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The deoxygenation of benzoic acid as a probe reaction to determine the impact of superficial oxygen vacancies (isolated or twin) on the oxidation performances of Mo-based oxide catalysts

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Abstract

The deoxygenation of benzoic acid (DBA) is a probe reaction of the organisation of oxygen vacancies at the surface of molybdenum based oxide catalysts. In the present work, the DBA was used in coupling with the selective oxidation of propylene so that it could offer an insight into the nature of oxygen vacancies involved in the later reaction. By correlating the superficial oxidation state of the catalytic elements measured by X-ray photoelectron spectroscopy with the information provided by the DBA probe reaction, it was possible to progress in the description of the atomic scale architecture of the oxidation sites at work. Sites bringing boosted performances in the oxidation of propylene are those which are slightly reduced thanks to the presence of single (isolated) oxygen vacancies. Conversely, twin oxygen vacancies do not participate in the oxidation reaction.

Keywords: Benzoic acid; Oxidation; Mo-based oxides; Oxygen vacancies

1. Introduction

Many authors have reported that alkane/alkene selective and total oxidation reactions take place on different catalytic sites [1,2]. Among the numerous proposed hypotheses, it has been suggested that the presence of reduced sites at the catalytic surface and thus the presence of oxygen vacancies, play a crucial role in the reactivity and selectivity of oxide catalysts [3,4].

In order to progress in the description of the atomic scale architecture of the oxidation sites at work, precisely to determine the nature of the oxygen vacancies (isolated or twin vacancies) promoting their performances, we have developed a new probe reaction for the real-time characterization of oxide catalysts in the selective oxidation reactions, namely of these catalysts ‘‘at work’’. The deoxygenation of benzoic acid (DBA) in the presence of hydrogen is reported as an adequate reaction to probe the organization of oxygen vacancies at the surface of oxide catalysts. According to these studies [5,6], (i) an oxide surface with isolated oxygen vacancies selectively produces benzaldehyde, (ii) twin oxygen vacancies selectively produce toluene, while (iii) benzene can be formed at the surface of the catalyst without the presence of any oxygen vacancies. Our innovative approach is to use benzoic acid in replacement of molecular oxygen in the selective oxidation of propylene. In such coupling, the oxygen atoms involved in the oxidation of the hydrocarbon thus come, indirectly through the superficial lattice of the oxide, from the acid molecule. As being carried out at the same time on the same catalyst, the two coupled reactions will simultaneously bring data concerning the oxidation performances (oxidation of propylene part of the coupling) and concerning the nature of oxygen vacancies present at the surface (deoxygenation of the acid part of the coupling). The correlation of the two sets of simultaneous information thus allows to progress towards the identification of the type of oxygen vacancies having an impact on the oxidation performances of the investigated catalysts. Fig. 1 illustrates this approach.

The coupling between propylene oxidation and the deoxygenation of benzoic acid was demonstrated to occur on a $CoMoO_4$ catalyst. In a recent work [7], we have established that CO_2 formation is closely proportional to the benzene and benzaldehyde productions. Although a part of carbon dioxide directly comes from the transformation of the acidic function of

