Catalytic behaviour of multiphasic oxide catalysts containing lanthanides (La, Ce, Pr, Sm, Tb) in the selective oxidation of isobutene to methacrolein

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The catalytic performances of five lanthanide oxides (La_2O_3, Sm_2O_3, CeO_2, Pr_6O_{11} and Tb_4O_7) for the selective oxidation of isobutene to methacrolein are evaluated within the framework of the remote control mechanism. Mechanical mixtures of these oxides with typical donor (Sb_2O_4) or acceptor (MoO_3) phases of spill-over oxygen were prepared and tested for their activity in the isobutene-to-methacrolein oxidation at 400°C. Amongst the five lanthanide oxides tested, only CeO_2 and Pr_6O_{11} were found to display significant cooperation effects for the investigated reaction, with enhanced yields and selectivity for partial oxidation and concomitant decrease of CO_2 production. The fresh and used catalysts were characterized by X-ray diffractometry, and the occurrence of solid state reactions between the partner oxides outside the reaction conditions was investigated in parallel in the temperature range 400–500°C. No new phase was observed in the case of the mixtures with La_2O_3, Sm_2O_3, CeO_2 and Tb_4O_7. Account taken of the absence of any new phase in the CeO_2–MoO_3 system, it can be concluded that CeO_2 is a potential donor of spill-over oxygen. The situation in the MoO_3–Pr_6O_{11} mixtures is more complex, owing to the generation of various praseodymium molybdates, together with the oxocarbonate Pr_2CO_5. The latter phase was shown to have no intrinsic tendency to produce methacrolein, but it seems that some of the praseodymium molybdates present in the working catalysts may exhibit noticeable catalytic properties.

Keywords: lanthanide oxides; selective oxidation; methacrolein; remote control

1. Introduction

Although the catalytic potential of lanthanides in oxidation catalysis seems to concern mainly total oxidation processes, experimental results suggest they could play an essential role in controlling selective oxidation [1–4]. However, pertinent information on the real role played by lanthanides in multiphasic oxidation catalysts is still rather scarce.

During the last few years, the catalytic performances of multiphasic oxide-based catalysts were analyzed within the framework of the "remote control" theory, based on the migration of active oxygen species ("spill-over" oxygen) from a donor to an acceptor phase. The keypoint of this mechanism is that cooperation occurs between two oxide phases, the one, the acceptor, being the catalytically active phase for the oxidation reaction, while the other one, the donor, which shows no intrinsic catalytic behaviour, governs the efficiency of the first one by creating and/or regenerating selective active sites on its surface. This mechanistic model has been successful in accounting for the synergetic effects observed on the yield and selectivity of a wide range of multiphasic oxidation catalysts [5,6]. To help to understand the overall behaviour of lanthanide elements in oxidation catalysis, it seemed therefore interesting to carry out a first approach by looking whether their oxides give rise to cooperation effects in the selective oxidation of isobutene to methacrolein, that could be rationalized within the above mentioned model.

Five different lanthanide oxides were selected in the present work: La_2O_3, Sm_2O_3, Pr_6O_{11}, Tb_4O_7 and CeO_2. Non-stoichiometry is a common property of the last three compounds. To evaluate the acceptor or donor role of these oxides, a systematic approach, based on the three following steps was adopted: (1) preparation of mechanical mixtures of various compositions between the oxides Ln_xO_y and either MoO_3 (typical acceptor of spill-over oxygen) or Sb_2O_4 (typical donor), prepared separately; (2) measurement of the catalytic performances in the partial oxidation of isobutene to methacrolein at 673 K; (3) bulk and surface characterization of fresh and used catalysts.

2. Experimental

Cerium(IV) oxide, CeO_2, praseodymium(III, IV) oxide, Pr_6O_{11}, and samarium(III) oxide, Sm_2O_3 were purchased from Janssen Chimica (purity: 99.9%).

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Lanthanum(III) oxide, La_2O_3 (99.99%) and terbium(III, IV) oxide, Tb_4O_7 (99.9%) were supplied by Aldrich. MoO_3 was obtained by calcination of a citrate-type precursor [7] at 673 K for 20 h. α-Sb_2O_4 was prepared by calcination of Sb_2O_3 in air at 773 K for 20 h.

