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NOTES

Reduction and Reoxidation Behaviour of γ-Bi_2MoO_6

Bismuth molybdenum oxides are well-known catalysts for the selective oxidation of olefins. For the oxidative dehydrogenation of 1-butene to butadiene, it was suggested (*1*) that γ-Bi_2MoO_6 (koechlinite) has the highest activity of these oxides, although subsequent results (*2*) implied that surface coatings of β-$Bi_2Mo_2O_9$ are primarily responsible for catalytic activity. The oxidation process has been demonstrated (*3–5*) to be an example of intrafacial catalysis, but the detailed chemistry of partially reduced catalysts remains unclear. For example, whereas X-ray diffraction patterns (*6*) of catalysts reduced in 1-butene at 470°C were attributed to $Bi_2MoO_{5.5}$, EPR (*7*) and XPS (*8*) measurements on hydrogen-reduced samples indicated the presence of Mo^{4+} (MoO_2) rather than Mo^{5+}. TPR investigations in conjunction with Auger electron spectroscopy revealed that samples reduced in propylene contained Bi and MoO_2 (*9*). Reoxidation occurred in two stages: at 158°C Mo^{4+} was oxidised to Mo^{6+} and Bi^0 to Bi^{m+} ($0 < m < 3$), whereas at 340°C complete oxidation to Bi^{3+} resulted. X-ray diffraction was unable to reveal the nature of this two-stage process. In an attempt to explain more fully the redox properties of γ-Bi_2MoO_6, partially reduced samples have been carefully examined using X-ray diffraction and thermal analysis.

γ-Bi_2MoO_6 samples were prepared using two methods described in the literature: these were slurry reactions between $BiONO_3$ and H_2MoO_4 (*10*), and precipitation from $Bi(NO_3)_3 \cdot 5H_2O$ and $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ solutions (*11*), respectively. The results discussed below were applicable to samples from both routes. The preparation of nonstoichiometric samples Bi_2MoO_{6-x} ($0 < x \leq 0.5$) was attempted by grinding together Bi_2O_3, MoO_3, and MoO_2 in appropriate stoichiometric proportions, sealing the mixtures in evacuated quartz tubes, and heating at 500°C for 6 h. Chemical reduction of γ-Bi_2MoO_6 samples was effected in a closed system of known volume using 1-butene and a range of pressures and temperatures. Reoxidation in flowing oxygen was examined by DTA and TGA using a Stanton-Redcroft STA 780 thermal analyser at a heating rate of 10 K min^{-1}. Powder X-ray diffraction patterns were recorded on a Philips 1050/70 diffractometer using Cu*Kα* radiation.

Attempts to prepare nonstoichiometric γ-Bi_2MoO_{6-x} in evacuated quartz tubes were unsuccessful and always resulted in detectable quantities of Bi and MoO_2 in X-ray diffraction patterns, even for an oxygen stoichiometry appropriate for $Bi_2MoO_{5.88}$. X-ray profiles for "$Bi_2MoO_{5.5}$" and Bi_2MoO_6 are compared in Figs. 1a and 1b. The variation of Bi content with overall composition was estimated by reference to the relative intensities of the most intense reflections, 014 for Bi and 131 for γ-Bi_2MoO_6. The Bi concentration decreased with x in Bi_2MoO_{6-x} and reached zero at an extrapolated value corresponding approximately to Bi_2MoO_6 (Fig. 2). The koechlinite phase thus appears unable to accommodate a significant degree of oxygen deficiency, which is contrary to a previous report (*6*).

Reduction of γ-Bi_2MoO_6 in 1-butene at 350°C produced a green material with an X-ray diffraction pattern identical to that of the original yellow catalyst irrespective of the initial pressure of 1-butene, i.e., the amount of reducing agent available to the

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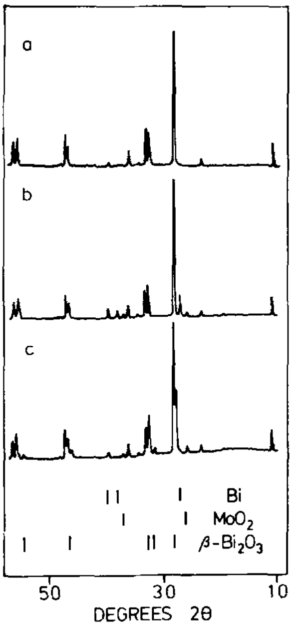

FIG. 1. X-ray diffraction patterns for (a) γ-Bi_2MoO_6, (b) "$Bi_2MoO_{5.5}$", and (c) γ-Bi_2MoO_6 reduced in 1-butene at 470°C and reoxidised at 225°C.

