ELSEVIER

Catalysis Today 32 (1996) 329–336

CATALYSIS TODAY

Impact of surface mobility in selective oxidation. Isotopic exchange of $^{18}O_2$ with $^{16}O_2$ on various oxides: MoO_3, SnO_2 and Sb_2O_4. Effect of a reducer gas

D. Martin [a,1], P. Kaur [a], D. Duprez [a], E. Gaigneaux [b,2], P. Ruiz [b], B. Delmon [b]

[a] *Laboratoire de Catalyse en Chimie Organique, URA-CNRS-350, Université de Poitiers, 40 Avenue du Recteur Pineau, 86022 Poitiers Cedex, France*

[b] *Unité de Catalyse et Chimie des Matériaux Divisés, Université Catholique de Louvain, Place Croix du Sud 1, 1348 Louvain-la-Neuve, Belgium*

Abstract

Isotopic oxygen exchange experiments were carried out on simple oxides (Sb_2O_4, MoO_3 and SnO_2) and mechanical mixtures of MoO_3 or SnO_2 (acceptor phase) with Rh/Al_2O_3 or Sb_2O_4 (donor phase). With Rh/Al_2O_3 a synergy effect is found: the amount of oxygen exchanged on the mixture is higher than the sum of oxygen exchanged on the two separate phases. This is a prove of oxygen mobility between donor and acceptor phases. With Sb_2O_4 this effect is less marked suggesting that the presence of a reducer gas is required. In presence of hydrocarbon, no isotopic exchange is observed: only total oxidation occurs. The presence of Sb_2O_4 decreases the rate of total oxidation by blocking, by oxygen spillover, the most active sites for oxidation.

Keywords: Remote control; Selective oxidation catalysts; Isotopic oxygen exchange

1. Introduction

Catalytic selective oxidations (CSO) are major processes in petrochemistry, for the production of alcohols, ketones, aldehydes and carboxylic acids used in the chemical industry [1]. The catalysts are multifunctional oxides. To explain the synergy effect between two (or more) oxide phases that is generally observed with these catalysts, Delmon and co-workers [2–8] have proposed a remote control effect based on the following assumptions:

(i) the catalyst is composed of two phases, an acceptor phase (A) and a donor phase (D) having well-defined coupled functions.

(ii) the acceptor phase is the center for hydrocarbon activation and can have, when alone, a low activity in CSO.

(iii) the donor phase generally has no CSO activity. Its role is to produce activated oxygen (O_{sp}) which spills over to the donor phase, accelerates the catalytic cycle and maintains it at a high rate.The existence of this oxygen spillover (O_{sp}) has been proved on the Sb_2O_4 +

---

[1] FAX: (33) 45 49 34 99.

[2] FAX: (32) 10 47 36 49.

PII S0920-5861(96)00092-2

MoO_3 catalysts, where Sb_2O_4 is the donor phase and MoO_3 is the acceptor phase. The first study carried out on this catalyst showed that ^{18}O could be incorporated into acrolein when using mechanical mixtures of $Sb_2^{18}O^{16}O_3 + Mo^{16}O_3$ for propene oxidation [9]. In a recent study based on Raman spectroscopy experiments [10], it was proved that MoO_3 can slowly exchange with $^{18}O_2$ at moderate temperatures when mixed with Sb_2O_4 while MoO_3 alone cannot exchange [11].

During the remote control process, the flux of O_{sp} from the donor phase D to the acceptor phase A is thought to be lower than the turnover frequency of the reaction: a large part of the gaseous oxygen (referred to as O_d) can be directly incorporated in the catalytic cycle. A mechanical equivalent of this chemical system is a wheel maintained at a high speed of rotation by small regular impulses. Actually the exact role of O_{sp} on the catalytic cycle or on the active site of phase A is not yet known and this point deserves in-depth studies, presently in progress. The aim of this work is to measure by means of oxygen isotopic exchange, the flux of O_{sp} species from D phases to A phases.

