Influence of the Grain Morphology of Molybdenum Trioxide on Its Catalytic Properties: Reduction of Nitric Oxide with Ammonia

A. BAIKER,[1] P. DOLLENMEIER, AND A. RELLER[2]

Department of Industrial and Engineering Chemistry, Swiss Federal Institute of Technology (ETH), ETH-Zentrum, CH-8092 Zurich, Switzerland

Molybdenum trioxide has been used in catalysts for high-temperature reduction of NO_x with NH_3 (*1*). Nevertheless, to our knowledge, the influence of the grain morphology on the intrinsic activity and selectivity of polycrystalline MoO_3 has not been studied for this reaction. Recent studies (*2*) on mild oxidation reactions (oxidations of propylene, methanol, 1-butene, and isobutene) carried out over MoO_3 of different grain morphology showed *structure sensitivity* (*3*); i.e., the activity and selectivity depended on the kind of crystallographic plane exposed on the surface. In the present work we have investigated the influence of the grain morphology of MoO_3 on its intrinsic activity for the reduction of nitric oxide with ammonia.

Two samples of morphologically and geometrically different molybdenum trioxide were prepared. Sample *A* consisted of large, thin platelets of orthorombic MoO_3 exposing predominantely the (010) plane and was obtained by fully oxidizing molybdenum metal sheets (99.99%) in air at 1050 K. Dimensions of the plates as determined by light microscopy were 0.5 to 3 mm along (001) (length), 0.2 to 1 mm along (100) (width), and 0.5 to 2 μm along (010) (thickness). Sample *B* consisted of microcrystalline MoO_3 with dimensions of 1 to 2 μm along (001), (100), and (010), respectively,

and was prepared by thermal decomposition of $(NH_4)_2MoS_4$ to amorphous MoS_3 and subsequent oxidation to MoO_3 in pure oxygen. This preparation process was monitored by thermogravimetry and simultaneous mass spectrometry. The BET surface areas as measured by krypton adsorption of the fresh samples were sample *A*, 0.045 ± 0.004 m^2/g, and sample *B*, 5.39 ± 0.007 m^2/g. Note that the BET surface area of sample *B* was about 120 times larger than that of sample *A*.

In order to compare semiquantitatively the contribution of the different exposed crystal faces to the surface area, the two MoO_3 samples were investigated by scanning electron microscopy and X-ray diffraction. Figure 1 depicts the electron micrographs of the platelets (*A*) and of the microcrystalline MoO_3 (*B*), which exhibits cubes and hexagonal prisms. The surface of the platelets (*A*) obtained by oxidation of molybdenum metal sheets is made up of at least 95% basal faces (010) and a few percent of side faces (100) as well as apical faces of the type (001) and (101), respectively. The surface of microcrystalline MoO_3 (*B*) is made up of not more than 50% basal faces (010) as well as equal portions of faces of type (001), (100), and (101), respectively. These results emerging from the electron microscopy studies are supported by X-ray analysis (Fig. 2). The platelets (*A*) formed oriented stacks in the X-ray sample holder, resulting in a considerable change in intensity, in particular, of the reflections

