Supported binary oxide monolayers as selective oxidation catalysts: $Bi_2Mo_3O_{12}/TiO_2$

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Monolayers of bismuth molybdates supported on low-area TiO_2 (anatase) catalyse the oxidation/isomerisation of 1-butene to butadiene and 2-butenes with combined selectivities of 80–100% and show significantly lower specific rates of deep oxidation than does α-$Bi_2Mo_3O_{12}$. As loadings are increased above 2 wt% (equivalent to one monolayer), selectivities remain high and, although the butadiene yields are generally only moderate, in some cases they exceed that shown by the unsupported α-phase.

Keywords: bismuth molybdate, titania, supported binary oxide monolayers, selective oxidation catalysts, 1-butene oxidation

1. Introduction

Most successful catalysts for the partial oxidation of hydrocarbons contain the cations of at least two different metals; many such catalysts contain stoichiometric binary oxides (e.g., bismuth molybdate). These reactions usually proceed by a Mars–van Krevelen mechanism in which the surface is continually reduced and re-oxidised, the immediate source of oxygen being the lattice oxygen. Much importance has been attached to the mobility of oxide ions within the lattice [1]. Recognition that a monolayer of a catalytically active oxide such as V_2O_5 supported on another suitable oxide such as TiO_2 could efficiently oxidise *o*-xylene to phthalic anhydride therefore came as a surprise [2], since such systems contain little or no reservoir of available bulk lattice oxygen. The conditions necessary to obtain stable single-oxide monolayers suitable for selective oxidations are now understood [3].

However, there has been only limited interest in extending this concept to supported monolayers of the *binary* oxides. We distinguish the use of an oxide support to stabilise and promote a monolayer of the active phase from the well known use of oxides as mechanical supports to improve the heat transfer properties and mechanical stability of catalysts [4]. Other possible advantages for supported binary oxides (SBO) include improved dispersion, the existence of new surface structures or phases, the stabilisation of volatile phases and a diminished role for bulk diffusion processes involving oxide ions or vacancies. The much smaller amount of active phase needed also allows the incorporation of elements which would have been considered too costly to use in the form of bulk oxides.

The older literature contains isolated references to "supporting" bismuth molybdates on silica [5,6], on which monolayers or high dispersions were unlikely to result. More recently, it was noted that the surfaces of multicomponent bulk oxides currently used for the propene to acrolein reaction tend to be enriched in bismuth and molybdenum [7]. This led to the deliberate preparation and testing of model catalysts comprising α-$Bi_2Mo_3O_{12}$ supported on $CoMoO_4$ and on $Co_{0.92}Fe_{0.08}MoO_x$, with surface areas of the order of 10 $m^2\,g^{-1}$; the former were inferior to unsupported α-$Bi_2Mo_3O_{12}$, but the latter were superior to it for loadings in the range of 1–10 monolayers. Isotopic tracer experiments indicated that it was only with the iron-doped support that the *support* lattice oxygen was available for reaction. Arora et al. examined a range of oxides supported on bismuth oxide [8]; perhaps not surprisingly molybdenum oxide was not stable on this surface, forming a compound upon calcination. The resulting surface mainly catalysed the deep oxidation of methanol, although calcination at higher temperatures improved the crystallinity of the bismuth molybdate and increased the selectivity to formaldehyde.

A number of attempts have also been made to prepare SBO catalysts containing vanadium, especially with phosphorus [3,9–16] but also with other elements such as antimony [17]. However, little effort was made to compare them with the unsupported oxides; the principal reason for the use of a support seems to have been to obtain a higher surface area, which is not necessarily a good thing for a *selective* oxidation catalyst. In one of these studies, V–P–O was supported on a low-area alumina, resulting in high conversion and moderate selectivity for the production of maleic anhydride from 1-butene [11]. In another, a silica-supported V–P–O catalyst of high area was prepared by grafting and this gave a better yield and selectivity for butane oxidation than a supported vanadium oxide alone [13]. Supported binary oxides such as V–Sb–O have also been successfully prepared by thermal spreading of the solid phases and mechanically in a solventless ball mill [18]. More recent work on supported V–P–O catalysts

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with loadings of the order of one monolayer has been to investigate the ways in which the structure and activity of the V–P–O phase are modified by the presence of the support. Overbeek et al. [19] have reported that V–P–O on Degussa P25 titania enhances the reducibility of the support; they propose that the improved low-temperature activity of this catalyst for the conversion of n-butane to maleic anhydride (MA) is a consequence of the "active oxygen" derived from the support. However, the selectivity at higher conversion was poor. A similar catalyst supported on Degussa P200 silica did not induce reduction of the silica and gave a lower dispersion of the V–P–O, with lower activity but improved selectivity. However, the selectivity still did not match that of the bulk V–P–O used for this reaction commercially. The authors concluded that for MA production a minimum particle size is critical for high selectivity [20]. A recent study in our own group of V–P–O on a low-area TiO_2 (anatase) has given selectivities for methanol oxidation to formaldehyde as high as 98% [21].

