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Synergy Effects in the Catalytic Properties of Bismuth Molybdates

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Different phases (α, β and γ) and intimate equimolar mixtures of the α and γ phases of bismuth molybdate have been investigated for the mild oxidation of propene into acrolein. The mixtures were prepared either as a coprecipitate or as intimately compressed and ground mixtures. A synergy effect between the α and γ phases was observed with an enhancement in activity and selectivity for an intimate equimolar mixture. A study by X-ray diffraction, X-ray photoelectron spectroscopy and infrared spectroscopy allowed us to follow the effect of mixing on the different phases in the bulk or at the outer layers. Changes in elemental composition in either Mo or Bi because of mixing or preparation conditions were not detected.

Bismuth molybdate catalysts for selective olefin oxidation have been the subject of many studies over the years and there are many aspects of this system that are well known (see Keulks *et al.*[1] and Grasselli and Burrington[2] for reviews). However, there is still much discussion about other aspects. For example, most authors agree that active bismuth molybdate catalysts have a Bi:Mo ratio between 2:3 and 2:1, but there is no agreement as to which phase (α, $Bi_2Mo_3O_{12}$; β, $Bi_2Mo_2O_9$; γ, Bi_2MoO_6) is the most active and selective of the three for selective oxidation. Kolchin *et al.*[3] stated that the activity follows the sequence $\beta > \alpha > \gamma$ for selective oxidation and ammoxidation of propene. The same sequence was also observed by German *et al.*,[4] while Monnier and Keulks[5] claimed the order is $\gamma > \beta > \alpha$ for the selective oxidation of propene and Burrington and Grasselli[6] found that the order is $\beta \simeq \alpha > \gamma$. In the oxidative dehydrogenation of butene, which is assumed to proceed *via* the π allyl intermediate as in the selective oxidation of propene,[1] Batist *et al.*[7] found that the activity follows the sequence $\gamma > \beta > \alpha$ and Matsuura *et al.*[8] stated that the order is $\beta > \alpha > \gamma$. This list is not exhaustive but it shows the large divergence of opinion. Of course, the catalysts were not prepared in the same manner, nor were the reaction conditions equivalent. Some of the early results were reported on a per gram basis and not per unit surface area.

For the selective oxidation of 1,1-dimethylethylene to methacrolein, it was shown[9] that the order of activity and selectivity for α, β or γ bismuth molybdate was different depending on the pressure of isobutene in the feed stream.

In the present work, results of catalytic activity experiments for the oxidation of

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propene to acrolein are reported for several well defined bismuth molbydates in order to add further insight to the discussion of which bismuth molybdate is the most active and selective catalyst.

EXPERIMENTAL

CATALYST PREPARATION

Several batches of catalyst with bismuth to molybdenum ratios of 2:1, 1:1 and 2:3 were prepared in the same manner by coprecipitation according to the following procedure:[10] 30 g of ammonium heptamolybdate [$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$] were dissolved in 250 cm^3 of ammonium hydroxide aqueous solution (5% NH_4OH) at pH 10. The solution was added dropwise at room temperature to a stirred nitric acid solution of 120 g $Bi(NO_3)_3\cdot 5H_2O$ in 500 cm^3 of 5 mol dm^{-3} HNO_3, until the desired stoichiometry was obtained. The final pH was brought to 7 by the addition of ammonium hydroxide. In all cases, the precipitate was white after the molybdate solution had been added. The ratio of bismuth to molbybdenum in the catalyst was controlled by varying the amount of heptamolybdate solution added to a fixed amount of the bismuth nitrate solution.

The precipitate and the mother solution were heated together, slowly, from 320 to 470 K until all of the water had been evaporated. At no time were the catalysts filtered or washed. The dried catalysts were calcined under static air from 470 to 720 K in steps of 50 K, with several hours at each step in order to ensure the complete decomposition of ammonium nitrate. Certain catalysts with a bismuth to molybdenum ratio of 1 were calcined a second time at temperatures ranging from 825 to 925 K. The areas of the catalysts were found to be between 0.5 and 5 m^2 g^{-1} by B.E.T. (N_2) measurements and decrease with increasing calcination temperature.

