

Coupling the deoxygenation of benzoic acid with the oxidation of propylene on a Co molybdate catalyst

F. Dury, S. Meixner, D. Clément, E.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

Received 31 January 2005; received in revised form 8 April 2005; accepted 9 April 2005

Available online 31 May 2005

Abstract

An innovating coupling between the deoxygenation of benzoic acid and the oxidation of propylene was set up and gave new information about the mechanism involved in the oxidation of propylene on a Co–Mo based oxide catalyst. The production of CO₂ during the catalytic reaction is bound to the formation of benzene and benzaldehyde. The first case corresponds to the removal of the carboxyl function of the benzoic acid. The second case is the evidence that benzaldehyde and products coming from the oxidation of propylene are formed on the same catalytic sites during the Mars and van Krevelen cycle. In this cycle, the oxygen atoms used for the oxidation come from the benzoic acid by the intermediate of the oxide lattice. In particular, it has been demonstrated that the oxidation of propylene involves lattice oxygen atoms far from each other in such a way that the reaction leaves single oxygen vacancies at the surface of the catalyst. Such coupling between a deoxygenation reaction and an oxidation one is reported for the first time.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Benzoic acid; Propylene; Oxidation; Co molybdate; MVK mechanism

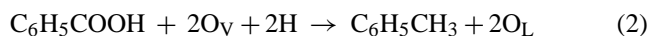
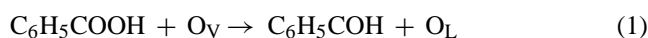
1. Introduction

Cobalt molybdates are well-known catalysts used with success, in their sulfidated forms, in hydro-desulphurisation processes. They are very active and exhibit high resistance to poisoning and deactivation. Some authors have studied cobalt molybdates in other processes like selective oxidation reactions, especially in the selective oxidation of propane [1–3], isobutene [4,5], propylene or acrolein [6,7]. Like Ni–Mo, Bi–Mo or Fe–Mo oxide catalysts, the good activity shown by these phases is not well understood yet. Several explanations are based on the oxidation state of the surface and/or of the bulk [8,9], some crystallographic considerations [10,11] or some complex mechanisms involving atom vacancies [7,12,13].

Our contribution to the understanding of the catalytic performances of Co–Mo catalysts, more specifically of oxides in selective oxidation reactions, consists in the development

of the deoxygenation of benzoic acid as a new probe reaction of oxide catalysts.

Deoxygenation of benzoic acid in presence of hydrogen is described in the literature as a reaction with selectivities to the different products depending on the arrangement of oxygen vacancies (O_V) at the surface of the catalysts. Poncet et al. have proposed that, on oxides like ZrO₂, Mn₃O₄ or MgO, benzaldehyde can be produced at the surface of catalysts exhibiting isolated oxygen vacancies Eq. (1) [14,15]. Moreover, twin oxygen vacancies, namely vacancies close to each other, catalyze the formation of toluene Eq. (2). In such a mechanism, the oxygen vacancies (O_V) are filled with the oxygen atoms coming from the benzoic acid.



with O_L representing lattice oxygen atoms and O_V representing oxygen vacancies.

A third product, benzene, can also be produced but without requiring oxygen vacancies [15,16]. Following the per-

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

performances of the deoxygenation of benzoic acid thus clearly allows to probe the catalysts surface state in terms of density and arrangement of the oxygen vacancies.

Our preliminary works have shown that the deoxygenation of benzoic acid in presence of molecular hydrogen on molybdenum oxides and suboxides leads to the deep reduction of the catalysts [17]. Although such a phenomenon is interesting to investigate, it does not directly reflect the surface state of the catalysts during the reaction in steady state conditions. Indeed, during the reaction, several crystalline phases appear and disappear sequentially, which makes the interpretation complex. To avoid such a modification of the catalysts, we have replaced hydrogen by a weaker reducer, namely propylene. Through this procedure, the redox character of the co-reactants is, a priori, better equilibrated. In addition, we have switched from the molybdenum suboxides to metal molybdates for three reasons: (i) metal molybdates are closer from a “real” and “industrial” catalytic system, (ii) metal molybdates are more stable than molybdenum suboxides during the reaction and (iii) deoxygenation of benzoic acid coupled with the oxidation of propylene does not need the presence of molecular hydrogen when performed on metal molybdates [18]. This allows to expect that the concerned catalysts remain stable during the whole course of the reaction.

Another important aspect in this innovative approach is the replacement of molecular oxygen used as oxidant agent in conventional oxidation reactions (as described by the Mars and van Krevelen mechanism [19]) by a more complex oxygen-donating molecule, benzoic acid. The catalytic system can thus be summarized like this: oxygen atoms needed to oxidize propylene into acrolein or CO/CO₂ comes, by the intermediate of the lattice oxygen, from the benzoic acid transformed in benzaldehyde or toluene.

It is the very first time that a selective oxidation reaction is coupled with the deoxygenation of a carboxylic acid. The interest of such a coupling between the deoxygenation of benzoic acid (DBA) and the selective oxidation of propylene (SOP) is its “probe reaction character”. It indeed permits to correlate in real time the performances of the investigated catalysts “at work” towards the formation of oxygenated molecules (acrolein, CO and CO₂) with their surface state, in particular the oxygen vacancies arrangement and indirectly the reduction state [17]. These characters will be deduced from the DBA selectivities. The objective of this paper is to provide the experimental evidence that such a coupling happens on Co–Mo oxide catalysts.

