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Description of active sites on molybdenum oxide as detected by isotope exchange between $C^{18}O_2$ and $Mo^{16}O_3$

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Abstract

The oxygen exchange reaction between $C^{18}O_2$ and $Mo^{16}O_3$ has been studied on well characterized MoO_3 crystallites. Temperature programmed desorption of adsorbed $C^{18}O_2$ has shown that the extent of surface oxygen exchange is higher on partially reduced samples exposing the (010) face. This has been related with the easier reducibility of the (010) face. Moreover, experiments in a recycle reactor at moderate reaction temperature (623K) suggest that surface oxygen exchange is more rapid on the basal (010) face. On the other hand, when the experiment is run at higher reaction temperature (773K), using a higher $^{18}O(C^{18}O_2)/^{16}O(MoO_3)$ ratio and for a longer period, a continuous oxygen exchange reaction occurs, specially with samples presenting lateral faces. In this latter conditions, two contributions to the exchange reaction can be distinguished. The first corresponds to a fast surface oxygen exchange. The second contribution which is more prominent over samples with (100) faces can be assigned to migration of oxygen atoms from lateral towards basal faces and/or to a slow migration of oxygen atoms from the bulk structure of MoO_3 towards the lateral faces. From the results of this study it is speculated on the importance of a preferential oxygen migration from the bulk MoO_3 towards the lateral faces, which is related with the selective partial oxidation of olefins observed on these faces.

Keywords: MoO_3; Surface oxygen mobility; Bulk oxygen mobility; Oxygen exchange with $C^{18}O_2$

1. Introduction

Catalytic properties of α-MoO_3 are known to be different depending of the mainly exposed faces on a given crystalline sample. This behaviour has been proved to work for oxidation reactions of olefins [1] and alcohols [2], and for reduction of nitric oxide [3]. For instance, propene oxidation is a so-called ''structure-sensitive'' reaction for which total oxidation occurs on the basal (010) face whereas acrolein is formed on stepped-like lateral faces [4]. Considering that mild oxidation reactions proceed following a redox mechanism, at least two steps can be distinguished: (1) dehydrogenation of propylene to yield allylic species, which takes place on Lewis acid sites associated to oxygen vacancies, and (2) oxygen insertion involving lattice oxygen, which require an easy transfer of oxygen ions from the oxide to the adsorbed allylic intermediate.

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During the last years, to understand the complete reaction mechanism we have carried out several studies by different methods, such as reactivity of allylic compounds [5] or $^{18}O_2$ tracer studies [6], and we have used various physic or chemical techniques for sample characterization [7]. Now our idea can be summarized as follows: oxygen is dissociatively adsorbed on (010) face and diffuses to lateral faces through the MoO_3 bulk by oxygen vacancy disordering. Furthermore, propene molecules are adsorbed and activated on stepped lateral faces and suffer the oxygen insertion by active lattice oxygen atoms.

In this paper the oxygen exchange reaction of $C^{18}O_2$ with MoO_3 samples exposing different crystalline structures has been studied. Compared to the $^{18}O_2/Mo^{16}O_3$ exchange reaction, which proceeds at temperatures above 873K [7], the $C^{18}O_2/Mo^{16}O_3$ exchange reaction allows us to have information about oxygen atom migration at temperatures close to those of the hydrocarbon reactions. Based on the results obtained it is speculated about the migration of oxygen atoms across the bulk structure of MoO_3 and this latter is related with the structure-sensitive character of various reactions on MoO_3 samples.

2. Experimental

Four MoO_3 samples have been used in this study. Two 100-oriented MoO_3, which were prepared by oxidation of Mo foils [8] at 893K for 24h and at 953K for 6h. Here after these samples will be designated as **A** and **B**, respectively. The surface of these samples is made up by truncated (110), (120) and (130) planes. A commercial MoO_3 powder (R.A. Merck), which mainly exhibits (010) face (sample **C**). Finally, MoO_3 crystallites prepared by evaporation-condensation under oxygen stream [9], for which at least 90% of the total surface corresponds to (010) face (sample **D**). The surface area (BET, N_2-77K) of these samples are 0.72, 0.30, 0.85 and 0.06 m^2/g for **A** to **D**, respectively [7].

