Available online at www.sciencedirect.com

SCIENCE DIRECT®

Catalysis Today 91–92 (2004) 105–110

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Influence of the reduction state in the bulk and at the surface on the behavior of MoO_3 catalysts in the reaction of 2-butanol (dehydration versus oxidation) in the presence of oxygen

F. Bertinchamps, E.M. Gaigneaux*, [1]

Unité de catalyse et chimie des matériaux divisés, Université catholique de Louvain, Croix du Sud 2/17, B-1348 Louvain-la-Neuve, Belgium

Abstract

The reaction of 2-butanol (dehydration to butenes versus total oxidation to CO_2 and water) in the presence of oxygen is used as a probe of the influence of the reduction state of MoO_3-based catalysts on their behavior. Two different behaviors are revealed depending on the extent of the reduction and on the manner by which this reduction is accommodated by the catalysts. Reduction accommodated through the stabilization of bulk Mo sub-oxide phases is detrimental in terms of exchangeability of oxygen atoms. Such catalysts preferentially promote the dehydration of 2-butanol on Brönsted sites, but do not succeed to oxidize it efficiently. In other words, they do not succeed to transfer oxygen atoms into hydrocarbons through the MVK mechanism. At the opposite, a slight reduction localized at the catalyst surface through the presence of Mo^{5+} species increases the exchangeability of surface lattice oxygen atoms. This makes the corresponding catalysts highly efficient in the oxidation of 2-butanol, and most generally in oxidation reaction proceeding through the MVK mechanism.

Keywords: Mo suboxides; MVK mechanism; Dehydration and oxidation of 2-butanol

1. Introduction

This work brings further understanding on the nature and working mechanism of active sites on oxide catalysts. More precisely, some light is shed towards the identification of the most active MoO_3-based catalysts in oxidation processes. The influence of the extent of the reduction of the catalyst and of the manner by which the latter accommodates the reduction (i.e. its location in the bulk or at the surface) is shown to have a crucial influence on the performances.

The Mars and van Krevelen (MVK) mechanism dictates the performances of MoO_3 and molybdate-based catalysts in oxidation processes [1]. The incorporation of oxygen into hydrocarbons is due to oxygen atoms belonging to the outermost atom layer of the oxide lattice. For sake of clarity, we shall term these oxygen atoms “surface lattice oxygen atoms” (O_{sl}). Surface lattice oxygen atoms are not mere adsorbed oxygen species but they are part of the near surface layer of the bulk. Following the MVK concept, it could thus be speculated that the oxides with the highest oxidation state would bring the highest oxidation activities, because they possess more oxygen atoms that can be used for the hydrocarbon oxidation. But the activity of an oxide in oxidation reactions is also dictated by the energy needed to transfer their O_{sl} atoms to the hydrocarbon. This energy likely depends on the global oxidation state of the catalyst. It should thus be envisaged that the most efficient state of the catalyst for promoting oxidation reactions might not be the fully oxidized one.

Several investigations of selective oxidation processes have indeed suggested that a key to maximize the performances of oxide catalysts (mainly VPO, MoO_3 and molybdates) is to stabilize them in a slightly reduced state [2–7]. In the case of MoO_3, the presence of superficial Mo^{5+} species, i.e. Mo atoms with an oxygen vacancy in their coordination sphere, has a beneficial influence on the performances of the catalysts [4–7], and Mo sub-oxide phases are found in the bulk of active catalysts [3,4]. Nevertheless, several questions still remain unanswered concerning: the role of Mo^{5+} in the active sites and the mechanism by which Mo^{5+} species influence the reactivity of the active

---

* Corresponding author. Tel.: +32-10-47-36-65; fax: +32-10-47-36-49.
E-mail address: gaigneaux@cata.ucl.ac.be (E.M. Gaigneaux).

[1] He is research associate of the Belgian Fonds National de la Recherche Scientifique.

0920-5861/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2004.03.017

sites, the optimal concentration of Mo^{5+} species and their best location (surface or bulk), the role of sub-oxide phases and shear plane structures on the catalytic mechanism, in particular on oxygen mobility and exchangeability, the necessity to stabilize such features in the catalysts to obtain high oxidation performances, etc.