2. Experimentals and methods

2.1. Preparation of Co–Mo oxide

Co–Mo oxide was prepared as follows: 13.2855 g Co (NO₃)₂·6H₂O (Merck, 99%) and 8.0337 g of (NH₄)₆Mo₇O₂₄·7H₂O (Aldrich, 99%) were dissolved separately in

100 ml of distilled water at room temperature (solutions A and B). When complete dissolution was reached, 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%), 12.5241 g in 100 ml of water, was added dropwise to the Co–Mo precursors solution. 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. Characterization of the Co–Mo catalyst

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 prior to the analysis at 10⁻⁶ bar and 423 K for 1 h. To confirm the crystallographic form of Co–Mo compound before and after catalytic test, X-ray diffraction (XRD) was performed on a Siemens D5000 diffractometer using the K α 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 K α radiation. Mo 3d, Co 2p, 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 Moⁿ⁺ species, are given elsewhere [20].

2.3. Catalytic activity measurement

Three different catalytic experiments were realized at atmospheric pressure in a fixed bed microreactor. (i) In experiment BAC3, the reaction feed contained 635 ppm of benzoic acid (Aldrich, 99%) and 318 ppm of propylene (Indugas, 2.01% vol. in He). Helium (Indugas, 99.996%) was the gas balance. (ii) In experiment BA, the reaction feed contained 635 ppm of benzoic acid (Aldrich, 99%) diluted in helium (Indugas, 99.996%) as the gas balance. (iii) In experiment C3, the reaction feed contained only 318 ppm of propylene (Indugas, 2.01% vol. in He) in helium (Indugas, 99.996%) as the gas balance. All the parts of the reactor were maintained above 405 K to avoid the solidification of benzoic acid in the lines. The total flow was adjusted to 100 ml min⁻¹. Three hundred milligrams of catalyst with a granulometry of 100–315 μ m were used. For all the catalytic conditions, the performances were measured at 723 K for 16 h. On-line GC analyses were performed by using a flame ionization detector (FID) for the detection of the reactants (benzoic acid and/or propylene) and the selective products (benzene, toluene, benzaldehyde, acrolein) and a catharometric detector (TCD) for the detection of CO and CO₂. Since quantities involved during the reaction are very

low (maximum 954 ppm), the error made on the measured raw data are not negligible and must be considered for the calculation of the selectivities. For information purposes, errors on the benzoic acid, benzaldehyde, benzene, propylene, CO and CO₂ concentrations correspond respectively, to 10, 1, 4, 4, 1 and 1 ppm. Moreover, due to the system design and the use of benzoic acid which requires high temperature in whole the catalytic system (temperature higher than 405 K to avoid the solidification of the acid), we were unable to detect acrolein in a quantitative way. Indeed, such a temperature is high enough to induce its polymerisation or thermal degradation. Moreover, the small potential amount of acrolein formed during the reaction (maximum 318 ppm) is below the threshold of detection of the GC apparatus (2000 ppm).

Raw data were analysed by statistical methods using Pearson product-moment correlation coefficient Eq. (3) and a commercial software (STATISTICA).

$$r = \frac{\sum(X - \bar{X})(Y - \bar{Y})}{N\sigma_X\sigma_Y} \quad -1 \leq r \leq 1 \quad (3)$$

where \bar{X} , \bar{Y} are the mean, σ_X , σ_Y are the standard deviations and N the number of considered samples.

According to this mathematical definition Eq. (3), r will be equal to zero if no relation can be found between two variables X and Y . A negative value means that when X or Y increases, Y or X decreases at the same time. On the contrary, a positive value means that when X or Y increases, Y or X also increases.

3. Results

3.1. Catalytic activity measurement

Fig. 1A describes the performances measured for the deoxygenation of benzoic acid and the oxidation of propylene in the experiment BAC3. Concerning the benzoic acid side, initial conversion is 100% and decreases with time on stream to stabilize at 40% after 15 h of reaction. Two products of reaction are identified: benzaldehyde and benzene, corresponding respectively to 3 and 97% of selectivity in the first hour of reaction. The selectivity to benzaldehyde increases with time on stream to the detriment of the benzene production and reaches 18% in the last hour of reaction. Toluene was