CATALYST ACTIVITY

A microreactor was used at atmospheric pressure and at 663 K in a single-pass flow system, which has been described previously.[11] The reaction volume was *ca.* 2 cm^3 and typically 200 mg of catalyst were used with a total gas flow rate of 1–2 cm^3 s^{-1}. The partial pressure of propene used in activity measurements ranged from 100 to 200 Torr,* as did the partial pressure of oxygen. The conversion levels were kept low ($< 4\%$) to avoid temperature gradients in the catalyst bed (for every 1 Torr of propene which reacts, there is an adiabadic rise in the temperature of the gas of *ca.* 15 °C). The propene, oxygen and nitrogen were obtained from Air Liquide, N20 grade, and were used without further purification. The effluent gases were analysed chromatographically, on stream, and the peaks were integrated by an Autolab System IV microprocessor. Carbon balances of better than 10% were attained.

PHYSICAL METHODS

ESCA measurements were performed on a Hewlett-Packard HP 5950 A spectrometer at room temperature. A computer was used to smooth the points of the spectra as well as calculate the peak's area. Qualitative analysis of the ESCA peaks, in terms of elemental ratios, was carried out as described previously[12] and the estimated error in such an analysis is approximately 10%.

Infrared spectra were recorded using a Perkin-Elmer 580 spectrometer with KBr pellets. X-ray powder spectra were recorded using Cu *Kα* radiation.

RESULTS

The catalysts with bismuth:molybdenum ratios of 2:1 and 2:3 prepared according to the above procedure were found to be virtually pure γ and α bismuth molybdates, respectively. This can be seen from the infrared spectra and the X-ray data shown in fig. 1 and table 1.

Characteristic Mo—O stretching vibrations can be seen in the 950–700 cm^{-1} region of the infrared spectrum of the 2:3 catalyst (fig. 1) and Bi—O stretching vibration

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* 1 Torr = 131.6 Pa.

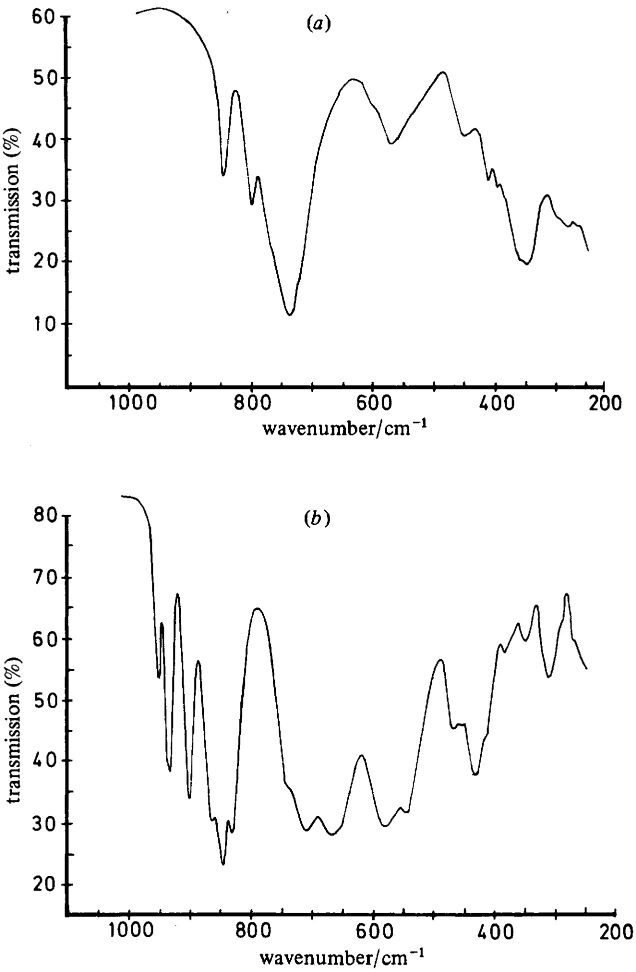

Fig. 1. Infrared spectrum of lattice vibrational bands for (*a*) γ and (*b*) α phases.

and deformation vibration in the 600–400 cm^{-1} region, which corresponds to previously published i.r. spectra for the α phase. The X-ray spectrum also corresponds to previously published X-ray spectra of well crystallised α bismuth molybdate:[13] The X-ray data in table 1 also show traces ($< 5\%$) of the γ phase.