We now report the preparation, characterisation and catalytic behaviour in the oxidation of 1-butene of bismuth–molybdenum oxides supported on titania. A Bi : Mo ratio of 2 : 3 was used in expectation of forming a supported analogue of α-bismuth molybdate ($Bi_2Mo_3O_{12}$), which is the most stable bulk phase.

2. Experimental

A procedure based on that of Peacock et al. [5] was used to make the unsupported bismuth molybdate and was modified slightly to make the supported analogues. The loading and Bi/Mo ratio were controlled by taking the appropriate weights of the bismuth, molybdenum and titanium compounds. A solution of $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ in 40 cm^3 of 0.34 M aqueous NH_4OH was added to 180–200 cm^3 of an aqueous stirred suspension of the support (10 cm^3 per 1 g TiO_2), followed by a solution of $Bi(NO_3)_3{\cdot}5H_2O$ in 25 cm^3 of 3 M aqueous HNO_3. The total volume at this stage, including rinsing, was about 320 cm^3. The pH was then slowly raised to 5 by dropwise addition of 9 M NH_4OH_{aq}, causing the precipitation of a bismuth molybdate precursor. The mixed suspension was stirred at 333 K for 1 h and then left for 24 h at room temperature. The water was evaporated at 373 K to form a cake which was ground to a powder and then calcined in flowing air at 773 K for 5 h. The pure titania and bulk α-$Bi_2Mo_3O_{12}$ were treated/prepared identically, omitting the bismuth and molybdenum salts or the titania as appropriate. The supports used were Tioxide pigmentary anatase (TPA) (10 $m^2\,g^{-1}$, containing a number of trace elements and additives, particularly 0.23 wt% K_2O and 0.47 wt% P_2O_5) and a Rhône–Poulenc anatase (RPA) (10 $m^2\,g^{-1}$, with somewhat more sulphate and zirconia impurity than TPA, but only half the amount of P_2O_5 and just 0.04 wt% K_2O). The loadings were 1–10 wt%. We *define* one monolayer (1 ML) as one Bi or Mo cation per titanium ion in the surface; on this basis, the loadings equate to roughly 0.5–6 ML.

For the oxidation of 1-butene, 1 g of catalyst in a tubular flow reactor was tested at temperatures in the range 673–773 K, under lean conditions (0.83% 1-butene in air) at a total flow rate of 60 $cm^3\,min^{-1}$. The products were analysed by GC, taking 200 μdm^3 samples in a gas syringe after liquid products (mainly water) had been condensed in a trap at 0 °C. The principal products were *cis*- and *trans*-2-butene and butadiene, but the *cis* isomer was not fully separated from the butadiene on our column (appearing as a shoulder) and it was assumed that the *cis* : *trans* ratio was exactly one. This assumption is based on previous observations of 1-butene reaction with bulk bismuth molybdate phases under similar conditions [22], implying kinetic rather than thermodynamic control of the isomerisation product ratio. The amount of "waste" products (assumed to be mainly CO_2) was calculated from a carbon mass balance. Characterisation was by means of XRD (Cu K_α radiation), TEM, single-point BET surface area determination and Raman spectroscopy (LRS). For the LRS, 100 scans were averaged at 4 cm^{-1} resolution using 1064 nm exciting radiation at 0.2 W.