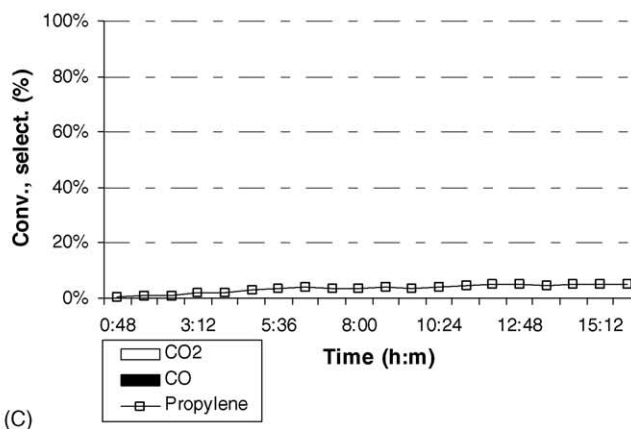
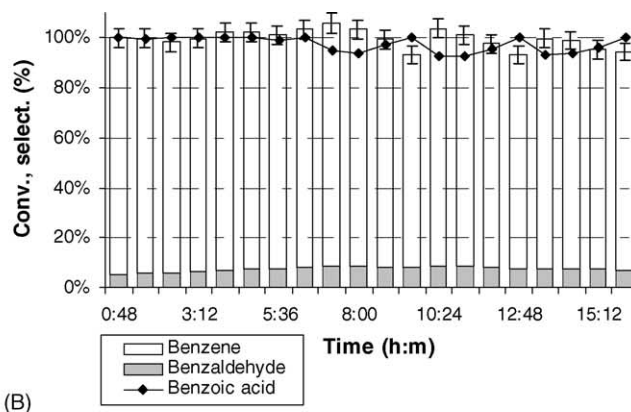
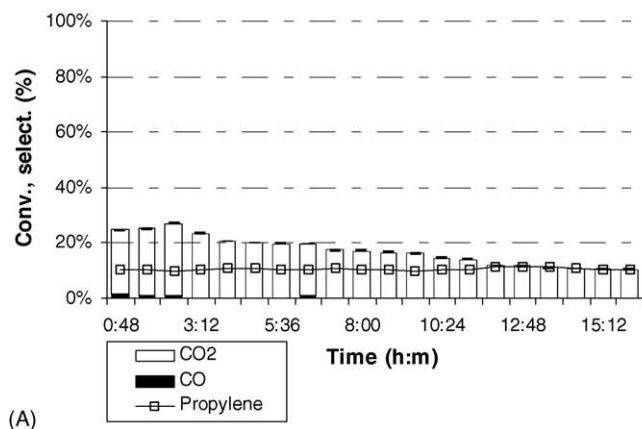
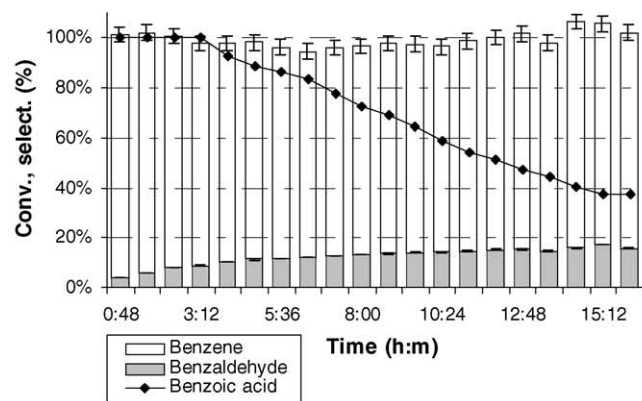


Fig. 1. (A) Conversion of benzoic acid and selectivities in benzaldehyde and benzene with time on stream at 723 K (upper graphic), conversion of propylene and selectivities in CO and CO₂ with time on stream at 723 K (bottom graphic) (experiment BAC3), (B) conversion of benzoic acid and selectivities in benzaldehyde and benzene with time on stream at 723 K (experiment BA), (C) conversion of propylene and selectivities in CO and CO₂ with time on stream at 723 K (experiment C3).

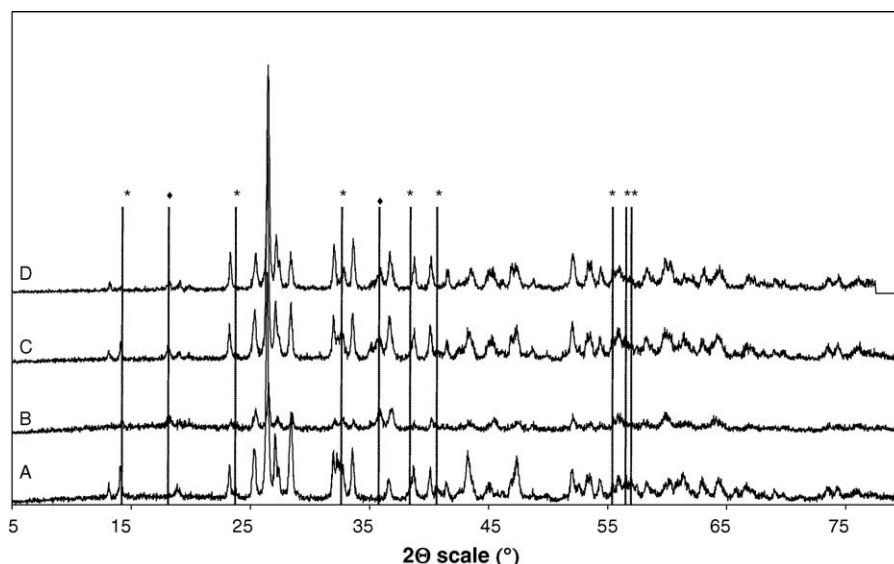


Fig. 2. X-ray diffractograms of (A) fresh Co–Mo oxide, (B) Co–Mo oxide used in experiment BAC3, (C) Co–Mo oxide used in experiment BA, (D) Co–Mo oxide used in experiment C3. (*) Indicates X-ray peaks attributed to CoMoO_4 (JCPDS n°25-1434), (◆) indicates X-ray peaks attributed to CoMoO_3 (JCPDS n°21-0869).

not detected during the whole duration of the catalytic test. The total selectivity in aromatic compounds is thus complete considering the error due to the GC apparatus.