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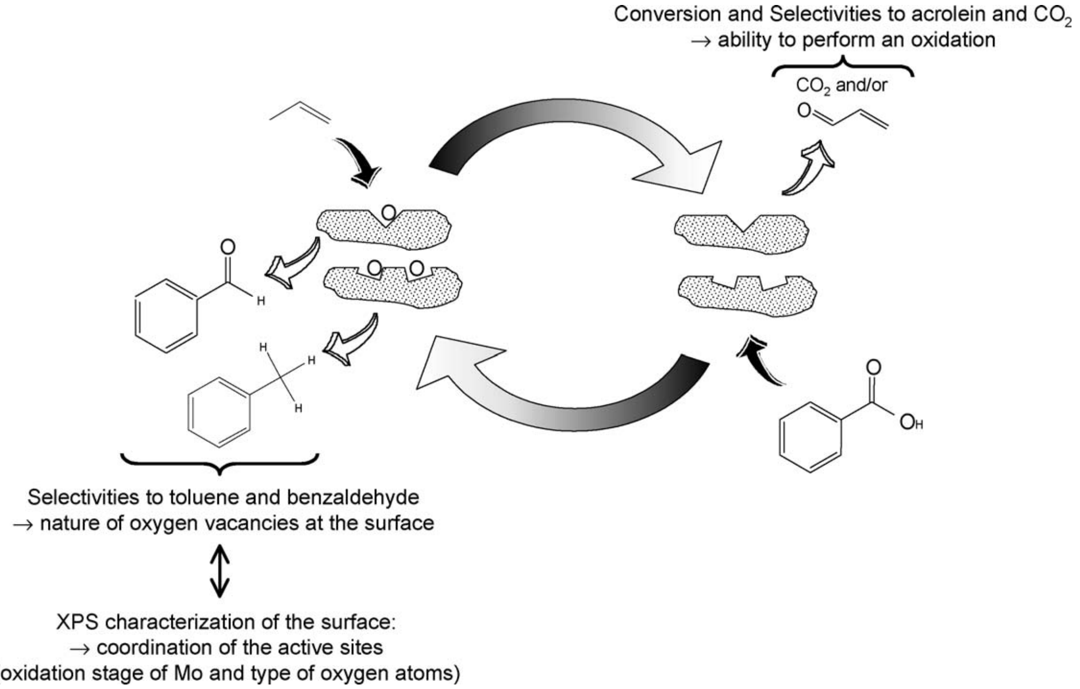

Fig. 1. Schematic representation of the concept of coupling the deoxygenation of benzoic acid and the oxidation of propylene at the surface of a catalyst possessing either single (isolated) oxygen vacancies or twin oxygen vacancies. The different sets of data correlated in our approach are indicated.

benzoic acid leading to the formation of benzene, there is another origin for a small amount of CO_2. Our hypothesis is that such a small amount is formed on the same catalytic sites as those where benzaldehyde is formed, demonstrating in this way the coupling between the oxidation of propylene and the DBA.

In the present work, the performances of about one hundred Mo-based oxide catalysts have been measured in the deoxygenation of benzoic acid either in the presence of hydrogen or in coupling with the oxidation of propylene. In addition to these measurements, the systematic characterization of the about one hundred corresponding tested samples by X-ray photoelectron spectroscopy allows us to use statistical tools in order to correlate some surface properties, like oxidation states of the active elements, with the catalytic activity in the deoxygenation of benzoic acid and the oxidation of propylene. This strategy gives us the opportunity to describe the active sites responsible for the activity in the oxidation reaction, in particular to point to the type of oxygen vacancies having an influence on the performances, as well as to their environment on the surface (oxidation state of active Mo atoms and coordination, type of oxygen atoms).

2. Experimental and methods

2.1. Catalysts preparation

Several Mo based oxide catalysts were synthesized: molybdenum (sub)oxides (MoO_3, Mo_8O_{23}, Mo_9O_{26}, Mo_4O_{11} and MoO_2) and metal molybdates ($NiMoO_4$, $Bi_2Mo_2O_9$, Bi_2MoO_6, $Bi_2Mo_3O_{12}$, $Fe_2Mo_3O_{12}$ and $CoMoO_4$).

MoO_2 (Aldrich, 99%) was pre-treated under a 60 ml min^{-1} flow of 5% H_2 in nitrogen (Indugas, 99.95% pure) at 723 K during 1 h. Similarly, MoO_3 (Aldrich, 99.5%) was oxidized in a 60 ml min^{-1} flow of pure oxygen (Indugas, 99.995% pure) at 623 K during 2 h. Concerning the synthesis of Mo suboxides, predetermined amounts of ‘‘reduced’’ MoO_2 and ‘‘oxidized’’ MoO_3 were closely mixed in an agathe mortar during 20 min and introduced in a specific quartz reactor between two walls of quartz wool. The quartz reactor was then sealed under a vacuum of 10^{-3} Pa. The cell was then heated at a specific temperature depending on the final phase desired [8–12]. The molar ratio between the two precursor compounds was adjusted to obtain the appropriate mean oxidation state in the final phase.

Metal molybdates were prepared by the ‘‘citrate method’’ using ammonium heptamolybdate as the first precursor and the nitrate of the corresponding metal as second precursor. They were dissolved separately in 100 ml of distilled water at room temperature (solutions A and B). The mixture of the solutions A and B was adjusted to pH 1 with nitric acid (Aldrich, 25%). Then, a citric acid solution (Merck, 99%) was added drop-wise to the precursors solution. The amount of citric acid was calculated in order to achieve the charge balanced complexation of the metallic species in solution with citrate anions, so avoiding the occurrence of any precipitation. Afterwards, water was evaporated at 310 K under reduced pressure and the obtained solid was dried overnight at 353 K under vacuum. The dried solid was calcined in air first at 573 K during 20 h then a second time at 723 K during 20 h.

