

Gas phase hydrogenation of benzaldehyde over supported copper catalysts

A. Saadi^a, Z. Rassoul^a, M.M. Bettahar^{b,*}

^a *Laboratoire de Chimie du Gaz Naturel, Institut de Chimie, USTHB, BP32 El-Alia, 16111 Bab-Ezzouar, Algeria*

^b *Laboratoire de Catalyse Hétérogène, UMR-CNRS 7565, Université Henri Poincaré, Nancy-I, Faculté des Sciences, BP 239, 54506, Vandoeuvre-lès-Nancy Cedex, France*

Received 29 September 1999; received in revised form 20 February 2000; accepted 28 February 2000

Abstract

Benzaldehyde hydrogenation over copper catalysts supported on Al₂O₃, SiO₂, TiO₂, CeO₂ and ZrO₂ has been studied at atmospheric pressure and 100–350°C. The reaction competitively produced benzylalcohol, toluene and benzene with yields depending on the nature of the support and reaction temperature. The obtained order of activity was attributed to metal and acid–base surface properties. The important gap in activity (multiplied by 2 to 23) between 300°C and 350°C, observed for all catalysts except Cu/SiO₂, was attributed to an adsorption phenomenon, i.e. base sites or low reaction temperature inhibited the reaction course, whereas acidic sites or high reaction temperature enhanced the catalyst activity. Benzylalcohol was obtained with high selectivity (83% at 68% of conversion) from only 100°C with the SiO₂ acidic support, whereas selective formation of toluene or benzene was observed at higher reaction temperature and depended on the nature of the support. The relative selectivity of toluene and benzylalcohol was governed by the adsorption strength the alcohol OH function on the catalyst surface. High selectivity to benzene was attributed to the easiness of the catalyst to break the C–H aldehydic bond and stability of the surface organic entity formed. The parallel study of the reduction of benzaldehyde under N₂ flow threw some light on the relation between metal and acid–base surface properties of the catalysts and reaction paths in benzaldehyde hydrogenation. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Copper; Catalysts; Supports; Benzaldehyde; Hydrogenation

1. Introduction

The selective hydrogenation of unsaturated carbonyl compounds has recently received a growing interest since it is an important step in the preparation of fine chemicals [1–6]. It was found in liquid phase that, in general, aldehydes are more reactive than ketones, which in turn were more reactive than olefins and a phenyl substituent activated both C=O and

C=C bond hydrogenation [7–9]. On the other hand, copper-based catalysts, mainly copper chromite, are known to preferentially hydrogenate the carbonyl group [7–10]. In the hydrogenation of aromatic compounds, the benzene ring and the carbonyl group should be hydrogenated but hydrogenolysis should also compete with hydrogenation [4–6]. The obtained selectivities mainly depended on the nature of the catalyst [4,5,11–13].

Until recently, the studies on the selective hydrogenation of benzaldehyde to benzyl alcohol have been largely devoted to the liquid phase system [7,10,14–21], whereas relatively few studies have

* Corresponding author. Tel.: +33-3-83-912066 ext. 3125;

fax: +33-3-83-912181.

E-mail address: bettahar@lcah.u-nancy.fr (M.M. Bettahar).

been reported for the gas phase system [4–6]. In the latter case, metal [4,5] and metal oxide [6] catalysts were used. The hydrogenation of benzaldehyde over Pt catalysts supported on TiO_2 , Al_2O_3 and SiO_2 in the range temperature of 60–220°C was reported [4]. No hydrogenation of the aromatic ring was found for Pt/ TiO_2 but an important metal-support interaction and a high temperature H_2 pre-treatment effect, which enhanced both conversion and selectivity to benzylalcohol. These performances were attributed to special sites formed at the interface of platinum and titania phases, which activate C=O bond hydrogenation [4]. It was shown that benzene and toluene by-products were formed directly from benzaldehyde and benzylalcohol, respectively, and a Langmuir–Hinshelwood model, with the addition of the second hydrogen atom as rate determining step, fits the data satisfactorily. The hydrogenation of benzaldehyde and *o*-tolualdehyde to the corresponding alcohols was studied over Ni/ SiO_2 in the temperature range of 110–300°C [4]. No ring hydrogenation was detected and the by-products arose from the direct hydrogenolysis of the aryl–carbonyl C–C bond [5]. As to metal oxides as catalysts, one of us have shown that their catalytic properties in the hydrogenation of benzaldehyde to benzyl alcohol depends on their reducibility and, also, on their surface acid–base properties [6]. Toluene and benzene by-products arose from benzylalcohol and benzaldehyde hydrogenolysis, respectively [6].

According to the above data, one can expect changes in the metal active phase properties by interaction with the support. Also, we have undertaken the study of the hydrogenation properties of 10% copper catalysts impregnated on Al_2O_3 , SiO_2 , TiO_2 , ZrO_2 and CeO_2 supports: Al_2O_3 and SiO_2 are both irreducible oxides and, also, amphoteric and weakly acidic, re-

spectively; TiO_2 , ZrO_2 and CeO_2 are reducible oxides and, in addition, behave as acidic or basic oxides [6]. In the present paper, we report the results obtained in the hydrogenation of benzaldehyde over the copper catalysts at atmospheric pressure in the reaction temperature range of 100–350°C. The catalysts activity was related to their reducibility and acid–base properties as determined by TPR measurements and behaviour in the reduction of benzaldehyde under N_2 flow [6].

2. Experimental

2.1. Catalysts preparation, BET surface area, reducibility

The catalysts were prepared by impregnation of an aqueous suspension of the support by copper nitrate, then evaporating the solvent at 80°C and drying at the same temperature for 12 h. The obtained precursors were calcined in air for 3 h. All the supports were commercial materials (Table 1) and calcined for 2 h at 500°C in air before impregnation.

The specific area measurements were performed by the classical BET method on a Coultronics 2100 E device using N_2 as probe molecule. The reducibility experiments were carried out on a pulse chromatographic reactor. The sample (0.3 g) was dried at 150°C for 2 h in argon (99.95%, Air Liquide) and then cooled to room temperature under argon flow. The flow was then switched to hydrogen (99.995%, Air Liquide) and the sample heated up to 500°C at a rate of 4°C min^{-1} . The degree of reduction of copper was calculated assuming its oxidation state was +2 after calcination.