The infrared spectrum of the 2:1 catalyst (fig. 1) corresponds to previously published infrared spectra for the γ koechlinite phase,[14] especially in the 800 cm^{-1} region of MoO stretching vibrations. The narrow lines in the X-ray spectrum also confirm that the 2:1 catalyst is well crystallised γ bismuth molybdate (koechlinite). No crystallised trace impurities were detected in the X-ray spectrum.

The infrared spectrum of the 1:1 catalyst (fig. 1) corresponds to previously reported infrared spectra for the β phase[14] (characterised by a broad featureless band in the 800 cm^{-1} region) only when the catalyst was calcined above 870 K. When the calcination temperature was < 770 K, the infrared spectrum was a superposition of the α and γ phases (fig. 2). This assessment was corroborated by the X-ray data, which correspond to an equimolar mixture of well crystallised α and γ bismuth molybdate

Table 1. X.r.d. peaks observed for the different bismuth molybdate phases;

α phase		β phase		γ phase	
$I_{\text{obs.}}s/10$	$d_{\text{obs.}}/10^{-10}$ m	$I_{\text{obs.}}s/10$	$d_{\text{obs.}}/10^{-10}$ m	$I_{\text{obs.}}$	$d_{\text{obs.}}/10^{-10}$ m
2	7.80*	1	8.02	2	804*
3	6.90*	2	6.67	1	4.54*
2	6.30*	2	5.96	1	3.78*
1	5.99*	1	5.22	1	3.26*
1	5.78*	1	4.92	10	3.15*
1	5.02*	1	4.78	4	2.75*
4	4.90*	1	4.22	3	2.70*
2	4.58*	1	3.93	1	2.60*
1	3.75*	1	3.80	1	2.50*
2	3.60*	1	3.44	1	2.43*
2	3.58*	1	3.30	1	2.27*
1	3.40*	10	3.20	1	2.00*
2	3.34*	1	3.19	3	1.94*
3	3.27*	1	3.16	3	1.92*
10	3.19*	1	3.08	1	1.89*
1	3.13	1	2.99	1	1.78*
8	3.05*	1	2.98	3	1.65*
5	2.88*	1	2.82	3	1.63*
1	2.79*	6	2.80	2	1.58*
1	2.65	5	2.70		
1	2.64	1	2.59		
1	2.57	1	2.55		
1	2.54	1	2.46		
1	2.50*	1	2.44		
2	2.48*	1	2.40		
1	2.44	1	2.39		
1	2.34*	1	2.32		
1	2.32	1	2.28		
1	2.29*	1	2.27		
1	2.27*	3	2.20		
2	2.24*	2	2.18		
		1	2.15		
		1	2.05		
		1	2.04		
		4	2.00		

* Peaks observed for the ($\alpha+\gamma$) phase.

and by the i.r. spectrum of an equimolar mixture of α and γ phases, as shown in fig. 2 (dotted-line spectrum). When this mixture was calcined above 870 K, the X-ray spectrum was found to correspond to the β form.

By elemental chemical analysis, the ratios of bismuth to moybdenum in all of the calcined catalysts were found to be exactly the same as the theoretical ratios from the catalyst preparation. This is not surprising since the precipitates were neither washed nor filtered, thus insuring the final bismuth:molybdenum ratios.

