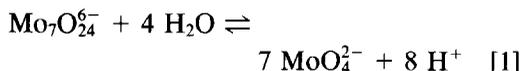


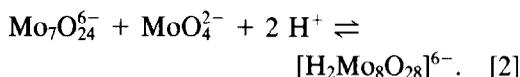
On the Adsorption of Heptamolybdate Ions on $\gamma\text{-Al}_2\text{O}_3$ and TiO_2

There is a continued interest in characterizing $\text{Mo}/\text{Al}_2\text{O}_3$ catalysts prepared via equilibrium adsorption from aqueous molybdate solutions (1-3) in view of the implications for the preparation of hydrotreating-type catalysts. Unfortunately, however, adsorption conditions are not always adequately controlled. In a previous publication (4) we pointed out that the use of too concentrated ammonium heptamolybdate (AHM) solutions may lead to precipitate formation instead of adsorption in the proper sense of the word. This phenomenon may pass undetected if powdered Al_2O_3 samples are used, the finely crystalline precipitate not being detectable by eye in a very intimate mixture with powdered alumina. In this note we submit that precipitate formation can easily be detected via measurement of the pH in the AHM solution after completion of the adsorption experiment. With regard to AHM adsorption on TiO_2 , recent papers (5, 6) report maximum Mo loadings differing (per unit area) by about a factor of 2 and we have, therefore, ascertained whether precipitate formation could play a role here as well.

The striking fact about aqueous AHM solutions is that the pH rises as the AHM concentration increases (Fig. 1), as already reported by Tsigdinos *et al.* (7). This means that apart from the well-known equilibrium

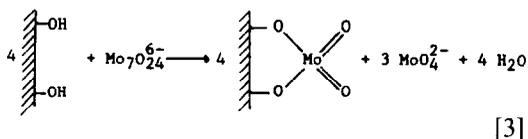


another process (or processes) must be involved. Tsigdinos *et al.* (7) suggested that the effect is caused by impurities; however, more important would seem to be an equilibrium which we may write as



This octamolybdate species tends to polymerize and eventually a precipitate is formed (8, 9). It is known that H_2O_2 stabilizes aqueous molybdate solutions (7). Bearing in mind decomposition of heptamolybdate ions (10), but less polymerization, on the basis of the above scheme one would expect H_2O_2 -containing solutions to have a lower pH than their AHM-only counterparts, and this is in fact observed (Fig. 1). Also, when a precipitate is formed, one would expect the pH to rise (cf. Eq. [2]) and this is observed as well: values as high as 7.5 to 8 can be reached.

We consider first adsorption on $\gamma\text{-Al}_2\text{O}_3$. The alumina used in the experiments reported here was a Shell $\gamma\text{-Al}_2\text{O}_3$, with a surface area of $250 \text{ m}^2 \text{ g}^{-1}$. With respect to AHM $\gamma\text{-Al}_2\text{O}_3$ has two adsorption sites (4, 11), namely basic hydroxyl groups and, probably, Lewis acid (coordinatively unsaturated Al^{3+}) centers. In the first instance HM ions react with the basic OH groups according to



As long as [AHM] is low enough for Reaction [3] not to proceed to completion, there are still basic OH groups left, which, since the pH is lower than the isoelectric point of the $\gamma\text{-Al}_2\text{O}_3$, can dissociate from the surface, so that a rise in pH can be observed. However, at higher AHM concentrations

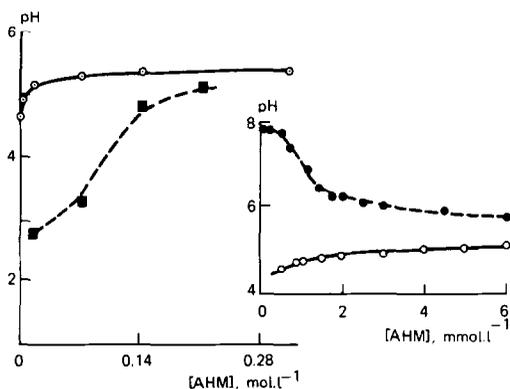


FIG. 1. pH as function of AHM concentration. Aqueous solutions in the absence (○) and presence (■) of 3% H_2O_2 . Inset: pH before (○) and after (●) adsorption; adsorption conditions: 2 g $\gamma\text{-Al}_2\text{O}_3$, 100 ml AHM solution, $t = 1$ week.

no basic hydroxyls are left and, since adsorption on Lewis acid centers does not involve protons or hydroxyls, the pH shifts observed under these conditions are relatively small (Fig. 1). Thus, when upon increasing the $[\text{AHM}]$ still further the pH in solution is found to start rising strongly again during the adsorption experiment, this is obviously due not to an adsorption reaction, but to precipitate formation, Eq. [2] *et seq.* This conclusion is corroborated by the fact that when use is made of whole $\gamma\text{-Al}_2\text{O}_3$ extrudates instead of a powder, the precipitate can be isolated as a separate phase, while the Mo loading on the extrudates does not exceed that consistent with adsorption via basic OH and Al^{3+} .