Exchange experiments were carried out using 50–200 mg of sample held inside a quartz reactor coupled to a grease free standard vacuum system. The gas phase was analysed with an on-line mass quadrupole spectrometer (Balzers QMG 421 C) connected to the reactor through a metering leak valve. In the temperature programmed desorption (TPD) experiments, the samples were reduced by outgassing at 873K, and after cooling at room temperature a pulse of $C^{18}O_2$ was introduced in the reactor. After removing the gaseous $C^{18}O_2$ under vacuum at 298K, the sample was heated at $10 K min^{-1}$ up to 850K with continuous analysis of the gaseous products ($C^{18}O_2$, $m/z = 48$; $C^{18}O^{16}O$, $m/z = 46$; $C^{16}O_2$, $m/z = 44$; ...). In the circulatory experiments the gas phase is recirculated by a stainless steel mechanic pump (Metal-Bellows Corp). Previously the samples were oxidised under $^{16}O_2$ at 623K for 1h and evacuated for 5 min at the same temperature. Then, a known amount of $C^{18}O_2$ was admitted into the recycle reactor; the reaction was performed at 623K with a ^{18}O(from $C^{18}O_2$ gas)/^{16}O(from $Mo^{16}O_3$ solid) atom ratio of 2/100 or at 773K with a $^{18}O/^{16}O$ ratio of 25/100.

3. Results and discussion

Fig. 1 shows the TPD of $C^{18}O_2$ adsorbed at room temperature on MoO_3 samples reduced under vacuum at 873K. First at all, the only desorbed product is $C^{16}O_2$. So, a total oxygen exchange takes place between the reduced surface and the chemisorbed CO_2 species. Considering the lower surface area of sample MoO_3 **D** compared to the MoO_3 **A**, the higher amount of $C^{16}O_2$ desorbed from sample **D** and the high proportion of (010) face in this latter, it is may be deduced that this desorbed $C^{16}O_2$ mainly comes from the basal face. Given that the (010) face of MoO_3 is reduced much more easily than lateral faces, and that this reduction originates anion vacancies and creates crystallographic shear planes [10]; it seems that the CO_2 chemisorption and its oxygen exchange with the surface may be related to the oxygen vacancies of the (010) face. Furthermore, the exchange of the two oxygen atoms of CO_2 suggests that these oxygen vacancies are in a close proximity on the (010) face of MoO_3.

Another way to obtain information about the oxygen exchange between $C^{18}O_2$ and $Mo^{16}O_3$ is the study of the isotopic composition when carbon dioxide is recirculated over the MoO_3 samples. Fig. 2 shows the isotopic exchange profiles obtained for the different samples at a reaction temperature of 623K and with a $^{18}O/^{16}O$ ratio of 2/100. The results presented in Fig. 2 clearly indicate that the oxygen exchange is more rapid on MoO_3 samples **C** and **D**, in comparison with the **A** and **B** ones. Considering the low $^{18}O/^{16}O$ ratio, the reaction temperature and the time under circulation, the oxygen exchange process in these experiments should be mainly limited to the surface. Then, for a quantitative comparison these results should be referred to the unity of surface area. However, the very low surface area of these MoO_3 samples implicates that the measurements could have a large uncertainty. Therefore, our results are compared on the base of MoO_3 weight. Also, it is worth noting that even if the surface areas of samples **A** and **B** are higher than that of **D** [7], the isotopic exchange is easier over the last one. So, considering the faces exposed for each sample, it can be deduced that (010) face of MoO_3 is a more rapid oxygen exchanger with CO_2 molecules. Very probably this phenomenon is related to the presence of oxygen vacancies on the basal face, which cannot be filled with oxygen atoms coming from the bulk structure of MoO_3. So, the (010) surface exposes oxygen atoms coming from the gas phase contrarily to the lateral faces which exchange ability is limited. From the point of view of the partial oxidation of olefins this finding can explain the mechanism of the

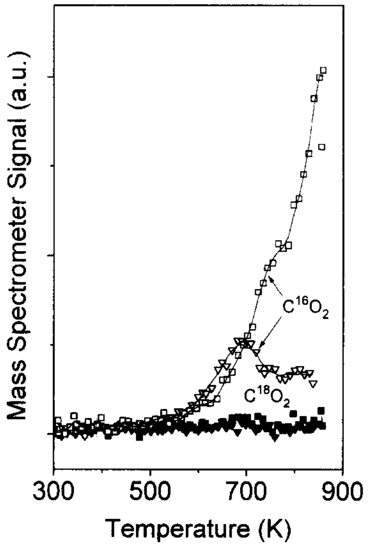

Fig. 1. Temperature programmed desorption of chemisorbed $C^{18}O_2$ on samples reduced under vacuum at 873K: (▽, ▽) MoO_3 **A** and (□, ■) MoO_3 **D**, open symbols correspond to $C^{16}O_2$ and solid ones to $C^{18}O_2$.

