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# Probing the reduction state of Mo oxide catalysts by the deoxygenation of carboxylic acid

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**Abstract**

This work investigates the potentiality of the deoxygenation of benzoic acid in the presence of hydrogen as a probe of the reduction state of molybdenum oxide in catalytic processes. On one hand, a complicated hysteresis phenomenon is observed when measuring the conversion of benzoic acid and selectivities to benzene, toluene and benzaldehyde of $Mo_8O_{23}$ along a cycle of temperatures between 628 and 723 K. On the other hand, $Mo_8O_{23}$ undergoes a reduction to $Mo_4O_{11}$ and $MoO_2$ throughout the catalytic reaction. These results, together with the performances of $Mo_4O_{11}$ and $MoO_2$ under the same conditions, allow to understand the reduction pathway of $Mo_8O_{23}$. The proposed pathway fits with that suggested in the literature, thus confirming the deoxygenation of benzoic acid as a promising probe reaction of the behavior of molybdenum based oxides at work.

*Keywords:* Deoxygenation; Benzoic acid; Hydrogen

## 1. Introduction

It progressively becomes well accepted that a key to optimize the performances of Mo oxide catalysts in selective oxidation processes is to stabilize them in a slightly reduced state during the reaction [1–4]. Now, a crucial aspect to be understood in order to further improve performances of such processes is to identify the optimal reduction state of the catalysts in terms of location and of concentration of the reduced features. To progress in this direction, a major difficulty comes from the fact that Mo oxides at work are not static during oxidation reactions. The bulk and the surface can equilibrate their coordination and structure with the composition (i.e. the reduction/oxidation strength) of the reaction gas and the temperature, eventually resulting in reconstruction phenomena [2,3]. In situ characterization (with the catalysts maintained in reaction conditions during the characterization) and operando characterization (an in situ characterization coupled to a simultaneous measurement of the catalytic performances) are efficient approaches to handle such a delicate behavior. But this work aims at developing a parallel approach, namely the use of “probe reactions” that allow to monitor the properties of the catalysts through the distribution of the reaction products.

Precisely, this work envisages the potentiality of the deoxygenation of benzoic acid as a probe of the presence and the mutual organization of oxygen vacancies at the surface of Mo suboxide catalysts. An oxide with its surface presenting isolated oxygen vacancies is indeed suggested to produce benzaldehyde, while twin oxygen vacancies would selectively produce toluene [5]. Benzene would likely be formed by a radical-like mechanism at the catalyst surface that would not involve oxygen vacancies. Practically, we investigated the behavior of $Mo_8O_{23}$ in the deoxygenation of benzoic acid in the presence of hydrogen. We directed our attention to correlate the performances (conversion and selectivities) with the modifications undergone by the catalyst in the course of a temperature cycle.

## 2. Experiments

### 2.1. Preparation of the catalysts

$Mo_8O_{23}$ was synthesized by heating a mixture of $MoO_3$ (Aldrich, 99.5% pure) and $MoO_2$ (Aldrich, 99% pure) in a quartz reactor sealed under a vacuum of $10^{-8}$ atm. The

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molar ratio of the mixture was adjusted to 7:1. The cell was heated at 1023 K during 96 h.

### 2.2. Catalytic activity measurements

Deoxygenation of benzoic acid was performed at 1 atm in a fixed bed microreactor. The reaction feed contained 574 ppm of benzoic acid (Aldrich, 99% pure) and 5% of hydrogen (Indugas, 99.95% pure) while helium (Indugas, 99.99% pure) was the gas balance. The total flow was adjusted to 100 ml $\mathrm{min}^{-1}$. One hundred milligram of catalyst with a granulometry of 100–315 μm were used. The catalytic test consisted in a three step temperature cycle. The performances were first measured at 473, 523, 573, 623, 638, 653, 673 and 723 K, then at the same temperatures during the cooling down of the reactor, then again during a second rise of temperature. The reaction was run at each temperature during 2 h. Additional experiments were conducted following the same procedure but stopped at different moments of the test. In all cases, catalysts were recovered after a fast cooling to room temperature (105 K $\mathrm{min}^{-1}$) in the flow of reaction gas. Remaining acid, benzaldehyde, toluene and benzene were measured at the reactor outlet by on-line GC-FID.