The exchange of ^{18}O with ^{16}O has been studied for many years and a number of reviews dealt with the early works [12–15]. Isotopic exchange reactions allow us to obtain an insight into the mechanisms of oxidation reactions, the nature of oxygen bonds and oxygen mobility at the catalyst surface. The exchange reaction may be studied by mass spectrometry where masses 32 ($^{16}O_2$), 34 ($^{16}O^{18}O$) and 36 ($^{18}O_2$) are monitored throughout the reaction. There are two types of isotopic exchange:

(i) The first one, named 'homophase equilibration,' is an exchange between adsorbed atoms without a participation of the oxygen atoms of the solid [Eq. (1)]. This is the R mechanism of Boreskov and Novakova [14,15]:

$$^{16}O_{2(g)} + {}^{18}O_{2(g)} \rightarrow 2\,{}^{16}O^{18}O_{(g)} \qquad (1)$$

The only role of the solid is to catalyse the dissociation of adsorbed oxygen species. The concentration of isotopic oxygen in each phase, gas and solid, does not change during the reaction.

(ii) The second one, named 'heterophase exchange,' concerns the exchange of gas phase $^{18}O_2$ with ^{16}O of the solid oxide and may be sub-divided into two groups according to the mechanism:

* Monomolecular or Simple Exchange: (mechanism R′ in [14,15]) one oxygen atom of the gas phase is exchanged with one atom of the solid surface [Eq. (2)]:

$$^{18}O_{2(g)} + {}^{16}O_{(s)} \rightarrow {}^{18}O^{16}O_{(g)} + {}^{18}O_{(s)} \qquad (2)$$

* Bimolecular or Multiple Exchange: (mechanism R″ in [14,15]) both oxygen atoms of the molecule of dioxygen are exchanged at once with two oxygen atoms of the solid surface [Eq. (3)]:

$$^{18}O_{2(g)} + {}^{16}O..{}^{16}O_{(s)} \rightarrow {}^{16}O_{2(g)} + {}^{18}O..{}^{18}O_{(s)} \qquad (3)$$

Both mechanisms involve three principal steps which are: dissociative adsorption of molecular oxygen, exchange of the adsorbed atoms or ions with ions from the oxide and associative desorption of molecular oxygen.

The research strategy is based upon the measurement of $^{18}O_{2(g)}/{}^{16}O_{(s)}$ isotopic exchange on D and A oxides. Two donor type oxides (Sb_2O_4, Rh/Al_2O_3) and two acceptor type oxides (MoO_3, SnO_2) were used. Although it is not a selective oxidation catalyst, Rh/Al_2O_3 was investigated because it is one of the most powerful oxygen donor [16,17]. It allows us to study the behavior of acceptor phases (MoO_3, SnO_2) in the presence of spillover oxygen. The first part of this paper is devoted to in-depth studies of $^{18}O_{2\ (g)}/{}^{16}O_{\ (s)}$ exchange of the individual oxides. The second part of this paper will deal with oxygen exchange on D + A mechanical mixtures. Amounts of spiltover oxygen (O_{sp})will be deduced from the excess of oxygen exchanged in the mixtures. In the third part of this paper we will examine the effect of a reducer gas (methane and propene) onto oxygen isotopic exchange with simple oxides and then with D + A mechanical mixtures.

2. Experimental

2.1. Materials

Studies have been carried out on three oxides MoO_3, SnO_2, Sb_2O_4, and a supported metal catalyst Rh/Al_2O_3. The oxides were prepared by sol–gel method (MoO_3), precipitation (SnO_2) and calcination (Sb_2O_4) [18,19]. They were calcined at 800°C for 4 h except MoO_3 (600°C for 4 h). The 0.05 wt% Rh/Al_2O_3 metal catalyst was prepared by impregnation of α-Al_2O_3 (Rhône Poulenc SCS 9) with the required volume of an aqueous Rh nitrate solution. The sample was dried at 120°C and calcined at 450°C for 4 in air. Single point BET measurements were carried out on both fresh and calcined samples.

2.2. Isotopic exchange experiments

Isotopic exchange experiments were carried out in a recycle reactor coupled to a mass spectrometer described elsewhere [20]. Precalcined samples (0.5 g) were oxidised in-situ at 450°C for 15 min, they were then outgassed at 450°C for 15 min. Pure $^{18}O_2$ (100 or 50 mbar for heterophase exchange) or an equimolecular mixture of $^{18}O_2 + {}^{16}O_2$ (50 mbar of each for homophase equilibration) was then introduced to the recycle system and the partial pressures P_{32} ($^{16}O_2$), P_{34} ($^{16}O^{18}O$) and P_{36} ($^{18}O_2$) were monitored by mass spectrometry throughout the reaction.