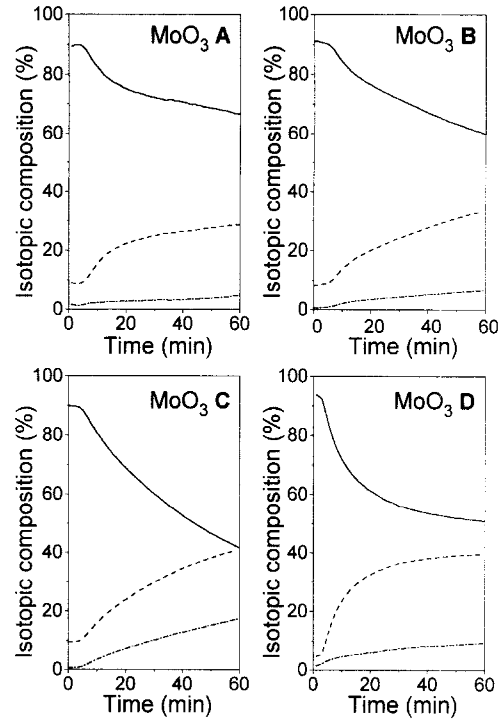

Fig. 2. Isotope exchange between $C^{18}O_2$ and $Mo^{16}O_3$ at 623K over the differnt crystalline samples. (————) $C^{18}O_2$, (– – –) $C^{18}O^{16}O$, (– · –) $C^{16}O_2$.

non-selective oxidation of allylic species on the (010) face and the selective oxidation on the (100) face [5,6]. It is generally accepted that total oxidation reactions involve gas phase oxygen atoms, while for partial oxidation of hydrocarbons oxygen atoms from the oxide lattice are incorporated into the oxidation product [6].

When the exchange reaction temperature is increased up to 773K (Fig. 3), it can also be observed that the oxygen isotopic exchange with $C^{18}O_2$ is initially more rapid on MoO_3 samples **C** and **D**. These samples exhibit a larger proportion of basal (010) face. This fact agrees with the exchange behaviour found at 623K (Fig. 2) over the various MoO_3 samples. In experiments reported on Fig. 3 not only the reaction temperature was increased, but also the time on reaction was extended up to 150 min and the initial ratio $^{18}O/^{16}O$ in the reactor was increased to 25/100. Under these conditions, the oxygen exchange reaction is practically finished after 50 min on samples **C** and **D**, while over samples **A** and **B** a continuous reaction is occurring. To better illustrate these features, it has been represented in Fig. 4 the evolution with the time in reaction of the isotopic labelling of gaseous CO_2, $F(^{18}O)\% = (I(46) + 2I(48))/2(I(44) + I(46) + I(48))$. $F(^{18}O)$ values give a indication of the exchange kinetic. If only an initial surface reaction takes place, the $F(^{18}O)$ will become constant after a given time in reaction. However, if a diffusion of oxygen atoms from the bulk oxide is occurring, a continuous decrease of $F(^{18}O)$ should be observed. This latter is the case of our MoO_3 samples; but, it is worth noting that the slope of the $F(^{18}O)$ is higher for samples **A** and **B** than for **C** and **D**. These evidence indicate that on (010) face the reaction is interrupted after a rapid exchange of the surface oxygen atoms. This interruption may be related to the absence of oxygen atom migra-

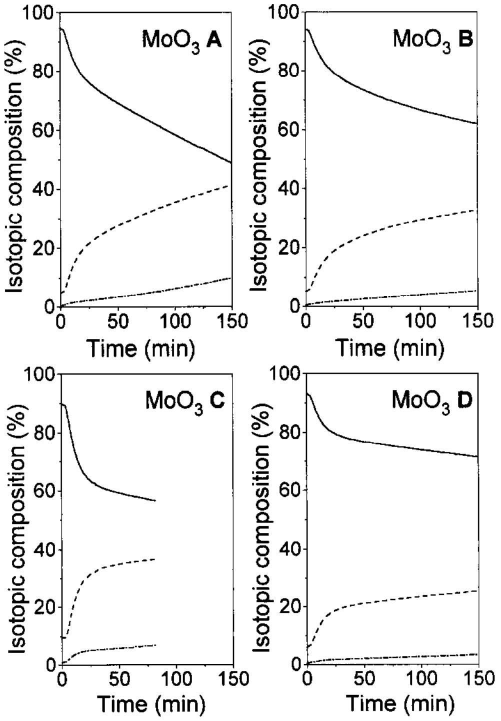

Fig. 3. Isotope exchange between $C^{18}O_2$ and $Mo^{16}O_3$ at 773K over the different crystalline samples. (————) $C^{18}O_2$, (– – –) $C^{18}O^{16}O$, (– · –) $C^{16}O_2$.

