Study of surface and lattice oxygen atoms over magnesium vanadate phases by isotopic exchange with $C^{18}O_2$

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Different magnesium vanadate phases, V–Mg–O phases (α-$Mg_2V_2O_7$, $Mg_3V_2O_8$ and β-MgV_2O_6), MgO and V_2O_5 oxides have been compared with respect to their surface properties and their oxygen exchange capacities with $C^{18}O_2$ in the gas phase. By temperature-programmed desorption of carbon dioxide, the absence of any basic impurities (i.e., MgO or residual oxidised K impurities resulting from the preparation) has been evidenced on the surface of magnesium vanadate phases. This demonstrates that the catalytic properties of the magnesium vanadate phases for oxidative dehydrogenation of propane as previously studied cannot be explained by synergetic effects due to the presence of any basic component impurities since they are absent in this case. While on MgO an important surface exchange process occurs with $C^{18}O_2$ of the gas phase, this exchange is very low on V_2O_5 and pure V–Mg–O phases. A comparison of the different magnesium vanadate phases in the same experimental conditions indicates that the α-$Mg_2V_2O_7$ phase (which exhibited the highest selectivity for oxidative dehydrogenation of propane to propene) shows the lowest lattice oxygen exchange with $C^{18}O_2$ of the gas phase. This is another specificity of this phase.

Keywords: magnesium vanadate phases, oxygen species mobility, alkane oxidative dehydrogenations, isotopic oxygen exchange

1. Introduction

Catalytic oxidative dehydrogenation of low alkanes (C_3–C_5) has been extensively investigated over vanadium-oxide materials [1–14]. Much research has aimed to attribute catalytic performances to single V–Mg–O phases [1–5,7,8]. However, the conclusions drawn on the activity and selectivity of these catalytic materials are still controversial and the exact nature of their surface sites is not well known. For Kung et al. [1,2], magnesium orthovanadate, $Mg_3V_2O_8$, is the active phase for alkene formation. But, Volta and co-workers [3] attributed the higher selectivity for propane dehydrogenation to propene to pyrovanadate, α-$Mg_2V_2O_7$. This contradiction was considered to arise from the preparation method of the phases and the resultant purity of these latter due to potassium contamination during the sample preparation that can affect the reactivity of V–Mg–O catalysts [4]. Furthermore, Delmon et al. [7,8] show that selectivity of $Mg_3V_2O_8$ phase can be improved by the presence of an excess of MgO in intimate contact. These authors also found that α-$Mg_2V_2O_7$ is the more selective phase compared with $Mg_3V_2O_8$ and β-MgV_2O_6, in agreement with Volta's group. The above described results mainly concern the selective oxidation of propane to propene. For the selective oxidation of *n*-butane [4] or pentane [13], the ortho phase exhibits an enhanced selectivity in comparison with the pyro phase, but over this latter a higher specific activity has been observed [13]. The nature of the hydrocarbon being activated appears to influence also the catalyst performance.

On the other hand, with regard to the reaction mechanism it is generally accepted that the alkane activation by breakage of a C–H bond is the rate limiting step [15]. Also, it has been proposed that the reaction mechanism over V–Mg–O is of a Mars–Van Krevelen redox type [16] and that the selectivity can be controlled by the binding energy of lattice oxygen. Following this hypothesis the redox properties of catalysts have been found to correlate with the selectivity [7] and an easier reducibility of the α-$Mg_2V_2O_7$ phase compared to other phases has been observed [17,18]. Furthermore, the higher selectivity of pyrovanadate has been attributed to the ability of this phase to stabilize V^{4+} ions associated with surface oxygen vacancies [17]. The importance of the appropriate combination of surface vanadium ions with anionic vacancies for the control of redox properties of the active phase (a key parameter in the Mars–Van Krevelen mechanism) has also been considered in a study on MgO-supported V–Mg–O phases [14].