The ESCA results, which give the mole ratios of the atomic elements at the surface

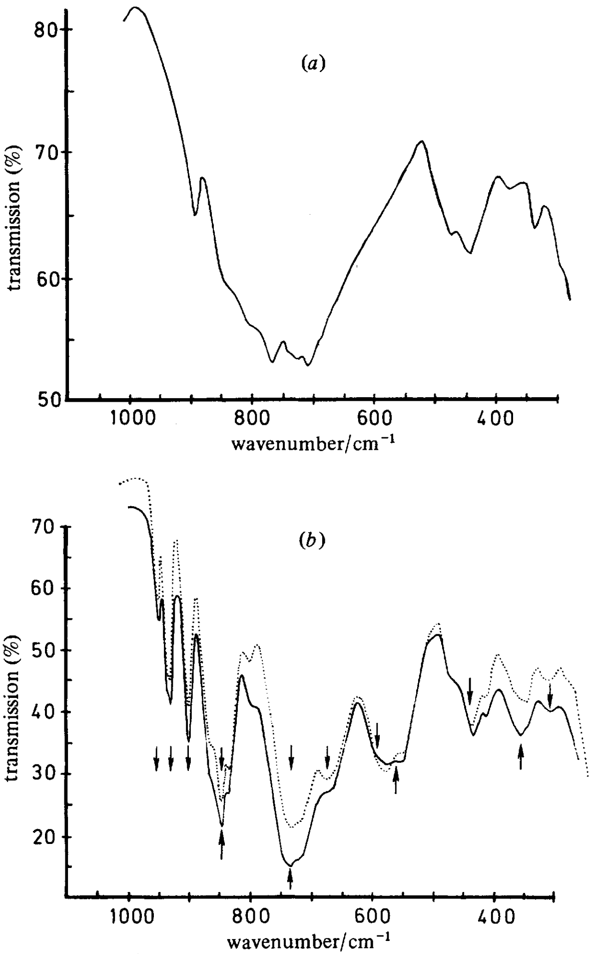

Fig. 2. Comparative infrared spectrum for (*a*) β and (*b*) coprecipitated $\alpha+\gamma$ phases (full line) and equimolar and ground mixture of α and γ phase (dotted lines). The arrows correspond to the position of the most intense i.r. bands for pure α (↓) and γ (↑) phases.

up to a depth of 5 nm into the catalysts, are shown in table 2. Within experimental error, the surface ratio of Bi to Mo reflects that of the bulk for all of the catalysts, both before and after 24 h use in the reactor. This result is particularly interesting for the catalyst designated ($\alpha+\gamma$) which is a mixture of two phases with different Bi:Mo ratio (2:3 and 2:1). Since the average surface Bi:Mo ratio for this catalyst is 1:1, we conclude that the catalyst is a true mixture of the α and γ phases, and that one phase is not supported by the other.

Note that the (Mo+Bi):O ratio given by X.p.s. measurement (table 2) is smaller for used catalysts than for the starting samples. The i.r. spectrum then shows the presence, after catalytic reaction, of an oxygenated compound strongly adsorbed on the surface. The presence of such a compound and eventually of adsorbed water from the reaction explains the increase in the O 1*s* X.p.s. peak and the subsequent decrease of both Mo and Bi X.p.s. peaks due to the adsorbed layers. Quantitative

Table 2. X.p.s. data in atomic ratios for the different samples before and after use. Theoretical (Bi + Mo):O ratios are calculated from chemical formulae.

	Bi:Mo		(Bi+Mo):O		Bi:O		Mo:O		
sample	X.p.s.	chemical analysis	X.p.s.	theoretical	X.p.s.	theoretical	X.p.s.	theoretical	remarks
α	0.65	0.67	0.39	0.42	0.15	0.17	0.24	0.25	starting samples
$\alpha+\gamma$	1.1	1.0	0.43	0.44	0.23	0.22	0.20	0.22	
β	1.1	1.0	0.27	0.44	0.12	0.22	0.13	0.22	
γ	2.4	2.0	0.51	0.50	0.36	0.33	0.15	0.17	
α	0.65	0.67	0.35	0.42	0.14	0.17	0.21	0.25	samples after 24 h reaction
$\alpha+\gamma$	1.2	1.0	0.31	0.44	0.17	0.22	0.14	0.22	
β	1.1	1.0	0.16	0.44	0.08	0.22	0.08	0.22	
γ	2.2	2.0	0.26	0.50	0.18	0.33	0.08	0.17	

