Nature of the β -Phase of Bismuth Molybdate

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Infrared and Raman spectroscopies, X-ray diffraction and d.s.c. analysis have confirmed that the β -phase (B mixture) is different from an equimolar mixture of the α - and γ -phases (A mixture) of bismuth molybdate. A comparison of the catalytic properties between A and B mixtures in the partial oxidation of propene and the dehydrogenation-dehydration of isopropanol also confirms this difference. The β -phase is a defined phase of the bismuth molybdate system and is metastable at room temperature, but is stable enough to be used in catalytic tests. The enthalpy of transformation of mixture A to mixture B at 560 °C was found to be 6330 J mol⁻¹.

The kinetics and mechanism of propene oxidation over bismuth molybdate catalysts have been studied in considerable detail and are the subject of several extensive reviews.¹⁻⁴ The three phases showing simultaneously high activity and selectivity for the partial oxidation of hydrocarbons are Bi_2MoO_6 (y-phase), $Bi_2Mo_2O_9$ (β -phase) and $Bi_2Mo_3O_{12}$ (α -phase). Some researchers^{5, 6} thought that the β -phase was only a mixture of the α - and γ -phases and not a distinct phase, while others^{7,8} believed that the β -phase was unstable at the high temperatures required for propene oxidation.

Thermal decomposition or reduction by butene of the β -phase decomposed it into the γ -phase and MoO₂^{9,10} or into the α - and γ -phases.¹¹

Monnier has verified that the β -phase is a pure phase of the bismuth molybdate system and is stable at the temperatures required for an in-depth study of the kinetics of propene oxidation.12

Grasselli et $al.^5$ thought that the best catalyst among these bismuth molybdates is $Bi_{a}Mo_{a}O_{a}$. The structure of the β -phase was controversial because of its thermal instability. Van den Elzen and Riek¹³ published a structure for the β -phase based on Xray powder data. Sleight and Chen¹⁴ obtained a suitable single crystal of the β -phase and an accurate structure was reported. X-Ray, i.r. and Raman spectra of the β -phase have been reported in many articles.12, 15, 16

Thermal methods and catalytic studies are often used to characterize the properties of solid materials, such as heterogeneous catalysts. Thermal analysis gives an idea about the stability of the catalyst and its chemical evolution. By microcalorimetric studies we can determine not only the temperature of the typical d.s.c transformation, but also the corresponding heat evolved.

Catalytic properties which depend strongly on the surface compositions give an idea about the nature of catalytic sites.

We have investigated this system in order to confirm the difference between the β phase and the equimolar mixture of α - and γ -phases and to obtain an insight into the stability of the β -phase under catalytic and laboratory conditions.

Experimental

Catalyst Preparation

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The β -phase catalyst used in this study was prepared by calcination in air at 560 °C of a hand-ground equimolar mixture of α - and γ -phases (A mixture) for 2 days. The α - and 3169

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 γ -phases were prepared according to the method of Batist.¹⁶ Details regarding their purity have been discussed previously.¹⁸

D.s.c. studies were carried out with a differential scanning calorimeter (DSC 111) from Setaram. The high sensitivity of this heat-flow microcalorimeter allows a heating rate up to 30 °C min⁻¹ and the use of a very small amount of solid. The experimental study was carried out from room temperature to 700 °C.

I.r. and Raman spectra were recorded using a Perkin-Elmer 580 spectrophotometer with KBr discs and a DILOR, OMARS 89 spectrograph, respectively. X-Ray powder spectra were recorded using Cu K_{α} radiation.

We studied two catalytic reactions: partial oxidation of propene in comparison with the published results, and dehydration-dehydrogenation of isopropanol to estimate the acid-base properties.^{19, 20}

The microreactor which was used to measure the catalytic activity consisted essentially of a single-pass flow system, and has been described previously.²¹ The tests were carried out in the temperature range 300-400 °C under atmospheric pressure. The total gas flow was 1 cm³ s⁻¹. Propene oxidation was studied with the ratio C_3H_6 : $O_2: N_2 = 100: 100: 560$. The conversion level was less than 4% in order to maintain a homogeneous temperature in the catalytic bed.

