JOURNAL OF CATALYSIS **32**, 497–498 (1974)

Formation of $Al_2(MoO_4)_3$ on MoO_3/γ-Al_2O_3 Catalyst Systems as Studied by Luminescence Spectroscopy

Catalysts of the type Co/Mo/γ-Al_2O_3 are widely used in the oil and chemical industries. Their structure has been studied by several investigators (*1–4*), but there is considerable disagreement as to the occurrence of compounds such as $CoMoO_4$, $CoAl_2O_4$, and $Al_2(MoO_4)_3$. On the basis of reflectance spectroscopic data Lipsch and Schuit (*2*) and van Sint Fiet (*3*) concluded that in the Mo/γ-Al_2O_3 system an MoO_3 monolayer is formed on the γ-Al_2O_3 support. The reflectance spectra obtained by Krylov and Margolis (*4*) seemed to be indicative of the generation of $Al_2(MoO_4)_3$, but no such evidence was found by Miller *et al.* (*5*) from their X-PES results. The $Al_2(MoO_4)_3$ particles, if formed, are generally too small and too poorly crystallized to be detectable by X-ray diffraction techniques.

In an attempt to clarify this situation we investigated several MoO_3/γ-Al_2O_3 samples by a new method which makes use of the luminescence from Cr^{3+} tracer ions. The method is based on the fact that the wavelength of Cr^{3+} emission depends on the lattice in which the ion is incorporated. Thus, emission from Cr^{3+} in the supported catalyst shows up as several signals, corresponding to the various compounds present. By preparing and measuring the relevant Cr^{3+}-doped compounds [γ-Al_2O_3, MoO_3, $Al_2(MoO_4)_3$] separately, the compounds present in the catalyst can be identified from a comparison of the spectra.

The luminescence spectra were recorded on the spectrometer described previously (*6*). Since the Cr^{3+} *R* line emission in $Al_2(MoO_4)_3$ has a relatively short decay time (<0.5 ms) the equipment was rearranged for fluorescence measurements by placing the slots of the two chopper discs of the Becquerel-type phosphoroscope in phase (*6*). Scattered light, which can be very intense in this arrangement, was efficiently suppressed with the aid of "crossed filters."

$Al_2(MoO_4)_3$:Cr was prepared from a solution containing stoichiometric amounts of $Al(NO_3)_3$ and ammonium heptamolybdate, together with a trace of $Cr(NO_3)_3$ [0.1% w Cr on $Al_2(MoO_4)_3$]. The solution was evaporated to dryness and the residue successively calcined at 500°, 700°, and 900°C. Identification of $Al_2(MoO_4)_3$ was achieved by X-ray analysis. The powder pattern of this compound was simulated using the single crystal data of the isomorphous $Al_2(WO_4)_3$ (*7*) together with molybdenum scattering factors and the $Al_2(MoO_4)_3$ lattice parameters.

MoO_3/γ-Al_2O_3 catalysts (up to 20% w Mo) containing 0.01% Cr were prepared by adding $Cr(NO_3)_3$ to the ammonium heptamolybdate impregnation solution. The γ-Al_2O_3 support was prepared from crystalline boehmite (surface area 120 m^2/gm). After dry impregnation the catalyst was dried and calcined at 500°C.

Figure 1 shows the emission spectrum of $Al_2(MoO_4)_3$:Cr. The two sharp peaks at about 740 nm are attributed to phosphorescence emissions from the ${}^2E_g$ level. The broad band around 810 nm is due to fluorescence from the ${}^4T_{2g}$ level. The spectrum is characteristic of $Al_2(MoO_4)_3$:Cr since Cr emissions in oxide lattices are normally found at lower wavelengths, between 690 and 720 nm (*8*).

The emission spectra of γ-Al_2O_3:Cr in the fluorescence and the phosphorescence mode were identical, consisting of a peak at 703 nm with a shoulder at 720 nm. MoO_3:Cr gave no measurable emission.

The emission, measured in the fluorescence mode, from the 10% Mo/γ-Al_2O_3 catalyst is shown in Fig. 2. Comparison with

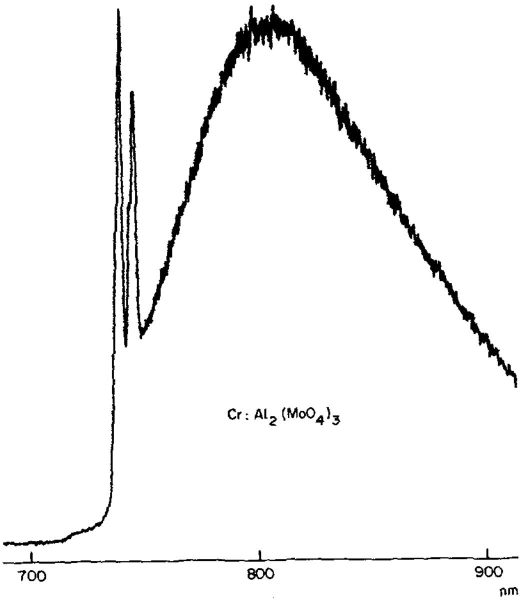

FIG. 1. Emission spectrum of $Al_2(MoO_4)_3$:Cr.

