loop and expanded into the reactor. The drop in pressure was monitored and the reaction was terminated by carefully evacuating the residual H_2 through the trap. Evacuation was continued for 1 hr. After this time no further H_2O was being released by the catalyst as noted by isolating the catalyst and looking for a response on a Hg manometer. The water collected in this step was then measured. Oxidation of the reduced catalyst was carried out in a similar manner using O_2 in place of H_2.

TREATMENT OF DATA

Basically, the experiment consisted of a redox cycle. In the first step (reduction), H_2 consumption and H_2O released were measured; in the second step (oxidation), only O_2 consumption was required, but as noted above the H_2O released in 1 hr was usually measured. In the first step, Mo is reduced from the +6 state to a lower valence state with a concurrent but not stoichiometric loss of oxygen in the form of H_2O. At this point hydrogen remained held by the catalyst (consumption $\gg H_2O$ evolution), but some of this was removed during the evacuation and this could not be measured directly. The oxidation step replenished the lost oxygen, reoxidized the Mo back to +6, and reacted with any bound hydrogen to form H_2O.

In attempting to analyze the data in terms of bound hydrogen, it soon became evident that at least two types of adsorbed H had to be present on the reduced catalyst in the presence of gaseous H_2—that which was desorbed within 2 hr under vacuum (reversible) and that which was still retained by the catalyst after extensive evacuation at reaction temperature (irreversible). In addition, a closed loop material balance was not obtained at the end of the redox cycle, i.e., after reaction with oxygen and subsequent evacuation for 1 hr, even after accounting for the reversible H_2 which was removed by evacuation after the reduction step. It was anticipated from related microbalance results (*3*), that the problem resided in water retention by the oxidized catalyst.

With these points in mind, the following material balance statements can be written:

$$\begin{aligned}[H_2] &= [W_R] + H_R + H_I,\\ 2[O_2] &= [W_R] + H_I, \qquad (1)\\ [W_O] &= H_I - W_A,\end{aligned}$$

where

$[H_2]$	H_2 consumption in reduction step
$[W_R]$	H_2O formed in reduction step
$[O_2]$	O_2 consumption in oxidation step
$[W_O]$	H_2O formed in oxidation step
H_R	H_2 adsorbed in reduction step, which is reversibly removed by evacuation
H_I	ditto, but not removed by evacuation
W_A	H_2O retained by catalyst after the oxidation step and subsequent evacuation.

These equations can be solved explicitly for the three unknowns, viz,

$$\begin{aligned}H_R &= [H_2] - 2[O_2],\\ H_I &= 2[O_2] - [W_R], \qquad (2)\\ W_A &= 2[O_2] - [W_R] - [W_O].\end{aligned}$$

The degree of reduction of the catalyst after the first step is defined by the extent of oxygen loss (measured as W_R) relative to the total oxygen available for reduction, viz,

$$\%\ \text{reduction} = \frac{[W_R]}{3[\text{Mo}]} \times 100, \qquad (3)$$

where $[W_R]$ is as before and [Mo] is the molybdenum content of the catalyst, both in units of moles per gram of catalyst. Alternatively, vacancies formed in reduction ($\square$), may be related to oxygen loss from the catalyst by the relationship:

$$\square/\text{Mo} = [W_R]/[\text{Mo}]. \qquad (4)$$

It should be noted that calculation of the desired quantities, H_R, H_I, and percentage reduction does not depend upon the adsorbed H_2O left on the reoxidized catalyst, which quantity varies with time of evacuation.

Results

The data from the redox experiments are given in Table 1 in terms of volumes

TABLE 1
Reduction–Oxidation Cycles on 8% Mo/Al_2O_3 Catalyst[a]