A typical problem found in studies over metal oxides for oxidation reactions is the determination of the role of lattice oxygen in the reaction mechanism [19]. For this purpose isotopic exchange with $^{18}O_2$ has widely been applied to characterize and classify metal oxides. But generally the isotopic exchange with $^{18}O_2$ takes place at temperatures far away from those used in catalysed reactions [20]. The oxygen isotopic exchange with $C^{18}O_2$ presents the advantage of occurring at relatively low temperatures (600–700 K), closer to catalytic reaction conditions. This latter technique has been applied to analyse lattice oxygen diffusion over single oxides, such as V_2O_5 [21] or MoO_3 [22], as well as to compare exchange properties of MoO_3 crystallites with different microcrystalline structures [23]. The oxygen isotopic exchange with $C^{18}O_2$ is tested here with V–Mg–O pure phases previously prepared and studied as catalysts [3]. Our aim is to investigate and to compare these catalysts (α-$Mg_2V_2O_7$, $Mg_3V_2O_8$, β-MgV_2O_6) from the point of view of oxygen surface exchange and with respect to their lattice oxygen migration. As noted above, these properties can control the catalytic performance of these samples for selective oxidation of hydrocarbons. Also, pure V_2O_5 and MgO have been studied.

2. Experimental

Six samples have been used in this study. Three magnesium vanadates, β-MgV_2O_6, α-$Mg_2V_2O_7$ and $Mg_3V_2O_8$, whose preparation and characteristics have been described elsewhere [3,17,18]. The surface areas (BET, N_2 - 77 K) of these samples are 0.1, 1.7 and 0.9 $m^2\ g^{-1}$, respectively. Two pure V_2O_5, the first is a commercial one (Merck, R.A.) with a surface area of 0.3 $m^2\ g^{-1}$, here designated V_2O_5-L. The second (V_2O_5-H) was prepared by the flame reactor method [24], and its surface area is 25.7 $m^2\ g^{-1}$. Also for comparison purposes, a commercial MgO sample (UCB, surface area of 16 $m^2\ g^{-1}$) was studied.

Exchange experiments with $C^{18}O_2$ (Isotec Inc., isotopic purity 95%) were carried out using 10–100 mg of sample held inside a quartz reactor coupled to a grease-free standard vacuum system [23]. The gas phase was analysed by an on-line mass quadrupole spectrometer (Balzers QMG 421C) connected to the reactor through a metering leak valve. Ion current of the various products ($C^{18}O_2$, $m/z = 48$; $C^{18}O^{16}O$, $m/z = 46$; $C^{16}O_2$, $m/z = 44$ and some secondary peaks) and the temperature of the sample were simultaneously collected in a personal computer. In these experiments the gas phase is recirculated through the sample bed by a low volume stainless steel mechanic pump (Metal-Bellow Corp). Previously the samples were pretreated under $^{16}O_2$ at 823 K for 1 h and evacuated at 723 K for 30 min. Then, a known amount of $C^{18}O_2$ (pressure around 2.6 kPa) was admitted into the recycle reactor. The exchange reaction was performed at 723 K using percentages of ^{18}O atoms in the system ($\%^{18}O = 2N(C^{18}O_2)_{gas}/[2N(C^{18}O_2)_{gas} + xN(M^{16}O_x)_{solid}]$, N = number of molecules and x = number of oxygen atoms for each metal oxide) between 8 and 42%. Temperature-programmed desorption experiments were conducted in the same apparatus, the samples were pretreated under vacuum at 823 K for 1 h and, once at room temperature, contacted with a pulse of $C^{16}O_2$ (3 kPa for 30 min). After evacuation at room temperature for 30 min the samples were heated up to 873 K at 10 K/min and the evolved products analysed by mass spectrometry [25].

3. Results and discussion

An important aspect when performing studies over pure phase mixture oxides is their purity. The samples used in this work have been characterized and controlled by different techniques: X-ray analysis, infrared spectroscopy, ^{51}V MAS NMR, ESR, XPS, electrical conductivity [3,17,18]. Here we like to focus on the possible presence of "basic" impurities, such as residual potassium or segregated MgO. A careful inspection of the photoelectronic spectra (XPS) obtained for the pure phases α-MgV_2O_6, β-$Mg_2V_2O_7$ and $Mg_3V_2O_8$ in the region of binding energies of 290–300 eV, shows that peaks corresponding to K $2p_{3/2}$ or K $2p_{1/2}$ transition levels are absent. Consequently, in these samples the level of potassium, if any, is extremely low.