To shed some light on these aspects, the reaction of 2-butanol in the presence of oxygen was used as a probe of the influence of the reduction state of MoO_3-based catalysts on their behavior. In this reaction, 2-butanol reacts following two distinct routes. Dehydration to butenes happens on protonated superficial O_{sl} atoms acting as Brönsted acid sites, while oxidation also happens either to methyl-ethyl-ketone (MEK) through selective oxidative dehydrogenation or to combustion products [8]. The two routes differ by the fact that, in the oxidation route, O_{sl} atoms are transferred from the oxide surface to the alcohol following the MVK mechanism, while such transfer does not occur in the dehydration route. The comparison of the selectivity of the two routes thus constitutes a direct probe of the exchangeability of O_{sl} atoms and of the ability of the catalysts to perform oxidation processes.

The strategy of our work consisted in measuring the performances of MoO_3 catalysts in the reaction of 2-butanol in the presence of oxygen under conditions with different oxido-reduction strengths. The reduction state of MoO_3 was thus delicately tuned during the reaction following two approaches. First, the reaction was run with different ratios O_2:2-butanol in the gas feed. Second, MoO_3 was used in the reaction alone and in the presence of Sb_2O_4. This approach is based on the fact that Sb_2O_4 is able to keep Mo atoms in higher oxidation states during catalysis in the presence of oxygen [9]. The reduction state of the catalysts under the different conditions was systematically characterized by various physico-chemical techniques.

2. Experiments

2.1. Preparation of the catalysts

MoO_3 and Sb_2O_4 were synthesized following procedures described elsewhere [4]. This led to a fully oxidized Mo trioxide material as ascertained by X-ray diffraction (XRD, obtention of molybdite JCPDS file no. 05-0508, absence of Mo sub-oxide), X-ray photoelectron spectroscopy (XPS, more than 99 at.% of the superficial Mo is in the 6+ state) and confocal Raman microscopy (CRM, Mo is only present in the octahedral coordination). The specific area of the sample was $0.36\,m^2\,g^{-1}$. Concerning Sb_2O_4, the α-phase was obtained as ascertained by XRD (cervantite JCPDS file no. 11-0694). The specific area of the sample was around $1.5\,m^2\,g^{-1}$.

Two physical mixtures of the obtained MoO_3 and Sb_2O_4 powders were prepared with two different mass fractions of Sb_2O_4, namely 0.5 (mixture hereafter noted as 1/1) and 0.666 (mixture hereafter noted as 1/2). Both mixtures were obtained by delicately interdispersing the two oxides with a spatula, and without applying any further thermal or chemical treatment.

2.2. Catalytic activity measurements

The reaction of 2-butanol was conducted in a fixed bed microreactor at 493 K. The tests with the different catalysts were conducted at constant mass of MoO_3 (500 mg) in the reactor. The partial pressure of 2-butanol (Acros, 99%) was 70.8 mmHg for a total flow of gas He (Indugas, 99.995%) + O_2 (Indugas, 99.995%) of $70\,ml\,min^{-1}$. In order to tune the ratio O_2:2-butanol in the reaction feed, the flow of O_2 was adjusted between 0 and $39\,ml\,min^{-1}$, with correspondingly the flow of He adjusted to keep the total gas flow constant. O_2:2-butanol ratios investigated were 0, 0.25, 0.5, 0.75, 1, 2, 3, 4, 5 and 6.

2.3. Characterization

The catalysts were characterized before and after the catalytic tests by specific area measurements, XRD, XPS and CRM. XRD was carried out on a Siemens Kristalloflex D-5000 equipment in $\theta/2\theta$ mode using Cu Kα radiation for 2θ angles going from 5 to 70°. The scan rate was $0.45^\circ\,min^{-1}$. Specific area measurements were performed with a Micromeritics ASAP 2000 equipment. The analysis was based on the adsorption of Kr at 77 K after that the samples were degassed at 423 K and 0.3 Pa during 90 min. XPS was performed with an Axis Ultra spectrometer from Kratos working with a monochromatic Al Kα radiation. Mo 3d, O 1s, Sb 3d and C 1s bands and survey spectra were recorded. CRM was performed with a Labram spectrometer (Dilor) working with a He–Ne laser (632.8 nm) at 10 mW. Further details on XPS and CRM experiments and corresponding data treatments are provided elsewhere [10].

