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COOPERATION BETWEEN MoO_3 AND OTHER METAL OXIDES IN SELECTIVE OXIDATION OF ISOBUTENE TO METHACROLEIN

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Summary

A synergy is observed in the selective oxidation of isobutene to methacrolein when MoO_3 is mixed mechanically with other metal oxides, either simple (Sb, Bi, Te) or binary (Cu—Sb, Bi—P, Zn—Fe, Ni—Mo, Co—Mo, Fe—Mo and Cu—Mo). In most cases, the effect can be explained by a remote control mechanism, namely the control of active sites of MoO_3 through spillover oxygen emitted by the other phases. Roles of these admixed phases can be related to the ionicity of the bonds in their structure. The results strongly suggest that TeO_2 behaves as an intermediate oxide, either as a donor when mixed with a strong acceptor or an acceptor when mixed with a strong donor.

Introduction

Selective oxidation of isobutene to methacrolein has received much attention because it constitutes the base of one of the new routes to produce MMA (methyl methacrylate), which is an important monomer for the fabrication of transparent sheets, molding products, paints etc. [1]. Compared with the conventional method of producing MMA, namely the acetone cyanohydrin process, the direct oxidation of isobutene with oxygen has many advantages [2]. Much research has focused on the search for efficient catalysts, as well as establishing the chemical kinetic parameters for optimization of the process [3–5].

The catalysts used for this reaction are similar to those used for other allylic oxidations (*e.g.* propylene oxidation). The most efficient catalysts are usually those containing several metallic elements (multicomponent catalysts), and they usually contain several phases. The explanations for the presence of several phases in these catalysts are multiple: increasing the mechanical strength of the catalysts, preventing deactivation, promotion of selectivity or activity, etc.

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For several years, our interest has centered on the cooperation between separated oxide phases. A series of studies on mechanical mixtures, *e.g.* MoO_3–α-Sb_2O_4 [6–8], SnO_2–α-Sb_2O_4 [9], $Sb_xSn_{1-x}O_2$–α-Sb_2O_4 [10], Bi_2MoO_6–α-Sb_2O_4 [11], $ZnFe_2O_4$–α-Sb_2O_4 [12], in the selective oxidation of isobutene to methacrolein, the oxidative dehydrogenation of n-butene or the oxygen-aided dehydration of N-ethyl formamide has revealed that the cooperation between these separated phases can be explained by a remote control mechanism. According to this mechanism, one of the oxides, called the acceptor (A), such as MoO_3, SnO_2, $Sb_xSn_{1-x}O_2$, Bi_2MoO_6 or $ZnFe_2O_4$, possesses the necessary functions for the catalytic reaction, while the other one, called the donor (D), such as α-Sb_2O_4, dissociates or activates molecular oxygen into oxygen species which migrate onto the surface of the former to improve its catalytic properties. The assumption on which this mechanism rests, namely the migration of oxygen species from one phase to another, has been proven recently by a specially designed experiment using ^{18}O [13].

The improvement of the catalytic properties is due to the creation and/or regeneration of active sites on the surface of the acceptor phase by the action of spillover oxygen emitted by the donor. In the case of the oxygen-aided dehydration of formamide, it has been demonstrated that the active sites on MoO_3, namely Brönsted sites, are created as a consequence of the presence of the donor α-Sb_2O_4 and oxygen [14]. Another effect of spillover oxygen is to regenerate the sites which are deactivated during catalytic reaction, *e.g.* due to deep reduction or the deposition of coke. This has been also demonstrated in specially designed experiments: the presence of α-Sb_2O_4 could greatly enhance both the reoxidation of reduced MoO_3 and the burning of coke artificially deposited on MoO_3 [14]. Another interesting study showed that α-Sb_2O_4 can inhibit the segregation of ZnO from $ZnFe_2O_4$ in the oxidative dehydrogenation of butene, thus impeding deactivation [12]. These investigations showed that the most important feature of the remote control effect is the improvement of the selectivity.

The purpose of the present work is to expand our studies to other systems. We shall present new results concerning other mechanical mixtures in which MoO_3 is associated with other metal oxides (simple or binary). These oxides are α-Bi_2O_3, TeO_2, MgO, $BiPO_4$, $ZnFe_2O_4$ and some molybdates (of Cu, Fe, Ni, Co and Mg). We compare their action on MoO_3 with that of α-Sb_2O_4. Our aim is, on the one hand, to refine our interpretation of the observed synergy phenomena and, on the other hand, to propose some bases for comparing the abilities of the respective donor phases in order to select the best ones. This information is necessary for designing efficient multiphase catalysts.