Two kinds of isotopic heteroexchange experiments ($^{18}O_{2(g)}/{}^{16}O_{(s)}$) were done: (i) temperature programmed exchanges (TPE) conducted on simple oxide phases between 25 and 800°C (except for MoO_3: 600°C) at a rate of 2°C/min, (ii) isothermal exchanges (IE) carried out at 500°C onto simple oxides and D + A mechanical mixtures. Homoexchange experiments ($^{18}O_{2(g)}/{}^{16}O_{2(g)}$) were carried out at 500°C. The whole calculations that allow us to determine the rates of exchange and the numbers of oxygen species exchanged during TPE and IE experiments are described in a previous work [20].

To study the possible effect of a reducer on the rate of exchange, a 1:1 mixture of $^{18}O_2$ and hydrocarbon was introduced on the sample at 500°C. The hydrocarbon conversion was followed by mass 16 for methane and mass 41 for propene.

3. Results and discussions

3.1. Surface area measurements

Surface areas are given in Table 1. MoO_3 sample was found to be unstable above 600°C. Sublimation occurs at 800°C in flowing air, and crystals were found on the wall of the reactor at the outlet in accordance to previous works [21,22]. SnO_2 was found to be stable keeping a BET area of 5 $m^2\ g^{-1}$ even at 800°C. No change in the total surface area was observed with Sb_2O_4 before and after calcination. However the initial area of this sample was very low.

3.2. Isotopic oxygen exchange on simple oxides

Fig. 1 gives isotopic exchange profiles (TPE) for each simple oxide, where the partial pressures P_{32} ($^{16}O_2$), and P_{34} ($^{16}O^{18}O$) are plotted

Table 1
Oxides surface area versus calcination temperature

Samples	BET area ($m^2\ g^{-1}$) vs. T_{calc}.			
	Fresh	600°C	700°C	800°C
MoO_3	1.6	1.0	0.5 [a]	
Sb_2O_4	0.7		0.7	0.7
SnO_2	5.1		5.0	5.0
α-Al_2O_3	7.6			7.6
Rh/Al_2O_3	7.6			7.6

[a] Sample calcined in static air.

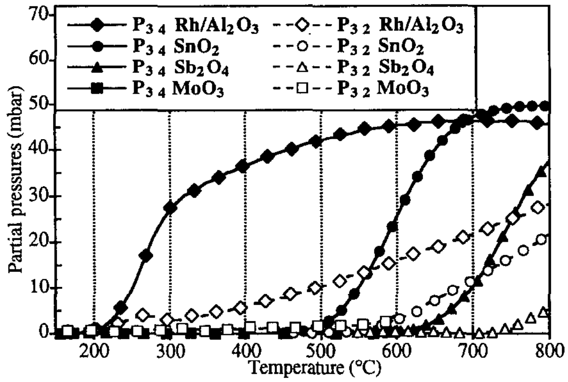

Fig. 1. Temperature programmed exchange on simple oxide phases.

against temperature. From these data, the temperature range of oxygen exchange for each oxide and the mechanisms involved could be deduced from the evolution of the partial pressure of each product ($^{16}O_2$ and $^{16}O^{18}O$).

3.2.1. MoO_3

Isotopic exchange experiments were conducted between 25 and 600°C only on MoO_3 because of the instability of the sample at higher temperatures. No significant isotopic exchange was observed between 25 and 600°C (see Fig. 1), even after reduction at 500°C. The sample was then left at 600°C for approximately 1 h to see if an exchange process occurs, indeed a very slow exchange was observed. An isothermal study conducted at 600°C over MoO_3 degassed at 25°C, confirmed that exchange occurs on this sample, however in this experiment a slow increase of mass 34 was observed. This increase shows that oxygen exchange onto MoO_3 follows a very slow R′ mechanism. On the other hand, MoO_3 was shown to catalyse the homophase equilibration at 600°C. MoO_3 is thus capable of dissociating gaseous oxygen at a significant rate but O_{ads} cannot easily exchange with oxygen atoms of MoO_3.

3.2.2. Sb_2O_4

TPE experiments conducted between 25 and 800°C show that isotopic exchange is incomplete within this temperature range (Fig. 1). $^{18}O^{16}O$ appears at 640°C attesting that oxygen exchange proceeds by R′ mechanism on Sb_2O_4 (650–800°C) .