3. Results and discussion

3.1. Physical characterisation

Signals generated by 0.5 wt% (0.25 ML) loadings approached the limits of detection for our instruments, but, nonetheless, it is clear from the XRD and LRS results (figures 1 and 2) that at 0.5 and 1 ML loadings most of the Bi–Mo–O is *not* present as crystallites of α-, β- or γ-bismuth molybdates. There are small, reproducible peaks in the diffractograms which are not readily identifiable with known phases, but, by comparison with a 2 wt% physical mixture of α-$Bi_2Mo_3O_{12}$ and TPA, we conclude that less than one fifth of the Bi–Mo–O present at 1 ML is crystalline. The Raman spectra are dominated by a broad band peaking at about 950 cm^{-1} with intensity tailing to the anatase peak at $\sim$790 cm^{-1}: this broad band was not observed in a detailed study of the bulk bismuth molybdates by LRS [23]. Such a band has been observed with supported molybdenum oxides and is usually identified with a surface polymolybdate [24–28]; its presence is consistent with the suggestion below that a bismuth-rich crystalline phase is also present. The 950 cm^{-1} feature is also present in the 2 ML samples, but whilst it dominates the LRS of the 2 ML/TPA catalyst the main feature in the LRS of the 2 ML/RPA catalyst is a peak at about 890 cm^{-1}. The principal feature of interest in the XRD of the 2 ML/TPA sample is a broad peak between $2\theta = 27$ and 28°. (In the TEM, the TPA-supported samples with loadings up to 2 ML were indistinguishable from the clean TPA.) The 2 ML/RPA sample gives a sharper peak at $2\theta = 27.95°$; its sharpness indicates that some of the Bi–Mo–O is present as crystallites greater than 10 nm in size. These features would seem to indicate that bismuth-rich crystalline phases such as

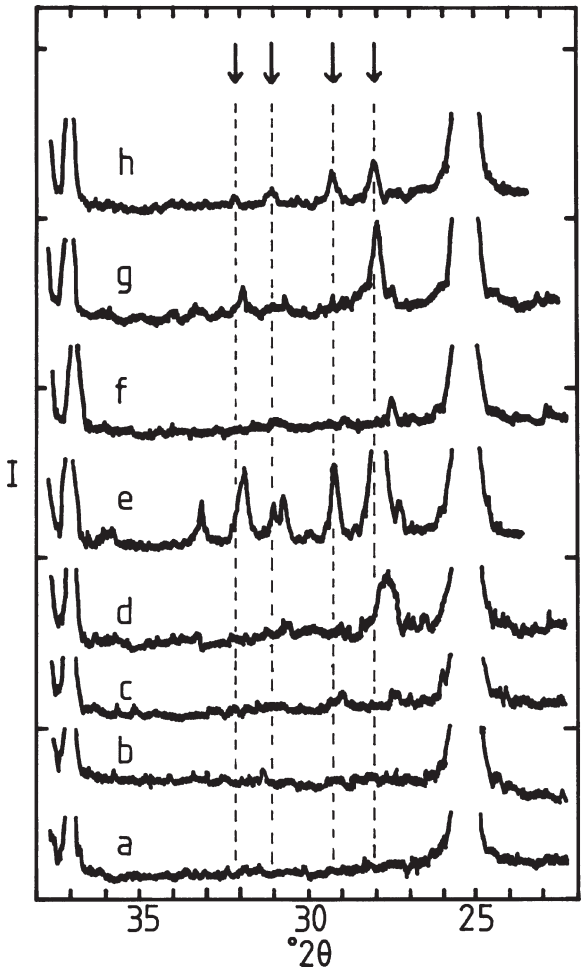

Figure 1. X-ray diffractograms, internally referenced to the anatase peaks at 25.30 and 36.98° 2θ. (a) Pure TPA; (b) 1 wt% A/TPA; (c) 2 wt% A/TPA; (d) 4 wt% A/TPA; (e) 10 wt% A/TPA; (f) 2 wt% A/RPA; (g) 4 wt% A/RPA; (h) physical mixture of 2 wt% bulk α-$Bi_2Mo_3O_{12}$ + 98 wt% pure TPA. The arrows emphasise the positions of the four most intense peaks from bulk α-$Bi_2Mo_3O_{12}$. "A" refers to a Bi : Mo ratio of 2 : 3.