The mechanical mixtures were obtained by dispersing the adequate amount of the concerned oxides under ultrasonic stirring in 100 ml distilled *n*-heptane, during 15 min, and removal of the hydrocarbon under vacuum at room temperature up to dryness. This procedure was selected in order to minimize, as far as possible, any damage to the crystallites during the mixing procedure, as would actually be expected to occur more easily upon dry grinding in a mortar, and was also shown to provide better homogeneity than the latter. In addition, the preparation was carried out under a dry nitrogen atmosphere to protect the oxides against hydrolysis and carbonation. The catalysts were stored under inert atmosphere and used in the catalytic tests without any further treatment.

Powder X-ray diffraction spectra were measured on a Siemens 500 diffractometer equipped with a copper anode. The BET specific surface areas of the powders were measured with a Micromeritics ASAP 2000 analyser, using krypton at 77 K.

Selective oxidation of isobutene to methacrolein was carried out in a fixed-bed U-shaped reactor system working under atmospheric pressure. The experiments were conducted with 600 mg catalyst (particle size 500–800 mm) under the following reaction conditions: molar composition of the reactant mixture i-$C_4H_8/O_2/N_2$: 8.3/19.3/72.4; total flow rate: 30 ml/min., $T = 673$ K. Gaseous reactants and products were analyzed with a Di200 gas chromatograph from DELSI Instruments.

Table 1
Catalytic results

1 Catalyst	2 x_m [a]	3 S_{BET} [b] ($m^2\,g^{-1}$)	4 X_{ISO}/S_{BET} ($\%\,g\,m^{-2}$)	5 Y_{meth}/S_{BET} ($\%\,g\,m^{-2}$)	6 S_{meth} (%)	7 $(Y_{CO_2}/4)/S_{BET}$ ($\%\,g\,m^{-2}$)	8 $(\Delta Y_{AB})_{meth}$ [c] (%)	9 $(\Delta Y_{AB})_{CO_2}$ [c] (%)
MoO_3	–	1.5	13.8	4.5	33.3	3.7	–	–
Sb_2O_4	–	0.7	5.3	1.6	29.1	0	–	–
Pr_6O_{11}	–	6.2	3.7	0.1	3.5	1.8	–	–
MoO_3/Pr_6O_{11}	0.25	2.0	9.3	2.2	23.9	2.8	11	10
MoO_3/Pr_6O_{11}	0.50	3.6	5.1	1.4	26.9	1.4	41	–36
MoO_3/Pr_6O_{11}	0.75	3.2	4.1	1.2	30.1	1.3	166	–30
MoO_3/Pr_6O_{11}	0.83	3.0	3.9	1.2	30.4	1.1	256	–40
MoO_3/Pr_6O_{11}	0.89	3.6	3.9	0.7	17.9	1.3	170	–28
Sb_2O_4/Pr_6O_{11}	0.25	0.7	3.6	1.3	36.4	0	160	–100
Sb_2O_4/Pr_6O_{11}	0.50	1.3	4.0	0.8	21.8	0	207	–100
Sb_2O_4/Pr_6O_{11}	0.75	2.6	7.2	0.3	4.9	3.2	91	88
Sm_2O_3	–	1.6	4.3	0.3	7.4	1.3	–	–
MoO_3/Sm_2O_3	0.50	2.0	9.1	2.3	25.6	2.7	ca 0	–15
Sb_2O_4/Sm_2O_3	0.50	1.1	5.9	0.9	15.0	0	ca 0	–100
La_2O_3	–	0.6	6.1	0.9	15.1	0	–	–
MoO_3/La_2O_3	0.50	0.9	12.3	4.3	35.0	2.5	20	ca 0
Sb_2O_4/La_2O_3	0.50	0.6	8.3	1.5	18.6	0.5	ca 0	ca 0
CeO_2	–	2.4	9.0	0.3	3.3	5.2	–	–
MoO_3/CeO_2	0.25	1.2	18.7	6.7	35.9	4.7	116	0
MoO_3/CeO_2	0.50	1.4	14.3	3.8	27.2	4.3	95	–19
MoO_3/CeO_2	0.75	1.4	16.1	4.8	30.0	5.0	345	–17
Sb_2O_4/CeO_2	0.25	0.5	10.6	2.8	26.1	0	200	–100
Sb_2O_4/CeO_2	0.50	0.9	1.1	1.1	–	0	72	–100
Sb_2O_4/CeO_2	0.75	1.2	6.2	1.4	23.3	0.7	195	–87
Tb_4O_7	–	0.2	4.6	0.7	15.7	1.1	–	–
MoO_3/Tb_4O_7	0.50	0.7	19.4	6.6	33.9	6.3	47	60
Sb_2O_4/Tb_4O_7	0.50	0.3	18.0	3.7	19.8	0	74	–100
$Pr_2O_2CO_3$	–	5.6	5.0	0.2	3.3	2.5	–	–
$Pr_2Mo_3O_{12}$	–	0.6	2.3	2.3	100	0	–	–
Pr_2MoO_6	–	6.2	1.2	0.3	21.8	0.2	–	–
Pr_6MoO_{12}	–	13.1	2.2	0.1	3.2	1.1	–	–

