

## EPR Studies on the Influence of NO Adsorption on Sulfided Co-Mo Hydrodesulfurization Catalysts

A large number of EPR studies on hydrodesulfurization (HDS) catalysts have been carried out [see Ref. (1), e.g., and references therein]. Recently, we investigated (1) by EPR unsupported and alumina-supported sulfided Co-Mo catalysts (Co/Mo = 0-2.3) and observed three distinct EPR signals which we called MO, MS, and CMS. MO corresponds to oxo-Mo<sup>5+</sup> ions interacting with alumina; MS was assigned either to bulk defects in a MoS<sub>2</sub> phase or to thio-Mo<sup>5+</sup> species at the edges of the layered MoS<sub>2</sub> crystallites. In the presence of Co, signal CMS was observed. Its intensity was found to parallel the HDS activity and also the amount of Co present at MoS<sub>2</sub> edges (as Co-Mo-S) studied also by Mössbauer emission spectroscopy. A similar signal has been found by Konings *et al.* (2, 3). They interpreted their signal in terms of Mo<sup>3+</sup> coupled via superexchange to Co<sup>2+</sup> ions. We (1) suggested a more likely model based on antiferromagnetic coupling between Co<sup>2+</sup> and Mo<sup>4+</sup>. This leads to a ground state with  $S = \frac{1}{2}$  in agreement with the experimental data.

We discuss below the effect of NO adsorption on the EPR signals CMS and MS.

The Co-Mo/Al<sub>2</sub>O<sub>3</sub> catalyst used was analogous to those described previously (4, 5). A molar Co/Mo ratio of 0.25 was chosen. The calcined precursor was heated to 673 K at a rate of 2 K min<sup>-1</sup> in an atmosphere of 2% H<sub>2</sub>S in H<sub>2</sub>. After 2 h at this temperature the samples were allowed to cool to room temperature, evacuated to  $3 \times 10^{-2}$  mbar, and subsequently exposed to NO at 130 mbar. At this pressure no EPR

lines from NO in the gas phase are seen. The EPR spectra were recorded using a Bruker BER-420 spectrometer operating at 77 K and X-band frequency under conditions previously described (1).

Figure 1 shows the EPR spectra of the sulfided catalyst (A) and after (B) chemisorption on NO. It is evident that the signals CMS and MS disappear after exposure to NO.

NO adsorption has been followed by IR spectroscopy (5) and shown to occur at the edges of the crystallites, preferentially. The amount of NO adsorbed parallels the amount of CMS and the HDS activity. By this technique, therefore, it is possible to "titrate" the active edge sites.

The present EPR results show that the species corresponding to signals CMS and MS, with spin  $S = \frac{1}{2}$ , are both accessible at the edges. Upon formation of complexes with NO, also having  $S = \frac{1}{2}$ , the spins obviously interact. If the interaction is static and mononitrosyl complexes are formed, singlet ground states result. The corresponding triplet states are not populated to any measurable degree under the experimental conditions. Due to zero-field splittings EPR signals from such triplets could be expected at almost any field available. A partly spin-forbidden line at  $g \approx 4$  is, however, expected from a triplet state. No such triplet lines could be detected. If dynamic interactions occur and if dinitrosyl complexes are formed the quenching of the signal can also be explained whether their chemical integrity is retained or not.

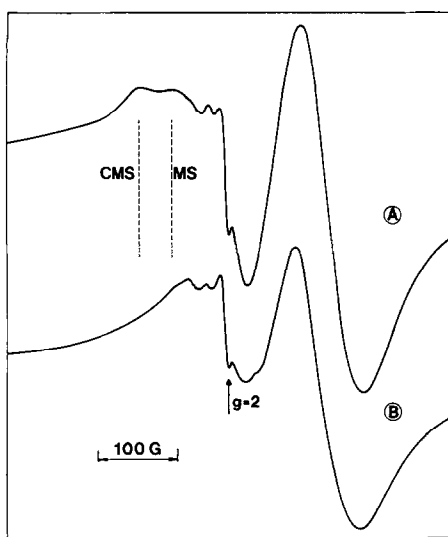


FIG. 1. X-band EPR spectra at 77 K of alumina-supported sulfided Co-Mo catalysts with Co/Mo = 0.25: (A) *in vacuo* and (B) in NO at 130 mbar.

The nitrosyl complex formed with CMS may be related to model compounds such as  $((\text{NO})_2\text{Co}(\text{MoS}_4))^{-n}$  and related bimetallic nitrosyl complexes which have been recently synthesized (6).

The unpromoted MS sites have low catalytic activity compared with the promoted Co-containing CMS edge sites (7). The present measurements provide further evidence that rather than being bulk defects (8), they are located at the edges of the  $\text{MoS}_2$  crystallites as thio- $\text{Mo}^{3+}$  species, as also suggested in Ref. (2).

#### REFERENCES

1. Derouane, E. G., Pedersen, E., Clausen, B. S., Gabelica, Z., Candia, R., and Topsøe, H., *J. Catal.* **99**, 253 (1986).
2. Konings, A. J. A., Brentjens, W. L. J., Koningsberger, D. C., and de Beer, V. H. J., *J. Catal.* **67**, 145 (1981).
3. Konings, A. J. A., Valester, A., de Beer, V. H. J., and Prins, R., *J. Catal.* **76**, 466 (1982).
4. Wivel, C., Candia, R., Clausen, B. S., Mørup, S., and Topsøe, H., *J. Catal.* **68**, 453 (1981).
5. Topsøe, N.-Y., and Topsøe, H., *J. Catal.* **84**, 386 (1983) and references therein.
6. Topsøe, H., Müller, A., Clausen, B. S., Topsøe, N.-Y., Pedersen, E., Lengeler, B., and Nieman, W., *J. Chem. Soc. Faraday Trans. I* (1987).
7. Candia, R., Clausen, B. S., Bartholdy, J., Topsøe, N.-Y., Lengeler, B., and Topsøe, H., in "Proceedings, International Congress on Catalysis, 8th—Berlin, 1984," Vol. II, p. 375. Verlag Chemie, Weinheim, 1984.
8. Silbernagel, B. G., Pecoraro, T. A., and Chinanelli, R. R., *J. Catal.* **78**, 380 (1982).

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Received February 18, 1987; revised May 19, 1987

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