On the other hand, the TPD of adsorbed CO_2 reflects the basic properties (e.g. concentration and strength of basic sites) of metal oxide surfaces [25,26]. Comparison of the fingerprint CO_2 TPD spectra of MgO and V_2O_5 with those corresponding to V–Mg–O samples can inform us about the presence of segregated phases. In figure 1 are shown the CO_2 TPD spectra of the various samples. It is seen that on pure MgO two desorption peaks at 383 and 523 K can be resolved. This profile is similar to others reported in the literature for desorption of CO_2 from MgO [26]. For V_2O_5 a desorption peak at higher temperature (660 K) was obtained. The three magnesium vanadates show a continuous desorption starting at 650 K, without significant differences

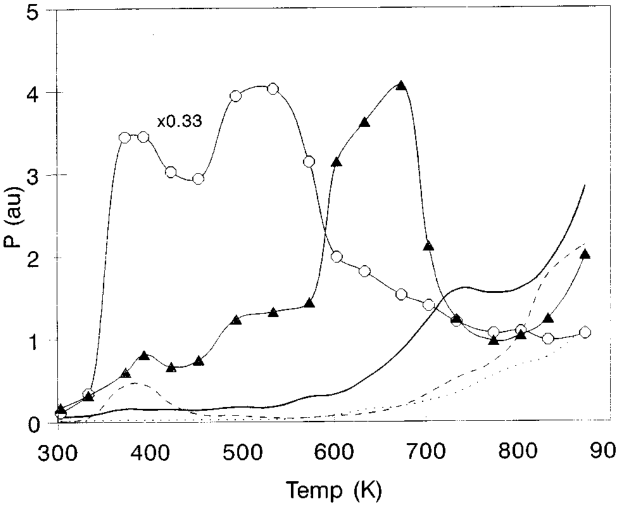

Figure 1. TPD profiles of CO_2 for: (○) MgO, (▲) V_2O_5-L, (——) α-MgV_2O_6, (- - -) $Mg_3V_2O_8$ and (. . .) β-$Mg_2V_2O_7$.

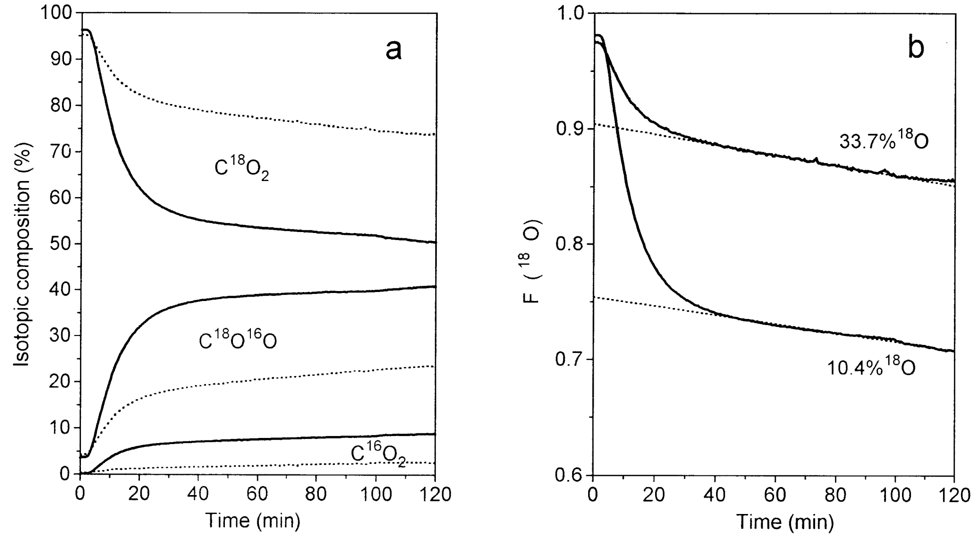

Figure 2. Oxygen exchange reaction between $C^{18}O_2$ and $Mg^{16}O$ at 723 K. (a) Isotopic composition versus time in reaction for a ^{18}O percentage of 33.7% (full line) and 10.4% (dotted line). (b) Isotopic labelling of gaseous CO_2 during the reaction (full line) and fitted slope (dotted line).

