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Multilayer Structure of Molybdena/γ-Alumina Catalysts Prepared Using Different Methods

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The apparent surface coverage by molybdena in three series of $MoO_3/\gamma\text{-}Al_2O_3$ catalysts prepared by different methods was determined by electrophoretic migration. These methods were designed to vary the extent of clustering (polymerization) in the solutions and on the wet catalysts. The combined use of electrophoretic migration and molybdenum extraction measurements showed that in alumina-supported molybdena catalysts with content below 14 wt%, molybdenum is present in both monolayer and multilayer forms over the entire range of molybdenum loading studied, irrespective of the method of catalyst preparation used.

INTRODUCTION

Great efforts using different techniques have been devoted to elucidating the structure of Mo-based hydrodesulfurization catalysts and in particular, promoted molybdena on alumina support. For many years it has been generally accepted that in the calcined state (for loadings below about 15% of MoO_3) the Mo is highly dispersed over the alumina surface. In contrast, controversial opinions exist on the exact structure of the sulfided catalyst forms; various models have been proposed, including the monolayer model (*1, 2*), the pseudointercalation model (*3, 4*), the synergy by contact model (*5, 6*), and the Co–Mo–S model (7–9).

For a better understanding of the final sulfided catalyst, it is necessary to know whether the Mo in the calcined catalysts is present on the alumina surface as a molybdate disrupted monolayer, or whether Mo is also present in a multilayer form (three-dimensional polymeric structure), i.e., is there coexistence on the alumina surface of both monolayer and cluster structures? Early results of oxygen chemisorption and molybdenum extraction (*10, 11*) have shown the presence of patches of three-dimensional polymeric species in both promoted and unpromoted molybdena supported catalysts, prepared by the wet impregnation method. In the same connection Hall *et al.* (*12–14*) using Raman and reflectance spectroscopy have shown that small islands of molybdenum atoms in two layers thick may exist in catalysts prepared by the equilibrium adsorption method. It is not clear, however, if any of these "non-monolayer-phases" are present even at low molybdena content in catalysts prepared by any procedure.

The purpose of this study was, therefore, to investigate these two important questions. Our hypothesis was that if molybdenum is present exclusively as a monolayer, then the decrease of the molybdenum loading by an extraction treatment (with ammonia solution) must be equal to the decrease of the surface fraction coverage by molybdenum. We compared the "apparent surface coverage" of three series of molybdena γ-alumina catalysts before (fresh samples) and after (extracted samples) the molybdena was partially extracted by ammonia solutions. The catalysts were prepared by wet and incipient wetness impreg-

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nation methods using water and NH_4OH or H_2O_2 solutions, respectively). The apparent surface coverages by molybdenum were determined by electrophoretic method (*15*) as outlined below.

EXPERIMENTAL

Catalysts. A Girdler T-126 alumina, with BET surface area of 188 $m^2\ g^{-1}$ and a pore volume of 0.39 $cm^3\ g^{-1}$ was used as support.

Catalyst samples with different molybdena content were prepared by three different methods:

(A) The "wet" impregnation method in which the ammonium–heptamolybdate (Merck p.a.) was impregnated using water in excess of the pore volume. The pH of Mo impregnation solution was 5.2.

(B) The NH_4OH incipient wetness method in which the ammonium-heptamolybdate was impregnated using the pore volume of NH_4OH solution. The pH of Mo impregnation solution was 9.9.

(C) The H_2O_2 incipient wetness method in which the ammonium–heptamolybdate impregnated using the pore volume of H_2O_2 solution. The pH of Mo impregnation solution was 5.4.

In the three methods the solvent was evaporated at 350 K and 27 K N m^2 in a rotary evaporator. Then, the samples were treated in a forced flow of air at 650 K for 2.5 h and finally calcined at 823 K for 4.5 h. The MoO_3 content was determined by atomic absorption spectroscopy.

Extraction by ammonia. For the partial molybdenum extraction of the samples, the method described by N. Giordano (*16*) was used: 0.100 g of $MoO_3/\gamma\text{-}Al_2O_3$ samples was immersed in 100 ml of a dilute ammonia solution (3 wt%) for 48 h with shaking. Then the solid samples were washed with H_2O and centrifugated twice and finally dried at 100°C for 6 h. This procedure removes polymeric octahedral molybdena but does not attack bound monomer (*16*). The molybdena removed was determined by atomic adsorption.

