

Oxygen Depletion of Bismuth Molybdates

Bismuth molybdates are well known as selective oxidation catalysts (1). Activity for olefin oxidation is found particularly for the compounds $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ (α phase), $\text{Bi}_2\text{Mo}_2\text{O}_9$ (β phase), and Bi_2MoO_6 (γ phase). The α phase is only weakly active, whereas the β and γ phases have comparable activity; various authors have claimed that either the β (2) or the γ (3, 4) is the most active phase. The role of lattice oxygen in the oxidation process has been demonstrated (5, 6); the mobility of the lattice oxygen is thus important in determining the catalytic activity. Ruckenstein *et al.* (7) have recently described measurements of O_2 evolution (*in vacuo*) from fully oxidized bismuth molybdates at high temperature, from which they calculated the diffusion coefficient for oxygen in the γ phase to be an order of magnitude higher than that in the α and β phases. We wish to report here measurements of oxygen depletion in partially reduced α and γ bismuth molybdates. Since bismuth molybdates are readily reduced in the presence of olefins (8), measurements made on partially reduced catalysts are more relevant to the catalytic process than those made on fully oxidized catalysts. EPR spectra of the reduced catalysts were also obtained.

EXPERIMENTAL METHODS

The α and γ bismuth molybdates were prepared by methods described in the literature (4, 9) and characterized by x-ray diffraction. The surface areas were 1.6 (α) and $2.1 \text{ m}^2 \text{ g}^{-1}$ (γ).

Reduction and reoxidation experiments were carried out in a circulation system similar to that described by Hall and Massoth (10), consisting of a quartz reactor, glass circulation pump, liquid nitrogen cold trap, and manometer. About 2.5 g of catalyst was pretreated in oxygen overnight at the temperature of the experiment, then evacuated for 1 hr, and a known amount of hydrogen was admitted. Measurement of the hydrogen pressure as a function of time gave a figure for hydrogen consumed in the reduction process. Excess hydrogen was removed by evacuation through the trap for 1 hr; then the water collected was measured volumetrically. Oxidation of reduced catalysts was carried out in a similar manner using oxygen in place of hydrogen.

EPR spectra were recorded at room temperature or 77°K with a Varian E-115 spectrometer operating at 9.15 GHz. Catalyst samples were transferred to a side arm on the quartz reactor, after completion of hydrogen uptake measurements, and their spectra were recorded *in vacuo*.

RESULTS AND DISCUSSION

Results of reduction-reoxidation measurements for α and γ bismuth molybdate are given in Table 1. For each temperature and reduction time, data are given for the volumes of hydrogen consumed ($[\text{H}_2]$) and water formed ($[\text{W}_\text{R}]$) in the reduction step, the number of anion vacancies produced (equal to W_R), and the volumes of oxygen consumed ($[\text{O}_2]$) and the water formed ($[\text{W}_\text{O}]$) in the subsequent reoxida-

tion step (at the same temperature). If no hydrogen is retained by the catalyst sample, $[H_2]$ will be equal to $[W_R]$; i.e., each hydrogen molecule removes one lattice oxide ion to form one molecule of water and leave an anion vacancy. In all experiments, $[W_R]$ was found to be slightly less than $[H_2]$, indicating some retention of hydrogen by the catalyst. The volume of water formed during the reoxidation is a measure of the amount of H_2 adsorbed irreversibly (retained by the catalyst after evacuation). This volume is in all cases extremely small, indicating that most of the hydrogen retained at the end of the reduction step is removed by the evacuation procedure prior to reoxidation. The volume of oxygen consumed on reoxidation should be equal to one half $[H_2]$ if no hydrogen is reversibly retained during reduction, or less than one half $[H_2]$ if some reversible retention occurs:

$$2[O_2] = [H_2] - H_R$$

Thus the quantity $2[O_2] - [H_2]$ should be zero or slightly negative.

As shown in the table, such was found to be the case for the α phase. For the γ phase, however, $2[O_2] - [H_2]$ was found

to be non-zero and positive and to increase with the extent of reduction. The excess oxygen is evidently required to fill additional anion vacancies formed during outgassing subsequent to the reduction step. The number of additional anion vacancies is given in the last column of the table.