Experimental

Catalyst preparation and characterization

Pure oxides

MoO_3 was prepared by calcination of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (p.a. Merck) at 500 °C for 20 h.

α-Sb_2O_4, α-Bi_2O_3 and MgO were obtained by calcining respectively Sb_2O_3, $Bi(NO_3)_3{\cdot}5H_2O$ and $Mg(NO_3)_2{\cdot}6H_2O$ (p.a. Merck) at 500 °C for 20 h.

TeO_2 was prepared by precipitation from $TeCl_4$ (Aldrich, 99%), followed by filtration, washing and finally calcination at 500 °C for 20 h.

$ZnFe_2O_4$, $Cu_2Mo_3O_{10}$, $NiMoO_4$, $CoMoO_4$, $Fe_2Mo_3O_{12}$, $MgMoO_4$ and $BiPO_4$ were prepared by the citrate method [15]. The starting materials used were respectively: $Zn(NO_3)_3{\cdot}6H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$, $Cu(NO_3)_2{\cdot}3H_2O$, $Ni(NO_3)_2{\cdot}6H_2O$, $Co(NO_3)_2{\cdot}6H_2O$, $Mg(NO_3)_2{\cdot}6H_2O$, $Bi(NO_3)_3{\cdot}5H_2O$, $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ and H_3PO_4 (all are p.a. from Merck). The main preparation steps of the citrate method are the following, taking $ZnFe_2O_4$ as an example:

(i) Preparation of an aqueous solution of Zn^{2+} and Fe^{3+} with an atomic ratio of $Zn/Fe = 1/2$.

(ii) Addition of a small amount of HNO_3 in order to avoid coprecipitation or precipitation.

(iii) When the solution becomes transparent, addition of citric acid in such a manner that the molar number of anions (3 ions per molecule of citric acid) is equal to that of cations (Zn^{2+} and Fe^{3+}).

(iv) Evaporation of the obtained solution in a Rotavapor, initially at 60 °C under reduced pressure until the solution becomes viscous, and then at *ca.* 90 °C until a solid is obtained (amorphous organic precursor).

(v) Decomposition of the obtained solid at 380 °C for 16 h and finally calcination at 500 °C for 18 h.

Sb(Cu)O (5 at.% Cu) was obtained by coprecipitation of Cu^{2+} and Sb^{3+} from a solution of $Cu(NO_3)_2{\cdot}3H_2O$ and $SbCl_3$ (Aldrich 99%) with NH_3 at pH near 6.5, followed by filtration, washing and drying at 100 °C overnight. The sample was finally calcined at 500 °C for 20 h.

The surface areas (Table 1) of the samples were determined gravimetrically by the BET method (Setaram microbalance MT 10-8) using N_2 as

TABLE 1

Surface area and XRD phase of oxides

Samples	XRD phase	Surface area ($m^2\,g^{-1}$)
MoO_3	MoO_3 (orthorh.)	2.3
α-Sb_2O_4	α-Sb_2O_4 (orthorh.)	2.2
α-Bi_2O_3	α-Bi_2O_3 (monoclinic)	1.9
MgO	MgO (cubic)	2.3
TeO_2	TeO_2 (tretragonal)	2.7
$NiMoO_4$	$NiMoO_4$ (monoclinic)	29.7
$CoMoO_4$	$CoMoO_4$ (monoclinic)	8.2
$Fe_2Mo_3O_{12}$	$Fe_2(MoO_4)_3$ (monoclinic)	4.3
$MgMoO_4$	$MgMoO_4$ (monoclinic)	4.1
$Cu_2Mo_3O_{10}$	$CuMoO_4 + MoO_3$ (tricl. + orthorh.)	4.0
$ZnFe_2O_4$	$ZnFe_2O_4$ (spinel)	25.4
$BiPO_4$	$BiPO_4$ (monoclinic)	4.3
Sb(Cu)O	α-Sb_2O_4 (orthorh.)	5.3

adsorbant at 77 K. The nature of the crystallographic phases (Table 1) of the samples were identified with an X-ray diffractometer (Krystalloflex 805 Siemens) using the Ni-filtered CuK_α radiation.

The sample mentioned as $Cu_2Mo_3O_{10}$ in this table is a mixture of $CuMoO_4$ and MoO_3. For Sb(Cu)O, only α-Sb_2O_4 was observed. The other samples are pure oxides.

Mechanical mixtures

Mechanical mixtures were prepared by dispersing the two powders, in equal proportion, in *n*-pentane and mixing for 10 min. This operation was followed by evaporation of the solvent under reduced pressure and finally drying at 80 °C overnight. The physicochemical characteristics of the mixtures are reported in Table 2.