The oxidation (or reduction) state in the bulk and at the surface of the catalysts was evaluated on the basis of the presence and intensity of diffraction peaks typical of Mo sub-oxide phases (principally the peaks at 25.3 and 38.3° for Mo_9O_{26}—JCPDS file no. 12-0753, and at 33.9 and 46.7° for Mo_4O_{11}—JCPDS file no. 05-0337), of Raman peaks typical of tetrahedrally coordinated Mo species (principally the peak at $888\,cm^{-1}$ corresponding to the tetrahedral ν OMo_2 vibration), and of Mo^{4+} and Mo^{5+} contributions in the Mo 3d band (Mo $3d_{5/2}$ at about 230.4 and 232.0 eV, respectively; Mo^{6+} $3d_{5/2}$ being observed at 233.3 eV).

3. Results

Independent of the catalyst and the composition of the gas feed, 2-butanol only undergoes the dehydration and the total oxidation routes. But no MEK is formed. The evolution of the catalytic performances with the O_2:2-butanol ratio in

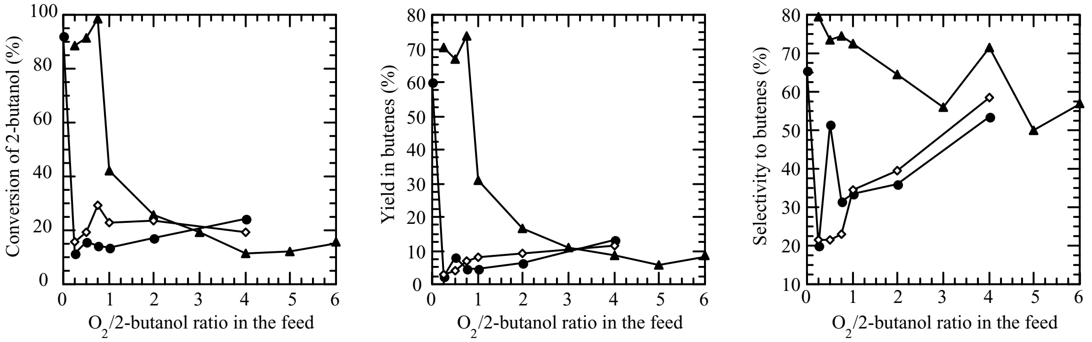

Fig. 1. Performances as a function of the O_2:2-butanol ratio in the gas feed: (▲) pure MoO_3; (●) mixture MoO_3/Sb_2O_4 1/1; (◇) mixture MoO_3/Sb_2O_4 1/2. Data correspond to performances measured after 10 h of reaction.