[a] Weight ratio of the lanthanide oxide in the mixture.
[b] Experimental specific surface area of the AB mixture.
[c] Synergy on methacrolein or CO_2 yield as defined by eq. (3).

Successive measurements performed during 2 h at constant temperature indicated that the catalytic performances remained unchanged over that period of time.

3. Results and discussion

The catalytic performances of the various mixtures and the corresponding pure oxides are listed in table 1, together with their mass composition (expressed as x_m with respect to the lanthanide oxide) and experimental surface areas. These areas were measured after submitting all the samples to the standard ultrasonic stirring described above. The conversion and yield values reported in table 1 were normalized with respect to the corresponding surface areas. Synergetic effects were investigated for the four following parameters: isobutene conversion rates (X_{iso}), methacrolein yield (Y_{meth}) and selectivity (S_{meth}), and CO_2 yield (expressed as: $Y_{CO_2}/4$ to allow a direct comparison with isobutene conversion). Apart from methacrolein and CO_2, the main side products were found to be CO and formaldehyde. The extent of coke formation on the catalysts was determined by elemental analysis and was shown to be negligible (yield in carbon less than 2%).

Except in two cases (Pr, Tb), the differences between the specific surface areas of the pure lanthanide oxides involved in the mixture and those of Sb_2O_4 or MoO_3 are not very important. Nevertheless, to check whether the increase of catalytic performances in the mechanical mixtures might be assigned to a real cooperation effect or merely reflects the enhancement of the global specific surface area of the mixture, we calculated the intrinsic yield, i.e. the yield normalized for a standard specific surface area of 1 m^2/g. The synergy will then be evaluated from the difference between the real intrinsic yield of the mixture Y^*_{AB}, and the theoretical intrinsic yield, $(Y^*_{AB})_{th}$, i.e. the one that would be obtained in the absence of any cooperation, assuming zero-order reactions as a first approximation. These parameters are defined in the following way:

(1) Theoretical intrinsic yield of AB mixture, $(Y^*_{AB})_{th}$:

$$(Y^*_{AB})_{th} = [Y_A x_A + Y_B x_B]/[(S_{BET})_A x_A + (S_{BET})_B x_B]\,, \tag{1}$$

where $(S_{BET})_i$ is the experimental specific surface area of compound i, x_i is the weight ratio of component i in the mixture AB.

(2) Real intrinsic yield of AB mixture, Y^*_{AB}:

$$Y^*_{AB} = [Y_{AB}]/[(S_{BET})_{AB}]\,, \tag{2}$$

where $(S_{BET})_{AB}$ is the experimental specific surface area of the mixture AB, Y_{AB} is the experimental yield of the mixture AB.

(3) Synergy on yield for the AB mixture, ΔY_{AB}:

$$\Delta Y_{AB} = [Y^*_{AB} - (Y^*_{AB})_{th}]/[(Y^*_{AB})_{th}]\,. \tag{3}$$

These values are given in the last two columns of table 1, for methacrolein and CO_2, respectively.