2.2. Catalytic activity measurements

Deoxygenation of benzoic acid was performed at atmospheric pressure in a stainless steel fixed bed microreactor. Helium (Indugas, 99.996%) was used as carrier gas. Benzoic acid was introduced in the feed by first flowing the carrier gas through a saturator filled with a bed of solid benzoic acid flakes diluted with carborundum grains then flowing the obtained saturated gas in the reactor. The saturator was maintained at the temperature of 371 K corresponding to a concentration of benzoic acid of 644 ppm. Experiments were thus performed with the gas mixture containing either 574 ppm benzoic acid after dilution with 50,000 ppm hydrogen (Indugas, 99.95%), either 574 ppm benzoic acid after dilution with 167,000 ppm (16.7%) of propylene (Indugas, 99.8%), or 635 ppm benzoic acid after dilution with 318 ppm of propylene in Helium (Indugas, 2.01 vol.% of propylene in He). Total flow was adjusted to 100 ml min^{-1}. All the catalytic tests were performed at 723 K for 10 h. Reactants and products were analysed by gas chromatography.

2.3. Characterization of the Co–Mo catalyst

The catalysts were characterized before and after the catalytic tests by X-ray photoelectron spectroscopy (XPS). An Axis Ultra spectrometer from Kratos was used with a monochromatic Al Kα radiation (15 kV, 10 mA), setting the bias of the charge compensation device provided by the manufacturer at −1.8 V. The absence of charging effect was ascertained by checking for each samples the identity of the kinetic energy measured for the C 1s photoelectrons at the beginning and at the end of the analysis. Pass energy for the analyser was 40 eV and the spot size was 700 μm × 300 μm corresponding to a full width at half maximum (FWHM) of 0.92 eV for the Ag $3d_{5/2}$ band of a freshly sputtered silver standard. The precision on the energy measurements is of about 0.2 eV. The binding energies were calibrated by fixing the *C*–(C, H) contribution of the C 1s adventitious carbon at 284.8 eV. Peaks were considered to be combinations of Gaussian and Lorentzian functions in a 70/30 ratio, working with a linear baseline (following recommendations from the manufacturer). For the quantification of the elements, sensibility factors provided by the manufacturer were used. C 1s, O 1s, Mo 3d were systematically recorded in all the samples. Ni 2p, Co 2p, Bi 4f and Fe 2p were also measured according to the sample. The absence of contamination in the analyzed surfaces by undesired elements was checked for every sample by ascertaining that a survey spectrum only exhibited peaks of the expected elements. Decomposition of the Mo 3d doublets to Mo^{n+} species was done by fixing as constraints an energy difference of 3.13 eV [13], and an area ratio of 2/3 between the Mo 3d3/2 and the Mo $3d_{5/2}$ bands. As another constraint, FWHM's of the two contributions of the Mo 3d doublet were kept identical during the whole decomposition process. The validity of the decomposition was ascertained by checking that the binding energies for the different Mo^{n+} eventually found fitted with those commonly accepted and that an energy gap around 1.2 eV existed between corresponding bands of two successive Mo^{n+} species. Oxygen (O 1s) and carbon (C 1s) contributions were also decomposed in several species with their respective FWHM's kept identical as only constraint.

2.4. Data treatment

Raw data, i.e. all the results of the catalytic tests and their corresponding XPS measurements, were analysed by statistical

