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The influence of the hydrogen origin at the surface of Mo suboxide during the deoxygenation of carboxylic acid

Frédéric Dury, Didier Clément, Eric M. Gaigneaux *

Unité de Catalyse et Chimie des Matériaux Divisés, Université Catholique de Louvain,
Croix du Sud 2/17, B-1348 Louvain-la-Neuve, Belgium

Abstract

This work investigates the reactivity of a molybdenum suboxide in the deoxygenation of benzoic acid in the presence of hydrogen or propylene. Major differences are highlighted with Mo_8O_{23} as the active phase. When the reaction is performed in the presence of hydrogen as the reductant, benzoic acid is converted to benzaldehyde, toluene and benzene. If molecular hydrogen is replaced by propylene as a weaker reductant, the only product formed during the reaction is benzaldehyde. It is demonstrated that, in absence of molecular hydrogen in the reaction mixture, a large amount of benzoic acid remains irreversibly adsorbed on the catalyst surface. The comparison of the two series of catalytic tests allows to somehow discriminate how the nature and the mobility of the hydrogen atoms involved in the reaction dictate the behaviour of the catalyst.

Keywords: Benzoic acid; Deoxygenation; Propylene; Molybdenum suboxide

1. Introduction

The deoxygenation of benzoic acid in the presence of hydrogen is an adequate reaction to probe the organization of oxygen vacancies at the surface of oxide catalysts. It is suggested that an oxide whose surface presents isolated oxygen vacancies selectively produces benzaldehyde, while twin oxygen vacancies selectively produce toluene. Benzene is likely formed by a radical-like mechanism at the surface of the catalyst without needing oxygen vacancies [1–4]. Recently, we used this reaction with success to demonstrate the reduction pathway of Mo_8O_{23} [5]. This was possible because the large excess of hydrogen and the nature of the solid (Mo suboxide) induced a deep reduction of our catalyst toward MoO_2.

The present work is dedicated to the experimental study of the organization of oxygen vacancies at the surface of Mo_8O_{23} under less reducing conditions to avoid such a deep reduction of the catalyst. Catalytic tests were, therefore, performed by replacing molecular hydrogen by a weaker reductant: propylene. The comparison of the catalytic behaviour of Mo_8O_{23} in the presence of hydrogen or in the presence of propylene provides some insight into the nature of the hydrogen species involved in the deoxygenation of benzoic acid. Some understanding on the role of hydrogen mobility in such a system is additionally obtained.

2. Experimental

2.1. Preparation of Mo_8O_{23}

Mo_8O_{23} was synthesized by heating a mixture of commercial MoO_3 and MoO_2 in a quartz reactor. The cell was heated under vacuum at 1023 K during 96 h. The molar ratio between the two precursor compounds was adjusted to obtain the appropriate mean oxidation state in the final phase [6].

2.2. Characterization of Mo_8O_{23}

The catalysts were characterized before and after the catalytic reactions. Specific areas were measured with a Micromeritics ASAP 2000 instrument using the adsorption of Kr at 77 K; therefore, the samples were degassed at 10^{-6} bar and 423 K for 1 h. With these experimental conditions, the precision of the measurement is 0.03 $m^2\ g^{-1}$. X-ray diffraction (XRD) was performed on a Siemens D5000 diffractometer

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* Corresponding author. Tel.: +32 10 473665; fax: +32 10 473649.
E-mail address: gaigneaux@cata.ucl.ac.be (E.M. Gaigneaux).

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using the Kα radiation of Cu for two-Θ angles scanned between 5° and 80° at a rate of 1.2° min^{-1}. X-ray photoelectron spectroscopy (XPS) was performed with an axis ultra spectrometer from Kratos working with a monochromatic Al Kα radiation. Mo 3d, O 1s and C 1s bands and survey spectra were recorded. The binding energies were calibrated by fixing the C–(C–H) contribution of the C 1s adventitious carbon at 284.8 eV. Further details on the XPS experiments and corresponding data treatments concerning the decomposition of the Mo 3d band to the different Mo^{n+} species, are given elsewhere [7].

2.3. Catalytic activity measurements

Deoxygenation of benzoic acid was performed at atmospheric pressure in a stainless steel fixed bed microreactor with 100 mg of catalyst. The reaction mixture invariably contained 574 ppm of benzoic acid (BA) which was mixed with either 50,000 ppm of hydrogen (experiment H) or 167,000 ppm of propylene (C3) (experiment P). In both cases, helium was the gas balance. Total flow was adjusted to 100 ml min^{-1}. All catalytic tests were performed at 723 K for 10 h. Benzoic acid, propylene, benzaldehyde, toluene, benzene, CO_2 and CO were analysed by gas phase chromatography.