As shown in columns 4, 5 and 7 of table 1, CeO_2 and Pr_6O_{11} are the most active oxides and produce mainly CO_2. All five lanthanides generate very little methacrolein under the present reaction conditions.

When mixed with MoO_3, the oxides La_2O_3 and Sm_2O_3 exhibit no synergetic effect, whereas Tb_4O_7 gives rise to enhanced yields of both partial and total oxidation. Most mixtures with Sb_2O_4 result in a negative synergy on CO_2 production. In particular, total oxidation is totally inhibited in the 1/1 mixtures with Sm_2O_3, Tb_4O_7, and in the Sb-rich mixtures with CeO_2 or Pr_6O_{11}. Because the cooperation effects were more pronounced when cerium or praseodymium oxides were involved, the behaviour of these mixtures was investigated in a deeper way.

In the Pr_6O_{11}–MoO_3 mixtures, the addition of increasing amounts of Pr_6O_{11} causes the conversion rate of isobutene to decrease with an apparent minimum close to the composition corresponding to $x_m = 0.83$. Along the same series, synergetic effects appear essentially on the methacrolein yield, which reaches a maximum at the same composition as above. As shown in table 1, these conclusions remain valid when considering the intrinsic yields, confirming that the observed effects cannot be assigned to changes in the specific surface area. In most cases, when positive synergetic effects are noted on the yield in the partial oxidation product, a simultaneous decrease of total oxidation is observed.

In the CeO_2–MoO_3 mixtures, positive synergetic effects on methacrolein production are observed and appear to increase when the CeO_2/MoO_3 ratio is high. They are accompanied by a significant decrease in CO_2 production.

In Sb_2O_4-rich mixtures with Pr_6O_{11}, overall isobutene conversion is decreased and CO_2 production is completely inhibited, resulting in a pronounced positive synergy on the selectivity for methacrolein. Similar observations were made in the CeO_2–Sb_2O_4 mixtures, the most important synergetic effects on methacrolein selectivity appearing on both sides of the composition range. In comparison with the effects noted in the mixtures with MoO_3, these variations were however found to be less pronounced.

To understand the cause of the synergetic effects observed with Pr_6O_{11} and CeO_2, independent investigations were carried out in parallel. The key question was whether these effects could be explained by the occurrence of solid state reactions between the concerned oxides in the temperature range 673–773 K. Whereas XRD gave no indication of any new phase in the samples heated at 673 K, whatever the nature of the lanthanide be, ternary Pr–Mo–O compounds were found to appear at 773 K in the Pr_6O_{11}–MoO_3 mixtures. In a previous work [8], we reported the formation of $Pr_2Mo_3O_{12}$ from the thermal degradation of praseodymium formate on MoO_3 at 823 K. Because the reaction conditions could change the reactivity of these oxides and generate new phases during the catalytic tests, XRD measurements were performed also on the used catalysts for the two systems (MoO_3/Pr_6O_{11} and MoO_3/CeO_2) for which clear cooperation effects were observed. In the Pr case, various praseodymium molybdate and oxocarbonate phases ($Pr_2Mo_3O_{12}$, Pr_6MoO_{12}, Pr_2MoO_6, $Pr_2O_2CO_3$) appear after catalytic tests. In the Ce case, the absence of any ternary phase in the catalysts is in line with the fact that, according to the literature, much higher temperatures are required to generate cerium molybdates [9]. Occasionally, partial reduction of MoO_3 and Sb_2O_4 into MoO_2 and Sb_2O_3 was observed.