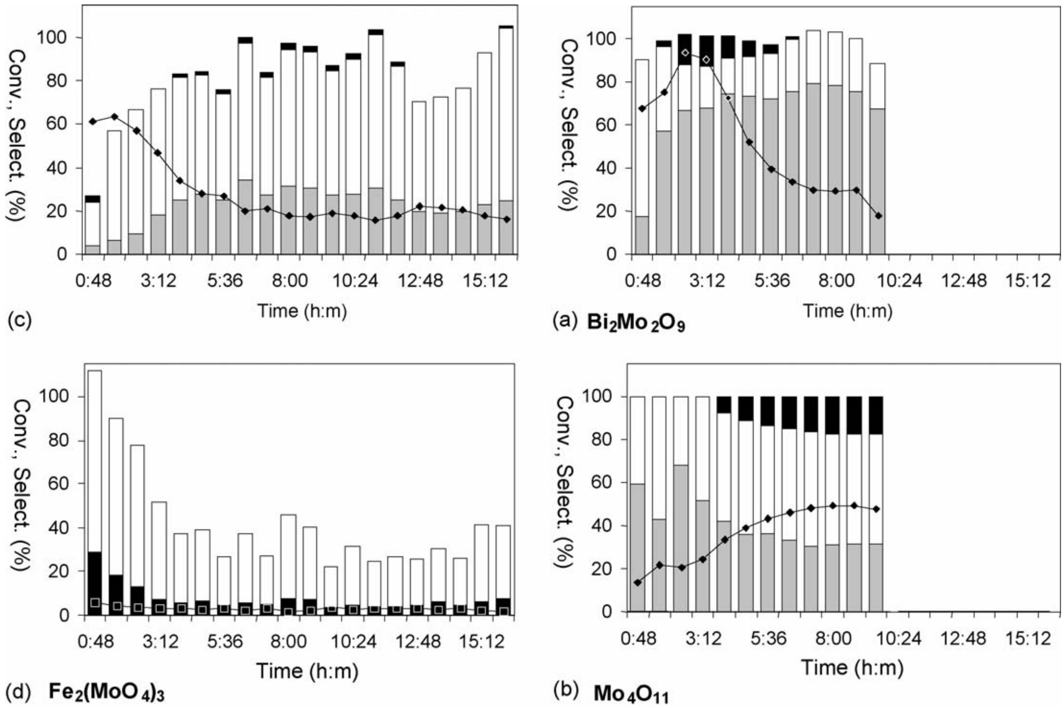

Fig. 2. (a) Evolution with time on stream of the conversion of benzoic acid (◆) and selectivities in benzaldehyde (grey bars), toluene (black bars) and benzene (white bars) obtained at 723 K on $Bi_2Mo_2O_9$ in the presence of hydrogen. (b) Same data collected on Mo_4O_{11}. (c) Evolution with time on stream of the conversion of benzoic acid and selectivities in benzaldehyde, toluene and benzene (same code of colors) obtained at 723 K on $Fe_2(MoO_4)_3$ in the presence of propylene. (d) Evolution with time on stream of the conversion of propylene (☐) and selectivities in CO (black bars) and CO_2 (white bars) obtained at 723 K on $Fe_2(MoO_4)_3$. Data presented in (c) and (d) are collected simultaneously in an experiment consisting in the coupling of the deoxygenation of benzoic acid and of the oxidation of propylene.

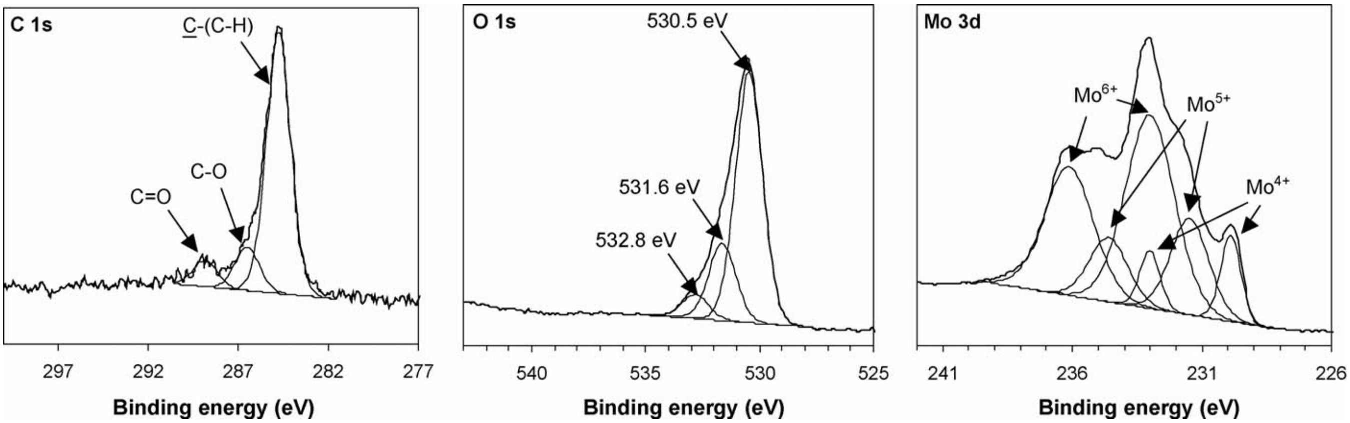

Fig. 3. Typical X-ray photoelectron spectroscopy results obtained on molybdenum based oxide catalysts.