between them. Only $Mg_3V_2O_8$ displays a small peak at 380 K which could be due to some MgO impurity on this sample (note a peak at ~ 380 K for MgO). From the CO_2 TPD experiments it can be seen that surface basic sites on magnesium vanadate phases are different to those exhibited by MgO and V_2O_5 pure oxides. In short, the XPS and CO_2 TPD experiments indicate that magnesium vanadate pure phases used in this work are not contaminated by basic impurities.

As introduced above, the catalytic selectivity in the hydrocarbon selective oxidation reaction may be controlled by the reactivity of oxygen ions, either surface adsorbed species or reactive lattice oxygen. We have attempted to gain insight in the study of this aspect by analysing the oxygen exchange behaviour with $C^{18}O_2$ of well characterized pure phases: α-MgV_2O_6, β-$Mg_2V_2O_7$, $Mg_3V_2O_8$, V_2O_5 and MgO. In spite of the various surface areas of these samples and because the surface oxygen exchange of the vanadium containing samples is very limited (see below), a key parameter in the exchange reaction of the lattice oxygen is the amount of ^{18}O atoms (from $C^{18}O_2$) relative to that of ^{16}O atoms (from the oxide sample). Therefore, we have introduced in the circulation reactor precise percentages of ^{18}O (%^{18}O) for each experiment. Figure 2a shows the isotopic composition of gaseous carbon dioxide during oxy-

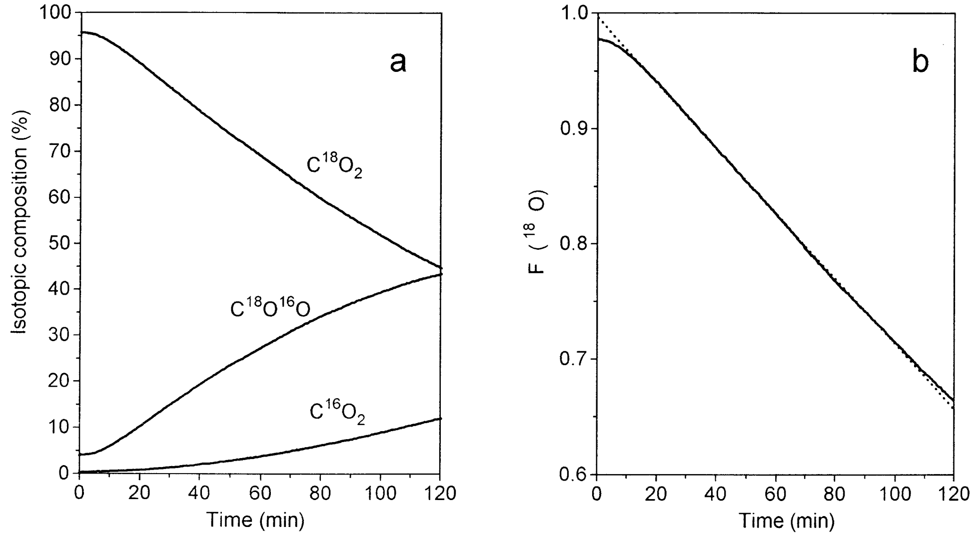

Figure 3. Oxygen exchange reaction between $C^{18}O_2$ and $V_2{}^{16}O_5$-H at 723 K. (a) Isotopic composition and (b) isotopic labelling of CO_2 during reaction (full line) and fitted slope (dotted line).