Table 1
BET surface area and reducibility of the copper catalysts

Catalyst	Cu/ SiO_2	Cu/ $\gamma\text{-Al}_2\text{O}_3$	Cu/ TiO_2	Cu/ ZrO_2	Cu/ CeO_2
% Cu (w/w)	7.4	7.9	7.4	8.1	9.2
Support origin	Fluka	Fluka	Merck	Merck	Labosi
Support BET surface area ($\text{m}^2 \text{g}^{-1}$)	200.0	72.0	80.0	50.0	100.0
Catalyst BET surface area ($\text{m}^2 \text{g}^{-1}$)	162.0	52.2	53.0	38.0	35.5
$T^\circ\text{C}$ of peak of reduction	260 (40%) ^a	350 (95%)	370	330 (40%)	350 (99%)
	360 (60%)	420 (5%)	(100%)	380 (60%)	490 (1%)
% of reduction	73.7	100	59.3	81.3	62.3

^aProportion of the surface area of the temperature peak.

2.2. Catalytic testings

Benzaldehyde (Aldrich, 99.98%) was degassed under nitrogen purge before use. H₂ and N₂ (Air Liquide) were passed through Supelco molecular sieve traps and Oxytraps (Altech).

The catalytic performances were carried out in a fixed-bed glass tubular reactor with 0.2 g samples at atmospheric pressure and the total flow rate was 50 cm³ min⁻¹. The reactant gas feed consisted of 3.2 Torr of benzaldehyde and 250 Torr of H₂ diluted in N₂. Gaseous benzaldehyde was obtained by bubbling N₂ in liquid benzaldehyde maintained at constant temperature (50°C) in a suitable saturator. Before testing, the catalysts were in situ reduced for 2 h at 350°C in a current of H₂ with a flow rate of 20 cm³ min⁻¹.

The gaseous reactant and products were heated upstream and outstream in order to avoid their condensation and analyzed on line by a FID gas chromatograph (Delsi IGC 121 ML) equipped with a carbosieve column. Each reaction temperature was maintained constant until the corresponding steady-state was reached as indicated by the gas chromatograph analysis of the exit gas samples. For each catalyst the reaction temperature was changed in a crossing order: 350°C, 150°C, 250°C, 100°C, 300°C. An ascending order did not sensibly modify the obtained steady-state activities. Varying the flow rate in the range from 10 to 80 cm³ min⁻¹ showed that no mass transfer limitations occurred when the sample weight was ≤0.2 g.

3. Results

3.1. Catalysts characterization

The BET surface area and reducibility properties of the catalysts are reported in Table 1.

The specific area of the catalysts increased with that of the corresponding supports and were in the range of 38–162 m² g⁻¹. However, this range of specific area is lower than that of the supports (72–200 m² g⁻¹), that is, the support lost from 20% to 60% of its area after impregnation of the copper phase. During the impregnation stage of the preparation, surface hydroxyl groups (OH_{surf}) of the support were consumed by re-

action with the active phase precursor. Such a surface reaction may have caused the decrease of available surface area of the support, probably by closure of the pores.

In other respects, the XRD spectra showed the characteristic bands of the copper phase and support [22]. The pattern for the supports was that of crystallized materials with well-defined bands except for the amorphous SiO₂ support. The copper phase consisted of small particles with a mean size of about 4–5 nm (for the Cu/SiO₂ and Cu/Al₂O₃ catalysts) and 7–10 nm (for the Cu/TiO₂, Cu/ZrO₂ and Cu/CeO₂ catalysts). In addition, for the Cu/ZrO₂ catalyst, STEM experiments showed small metal copper particles, well dispersed both on the surface (mean size of about 15 nm) and in the bulk (mean size of about 8 nm) of the solid [22].

Under H₂ atmosphere, the supported CuO phase was reduced to two steps as illustrated in Fig. 1, except for the Cu/TiO₂ catalyst for which only one step was observed. The reduction was uncomplete (60–80%), except for the Cu/Al₂O₃ catalyst (Table 1). The first peak of reduction should correspond to isolated and easily reducible CuO particles, whereas the second peak should correspond to larger CuO particles or/and CuO particles more strongly interacting with the support. These assumptions are in good accordance with the STEM experiments in the case of the Cu/ZrO₂ catalyst [22]. The uncomplete reduction of the catalysts should also be explained by the existence of copper particles strongly bounded to the support.

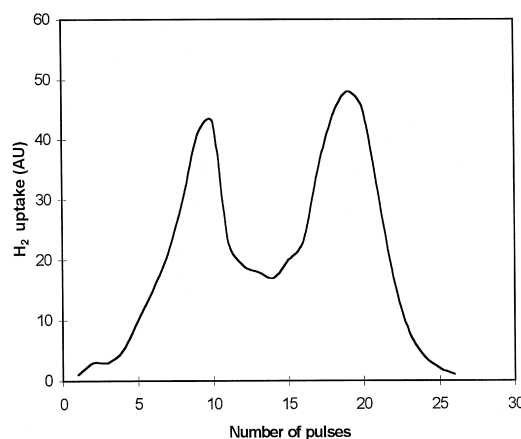


Fig. 1. TPR profile of the Cu/SiO₂ catalyst.

3.2. Catalytic activity

3.2.1. Hydrogenation of benzaldehyde

The bare oxides were almost all inactive in benzaldehyde hydrogenation in the whole range of reaction temperature: only a very little activity (conversion of about 5%) and at high reaction temperature (350°C) was found in the case of the reducible TiO₂, ZrO₂ and CeO₂ bare oxides. Toluene and benzene were formed in the latter case. Much higher conversions were obtained in the presence of copper, notably at 350°C, indicating that the latter is the main component of the active site.

The copper catalysts exhibited initial deactivation before the steady-state was established and the degree (10–30%) and duration (1–3 h) of deactivation depended on the nature of the support and reaction temperature. Fig. 2 reports activity results with time on stream at 350°C. It can be noted in this figure that no initial deactivation occurred at 350°C for the Cu/SiO₂ and Cu/Al₂O₃ catalysts but, for the latter, a drop of conversion from 100% to 60% is observed after about a 4-h work. The decrease of activity is attributable to poisoning by carbonaceous overlayer since the activity was almost totally recovered after regeneration by calcination then re-reduction.