### 2.3. Characterization

The catalysts were characterized before and after the catalytic reactions and additional experiments. Specific areas were measured with a Micromeritics ASAP 2000 instrument using the adsorption of Kr at 77 K after the samples were degassed at $10^{-6}$ atm and 423 K for 1 h. X-ray diffraction (XRD) was performed on a Siemens D5000 diffractometer using the Kα radiation of Cu for $2\theta$ angles scanned between 5° and 80° at a rate of 1.2° $\mathrm{min}^{-1}$. Photoelectron spectroscopy (XPS) was performed with a Kratos Axis Ultra instrument working with a monochromatic Al Kα radiation. Mo 3d, O 1s and C 1s bands and survey spectra were recorded. Binding energies were calibrated by fixing the C–(C–H) contribution of C 1s at 284.8 eV. Further details on XPS experiments and data treatments are given elsewhere [6]. Scanning electron microscopy (SEM) was realized on a PHILIPS XL30 ESEM-FEG microscope in high vacuum mode using secondary electrons and an acceleration tension of 10 or 20 kV. Catalysts were analyzed by spreading them on a carbon tape. All characterizations were carried out ex situ. The possibility that the obtained data do not reflect the real state of the catalyst at work must however be discarded as a very rapid cooling rate (105 K $\mathrm{min}^{-1}$) under reaction mixture has been applied at the end of each test. The catalyst cannot transform significantly during this step. In addition, the same cooling procedure was applied to all the catalysts thus if a slight transformation should happen (only a minor reduction may occur), it is systematic for all samples. Tendencies in the characterizations data reported hereafter can be correlated with the catalytic performances.