[1] To whom all correspondence should be addressed.
[2] Present address: Institute of Inorganic Chemistry, University of Zürich, CH-8057 Zürich, Switzerland.
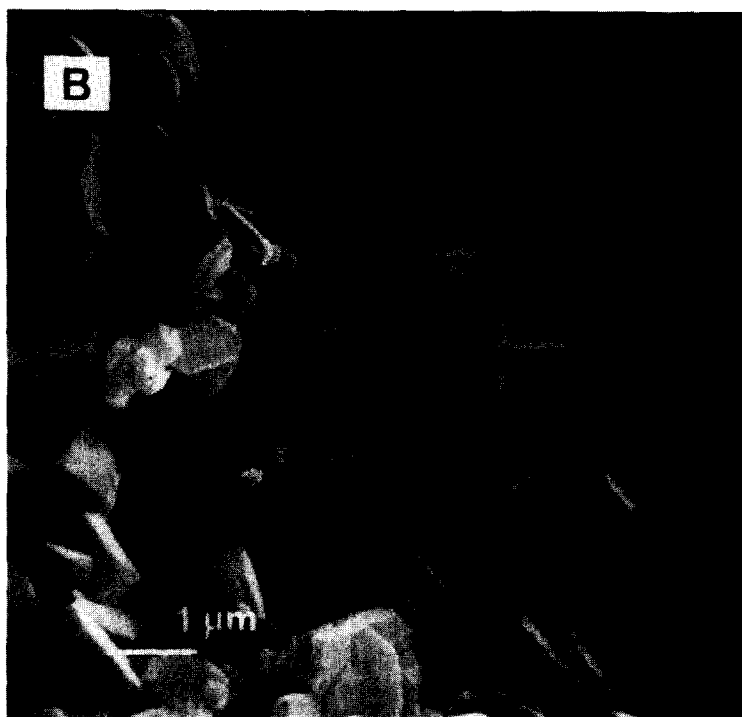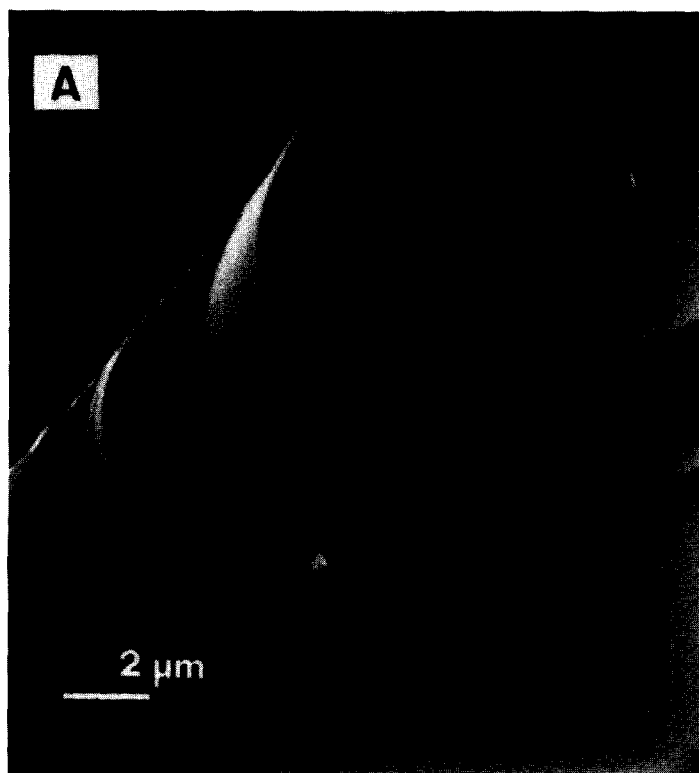
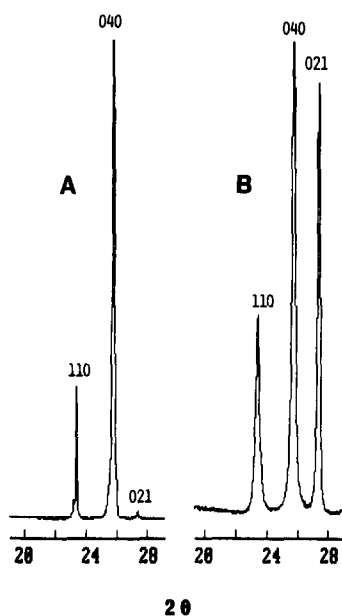FIG. 1. Scanning electron micrographs showing grain morphologies of MoO₃ samples A and B.

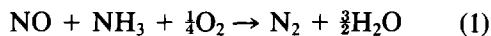FIG. 2. Comparison of intensities of X-ray (CuKα) reflections (110), (040), and (021) of MoO₃ samples A and B.

(110), (040), and (021) as compared to the intensities of the nonoriented sample (B).