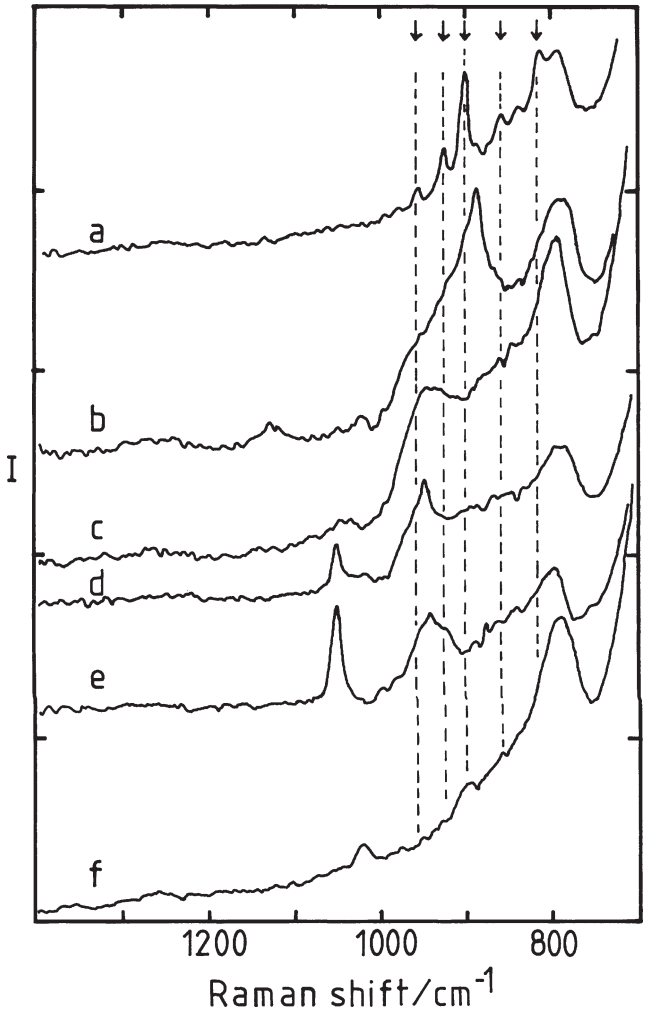

Figure 2. Raman spectra. (a) Physical mixture of 2 wt% bulk α-$Bi_2Mo_3O_{12}$ + 98 wt% pure TPA; (b) 4 wt% A/RPA; (c) 2 wt% A/RPA; (d) 4 wt% A/TPA; (e) 2 wt% A/TPA; (f) pure TPA. The features at 1022–1052 cm^{-1} are not always present: they develop with exposure to the atmosphere and are assigned to carbonate ion [35]. The arrows emphasise the positions of the five most intense peaks from bulk α-$Bi_2Mo_3O_{12}$. "A" refers to a Bi : Mo ratio of 2 : 3.

Bi_6MoO_{12} are present [29–31], although one cannot rule out the presence of a smaller amount of α-$Bi_2Mo_3O_{12}$ as well. The LRS of Bi-rich phases ($Bi_6Mo_2O_{15}$ and $Bi_{38}Mo_7O_{78}$) show peaks at ~870–880 and 800 cm^{-1} [23]: in figure 2 (b) and (d), there is clearly Raman intensity at these wavenumbers, although discrete peaks are not resolved for the latter (TPA support). The XRD of the 2 ML samples shows little evidence of crystalline MoO_3 or MoO_2. Presumably the excess molybdenum is present in X-ray amorphous form; the surface polymolybdates mentioned above are amorphous [25–27]. However, all the catalysts except the 0.5 ML A/TPA sample seem to include a small amount of crystalline Bi_2O_3 (less than 0.4 wt%).

The preferential adsorption of one component (the phosphorus oxide) has also been observed with supported V–P–O catalysts [32,33]. Given the known affinity of MoO_x for titania and its ability to spread over this surface [28], coupled with the existence of stable bismuth-rich phases of bismuth molybdate, in retrospect it is perhaps not surprising that at higher loadings our catalysts comprise, at least in part, a highly dispersed polymolybdate "monolayer" phase and a bismuth-rich crystalline phase. Work now in progress in our laboratories aims deliberately to form a molybdenum oxide monolayer and then to precipitate bismuth molybdate on top of this and to try to form a chosen bismuth molybdate phase in a "one-pot" reaction by including sufficient excess molybdenum ions to form the monolayer.