The XRD phases in the mechanical mixtures are those characteristic of the starting oxides. No new phases were observed.

The surface area of the mechanical mixture is, within the experimental error, the properly weighted sum of those of the pure oxides.

Catalytic selective oxidation of isobutene

Selective oxidation of isobutene to methacrolein was carried out in a conventional fixed bed reactor under atmospheric pressure. The reactor was a Pyrex tube of 8 mm i.d., into which a small tube of 4 mm o.d. was introduced for loading a thermocouple for measuring the temperature of the catalytic bed. The catalyst was screened and 800 mg of the fraction 500–800 μm were used for each run. The standard reaction conditions were the following: iso-$C_4H_8/O_2/N_2$ (diluting gas) = 1/2/7 (vol.), total feed = 30 ml min^{-1}, reaction temperature: 380–400 °C.

The reactants and products were analyzed by 'on-line' gas chromatography (Intersmat, IGC 120 ML). Two columns were used, one containing Tenax

TABLE 2

BET surface area and XRD phase of mechanical mixture

Mechanical mixtures	XRD phase	BET surface ($m^2 g^{-1}$)
MoO_3–α-Sb_2O_4	MoO_3 + α-Sb_2O_4 (orth. + orth.)	2.2
MoO_3–α-Bi_2O_3	MoO_3 + α-Bi_2O_3 (orth. + monocl.)	2.0
MoO_3–MgO	MoO_3 + MgO (orth. + cubic)	2.1
MoO_3–TeO_2	MoO_3 + TeO_2 (orth. + tretrag.)	2.7
MoO_3-$NiMoO_4$	MoO_3 + $NiMoO_4$ (orth. + monocl.)	15.9
MoO_3–$CoMoO_4$	MoO_3 + $CoMoO_4$ (orth. + monocl.)	10.7
MoO_3–$Fe_2Mo_3O_{12}$	MoO_3 + $Fe_2(MoO_3)_4$ (orth. + monocl.)	3.4
MoO_3–$MgMoO_4$	MoO_3 + $MgMoO_4$ (orth. + monocl.)	3.8
MoO_3–$Cu_2Mo_3O_{10}$	MoO_3 + $CuMoO_4$ (orth. + tricl.)	3.2
MoO_3–$ZnFe_2O_4$	MoO_3 + $ZnFe_2O_4$ (orth. + spinel)	12.6
MoO_3–$BiPO_4$	MoO_3 + $BiPO_4$ (orth. + monocl.)	3.5
MoO_3–Sb(Cu)O	MoO_3 + α-Sb_2O_4 (orth. + orth.)	4.1

for analyzing the methacrolein and other oxygenated products (acrolein, acetone, etc.) and the other containing Porapak Q for isobutene, CO/CO_2, N_2 and water.

The reaction conversion (C) was defined as the total percentage of converted isobutene. The methacrolein yield (Y) was the percentage of the starting isobutene converted to methacrolein. The methacrolein selectivity (S) was thus easily calculated as being the ratio of yield over conversion.

We shall need to compare the activities of oxides having different surface areas. In what follows we shall thus use the quantities corresponding approximately to intrinsic activities, namely methacrolein yield or isobutene conversion divided by specific surface area (S). The respective intrinsic yield and conversion will be represented as y and c.

For the mechanical mixtures, the magnitudes of the cooperation (or synergy) between two oxides will be calculated as follows:

Supposing that we have two oxides A and B with specific surface area S_A and S_B; if no interaction between the oxides takes place (or no cooperation exists), the total methacrolein yield ($\bar{\mathrm{Y}}_{AB}$), methacrolein selectivity ($\bar{\mathrm{S}}_{AB}$) and specific surface area ($\bar{S}_{AB}$) will be:

$$\bar{\mathrm{Y}}_{AB} = 0.5S_A y_A + 0.5S_B y_B = 0.5(S_A y_A + S_B y_B) \tag{1}$$

$$\bar{\mathrm{S}}_{AB} = \frac{(0.5\mathrm{Y}_A + 0.5\mathrm{Y}_B)}{(0.5\mathrm{C}_A + 0.5\mathrm{C}_B)} = \frac{(\mathrm{Y}_A + \mathrm{Y}_B)}{(\mathrm{C}_A + \mathrm{C}_B)} \tag{2}$$

$$\bar{S}_{AB} = 0.5(S_A + S_B) \tag{3}$$

and thus the intrinsic yield will be:

$$\bar{y}_{AB} = \frac{\bar{\mathrm{Y}}_{AB}}{\bar{S}_{AB}} = \frac{S_A y_A + S_B y_B}{S_A + S_B} \tag{4}$$

We define the magnitudes of synergetic effects for intrinsic methacrolein yield (Δy) and selectivity ($\Delta \mathrm{S}$) as:

$$\Delta y = y_{AB} - \bar{y}_{AB} \tag{5}$$

$$\Delta \mathrm{S} = \mathrm{S}_{AB} - \bar{\mathrm{S}}_{AB} \tag{6}$$

where y_{AB} and S_{AB} are the real intrinsic yield and selectivity of mechanical mixture respectively.