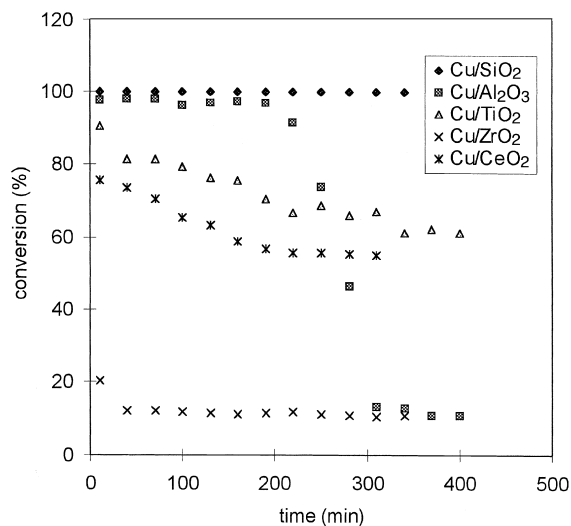


Fig. 2. Conversion of benzaldehyde with time on stream at 350°C under H₂ flow for the supported copper catalysts. Pre-treatment: H₂/350°C.

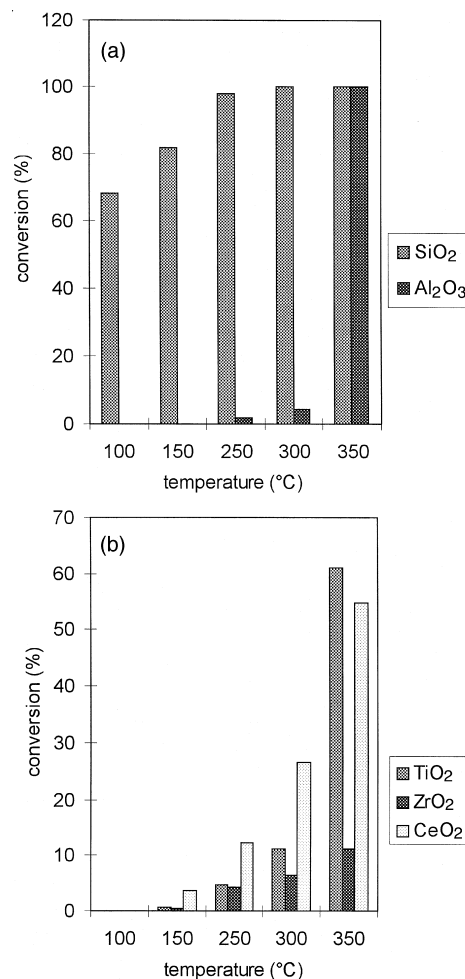


Fig. 3. Steady-state conversion of benzaldehyde under H₂ flow as a function of the reaction temperature for: (a) Cu/SiO₂ and Cu/γ-Al₂O₃; (b) Cu/TiO₂, Cu/ZrO₂ and Cu/CeO₂. Pre-treatment: H₂/350°C.

3.2.1.1. Activity. The steady-state conversion increased with the reaction temperature for all catalysts (Fig. 3). The level and order of conversions depended on both the reaction temperature and nature of the support. The Cu/SiO₂ catalyst showed high activity from 100°C (68.2% of conversion), whereas the other catalysts began to be active only from 150°C (<5% of conversion). On the other hand, the maximum of conversion was very high (100%) for the Cu/SiO₂ and Cu/Al₂O₃ catalysts, whereas it reached lower values (11.2–61.1%) for the other catalysts. The highest ac-

tivity was observed at 250°C for Cu/SiO₂ and 350°C for the other catalysts.

On the other hand, strikingly, a gap of activity was observed between 300°C and 350°C in the case of the Al₂O₃ supported catalyst, the conversion of which was multiplied by 23 (Fig. 3a). Although to a lesser extent, a similar behaviour was also observed for the reducible supports: in the same range of temperature, the activity was multiplied by 5.4 for TiO₂ and about 2 for CeO₂ and ZrO₂ (Fig. 3b). For the SiO₂-supported catalyst the conversion increased gradually in the whole range of reaction temperature (Fig. 3a).

3.2.1.2. Selectivity. The reaction products were benzyl alcohol, toluene and benzene. No aromatic ring hydrogenation was observed.

- Benzyl alcohol was produced only on the Cu/SiO₂ catalyst and at the reaction temperature of 100°C (83.5% selectivity at 68.2% of conversion). No benzyl alcohol (or only traces as for Cu/CeO₂) was observed for the other catalysts, whatever the reaction temperature.

- High selectivity to toluene (>90%) was observed for the Cu/SiO₂, Cu/CeO₂ and Cu/TiO₂ catalysts, whereas, the Cu/Al₂O₃ and Cu/ZrO₂ catalysts exhibited lower selectivity values (<70%) (Fig. 4). The maximum of selectivity to toluene appeared at low reaction temperature for Cu/SiO₂, Cu/Al₂O₃ and Cu/CeO₂ (≤250°C) but at higher reaction temperature for Cu/TiO₂ and Cu/ZrO₂ (350°C).

- The most selective catalyst to benzene was Cu/TiO₂ (100% at 150°C), whereas the least selective was Cu/SiO₂, even at a high reaction temperature (<10% at 350°C) (Fig. 5). In contrast to toluene, the selectivity to benzene increased with the reaction temperature for the Cu/SiO₂, Cu/Al₂O₃ and Cu/CeO₂ catalysts but decreased in the case of the Cu/TiO₂ and Cu/ZrO₂ catalysts (Fig. 5). The maximum of benzene selectivity was obtained at a high reaction temperature (350°C) for Cu/SiO₂ (8.0%), Cu/Al₂O₃ (64.8%) and Cu/CeO₂ (90.3%), and at lower temperature (150°C) for Cu/TiO₂ (100%) and Cu/ZrO₂ (65.9%) (Fig. 5).

- It is worth to note that, during the steady-state setting-up of the Cu/SiO₂ catalyst, toluene was formed as primary product and benzylalcohol as secondary product (Fig. 6). Benzene also arose as primary product, which disappeared after the steady-state activity was reached.

