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JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

J. Am. Chem. Soc., 1997, 119(42), 10137-10146, DOI: [10.1021/ja971981r](https://doi.org/10.1021/ja971981r)

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Ligand-promoted alumina dissolution in the preparation of $\text{MoO}_x/\gamma\text{-Al}_2\text{O}_3$ catalysts: evidence for the formation and deposition of an Anderson-type aluminoheteropolymolybdate.

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Supporting Information

Synthesis of the reference heteropolyanion salt $\text{K}_3[\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}]$

$(\text{NH}_4)_3[\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}]$ was prepared by dissolving 0.24 g aluminum chloride ($\text{AlCl}_3 \cdot 6 \text{H}_2\text{O}$, Merck) and 1.06 g ammonium heptamolybdate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4 \text{H}_2\text{O}$, Merck) in 100 ml water (molar ratio Al/Mo = 1/6). The initial pH was 2.4; it was adjusted to 3.5-4.0 with concentrated NH_3 . The solution was initially cloudy but became clear and colorless after one hour stirring.

The obtained solution of the ammonium salt was converted to the potassium salt by ion-exchange over an Amberlite IR-120 resin (Prolabo) previously saturated with KCl. A precipitate is formed within hours for an aluminum concentration = $1 \cdot 10^{-2}$ M.

X-ray Diffraction Measurements on the reference $\text{K}_3[\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}]$

The powder diffractograms were recorded on a Siemens D 500 diffractometer with a $\theta/2\theta$ setting, using the Cu $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). The scan rate was $0.02^\circ/2\theta/\text{s}$.

The theoretical powder diffractogram of $\text{K}_3[\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}]$ was calculated from published crystallographic data using Rietveld's method with the FullProf software (1991) which is a modification of the DBW3.2 code (1987) {Wiles, 1981 #37}. The experimental powder diffractogram (a) of $\text{K}_3[\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}]$ is presented in figure A, together with the theoretical powder diffractogram (b) computed from the single crystal crystallographic data reported by Lee et al. {Lee, 1991 #38}. The very good agreement between the computed and experimental spectra confirms the identity of the synthesised product.

UV-visible spectroscopy

UV-vis-NIR spectra were recorded on a Cary 5 spectrometer working in the 190-2500 nm range, equipped with an integration sphere. The spectra are given as the SKM function $(1-R_\infty)/2(R_\infty)^2$ versus the wavelength λ , where R_∞ is the reflectance of a sample with an infinite thickness ($\sim 4 \text{ mm}$). Barium sulfate was used as a reference. The UV-Visible solid-state spectra of $\text{K}_3[\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}]$ and $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ are shown in Figure B. Their similarity precludes the utilisation of UV-visible to discriminate the two anions.

Computation of Equilibrium Concentrations in aqueous solutions.

One problem in computing equilibrium curves is to take into account correctly the effect of the ionic strength of our medium.

Indeed, it seems impossible to know the precise concentrations and the charges of the different species we are considering within the whole duration of our experiments. For instance, the molybdenum species in solution can have a charge of 6- (heptamolybdate), 3- (AlMo_6) or 2- (monomolybdate). Furthermore the relative concentrations of these different species will vary during the experiment. The only way to by-pass this problem is to keep the ionic strength constant with an appropriate ionic salt (Öhman, L.O.; Sjöberg, S. *Coord. Chem. Rev.* **1996** 149,37-39}. However this procedure cannot be used in catalyst preparation as the salt (NaCl for example) could drastically modify the adsorption process.

So, for the sake of clarity we decided to compute all the equilibria with a theoretical ionic strength of 0 (i.e, activity=concentration).

Quantitativity of liquid-state NMR measurements

Figure C compares the total Al concentrations in the filtrates obtained by elemental analysis with the Al concentrations deduced from the integrated intensities of NMR peak. No significant differences are observed between the two sets of values, indicating that all the Al in solution is detectable by NMR.