Fig. 1 unambiguously shows that this is the spectrum due to Cr in $Al_2(MoO_4)_3$, thus indicating the presence of this compound in catalysts calcined at 500°C. The emission due to γ-Al_2O_3:Cr measured in the fluorescence mode was extremely weak.

$Al_2(MoO_4)_3$ formation was also established for catalysts with lower loadings: with 3% Mo and after 3 hours calcination at 500°C, the compound could still be detected. Its generation in catalysts with high Mo loadings was confirmed by X-ray diffraction.

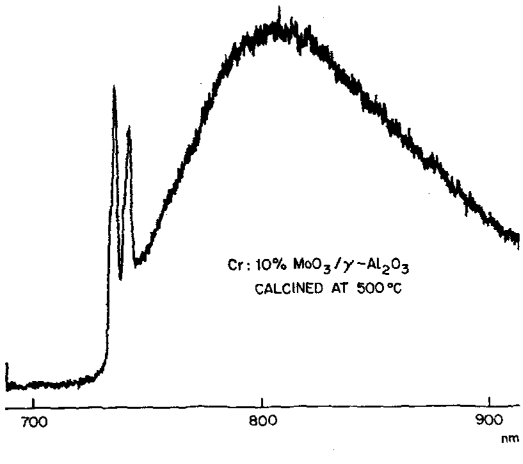

FIG. 2. Emission spectrum of 10% MoO_3/γ-Al_2O_3:Cr.

In conclusion, our results clearly demonstrate the existence of $Al_2(MoO_4)_3$ on the catalyst. From the sharpness of the emission bands it is evident that the compound is formed in more than a monolayer and is reasonably well crystallized. The occurrence of small MoO_3 crystallites, however, cannot be entirely ruled out. In the formation of $Al_2(MoO_4)_3$, Mo^{6+} ions change from octahedral to tetrahedral coordination (*9*).

Similar results (*10*) were obtained by us for the WO_3/γ-Al_2O_3 system, where Raman and Cr^{3+} phosphorescence spectra established the formation of $Al_2(WO_4)_3$.

REFERENCES

1. ASHLEY, J. H., AND MITCHELL, P. C. H., *J. Chem. Soc. A.* **1968**, 2821; ibid. **1969**, 2730; RICHARDSON, J. T., *Ind. Eng. Chem. Fundamentals* **3**, 154 (1964); DE BEER, V. H. J., VAN SINT FIET, T. H. M., ENGELEN, J. F., VAN HAANDEL, A. C., WOLFS, M. W. J., AMBERG, C. H., AND SCHUIT, G. C. A., *J. Catal.* **27**, 357 (1972).

2. LIPSCH, J. M. J. G., AND SCHUIT, G. C. A., *J. Catal.* **15**, 163, 174, 179 (1969).

3. VAN SINT FIET, T. H. M., *Thesis, Eindhoven (The Netherlands)*, 1973.

4. KRYLOV, O. V., AND MARGOLIS, L. YA., *Kinetics and Catalysis (USSR) (Eng-. Transl.)* **11**, 358 (1970).

5. MILLER, A. W., ATKINSON, W., BARBER, M., AND SWIFT, P., *J. Catal.* **22**, 140 (1971).

6. POTT, G. T., AND MCNICOL, B. D., *J. Chem. Phys.* **56**, 5246 (1972).

7. CRAIG, D. C., AND STEPHENSON, N. C., *Acta Cryst.* **B24**, 1250 (1968).

8. POTT, G. T., AND MCNICOL, B. D., *J. Solid State Chem.* **7**, 132 (1973).

9. NASSAU, K., LEVINSTEIN, H. J., AND LOIACONO, G. M., *J. Phys. Chem. Solids* **26**, 1805 (1965).

10. STORK, W. H. J., AND POTT, G. T., to be published.

W. H. J. STORK
J. G. F. COOLEGEM
G. T. POTT

Koninklijke/Shell-Laboratorium, Amsterdam
Badhuisweg 3
Amsterdam-N, The Netherlands

Received August 8, 1973