Results

Pure oxides

The intrinsic isobutene conversion and selectivity of the isolated oxides at 380 and 400 °C are reported in Figs. 1-a and 1-b respectively. Pure α-Sb_2O_4 is inactive. MgO is poorly active and not selective. α-Bi_2O_3 is moderately active, but no methacrolein is produced. MoO_3 is relatively active

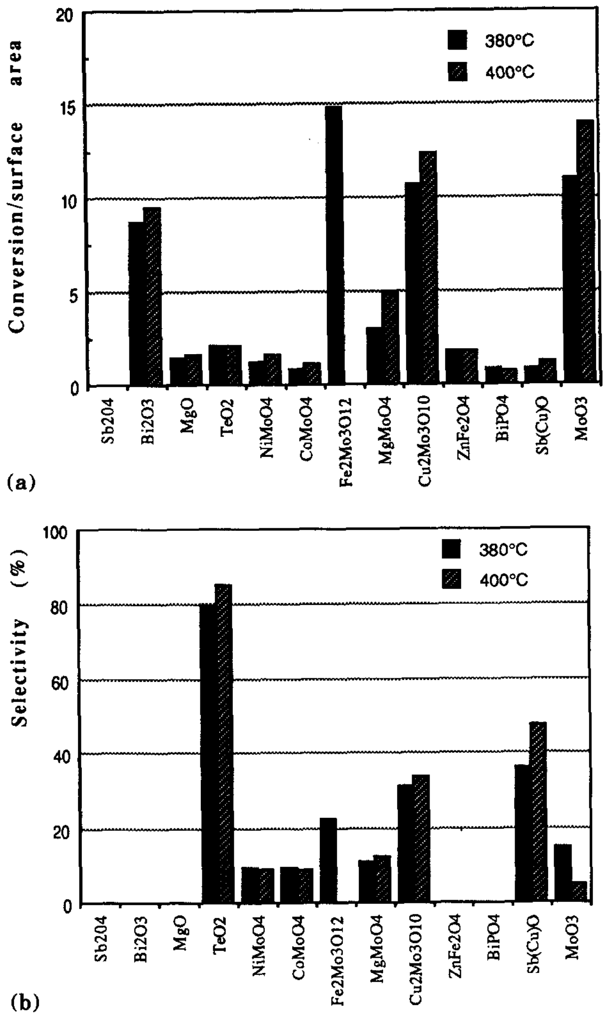

Fig. 1. (a) Intrinsic conversions of isobutene for various oxides at 380 and 400 °C respectively; (b) Methacrolein selectivites for various oxides at 380 and 400 °C respectively.

but its selectivity is poor. The most efficient simple oxide in our case is TeO_2. It has a very high selectivity to methacrolein ($\cong$80%) although its activity is not excellent.

Except $Fe_2Mo_3O_{12}$ and $Cu_2Mo_3O_{10}$, all binary oxides have the intrinsic activities (conversion) lower than that of pure MoO_3. Among the molybdates, the intrinsic conversion follows order: $Fe_2Mo_3O_{12} > Cu_2Mo_3O_{10} \gg MgMoO_4 > NiMoO_4 \cong CoMoO_4$, and the selectivity to methacrolein: $Cu_2Mo_3O_{10} > Fe_2Mo_3O_{12} > MgMoO_4 > NiMoO_4 \cong CoMoO_4$. Sb(Cu)O is more active than α-Sb_2O_4. The selectivity of Sb(Cu)O is the highest among the mixed oxides (but it has a very low activity). Two binary oxides exhibit no activity to the formation of methacrolein: $ZnFe_2O_4$ and $BiPO_4$. If we take into account both the intrinsic activity and methacrolein selectivity, the most efficient catalysts are $Cu_2Mo_3O_{10}$ and $Fe_2Mo_3O_{12}$.

Mechanical mixtures

Figures 2-a and 2-b present the intrinsic methacrolein yield and selectivity of the mechanical mixtures of MoO_3 with other oxides at 380 and 400 °C respectively.