Samples were also characterized for isopropanol reaction in the air flow at temperatures ranging between 100 and 250 °C with $C_3H_7OH:O_2:N_2 = 10:150:600$. The total gas flow was 0.32 cm³ s⁻¹. The products were either propene (dehydration reaction due to acidic sites) or acetone (dehydrogenation due to redox or basic sites).

Results and Discussion

D.S.C.

The d.s.c. curve of the γ -phase shows two endothermic peaks. The smaller peak at 607 °C ($\Delta H = 282 \text{ J mol}^{-1}$), corresponds to the transition of γ - to γ'' -phase,²² and the second, more intense one at 658 °C ($\Delta H = 10065 \text{ J mol}^{-1}$) is attributed to the transition of γ'' - to γ' -phase,²² while the d.s.c. curve of the α -phase does not show any peak between 0 and 650 °C. The metastability of the γ'' -phase, and the low value of the enthalpy of the transition of γ - to γ'' -phase explain the controversy about the existence of this phase.^{22, 23}

The d.s.c. curve of a hand-ground mixture of the α - and γ -phases (A mixture) shows an endothermic peak at 560 °C ($\Delta H = 6330 \text{ J mol}^{-1}$). This peak corresponds to the chemical reaction of the α - and γ -phases to give the β -phase according to the reaction

$$Bi_2Mo_3O_{12} + Bi_2MoO_6 \rightarrow 2Bi_2Mo_2O_9$$
.

The endothermic value of the peak shows the evolution of the system to a more organized one. This reaction was evidenced by the following spectroscopic studies.

Spectroscopic Studies

The i.r. and Raman bands of bismuth molybdates are situated below 1000 cm^{-1} . Characteristic Mo—O stretching vibrations can be seen in the 950-800 cm⁻¹ range, and the Bi—O—Mo and/or Bi—O stretching vibrations in the 750-550 cm⁻¹ range. Finally, the bands in 400-200 cm⁻¹ range are assigned to Mo—O and Bi—O bending vibrations. It is therefore doubtful whether evidence from i.r. and Raman spectroscopy can be used to make a distinction between an 'octahedral' or 'tetrahedral' environment of the molybdenum in this case.

The i.r. spectrum of the A mixture before calcination shows only the α and γ bands (fig. 1). There are three bands between 950 and 900 cm⁻¹ characteristic of the α -phase,

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Fig. 1. I.r. spectra of equimolar mixture of α - and γ -phases before (a) and after (b) calcination at 560 °C for 2 days in air.

	c	r		Ŷ	mixture A		mixture B		
-	d	I _r	d	I _r	d	I _r	d	I _r	
			8.10	8.5	8.10	10			
	6.94	20			6.94	17	5.94	12	
	4.87	23			4.87	22	4.9	16	
	3.18	100			3.18	100	3.20	100	
		<u></u>	3.15	100	3.15	100	3.1	14	
	3.05	67			3.05	60	<u> </u>		
	2.86	28			2.86	33	2.8	29	
		_	2.74	15	2.74	20	2.69	17	
		_	1.94	19	1.94	14	1.68	18	
		—	1.65	17	1.65	18	1.64	16	

Table 1. X-Ray diffraction peaks observed for different bismuth molybdate samples

Mixture A: a hand-ground equimolar mixture of α - and γ -phases. Mixture B: β -phase. I_r , relative intensity defined by $100I/I_{max}$; d, inter-reticular distance defined by the Bragg equation: $n\lambda = 2d \sin \theta$, with d in Å.