The main feature in the XRD of the 6 ML/TPA sample is a relatively intense sharp peak at $2\theta = 27.95°$, which probably results from the bismuth-rich phase mentioned earlier. In one catalyst prepared with this loading sharp peaks due to the γ-phase (also bismuth-rich with respect to the α-phase) were present as well, plus an unidentified peak at $2\theta = 26.6°$: The activity of this material was almost as good as that of bulk α-$Bi_2Mo_3O_{12}$, but we have not yet been able to reproduce this catalyst so we present no further results from it; it seems to have had a non-standard

Table 1
Selective oxidation of 1-butene by titania-supported bismuth molybdate catalysts.[a]

Catalyst[b]	ML	T (°C)	1-butene C (%)	Butadiene Y (%)	Butadiene S (%)	Butadiene + 2-butenes S (%)
Pure TPA	0	500	81	11	13	19
1 wt% A/TPA	0.5	500	46	33	71	82
2 wt% A/TPA	1	500	20	16	81	91
2 wt% A/TPA[c]	1	500	11	8	77	89
4 wt% A/TPA	2	500	51	40	79	84
4 wt% A/TPA[c]	2	500	50	38	76	82
10 wt% A/TPA	6	500	59	44	74	84
Bulk α-$Bi_2Mo_3O_{12}$	–	500	89	69	77	82
2 wt% A/RPA	1	500	93	47	50	59
4 wt% A/RPA	2	500	96	39	41	48
2 wt% A/TPA	1	400	6	2	38	54
4 wt% A/TPA	2	400	19	10	50	64
10 wt% A/TPA	6	400	24	17	72	100
2 wt% A/RPA	1	400	63	38	60	89
4 wt% A/RPA	2	400	77	46	60	88
Bulk α-$Bi_2Mo_3O_{12}$	–	400	64	30	47	63

[a] Table headings: monolayer equivalent loadings; reactor temperature; 1-butene conversion; butadiene yield and selectivity; and butadiene + 2-butenes selectivity. The uncertainties in the results vary significantly according to both conversion and selectivity but the % values in the table are no worse than ±10.
[b] "A" refers to a Bi : Mo ratio of 2 : 3.
[c] Indicates a repeat test on an independently prepared sample.

thermal history. It is clear that the nature of the support is also critical: using a Degussa P25 titania (surface area 55 $m^2\,g^{-1}$) a significant amount of crystalline α-$Bi_2Mo_3O_{12}$ was formed for a 6 ML loading.

3.2. Catalytic activity measurements

A selection of the catalytic activity results is shown in table 1 (the isomerisation products are included in this table because a common step in both oxidation and isomerisation is believed to be the formation of adsorbed C_4H_7 [1]). For 1-butene oxidation, these catalysts reached a steady state within 30 min and maintained their activity over several hours (we have not yet tested them over longer periods). The deep oxidation activity which is characteristic of the bare TiO_2 is almost completely suppressed by a loading of one monolayer: indeed, it is largely suppressed by 0.5 ML (tables 1 and 2). *This provides compelling evidence that at these loadings most of the Bi–Mo–O is spread out in a monolayer rather than aggregated*. Furthermore, as shown in table 2, the specific rate of CO_2 production for the supported catalysts with loadings in the range 0.5–6 ML is *always* less than that for bulk α-$Bi_2Mo_3O_{12}$, i.e., *most of the Bi–Mo–O is present in a form which has much lower intrinsic deep oxidation activity than the bulk α-phase*. This is obviously very desirable for a selective oxidation catalyst. There is a school of thought which prefers to compare selective oxidation catalysts at constant conversion; certainly, this is the appropriate comparison when screening catalysts for commercial use. However, for a piece of work at "proof of concept" stage, where we are trying to establish the effects of supporting the oxide phases, we believe that it is more informative to compare the supported and bulk phases under constant experimental conditions, namely temperature, flow rate, air/fuel ratio and mass of catalyst. We will report measurements made at constant conversion in the full paper on this work.

Table 2
The variation of BET surface area and specific rate of CO_x production at 500 °C with loading.

Catalyst[a]	Area ($m^2\,g^{-1}$)	Specific rate × 10^8 ($mol(C_4)\,s^{-1}\,m^{-2}$)
Pure TPA	8	2.82
1 wt% A/TPA	6	0.44
2 wt% A/TPA	9	0.07
4 wt% A/TPA	10	0.27
10 wt% A/TPA	8	0.40
Bulk α-$Bi_2Mo_3O_{12}$	5	1.08

[a] "A" refers to a Bi : Mo ratio of 2 : 3.