	Reduction					Oxidation		Surface concn[d] (ccNTP)		
Temp[b] (°C)	Time (min)	Final press (Torr)	H_2 consumed (ccNTP)	H_2O formed (ccNTP)	Reduction[c] (%)	$2O_2$ consumed (ccNTP)	H_2O formed (ccNTP)	H_I	H_R	W_A
500	120	248	16.69	10.69	19.9	14.59	2.78	3.90	2.10	1.12
500R	120	217	16.26	10.09	18.7	14.16	2.71	4.07	2.10	1.36
400R	30	280	10.05	4.29	8.0	8.64	2.67 (3.55)[e]	4.35	1.41	1.68 (0.80)[e]
600R	120	146	21.44	14.36	26.7	18.66	—	4.30	2.78	—
400	20	134	7.26	3.01	5.6	5.99	3.03[f]	2.98	1.27	−0.05[f]
400R	5	153	4.44	1.59	2.9	3.92	—	2.33	0.52	—
400R	45	205	7.10	3.06	5.7	—	—	3.40	0.64	—
550[g]	—	—	−0.02[h]	2.96	—	6.46	—			

[a] Basis: 1 g of charge. Water loss on heating overnight was 5–6 wt%.

[b] R signifies sample was used in a previous redox cycle.

[c] Calculated from Eq (3).

[d] Calculated from Eq (2). Values pertain to reduced state prior to evacuation (cc H_2 or H_2O).

[e] Values in parentheses are for extra 6-hr evacuation through cold trap (cumulative).

[f] Water collected over 20-hr period.

[g] Sample heated in vacuum to 550°C and held for 1 hr prior to oxidation at 550°C.

[h] H_2 evolved.

TABLE 2

Surface Concentrations of Reduced Catalyst

Temp[a] (°C)	□/Mo[b]	H_I/Mo[c]	H_R/Mo[c]
500	0.593	0.433	0.233
500R	0.560	0.452	0.233
400R	0.237	0.483	0.156
600R	0.795	0.477	0.308
400	0.166	0.331	0.141
400R	0.088	0.260	0.058
400R	0.170	0.377	0.071

[a] Same series as in Table 1.

[b] Vacancy site/Mo.

[c] Atom per atom Mo.

of gas consumed in the reduction and oxidation steps and as surface concentrations in Table 2. Differing extents of reduction were achieved by varying the temperature, pressure and/or time in contact with H_2. In some experiments a fresh catalyst sample was used while in others the same sample was used as in a previous redox cycle. In the latter case, the sample was treated in O_2 overnight at the temperature of the next experiment.

The rate of H_2 consumption was rapid initially, but became slower as the reduction proceeded. In no experiment was reduction complete in the time–temperature region studied. Reoxidation, on the other hand, was very rapid and essentially complete within 0.5 hr. These results agree with earlier work (3).

Previous investigation (3) had shown that a 1-hr purge in N_2 was sufficient to obtain a constant catalyst weight after the reduction step. However, after the oxidation step, catalyst weight was greater than its original oxidized value, but slowly decreased in purging with N_2 due to gradual desorption of water. In order to check this latter point, evacuation was continued for an additional 6 hr beyond the standard 1 hr (3rd run), whence the amount of water remained adsorbed on the catalyst dropped by one-half. In another experiment (5th run), the oxidized catalyst was subjected to a mixture of O_2 and He for overnight with continuous circulation through the water trap. From the total water collected by this treatment, W_O, and the other quantities measured in the experiment, a good material balance was obtained, i.e., W_A in Eq. (2) was zero within experimental error. Hence, in this case,

$$H_I = 2[O_2] - [W_R] = [W_O],$$

confirming that the water from the oxidation derived directly from the irreversibly retained H. Having satisfied ourselves on this point, it was deemed sufficient to omit (or ignore) the water from the oxidation step and use the measured quantities $[H_2]$, $[O_2]$ and $[W_R]$ for calculating the desired values of H_I and H_R according to the first two relationships in Eq. (2).

Figure 1 presents a plot of H_I vs the

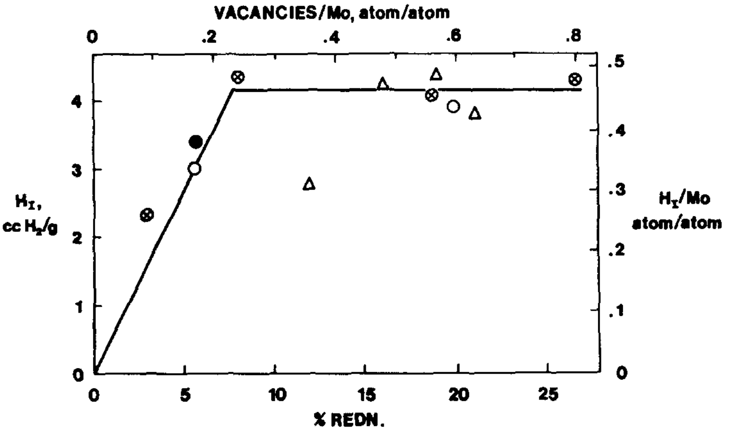

Fig. 1. Correlation between irreversibly adsorbed hydrogen (H_I) and reduced state of the catalyst. (○) Fresh catalyst, (⊗) regenerated, (●) Run 7, (△) data of Ref. (3).