3. Results

3.1. Catalytic activity measurements

Results from experiment H are presented in Fig. 1A. In the presence of hydrogen as reductant, the conversion of benzoic acid increases with time on stream and reaches 35% after 5 h. Next, the conversion is 30% until the end of the catalytic test. Initially, benzene and toluene are formed, respectively, with 79 and 21%. But, after 60 min of reaction, benzaldehyde is produced to the detriment of benzene. Meanwhile, the selectivity to toluene increases. After 10 h of catalytic reaction, selectivities to benzaldehyde, toluene and benzene are, respectively, 20, 45 and 35%.

In experiment P, the conversion of propylene is very low (less than 5% of conversion), and can thus not be discussed in detail. CO is detected in trace. Concerning the conversion of benzoic acid (Fig. 1B), major differences with experiment H appear: (i) the conversion of benzoic acid for the first 3 h is less than 10% and increases only to 18%, (ii) only benzaldehyde is detected and (iii) a gap in the total selectivity indicates a large deficit in the carbon balance while the carbon balance was reached in experiment H.

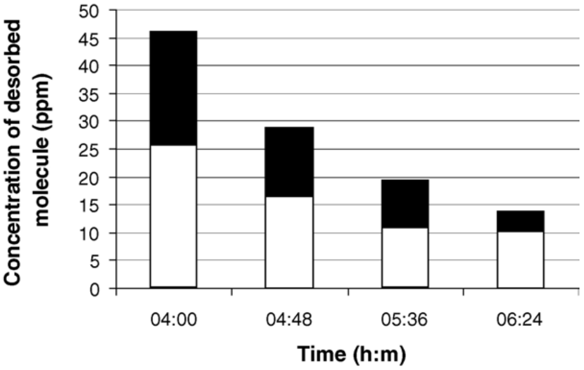

Fig. 2. Concentration in toluene (black) and benzene (white) during the desorption procedure under diluted hydrogen at 723 K.

In order to understand the origin of these differences, experiment P was repeated twice under identical conditions but after 3 h of reaction, the gas feed was suddenly changed either to pure helium or to 5% hydrogen in helium. No more benzoic acid nor propylene were thus added to the feed. No products were detected while flushing under pure helium at 723 K. Fig. 2 illustrates the compounds detected at the outlet of the reactor during the flushing with hydrogen at 723 K. No benzaldehyde is detected. On the contrary, significant amounts of benzene and toluene are desorbed from the catalyst (respectively, 25 and 20 ppm during the very first minutes). The desorption proceeds during 3 h, with the concentrations of desorbed benzene and toluene at the reactor outlet decreasing with time under hydrogen.

3.2. Characterizations

The specific area of the fresh catalyst is 0.2 $m^2 g^{-1}$. After experiment H and P, these values, respectively, increase to 1.8 and 1.3 $m^2 g^{-1}$.

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. After catalytic tests (both experiments H and P), characteristic peaks of MoO_2 were found in addition to the phases detected in the fresh sample.

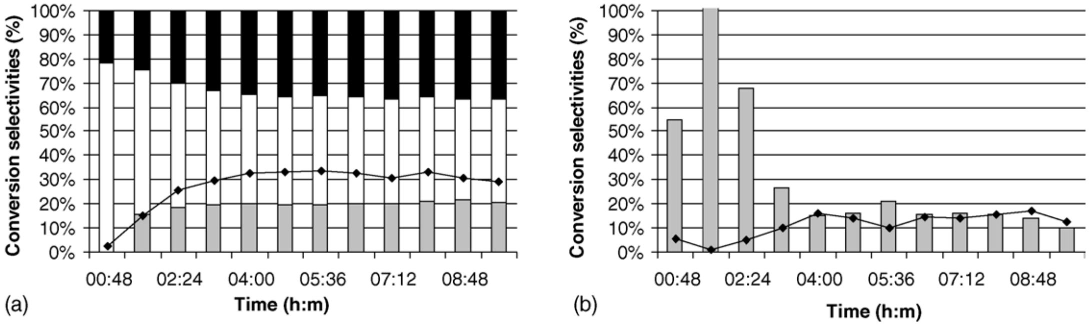

Fig. 1. Conversion of benzoic acid (◆) and selectivities to benzaldehyde (grey), toluene (black) and benzene (white) during experiments H (A) and P (B).