methods using Pearson product–moment correlation coefficient (Eq. (1)) and a commercial software (STATISTICA)

$$r = \frac{\sum (X - \overline{X})(Y - \overline{Y})}{N \sigma_X \sigma_Y} \tag{1}$$

where $\overline{X}$, $\overline{Y}$ are the means, σ_X, $\sigma_Y$are the standard deviations and N the number of considered samples. According to this mathematical definition (Eq. (1)), r will be equal to zero if no relation can be found between two variables X and Y. A negative value of r means that when X increases, Y decreases at the same time (or vice versa). On the contrary, a positive value of r means that X and Y increase (or decrease) together. The confidence function, or p-level, was also selected as it reflects the reliability of a considered relation between variables: a relation becomes less reliable when its p-level increases. The p-level is automatically delivered by the software. A p-level of 0.05 is usually admitted as the upper-limit for considering a relation as reliable.

3. Results

More than 100 catalytic tests were performed using molybdenum based oxide catalysts in the presence of either hydrogen or propylene as reducing gas. Previous publications indicate the obtained catalytic data [6,7]. In order to illustrate the type of results collected, we present here the data from three different tests (Fig. 2). A first category of catalytic tests is illustrated on the basis of those performed with $Bi_2Mo_2O_9$ (Fig. 2a) and Mo_4O_{11} (Fig. 2b) and is related to the use of hydrogen as the reducing gas. One can summarize the corresponding observations like this: (i) three products coming from the deoxygenation are identified: benzene as the main product, benzaldehyde and toluene, (ii) the sum of the selectivities to these three products reaches 100% in most of the cases. A second category of catalytic tests is related to the use of propylene as the reducing gas and is illustrated on the basis of a test performed with $Fe_2(MoO_4)_3$ (Fig. 2c and d). One notices that: (i) benzaldehyde, toluene and benzene are the main products obtained from the deoxygenation of benzoic acid (Fig. 2c) but sometimes an additional unidentified molecule is detected, (ii) the sum of the selectivities to the three identified products thus does not reach 100% when the unknown product is detected, and (iii) concerning the oxidation of propylene (Fig. 2d), CO and CO_2 are produced. No acrolein is detected as due to two technical limitations: (i) the high temperature (>405 K) maintained in all the catalytic system to avoid the solidification of the benzoic acid in the lines ($MP_{benzoic\ acid}$ = 394 K) is sufficient to induce the thermal degradation or the polymerisation of the acrolein, (ii) the maximum concentration of acrolein potentially produced in this system is below the threshold of the GC apparatus (2000 ppm). As a consequence, the carbon balance is not complete [7].

The second series of data consists in the statistical results based on all the XPS and catalytic results collected when performing the reaction on molybdenum based oxides catalysts. As examples of our data, we report typical X-ray photoelectron spectroscopy results in Fig. 3. C 1s, O 1s and Mo 3d contributions are decomposed with respect to the rules fixed in Section 2. Concerning the peaks related to Fe, Co, Ni and Bi, for none of the samples, no significant difference in the binding energies measured before and after catalytic tests were observed: respectively the binding energies measured for Fe 2p, Co 2p, Ni 2p and Bi 4f were 711, 781, 856 and 160 eV.