percentage reduction. This quantity was the hydrogen retained after the evacuation following the reduction step. A direct correlation between H_I and percentage reduction obtains at low reductions, but at higher reductions H_I becomes independent of percentage reduction. Since the percentage reduction is defined by the water lost in the reduction step, it is also a direct measure of the oxygen lost by the catalyst. The oxygen lost can be equated with oxide surface vacancies. In these terms, the correlation at low vacancy density gives an H_I/vacancy ratio of unity, or two atoms of H retained per vacancy. On the flat maximum portion of Fig. 1, no further increase in H_I occurs with further reduction suggesting that a second process sets in.

In order to establish whether the irreversibly retained H_2 could be characterized as some form of strongly chemisorbed hydrogen, a special experiment was performed (7th run, Table 1). The catalyst was reduced at 400°C, evacuated for 1 hr, and the H_2 consumption and H_2O formed were measured. The catalyst was then heated to 550°C in circulating He for 1 hr. In this step, very little H_2 gas was evolved (<0.02 cc/g) as evidenced by the small net change in pressure (when corrected for reactor tube temperature change), but appreciable H_2O was produced. Finally, the oxygen uptake was determined at 550°C. Analysis of the data, using the H_2 and H_2O values at 400°C and the O_2 value at 550°C, gave the solid point falling on the straight line of Fig. 1. This could only occur if the H_I was removed as H_2O and not as H_2 in the heat-up step added after reduction. If the H_I was predominately removed as H_2, the O_2 uptake would be lower than obtained, reflecting only that added to the vacancies, little H_I being left available to react. On the other hand, removal of the H_I as H_2O, via dehydroxylation of OH, would create additional vacancies of exactly equal number to the H_I removed; consequently the O_2 uptake would be identical to that which would normally be obtained at low temperature oxidation. Furthermore, the H_2O released in the heat-up step (2.96 cc) was not an insignificant fraction of the calculated H_I. This H_2O can come from two sources, viz, dehydroxylation of OH_I, and extra loss from the Al_2O_3 portion of the catalyst. In order to estimate these contributions, a separate experiment was carried out in a microbalance. The catalyst was heated overnight in air at 400°C. Upon raising the temperature to 550°C, a weight loss equivalent to 1.4 cc H_2O/g was measured. Subtracting this value from that obtained in the heat-up step of the 7th run still leaves 1.6 cc H_2O/g generated from H_I. Thus, more than half of the H_I present after the low temperature reduction was removed in the heat-up step.

In Fig. 2a, the relation between H_R and the percentage reduction is similarly depicted. The approximately linear relation suggests that H_R is associated with vacancies. This notion is supported by the data of Fig. 2b as the different vacancy densities were mainly achieved by employing different temperatures. Presuming this H_2, which is readily removed upon evacuating

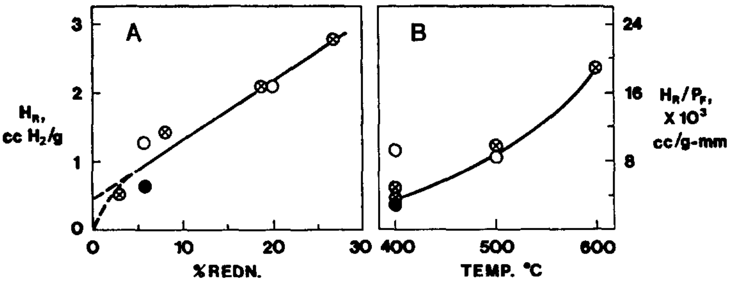

FIG. 2. Correlation between reversibly adsorbed hydrogen (H_R) and: (A) % reduction of the catalyst and (B) temperature. Symbols same as for Fig. 1.

the reduced catalyst, to be weakly adsorbed, it might be expected to be proportional to the gaseous H_2 pressure during the experiment; this partly reduced the scatter, but not entirely, as seen in Fig. 2b. An Arrhenius-type plot of H_R/p_f (where p_f is the final H_2 gas pressure just prior to evacuation) and temperature gave an activation energy of about 4 ± 1 kcal/mole.