Electrophoretic migration measurements. The isoelectric points (IEP) of the support (γ-alumina) and supported phases (MoO_3) and the zero points of charge (ZPC) of the fresh and extracted $MoO_3/\gamma\text{-}Al_2O_3$ catalysts were determined by measuring the zeta-potentials as a function of the solution pH. The zeta potentials were obtained using the Smoluchowski equation (*17*) $\overline{V} = \frac{1}{4}\ \varepsilon\xi/\pi\eta$ by measuring the electrophoretic migration rate in a Zeta-Meter Inc. instrument, model ZM-77 provided with an automatic sample transfer Assembly (peristaltic pump and special electric purchclamp) to avoid sample sediment problems. In this equation $\overline{V}$ is the electrophoretic mobility, ε the permittivity, ξ the zeta-potential, and η the dynamic viscosity. Experiments were carried out using 20 mg of ~2 μm powder samples suspended in 200 ml of 10^{-3} *M* KCl, adjusting the pH value with 10^{-3} *M* KOH and HCl solution.

Coverage determinations. The "apparent surface coverages" (ASC) of the samples were calculated according to the electrophoretic migration method previously described (*15*). It is based on the fact that the zero point of charge (ZPC) of a surface "support-supported" falls between the isoelectric point (IEP) of the support (S) and the IEP of the supported phases (M). From this principle Eq. (1)

$$\begin{aligned}\mathrm{ASC} = M_{\mathrm{s}}^{-1}(\mathrm{IEP_s} - \mathrm{ZPC})/(M_{\mathrm{M}}^{-1} \\ - M_{\mathrm{S}}^{-1})(\mathrm{ZPC} - \mathrm{IEP_S}) \\ + M_{\mathrm{M}}^{-1}(\mathrm{IEP_S} - \mathrm{IEP_M}) \times 100 \quad (1)\end{aligned}$$

was developed (*15*). It permits us to determine the surface fraction covered by any supported phase (ASC), supplied by the molecular weight (*M*) of the support ($M_{Al_2O_3}$ = 101.96 g mol^{-1}) and by the molecular weight of the supported phase (M_{MoO_3} = 143.94 g mol^{-1}). The ASC obtained for $MoO_3/\gamma\text{-}Al_2O_3$ catalysts from Eq. (1) were in agreement with those previously obtained from oxygen chemisorption (*18*).

RESULTS AND DISCUSSION

Table 1 shows the chemical composition,

TABLE I

Chemical Composition, Zero Point of Charge (ZPC), and Apparent Surface Coverage (ASC) of Fresh and Extracted $MoO_3/\gamma\text{-}Al_2O_3$ Catalysts, Prepared by Different Procedures

Catalysts	Fresh				Extracted			
	MoO_3[a] (%)	Mo/g catalysts 10^{-20}	ZPC (pH)	ASC[b] (%)	MoO_3 (%)	Mo/g catalysts 10^{-20}	ZPC (pH)	ASC[b] (%)
$Al_2O_3(H_2O)$	—	—	8.80[c]	—	—	—	8.80[c]	—
$Mo(H_2O)$ − 1	1.1	0.46	8.65	8	0.2	0.08	8.65	8
$Mo(H_2O)$ − 2	4.1	1.64	8.50	16	0.7	0.29	—	—
$Mo(H_2O)$ − 3	7.8	3.03	8.30	26	1.6	0.66	8.40	21
$Mo(H_2O)$ − 4	11.4	4.29	8.00	39	2.0	0.82	8.30	25
$Mo(H_2O)$ − 5	13.8	5.07	7.85	46	2.5	1.02	8.15	32
$Al_2O_3(H_2O_2)$	—	—	8.70[c]	—	—	—	8.70[c]	—
$Mo(H_2O_2)$ − 1	2.5	1.02	8.70	26	0.8	0.31	8.40	16
$Mo(H_2O_2)$ − 2	6.5	2.55	7.95	37	1.4	0.58	8.20	26
$Mo(H_2O_2)$ − 3	13.8	5.07	7.40	61	2.3	0.94	7.90	40
$Al_2O_3(NH_3)$	—	—	8.50[c]	—	—	—	8.50[c]	—
$Mo(NH_3)$ − 1	2.3	0.94	8.40	6	0.9	0.37	8.40	6
$Mo(NH_3)$ − 2	6.5	2.55	8.20	18	2.3	0.94	8.30	12
$Mo(NH_3)$ − 3	13.9	5.10	8.00	29	2.9	1.19	8.20	18
MoO_3	—	—	6.25[c]	—	—	—	—	—

[a] Gram of MoO_3 per 100 g of dried $\gamma\text{-}Al_2O_3$.
[b] From Eq. (1).
[c] Isoelectric point (IEP).

zero point of charge (ZPC) of the three series of $MoO_3/\gamma\text{-}Al_2O_3$ samples (fresh and extracted) and the isoelectric points (IEP) of unsupported MoO_3 and $\gamma\text{-}Al_2O_3$, together with the "apparent surface coverage" (ASC) determined following the electrophoretic method. As shown in Table 1, the IEP of the $\gamma\text{-}Al_2O_3$ treated with H_2O, H_2O_2, or NH_4OH solutions were slightly different. This behavior is probably related to small variations in the surface of the support as a result of the treatment with the three different solutions and the subsequent calcination. On the other hand, comparison of the IEP values of the fresh and extracted samples of the treated $\gamma\text{-}Al_2O_3$, nominally $Al_2O_3(H_2O)$, $Al_2O_3(H_2O_2)$, and $Al_2O_3(NH_3)$, shows that no substantial modifications in the surface of the $\gamma\text{-}Al_2O_3$ occurred as a consequence of the extraction treatment with ammonia solutions.