Three components are found in the carbon contribution. The main peak is centred at 284.8 eV and corresponds to the *C*–(C, H) contribution. The second peak is centred at 286.5 eV and is generally attributed to carbon atoms simply bonded to oxygen atoms (*C*–O). The last component is located at 288.8 eV and can be attributed to carbon atoms doubly bonded with an oxygen atom (*C*=O) [14,15]. Fig. 3 also shows the oxygen spectrum of the same sample. The oxygen line shape seems asymmetrical and could only be fit with three components with an identical FWHM. The components are centred at 530.5 eV (O_I), 531.6 eV (O_{II}) and 532.8 eV (O_{III}). The last XPS spectrum reported in Fig. 3 concerns the molybdenum contribution. The complex shape observed for this element is due to two factors: (i) Mo 3d is a doublet and, (ii) molybdenum atoms are present at the surface of the sample in three oxidation states (Mo^{6+}, Mo^{5+} and Mo^{4+}). The decomposition shown here fits quite well with the experimental shape. The $3d_{5/2}$ contribution of each oxidation stage has respectively a binding energy of 233.0, 231.5 and 299.9 eV. This kind of results is found in almost all

Table 1

Pearson product–moment correlation coefficients at p-level <0.05 ($N = 104$) between the different components of C 1s and O 1s

Pearson product–moment correlation coefficients (r)	C 1s (C=O)	C 1s (C–O)	C 1s (*C*–(C, H))
O1s (532.8 eV)–O_{III}	*−0.23*	*−0.25*	*0.28*
O1s (531.6 eV)–O_{II}	0.06	0.06	−0.06
O1s (530.5 eV)–O_{I}	0.04	0.06	−0.06

Italic values mark the significant coefficients according to the p-level.

Table 2

Pearson product–moment correlation coefficients at p-level <0.05 ($N = 104$) between the different components of Mo 3d and O 1s

Pearson product–moment correlation coefficients (r)	O1s (532.8 eV) O_{III}	O1s (531.6eV) O_{II}	O1s (530.5 eV) O_{I}
Mo^{6+}	*−0.75*	*−0.64*	*0.72*
Mo^{5+}	*0.59*	*0.41*	*−0.50*
Mo^{4+}	*0.75*	*0.69*	*−0.76*

Italic values mark the significant coefficients according to the p-level.

Table 3

Pearson product–moment correlation coefficients at p-level < 0.05 ($N = 57$) between the different components of Mo 3d, O 1s and the concentrations in benzaldehyde, toluene and benzene

Pearson product–moment correlation coefficients (r)	Benzaldehyde concentration	Toluene concentration	Benzene concentration
Mo^{6+}	0.15	*−0.30*	*0.28*
Mo^{5+}	−0.01	−0.17	−0.26
Mo^{4+}	−0.17	*0.46*	*−0.27*
O1s (532.8 eV)–O_{III}	−0.07	*0.26*	−0.08
O1s (531.6 eV)–O_{II}	−0.20	*0.45*	−0.18
O1s (530.5 eV)–O_{I}	0.16	*−0.43*	0.16

Italic values mark the significant coefficients according to the p-level.

the molybdenum based catalysts analysed before and after catalytic tests.

Benefiting from the large number of data, we sought correlations between the different variables like the molybdenum oxidation state, the concentration of products derived from the benzoic acid or the three oxygen "species" detected by XPS. Hereafter, we report three tables providing interesting insights towards the atomic description of the active oxidation site on molybdenum based catalysts. It is well-known that the O 1s shift observed in Fig. 3 could be the consequence of the presence of an oxygenated carbonaceous content at the surface of the samples. Therefore we have first checked the existence of some correlations between the C 1s and O 1s (Table 1). Three coefficients were found to be significant. A positive linear dependence is found between the *C*–(C, H) component and O_{III}. Two negative linear dependences exist respectively between the O_{III} and the *C*=O or *C*–O components. The other combinations do not indicate any reliable dependence between these variables. In a similar way, we have tested the correlations between the Mo 3d and O 1s components (Table 2). It appears that the oxygen peak found at 530.5 eV (O_I) is positively correlated with the presence of Mo^{6+} and negatively correlated with the other molybdenum species. On the contrary, O_{II} and O_{III} are positively correlated with the reduced molybdenum species (Mo^{5+} and Mo^{4+}) while a negative correlation is highlighted with the fully oxidized Mo^{6+} molybdenum atoms. In a third step, we tried to check the existence of correlations between the products formed during the catalytic tests, namely benzaldehyde, toluene and benzene, and the oxidation state at the surface of the molybdenum based oxide catalysts (Table 3). Several important facts are observed: (i) the benzene concentration is positively linked with the atomic percentage of Mo^{6+} and negatively linked with the reduced molybdenum species, (ii) the toluene concentration is positively correlated with the Mo^{4+} and negatively correlated with the Mo^{6+}, (iii) a poor dependence is suspected between the benzaldehyde concentration and the atomic percentage of Mo^{6+}, (iv) a weak negative correlation is also suggested between the benzaldehyde concentration and the atomic percentage of Mo^{4+}, (v) no correlation exists between the benzaldehyde concentration and the atomic percentage of Mo^{5+} as suggested by $r = -0.01$.