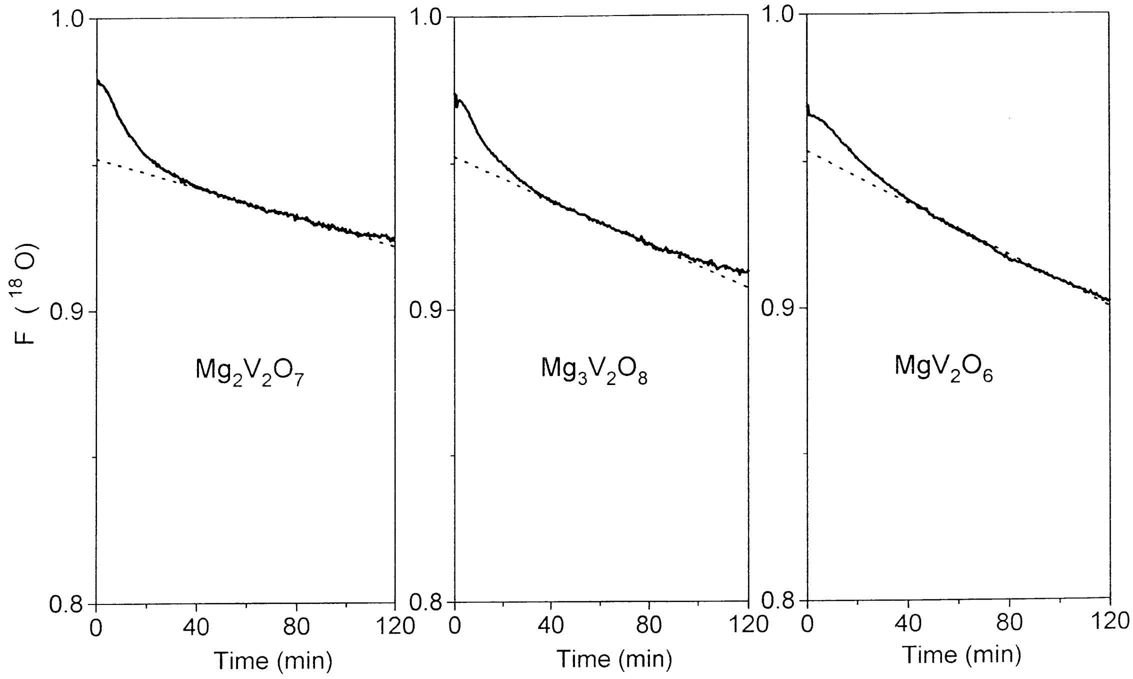

Figure 4. Oxygen exchange reaction between $C^{18}O_2$ and the V–Mg–O phases at 723 K. Isotopic labelling of gaseous CO_2 (full line) and fitted slope (dotted line).

gen exchange reaction over MgO with two different ^{18}O percentages, 10.4 and 33.7%. In figure 2b the results are presented as evolution of the isotopic labelling of gaseous carbon dioxide ($F(^{18}O)$) with the time in reaction. $F(^{18}O)$ is defined as: $F(^{18}O) = [I(46) + 2I(48)]/\{2[I(44) + I(46) + I(48)]\}$; I = intensity in the mass quadrupole for a m/z peak. $F(^{18}O)$ values give an indication of the exchange kinetics. The curves presented in figure 2b clearly show two contributions to the oxygen exchange reaction. First, an oxygen exchange reaction with the surface of the metal oxide which is characterized by a rapid isotopic labelling decrease up to reaction times of 40 min. Obviously, the rate and extent of the surface oxygen reaction depend on the MgO mass in an experiment (the square meters of MgO introduced in the reactor) for a given amount of $C^{18}O_2$. At reaction times longer than 40 min the exchange reaction becomes slower, the slope of this second part of the curve being 0.00044 and 0.00039 for 33.7 and 10.4% of ^{18}O, respectively. This second contribution to the oxygen exchange reaction is due to lattice oxygen exchange and is independent of the surface area of MgO available for reaction, as revealed by the similarity in the slopes of these two experiments.

Figure 3 displays the results of the oxygen exchange reaction with $C^{18}O_2$ for the V_2O_5-H sample under 8.6% of ^{18}O. One can see the absence of exchange reaction with the surface although the surface area of this sample (25.7 $m^2\ g^{-1}$) is higher than that of the MgO sample (16 $m^2\ g^{-1}$). Only the second contribution to the oxygen exchange reaction, i.e. that due to the lattice oxygen, is observed (figure 3b). Similar profiles were obtained over the V_2O_5-L sample and also over all the magnesium vanadates. Figure 4 displays the curves corresponding to the isotopic labelling of gaseous carbon dioxide for the three V–Mg–O phases. As can be seen, under our experimental conditions, the surface oxygen exchange of vanadium containing samples with labelled carbon dioxide is very small.