The precipitate can easily be detected by temperature-programmed reduction (4) and Raman spectroscopy. A representative set of Raman spectra is shown in Fig. 2. The conditions under which precipitate formation takes place were first defined employing Al_2O_3 extrudates, in which case it can be established by visual inspection whether a precipitate has formed or not, and the samples for Raman analysis were subsequently prepared employing an alumina powder, thus effectively assuming that the physical state of the alumina does not

greatly influence the precipitation process (*vide infra*). It is evident that the precipitate gives rise to a spectrum that can easily be distinguished from those due to the adsorbed species. It is to be noted, however, that the Raman spectrum of the precipitate as it is formed during an adsorption experiment is not identical to that of $[(\text{NH}_4)_6\text{Mo}_8\text{O}_{27}]_n$ which is formed in the absence of $\gamma\text{-Al}_2\text{O}_3$ (8, 12) (Fig. 2). Apparently, the alumina has an influence on the polymerization/precipitation process, which indeed also shows up in the fact that precipitate formation in the presence of $\gamma\text{-Al}_2\text{O}_3$ occurs at lower $[\text{AHM}]$ (or shorter times) than in its absence. In fact, the Raman spectrum of the phase formed in the presence of $\gamma\text{-Al}_2\text{O}_3$

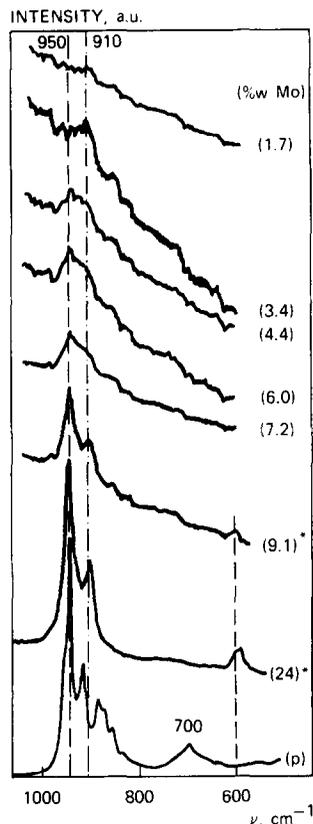


FIG. 2. Raman spectra of $\text{Mo}/\text{Al}_2\text{O}_3$ samples obtained via "equilibrium adsorption." The asterisk indicates samples in which a precipitated phase is present. The bottom spectrum (p) is that of $(\text{NH}_4)_6\text{Mo}_8\text{O}_{27} \cdot 4\text{H}_2\text{O}$.

extrudates is virtually identical to that shown in Fig. 2 for 24 wt% Mo/Al₂O₃, viz., a doublet at 950 and 905 cm⁻¹, and a weaker feature around 590 cm⁻¹. Although, therefore, the exact structure of the precipitate remains as yet unknown, its nature as such is not in doubt.

In the light of the above, it is significant that the authors who reported that high Mo loadings (i.e., >3–4 μmol m⁻²) can be achieved via equilibrium adsorption (2, 3, 7) used powdered alumina samples, and did not employ Raman spectroscopy in the characterization of the adsorbed phases. However, as explained above, precipitate formation is accompanied by a relatively large pH shift, which can serve as a diagnostic criterion. In fact, Cáceres *et al.* (3) report such pH shifts (their Table 1), and thus the observed high Mo loadings can be safely ascribed to the presence of a precipitated rather than an adsorbed phase (adsorption under the conditions of Tsigdinos *et al.* (7) also leads to a precipitate in our hands (4)).