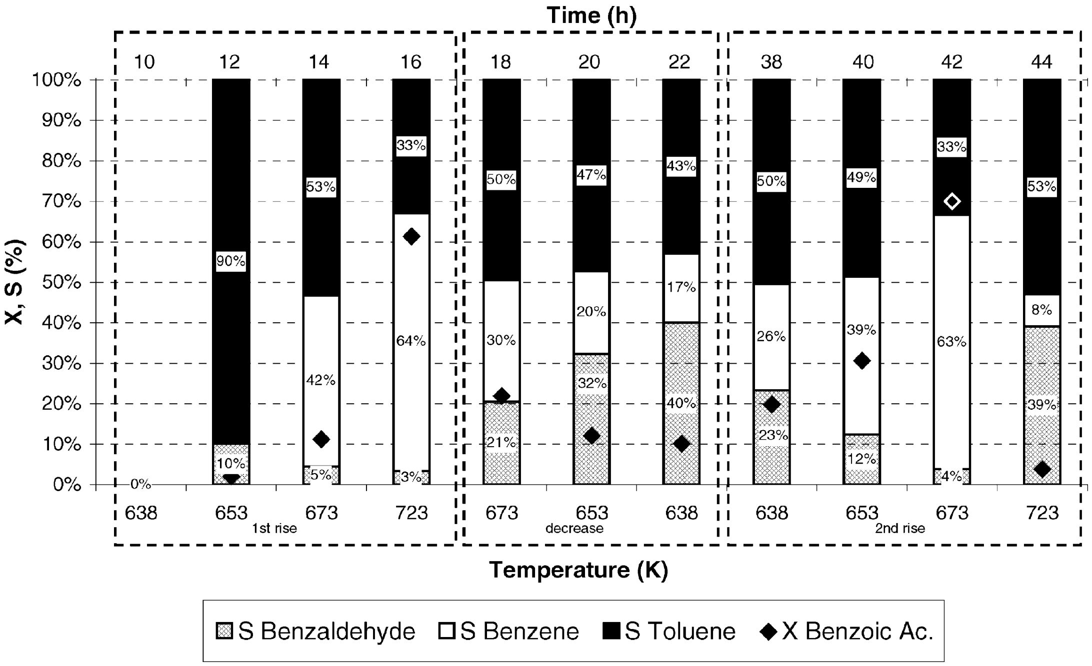

Fig. 1. Evolution of the conversion of benzoic acid (X) and the selectivities (S) through the three steps of a catalytic test. No activity was observed at temperatures lower than 638 K and was not reported for the sake of clarity. One must thus be careful not to compare the data at 638 K (decrease temperature step) and those at 638 K (second rise) as they are separated by several measurements as shown by the timescale. The timescale points to the beginning of the 2 h during which measurements were made at each temperature. Performances were stable within each of these 2 h periods.

## 3. Results

### 3.1. Catalytic activity measurements

Catalytic performances obtained in the course of the temperature cycle are plotted in Fig. 1. Comparing the different steps of the cycle, hystereses are observed for the conversion of benzoic acid and the selectivities to the different products. For example, in the first rise of temperature, the conversion of benzoic acid at 653 K is 2% whereas at the same temperature, it is, respectively, 12 and 31% in the decrease and the second rise of temperature. Similar tendencies are observed at other temperatures. Conversions are thus systematically higher at a given temperature following the order first rise $<$ decrease $<$ second rise. Only one exception is found at 723 K (second rise) during which the conversion drops dramatically to 4%, i.e. below what was obtained in the first rise.

At 653 K (first rise) only benzaldehyde and toluene are formed. But in all other cases, benzaldehyde, toluene and benzene are always formed together. In the first rise of the cycle, the increase of temperature induces an increase of the selectivity to benzene while the selectivities to toluene and benzaldehyde both decrease. During the cooling step, an opposite tendency is found, namely a decrease of the selectivity to benzene and an increase of the selectivity to benzaldehyde. The selectivity to toluene only slightly decreases. In the second rise of temperature, two tendencies are distinguished: (i) from 638 to 673 K, the tendency is identical to that in the first rise: selectivities to toluene and benzaldehyde decrease and the selectivity to benzene strongly increases; (ii) at a higher temperature (723 K), the selectivity to benzaldehyde and toluene suddenly increases and the selectivity to benzene decreases. Let us remind that at the same moment of the test, the conversion of acid undergoes a dramatic drop.

### 3.2. Characterization

The specific area of the fresh catalyst is 0.2 m$^2$ g$^{-1}$. At the end of the test, it increases to 3.0 m$^2$ g$^{-1}$. The catalysts recovered at intermediate moments of the test have specific areas between these two values depending on the duration of the experiments. The main XRD peaks for the fresh sample are typical of $Mo_8O_{23}$ (JCPDS no. 5-0339). The presence of $Mo_9O_{26}$ (JCPDS no. 12-0753) is also revealed. $Mo_8O_{23}$ and $Mo_9O_{26}$ are still present after the first rise of temperature. But $Mo_4O_{11}$ (JCPDS no. 5-0337) and $MoO_2$ (JCPDS no. 32-0671) appear as two minor phases after the first step of the reaction test. After the cooling step and the second rise of temperature, three main phases are detected: $Mo_9O_{26}$, $Mo_4O_{11}$ and $MoO_2$. After these treatments, the lines of $Mo_8O_{23}$ have totally vanished. For the samples recovered at intermediate moments, progressing along the test, $Mo_4O_{11}$ first becomes the main phase until 673 K (second rise) but then vanishes, likely transforming to $MoO_2$. Small peaks attributed to $Mo_9O_{26}$ are still present. The phases found along the test are summarized in Table 1.