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Fig. 2. Raman spectra of an equimolar mixture of α - and γ -phases before (a) and after (b) calcination at 560 °C for 2 days in air.

and a band at 360 cm⁻¹ which corresponds to the γ -phase.^{15,17} There is no enhanced intensity or new band.

After calcination of mixture A at 560 °C (mixture B), the i.r. spectra show an important change (fig. 1): the α and γ bands disappear. There is an intense band at 740 cm⁻¹ which corresponds to the β -phase.^{15,17} Detailed study of this spectrum leads us to conclude that the α - and γ -phases are transformed to the β -phase and that the B mixture corresponds only to the β -phase. This conclusion was confirmed by the X-ray data. The A mixture corresponds to an equimolar mixture of well crystallized α - and γ -phases (table 1),¹⁵⁻¹⁷ but when the A mixture is calcined above 560 °C, the X-ray spectrum is found to correspond to the β -phase, characterized by the presence of two peaks at 3.20 and 2.80 Å¹⁵⁻¹⁷ (table 1).

The Raman spectra of mixtures A and B are shown in fig. 2. The Raman spectrum of mixture A shows three bands at 955, 925 and 900 cm⁻¹, which correspond to the α -phase and a band at 842 cm⁻¹, corresponding to the γ -phase.¹⁷ The B mixture shows the presence of a strong band at 885 cm⁻¹, characteristic of the β -phase.¹⁷

I.r. and Raman spectroscopies and X-ray diffraction and d.s.c. analysis show that the β -phase is different from an equimolar mixture of α - and γ -phases. The β -phase is a defined pure phase of the bismuth molybdate system.

The B mixture (β -phase) remains stable under catalytic conditions, as shown by i.r. and X-ray spectra of the solids used in propene oxidation and in isopropanol reactions. However, the i.r. and X-ray spectra of the β -phase which had been aged over 2 years under laboratory conditions (pressure = 10⁵ Pa, temperature = 23 °C) show the presence of traces of α - and γ -phases. This implies that the β -phase is a metastable phase which involves decomposition with time into a mixture of α - and γ -phases.

Catalytic Study

The results for selectivity for the two catalytic reactions studied are given in table 2. The selectivity of propene to acrolein was found to follow the order: mixture A > mixture

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	propene selectivity (%)		isopropanol selectivity (%)		C(DET)
	acrolein	CO2	acetone	propene	$/m^2 g^{-1}$
mixture A	95	3	88	12	4.7
mixture B	90	6	72	28	0.3

Table 2. Selectivity in propene oxidation and in dehydration-dehydrogenation of isopropanol

Mixture A: Hand-ground equimolar mixture of α - and γ -phases. Mixture B: Bi₂Mo₂O₉ (β -phase). Catalytic conditions for the partial oxidation of propene: mass = 0.1 g, T = 380 °C. Catalytic conditions for isopropanol dehydration-dehydrogenation: mass = 0.1 g, T = 190 °C.

B (β -phase). The A mixture is more selective than the β -phase in the partial oxidation of propene. This result is in agreement with the work of Carson *et al.*, and the effect is explained by a synergetic effect.^{16,18}

The selectivity for the dehydration of isopropanol was found to follow the order mixture B (β -phase) > mixture A. This suggests that the β -phase shows a stronger superficial acidity than the A mixture. Comparison of catalytic properties confirms that the β -phase is significantly different from an equimolar mixture of α - and γ -phases.

Conclusions

D.s.c. analysis and spectroscopic studies have shown that a chemical reaction occurs between the α - and γ -phases to give rise to the β -phase. The i.r., Raman and X-ray spectra of the β -phase are very different from those of an equimolar mixture of α - and γ -phases, confirming that the β -phase is a well defined phase of the bismuth molybdate system. After a long time the β -phase begins to decompose at room temperature into the α - and γ -phases.

The β -phase can also be differentiated from an equimolar mixture of α - and γ -phases of bismuth molybdate by the selective oxidation of propene and the dehydration of isopropanol to propene.

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