3.2.3. SnO_2

This sample was found to be the most active oxide studied. Exchange occurs between mass 36 and 34 with some contribution of mass 32 at higher temperatures (Fig. 1). An exchange temperature of 450–520°C has been reported by Winter [13]. Indeed we observed that isotopic exchange starts at 450°C with the appearance of mass 34, indicative of an R′ mechanism and above 550°C (Fig. 1) the increase of mass 32 is indicative of an R″ mechanism as previously observed [23]. An isothermal study conducted at 500°C over SnO_2 allows us to measure the slope of mass 34 (see Table 2) and the number of oxygen exchanged (Fig. 2).

3.2.4. Rh/Al_2O_3

As expected on this rhodium supported sample, oxygen exchange occurs at very low temperature (200°C) following the R′ mechanism predominantly. This mechanism is imposed by the presence of rhodium oxide particles supported onto alumina that act as a porthole for oxygen exchange [16]. On the other hand alumina is known to present a high oxygen mobility [20] and this sample will be an excellent oxygen donor phase in the following experi-

Table 2
Mass 34 slopes for simple and mechanical mixtures of oxides measured (see Fig. 2)

Sample composition	SnO_2	Rh/Al_2O_3	Rh/Al_2O_3 + MoO_3	Rh/Al_2O_3 + SnO_2	Rh/Al_2O_3 + Sb_2O_4	Sb_2O_4 + MoO_3	Sb_2O_4 + SnO_2
Initial P_{34} slope (mbar min^{-1})	0.02	0.06	0.09	0.15	0.10	n.a. [a]	0.03

[a] Not available: value too small to be accurate.

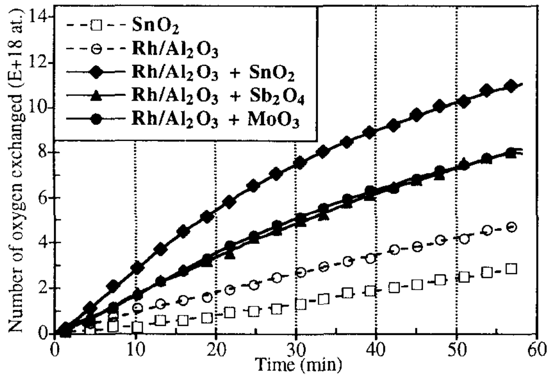

Fig. 2. Evolution of the number of oxygen exchanged at 500°C with time over simple phase samples (10 mg Rh/Al_2O_3 and 90 mg oxide) and mechanical mixtures (10 mg Rh/Al_2O_3 + 90 mg oxide).

ments. An isothermal study conducted at 500°C over this sample allows us to measure the slope of mass 34 (see Table 2) and the number of oxygen exchanged (Fig. 2).

3.3. Isotopic oxygen exchange on donor + acceptor mechanical mixtures

With Rh/Al_2O_3 as donor, the mixtures were made with 10 mg of donor phase and 90 mg of acceptor phase while with Sb_2O_4 as donor, the mixtures were made with 90 mg of each phase. When alone, Sb_2O_4 and MoO_3 are inactive at 500°C while Rh/Al_2O_3 and SnO_2 exchange oxygen at this temperature according to the heterophase R′ mechanism. The mixtures also exchange by the simple mechanism and hence only the slopes of mass 34 were reported in Table 2. To evaluate the flux of O_{sp} on these samples the evolution of the number of oxygen exchanged versus time at 500°C are represented in Fig. 2.

3.3.1. Mechanical mixtures with Rh/Al_2O_3 as donor phase

It can be seen from Fig. 2 that the increase in the amount of oxygen exchanged is more significant over the mixture formed between Rh/Al_2O_3 and SnO_2. Moreover the number of oxygen atoms exchanged on this mixture is higher than the sum of oxygen exchanged recorded on separate phases. This fact proves an actual synergy effect between Rh/Al_2O_3 and SnO_2. The amounts of oxygen exchanged in the mixtures $Rh/Al_2O_3 + MoO_3$ and $Rh/Al_2O_3 + Sb_2O_4$ are higher than on Rh/Al_2O_3 alone even though MoO_3 and Sb_2O_4 are inactive alone. These observations provide evidence of oxygen mobility between donor and acceptor oxides in these mechanical mixtures. Compared to the sum of oxygen exchanged on the two separate phases, the O_{sp} flux is about 6.3×10^{17} atom min^{-1} g^{-1} for $Rh/Al_2O_3 + SnO_2$ sample and about 6.2×10^{17} atom min^{-1} g^{-1} for $Rh/Al_2O_3 + MoO_3$ and $Rh/Al_2O_3 + Sb_2O_4$ samples.