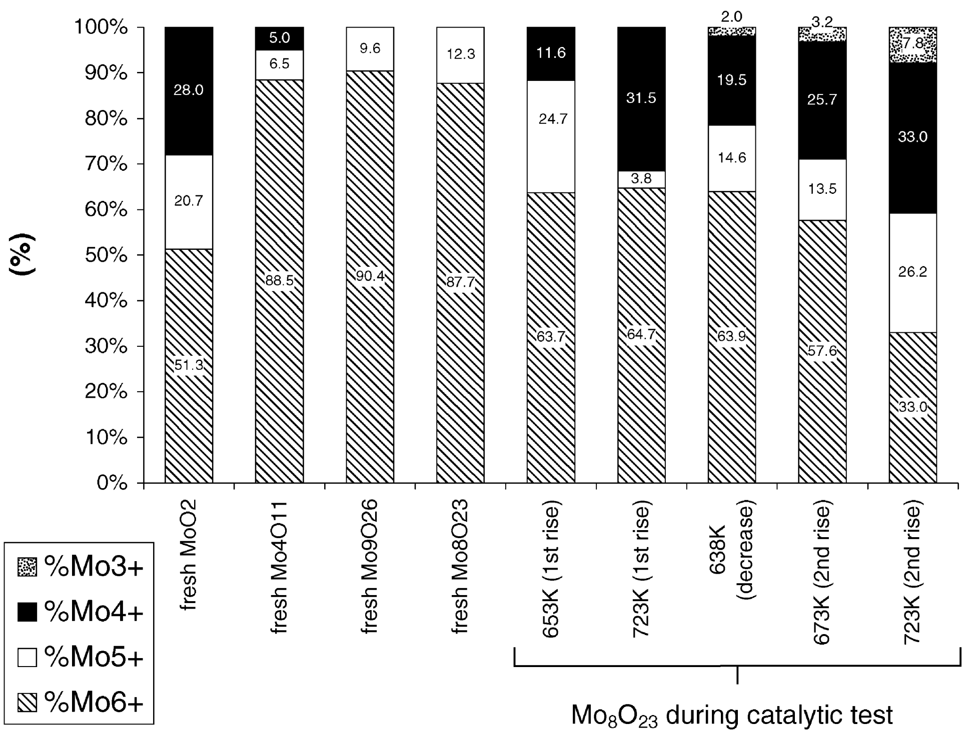

Fig. 2. Importance of the Mo$^{n+}$ contributions found by XPS for fresh $Mo_8O_{23}$ and catalysts recovered at different moments of the catalytic tests. Data for $MoO_2$, $Mo_4O_{11}$ and $Mo_9O_{26}$ reference compounds are also given.

Table 1
Crystalline phases detected by XRD for fresh $Mo_8O_{23}$ and the catalysts recovered at different moments of the catalytic test after fast cooling down to room temperature