Account taken of the results obtained in the Pr case, additional experiments were necessary. The formation of oxocarbonates is obviously due to partial trapping of CO_2 generated during the reaction in the Pr-based catalysts. Two different praseodymium oxocarbonates $Pr_2O_2CO_3$ and $Pr_2O(CO_3)_2$ are mentioned in the literature as produced by the thermal decomposition of Pr carbonates and hydroxocarbonates [10–13] or carboxylates [8,14,15]. These phases are also reported to form upon carbonatation of praseodymium oxides or hydroxides [10,11]. In the course of a recent and well documented investigation by Hussein [13], $Pr_2O_2CO_3$, which is undoubtedly the major phase in this system, was shown to appear as intermediate product during the thermolysis of Pr oxalate at 718 K and to be converted into Pr_6O_{11} when heated further under O_2 at 823 K. Formation of $Pr_2O_2CO_3$ at still lower temperatures (673–723 K) was observed during the thermal degradation of Pr acetate [14]. Poisoning effects related to the generation of surface oxocarbonate species in lanthanum oxide catalysts were reported in the conversion of propanal to pentan-3-one and were found to be more extensive with La than with Pr [15]. In some particular cases, the presence of oxocarbonate in lanthanide-based catalysts was thought to exert a positive influence on the catalytic performances, like the improvement of C_{2+} selectivity in the La_2O_3-catalyzed oxidative coupling of methane [16]. Because the stability of lanthanum oxocarbonate under the reaction conditions was questionable, its generation by surface processes has been investigated carefully with spectroscopic techniques [17]. More recent in situ XRD investigations of working catalysts concluded, however, to the absence of a simple relationship between the amount of bulk lanthanum oxocarbonates and the selectivity to C_2 products during the oxidative coupling of methane [18]. To explore the possible influence of the similar praseodymium oxocarbonate phase on the catalytic properties of our samples, we prepared $Pr_2O_2CO_3$ in a pure form by carbonatation of Pr_6O_{11} under CO_2 at 873 K during 16 days. After checking its purity by X-ray diffractometry, this sample was engaged into our standard catalytic tests. When used alone, this phase was shown to produce mainly CO_2, but without substantial decarbonatation, and very little methacrolein formation. Although more experiments would be necessary to draw a definitive conclusion, it seems that the occurrence of this phase in our catalysts plays no significant role in the observed enhancement of partial oxidation. However, its presence has to be taken into account when calculating the mass balance during the reaction.

The same is not true for the various Pr molybdate phases. Independent investigations were therefore undertaken with the pure $Pr_xMo_yO_z$ phases and their catalytic performances are reported in table 1. If the performances are normalized with respect to the respective surface areas of these phases, it appears that Pr_2MoO_6 exhibits no significant activity, while the $Pr_2Mo_3O_{12}$ and the Pr_6MoO_{12} phases are fairly active for partial or total oxidation, respectively.

Finally, a last comment should be made on the observation of synergetic effects in the mixtures between Pr_6O_{11} or CeO_2 and Sb_2O_4, which is a typical oxygen donor. These results suggest that the behaviour of these lanthanide oxides could be similar to that of tin(IV) oxide or some bismuth molybdates, which exhibit a dual role in the sense that they behave as oxygen donor or acceptor. These oxides were actually found to play the role of either oxygen donor, when put in presence of an acceptor, or oxygen acceptor, when mixed with a donor, according to a donor–acceptor scale of spill-over oxygen described by Weng et al. [5].

4. Conclusions

Amongst the five lanthanide oxides studied (La_2O_3, Sm_2O_3, CeO_2, Pr_6O_{11}, Tb_4O_7) in mixtures with Sb_2O_4 or MoO_3 oxides, CeO_2 and Pr_6O_{11} are found to give rise to the more pronounced cooperation effects. At the present stage, care should be exercised in attempting to rationalize these results within the framework of the remote control theory. The behaviour of cerium oxide may be interpreted rather easily because cooperation effects occur without apparent formation of new phases during catalytic tests. CeO_2 is therefore a potential donor phase of spill-over oxygen. In the case of praseodymium oxide, the situation is more complex owing to the appearance of praseodymium molybdate phases under the reaction conditions. Work is presently under progress to evaluate the stability and investigate more thoroughly the catalytic properties of the various $Pr_xMo_yO_z$ phases for the selected reaction within the frame of the remote control theory. In addition, the results obtained in the combinations with Sb_2O_4 suggest that some cerium or praseodymium oxides might possess simultaneously some acceptor properties, which need to be examined further.

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