The evolution of the activity measured at the same time for the oxidation of propylene is totally different: a conversion of 10% is observed and remains constant during the whole reaction. Concerning the selectivities, some important modifications between the different products are observed. After the first hour of reaction, selectivity to CO_2 decreases from 23 to 10% in 16 h. CO is only detected in traces. For the propylene side, the carbon balance could not be reached but no additional products are detected.

The catalytic results of experiment BA are described in Fig. 1B. This catalytic test is performed only with benzoic acid in the gaseous feed. Until the sixth hour of reaction, conversion is maximum. After that, some oscillations between 100 and 95% of conversion are observed. Three products of reaction are formed: benzaldehyde and benzene, respectively

with 8 and 92% of selectivity (on average) and CO_2 with a rather constant concentration of 35 ppm. No other products are detected.

Fig. 1C shows the results obtained in the conditions of experiment C3, i.e. with propylene in the feed but without benzoic acid. The conversion of propylene is low (less than 10%) and increases slightly with time on stream. No acrolein, CO, CO_2 nor any unknown product are detected with the direct consequence that carbon balance is not reached. But, remembering that the detection threshold of acrolein is 2000 ppm and as our GC apparatus is able to detect concentrations of CO_x as low as 35 ppm, one could assume that the selective product is formed with a selectivity near 100%.

3.2. Characterization of Co–Mo catalysts

The specific area of the fresh catalyst is $11.3 \text{ m}^2 \text{ g}^{-1}$. After experiments BAC3, BA and C3, these values, respectively increase to 13.8, 13.1 and $12.1 \text{ m}^2 \text{ g}^{-1}$.

X-ray diffraction analysis (Fig. 2) performed on fresh Co–Mo oxide catalyst reveals the presence of two crystallographic phases corresponding to CoMoO_4 (JCPDS n°25-1434) and CoMoO_3 (JCPDS n°21-0868). These two phases only differ by the cell sizes. In addition to those phases, two peaks attributed to CoMoO_3 (JCPDS n°21-0869) are detected in the three samples recovered after experiments BAC3, BA and C3.

Atomic concentrations measured by XPS are reported in Fig. 3. The histogram shows an important increase in the carbon content at the surface of the used catalysts which makes inconsistent the calculation of any elemental ratio relative to carbon or oxygen. Co/Mo atomic ratios are in slight diminution in all the samples recovered after catalytic test: 0.85 (BAC3), 0.80 (BA), 0.85 (C3) against 1.07 in the fresh

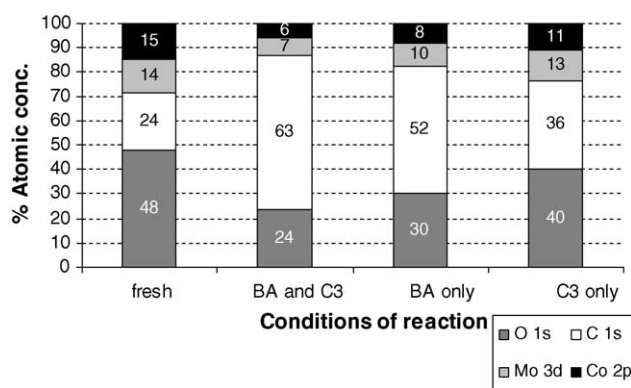


Fig. 3. Atomic concentration measured by XPS in fresh and samples corresponding to BAC3, BA and C3 experiments.

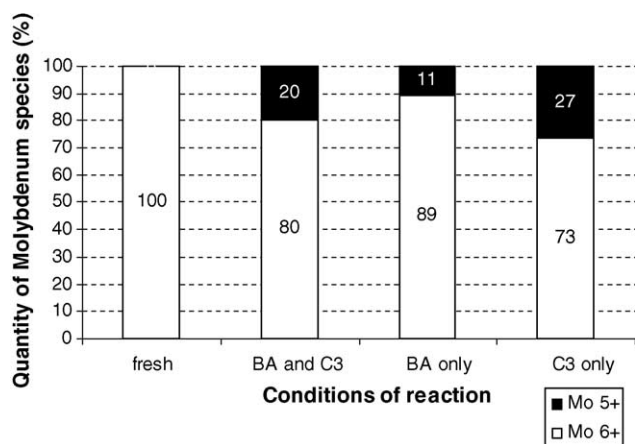


Fig. 4. Molybdenum species detected by XPS in fresh material and samples corresponding to BAC3, BA and C3 experiments.

catalyst. Fig. 4 gives the importance of the different Mo^{n+} detected for the fresh catalyst and after the different tests. Compared to the fresh material, the catalyst recovered after the test with propylene only (experiment C3) is the most reduced one. The sample recovered after the test with benzoic acid only (experiment BA) is the most oxidized one after the fresh catalyst. The sample recovered after the test in presence of both benzoic acid and propylene (experiment BAC3) presents an intermediate reduction degree between the BA and C3 samples.