4. Discussion

The statistical analysis of the results highlights several reliable negative or positive correlations between spectroscopic and catalytic data. But another interesting point is the asymmetry of the oxygen peak on the high binding energy side and its relation with the different molybdenum oxidation levels. After repeating the analyses and checking that all the precautions were taken (absence of charging effect and contamination by undesired elements), we have validated these results. Such an observation is possible thanks to the excellent resolution in the binding energy scale (about 0.2 eV) and sensitivity of the available XPS apparatus. Concerning the three oxygen components, we have first checked the independence between the carbon contributions and the oxygen. Indeed, the presence of oxygen-containing carbon deposit (coke) or some organic molecules could explain the oxygen chemical shift. This is commonly observed on several biological and synthetic organic compounds like glucose 6-phosphate [14] or polycarbonate [15]. In the present case, Table 1 shows that one correlation exists between the most shifted oxygen component (O_{III}, binding energy of 532.8 eV) and each component of the C 1s. Whereas these are significant, they are not reflecting some direct chemical relationships: the best demonstration is provided by the positive correlation between O_{III} and C 1s (*C*–(C, H)). Such a positive correlation has no significance since the C 1s contribution at 284.8 eV is the well-known binding energy of a carbon atom bonded with another carbon atom or a hydrogen atom but not with an oxygen atom [14,15]. So, this relation is indirect and could indicate that both C 1s (*C*–(C, H)) and O_{III} are correlated, but in an independent manner, with a third identical parameter.

Now that we have discarded the link between the oxygen and the carbon content, the alternative way that we have suggested in Table 2, i.e. the correlations between the oxidation levels of molybdenum and the chemical shifts of oxygen, can be considered as a real property of the molybdenum based oxide catalysts and not as an artefact. It is clearly suggested that the most oxidized molybdenum species (Mo^{6+}) are only bonded with the ‘‘normal’’ oxygen component found at 530.5 eV (O_I) while the Mo^{5+} and Mo^{4+} are both linked with the presence of the O 1s components at 531.6 eV (O_{II}) and 532.8 eV (O_{III}).

According to Dupin et al. [16], O_I can be considered as an oxygen with a strong ionic character, namely O^{2-} bonded with a metal atom fully coordinated. Moreover, the work of Jimenez et al. [17] suggests that O_{II} and O_{III} could be the signature of some oxygen atoms bonded with metal atoms whose coordination is lower. Thanks to the new probe reaction that we have developed, we are able to confirm this hypothesis. Indeed, the correlations provided in Table 3 reveals that the O_{II} and O_{III} are both significantly linked with the toluene concentration. According to the principle of our probe reaction, the production of toluene occurs at the surface of the oxide catalysts presenting twin oxygen vacancies, namely two oxygen vacancies close to each other at a distance of around 2 Å. Thus, the transformation of benzoic acid to toluene occurs by filling two superficial oxygen vacancies with the two oxygen atoms coming from a single benzoic acid molecule. The obvious corollary to this mechanism is that a molybdenum atom near of the oxygen vacancies has two oxygen atoms missing in its surrounding. Such atom is thus coordinatively unsaturated compared to molybdenum atoms related to a fully oxidized surface whose characteristics are: (i) the +6 oxidation level, (ii) the correlated O_I component and (iii) the correlated concentration of benzene whose formation does not necessitate the presence of oxygen vacancies.

