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Characterization of Mo/Al_2O_3 Catalysts by Low-Temperature Oxygen Chemisorption

Low-temperature oxygen chemisorption (LTOC) has recently come out as an important surface specific tool for characterizing reduced (*1–11*) as well as sulfided (*12–27*) hydroprocessing catalysts. It is generally accepted (*27–32*) that coordinately unsaturated Mo ions (CUS) on reduced and sulfided catalysts are the active sites for hydrogenation (HYD) and hydrodesulfurization (HDS) reactions; and that oxygen, when chemisorbed at temperatures around −78°C does so dissociatively (*12, 19*) and selectively on the CUS (*8, 12, 17, 19*). However, on analyzing the results of LTOC on Mo/Al catalysts, it is observed consistently that only a small fraction (about 0.2) of the total CUS is titrable by LTOC. This conclusion is derived from the low oxygen (as determined by LTOC)-to-Mo ratio (O/Mo) as reported by various workers and compiled in Table 1. This ratio is significantly lower than what is expected from the fact that under the normal conditions of reduction of supported Mo/Al catalysts about 75% of Mo^{6+} is converted to Mo^{4+} (*16, 28*) generating an equivalent amount of CUS that should, in principle, serve as potential centers for oxygen chemisorption. The low O/Mo ratio, therefore, implies that not all of the CUS, but only a minority group, are capable of holding chemisorbed oxygen at low temperatures. This interesting phenomenon has not received proper attention so far. Therefore, an effort is made in this communication to understand the implications of the above findings on the surface structure of the Mo oxide (supported) catalysts as well as on the genesis of the sulfided state from the oxide precursors. For the sake of simplicity, we will devote ourselves only to the unpromoted Mo/Al catalysts.

In order to complement the data presented in Table 1, low-temperature oxygen chemisorption was performed on a series of Mo/Al catalysts. The Mo/Al catalysts with Mo loading varying between 2 and 12% were first prepared by incipient wetting of a Harshaw γ-Al_2O_3 (204 m^2g^{-1}, 0.6 ml g^{-1}) by stoichiometric solutions of ammonium heptamolybdate at pH 8. The alumina support was calcined at 540°C for 16 h prior to impregnation. The impregnated samples were dried at 120°C and then calcined at 540°C, both for 16 h. Reduction of the calcined catalysts was done *in situ* by flowing hydrogen (40 ml min^{-1}) for 6 h at 500°C. Sulfidation of the calcined catalysts was done at 400°C for 2 h by passing CS_2-saturated H_2 (at 25°C). The catalyst, thus reduced (or sulfided), was evacuated at the temperature of reduction (or sulfidation) for 2 h at 10^{-6} Torr, followed by an additional evacuation for 2 h at −78°C prior to chemisorption, which was performed in a static high-vacuum system. Experimental details on the LTOC have been given elsewhere (*26, 35*).

The results are shown in Fig. 1. It is observed that the uptake of oxygen, normalized to unit surface area of the reduced (or sulfided) catalysts, increases linearly as a function of surface coverage up to a certain value and then tends to level off. It is interesting to note that the leveling off in the oxygen uptake capacity starts at a surface coverage of about 4.5 μmol m^{-2}—a value that corresponds to the monolayer cover-

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TABLE 1

Results of Oxygen Chemisorption on Mo/Al Catalysts Taken from Various Works

Catalyst: % Mo on Al_2O_3	State of catalyst	O/Mo ratio	Temp. of oxygen chemisorption, (°C)	Reference
2–12	Reduced	0.15–0.075	−78	This work
2.4–9.5	Reduced	0.24–0.09	−78	Weller (*7*)
0.75–18.24	Reduced	0.32–0.13[a]	+25	Yao (*36*)
8	Reduced	0.005[a]	R.T.[b]	Okamoto (*45*)
8	Reduced	0.35	−78	Hall (*8*)
8	Sulfided	0.02[a]	R.T.[b]	Okamoto (*36*)
8	Sulfided	0.22[a]	−78	Hall (*12*)
8	Sulfided	0.20	−78	Hall (*12*)
8	Sulfided	0.04	−78	Massoth (*17*)
1.3–13.3	Sulfided	0.16–0.09	+27	Jung (*25*)
5–18	Sulfided	0.20–0.11	R.T.[b]	Burch (*24*)
8.6	Sulfided	0.1	−78	Topsøe (*27*)
2–12	Sulfided	0.10–0.04	−78	This work

[a] These values are obtained from the NO chemisorption data by assuming that four NO molecules can adsorb on sites where one O_2 can adsorb as per the findings of Hall (*12*).

[b] Room temperature.

age (*33, 36*) of alumina surface by Mo oxide.

In order to elicit further information, O/Mo ratio has been plotted as a function of surface coverage in Fig. 2. The low values of O/Mo and its monotonic decrease as a function of surface coverage are the two most important features to be noted in Fig. 2. The parallelism between the curves related to reduced and sulfided catalysts is also remarkable. These results are in perfect accord with other published results as documented in Table 1.