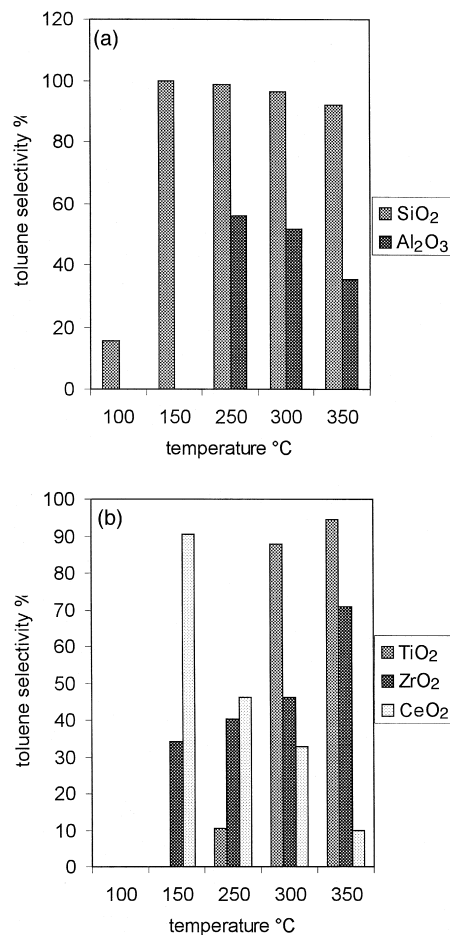


Fig. 4. Steady-state selectivity to toluene under H₂ flow as a function of the reaction temperature for: (a) Cu/SiO₂ and Cu/γ-Al₂O₃; (b) Cu/TiO₂, Cu/ZrO₂ and Cu/CeO₂. Pre-treatment: H₂/350°C.

3.2.2. Reduction of benzaldehyde under N₂ flow

Under N₂ flow, benzaldehyde was reduced stoichiometrically to benzylalcohol (100% of selectivity) at 100°C and catalytically to benzene (100% of selectivity) at 350°C (Figs. 7 and 8; Table 2). Carbon monoxide was co-produced with benzene. The observed reaction path depended on the nature of the catalyst or pre-treatment and reaction temperature.

Benzylalcohol appeared only with the Cu/CeO₂ and Cu/ZrO₂ catalysts (initial conversion of 3.4% or 1.2%, respectively; Fig. 7) pre-treated under N₂ flow or the Cu/SiO₂ catalyst (initial conversion of 38%; Fig. 8) pre-treated under H₂ flow. In contrast, benzene was produced with all the catalysts (Table 2) and the yield

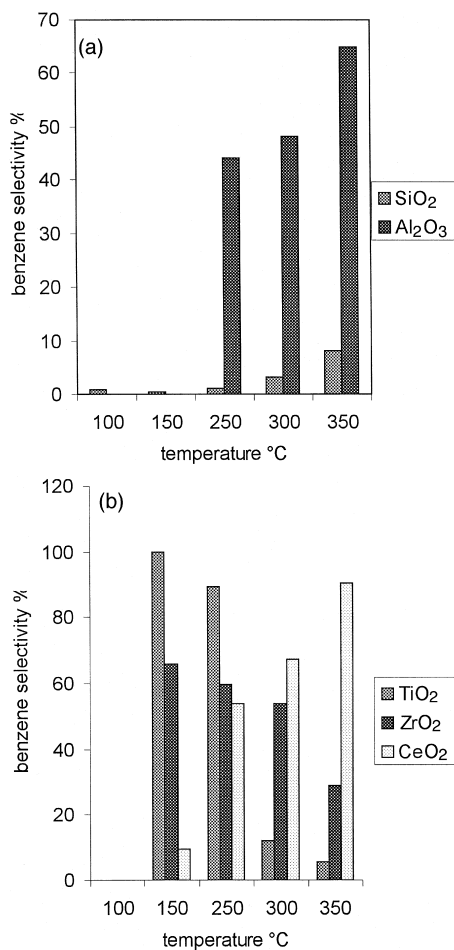


Fig. 5. Steady-state selectivity to benzene under H₂ flow as a function of the reaction temperature for: (a) Cu/SiO₂ and Cu/γ-Al₂O₃; (b) Cu/TiO₂, Cu/ZrO₂ and Cu/CeO₂. Pre-treatment: H₂/350°C.

was higher when the pre-treatment was H₂ (up to 88%) than N₂ (up to 28.8%) flow. For the catalysts supported on the irreducible oxides, alumina gave better conversion (28.8% or 88.8% as compared to 12.5% or 51.0%) whatever the pre-treatment, whereas, the order of activity depended on the pre-treatment for the reducible supports:

Cu/ZrO₂ > Cu/TiO₂ > Cu/CeO₂
N₂ flow pre-treatment

Cu/ZrO₂ > Cu/CeO₂ > Cu/TiO₂
H₂ flow pre-treatment

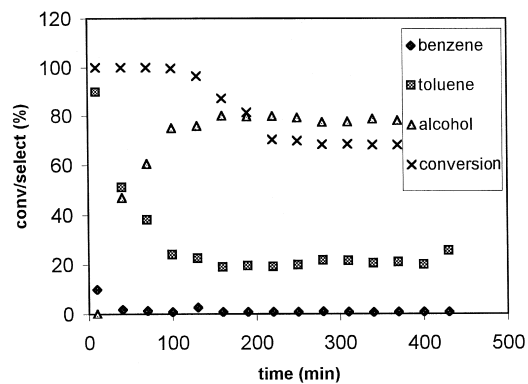


Fig. 6. Conversion of benzaldehyde with time on stream at 100°C under H₂ flow for the Cu/SiO₂ catalyst. Pre-treatment: H₂/350°C.

The latter order is different from that observed in benzene yield in benzaldehyde hydrogenation at the same reaction temperature (Table 2).

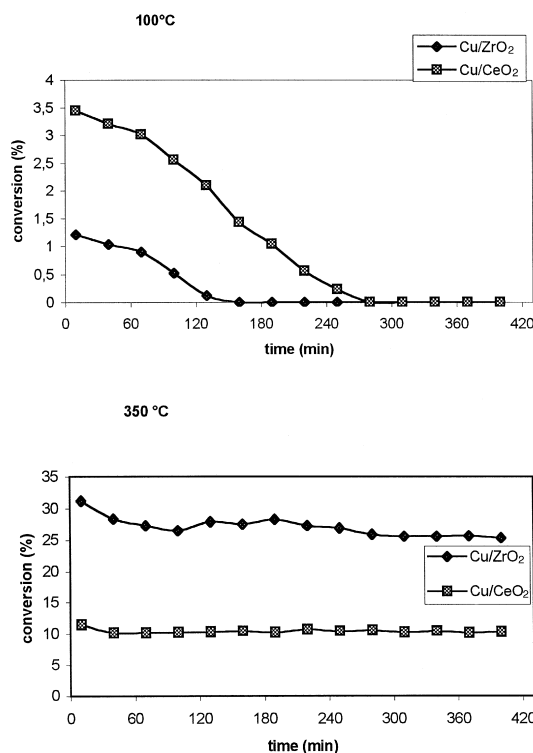


Fig. 7. Conversion of benzaldehyde with time on stream at 100°C and 350°C under N₂ flow for the Cu/ZrO₂ and Cu/CeO₂ catalysts. Pre-treatment: N₂/350°C.