The molybdena coverages on Al_2O_3 given in Fig. 1 are in close agreement with the previous results (*11, 18*). It is clear that the coverages are strongly dependent on the preparation of the catalysts. The ASC values of the catalysts prepared in H_2O_2 medium were higher than those prepared in H_2O and much higher than those prepared in NH_4OH medium. It is inferred therefore that a different distribution of molybdena on the Al_2O_3 surface takes place as a result of varying the molybdenum impregnation method. These differences between the $Mo(H_2O)$ and $Mo(NH_3)$ catalyst series may be interpreted in the light of the mechanism of adsorption of molybdenum ions as a function of the pH solution (*11–13*). At pH values above the IEP of the Al_2O_3 used ($pH \simeq 8.8$) the adsorption of the MoO_4^{2-} or $Mo_7O_{24}^{-6}$ anions is not favored. Thus, in the case of the $Mo(NH_3)$ series (pH 9.9) the amount of Mo retained by adsorption, presumably as MoO_4^{2-}, might be very small

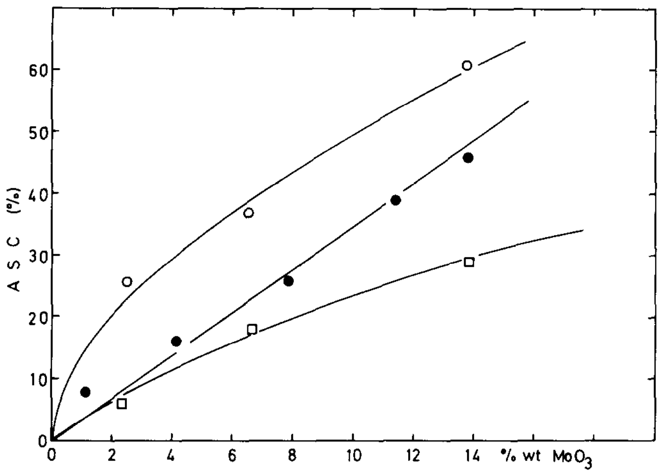

FIG. 1. Apparent surface coverage (ASC) of fresh MoO_3/γ-Al_2O_3 catalysts prepared in H_2O (●) pH 5.2; H_2O_2 (○) pH 5.4; and NH_4OH (□) pH 9.9 solution.

compared with that retained by deposition. Therefore it is expected that the deposited molybdenum may lead to a poor dispersion of it. However, in the $Mo(H_2O)$ series, as the pH of the impregnation solution (pH 5.2) was below the IEP of the Al_2O_3 (IEP = 8.80), a higher fraction of adsorbed molybdenum, compared with the deposited Mo, is expected. Accordingly, in the $Mo(H_2O)$ series the dispersion of molybdenum may be higher than in the $Mo(NH_3)$ series. These findings are similar to those reported recently by Houalla *et al.* (*19*).

The adsorption of molybdates from a peroxy solution (*20*) onto γ-Al_2O_3 occurs by the same ion exchange mechanism described for the aquo solution (*14*), and consequently it is also affected by the pH. The differences between the ASC of $Mo(H_2O)$ and $Mo(H_2O_2)$ samples cannot be explained by differences in the pH of the solution because both have a very similar pH (5.2 and 5.4, respectively). The high ASC of the $Mo(H_2O_2)$ catalyst series can be explained therefore in terms of the higher solubility and stability of the peroxy solutions than of the aquo solution of ammonium heptamolybdate (*20*). The formation of peroxymolybdate species may prevent and/or delay the appearance of precipitates of polymolybdates when the ammonium heptamolybdate solution is highly concentrated, i.e., during removal of the last H_2O or NH_3. Thus, if the Mo ions are allowed to remain in solution for a longer period, a higher fraction of Mo ions may be adsorbed on the alumina surface area and, consequently, a higher dispersion of Mo may occur.

Since the molybdenum loadings in the three catalyst series were similar, while the ASC values were different, it appears that molybdenum must be distributed differently. If it occurred only as monolayer, then all the ASC values of the three catalyst series should be in the same straight line. Figure 1 shows, however, that the data fall into three well differentiated lines, one for each catalyst preparation. Thus the presence of a fraction of molybdenum forming multilayers affords a reasonable explanation, as was previously suggested (*11–14*).