4. Discussion

Let us discuss the primary available results. Thanks to the probe reaction mechanism, the detection of benzaldehyde formed during the deoxygenation of benzoic acid on Co molybdate catalyst and the absence of toluene (both observed in both tests BA and BAC3) reveal that only single oxygen vacancies are present at the surface of the catalyst. However, the large amount of benzene also indicates that these single oxygen vacancies are scarce at the surface of the Co molybdate.

Besides, the BA experiment highlights a small and constant production of CO_2 , namely 35 ppm. In a first approach, one could discuss the relevance of assigning the origin of this carbon dioxide to the total oxidation of benzoic acid. This hypothesis would be supported by the fact that a slight reduction of the catalyst corresponding to the experiment BA is detected by XPS. This reduction would be due to the fact that the envisaged total oxidation of benzoic acid proceeds without oxygen in the feed, i.e. by using the O_L of the catalyst only. If a total oxidation reaction occurs, one should observe: (i) a diminution of the total concentration in aromatic compounds in the outlet flow, i.e. a total selectivity in aromatic compounds of less than 100%, (ii) a concentration of CO_2 at the outlet of the reactor corresponding to the generation of seven molecules of CO_2 per molecule of benzoic acid burned,

(iii) the probable presence of other products from (almost) total oxidation, namely CO. None of these three expectations were validated by our experiments. Therefore, although one cannot discard it absolutely, one must admit that the total oxidation of benzoic acid, if it occurs, is marginal compared to the formation of benzaldehyde and benzene. This view matches well with the observations concerning the formation of benzaldehyde. Namely, starting from a fully oxidized surface of Co molybdate (see XPS), the catalyst is not able to produce benzaldehyde as it misses O_V . The total oxidation of benzoic acid would be responsible for the creation of some scarce single oxygen vacancies, which are detected by the probe reaction accordingly with the observed selectivity to benzaldehyde in experiment BA.

Focussing on the second side of the coupling reaction, namely the propylene oxidation, the available literature reports Co molybdate as an active and very selective catalyst in the selective oxidation of propylene [6,7,21]. In the experiment BAC3 and C3, whereas a significant conversion of propylene is measured, no selective products are detected and an important lack of selectivity is observed. There are two possible reasons to explain such a major lack in the carbon balance: (i) the technical limitation exposed above makes impossible the detection of the formed acrolein and (ii) a part of the propylene and/or acrolein contributes to form a coke deposit at the surface of the catalyst. The first cause is unfortunately a certainty verified by the measurement of the GC detection threshold of the acrolein. The second reason cannot be neither discarded: acrolein and/or propylene can be precursors of coke. Indeed, XPS results show that the carbon content increases in both BAC3 and C3 tests, to 63 and 36%, respectively whereas the carbon content at the surface of the fresh catalyst is only 24%. However, one cannot conclude that no acrolein is formed in our catalytic conditions since the carbon increase observed in the case of the C3 experiment is acceptable for a catalyst used in a selective oxidation reaction. Moreover, the noticeable difference of the carbon contribution between C3 and BAC3 indicates that the benzoic acid, when it is present, is involved in the coke formation. The arguments to discuss this point will be provided later in the text.

The raw data discussed until now do not show any direct and concluding information to reach our objectives. But, by refining these results, major new evidences for the feasibility of the coupling are highlighted.

Refined data are summarized in Figs. 5 and 6. Yield to CO_2 is plotted as a function of the benzoic acid conversion. By applying a linear regression to the available points ($R^2 = 0.99$), it appears that a correlation binds the benzoic acid conversion with the formation of CO_2 . A previous part of this discussion established that benzoic acid is only marginally burned, whereas Fig. 1A shows that benzoic acid is mainly converted to benzene and benzaldehyde. Taking this into account, the correlation between benzoic acid and carbon dioxide thus suggests that at least one relation must exist between benzene and CO_2 and/or between benzaldehyde and CO_2 . Four

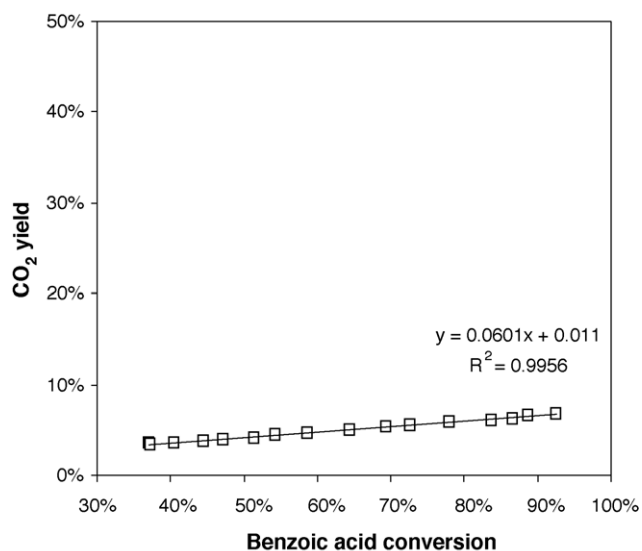


Fig. 5. CO₂ yield as a function of benzoic acid conversion.