The synergies for intrinsic methacrolein yield (Δy) and selectivity (ΔS),

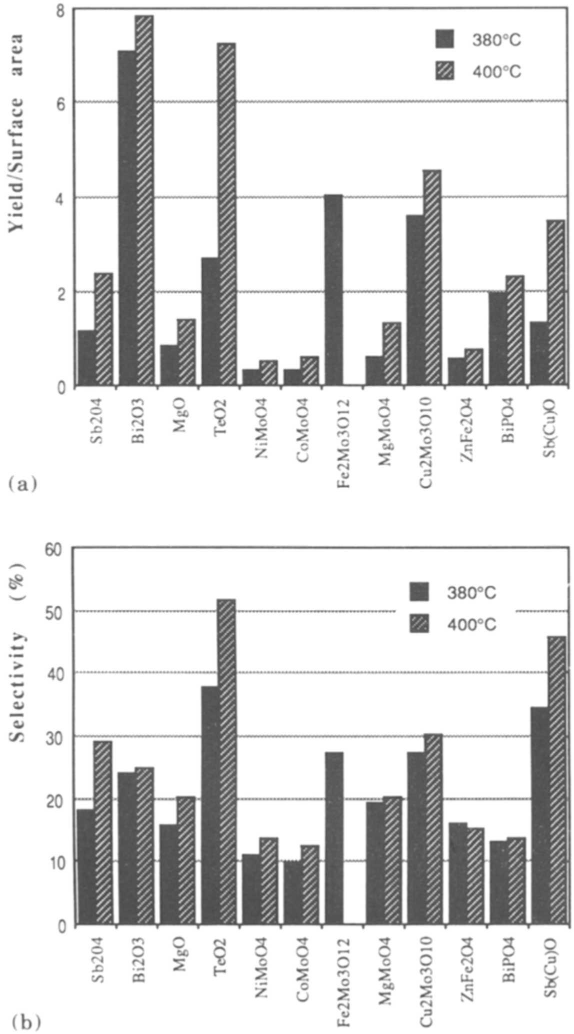

Fig. 2. (a) Intrinsic methacrolein yields for mechanical mixtures of MoO_3 with various added oxides at 380 and 400 °C respectively; (b) Methacrolein selectivities for mechanical mixtures of MoO_3 with various added oxides at 380 and 400 °C respectively.

as expressed by formulae (5) and (6), are presented in Figs. 3-a and 3-b respectively. In most cases, a conspicuous synergy between MoO_3 and other added oxides is observed. The higher synergies for intrinsic methacrolein yield were observed for MoO_3–α-Bi_2O_3, MoO_3–TeO_2 and MoO_3–Sb(Cu)O, while Sb(Cu)O, TeO_2, α-Bi_2O_3 and α-Sb_2O_4 were the most efficient added phases for increasing methacrolein selectivity. The calculated synergies increase with reaction temperature.

The effects of molybdates (Fe, Co, Ni, Cu and Mg) on the increase of intrinsic yield (Δy) and selectivity (ΔS) are very different when mixed with MoO_3. Ni and Co molybdates have a small positive effect on methacrolein

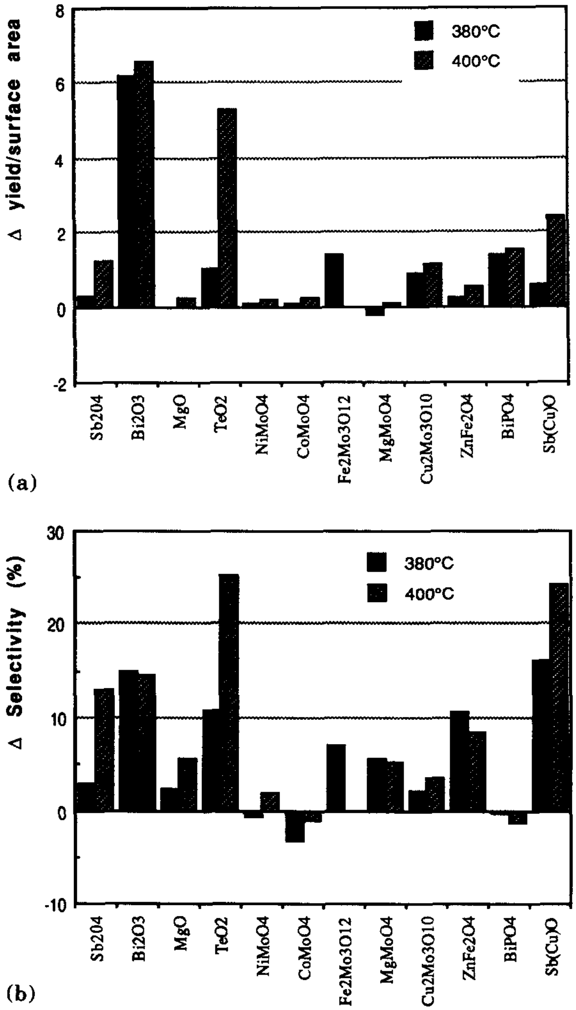

Fig. 3. (a) Calculated synergies on intrinsic yield (Δy) for different mechanical mixtures; (b) Calculated synergies on selectivity (ΔS) for different mechanical mixtures.