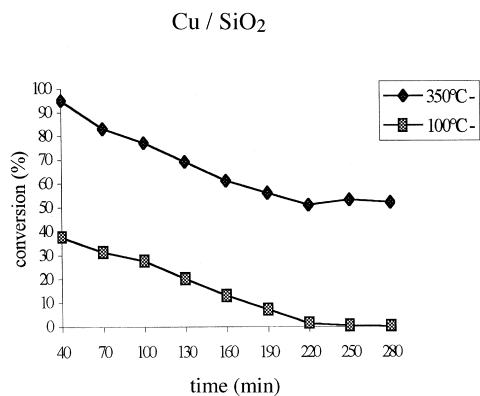


Fig. 8. Conversion of benzaldehyde with time on stream at 100°C or 350°C under N₂ flow for the Cu/SiO₂ catalyst. Pre-treatment: H₂/350°C.

Table 2

Steady-state benzene yield in the reduction of benzaldehyde under N₂ or H₂ flow over the copper catalysts

Catalyst	Reaction PhCHO/N ₂ /350°C		Reaction PhCHO/H ₂ /350°C
	Pre-treatment		Pre-treatment
	N ₂ /350°C (%)	H ₂ /350°C (%)	H ₂ /350°C (%)
Cu/SiO ₂	12.5	51.0	8.0
Cu/γ-Al ₂ O ₃	28.8	88.0	64.8
Cu/TiO ₂	18.4	24.0	3.4
Cu/ZrO ₂	28.4	40.0	3.4
Cu/CeO ₂	10.1	39.0	49.6

4. Discussion

In the discussion of the results of benzaldehyde hydrogenation, we have to bear in mind the nature of both the copper active site and organic molecules.

It is now well recognized that the active site in copper catalyzed hydrogenation reactions is the association of copper(I) in an octahedral environment with hydride ion [9,23–28]. The ionic character of this site explains its strong reactivity toward the highly polarized C=O double bond of carbonyl compounds [7–9,23–30] but also with the C–O simple bond of the alcohol product [4,24,30] and, as a consequence, the competitive adsorption between the reactant and product. In turn, this competitive adsorption should influence the reaction yields and lead to secondary

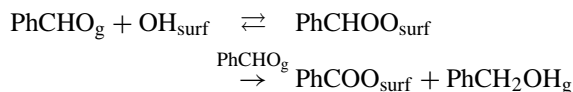
reactions of the alcohol product [4–6,24,30]. On the other hand, aldehydes are known as reductants through hydride release [30], then benzaldehyde should decompose to benzene [4–6,31]. In addition, all these paths should be accelerated or inhibited according to the nature of the support and reaction conditions. The support may both modify the electronic structure of the copper active site and play an important role in the adsorption and desorption of the reactant and product molecules.

Let us then discuss in more detail the obtained results in this study. We first consider the results obtained in the reduction of benzaldehyde under N₂ flow because they give useful information on the acid–base and reducibility properties of the catalysts.

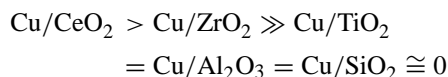
4.1. Reduction of benzaldehyde under N₂ flow

4.1.1. Reaction at 100°C. Formation of benzylalcohol

(i) After N₂ pre-treatment, only benzylalcohol was obtained as a result of the Cannizzaro reaction for the Cu/ZrO₂ and Cu/CeO₂ catalysts [6]. This reaction stoichiometrically consumes surface OH_{surf} groups then ends up (Fig. 7). It concomitantly forms benzyl alcohol and benzoate surface species (PhCOO_{surf}) and the overall process should be written as follows:



In this process, the pre-equilibrium step is probably rate limiting, then it follows that the obtained results reflect the surface mobility (or nucleophilicity) or concentration order of the OH_{surf} groups in the case of the oxidized catalysts, that is:



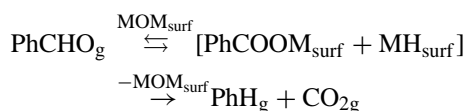
Moreover, the Cannizzaro reaction probably mainly proceeded through the support surface. Indeed, we have shown elsewhere [32], that, in the same reaction conditions, the bare CeO₂ support was much more active (25.0% of conversion) than the corresponding copper catalyst (3.4% of conversion, Table 2). Although less marked, similar behaviour was observed for the bare ZrO₂ support (2.0% of conversion instead of 1.2%). As to other bare TiO₂, Al₂O₃, SiO₂

supports, they were totally inactive [32] as were the corresponding copper catalysts (Table 2). It may be concluded that the oxidized supported copper catalysts contained lesser amount of active OH_{surf} groups than the bare supports. By the way, a similar decrease in active OH_{surf} groups concentration should have occurred during the impregnation step of the catalyst preparation, probably by reaction between these groups and the copper precursor, thus leading to the decrease of the BET specific area as reported above (Table 1).

(ii) Benzylalcohol obtained after H_2 pre-treatment for the Cu/SiO_2 catalyst was probably a result of hydrogen spillover. This behaviour is in good agreement with the reducibility (Table 1) and hydrogenation activity results (Fig. 3): the reduced copper phase was shown to be active from 100°C only on the silica support (see also discussion below). Further, the lack of activity in the case of the Cu/ZrO_2 and Cu/CeO_2 catalysts in the reduced state should indicate that the surface OH groups, active in the Cannizzaro reaction (Fig. 7), have been removed by the H_2 pre-treatment [6].

4.1.2. Reaction at 350°C . Formation of benzene

Benzaldehyde is known to dissociatively adsorb as benzoate species on basic oxides at room temperature [6,33] and subsequent heating leads to the decomposition of these species into benzene and CO_2 [6,33–35]. The mechanism is believed to be an oxido-reduction process where the metal oxide surface (denoted MOM_{surf}) is reduced by gaseous benzaldehyde [6,34]:

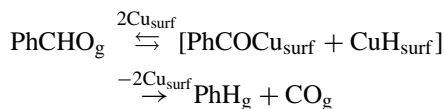


to metal benzoate (denoted $\text{PhCOOM}_{\text{surf}}$) and hydride (denoted MH_{surf}) surface species. This step, corresponding to the C–H bond breaking, is probably rate limiting. The formation of the benzoate species should proceed either in one single step or through that of the ketal-like intermediate ($\text{PhCHOOM}_{\text{surf}}$) [6,35].