Table 3. Activity and selectivity in propene oxidation. $O_2:C_3H_6:N_2 = 200:100:460$ Torr; $T = 660$ K; gas flow = 1 $cm^3\ s^{-1}$

solid (phase)	activity/10^{-8} mol s^{-1} m^{-2}			selectivity for acrolein (%)			surface area/m^2 g^{-1}
	(*a*)	(*b*)	(*c*)	(*a*)	(*b*)	(*c*)	(*c*)
α	28	45	37	85	90	88	0.6
$\alpha+\gamma$	30	60	47	92	97	94	3.2
β	26	17	16	55	75	65	0.5
γ	3	12	8	59	71	66	2.7

[a] Minimum experimental value; [b] maximum experimental value; [c] typical experimental value.

ratios are obtained by measuring the area (A) of the peaks after subtracting the background. The approximate relationship:

$$\frac{n_1}{n_2} \approx \frac{A_1}{A_2}\frac{\sigma_2}{\sigma_1}\frac{E_{k_2}^{1/2}}{E_{k_1}^{1/2}}$$

is used, where σ as the cross-section of the electron (tabulated by Scofield[12]) and E_k its kinetic energy. The case of the β-phase sample is more striking since, even for the starting sample, the (Mo + Bi):O ratio is much smaller than the theoretical value. This is presumably due to an oxygen species strongly adsorbed on the surface, since it is not eliminated by outgassing overnight under high vacuum (10^{-9} Torr) at 330 K. Unfortunately, no non-overlapping signals of the O 1*s* peak could be detected. It is tempting to relate such an intense O 1*s* peak and the relatively poor catalytic properties of the β-phase sample with respect to those of the ($\alpha+\gamma$) phase.

In all, 20 catalysts were tested. The results for the activity and selectivity are given in table 3 for the four classes of catalysts (the pure phases, α, β and γ, and the mixture $\alpha+\gamma$).

The catalytic activity and selectivity were found to follow the order $\gamma <$

Table 4. Synergy effect for the intimate mixture of α and γ phases in propene oxidation $O_2:C_3H_6N_2 = 100:200:460$ Torr; $T = 653$ K; gas flow = 1 $cm^3\ s^{-1}$

	without grinding and compression			after grinding and compression (4 tonne cm^{-2})		
solid	selectivity for acrolein (%)	surface area /$m^2\ g^{-1}$	activity /10^{-8} mol $s^{-1}\ m^{-2}$	selectivity for acrolein (%)	surface area /$m^2\ g^{-1}$	activity /10^{-8} mol $s^{-1}\ m^{-2}$
α	86	0.6	40	86	1.9	30
γ	67	2.7	19	56	4.2	20
average $\frac{1}{2}(\alpha+\gamma)$ (theoretical)	73	1.6	23	68	3.0	23
mechanical mixture $\alpha+\gamma$ (experimental)	71	1.3	21	89	2.7	13

$\beta < \alpha < (\alpha+\gamma)$. Note that the mixture $\alpha+\gamma$ is more active and more selective than either of its two constituents. Also, after the phase transformation $\alpha+\gamma \rightarrow \beta$, the activity and selectivity drop almost to the level of γ bismuth molybdate which is only slightly active. α bismuth molybdate is only slightly less active and selective than the $\alpha+\gamma$ catalyst.

To investigate the synergetic effect between the α and γ phases, catalytic activity experiments were carried out on a mechanical mixture of the α and γ phases (50 moles of each) after simple mixing and after the mechanical mixture was ground and compressed (4 tonne cm^{-2}). The α- and γ-phase catalysts were also tested after being compressed, for comparison. The results are shown in table 4.