formation but have almost no or even negative influence on the selectivity. The reverse was observed for $MgMoO_4$. Only Fe and Cu molybdates have a positive effect on both yield and selectivity.

$ZnFe_2O_4$ and $BiPO_4$, which are not selective for methacrolein formation when alone, have a highly positive influence on intrinsic methacrolein yield. The interesting point is that the former has a positive effect on selectivity while the latter has almost no effect on it.

It is interesting to note that almost no gain in the intrinsic methacrolein yield was observed when MoO_3 was mixed with oxides containing Mg (MgO and $MgMoO_4$). But these oxides greatly increase methacrolein selectivity.

In summary, the catalytic synergy for intrinsic methacrolein yield varies in the following order: α-$Bi_2O_3 > TeO_2 > Sb(Cu)O > BiPO_4 \cong Fe_2Mo_3O_{12} \cong Cu_2Mo_3O_{10} \cong \alpha$-$Sb_2O_4 > ZnFe_2O_4 > NiMoO_4 \cong CoMoO_4 \cong MgO > MgMoO_4$ and for selectivity: $TeO_2 \cong Sb(Cu)O > \alpha$-$Sb_2O_4 \cong \alpha$-$Bi_2O_3 > ZnFe_2O_4 > Fe_2Mo_3O_{12} \cong MgMoO_4 \cong MgO > Cu_2Mo_3O_{10} > NiMoO_4 \cong CoMoO_4 \cong BiPO_4$.

From the point of view of both methacrolein yield and selectivity, the best catalytic systems in all the mechanical mixtures are MoO_3–α-Bi_2O_3, MoO_3–Sb(Cu)O, MoO_3–TeO_2 and MoO_3–$Cu_2Mo_3O_{10}$.

Discussion

It is striking that there exists a pronounced synergy between MoO_3 and almost all added oxides, either simple or binary.

In general, the catalytic synergy can be explained by one of the following possibilities:

(i) *formation of a new phase* which is more active than either of the starting oxides;

(ii) *contamination* of one phase by a small amount of element coming from the other, creating an active overlayer;

(iii) *classical bifunctional catalysis, i.e.* a mechanism by which an intermediate (semi-reacted product) formed on one phase desorbs from that phase and adsorbs onto the other phase where it is transformed to the final product;

(iv) the presence of *structurally coherent phase boundaries* (epitaxy) between two phases [16–20] and

(v) *the creation and/or regeneration of the catalytic sites* on one phase by the mobile oxygen species emitted by the other (*remote control mechanism*).

A classical bifunctional mechanism must be excluded in the case of allylic oxidation where the allylic intermediate obtained after the first hydrogen abstraction is strongly bound to the surface [21]. Such a classical bifunctional catalytic mechanism has never been contemplated in the case of allylic oxidation. A conceptionally similar mechanism could be that by which a surface migration rather than desorption–adsorption would occur. This possibility has sometimes been mentioned in literature when discussing the role of two distinct sites existing on a given phase. But the surface migration of an allylic species from one phase to another has never been envisaged and such a process seems very unlikely, in view of the size of the allylic radical. A much more likely candidate for surface migration is instead oxygen (a single atom, compared to 11 atoms constituting the isobutene allylic radical); its migration has been proven experimentally [13].

In principle, the remaining possibilities (i), (ii), (iv) and (v) may be contemplated for explaining the results of our experiments. The explanation for the observed synergies may differ from one system to another. Since not all mechanical mixtures studied in this work have been investigated by surface sensitive techniques (XPS, ISS, etc.), much care should be taken in explaining the results. Therefore, in what follows, we shall first discuss the results obtained with some systems for which the physico-chemical characterization has been reported, either by our laboratory or in the literature. We shall see that the most likely explanation is a remote control effect, and that, in these cases, synergy can be logically explained. The case of the other oxides will be discussed afterwards, especially that of TeO_2, which seems to act as an 'intermediate' oxide.