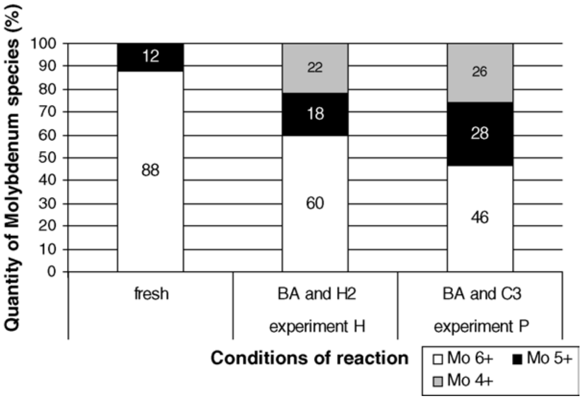

Fig. 3. Mo^{n+} contributions measured by XPS on fresh catalyst, after experiments H and P.

XPS analyses reveal that after catalytic test, the carbon content at the surface of the catalyst increases significantly. Whereas in the fresh material, there was only 24% of carbon, for the test ran in presence of hydrogen, the C 1s contribution increases to 70%. With propylene as the reductant, the carbon content is 42%. The analysis of Mo 3d region (Fig. 3) shows that the fresh catalyst has only Mo^{6+} (88%) and Mo^{5+} species (12%). The catalysts used in experiments H and P are more reduced than the fresh one since Mo^{4+} species is detected in considerable amount (22 and 26%, respectively).

4. Discussion and conclusions

The comparison of experiments P and H shows that: (i) in the absence of molecular hydrogen in the feed (experiment P), a part of benzoic acid remains irreversibly adsorbed at the surface of the catalyst and (ii) the benzene and toluene synthesis is only possible in presence of molecular hydrogen in the gas feed (experiment H). Without any doubt, the mechanism of the products formation (benzaldehyde, toluene and benzene) is dictated by the nature of the reductant used during the catalytic test. Two hypotheses could be envisaged to explain the difference of reactivity between experiments H and P: (i) a modification of the main crystallographic phase in relation with the reductant used could induce a major difference in the nature of the catalytic sites available at the surface of the catalyst and (ii) the nature and the reactivity of hydrogen atoms introduced either by molecular hydrogen (experiment H) or by propylene (experiment P) and benzoic acid could be the determining factor in the formation of the deoxygenation products.

The first hypothesis can be rejected because, in both experiments H and P, the catalyst undergoes a similar reduction to MoO_2 (surface and bulk). Moreover, we know from present and previous sets of catalytic tests that, in presence of hydrogen, Mo_9O_{26} is inactive, Mo_8O_{23} mainly produces toluene and MoO_2 is mainly responsible for the production of benzaldehyde [5]. In the present situation, catalytic activity is different but the catalysts used in experiments H and P undergo the same reduction towards MoO_2. As a consequence, the difference cannot be only attributed to the nature of the catalyst itself.

The other hypothesis is related to the nature of the reactants. The mobility and the nature of hydrogen atoms coming from the dissociation of molecular hydrogen are likely different from those resulting from the acidic function of benzoic acid or from the total oxidation of propylene. Our results suggest that the first species would be needed for the formation of benzene and toluene, whereas the second and third ones could only take part to the formation of benzaldehyde, allowing its desorption. A piece of answer is that on one side the activation of molecular hydrogen is easier than the activation of several C–C and C–H bonds. This is reflected by the very low conversion of propylene (experiment P) with as a consequence, small quantities of hydrogen atoms available to transform the benzoic acid molecules. The hydrogen provided by propylene would not come from its dehydrogenation to propyne (no propyne detected in the test) but it would rather come from the abstraction of the α-hydrogen atom of the olefin. On the other side, dissociative adsorption of molecular hydrogen could occur on catalytic sites different from those responsible for the propylene transformation. Indeed, in our system, hydrogen (whatever its origin) can be fixed by molybdenum atoms or by oxygen atoms. These two species are thus quite different since the first one is richer in electron than the second one. This explanation is reinforced by others results presented elsewhere [8]: when the experiment P is reproduced on a Co molybdate catalyst, the conversion of propylene is higher and molecular hydrogen is not needed at all to allow the desorption of benzene. So, in presence of propylene, on Mo_8O_{23}, one can assume that one of the two hydrogen species is missing (or present in too small quantities) implying the non-formation of toluene and benzene.

In conclusion, this work highlights the specificity of the deoxygenation reaction pathway according to the source of hydrogen. More generally, data revealed in this paper can contribute to the understanding of the role of hydrogen in the Mo (sub)oxides behaviour at work in the deoxygenation of acids and related oxidation reactions.

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