The slope of the second part of the curve of $F(^{18}O)$ versus the time (figures 2b, 3b and 4) gives an indication of the kinetics of the lattice oxygen exchange reaction. The values of this slope for each sample (MgO, V_2O_5 samples and magnesium vanadates) and the main experimental conditions are included in table 1. It is seen that for a given value of $\%^{18}O$ the slope determined is independent of the surface area of the V_2O_5 sample (V_2O_5-L versus V_2O_5-H). So, this is another evidence that the process we are analysing cor-

Table 1
Slopes of the curves of isotopic labelling of CO_2 versus the relative amount of ^{18}O for reaction at 723 K

Sample	Relative amount of ^{18}O atoms	Slope ($\times 10^4$)
MgO	10.4	3.9
	33.7	4.4
V_2O_5-L	8.6	27.4
	33.8	16.7
V_2O_5-H	8.6	28.3
	41.4	16.1
α-$Mg_2V_2O_7$	34.5	2.5
$Mg_3V_2O_8$	32.5	3.8
β-MgV_2O_6	33.0	4.5

Table 2
Catalytic results for propane oxidative dehydrogenation at 823 K on the V–Mg–O phases [a]

V–Mg–O phase	Mass (%)	Conversion C_3H_8 (%)	Selectivity (%)				
			C_3H_6	CO_2	CO	oxygenates	
$Mg_3V_2O_8$	1.0	8.3	6.0	94.0	–	–	
α-$Mg_2V_2O_7$	0.2	6.9	53.5	18.8	10.4	acrylald. propanal acetic acid	12.0 3.5 1.0
β-MgV_2O_6	0.7	7.4	14.9	17.6	36.6	ethanal	30.2

[a] Catalytic conditions $C_3H_8/O_2/N_2$: 2/19.6/78.4, 760 Torr, 3 ℓ h^{-1} (from ref. [3]).

responds to the exchange reaction of lattice oxygen. Moreover, as expected, the percentage of ^{18}O remarkably changes the slope value for a given sample (V_2O_5). Comparison of the slope values of the various samples reveals that the lattice oxygen exchange is more rapid in V_2O_5 than in MgO and magnesium vanadate samples. This difference in oxygen exchange between magnesium vanadates and V_2O_5 could explain the lower selectivity towards partial oxidation obtained over V_2O_5 under similar conversion levels [3]. Table 2 gives the catalytic performances measured on the three V–Mg–O phases for propane oxidative dehydrogenation, as previously published [3]. It appears that the lattice oxygen exchange necessary to produce selective V–Mg–O catalysts for propane oxidative dehydrogenation should be relatively low, in our slope scale around 2–4 (table 1). Obviously, the presence of vanadium ions in a suitable environment is needed to activate the propane molecule.

Finally, from the experiments of oxygen exchange with $C^{18}O_2$ we have found significant differences among MgO, V_2O_5 and magnesium vanadate samples. These would account for their distinct catalytic behaviour in selective oxidation of alkanes. The α-$Mg_2V_2O_7$, which is the most selective for oxidation of propane to propene (table 2) [3,7], has the lowest value of the slope corresponding to the second part of the $F(^{18}O)$ versus time curve (table 1). Considering that these slope values are indicative of the lattice oxygen exchange kinetics, it can be inferred that a good catalyst for selective oxidation of saturated hydrocarbons should possess a minimum of lattice oxygen exchange with the gaseous phase.

In conclusion, the study of oxygen exchange reaction between $C^{18}O_2$ and different metal oxides samples has allowed us to determine a parameter (the slope of $F(^{18}O)$ versus time curve) characteristic of this exchange that can also depend on the binding energy of the lattice oxygen. A comparison of our results with previously reported catalytic data [3] leads us to suggest the dependency of selectivity for propane oxidative dehydrogenation not only upon the O^{2-} ions lability [3] but also upon a limited lattice oxygen exchange with the gas phase.

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