Experiments were performed to determine the number of anion vacancies formed on outgassing fully oxidized γ bismuth molybdate. Catalyst samples were pretreated in oxygen overnight at temperatures between 400 and 500°C, evacuated at the pretreatment temperature for 1 hr, then reoxidized at that temperature, and the volume of O_2 consumed was measured. In all cases, $[O_2]$ was found to be in the range of 0.01–0.02 cm³ NTP g⁻¹, corresponding to anion vacancy concentrations of the order of 1×10^{18} g⁻¹.

EPR spectra of the reduced α and γ phases at room temperature and 77°K showed a very weak asymmetric signal at $g = 1.9$ which resembled the signals assigned to Mo^{5+} in silica-supported bismuth molybdates (11–13). The intensity of the observed signal corresponded, however, to a spin concentration of less than 10^{14} spins g⁻¹ (determined by comparison with a

TABLE I
Oxygen Depletion Measurements

| Temperature (°C) | Reduction | | | Oxidation | | | | |
|---------------------|---------------|-----------|-----------|---------------------------------|-----------|-----------|------------------|----------------------------------|
| | Time (min) | $[H_2]^a$ | $[W_R]^b$ | Anion vacancies ^c | $[O_2]^a$ | $[W_o]^b$ | $2[O_2] - [H_2]$ | Excess vacancies ^c |
| α Phase | | | | | | | | |
| 350 | 30 | 0.65 | 0.53 | 1.4 | 0.33 | 0.04 | 0.01 | |
| 405 | 15 | 1.99 | 1.70 | 4.5 | 0.96 | 0.08 | -0.07 | |
| 400 | 30 | 3.43 | 2.91 | 7.8 | 1.69 | 0.04 | -0.05 | |
| 415 | 60 | 6.71 | 4.82 | 12.9 | 3.05 | 0.20 | -0.61 | |
| 570 | 20 | 5.08 | 4.86 | 13.0 | 2.58 | 0.16 | 0.08 | |
| γ Phase | | | | | | | | |
| 300 | 30 | 0.68 | 0.59 | 1.6 | 0.48 | 0.02 | 0.28 | 0.8 |
| 340 | 30 | 0.93 | .62 | 1.7 | 0.54 | 0.07 | 0.15 | 0.4 |
| 400 | 10 | 1.37 | 1.04 | 2.8 | 0.92 | 0.04 | 0.47 | 1.3 |
| 400 | 40 | 7.53 | 6.86 | 18.4 | 4.73 | 0.08 | 1.94 | 5.2 |
| 450 | 5 | 5.03 | 3.73 | 10.0 | 3.19 | 0.27 | 1.35 | 3.6 |
| 500 | 30 | 13.09 | 10.96 | 29.4 | 7.97 | 0.34 | 2.85 | 7.6 |

^a ± 0.05 cm³ (NTP) g⁻¹.

^b ± 0.1 cm³ (NTP) g⁻¹.

^c $\times 10^{-19}$ g⁻¹.

Varian weak pitch standard) and the signal intensity did not increase with the extent of reduction. This result is consistent with the XPS observations of Grzybowska *et al.* (14), who found that hydrogen treatment of unsupported bismuth molybdates caused direct reduction from Mo^{6+} to Mo^{4+} . The Mo^{5+} concentration observed by EPR is several orders of magnitude less than the values reported (10^{16} – 10^{17} spins g^{-1}) for silica-supported bismuth molybdates (11, 13).

It appears from the oxygen uptake measurements that lattice oxide ions in γ bismuth molybdate become more labile when the catalyst is in the partially reduced state, and to a greater extent than with the α phase. Temperature-programmed reduction and reoxidation studies indicate that the most labile oxide anions in γ bismuth molybdate are those bridging between bismuth and molybdenum layers in the koechlinite structure (15). The enhanced mobility of oxide anions under reaction conditions is likely to be responsible for the superior catalytic properties of the γ phase.

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