After grinding and compressing, the pure α and γ phases show the same selectivity and about the same specific activity despite the change of surface area.

Without grinding and compression the activity and selectivity of a mechanical mixture are the same as those expected from a simple arthimetical average of the values for both components. After grinding and compression an important effect was observed. The selectivity for acrolein increased and approached the selectivity of the coprecipitated $\alpha+\gamma$ catalyst (table 3), while the specific activity decreased. These results can be explained by a drop in the activity for CO_2.

DISCUSSION

The results of the present catalytic activity experiment show that there is a synergy effect between the α and γ phases of bismuth molybdate. That is, a catalyst composed of an intimate equimolar mixture of $Bi_2Mo_3O_{12}$ (α) and Bi_2MoO_6 (γ) is more active and selective than either of the pure phases alone. The synergy effect is emphasised in the mechanical mixing experiment. By simply mixing and compressing α and γ bismuth molybdates together, improving the contact between the two catalysts to imitate the coprecipitate $\alpha+\gamma$ catalyst, the selectivity surpasses either of the pure phases even when each pure phase is individually compressed in the same manner. The implication of this result is that small amounts of an impurity (α for example) on the surface of a pure catalyst (γ) may change the catalytic properties of the catalyst. How the two phases interact with each other to form the active surface is not clear.

Upon calcination at high temperatures ($\geqslant$ 825 K), the coprecipitated $\alpha+\gamma$ catalyst undergoes a phase transformation to the β phase[15] and loses its high activity and selectivity. In contrast, Grasselli and coworkers have observed a different effect. They state[16] that the most active phase for propene oxidation is the β phase and upon repeated reduction–oxidation cycles at reaction temperatures there is a phase partition into $MoO_{3-y}+Bi_2MoO_{6-x}$ and ultimately $Bi_2Mo_3O_{12}$ (α)+Bi_2MoO_6 (γ), and the high activity is lost. Kumar and Ruchenstein[17] have also studied the decomposition of the β phase in order to characterize the active surface. By electron diffraction they observed that thin films (several hundred ångströms) of β bismuth molybdate decompose into the γ phase plus MoO_2 at 625 K under vacuum or at 675 K in air, conditions that are similar to actual reaction conditions. They attribute the high activity of the phase to a thin surface layer of γ bismuth molybdate plus MoO_2 formed under reaction conditions. However, the instability of the surface of the β phase under reaction conditions makes it difficult to determine the structure of its active surface phase with certainty and indeed the surface may be structurally different for different reaction conditions. It is not surprising then that the activity of the β phase in the present study is low while other studies find it to be very active. On the other hand, it is not clear whether the active surface for the coprecipitated $\alpha+\gamma$ catalyst in the present study is the same as the active surface phase for the β bismuth molybdates studied by Grasselli and coworkers[16] or Matsuura *et al.*[8]

Grasselli and coworkers have also proposed[18] that the high activity of the β phase is due to an equal amount of Bi and Mo on the catalyst surface, maximising the pairs of α hydrogen-abstraction sites and oxygen-insertion sites. Indeed, Matsuura *et al.*[8] have prepared a series of bismuth molybdate catalysts with varying Bi:Mo ratios for the oxidative dehydrogenation of n-butene and they have found that any catalyst with a surface bismuth:molybdenum ratio of 1:1, no matter what phase (α, β or γ) is the supporting phase, has approximately the same activity as the pure β phase, which is the most active. Thus the present study is in agreement with Grasselli and coworkers[16] and Matsuura *et al.*[8] in that the most active bismuth molybdate catalyst is one with a surface Bi:Mo ratio of 1:1. However, the results of the present study show that it is not sufficient to have a catalyst with a surface Bi:Mo ratio of 1:1 because when the coprecipitated $\alpha+\gamma$ catalyst was transformed into the β phase the surface Bi:Mo ratio did not change, as shown by the ESCA measurements, but the activity dropped. This is also apparent in the decomposition of the β phase observed by Grasselli and coworkers accompanied by a loss in activity.

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