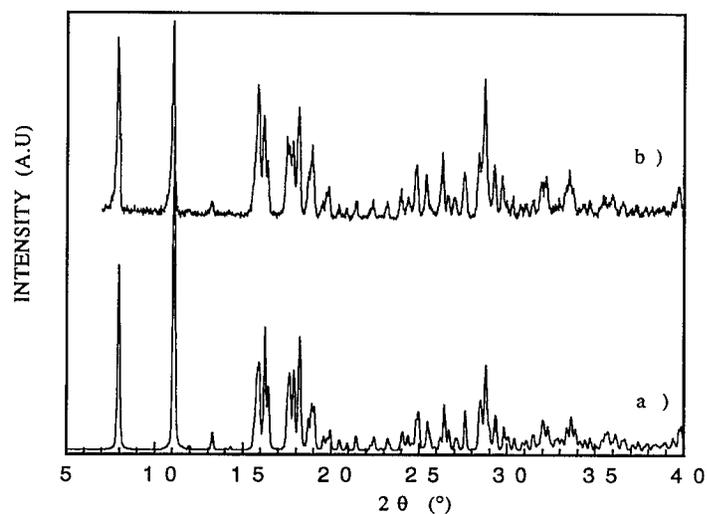


Figure A a) experimental powder diffractogram of $\text{K}_3[\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}]$, b) theoretical diffractogram of $\text{K}_3[\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}]$, computed from the data of Lee et al. (Lee, H. Y.; Park, K. M.; Lee, U.; Ichida, H. *Acta Cryst.* **1991**, C 47, 1959-1961).

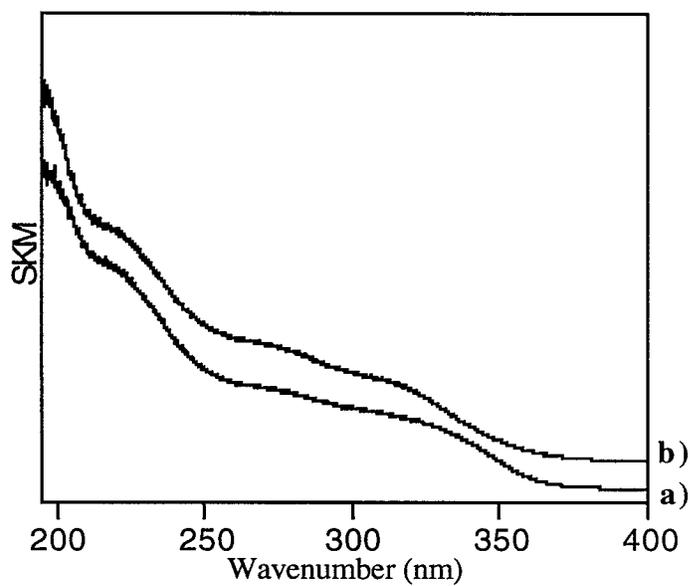


Figure B: UV-Visible solid-state spectra of a) $\text{K}_3[\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}]$ and b) $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$.

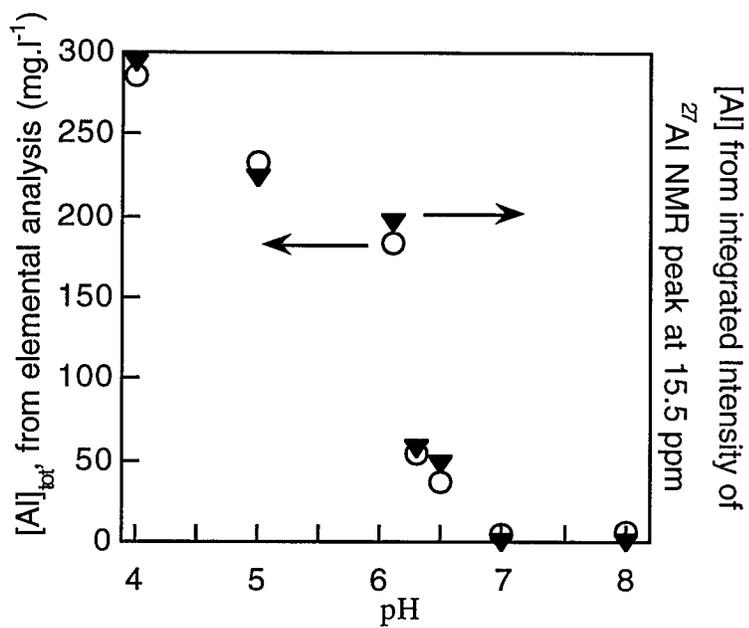


Figure C: Comparison of (○) the aluminum content in the filtrates found by elemental analysis with (▼) the integrated intensity of the ²⁷Al NMR peak at 15.5 ppm in each filtrates after 168 hours of equilibrium as a function of pH.