(i) A similar mechanism should proceed in the case of our unreduced (pre-treated under N_2 flow) copper catalysts at the reaction temperature of 350°C . Copper is probably involved in such a mechanism since, in the absence of copper, the bare support oxides were almost inactive in the same reaction conditions [32]. Besides,

copper is known for a long time ago as an efficient catalyst for the decarboxylation of benzoate salts in liquid medium [36]. Moreover, it has been shown that the actual catalyst is cuprous ion and the intermediate the cuprous salt of the aromatic acid [PhCOOCu(I)] [36]. Also, as far as reaction mechanisms in liquid medium hold for gas phase reactions and if one supposes that reduced copper is formed during the thermal pre-treatment or the setting of the steady-state, copper benzoate species ($\text{PhCOOCu}_{\text{surf}}$) may have been the reaction intermediate in the reduction of benzaldehyde to benzene on the present supported copper catalysts. In such a case, the oxygenate species, formed on the support, migrated on copper where it was subsequently reduced to benzene. Similar surface processes are often invoked in the case of oxygenate species evidenced on supported copper catalysts during the reduction of the carbon oxides [37,38].

(ii) The above mechanism should also hold for the reduced (pre-treatment under H_2 flow) catalysts. The increase in benzene yield after the reductive pre-treatment should be attributed to the increase of the amount of reduced active phase (Table 2). However, change in the reaction path on the reduced as compared to the unreduced copper phase have to be considered. Thus, the decomposition of benzaldehyde into benzene, over reduced copper particles instead of acid–base sites, is not excluded. The reaction intermediate should be the copper benzoyl surface species:



A similar entity, the carbonyl surface species, has also been invoked in the case of supported copper catalysts during the reduction of the carbon monoxide [37]. In any case, such a mechanism should be suitable in the case of copper supported on the acidic SiO_2 support on which the benzoate surface entity is less likely to form.

4.2. Hydrogenation of benzaldehyde

4.2.1. Activity

4.2.1.1. Copper supported on SiO_2 and Al_2O_3 irreducible supports. According to the TPR results

(Table 1), the high activity of Cu/SiO₂ as compared to that of Cu/Al₂O₃ may be related to its better reducibility. Indeed, the first peak of reduction of Cu/SiO₂ arose at 260°C, whereas, it appeared at 350°C only for Cu/Al₂O₃. However, the sudden increase of the conversion (from 5% to 100%) observed for the latter between 300°C and 350°C (Fig. 3) suggests that, besides reducibility properties, support acid–base properties of the catalysts should also be involved. In such a case, the activity of Cu/Al₂O₃ should be governed by the adsorption strength of the reactant or product molecules, as surface benzoate or alcoholate species [6,33–35], on acid–base sites of the support.

The inhibiting effect of stable surface oxygenated products has indeed been invoked for the hydrogenation of conjugated carbonyl compounds on copper-based catalysts [7–9,24,29,30,35,36]. Benzoate or alcoholate species formation was also invoked during the hydrogenation of benzaldehyde over copper catalysts supported on chromium oxide [8,9,23,24]. In addition, the IRTF study of the adsorption of benzaldehyde over metal oxides [35] strengthens the hypothesis of the intervention of the acid–base properties of the SiO₂ or Al₂O₃ supports in the case of copper catalysts. Indeed, the study [35] showed that the adsorption of benzaldehyde on silica occurs through a hydrogen bond of the oxygen atom of the C=O group to the surface silanol groups, whereas, for the rather basic alumina, it involves a nucleophilic attack at the carbonyl center by surface oxygen (or hydroxyl), producing surface benzoate species [36]. These species were stable up to 300°C even under hydrogen atmosphere [35]. Also, for the present alumina supported copper catalyst, intermediate oxygenated surface species formed should have acted as inhibiting entities, maintaining low activity up to 300°C. At higher reaction temperatures, these species readily decomposed, whereas, the metallic copper sites became more active, thus explaining why an important gap in conversion of benzaldehyde was observed (Fig. 3). For the Cu/SiO₂ catalyst, no or little base sites were available for strong adsorption of the reactant or product molecules; then no inhibition of the reaction course was detected.

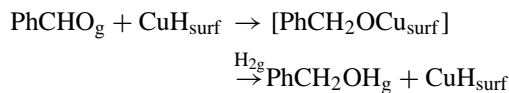
4.2.1.2. Copper catalysts supported on TiO₂, ZrO₂ and CeO₂ reducible oxides. The Cu/ZrO₂ catalyst exhibited the lowest activity in the whole range of

reaction temperature (Fig. 3). This behaviour may be explained by a strong metal–support interaction, which led to the insertion of part of the copper phase in the bulk [22] and, consequently, lowered the catalytic activity. Similar interaction may also exist for the Cu/TiO₂ and Cu/CeO₂ catalysts. In other respects, as suggested above for Cu/Al₂O₃, the gap of activity observed between 300°C and 350°C (Fig. 3) should also involve acid–base and not only metal properties of the copper catalysts supported on the reducible oxides. Further studies are needed to describe in more detail the involved chemical processes.

4.2.2. Selectivity

The fact that the aromatic nucleus is unreactive while the carbonyl substituent undergoes hydrogenation and hydrogenolysis suggests that the aromatic aldehyde reacts principally with the catalyst via the carbonyl function. It should be assumed that in the adsorbed benzaldehyde both the aromatic ring and the carbonyl group lie parallel to the active surface [5]. In such a case, the adsorbed hydrogen preferably attack the carbonyl group due to energy barriers [2,5,8].

4.2.2.1. Benzylalcohol selectivity. Benzylalcohol was produced with high selectivity at high conversion on copper supported on the acidic SiO₂ support only (Fig. 6). This support favoured the reduction of the carbonyl compound to the corresponding alcohol, even at high conversion, probably mainly through the inhibition of the adsorption of the benzylalcohol reaction product [4]. As to the chemical process of benzylalcohol formation, it can be supposed to be a 1–2 nucleophilic addition, with a high polarization of the transition state, as in the case of the hydrogenation of conjugated carbonyl compounds [2,7–9,23,24]:

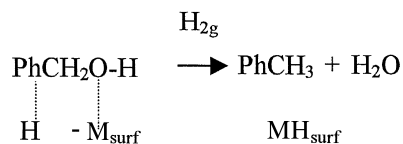


For the other more basic catalysts, no benzylalcohol was detected in the exit gas (Fig. 4) probably because, more strongly held on the catalyst surface, it was subsequently chemically converted before desorption.