3.3.2. Mechanical mixtures with Sb_2O_4 as donor phase

A very slow isotopic exchange was observed at 500°C for mixtures formed with the donor oxide Sb_2O_4 and the acceptor oxides SnO_2 or MoO_3 (Table 2). Concerning the flux of O_{sp}, the amount of oxygen exchanged with Sb_2O_4 as donor phase is just little upper (8%, i.e. 0.45×10^{17} atom min^{-1} g^{-1}) than when SnO_2 is alone (Fig. 3). In the mixture $Sb_2O_4 + MoO_3$ a very slow exchange is observed (O_{sp} flux about 1.7×10^{17} atom min^{-1} g^{-1}). Oxygen migration was observed for mechanical mixtures $Sb_2^{18}O^{16}O_3 + Mo^{16}O_3$ in propene oxidation ex-

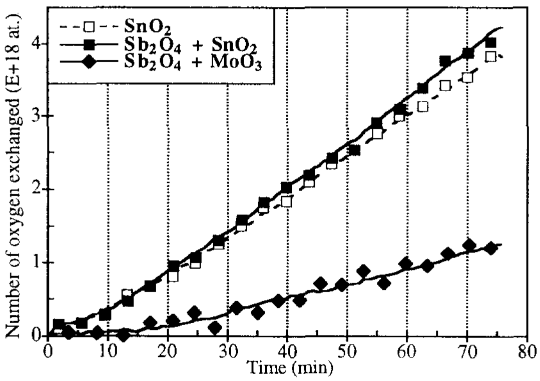

Fig. 3. Evolution of the number of oxygen exchanged at 500°C with time over simple oxide (90 mg SnO_2) and mechanical mixtures (90 mg Sb_2O_4 + 90 mg oxide).

periments by Weng et al. at 400°C [9]. In this latter case, the apparent rate of ^{18}O insertion in the products (acrolein, CO_x) was largely higher than the rate of exchange measured on the $Sb_2O_4 + MoO_3$ mixture. Two essential differences between the experimental conditions of [9] and those of the present study can explained the results: (i) the presence of large amounts of ^{18}O on the donor (while here, the donor has to activate molecular $^{18}O_2$) and (ii) the presence of a reducer which can act as a driving force for oxygen migration. So we will now examine the exchange behavior of the mechanical mixtures in the presence of methane and propene as a reducer gas.

3.4. *Effect of a reducer gas on isotopic exchange*

To study the influence of the reducer (methane or propene) on the oxygen exchange, the oxide phases Sb_2O_4, SnO_2 and MoO_3 were first tested alone prior to the mechanical mixtures. The results could not be quantified in terms of % conversion due to the recycle system used, but the initial evolution of the product partial pressures allows us to estimate which are the major and the primary products on each sample.

3.4.1. *Reaction with methane as reducer gas*

Contrarily to what was expected, no isotopic exchange was observed here (no $^{16}O^{18}O$ nor $^{16}O_2$). On SnO_2, methane oxidation was extremely fast, more than 90% of the $^{18}O_2$ being consumed within the first 10 min of reaction. The major products observed are $C^{18}O_2$ and $C^{18}O^{16}O$. Sb_2O_4 is inactive in the exchange reaction at 500°C and small quantities of CO and $C^{18}O$ are observed in reaction with methane, and again no oxygen exchange is observed. On MoO_3 no exchange nor oxidation is observed at 500°C.

MoO_3 alone or the mixture $MoO_3 + Sb_2O_4$ are inactive neither in isotopic exchange nor in methane oxidation at 500°C. When SnO_2 is mixed with Sb_2O_4, the oxidation reaction appears to be slower and again no oxygen exchange is observed. The major reaction products are again $C^{18}O_2$ and $C^{18}O^{16}O$. Most of the oxygen is consumed within 30 minutes of the reaction (slower than that observed for SnO_2 alone). The decrease in the rate of total methane oxidation when the donor phase is mixed with SnO_2 (see Table 3) could be interpreted by a deactivation of the active sites for total oxidation on SnO_2. This agrees with the general result of the decrease of the conversion and the increase of the selectivity in selective oxidation when the donor phase is mixed with the acceptor one [2,24]. It seems then that the presence of the donor phase (Sb_2O_4) increases the oxidation selectivity of SnO_2 by decreasing its activity in total oxidation. This deactivating effect could be due to a reoxidation of the partially reduced sites on SnO_2 with O_{sp} from Sb_2O_4.

