

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

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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.

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

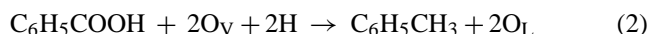
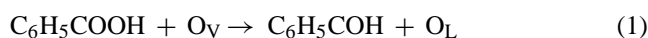
1. Introduction

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-

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formances 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 Mo^{*n*+} 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

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