4.2.2.2. Toluene selectivity. It is generally believed that toluene is the product of the consecutive reaction of hydrogenolysis of benzylalcohol [2–8].

Indeed, flowing the Cu/SiO₂ catalyst with benzylalcohol instead of benzaldehyde, selectively led to toluene production. However, benzylalcohol is a complex molecule possessing several active centers such as the acidic proton and basic oxygen of the O–H function and the reductive hydrogen of the C–H exocyclic function. All these centers may interact with the copper or support phase or dihydrogen molecule. Also several pathways can be envisaged for toluene formation from benzylalcohol.

(i) It has been reported that mixed copper oxides such as Cu–Cr–O [9,23], Cu–Zr–O [39], Cu–Zn–O [39–42] are hydrogen reservoirs and the occluded hydrogen postulated to be of hydridic nature [9,23,26,39]. On the other hand, the hydrogenolysis of allyl alcohol to the corresponding hydrocarbon was studied on copper supported on chromium oxide and it was shown that the Cr–H but not the Cu–H species was the active site [8,9]. The chromium ion was suggested to play the role of strong Lewis acid site interacting with the oxygen atom of the alcohol molecule and the mechanism postulated to be concerted [8,9]. Then, we think that the present oxide supports, except perhaps SiO₂ (see below), formed metal hydride as active species for the reduction of benzylalcohol to toluene:

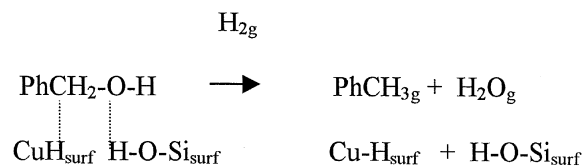


In other words, the active site should be bifunctional in nature on which the metal cation and hydride entities interacted with the oxygen and carbon atoms of the alcohol molecule, respectively. In such a case, the activity in toluene should reflect the aptitude of the support oxide to both adsorb the alcohol (Lewis acid property) and dissociate H₂ (metal property). This conclusion may hold for the TiO₂, ZrO₂ and CeO₂ reducible oxides, which are more prone to form metal hydride species.

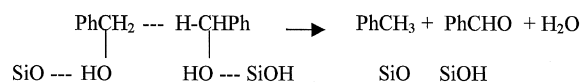
(ii) The copper mixed oxide Cu–Al–O has also been shown to be reservoir of occluded hydrogen of hydridic nature [26]. Also, the above mechanism can be postulated for the formation of toluene from benzy-

l alcohol in the case of copper supported on the Al₂O₃ irreducible oxide.

(iii) In the case of the Cu/SiO₂ catalyst, no Cu–Si–O mixed metal oxides were reported, to our best knowledge. On the other hand, we have above reported that benzaldehyde adsorption resulted in the interaction between its oxygen atom and the hydrogen atom of the silanol groups [35]. Also, one is allowed to think that toluene formation probably resulted in the protonation of the alcohol function on a silanol Brønsted acid site (H–O–Si_{surf}) followed by the hydrogenolysis of the protonated specie on an adjacent copper site:



(iv) We have shown that, strikingly, toluene appeared as a primary product over the Cu/SiO₂ catalyst at 100°C (Fig. 5). The formation of toluene as primary product and at a so low reaction temperature, suggests the existence of another reaction path than that described above. This path probably involves very active sites on which toluene quickly formed in the early stages of the reaction where the partial pressure of both reactants and products were low (time ≈ 0; Fig. 5). These sites were then poisoned at higher conversion (time > 100 min; Fig. 5) by the one or the other reactant molecule, even water. The possible route should be the benzylalcohol dimerization to toluene, benzaldehyde and water on the silica support [43–45]:



The reaction probably proceeds through hydride transfer between two adsorbed benzylalcohol molecules over specific acid–base sites of the support [43,44]. These sites should be poisoned with time on stream. Such a mechanism was reported for benzylalcohol dimerization to toluene over alumina catalyst [44]. The catalyst was shown to deactivate by prolonged usage or by water addition [44].

4.2.2.3. Benzene selectivity. In the catalytic hydrogenation of benzaldehyde, benzene is believed to be the product of the hydrogenolysis of the external C–C

bond of benzaldehyde [4,5]. Gas phase kinetic studies of benzaldehyde over platinum [4] or nickel [5] catalysts showed that benzene was produced directly from the reactant molecule and not from the alcohol or toluene intermediates. Carbon monoxide was identified as co-product of benzene [4]. However, no mechanistic route has been proposed for the reaction. As to copper catalysts, no studies have been reported on the hydrogenolysis of benzaldehyde to benzene. Moreover, it has been reported that this reaction not occurs on copper catalysts [20].

In the present case, benzene is formed in benzaldehyde hydrogenation on copper catalysts (Fig. 5). The above discussion suggests that the reaction path to benzene involves the intervention of an oxygenate surface precursor, the stability of which depends on the nature of the support and reaction temperature [6,32–34]. It is worth to note that, at the reaction temperature of 350°C, the benzene yield was higher in the absence (24.0–88.0%) than in the presence (3.4–49.6%) of H₂ (Table 2). These results may be attributed to the competitive formation of toluene under H₂ flow (Fig. 4). However, other factors such as the presence of water molecules formed in the reactive atmosphere or the nature of the H₂ reductant should also play a role in the observed yields. In the same way, for the Cu/ZrO₂ catalyst, the conversion of benzaldehyde was more important in the absence (40%; Table 2) than in the presence (11.2%; Fig. 3) of H₂. In this case, the presence H₂ in the reactive atmosphere seemed to inhibit the active sites of benzene formation. These facts show that other investigations are necessary to get more insight on the mechanism of reduction of benzaldehyde to benzene on supported copper catalysts.

5. Conclusions

The hydrogenation of benzaldehyde over copper catalysts supported on Al₂O₃, SiO₂, TiO₂, ZrO₂ and CeO₂ at atmospheric pressure and 100–350°C produced competitively benzylalcohol, toluene and benzene with yields depending on the nature of the support and the reaction temperature. The order of activity was attributed to both metal and acid–base properties of the catalysts. The latter properties induced adsorption phenomena which, for example, explained the important gap in activity (multiplied by 2 to 23)

between 300°C and 350°C observed for all catalysts except Cu/SiO₂: the lower the reaction temperature the strongly held were the benzaldehyde or benzylalcohol molecules the stronger was the inhibiting effect of the support on the reaction course; conversely, the higher the reaction temperature the lower the adsorption effect the higher the conversion of benzaldehyde. In connection, benzylalcohol was selectively obtained (83% at 68% of conversion) at 100°C with the copper catalyst supported on the acidic SiO₂ oxide. Toluene product arose from the hydrogenolysis of benzylalcohol on probably bifunctional sites involving metal hydride species. As to benzene, it resulted from benzaldehyde hydrogenolysis, probably through a copper surface oxygenate specie. Useful information on the surface properties of the catalysts and the reaction course were given by comparing the transformations of benzaldehyde under H₂ or N₂ atmosphere.