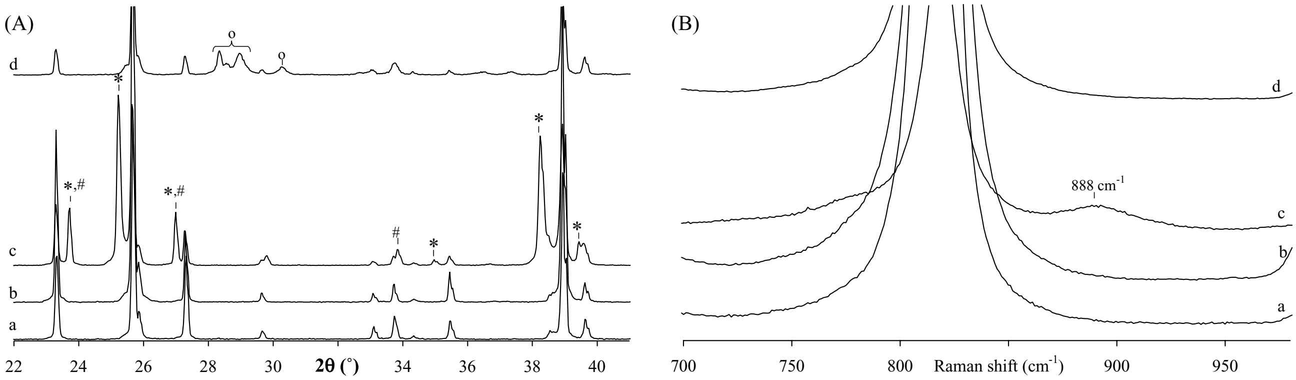

Fig. 2. (A) XRD and (B) CRM spectra of (a) fresh pure MoO_3, (b) pure MoO_3 after reaction under ratio O_2:2-butanol of 2, (c) pure MoO_3 after reaction under ratio O_2:2-butanol of 0.5, (d) the mixture MoO_3/Sb_2O_4 1/1 after reaction under the ratio O_2:2-butanol of 0.5: (∗) peaks of Mo_9O_{26}; (#) peaks of Mo_4O_{11}; (O) peaks of Sb_2O_4.

the reaction feed is plotted in Fig. 1 for pure MoO_3 and the mixtures with Sb_2O_4.

Pure MoO_3 does not undergo any modification when it is used in the reaction with O_2:2-butanol ratios higher than 0.75. But it clearly undergoes a reduction when it is used in the reaction with O_2:2-butanol ratios of 0.75 and lower. For the samples recovered after catalysis under these lower ratios, (i) XRD peaks of crystalline Mo_9O_{26} and Mo_4O_{11} phases are found. Their intensities grow when the O_2:2-butanol ratio decreases, and correspondingly, the peaks of MoO_3 vanish (Fig. 2A). (ii) Raman peaks typical of octahedrally coordinated Mo are less intense. As a counterpart, the peak at 888 cm^{-1} typical of tetrahedrally coordinated Mo appears (Fig. 2B). (iii) The contribution of Mo^{6+} species drops below 70% of the total superficial Mo, and those of Mo^{5+} and Mo^{4+} reach about 30 and 4%, respectively (Fig. 3). Independently of the gas feed composition, specific areas for pure MoO_3 after reaction do not present any significant difference from the fresh sample. All data remain in the range $0.4 \pm 0.1\,m^2\,g^{-1}$ and can thus not be evoked to account for any difference of performances.

As expected, Sb_2O_4 inhibits the reduction of MoO_3 during catalysis. For either mixture, diffraction peaks of Mo sub-oxides, Raman peaks of tetrahedrally coordinated Mo species and superficial Mo^{4+} species are never detected provided that O_2 is present in the reaction feed. Superficial Mo^{5+} species are detected with an increasing contribution when the ratio O_2:2-butanol decreases. As for pure MoO_3, specific areas for both mixtures after reaction do not present any significant difference from the fresh samples. All data remain in the range $1.6 \pm 0.1\,m^2\,g^{-1}$ for the mixture 1/1 and in the range $1.7 \pm 0.1\,m^2\,g^{-1}$ for the mixture 1/2 and can thus not be evoked to account for any difference of performances.

4. Discussion

No direct interpretation of the data shown in Fig. 1 could be found. The reason for that is likely that the observed variation of catalytic performances is induced by the simultaneous effect of two parameters, namely the ratio O_2:2-butanol in the feed and the proportion of Sb_2O_4 in the catalyst. A multi-variate approach was thus adopted. As the evoked parameters are both expected to influence the oxidation state of the catalysts at work, the performances were plotted versus the characterization data. Interesting results came from the correlation of the performances with the extent of the Mo^{5+} contribution at the catalyst surface.

Fig. 4 reveals the existence of two very different catalytic behaviors depending on the extent of the superficial Mo^{5+} contribution. Domain I gathers catalysts stabilized with a