Table 1 shows clearly that for both reduced and sulfided Mo/Al catalysts the O/Mo ratio is remarkably lower than what is expected from the reduction characteristics (*7–12*) of the catalysts as described earlier. Furthermore, if all of the CUS are to hold oxygen, the monotonic decrease in O/Mo ratio with increasing Mo loading (Fig. 2 and Table 1), does not conform with the well-

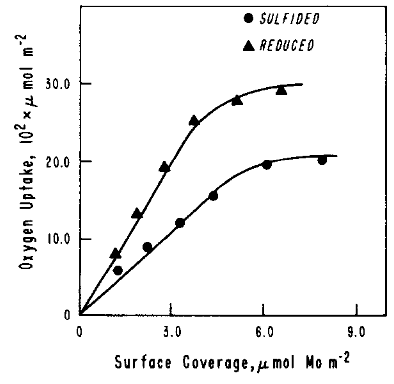


FIG. 1. Oxygen uptake at −78°C as a function of surface coverage.

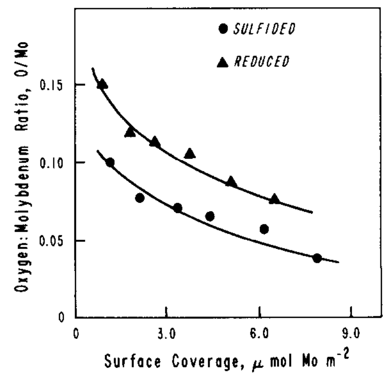
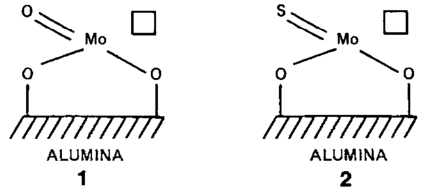


FIG. 2. Oxygen-to-molybdenum ratio, O/Mo, as a function of surface coverage.

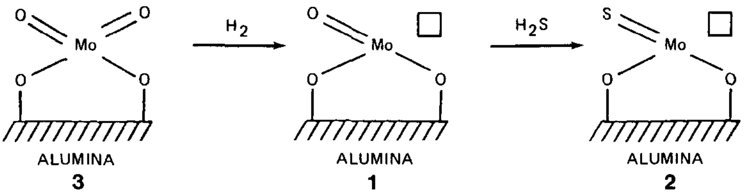
documented fact that with increasing Mo loading the fraction of more reducible octahedral Mo oxide Mo(O) increases (*16, 37–40*) with concomitant increase in the number of CUS (*8–12*) (on reduction). A monotonic increase (up to O/Mo = 1) as a function of Mo loading, rather than a decrease, in the O/Mo ratio should have been observed if all of the CUS generated by reduction could chemisorb oxygen. This conflicting behavior indicates, therefore, that only a selected group of surface Mo sites (CUS) with some special properties is capable of chemisorbing oxygen at low temperatures. These special properties are envisioned to include the chemical state of Mo (oxidation state), the distribution of the surface Mo oxide species to octahedral and tetrahedral coordination, and last, but not the least, the location of the CUS on the surface of the catalyst. It is well known (*12, 37–40*) that the coordination surrounding and the reducibility of the supported Mo oxide are strongly dependent on several factors including the nature of the exposed crystallographic plane and the surface concentration of the OH groups of the support, and the pH of the impregnating solution. For the γ-Al_2O_3-supported catalysts prepared by incipient wetting of the support by ammonium paramolybdate at pH around 8 and calcining at about 500°C, the arrangement of the surface OH groups of Al_2O_3 permits the formation of isolated tetrahedrally coordinated Mo(T) species at very low Mo loadings (*37*). With increasing Mo loading, however, the more reducible polymeric species with Mo(O) are formed in increasing proportion (*38*). The overall reduction behavior of the supported Mo oxide catalyst is strongly dependent on the distribution of the type of species, Mo(T) or Mo(O), on the alumina surface; and the nature of the oxide precursors and their reduction behavior are expected to have important bearing on the oxygen chemisorption. This is because LTOC is possible only on prereduced catalysts (*8*) that contain the CUS generated by the removal of oxygen from Mo oxide as H_2O by H_2 reduction (*28*).



SCHEME 1

As mentioned earlier, the isolated Mo(T) species are more difficult to reduce than the polymeric Mo–(O) species (*12, 15, 37–40*), presumably due to strong chemical interaction between Mo(T) and the carrier (*41*). The results presented in this article show unexpectedly that the reducibility of a Mo oxide species Mo(T) or Mo(O) does not necessarily reflect its oxygen chemisorption capacity. Had it been so, one would have observed an increasing O/Mo ratio in Fig. 2 and Table 1 as a function of surface coverage, rather than a decreasing trend. From the low as well as decreasing O/Mo ratio with increasing Mo loading, it appears that the isolated species **1**, which is generated by the partial reduction of isolated tetrahedral Mo(T) **3**, is the center for LTOC (Scheme 1). The importance of this type of species as active sites has been recognized by Hall *et al.* (*8, 10, 42, 43*); and according to Okamoto *et al.* (*44, 45*) species **1** acts as the precursor of the species **2** which serves as the active site for HDS reactions.