Adsorption isotherms, then, should not be accepted at face value, and the possibil-

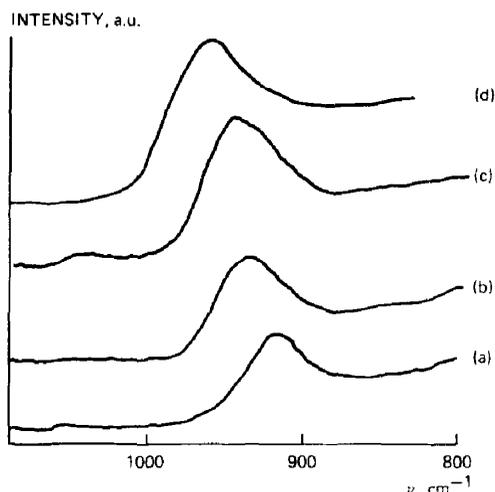


FIG. 3. Raman spectra of Mo/TiO₂ samples obtained via equilibrium adsorption of AHM. Mo loadings: (a) 1.3%, (b) 2.1%, (c) 3.5%, (d) 3.0%. To obtain spectrum (d) TiO₂ reacted with Fe(acac)₃ has been used.

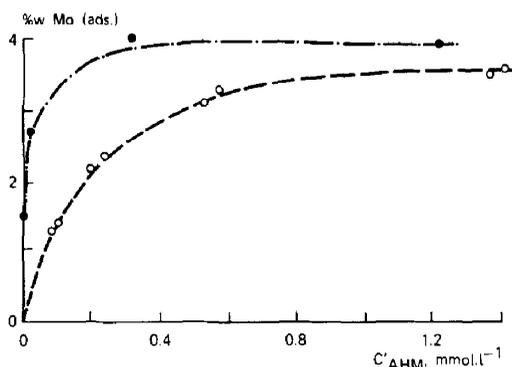


FIG. 4. Adsorption isotherm of AHM on TiO₂ (P25). (○) Neutral conditions, (●) pH 2 (solutions acidified with conc. HNO₃).

ity of precipitate formation should always be checked.

Turning now to TiO₂, the mechanism of AHM adsorption is similar to that on γ-Al₂O₃. Only basic hydroxyl groups and coordinatively unsaturated (cus) Ti⁴⁺ sites are involved in the adsorption process. This follows, for instance, from the fact that the difference in the amount of Mo adsorbed between an untreated TiO₂ sample and one whose hydroxyl groups have been reacted away with Fe(acac)₃ (13) is exactly equal to the amount calculated from the number of basic hydroxyl groups present using Eq. [3]. For example, P25 TiO₂ (ex Degussa, 50 m² g⁻¹) contains (13) 0.14 mmol basic OH g⁻¹ and this accounts for 0.7 wt% Mo adsorbed, the cus Ti⁴⁺ sites accounting for the remaining 3.3 wt%.

The fact that, just as in the case of γ-Al₂O₃, the reaction with the basic OH groups occurs first is shown by the relevant Raman spectra (Fig. 3). At low loadings the Mo=O stretch absorption band lies at relatively low wavenumber (920 cm⁻¹), and at higher loadings it shifts toward the position characteristic of AHM adsorbed on Ti⁴⁺ sites (spectrum (d)). Just as with γ-Al₂O₃, the adsorption equilibria lie more toward the adsorbed phase at lower pH, while maximum adsorption capacity is not significantly higher (Fig. 4).

Based upon the above, the maximum Mo

loading attainable via adsorption on a TiO_2 of $50 \text{ m}^2 \text{ g}^{-1}$ would appear to be of the order of 4–5 wt%, the precise amount depending on the extent of hydroxylation of the TiO_2 surface, i.e., on the relative number of cus Ti^{4+} and basic OH sites. This is in agreement with the results reported by Ng and Gulari (6), and by Shimada *et al.* (14), who found that 7 wt% Mo on a TiO_2 of $66 \text{ m}^2 \text{ g}^{-1}$ just exceeded the adsorption capacity of the latter (MoO_3 formation upon calcination). This leaves the high value reported by Wang and Hall (~10 wt%) (5) in need of an explanation. Since these authors conducted the adsorption experiments at rather low initial AHM concentrations we do not think precipitate formation could provide that explanation. However, we have reported before (4) that the Raman spectrum of one of our "adsorbed" samples showed the presence of an as-yet unidentified phase (strong Raman bands at 1057, 1044, 737, 530, and 352 cm^{-1}). Although this preparation could not be reproduced, the possible existence of nonadsorbed Mo is indicated, and the Raman spectra of the samples of Wang and Hall should turn out to be instructive.

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