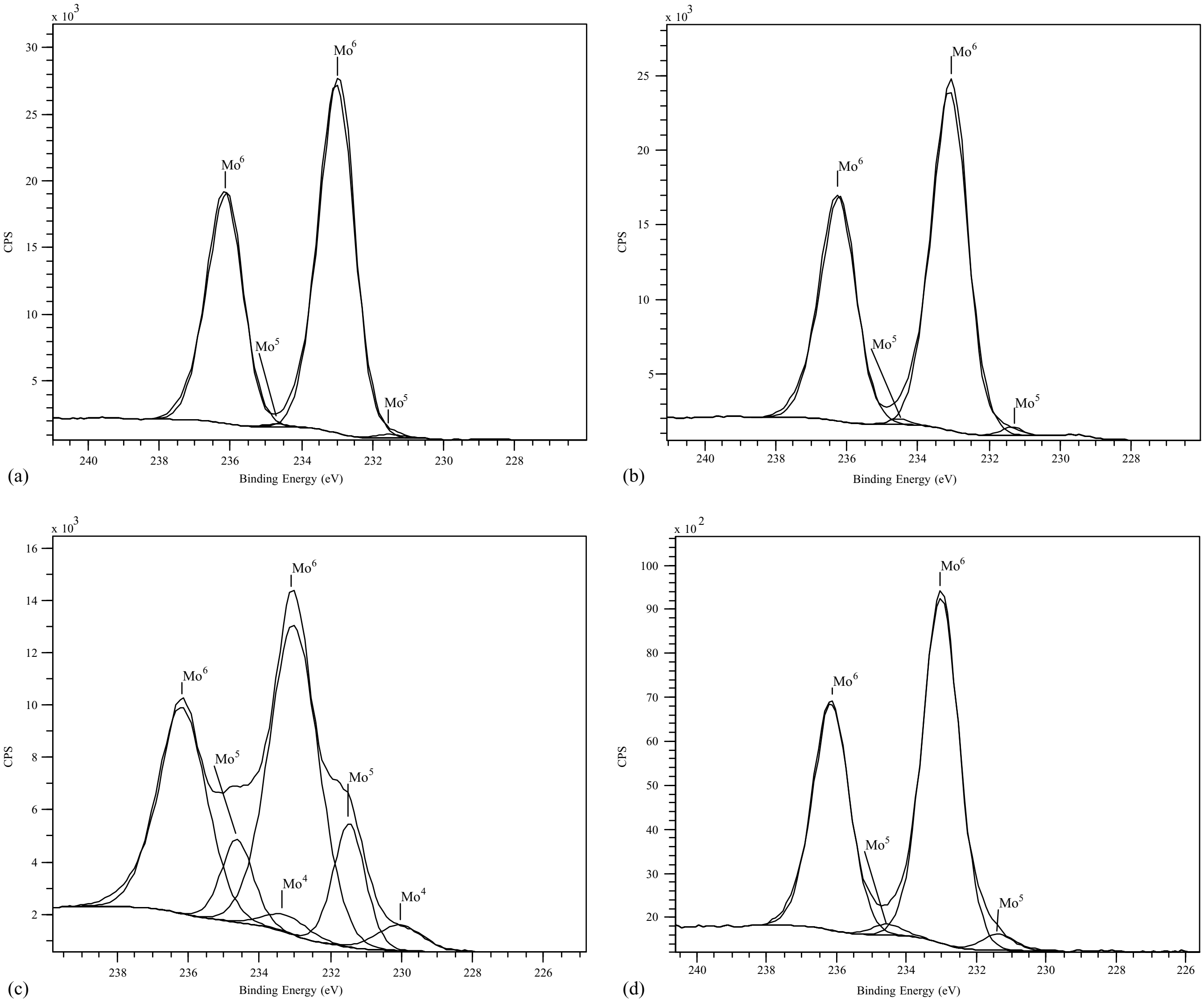

Fig. 3. Decomposition of the Mo 3d band (XPS) to Mo^{n+} species for: (a) fresh pure MoO_3, (b) pure MoO_3 after reaction under ratios O_2:2-butanol of 2, (c) pure MoO_3 after reaction under ratio O_2:2-butanol of 0.5, and (d) the mixture MoO_3/Sb_2O_4 1/1 after the reaction under the ratio O_2:2-butanol of 0.5.