Since extrapolation of the H_R vs W_R curve to zero reduction is uncertain from the data (Fig. 2A), it was deemed desirable to establish whether any H_2 adsorbed on the fully oxidized catalyst. Unfortunately, this could not be done at working temperatures due to rapid catalyst reduction. Therefore, the oxidized catalyst was exposed to H_2 at room temperature. No measurable H_2 adsorption was detected in this case.

The presence of adsorbed oxygen on the oxidized catalyst prior to reduction could complicate the interpretation of the results. The catalyst was pretreated in O_2 overnight and then evacuated for about 1 hr prior to the reduction step. Exposure of the catalyst to O_2 at this state at 600°C showed negligible O_2 adsorption.

DISCUSSION

The reduction characteristics of the Mo/Al_2O_3 catalyst have been fully discussed elsewhere (*3*). The results of this investigation clearly show that two distinct types of hydrogen are adsorbed on a reduced Mo/Al_2O_3 catalyst—irreversibly retained (H_I) and reversibly adsorbed (H_R). Although there may be experimental and theoretical difficulties in attempting to precisely separate each type, a reasonably quantitative measure was obtained with the 1-hr evacuation period employed. It is possible, however, that some additional H_I would be lost in a long-time evacuation.

The correlation between the H_I and the vacancy density at low reductions strongly implies an association of H_I with vacancies. It is plausible to assume attachment of the H_I to oxide ions neighboring the vacancy (*1*, *3*). Evidence supporting this interpretation is as follows: (1) H_I is still present even after extensive evacuation, (2) H_I is probably not present as adsorbed H_2O since introduction of O_2 caused an immediate release of H_2O whereas N_2 did not, (3) H_I is associated with Mo as none was detected with the Al_2O_3 support alone (*3*), and (4) H_I was removed as H_2O, not H_2, when the temperature of the reduced catalyst under vacuum was raised. Since this process represents a dissociative adsorption and reaction to form hydroxyl groups, a reducible cation is needed. For example, a simple reaction sequence may be envisioned as,

$$H_2 \rightleftharpoons H_R, \qquad (5)$$

$$Mo^{6+} + O^{2-} + \tfrac{1}{2} H_R \rightarrow Mo^{5+} + OH_I^{-}. \qquad (6)$$

Here we arbitrarily define the adsorbed hydrogen as the sum of H_R and H_I because evacuation will remove H_R but not H_I. Also, evacuation at elevated temperature will not remove H_I as H_2 although some H_I can be removed as H_2O by simple dehydroxylation of OH_I groups. Reaction with oxygen will also remove H_I as H_2O, but now oxidation of the Mo must occur concurrently, as for example,

$$Mo^{5+} + OH_I^{-} + \tfrac{1}{4} O_2 \rightarrow Mo^{6+} + O^{2-} + \tfrac{1}{2} H_2O. \qquad (7)$$

Much less of a definitive nature can be said about H_R. It represents an important fraction of the hydrogen held by the catalyst. It is easily desorbed, but whether it is adsorbed associatively or dissociatively is not known, nor its location. Possibly, it may be dissociatively adsorbed on Mo^{4+} exposed at a vacancy and adjoining oxide ion (not already covered with H_I), similar to that found for ZnO (*4*) or for Cr_2O_3 (*5*). Since the Mo^{4+} is coördinatively unsaturated, heterolytic adsorption of H_2 should be possible (*5*); this adsorption would be expected to be weak and reversible. There may be a contribution to H_R from the Al_2O_3 of the catalyst, but this should be low in the temperature range studied (*6*). H_R generally increased with defect density in contrast with H_I which reached a maximum.