Table 1

Pearson product-moment correlation coefficients at <i>p</i> -level < 0.05 (<i>N</i> = 21)	
Pearson product-moment correlation coefficients (<i>r</i>)	CO ₂ concentration
Benzoic acid conc.	-0.99
Propylene conc.	-0.57
Benzaldehyde conc.	0.59
Benzene conc.	0.99

relations are evaluated by the Pearson product-moment correlation coefficient method (Table 1). According to the *p*-level, all are significant. Among these, we notice that two positive correlations exist between the CO₂ concentration and the benzaldehyde or benzene concentrations. A more surprising negative but however significant correlation is found between CO₂ and propylene. To visualize the relations, data are plotted in Fig. 6 which presents the benzene and ben-

zaldehyde concentrations in the outlet feed as a function of the CO₂ concentration. The linear correlations obtained between CO₂ and benzene/benzaldehyde are both very strong ($R^2 = 0.98$ and 0.90 , respectively) and can then be considered. The R^2 of the respective correlation function indicates that the dependence between CO₂ and benzene or benzaldehyde is clearly the reflect of a specific mechanism of reaction. However, the fact that the corresponding angular coefficient for the two correlations is different indicates that the mechanism of reaction describing the formation of the two products are different. In order to elucidate the nature of these different mechanisms, it is crucial to discuss the origin of the CO₂.

After that a previous part of this discussion has established that CO₂ is only marginally coming from the total oxidation of benzoic acid, two hypotheses must be examined: (i) CO₂ could be the product formed by the removal of the carboxyl function from the benzoic acid when benzene is generated, (ii) CO₂ could be the total oxidation product from propylene. Further correlations shown in Fig. 6A and B permit us to elaborate an answer.

Concerning the relation between the benzene and the CO₂, a dependence is clearly significant regarding the angular coefficient of the linear regression (10.28). It can be assumed that carbon dioxide is formed co-linearly with the benzene. CO₂ would be the result of the carboxyl group removed from the benzoic acid. Such a hypothesis is not in contradiction with the literature. Indeed, it is proposed that benzene is formed by a radical-like rupture of the bond between the aromatic cycle and the acidic function of the benzoic acid molecule [22]. Nevertheless, this proposed mechanism is subjected to one condition: benzoic acid may lose its acidic proton and may be adsorbed on the catalyst in its benzoate form. No information are available on what happened to the acidic function but our results suggest that the acidic function is transformed into one CO₂ molecule. That transformation is stoichiometric but the desorption of CO₂ would not be quantitative as shown by Fig. 6A: there is only about one CO₂ molecule released for

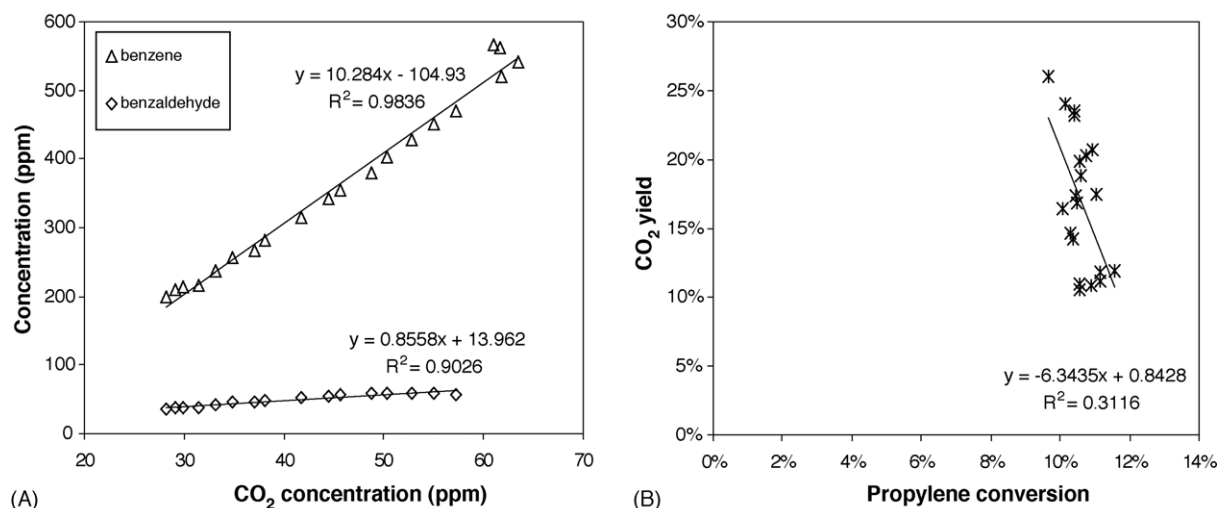


Fig. 6. (A) Concentration of benzene and benzaldehyde as a function of the CO₂ concentration, (B) CO₂ yield as a function of propylene conversion.