References

- [1] P. Gallezot, A. Giroir-Fender, D. Richard, in: W. Pascoe (Ed.), *Catalysis of Organic Reactions*, Marcel Dekker, New York, 1991, p. 1.
- [2] A. Chambers, S.D. Jackson, D. Stirling, G. Webb, *J. Catal.* 168 (1997) 301.
- [3] T.B.L.W. Marinell, V. Ponec, *J. Catal.* 156 (1995) 59.
- [4] M.A. Vannice, D. Poondi, *J. Catal.* 169 (1997) 166.
- [5] M.A. Keane, *Appl. Catal., A* 118 (1997) 261.
- [6] D. Haffad, U. Kameswari, M.M. Bettahar, A. Chambellan, J.C. Lavalley, *J. Catal.* 172 (1997) 85.
- [7] J. Jenck, J.E. Germain, *J. Catal.* 65 (1980) 141.
- [8] R. Hubault, J.P. Bonnelle, *J. Mol. Catal.* 55 (1989) 170.
- [9] R. Hubault, M. Daage, J.P. Bonnelle, *Appl. Catal.* 22 (1986) 231.
- [10] D. Nightingale, H.D. Radford, *J. Am. Chem. Soc.* 71 (1949) 1089.
- [11] M. Fiefelder, *Practical Catalytic Hydrogenation*, Wiley-Interscience, New York, 1971.
- [12] P.N. Rylander, *Catalytic Hydrogenation in Organic Synthesis*, Academic Press, London, 1979.
- [13] P.N. Rylander, *Hydrogenation Methods*, Academic Press, London, 1985.
- [14] H. Adkins, H.R. Billica, *J. Am. Chem. Soc.* 70 (1948) 695.
- [15] W.H. Carothers, R. Adams, *J. Am. Chem. Soc.* 46 (1924) 1675.
- [16] R. Menschke, W.H. Hartung, *J. Org. Chem.* 25 (1960) .
- [17] R. Baltzly, *J. Org. Chem.* 41 (1976) 928.
- [18] W.H. Carothers, R. Adams, *J. Am. Chem. Soc.*, 47 51925° 1047.
- [19] S. Paganelli, U. Matteoti, A. Scrivanti, C. Botteghi, *J. Organomet. Chem.* 397 (1990) 375.

- [20] J.A. Schreifels, P.C. Maybury, W.E. Swartz, *J. Org. Chem.* 46 (1981) 1263.
- [21] M. Herskowitz, in: M. Guisnet (Ed.), *Heterogeneous Catalysis and Fine Chemicals*, Elsevier, Amsterdam, 1991, p. 105.
- [22] A. Saadi, Z. Rassoul, M.M. Bettahar, J. Barrault, in preparation.
- [23] L. Jalowiecki, G. Wrobel, M. Daage, J.P. Bonnelle, *Appl. Catal.* 107 (1987) 375.
- [24] R. Bechara, G. Wrobel, M. Daage, J.P. Bonnelle, *Appl. Catal.* 16 (1985) 15.
- [25] M. Daage, J.P. Bonnelle, *Appl. Catal.* 16 (1985) 355.
- [26] F. Bali, G. Wröbel, L. Jalowiecki, J. Bonnelle, M.M. Bettahar, *New J. Chem.* 11 (1987) 715–720.
- [27] S. Siegel, *J. Catal.* 30 (1973) 139.
- [28] M. Amara, M.M. Bettahar, L. Gingembre, D. Olivier, *Appl. Catal.* 35 (1987) 153.
- [29] R. Hubault, J.P. Bonnelle, in: M. Guisnet (Ed.), *Heterogeneous Catalysis and Fine Chemicals*, Elsevier, Amsterdam, 1991, p. 287.
- [30] R. Hubaut, *React. Kinet. Catal. Lett.* 46 (1992) 25.
- [31] J. March, *Advanced Organic Chemistry, Int. Stud. edn.*, McGraw-Hill, Tokyo, 1997.
- [32] A. Saadi, Z. Rassoul, M.M. Bettahar, in preparation.
- [33] S.T. King, E.J. Strojny, *J. Catal.* 76 (1982) 274.
- [34] M. Coudurier, G. Wieker-Coudurier, C. Naccache, B. Vital-Mathieu, *Bull. Soc. Chim. Fr.* 4 (1969) 1121.
- [35] C.A. Koustal, P.A.J.M. Angeware, V. Ponec, *J. Catal.* 143 (1993) 573.
- [36] J. March, *Advanced Organic Chemistry, Int. Stud. edn.*, McGraw-Hill, Tokyo, 1997. p. 507.
- [37] F. Lepeltier, P. Chaumette, J. Saussey, M.M. Bettahar, J.C. Lavalley, *J. Mol. Catal. A: Chem.* 122 (1997) 131.
- [38] F. Lepeltier, P. Chaumette, J. Saussey, M.M. Bettahar, J.C. Lavalley, *J. Mol. Catal. A: Chem.* 132 (1997) 91.
- [39] F. Bali, M.M. Bettahar, G. Wröbel, J.P. Bonnelle, *J. Chim. Phys.* 92 (1995) 1405–1416.
- [40] D. Duprez, J. Barbier, Z. Ferhat-Hamida, M.M. Bettahar, *Appl. Catal.* 12 (1984) 219–225.
- [41] Z. Mesbah-Benyoucef, M.M. Bettahar, J. Barrault, A. Tranchant, P. Messina, *Mol. Chem.* 2 (1987) 33–46.
- [42] D. Duprez, Z. Ferhat-Hamida, J. Barbier, M.M. Bettahar, *J. Catal.* 124 (1990) 1.
- [43] E.A.I. Heiba, P.S. Landis, *J. Catal.* 3 (1964) 471.
- [44] M. Jayamani, C.N. Pillai, *J. Catal.* 82 (1983) 485.
- [45] M. Jayamani, N. Murugesan, C.N. Pillai, *J. Catal.* 85 (1984) 527.