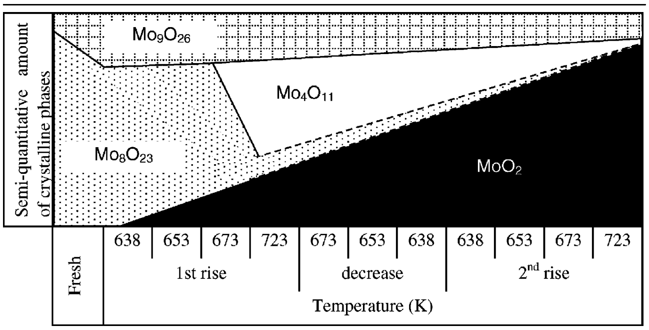

Fig. 2 summarizes the importance of the different $Mo^{n+}$ contributions found by XPS for fresh $Mo_8O_{23}$ catalyst and those recovered at different moments of the catalytic test. Corresponding data are also given for other suboxides prepared following procedures adapted from the literature [7–10]. Fresh $Mo_8O_{23}$ exhibits mainly $Mo^{6+}$ and a small amount of $Mo^{5+}$ species. A surface reduction of $Mo_8O_{23}$ starts during the first rise of temperature, as a significant increase of the $Mo^{5+}$ contribution is observed for the sample recovered at 653 K (first rise), while $Mo^{4+}$ species appear. Correspondingly the $Mo^{6+}$ contribution decreases. Further in the cycle, $Mo^{6+}$ contribution then remains constant with time-on-stream, but it decreases significantly at the end of the test (723 K, third step). Concerning the evolution of $Mo^{5+}$ and $Mo^{4+}$ species, the situation is more delicate. When the reaction is stopped during a rise of temperature, the $Mo^{4+}$ content tends to increase while that of $Mo^{5+}$ tends to decrease. Again, a different behavior is observed at the end of the second rise of temperature where the $Mo^{5+}$ content increases likely at the detriment of $Mo^{6+}$. $Mo^{3+}$ [11] is an additional species that appears in the second rise of temperature with a contribution always remaining below 10%.

SEM reveals an important transformation of $Mo_8O_{23}$ with time-on-stream (Fig. 3). Fresh $Mo_8O_{23}$ exhibits particles with a lamellar structure. But, after the reaction is stopped at 653 K (first rise), the extremities of the lamellae get fragmented and pits appear in the middle of the crystal faces. The crystal size is not significantly modified. The same tendency is more clearly observed for the catalysts recovered when the reaction is stopped at 723 (first rise) and 638 K (cooling step). After the reaction is stopped at