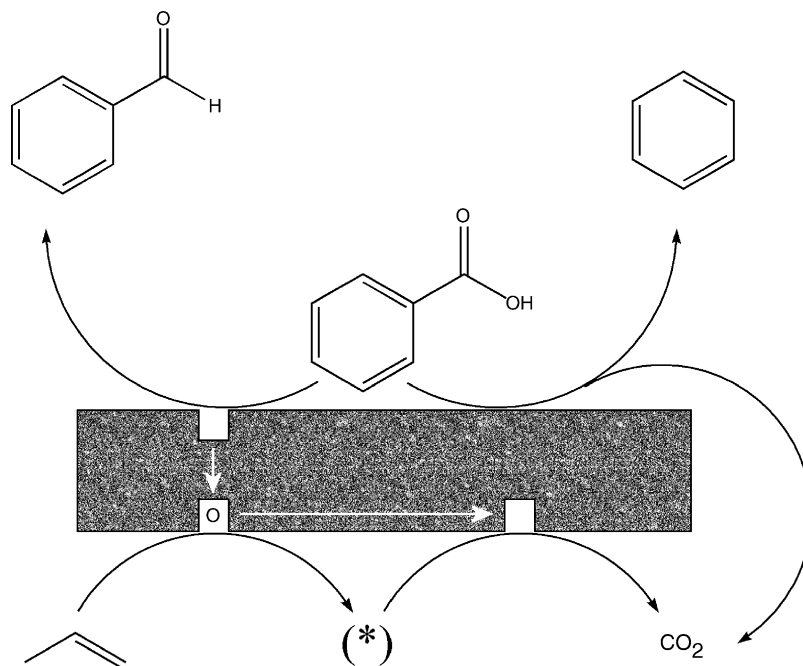


Fig. 7. Proposed mechanism for the coupling between the probe reaction and the total oxidation of propylene. (*) Represents the possible intermediate molecules formed during the total oxidation of propylene.

ten molecules of benzene whereas it could be expected that one CO₂ molecule would be released for each molecule of benzoic acid transformed to benzene. Experiment BA demonstrates that fact. Whereas a constant benzene concentration of about 570 ppm is measured, we only detect 35 ppm of CO₂ at the same time. It means that more than 90% of the CO₂ coming from the benzene formation remains at the surface of the catalyst and contributes mainly to the carbonaceous deposit detected by XPS.

The second hypothesis for the CO₂ formation is the total oxidation of propylene. Fig. 6B presents the yield to CO₂ as a function of propylene conversion. Although no strong correlation could be found, it is sure that a relation exists between the two compounds as demonstrated in Table 1. The poor correlation can be explained by the small range of propylene conversion which induces an important inaccuracy on the chromatogram integration. The surprising negative coefficient of that linear relation (-6.34) is a mathematical artefact which suggests that CO₂ is mainly coming from the benzene formation and only to a lower extent from the propylene reaction. The part of CO₂ coming from the decarboxylation of benzoic acid cannot be differentiated of the CO₂ coming from the total oxidation of propylene. Since the negative correlation calculated between the propylene and the benzene concentrations ($r = -0.45$) is significant, it fully explains why the coefficient in the linear relation between propylene and CO₂ is negative.

At this point of the discussion, it could be interesting to summarize the data: (i) a marginal part of CO₂ comes from the total oxidation of benzoic acid, (ii) CO₂ formation is bound to the benzaldehyde and benzene synthesis, (iii) a part of the

produced CO₂ comes from the transformation of benzoic acid to benzene, (iv) 90% of the CO₂ co-linearly produced with the benzene contribute to the carbonaceous species at the surface of the catalysts, (v) a small part of carbon dioxide comes from the total oxidation of propylene. One fact remains unexplained: why is the benzaldehyde formation strongly correlated with the CO₂?

Our hypothesis is totally innovative and based on the mechanism of the deoxygenation of benzoic acid. Remembering that deoxygenation occurs on oxygen vacancies at the surface of the catalyst, it can be suggested that the oxidation of propylene and the formation of benzaldehyde occurs consecutively on the same catalytic site (Fig. 7). In that scheme, benzoic acid gives one oxygen atom to one oxygen vacancy, forming benzaldehyde and a filled oxygen vacancy at the surface of the catalyst. In a second step, one propylene molecule is oxidized to acrolein or an intermediate molecule¹ on that filled oxygen vacancy (or another equivalent one). Afterward, the intermediate molecules could react on other oxygen lattice to give CO₂. Taking into account a stoichiometric reaction², 9 benzoic acid molecules are thus necessary to oxidize one propylene molecule and to produce three CO₂ molecules.

The comparison of the molybdenum oxidation state at the surface of CoMoO₄ used in different reaction conditions supports our hypothesis. While fresh catalyst has only Mo⁶⁺ species at its surface, used catalysts also exhibit Mo⁵⁺ species.

¹ By intermediate molecule, we consider a molecule in which an oxygen atom has been added.

² $C_3H_6 + 9C_6H_5COOH \rightarrow 3CO_2 + 9C_6H_5COH + 3H_2O$.

Mo⁴⁺ or Mo⁰ were never detected in any sample. Moreover, it appears that the catalyst used in presence of both benzoic acid and propylene is less reduced than the one used in presence of only propylene. Indeed, the Mo⁵⁺ content at the surface of the catalyst is lower when benzoic acid is used. This observation is in agreement with the mechanism of reaction described before. The lower reduction level of the catalyst when benzoic acid is present means that oxidation of the surface occurs during the coupling reaction. If an oxidation of the molybdenum atoms is possible, we must admit that an oxygen source is available for the oxidation. In our case, there is only one possibility: the oxygen atoms coming from the benzoic acid.