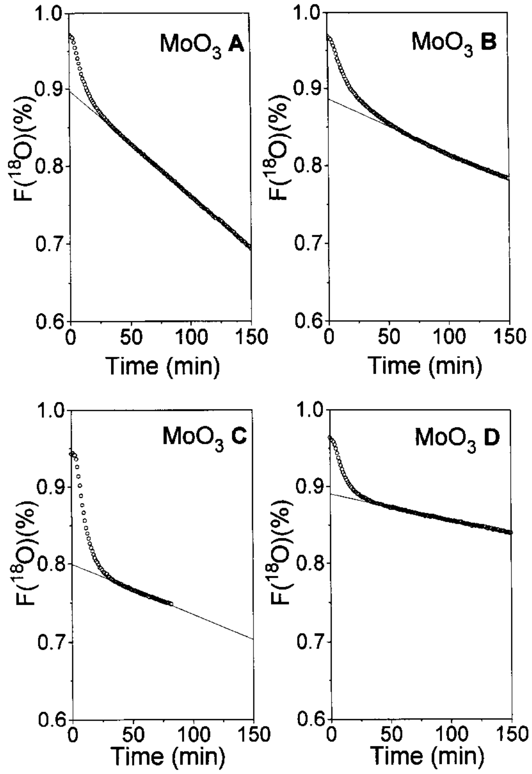

Fig. 4. Isotopic labeling of gaseous CO_2 during the time in reaction at 773K over the different crystalline samples.

tion from the bulk structure of MoO_3 towards this basal face. Contrarily, over samples exposing lateral faces (**A** and **B**) the exchange reaction progress into the bulk. The continuity in the oxygen exchange reaction may be interpreted as consequence of a preferential migration of oxygen atoms through the MoO_3 structure along [100] and [001] directions. This explanation is supported by earlier studies over the incorporation of ^{18}O atoms in these MoO_3 crystals under propylene oxidation conditions, using $^{18}O_2$ as reactant and analysing the solids by Secondary Ion Mass Spectroscopy [11].

Alternatively the results presented in Fig. 4 for samples **A** and **B** can be interpreted as due to a surface migration of oxygen ions from lateral faces towards the basal one. Supporting this explanation it can be considered that actually the structure of lateral faces for samples **A** and **B** may be described as step-surfaces composed of both (100) terraces and normal (010) steps [8]. However, given the low surface area of these MoO_3 solids ($< 1\ m^2 \cdot g^{-1}$), a relatively low amount of surface ^{16}O ions is placed on the surface of the MoO_3. On the other hand, the levels of ^{16}O atoms in the gaseous carbon dioxide after 150 min in reaction becomes about 40%. So, a contribution of bulk MoO_3 oxygen atoms in the exchange reaction has to be considered, and consequently the mechanism above described with a preferential migration of oxygen ions through the oxide structure is needed to understand the results presented in Fig. 4.

In conclusion, the use of $C^{18}O_2$ as probe of the reactivity of MoO_3 surfaces seems to be a useful tool, not only to study the surface reactivities but also to follow the possible ways of oxygen ion migration into the oxide structure. The oxygen migration may be the key parameter that controls the selective or non-selective oxidation of propylene over the different MoO_3 faces.

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References

[1] J.C. Volta, W. Desquesnes, B. Moraweck and J.M. Tatibouet, in Proc. 7th Int. Cong. Catal., Tokyo, 1980, p. 1398.

[2] J.M. Tatibouet, J,E. Germain and J.C. Volta, J. Catal., 82 (1983) 240.

[3] A. Baiker, P. Dollenmeier and A. Reller, J. Catal., 103 (1987) 394.

[4] J.C. Volta and J.L. Portefaix, Appl. Catal., 18 (1985) 1.

[5] A. Guerrero-Ruiz, M. Abon, J. Massardier and J.C. Volta, J.C.S. Chem. Comm., 1031 (1987).

[6] A. Guerrero-Ruiz, A. Massardier, D. Duprez, M. Abon and J.C. Volta, in Proc. 9th Int. Cong. Catal., Calgary, 1988, p. 1601.

[7] M. Abon, M. Roullet, J. Massardier and A. Guerrero-Ruiz, in New Developments in Select. Oxid. II, Stud. Surf. Sci. Catal., 82 (1994) p. 67.

[8] B. Mingot, N. Floquet, O. Bertrand, M. Treilleux, J.J. Heizmann, J. Massardier and M. Abon, J. Catal., 118 (1989) 424.

[9] J.M. Tatibouet, Thesis, University of Lyon, 1982.

[10] P.L. Gai-Boyes, Cat. Rev.-Sci. Eng., 34 (1992).

[11] A. Guerrero-Ruiz, J.M. Blanco, M. Aguilar, I. Rodriguez-Ramos and J.L.G. Fierro, J. Catal., 137 (1992) 429.