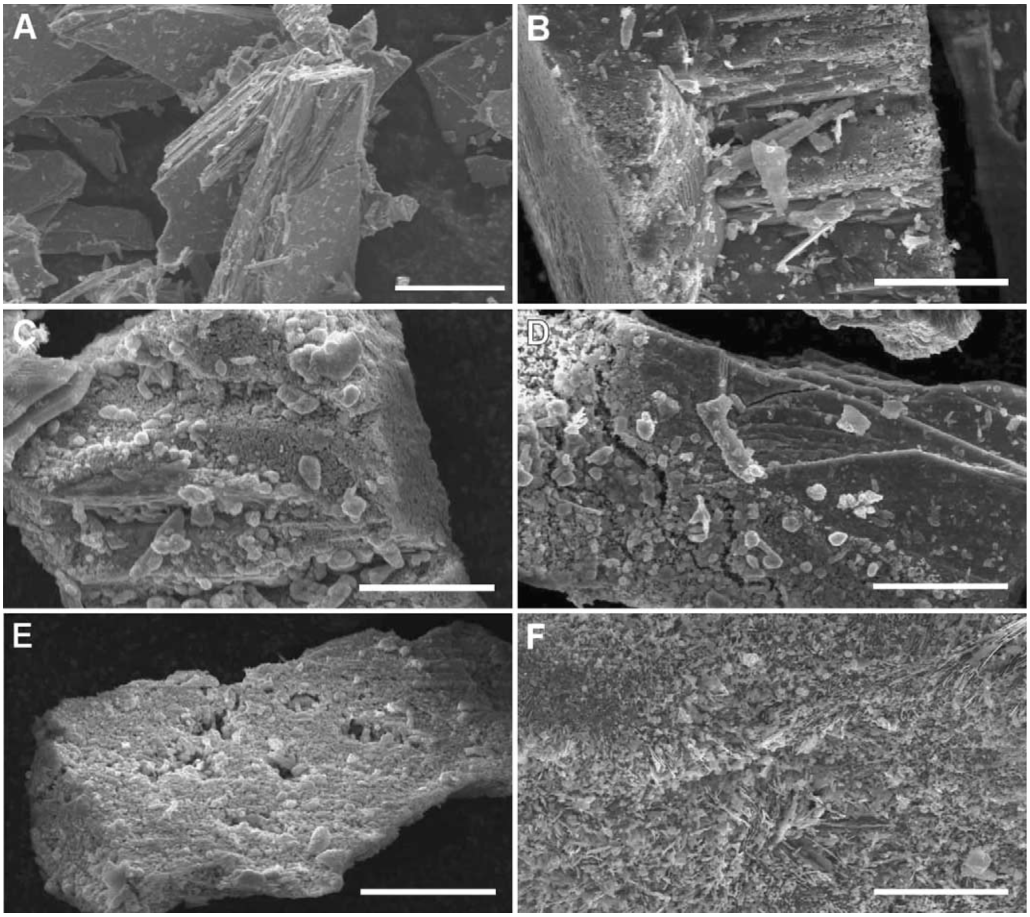

Fig. 3. SEM image of fresh $Mo_8O_{23}$ (A) and at different moments of the catalytic test: (B) first rise at 653 K; (C) first rise at 723 K; (D) decrease at 638 K; (E) second rise at 673 K; (F) second rise at 723 K. White lines represent 20 μm.

673 K (second rise), lamellae are no more visible, and the crystals appear completely reorganized, having undergone a recrystallization. This is further confirmed by the observation of the sample recovered at the very end of the test. Such a recrystallization is consistent with the increase of specific area with time-on-stream.

## 4. Discussion and conclusion

Several mechanisms accounting for the reduction of $MoO_3$ to $MoO_2$ have been proposed in the literature. According to Ressler et al. [12], the reduction pathway, precisely the formation or not of intermediate species, depends on the reduction temperature. Below 698 K, $MoO_3$ would reduce directly to $MoO_2$ without any intermediate species. But above 698 K, the $MoO_2$ resulting from the direct reduction of $MoO_3$ would react in situ with the "not yet reduced" remaining fraction of $MoO_3$, so leading to the formation of a third phase with a more distorted structure, namely $Mo_4O_{11}$.

The evolution of the crystalline phases throughout our catalytic test suggests that the reduction scheme described by Ressler also applies in our case. One nuance must be evoked, namely the fact that we work with $Mo_8O_{23}$ (in mixture with a small amount of $Mo_9O_{26}$) rather than with $MoO_3$. This difference is, however, not an argument to rule down the parallelism with the experiments of Ressler, on the contrary. $Mo_8O_{23}$ and $Mo_9O_{26}$ have indeed a structure very similar to that of $MoO_3$. Roughly, these suboxides can be described as a stacking of strips with corner-sharing arrangements of $MoO_6$ octahedra exactly as in $MoO_3$, glued together along shear planes [7–10]. The shear planes consist in edge sharing arrangements of octahedra compensating the oxygen deficiency of the suboxides. The main difference between $MoO_3$ and $Mo_8O_{23}$/$Mo_9O_{26}$ is thus the presence of shear planes. But these are known to allow easy diffusion of oxygen atoms from the bulk to the surface [13]. They thus most likely facilitate the reaction with $MoO_2$, which involves a transfer of oxygen to form $Mo_4O_{11}$.

In another set of experiments (not described here), $MoO_2$, $Mo_9O_{26}$ and $Mo_4O_{11}$ were tested and characterized following the same procedure as described above. $MoO_2$ produces benzaldehyde with a high selectivity but it loses its activity at the end of the cycle due to a severe surface reduction. $Mo_9O_{26}$ remains inactive and stable independently of the temperature investigated. The performances of $Mo_4O_{11}$ strongly depend on the temperature. At 623 K, an activity is obtained provided an activation of 4 h under the reaction conditions is respected. Then, benzene is the main product with small amounts of toluene. At 723 K, $Mo_4O_{11}$ does not need any activation period and produces benzene (main product) and benzaldehyde. Among the phases concerned here, $Mo_4O_{11}$ is the most active phase at temperatures higher than 673 K, and progressively reduces to $MoO_2$.