We may define a morphological factor f = I_{040}/I_{021} to assign the morphological differencies of the two samples, where I_{hkl} designates the intensity of the X-rays diffracted for the respective planes, measured for oriented samples prepared by standard smoothing in a sample holder. The morphological factors determined were f ≅ 67 for the well-developed platelets (A), and f ≅ 1 for the microcrystalline sample B. The latter value is in good agreement with measurements for nonoriented samples (4).
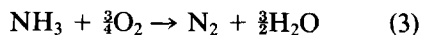
Catalytic reduction of NO with NH₃ was performed in a continuous flow fixed-bed reactor. The tubular reactor was constructed from 10-mm-diameter Pyrex glass tubing and was 60 cm long. The reactor tube was placed vertically in a tubular oven for temperature control. The catalyst bed temperature was measured by a Chromel–Alumel thermocouple positioned at the center of the catalyst bed and could be held within ±1°C of the desired value. Diluted

reactant gases, NO and NH₃ (about 2000 ppm of reactant in nitrogen), were taken without further purification from cylinders. Pressurized air was used as oxygen source. Mass flows were controlled by means of thermal flow controllers. Experiments were carried out in the presence of oxygen (1.85%) and with reactant concentrations (NO and NH₃) of less than 1000 ppm in the feed. Preliminary experiments indicated that a small oxygen partial pressure is necessary to avoid reduction of the MoO₃ catalyst by ammonia. Without oxygen in the feed, ammonia reduces MoO₃ to MoO₂ under the conditions used, as confirmed by X-ray analysis. All gases were premixed in the cold section of the tubing. Analysis of the reactor feed and of the product stream was carried out with a quadrupol mass spectrometer. The amount of nitrogen formed during the reaction was calculated by mass balance. The gas inlet system and the analyzer of the mass spectrometer were held at 200°C in order to avoid condensation of NH₃ and H₂O. The linearity of the ion currents was checked by calibrated gas mixtures. Concentrations were calculated from the parent peaks by taking into account necessary corrections due to the cross sensitivities of the analyzed species. The accuracy of the analysis of all species was better than ±2%.

Results of the NO reduction with NH₃ carried out over the two MoO₃ samples of different grain morphology are shown in Fig. 3. Steady-state compositions of the product gas mixtures measured at the reactor outlet at different reaction temperatures are compared. Note that NO is consumed in the simultaneously occurring reactions:

$$NO + NH_3 + \tfrac{1}{4}O_2 \rightarrow N_2 + \tfrac{3}{2}H_2O \qquad (1)$$

$$NO + NH_3 + \tfrac{3}{4}O_2 \rightarrow N_2O + \tfrac{3}{2}H_2O \qquad (2)$$

Besides these two reactions, oxidation of ammonia by oxygen (Eq. (3)) was found to be important at temperatures >550 K.

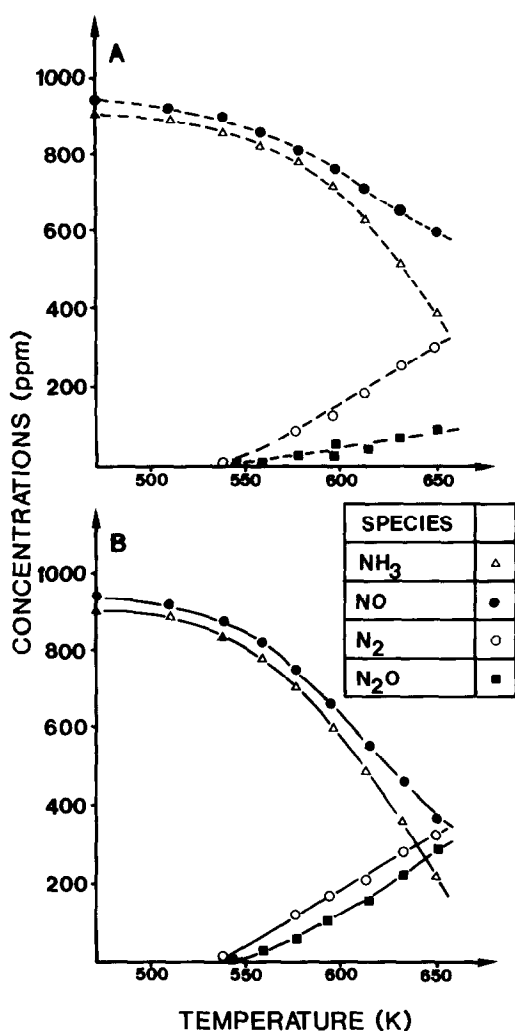$$NH_3 + \tfrac{3}{2}O_2 \rightarrow N_2 + \tfrac{3}{2}H_2O \qquad (3)$$

otherwise similar conditions. These experiments also indicated that reaction (3) is not significantly influenced by the grain morphology of MoO_3. The most important result emerging from Fig. 3 is that the rate of N_2O formation (Eq. (2)) depends on the grain morphology of MoO_3, whereas similar behavior is not observed for reactions (1) and (3).