It has been suggested that the reversibly adsorbed hydrogen is the active species for the hydrodesulfurization of thiophene (*2*). The Lipsch and Schuit (*1*) mechanism requires that the hydroxyl H is involved in the reaction. It seems likely that both are important via Eqs. (5) and (6) given above.

The finding of close stoichiometry between irreversibly retained H and vacancies seems to support the proposed mechanism of Lipsch and Schuit in detail. A fundamental question is: why are there exactly two H per vacancy? If we adopt the Lipsch and Schuit mechanism, two H attached to oxide ions neighboring a vacancy provide the proper assemblage of atoms (active site?) to accomplish the desulfurization reaction. However, there is no *a priori* reason why more or less H could not be present, even if exactly two per vacancy are involved in the desulfurization act, unless the chemisorption is heterolytic as found with ZnO (*4*). This would require a simple modification of the Lipsch and Schuit mechanism.

Since the ratio of $2H/\square$ was found at low reduction, a randomized adsorption can be ruled out, and a site-specific adsorption must be considered. Lipsch and Schuit visualized two H attached to two oxide ions adjoining the vacancy. This seems perfectly plausible but still leaves unanswered the question of why two and not one or three or some non-integer, average number. A reasonable hypothesis might be a surface geometric restriction. For example, one may envision a situation in which only two surface oxide ions are in nearest neighbor proximity to a vacancy; because of the cation exposed at the vacancy, these adjoining oxides become activated toward adsorption of H, forming hydroxyl ions. At low temperature, reduction is low and the H_I added (at a ratio of $H_I/\square = 2$) is stable. Now it must be recalled that the activation energy for reduction increases with degree of reduction (*3*). The significance of this is that higher temperatures are required to achieve higher degrees of reduction. This is evident from the data of Table 1. At the higher temperature, an increase in proton mobility may be expected, thus providing a mechanism for dehydroxylation as the protons hop over the surface oxygens. This may be the explanation of the loss in some H_I as H_2O (7th run) when the reduced catalyst at 400°C was heated to 550°C in the absence of H_2 gas. Although this created additional vacancies presumably capable of adding extra H_I, none could be added because the H_I removed was as H_2O and no H_2 gas was present to react.

Viewing the retained H as bonafide OH groups, their formation are nevertheless quite different from the normal hydration–dehydroxylation chemistry associated with familiar catalytic support materials, i.e.,

$$O^{2-} + \square + H_2O \rightleftharpoons 2OH^-, \qquad (8)$$

which does not formally involve a valence change in the support cation. Moreover, it should be noted that this reaction does not occur to any great extent with H_2 (*6*). On the other hand, the hydroxyl groups formed during reduction of the Mo catalyst does require a change in valence of the Mo. This is because each H_2 molecule adsorbed as H_I must contribute two electrons to the catalyst, the electron sink being the Mo cation. Thus, the process involves a true redox reaction in which the Mo is reduced to a lower valence state and the H is oxidized to H^+, for example as shown by Eq. (6). Thus, the percentage reduction as defined in this paper by Eq. (3) is equivalent to a vacancy concentration but not to an average reduced Mo valence state of the catalyst.

Any surface model of the Mo/Al_2O_3 catalyst must not only fulfill the requirement of an exact ratio of $OH_I/\square = 2$ at low reductions, but also a limiting value of $OH_I/Mo = 0.45$ at moderate extents of reduction; the straight lines in Fig. 1 represent these conditions. The sharp break at about 0.2 $\square/Mo$ (7% reduction) suggests that the reduction occurs in two stages, viz, one in which exactly 2H atoms are added per vacancy formed and one, in which no net H is added as additional vacancies are formed. Therefore, it appears likely that geometric restrictions come into play.

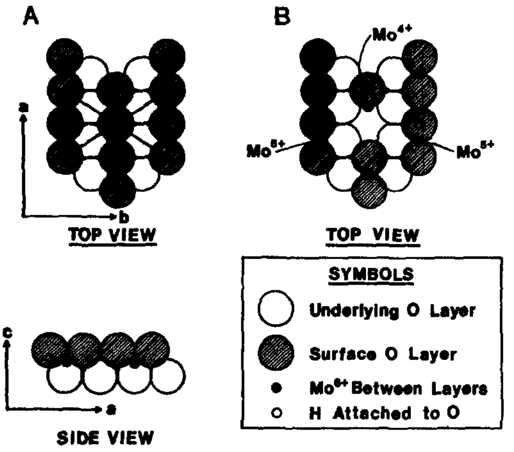

FIG. 3. Proposed surface of $Mo/\gamma\text{-}Al_2O_3$. (A) Oxidized catalyst, (B) reduced catalyst.