Mo^{5+} contribution up to 11% of the total superficial Mo. Other features are a Mo^{4+} contribution below 1% and, the absence of Mo sub-oxide phases in the bulk and of tetrahedrally coordinated Mo species. The conversion of 2-butanol remains low and is not significantly affected by a modification of the extent of the Mo^{5+} contribution at the surface of the catalysts. The yield to butenes decreases with the Mo^{5+} contribution increasing. But the most striking effect is the dramatic drop of selectivity to butenes undergone by the catalysts of domain I when the Mo^{5+} contribution at their surface increases. In other words, MoO_3 preferentially catalyzes the dehydration of 2-butanol when it has its surface in a near-fully oxidized state, but it catalyzes the oxidation of 2-butanol when its surface is slightly reduced.

Compared to domain I, domain II obviously corresponds to catalysts with a very different catalytic behavior. The features of the catalysts gathered in domain II are: more than 24% of the superficial Mo in the Mo^{5+} state and a Mo^{4+} contribution higher than 2%, the presence of sub-oxide phases in their bulk (Mo_9O_{26} and/or Mo_4O_{11}) and of tetrahedrally coordinated Mo. When the contribution of Mo^{5+} species increases, conversion of 2-butanol and yield in butenes slightly increase, and the selectivity to butenes remains high and constant. The increase of conversion and yield is nicely correlated with the amount of sub-oxide phases present in the samples as estimated from XRD data (correlation not shown here).

These results shed light on the nature and working mechanism of the active sites of MoO_3 involved in the reaction of 2-butanol in the presence of oxygen. Mo atoms stabilized at the surface of the catalyst in the 5+ state do not have the same effect on catalysts with a fully oxidized MoO_3 bulk, or on catalysts with their bulk at least partially stabilized during the reaction in a sub-oxide MoO_{3-x} state. The catalysts

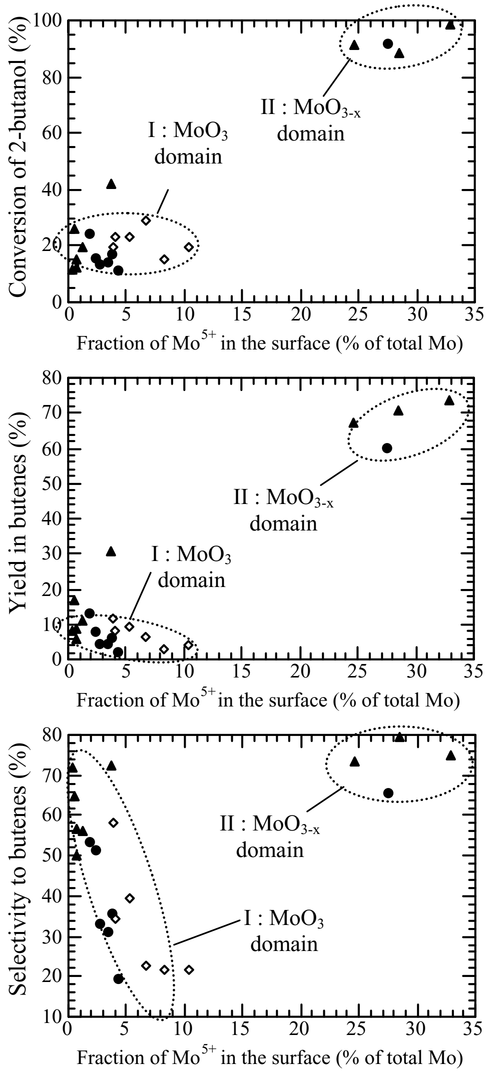

Fig. 4. Performances as a function of the fraction of Mo^{5+} species at the surface of the catalysts. Same symbols as for Fig. 1.

in domain II have a strong tendency to perform the dehydration of 2-butanol, but not to oxidize it. These catalysts thus have their surface lattice oxygen atoms almost not available for the MVK mechanism. Our work shows that the Brönsted acid sites of the catalysts with a MoO_{3-x} sub-oxide bulk are likely located on Mo^{5+} species. Oxygen atoms associated to these sites only have a weak tendency to be transferred from the catalytic surface and inserted into hydrocarbons. They are likely strongly bound to Mo and must thus be regarded as having only a poor efficiency in oxidation.