At this stage, one can now explain the evolution of the catalytic performances of $Mo_8O_{23}$ as shown in Fig. 1. At 653 K (first rise of temperature), $Mo_8O_{23}$ and $Mo_9O_{26}$ induce the production of toluene and benzaldehyde which reflects the presence of twin and single oxygen vacancies at their surface. $MoO_2$ resulting from their direct reduction at low temperature also likely contributes partially to the production of benzaldehyde. Increasing the temperature, and thus getting closer to the critical point of 698 K mentioned by Ressler, the formation of $Mo_4O_{11}$ is favored. This accounts for the observed increases of activity and of the selectivity to benzene. The latter suggests a lower concentration of oxygen vacancies at the surface of $Mo_4O_{11}$. In the cooling step, particularly below 698 K, two phenomena must be taken into account: (i) $Mo_4O_{11}$ formed during the first step of the cycle becomes inactive; (ii) the in situ formation of additional $Mo_4O_{11}$ is stopped. The consequences are the observed decrease of conversion and the shift of selectivity from the formation of benzene to benzaldehyde and toluene. The selectivity to benzaldehyde in the cooling step (which is higher than in the first rise) suggests the presence of a larger amount of $MoO_2$ in the catalyst.

The first part of the second rise of temperature (up to 673 K) is explained by the same behavior as evoked for the first. The explanation of the severe loss of activity observed at the end of the second rise is more delicate. It results from a combination of several phenomena. (i) $Mo_8O_{23}$ and $Mo_9O_{26}$ have completely disappeared from the system as a result of their reduction either to $MoO_2$ or to $Mo_4O_{11}$. (ii) The absence of $Mo_8O_{23}$ and $Mo_9O_{26}$ inhibits the further in situ formation of $Mo_4O_{11}$, which together with (iii) its progressive reduction to $MoO_2$, leads to (iv) the progressive decrease of the $Mo_4O_{11}$ content in the system. The sudden increase of selectivity to toluene and benzaldehyde definitely argues in favor of this hypothesis. Other elements may additionally reinforce the variations of performances, as (v) a deeper reduction of $MoO_2$ and (vi) a possible poisoning of the surface by an accumulation of carbonyl compounds due to the formation of benzene [14].

The above hypothesis to explain the catalytic behavior of $Mo_8O_{23}$ rests on the interpretation of XRD data that the catalyst undergoes a series of recrystallization with time-on-stream. SEM pictures actually strongly support this view, showing indeed the occurrence of such a phenomenon at the surface and in the bulk of the catalyst. Photoelectron spectroscopy data also support our hypothesis since the fluctuations between $Mo^{5+}$ and $Mo^{4+}$ (Fig. 2) fit quite well with the different crystalline phases met during the catalytic test. By comparison with the fresh reference compounds, more $Mo^{5+}$ (and less $Mo^{4+}$) species would mean that $Mo_8O_{23}$ is the phase at the surface of the catalyst during the first catalytic step and that $MoO_2$ is the superficial phase during the very last step. On the contrary, less $Mo^{5+}$ (and more $Mo^{4+}$) could indicate the presence of $Mo_4O_{11}$ as the superficial phase.

## 5. Conclusion

$Mo_8O_{23}$ undergoes a reduction to $MoO_2$ in the course of the deoxygenation of benzoic acid in the presence of hydrogen. The phenomenon is temperature dependent. Below 698 K, $Mo_8O_{23}$ reduces directly to $MoO_2$. But, above 698 K, the reduction proceeds through the formation of $Mo_4O_{11}$ as an intermediate phase. Measuring the performances of the phases involved in this reduction pathway reveals that $Mo_4O_{11}$ mainly produces benzene, $Mo_8O_{23}$ mainly produces toluene and $MoO_2$ mainly produces benzaldehyde. The combination of these data allows us to account for the obtention of a hysteresis when following the performances of $Mo_8O_{23}$ in the deoxygenation reaction carried out along a temperature cycle. Following the opposite approach, it should thus be possible, on the basis of its selectivity to the different products of the deoxygenation of benzoic acid, to predict the stabilized phases in a molybdenum oxide-based catalyst at work. In this way, the deoxygenation of benzoic acid appears as a promising probe of the reduction state of catalysts for the $MoO_{3-x}$ series at work.

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