Table 3
Initial slope (mbar min^{-1}) for methane oxidation on simple and mechanical mixtures at 500°C

Sample composition	$C^{16}O_2$	$C^{16}O^{18}O$	$C^{18}O_2$
Sb_2O_4	0.01	0.005	0.01
SnO_2	1.4	1.7	2.4
$Sb_2O_4 + SnO_2$	1.0	1.2	0.95

3.4.2. *Reaction with propene as reducer gas*

With propene all the simple oxide phases display activity in oxidation. Only total oxidation and no exchange are observed. The activity order for the different oxides is $SnO_2 >> MoO_3 > Sb_2O_4$. The major reaction products over SnO_2 are $C^{18}O_2$ and $C^{18}O^{16}O$ and minor products are $C^{18}O$, $C^{16}O$ and $C^{16}O_2$. The amounts of $C^{18}O_2$ and $C^{18}O$ produced decrease after about 20 min of reaction and the amounts of $C^{18}O^{16}O$, $C^{16}O$ and $C^{16}O_2$ continue to rise. On MoO_3 the major products formed is $C^{18}O$, while it is $C^{16}O$ over Sb_2O_4 (Fig. 4).

Concerning mechanical mixture $Sb_2O_4 + SnO_2$, the same activity as SnO_2 alone is observed and contrarily to previous work [25], no

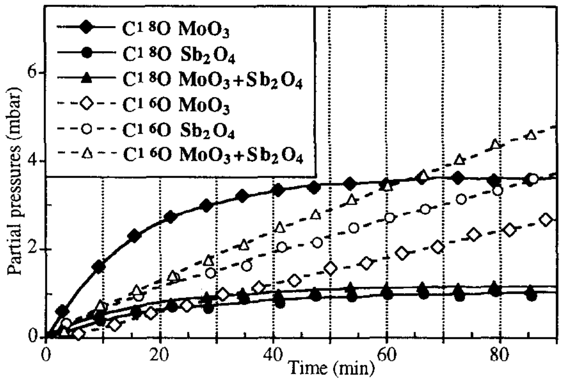

Fig. 4. Evolution of the major products formed during reaction at 500°C in presence of propene over simple oxide (90 mg) and mechanical mixtures (90 mg Sb_2O_4 + 90 mg MoO_3).

acrolein formation was observed due to the high temperature (500°C). On the $Sb_2O_4 + SnO_2$ sample, the most significant difference is that the decrease of $C^{18}O_2$, observed after about 25 min is clearly accompanied by an increase of $C^{16}O_2$ although all the initial amount of $^{18}O_2$ in gas phase is consumed. This fact could be interpreted as a re-exchange of carbon dioxide on oxide surface [23]. This secondary reaction is not observed on SnO_2 alone. The behavior of the mechanical mixture $Sb_2O_4 + MoO_3$ is similar to that of Sb_2O_4 (Fig. 4). For these samples, the major difference is based on the oxidation mechanism: on the mixture, as on Sb_2O_4 alone, $C^{16}O$ is the major product contrarily to MoO_3 those products mainly $C^{18}O$. As for reaction in presence of methane, Sb_2O_4 decreases the rate of the total oxidation. Moreover, on Sb_2O_4 containing samples, oxidation occurs with surface oxygen species (O_{sp}) by contrast with MoO_3 alone, where it is gaseous oxygen (O_d) that acts as oxidant.

4. Conclusion

Even if MoO_3 and Sb_2O_4 are inactive for isotopic exchange at 500°C, evidence of oxygen mobility was observed by an increase in the amount of oxygen exchanged (O_{sp} flux), between the acceptor oxides and the donor Rh/Al_2O_3. The most significant result was obtained for the mixture formed between Rh/Al_2O_3 and SnO_2, where a synergy effect was clearly demonstrated. No definite effect could be observed with Sb_2O_4 based mixtures. The amount of oxygen exchanged is practically the same in the $SnO_2 + Sb_2O_4$ mixture as in SnO_2 alone. However, it seems that Sb_2O_4 promotes a very slow oxygen exchange on MoO_3.