The Arrhenius plots for the NO consumption rates presented in Fig. 4 show that sample B exhibited a two to three times higher rate of NO conversion. This is attributed to the higher rate of N_2O formation on the microcrystalline MoO_3 B (Fig. 3). Note that the apparent activation energies of A ($E_A = 50.0 \pm 5$ kJ/mol) and B ($E_B = 48.7 \pm 5$ kJ/mol) are the same within the 95% confidence limits. This result indicates that the two simultaneously occurring reactions of NO have about similar activation energies.

To summarize, the reduction of NO by ammonia has been investigated in the presence of oxygen in the temperature range 500–650 K over MoO_3 of different grain
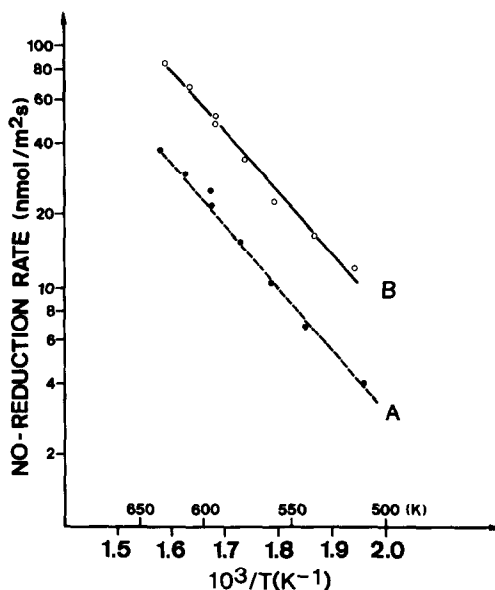
SPECIES	
NH_3	△
NO	●
N_2	○
N_2O	■

FIG. 3. Steady-state compositions of product gas mixtures measured during NO reduction over MoO_3 samples A and B, respectively. Conditions: total surface area of catalyst in reactor, 0.27 m²; total flow rate, 2.08 ml(NTP)/s; reactant concentrations in feed: NO, 940 ppm; NH_3, 900 ppm; O_2, 1.83%; diluent gas, nitrogen; total pressure, 1 bar.

Calculation of the ammonia mass balance based on the measured product distribution (Fig. 3) indicates that at 650 K about 20% of the ammonia in the feed is consumed by reaction (3). The reactions of ammonia with oxygen to form NO and N_2O became relevant at higher temperatures, $T > 650$ K only. This was confirmed by oxidation experiments performed without NO but under

FIG. 4. Arrhenius plots of NO reduction rates measured over MoO_3 samples A and B, respectively. For conditions see Fig. 3.

morphology. Under these conditions NO undergoes reduction to both N_2 and N_2O. Our results indicate that the reduction to N_2 is not markedly influenced by the kind of crystallographic faces exposed on the MoO_3 surface. Conversely, the reduction to N_2O is structure sensitive; i.e., side (100) and apical faces (001, 101) of MoO_3 are more active for N_2O formation than are the basal planes (010).

ACKNOWLEDGMENTS

REFERENCES

1. Wise, H., in "The Catalytic Chemistry of Nitrogen Oxides" (L. Klimisch and J. G. Larson, Eds.), p. 235. Plenum, New York, 1975.
2. Volta, J. C., and Portefaix, J. L., *Appl. Catal.* **18,** 1 (1985).
3. Boudart, M., "Advances in Catalysis" (D. D. Eley, P. W. Selwood, and P. B. Weisz, Eds.), Vol. 20, p. 153. Academic Press, New York, 1969.
4. Joint Committee on Powder Diffraction Standards, "ASTM Powder Diffraction File 5-0508." Pennsylvania, 1984.