In view of these facts, the low and decreasing O/Mo ratio can be explained as follows: At very low surface coverage, the majority, if not all, of the surface Mo remains as Mo(T); and the low reducibility of Mo(T) permits only a small fraction of total Mo, roughly about 0.2, to generate species **1** that does chemisorb oxygen. As the surface coverage increases, the proportion of polymeric Mo(O) also increases. Although Mo(O) has higher reducibility than Mo(T) (*16*), the CUS that are generated by reduction of Mo(O) probably do not hold chemisorbed oxygen, as is observed from the de-



SCHEME 2

creasing O/Mo ratio with increasing Mo(O) (i.e., increasing Mo loading). Rather, the increasing proportion of Mo(O) "dilutes" the proportion of Mo(T) to greater and greater extent, and this "dilution" effect is reflected by the decreasing O/Mo ratio.

Since the above hypothesis is rather speculative, it is worthwhile to seek an alternative interpretation from a different perspective. Hall (*42*) has recently proposed that, but for a very small fraction of difficultly reducible Mo(T), the Mo phase of the unreduced Mo/Al catalysts remains on the support surface as small "clusters" of Mo(O) oxide of two layers of thickness. On reduction, oxygen atoms at the edges and corners of the octahedral clusters are removed and the catalytically active CUS are generated. This "patch" model is consistent with the EXAFS results of Clausen *et al.* (*46*) which show a highly disordered Mo oxide phase in the calcined catalysts. As per the "patch" model, the reduced catalyst is envisaged (*42*) as supported submicrocrystallites of MoO_2 with the CUS. If this is so, then the low and decreasing O/Mo ratio should indicate that with increasing Mo loading, the patches grow in size along the alumina surface, thus permitting smaller and smaller fractions of Mo to be distributed to the edge or corner positions. Thus, the O/Mo ratio obtained by LTOC reflects a dispersion effect.

The parallelism between the oxygen chemisorption characteristics of the reduced and of the sulfided catalysts, as depicted in Figs. 1 and 2 and summarized in Table 1, indicates a "memory" effect which plays some part in the genesis of the sulfided state from the oxide precursor. These results give an impression that the surface state of the oxide precursor remains essentially intact even after sulfidation, at least for that fraction of Mo oxide which chemisorbs oxygen at low temperatures. All these results can be explained again by the works of Okamoto *et al.* (*44, 45*), who showed that at lower Mo loadings and especially under mild reduction conditions, as used in this work as well as in the works referred to in Table 1, catalytically active species like **2** are generated during the sulfidation step as per the reaction Scheme 2.

This scheme is consistent with the "monolayer" model of supported Mo sulfide catalysts as proposed by Massoth (*33*). According to Okamoto *et al.* (*44*) the species **2** with ratio S/Mo = 1 has the highest HDS activity. Since a correlation has also been reported between the number of chemisorbed oxygen atoms with HDS activity (*13–15, 18, 19, 23, 25, 26*) for similar catalysts with the same support material, we conclude that the species **2** is a likely candidate for oxygen chemisorption which occurs dissociatively (*12, 19*) on the CUS. Yang and Satterfield (*47*) have also recently proposed the species **2** as the active HDS site. The observations that the O/Mo is low and that it decreases with increasing Mo loading are consistent with the fact that only a very small fraction of total Mo can remain on the surface as strongly bound isolated Mo(T) species **3** (the precursor of **2**) and that the Mo(T)/Mo(O) ratio decreases (*15, 37–40*) with increasing loading.

In view of Hall's "patch" model of the oxide precursor, it is possible that the patches containing mainly Mo(O), on sulfidation, generate small crystallites of MoS_2 without changing their registry with the alumina surface. This is in line with Topsøe's (*48*) proposal that under mild sulfiding conditions, the Mo/Al catalysts are converted to small two-dimensional crystallites (about 10 Å) of MoS_2 which contain anion vacancies (CUS) on the edges and corners. These vacancies are the sites for HDS and HYD reactions and, as it turns out, also for LTOC. The remarkably low number of such sites, as titratable by LTOC, then indicates again that not all such vacancies, but only those on certain specific locations on the crystallites, are capable of LTOC. From the probable distribution of the edge and the corner sites on such small two-dimensional crystallites of MoS_2, it appears that the CUS at the corners are the sites for LTOC.

Finally, since the monolayer model, especially for the sulfided Mo/Al catalysts, has recently been found to be inadequate (*48*), the above explanations based on the "patch" model are preferable. However, further research is necessary to fully understand the mechanism.

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