Our work clearly confirms that such a coordinatively unsaturated molybdenum atom induces a chemical shift of the O 1s. In that precise case, the chemical shift towards the higher binding energy reflects the impoverishment of the core electron density around the oxygen atoms. It is related to the lower coordination state detected by the formation of toluene and characterized by the molybdenum atoms in the +4 and +5 oxidation levels (Fig. 4). These correlation suggests that when a +6 molybdenum atom looses two oxygen atoms in its coordination sphere, it will consequently attracts more core electrons of the four remaining oxygen atoms. As a result of this phenomenon, the molybdenum atom will switch to a lower oxidation state. The oxygen in the coordination sphere have thus less electrons. The remaining core electrons are more retained by the atom nucleus, so explaining why the core electrons appear to higher binding energy. This mechanism involves two consequences: (i) the Mo–O bond is thus less polarised, i.e. the charge of the oxygen atom is less negative when the charge of the molybdenum atom is less positive. (ii) The concerned molybdenum atoms are in a more reduced state and are detected as Mo^{5+} or Mo^{4+} in the XPS analysis thanks to the chemical shift.

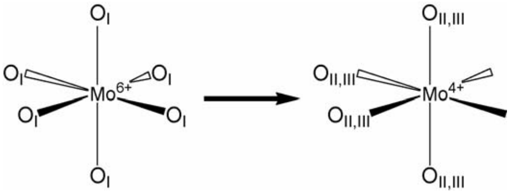

Fig. 4. Idealized octahedral coordination of Mo atoms in the fully oxidized state and after the removal of two oxygen atoms.

In contrast to the twin oxygen vacancies, the single oxygen vacancies seem not to modify the polarisation of the Mo–O bond as revealed by the negative correlation between the benzaldehyde concentration and the Mo^{4+}/O_{II} components.[1] This is reinforced by the weak but nevertheless positive correlation between the benzaldehyde formation and the presence of Mo^{6+}. These observations in addition to our previous work [6,7] could lead to a better description of the active site in the oxidation of propylene. Indeed, we have demonstrated that the oxidation of propylene to acrolein and/or CO_2 occurs in such way that single oxygen vacancies are formed at the surface of the catalyst [7]. This paper concerned $CoMoO_4$, but the present work confirms that under identical conditions the same hypothesis is verified for all the catalytic phases mentioned above.

Thus, it is now possible to reject the twin oxygen vacancies and its related coordinatively unsaturated molybdenum structure as a potential candidate in the participation of the propylene oxidation. This is definitively validated since we never detected any correlation between an oxidation product and the formation of toluene. Single oxygen vacancies are the key. As a reminder, (i) these are formed after the oxidation of a propylene molecule, (ii) they are surrounded by fully oxidized molybdenum atoms and (iii) they do not modify (in a detectable

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[1] This hypothesis must be considered with precautions since the correlations between benzaldehyde and Mo^{4+}/O_{II} are not significant at *p*-level <0.05 but these could provide some clues.

way) the polarisation of the Mo–O bond. Such a hypothesis is in phase with the results claimed by Bertinchamps et al. [3]. These authors argue that a slight reduction of MoO_3, namely the presence of a small quantity of Mo^{5+} at the surface of the catalyst induces an improved catalytic activity towards the oxidation of 2-butanol. According to this probe reaction, a better reactivity in oxidation instead of dehydration means that a few Mo^{5+} increases the exchangeability of surface lattice oxygen atoms. Our work thus highlights that the deep reduction of the surface, through the presence of large quantities of Mo^{5+} and Mo^{4+}, leads to a strong modification of the catalyst, especially in the electronic properties of oxygen and the activity of the catalyst. A slight reduction seems to be necessary for the oxidation reaction since it is less disturbing in the electronic behaviour of both the molybdenum and oxygen atoms.

5. Conclusions

Correlations between Mo oxidation state, O chemical shift, number and mutual disposition of oxygen vacancies have been revealed on molybdenum based oxide catalysts by the way of the deoxygenation of benzoic acid used as a probe reaction. A detailed investigation of the three O contributions detected by XPS and their relation with Mo oxidation level gives us a better understanding on the mutual disposition of Mo and O atoms in the catalytic site responsible for total or selective oxidation. In particular, this work allows to refine the concept that ‘‘Mo-based oxide catalysts become more oxidant when they are slightly reduced’’ by pointing to the type of oxygen vacancies having a beneficial influence on the performances. This work allows to discard the hypothesis that twin oxygen vacancies (i.e. oxygen vacancies separated by about 2 Å and related to a coordinatively unsaturated molybdenum atom) are beneficial for the oxidation of propylene. Conversely, single (isolated) vacancies seem not to induce significant electronic perturbation in the Mo and O vicinity. Single vacancies are thus pointed as the correct reduced site required at the surface of the catalyst to have its performances boosted in the propylene oxidation.

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