Similar behavior regarding the tendency of the ASC values was observed for the extracted samples, as Fig. 2 shows. The coverages were different for each extracted catalyst series: the values were higher for the $Mo(H_2O_2)$ and smaller for the $Mo(NH_3)$ compared with the $Mo(H_2O)$ series.

In Fig. 3 the relative decrease in molybdenum loading and ASC of the three catalyst series, which occurred by extraction treatment, are compared. The molybdenum

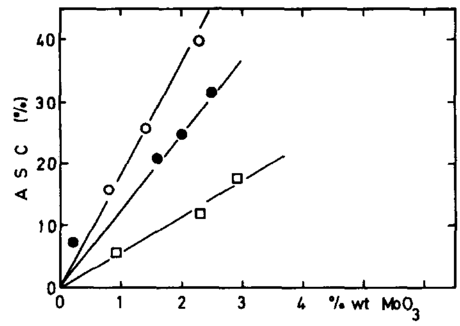

FIG. 2. Apparent surface coverage (ASC) of extracted $MoO_3/\gamma\text{-}Al_2O_3$ catalysts prepared in H_2O (●) pH 5.2; H_2O_2 (○) pH 5.4; and NH_4OH (□) pH 9.9 solution.

loading in the extracted samples decrease by about 80% compared with unextracted samples, whereas the ASC decreases about 20%. If all the molybdenum was present as a monolayer, in the extracted samples the decrease in molybdenum charge should lead to a similar decrease in ASC values. Our results show, however, that the decreases of both molybdenum content and ASC are substantially different. The presence of molybdenum as multilayers can account for the above results, since a preferential extraction of molybdenum forming multilayers would lead to a smaller variation in the surface fraction covered by molybdenum than in the molybdenum content. Thus, the preferential dissolution of octahedral molybdena shown in previous studies (*14, 16*) agrees with the dissolution of molybdenum present as MoO_3 or as multilayers. In the extraction conditions employed, the removed molybdenum must be present preferentially as a multilayer, which decreases the coverage mildly. It is inferred, therefore, that molybdenum is not only present as monolayer but also in multilayer form, as is shown in scheme 1.

$$\begin{array}{cc} \text{X X X X} & \\ \text{X X X X} & \\ \text{X X X X X X X X} & \text{X X X X X X X} \\ \hline Al_2O_3 & Al_2O_3 \\ \text{Fresh samples} & \text{Extracted samples} \end{array} \qquad (1)$$

According to this scheme, fresh catalysts must have ASCs equal to or somewhat greater than the extracted catalysts, but the MoO_3 loading for the fresh sample must be much greater than for the extracted one. This behavior was observed in the three series of samples studied. Scheme 1 cannot, however, be entirely correct because, if in all the extracted samples the molybdenum was present only as a monolayer (without Mo present as multilayer), then all the ASC values should fall in the same line. The different coverages of each extracted series suggest that in these samples there must be a "non-superficial-molybdenum-species" similar to the $Al_2(MoO_4)_3$ previously described (*21, 22*).

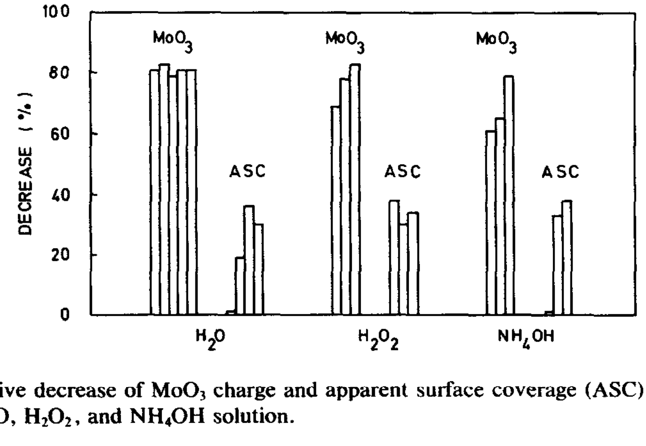

FIG. 3. Relative decrease of MoO_3 charge and apparent surface coverage (ASC) of $MoO_3/\gamma\text{-}Al_2O_3$ prepared in H_2O, H_2O_2, and NH_4OH solution.

CONCLUSIONS

Electrophoretic migration measurements of the apparent surface coverages show that in calcined $MoO_3/\gamma\text{-}Al_2O_3$ catalysts prepared by different methods, the molybdenum is present on the alumina surface not exclusively as a monolayer but also forming patches in multilayers, even at low loadings.

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