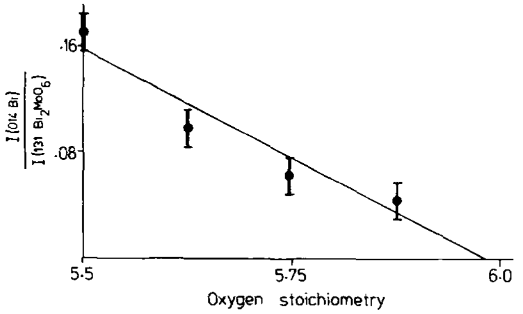

FIG. 2. Variation of Bi concentration with nominal oxygen content for reduced γ-Bi_2MoO_6 samples.

catalyst. DTA conducted under flowing nitrogen, however, indicated the presence of small amounts of Bi, since the endotherm at 261°C, Fig. 3a, is consistent with the melting point of Bi. The absence of Bi X-ray diffraction peaks suggested that either the Bi concentration was very low (in agreement with TGA results which showed no significant weight increase on reoxidation) or the particle size was very small. At this low temperature, Bi could possibly form as a film on the surface of the catalyst particles, and such surface reduction of $Bi_2O_2^{2+}$ layers has previously been proposed to explain the enhanced electrical conductivity of reduced bismuth molybdenum oxides (*12*).

For samples reduced at higher temperatures, e.g., 470°C, blue-black products were generally obtained, and X-ray diffraction patterns, which were similar to that shown in Fig. 1b, clearly indicated the presence of Bi and MoO_2 in addition to unreduced Bi_2MoO_6. The extent of reduction was determined by the initial pressure of 1-butene, and for very low levels of reduction samples were green rather than blue–black.

DTA traces for oxidation of a catalyst prereduced at 470°C exhibited two exothermic peaks with maxima at approximately 205 and 325°C (Fig. 3b). These peaks are consistent with the two-stage reoxidation observed in the previous TPR study (*9*). TGA for the reoxidation process (Fig. 3c) indicated a 69:31 ratio for oxygen absorbed at the lower and higher temperatures. The chemical changes occurring at these temperatures were investigated by X-ray diffraction. At the low-temperature step, Bi

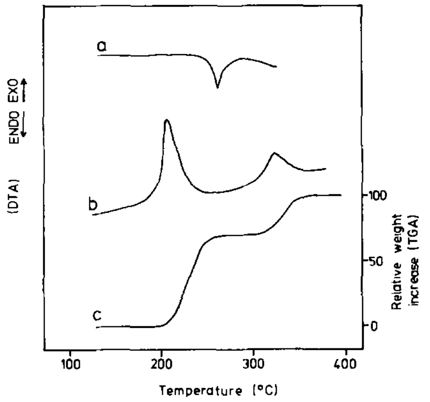

FIG. 3. DTA/TGA traces from γ-Bi_2MoO_6 prereduced in 1-butene: (a) DTA in nitrogen after reduction at 350°C, (b) DTA in oxygen after reduction at 470°C, and (c) TGA in oxygen after reduction at 470°C.

peaks disappeared from the diffraction pattern and were replaced by a β-Bi_2O_3 phase; peaks attributed to MoO_2, however, remained unchanged, as shown in Fig. 1c. The second step was found to relate to total oxidation to Bi_2MoO_6. A significant feature of the TGA data is their implication that the low-temperature stage actually corresponds to Bi oxidation to β-$Bi_2O_{2.78}$, with the subsequent process being the transformation of β-$Bi_2O_{2.78}$ and MoO_2 to Bi_2MoO_6. This observation appears consistent with Auger spectroscopy results (*9*), which suggested oxidation of Bi to Bi^{m+} $(0 < m < 3)$ during the low-temperature stage, although the nature of this material could not be established. The present study, however, does not support the view that simultaneous oxidation of Mo^{4+} to Mo^{6+} occurs at this temperature, since both X-ray diffraction and TGA results are consistent only with this oxidation relating to the high-temperature exotherm. This apparent disagreement may simply reflect differences between surface and bulk properties.

The initial oxidation product may seem unusual since β-Bi_2O_3 is generally regarded as metastable, with α-Bi_2O_3 being the stable low-temperature form (*13*). β-Bi_2O_3, however, has previously been observed during the reoxidation of a bismuth molybdenum oxide (*14*) and is the product of the thermal decomposition of $Bi_2O_2CO_3$ at 400°C. Since the $Bi_2O_2^{2+}$ layers present in $Bi_2O_2CO_3$ and γ-Bi_2MoO_6 have a Bi and O structural arrangement which is found in β-Bi_2O_3 but not α-Bi_2O_3 (*15*), it is possible that these layers act as nucleation sites for the preferential formation of β-Bi_2O_3.

The existence of oxygen-deficient β-Bi_2O_3 samples, e.g., $Bi_2O_{2.5}$ and $Bi_2O_{2.7}$, has previously been reported (*16, 17*) for thin film specimens. X-ray and electron diffraction studies revealed that the cation sublattice is essentially the same as that for the fully oxidised phase such that the oxygen stoichiometry cannot be established using X-ray diffraction. Treatment of β-Bi_2O_{3-x} films in oxygen was found to result in gradual oxygen uptake towards the stoichiometric material (*16*), and similar behaviour was observed in the present study of Bi oxidation on Bi_2MoO_6 catalysts, since maintaining samples at 220°C for 4 h produced a weight increase consistent with the formation of stoichiometric β-Bi_2O_3.

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