By admitting that the benzoic acid provides oxygen atoms to the catalyst, we can conclude that the coupling reaction between propylene and benzoic acid is a reality. So, propylene oxidation and benzaldehyde formation can be linked only if they occur on the same catalytic site. In other words, benzaldehyde is formed on a specific catalytic site presenting isolated oxygen vacancies whereas the products of the propylene oxidation, acrolein and CO₂, are generated on any equivalent catalytic sites in their oxidized form i.e. with filled oxygen vacancies.

5. Conclusions

The results described above indicate that the coupling between the deoxygenation of benzoic acid and the oxidation of propylene is possible and can give some new precisions about the working mechanism of oxides. In particular, the coupling reaction points out that the oxidation of propylene occurs in such a way that the reaction leaves single oxygen vacancies at the surface of the catalyst. Moreover, our results suggest that the total oxidation of propylene, i.e. the formation of carbon dioxide would be a multi-step mechanism involving several lattice oxygen atoms far from each other.

Such a coupling reveals all its interest for the understanding and optimization of the catalyst because direct correlations between products coming from different reactants indicated how they are synthesized as a function of the catalyst surface. Although the coupling between the deoxygenation of benzoic acid and the selective oxidation of propylene could not directly interest petrochemical industries as market demands in benzaldehyde and acrolein are too different, one can imagine that the coupling between the oxidation of a paraffin or of an olefin longer than propylene with the deoxygenation of benzoic acid could be of great interest. We would be able to produce benzene and/or benzaldehyde together with selective oxidation

product by the way of a cleaner and environment friendly process.

Acknowledgements

F.D. is granted by the Fonds pour la formation à la Recherche dans l'Industrie et dans l'Agriculture (FRIA) of Belgium. The authors thank the Fonds Spécial de la Recherche (FSR) of the Catholic University of Louvain (Belgium) for the financial support. Moreover, the authors acknowledge the involvement of their laboratory in the Coordinated Action "Concorde" and in the Network of Excellence "Fame" of the European Union 6th framework program, as well as in the IUAP network "Supramolecularity" sustained by the "Service public fédéral de programmation politique scientifique" of Belgium.

References

- [1] A. Maione, M. Devillers, J. Solid State Chem. 177 (2004) 2339.
- [2] Y.-S. Yoon, N. Fujikawa, W. Ueda, Y. Moro-oka, K.-W. Lee, Catal. Today 24 (1995) 327.
- [3] D.L. Stern, R.K. Grasselli, J. Catal. 167 (1997) 550.
- [4] S.R.G. Carrazan, C. Martin, V. Rives, R. Vidal, Appl. Catal. A: Gen. 135 (1996) 95.
- [5] F. Trifiro, G. Caputo, P.L. Villa, J. Less Common Metals 36 (1974) 305.
- [6] M.M. Bettahar, G. Costentin, L. Savary, J.C. Lavalley, Appl. Catal. A: Gen. 145 (1996) 1.
- [7] W. Ueda, Y. Moro-oka, T. Ikawa, J. Catal. 70 (1981) 409.
- [8] E. Godard, E.M. Gaigneaux, P. Ruiz, B. Delmon, Catal. Today 61 (2000) 279.
- [9] A.B. Anderson, D.W. Ewing, Y. Kim, R.K. Grasselli, J.D. Burrington, J.F. Brazdil, J. Catal. 96 (1985) 222.
- [10] M.W.J. Wolfs, P.H.A. Batist, J. Catal. 32 (1974) 25.
- [11] I. Matsuura, S. Mizuno, H. Hashiba, Polyhedron 5 (1986) 111.
- [12] E.M. Gaigneaux, H.M. Abdel Dayem, E. Godard, P. Ruiz, Appl. Catal. A: Gen. 202 (2000) 265.
- [13] J.F. Brazdil, L.C. Glaeser, R.K. Grasselli, J. Catal. 81 (1983) 142.
- [14] M.W. de Lange, J.G. van Ommen, L. Lefferts, Appl. Catal. A: Gen. 220 (2001) 41.
- [15] Y. Sakata, V. Ponc, Appl. Catal. A 166 (1998) 173.
- [16] Y. Sakata, C.A. Van Tol-Koutstaal, V. Ponc, J. Catal. 169 (1997) 13.
- [17] F. Dury, V. Misplon, E.M. Gaigneaux, Catal. Today 91–92 (2004) 111.
- [18] F. Dury, D. Clément, E.M. Gaigneaux, submitted in Catal. Today.
- [19] P. Mars, D.W. van Krevelen, Chem. Eng. Sci. 3 (1954) 41.
- [20] F. Dury, E.M. Gaigneaux, P. Ruiz, Appl. Catal. A: Gen. 242 (2003) 187.
- [21] J.M.M. Millet, H. Ponceblanc, G. Coudurier, J.M. Herrmann, J.C. Vedrine, J. Catal. 142 (1993) 381.
- [22] M.W. de Lange, J.G. van Ommen, L. Lefferts, Appl. Catal. A: Gen. 231 (2002) 17.