The introduction of a reducer (methane or propene) with $^{18}O_2$ only resulted in complete oxidation of the hydrocarbon. On simple oxide phases, with methane and propene SnO_2 is the most active oxide. Concerning reaction over mechanical mixtures, the major fact is that the oxidation of methane over the $Sb_2O_4 + SnO_2$ mixture was slower than that observed with SnO_2 alone. This deactivating effect could be explain by a blockage of the most active sites of SnO_2 for total oxidation, probably by oxygen spillover from Sb_2O_4. The most interesting consequence of this fact is an increase in selective oxidation by decreasing the rate of total oxidation on this mechanical mixture.

Acknowledgements

This work is supported by the Human Capital and Mobility Program of the European Community.

References

[1] B. Delmon and P. Ruiz, Catal. Today, 1 (1987) 1.
[2] P. Ruiz, B. Zhou, M. Remy, F. Aoun, B. Doumain and B. Delmon, Catal. Today, 1 (1987) 181.
[3] L.T. Weng, B. Zhou, B. Yasse, B. Doumain, P. Ruiz and B. Delmon, in M.J. Philips and M. Ternan, Editors, Proc. 9th Int. Congr. Catal., Calgary, Canada, Chemical Institute of Canada, Ottawa, Vol. 4, 1988, p. 1609.
[4] P. Ruiz and B. Delmon, Catal. Today, 3 (1988) 199.
[5] L.T. Weng, P. Ruiz and B. Delmon, in K.H. Steinberg, Editor, Proc. 2nd Int. Conf. Spillover, Leipzig, 1989, p. 37.
[6] B. Zhou, T. Machej, P. Ruiz and B. Delmon, J. Catal., 132 (1991) 183.
[7] L.T. Weng and B. Delmon, Appl. Catal., 81 (1991) 183.

[8] B. Delmon, in T. Inui, K. Fujimoto, T. Uchijima and M. Masai, Editors, 3rd Int. Conf. Spillover, Kyoto, Stud. Surf. Sci. Catal., 77 (1993) 1.
[9] L.T. Weng, P. Ruiz, B. Delmon and D. Duprez, J. Mol. Catal., 52 (1989) 349.
[10] G. Mestl, P. Ruiz, B. Delmon and H. Knözinger, J. Phys. Chem., 98(44) (1994) 11269.
[11] G. Mestl, P. Ruiz, B. Delmon and H. Knözinger, J. Phys. Chem., 98(44) (1994) 11283.
[12] E.R.S. Winter, Adv. Catal., 10 (1958) 196.
[13] E.R.S. Winter, J. Chem. Soc., 1 (1968) 2889.
[14] G.K. Boreskov, Advan. Catal., 15 (1969) 285.
[15] J. Novakova, Catal. Rev., 4 (1970) 77.
[16] D. Duprez, H. Abderrahim, S. Kacimi and J. Riviere, in K.H. Steinberg, Editors, 2nd Symp. Spillover, Karl Marx Universitat, Leipzig, 1989, p. 127.
[17] D. Martin and D. Duprez, in T. Inui, K. Fujimoto, T. Uchijima and M. Masai, Editors, Proc. 3rd Int. Conf. Spillover, Kyoto, Stud. Surf. Sci. Catal., 77 (1993) 201.
[18] E. Gaigneaux, P. Tsiakaras, D. Herlia, L. Ghenne, P. Ruiz and B. Delmon, American Chemical Society Annual Meeting, Symp., Catalysis and Photocatalysis on Metal Oxides, Chicago, IL, USA, 21–25 August 1995.
[19] E. Gaigneaux, D. Herlia, P. Tsiakaras, U. Roland, P. Ruiz and B. Delmon, American Chemical Society, Heterogeneous Hydrocarbon Oxidation Spring, ACS Meeting, New Orleans, LA, 24–29 March 1996.
[20] D. Martin and D. Duprez, J. Phys. Chem., 100 (1996) 9429.
[21] T. Lim and S.W. Weller, J. Catal., 108 (1987) 175.
[22] L. Dazhuang, Z. Lixiong, Y. Biguang and L. Jiaofeng, Appl. Catal., 105 (1993) 185.
[23] I. Brown and W.P. Patterson, J. Chem. Soc., Faraday Trans. 1, 79 (1983) 1431.
[24] J.C. Volta, P. Bussiere, G. Coudurier, J.M. Herrmann and J.C. Vedrine, Appl. Catal., 16 (1985) 315.
[25] J.R. Christie, D. Taylor and C.C. McCain, J. Chem. Soc., Faraday Trans. 1, 72 (1976) 334.