The MoO_3–α-Sb_2O_4 mixture mentioned in the introduction has a behavior which is very typical of two-phase systems. The mechanical mixtures before and after test have been characterized by several physico-chemical techniques such as XRD, AEM, XPS and ISS. No new phase has been observed, no mutual contamination has been detected [6–8]. This is further confirmed by the results obtained with catalysts prepared by impregnation or coprecipitation [8, 15]. In these studies, attempts were made to contaminate the surface of one oxide by the metallic ions of the other (by impregnation) or to form a Mo—Sb—O compound. The characterization showed that the artificial contamination disappeared after catalytic reaction and no Mo—Sb—O compound was formed. This result agreed well with the conclusions obtained by Parmentier *et al.*, namely that Mo—Sb—O compounds (Sb_2MoO_6, $Sb_2(MoO_4)_3$ [22], $Sb_{0.2}MoO_{3.1}$ and $Sb_{0.4}MoO_{3.1}$ [23]) which could be formed under particular conditions, decomposed into MoO_3 and Sb_2O_4 when calcined in air at temperatures of 300–400 °C, similar to our reaction temperatures. All these studies showed that the tendency of the MoO_3–α-Sb_2O_4 system is to form two separate oxides, instead of tending to mutual contamination. In such a case, it seems difficult to imagine a 'structurally coherent phase boundary' (epitaxy) between two phases. A similar conclusion has been reached for the MoO_3–$BiPO_4$ system [24]. The MoO_3–Sb(Cu)O system has also been characterized by XPS [25] and no mutual contamination has been detected. MoO_3 associated with other molybdates such as $NiMoO_4$ and $CoMoO_4$, prepared by coprecipitation or solid state reaction methods, has been characterized using different physicochemical techniques such as laser Raman, XRD, electron microscopy and XPS [26, 27] and only the separate phases, namely MoO_3 + molybdate (Ni or Co), have been observed. The only possible explanation of synergy in the case of all these catalysts is thus the remote control mechanism. MoO_3 possesses the necessary functions for selective oxidation while Sb(Cu)O, $BiPO_4$, $NiMoO_4$ and $CoMoO_4$ (which have little or no activity in methacrolein formation) play the same role as α-Sb_2O_4, *i.e.* that they produce spillover oxygen for improving the catalytic properties of MoO_3.

The $Cu_2Mo_3O_{10}$ we tried to prepare formed two phases after calcination: $CuMoO_4$ and MoO_3. The thermodynamic equilibrium situation for this system indeed corresponds to the formation of a two-phase catalyst. It is thus difficult to imagine that some mutual contamination between MoO_3 and $CuMoO_4$ would take place when MoO_3 is addeded. The same mechanism, namely remote control, is thus the more natural explanation of the phenomena observed with $Cu_2Mo_3O_{10} + MoO_3$.

The characterization of mixtures of MoO_3 with other molybdates (Fe and Mg) has not been carried out; it is thus impossible to reject *a priori* the existence of a mutual contamination. However, one could incline toward a mechanism where cooperation between phases, rather than contamination, would explain synergy. Iron molybdates have been extensively used in methanol oxidation, and it has been found that a good catalyst also corresponds to a two-phase system: $Fe_2(MoO_4)_3$ and MoO_3 [28]. These two phases also exist in our catalysts.

Bearing in mind these results and remarks, there is a ready explanation of the results obtained with the mixtures of MoO_3 and various molybdates. This is the existence of a remote control and indeed it is possible to arrive at a self-consistent picture of the processes involved.

The A phase (MoO_3) is common to all systems in our case, the magnitude of the catalytic synergy should directly depend on the ability of D to produce spillover oxygen. It is logical to suppose that a donor phase should be partially ionic in order to dissociate molecular oxygen (oxides with a weak ionic character, such as MoO_3, slowly form surface oxygen species, compared to α-Bi_2O_3, as shown in surface potential measurements [29] and the inability to carry out the reverse reaction, namely $2O^{2-} \rightarrow O_2$ [30]). On the other hand, much too ionic compounds would bring about the formation of electrophilic oxygen (O_2^- or O^-) in addition to O^{2-} and a corresponding loss of selectivity. Now let us look at the D phases (molybdates) in this perspective. All D phases in our case contain Mo^{6+}, the only difference is the cation. Taking account of the above results, it is logical to consider that it is the other metal cation that dissociates oxygen. Based on the study of oxygen adsorption on many complex oxides [31–32], it has been concluded that the ability of an oxide to generate oxygen ions decreases when the ionization potential of the cation at the surface increases [33]. According to the ionization potentials [34] of the cations associated with Mo in the considered binary oxides [Co^{2+} (33.5) < Ni^{2+} (35.2) < Cu^{2+} (36.8) < Fe^{3+} (54.8) ≪ Mg^{2+}(80.1)], their abilities to generate molecular oxygen to oxygen ions should vary in the following way:

$$CoMoO_4 > NiMoO_4 > Cu_2Mo_3O_{10} > Fe_2Mo_3O_{12} \gg MgMoO_4$$

but the proportion of nucleophilic oxygen (O^{2-}) should follow an inverse trend. If this is true, the synergistic effect on selectivity (ΔS) should increase from $CoMoO_4$ to $MgMoO_4$. This corresponds to the general trend in the experimental results. According to our explanation, the fact that ΔS of $CoMoO_4$ and $NiMoO_4$ is almost zero is due to the low proportion of nucleophilic and large production of electrophilic oxygen (O^-) by these oxides. The fact that no catalytic synergy for intrinsic methacrolein yield ($\Delta y \approx 0$) is observed with $MgMoO_4$ can be explained by the fact that the ionic properties of $MgMoO_4$ are so weak that very little spillover oxygen is available. If we take into account the two parameters which control a synergetic effect, *i.e.* quantity and quality of spillover oxygen, a good donor should be a 'moderately ionic' phase, such as $Cu_2Mo_3O_{10}$ and $Fe_2Mo_3O_{12}$, in conformity with observations.

Let us compare α-Sb_2O_4 and Sb(Cu)O. Although both oxides have the same α-Sb_2O_4 structure, Sb(Cu)O brings about a catalytic synergy (Δy) two times greater than pure α-Sb_2O_4. The first reason for this observation is that Sb(Cu)O has a surface area larger than α-Sb_2O_4. This increases the spillover oxygen-generating area and the number of contacts with MoO_3 and, consequently, the intensity of the oxygen flow on the surface of MoO_3 and, hence, the catalytic synergy. The second factor might be that the introduction of Cu into α-Sb_2O_4 modifies slightly (decreases) the Sb—O bond strength or increase its ionicity and favours the production of spillover oxygen.

Two oxides, namely α-Bi_2O_3 and $ZnFe_2O_4$, have been proposed as the active phases for the α-hydrogen abstraction from hydrocarbons in selective oxidation [33, 35]. In the MoO_3–α-Bi_2O_3 system, the formation of a new phase (a bismuth molybdate), in small amounts, or surface contamination of MoO_3 by α-Bi_2O_3, as proposed in the literature [36], could explain the effect, although XRD measurements did not detect this. However, taking into account the fact that both α-Bi_2O_3 and $ZnFe_2O_4$ are believed to have mobile oxygen on their surface [37, 38] and that the addition of these two oxides greatly enhances selectivity, we think that they may play roles similar to that of α-Sb_2O_4, namely of donors.

The MoO_3–TeO_2 system seems more difficult to explain because the binary compounds, Te—Mo—O, have been proposed as the active phase in literature [39], although our XRD measurements did not detect any of these phases. Without further reasoning, it could be advanced that because the presence of TeO_2 improved the selectivity, TeO_2 plays a role of donor. But the fact that pure TeO_2 is active and selective indicates that it possesses, on its

TABLE 3

Catalytic activity and selectivity for mechanical mixture TeO_2–α-Sb_2O_4

Temp (°C)	Intrinsic yield (%)	Selectivity (%)	Δy^a (%)	ΔS^a (%)
380	3.25	90.00	1.59	10.33
400	5.15	92.57	2.51	7.30

[a] Δy and ΔS are calculated with eqns. (5) and (6)

own, catalytic sites. This strongly suggests that TeO_2 may also play a role similar to that of MoO_3 (essentailly as an acceptor A). If this is the case, a catalytic synergy should be observed, especially in selectivity, when it is mixed with an excellent donor D, *e.g.* α-Sb_2O_4. This is demonstrated by the results presented in Table 3. It can thus be concluded that TeO_2 constitutes an 'intermediate' oxide, as a donor when mixed with a strong acceptor such as MoO_3, or an acceptor when mixed with a strong donor such as α-Sb_2O_4.

Conclusions

Several conclusions can be drawn from the present work:

(1) A conspicuous synergy exists between MoO_3 and other added oxides, either simple or binary, in the form of a mechanical mixture.

(2) The effects observed for most of the systems can be explained by a remote control mechanism. The best donor phases are: Sb(Cu)O, α-Sb_2O_4 and iron and copper molybdates.

(3) TeO_2 is very likely an intermediate oxide, either an acceptor when mixed with a strong donor, or a donor when mixed with a strong acceptor.

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