Concerning the catalysts of domain I, namely catalysts with a fully oxidized MoO_3 bulk, the decrease of the yield to butenes when the Mo^{5+} contribution increases at the expense of the Mo^{6+} species shows that Brönsted acid sites of these catalysts are located on Mo atoms in the 6+ state. But the drop of selectivity to butenes when the Mo^{5+} contribution increases indicates that the oxygen atoms associated to these Brönsted sites have their selectivity to the dehydration decreased in the neighborhood of Mo^{5+} atoms. O_{sl} are thus less strongly bound to a Mo^{6+} atom bridged to a Mo^{5+} atom than it is to a Mo^{6+} atom bridged to another Mo^{6+} atom. Such difference of bound strength could be tentatively interpreted at the atomic scale as due to a partial delocalisation of the unappariate electron of Mo atoms in the 5+ state and the resulting slightly negative charge on the oxygen atom bound to a neighbor Mo atom in the 6+ state. However, alternative and/or complementary interpretations could be evoked at a more macroscopic scale such as the high flexibility of sub-stoichiometric, eventually amorphous, oxide surfaces. Such flexibility makes slightly reduced oxides “breathing” and exchanging oxygen atoms more easily and additionally eventually induces the reconstruction of initial superficial crystalline structures to others with different oxygen species exposed, with corresponding likely different oxidant/exchangeable characters and selectivities [10].

5. Conclusion

Our work confirms that the extent of the reduction of MoO_3-based catalysts has a deep influence on their performances in processes involving oxygen. The most striking is the fact that depending on the manner by which this reduction is accommodated, the catalysts change of behavior and have their efficiency to participate in the MVK mechanism completely modified. Reduction accommodated through the stabilization of Mo sub-oxide phases in the bulk is shown to be detrimental in terms of oxygen exchangeability. Such catalysts may activate reactions involving surface lattice oxygen atoms without incorporation of these atoms into the reactant, like the dehydration on Brönsted sites, but they are poorly active in oxidation MVK processes. At the opposite, a slight reduction localized at the surface of a fully oxidized MoO_3 bulk through the presence of Mo^{5+} species increases the exchangeability of surface lattice oxygen atoms. Such catalysts activate with high efficiency the incorporation of oxygen into hydrocarbons through the MVK oxidation mechanism. Our results suggest that bulk Mo sub-oxides are not the absolute solution to promote oxidation processes. They also points to a paradox of heterogeneous catalysis that, despite they possess less oxygen atoms, slightly reduced MVK catalytic surfaces are more oxidant than fully oxidized ones.

Acknowledgements

The authors gratefully thank Prof. B. Delmon and Dr. J. Rouchaud for the fruitful discussions about the data presented in this paper. This work was supported by the Fonds National de la Recherche Scientifique (FNRS) of Belgium, the Fonds Spécial de la Recherche (FSR) of the Catholic University of Louvain, and the Région Wallonne of Belgium.

References

[1] P. Mars, D.W. van Krevelen, Chem. Eng. Sci. 3 (1954) 41.

[2] K. AitLachgar, A. Tuel, M. Brun, J.M. Hermann, J.M. Krafft, J.R. Martin, J.C. Volta, M. Abon, J. Catal. 177 (1998) 224.

[3] T. Ressler, J. Wienold, R.E. Jentoft, F. Girgsdies, Eur. J. Inorg. Chem. 2 (2003) 301.

[4] E.M. Gaigneaux, P. Ruiz, B. Delmon, Catal. Today 32 (1996) 37.

[5] E.M. Gaigneaux, P. Ruiz, E.E. Wolf, B. Delmon, Appl. Surf. Sci. 121/122 (1997) 552.

[6] E.M. Gaigneaux, M.J. Genet, P. Ruiz, B. Delmon, J. Phys. Chem. B 104 (2000) 5724.

[7] E. Godard, E.M. Gaigneaux, P. Ruiz, B. Delmon, Catal. Today 61 (2000) 279.

[8] Y. Okamoto, K. Oh-Hiraki, T. Imanaka, S. Teranishi, J. Catal. 71 (1981) 99.

[9] L.T. Weng, B. Delmon, J. Mol. Catal. 52 (1989) 349.

[10] F. Dury, E.M. Gaigneaux, P. Ruiz, Appl. Catal. A: Gen. 242 (2003) 187.