The unsupported α-phase behaved much as expected from the literature, with both 1-butene conversion and butadiene selectivity in the region of 70–90% (table 1). For the TPA-supported 0.5 ML Bi–Mo–O catalyst, at 500 °C the selectivity is only a few percent lower, although the yield of butadiene is only half that for the unsupported material. For higher loadings, the selectivities are similar or a few percent higher than that for the α-phase; the yields increase to about 40%, but even at 6 ML they do not approach that shown by the bulk α-phase. However, we saw above that a significant fraction of the Bi–Mo–O was present as small crystallites of a bismuth-rich phase and an X-ray amorphous Mo–O phase. MoO_3 and Bi-rich bismuth molybdates are known to have much lower activities for 1-butene oxida-

tion than α-$Bi_2Mo_3O_{12}$; MoO_3 shows poor selectivity to butadiene, whilst the Bi-rich phases have somewhat lower selectivities [22]. Our results then show a benefit from supporting these non-alpha phases and it is possible that their overall activity derives from their proximity on the support surface [34], but the increase in butadiene yield with loading (table 1) could also be due to the increasing reservoir of lattice oxygen in the bismuth-rich crystallites or an increase in the number of active sites.

It is interesting that the lowest yields of butadiene at both 400 and 500 °C are from the 2 wt% A/TPA catalysts with approximately a 1 : 1 ratio between surface titanium ions and bismuth + molybdenum ions. One could speculate that this might arise if at this loading on TPA most of the molybdenum spread out to form a monolayer on the titania, leaving almost pure, largely amorphous, bismuth oxide on top. At 1 wt%, both bismuth and molybdenum may be incorporated in the monolayer itself, and at 4 wt% and greater, a bismuth-rich bismuth molybdate would be supported on top of the molybdenum oxide monolayer; in each case giving a higher yield due to the proximity of the bismuth and molybdenum sites on these samples compared to the 2 wt% material.

Post-reaction XRD analysis of the 2 and 10 wt% A/TPA samples showed no change compared to the freshly calcined materials. It therefore seems unlikely that the reaction-induced spreading observed by Cai et al. [28] for supported oxides of vanadium and molybdenum is occurring in our samples – perhaps for no other reason than spreading is already complete following our calcination at 500 °C.

At 500 °C, the RPA-supported catalysts are significantly less selective than unsupported α-$Bi_2Mo_3O_{12}$. At lower temperatures, the 1-butene conversion falls for all catalysts, and for the α-phase and for the lower loading TPA-supported catalysts, the butadiene selectivity also falls. However, for the RPA-supported catalysts the selectivity remains moderately high or increases somewhat as temperature is lowered, such that at 400 °C the total C_4 selectivity is nearly 90%, i.e., 25% better than the α-phase under the same conditions. Also of interest is that negligible deep oxidation occurs with the 10% A/TPA catalyst at 400 °C. In terms of conserving feedstocks, running the reaction at 400 °C in a recycle reactor with either of these two catalysts, which contain a significant amount of the crystalline bismuth-rich phase (i.e., 10% A/TPA or 4% A/RPA), might be attractive.

4. Conclusions

A stable oxide "monolayer" containing bismuth and molybdenum ions (average Bi : Mo = 2 : 3) is readily prepared on low-area pigmentary anatase; the development of phases detectable by LRS, XRD and TEM at higher loadings appears to depend on the surface structure and concentration of additives, especially potassium. For most of the catalysts, the selectivity for the oxidation of 1-butene to butadiene at 500 °C is as good as that of unsupported α-$Bi_2Mo_3O_{12}$, implying that a *large* reservoir of lattice oxide ions is *not* a prerequisite for a selective oxidation catalyst, although the yield of butadiene is only moderate. When compared at 400 °C, supported crystallites of a bismuth-rich bismuth molybdate are better catalysts than the bulk α-phase. The demonstration of effective selective catalytic oxidation by highly dispersed supported binary oxides, as reported in the present work and by Moro-oka et al. [7] for bismuth molybdates, by the groups of Overbeek and Kung for vanadium phosphates [19,20] and by Grasselli and Knözinger for vanadium antimonates [18], greatly increases the choice of catalysts for such reactions. New phases may be stabilised at the surface or mixed phases formed in close proximity or volatile phases stabilised, and diffusion of bulk lattice oxygen and solid-state reactions can be minimised. When properly understood these materials may allow the control of activity and selectivity by appropriate choice and fine-tuning of the support and the active phase(s). Different loadings of the active phase(s), different surface areas and phases of the support and the use of promoters are all possible, for example. Elements which were too expensive to consider for use in bulk oxide catalysts could be economic in the much smaller amounts needed for a supported active phase. Given the limited range of preparations and reaction conditions explored so far for supported binary oxide "monolayer" catalysts, it seems likely that significantly better catalysts await invention.

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