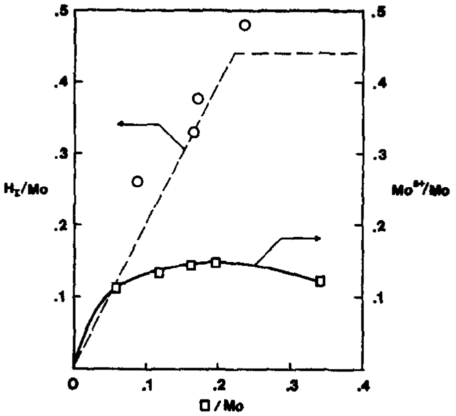

FIG. 4. Relationship between H_I and Mo^{5+}. ($\square$) ESR data on 10% $Mo/\gamma\text{-}Al_2O_3$ reduced at 300°C (*9*); (○) data of this study.

A surface model for the Mo/Al_2O_3 catalyst has been previously proposed (*3*) which involves two terminal oxide anions per Mo atom, and two interlayer oxide ions shared with Al atoms lying below the surface. Lippens (*7*) has concluded that the most favorable structure for $\gamma\text{-}Al_2O_3$ is that in which the surface takes on the 110 configuration. If MoO_3 is added epitaxially as a monolayer in small patches over the Al_2O_3 surface (about 40% of the Al_2O_3 surface would be covered with our catalyst) the 110 configuration can be maintained, but now the surface oxide ions are terminal oxides associated with the Mo. Each oxide ion in the surface layer can have two nearest neighbors (*a*-axis), two further removed (*b*-axis) and four more distant (diagonal) (see Fig. 3). If it is assumed that only the near neighbors to a vacancy can become activated for H_I adsorption, at low reduction, an isolated vacancy will be surrounded by three oxide ions bound to a Mo^{6+} cation, and one oxide ion to a Mo^{4+} cation. Addition of an atom of H_I to the latter oxide would be expected to further reduce the Mo^{4+} to the Mo^{3+} cation. Since the presence of Mo^{3+} on reduced $Mo\text{–}Al_2O_3$ catalysts has not been reported and attempts at detecting it by ESR have been unsuccessful (*8*), we would expect the stable locations to be the opposite $Mo^{6+}\text{–}O$ oxides, as depicted in Fig. 3b. On this basis, two Mo^{5+} cations would be formed for each $Mo^{4+}\text{–}\square$ site pair.

The absolute concentration of Mo^{5+} has been determined for similar Mo/Al_2O_3 catalysts under various reduction conditions (*9*). Also, these concentrations were correlated (*3*) with the extents of reduction as determined by microbalance measurements. Data for a 10% $Mo/\gamma\text{-}Al_2O_3$ catalyst reduced at 300°C are given in Fig. 4, plotted as Mo^{5+}/Mo vs $\square/Mo$. Superimposed is the H_I/Mo vs $\square/Mo$ relationship found in the present study. Even though the data are inadequate to form a firm conclusion, it can be seen that no inconsistency is present between the model and the ESR data taken in the range of the very low reduction. Obviously, an explanation is missing for the leveling of the ESR data as the vacancy density is increased above about 0.6 $\square/Mo$ and there are a couple of possible explanations for this. Therefore, further work is needed here.

Bulk MoO_3 showed little propensity toward H-retention. A sample of bulk MoO_3 which was reduced about 20%, gave less than 2% of the H_2 uptake as water upon reoxidation. By the same token, reduced MoO_3 (and Mo supported on SiO_2) showed practically no Mo^{5+} signal (*10*). These results are consistent with the thought that the Mo^{5+} arises from H_I addition to $Mo^{6+}O^{2-}$.

ACKNOWLEDGMENT

The assistance of Mr. James Marsh in the experimental portion of this investigation is gratefully acknowledged.

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