

Reduction of benzoic acid on CeO₂ and, the effect of additives

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Abstract

Catalytic behaviour of CeO₂ in the reduction of benzoic acid has been studied in the temperature range 523–723 K. Two types of catalytic behaviour are observed in the whole temperature range. One type is observed from 523 up to 723 K. In this range, the selectivity to benzaldehyde can be higher than 95% and the reaction proceeds by the redox (Mars and van Krevelen) mechanism, with the oxygen vacancy as the active site. The activity is controlled by the steady-state concentration of oxygen vacancies under reaction conditions. The second type behaviour is observed above 648 K. Under these conditions the conversion of benzoic acid achieves nearly 100%, but the selectivity to benzaldehyde decreases, while that to toluene and benzene increases. In this range of temperatures, the reaction proceeds too far, due to a very high concentration of vacancies. Besides the redox mechanism decarboxylation (hydrogenolysis) of the relative stable adsorbed benzoic acid takes place. The results observed with the reaction of adsorbed benzoic acid, under a flow of H₂ reflects the two types of reaction. The potential promotion effects by Al, Cr, Mn, Fe, Ga, Zr, In and Pb oxides added to CeO₂ were investigated. The catalytic behaviour of CeO₂ changes by the addition of the metal oxides, positive effects are observed after adding Mn, Zr, In and Pb oxides. © 1998 Elsevier Science B.V.

1. Introduction

Aldehydes, and particularly the aromatic aldehydes, are important materials for synthesis of organic fine chemicals. There are various ways to synthesize aldehydes and the two-step reduction of carboxylic acids is the most important method. Hereby, the carboxylic acid is first converted into an acid chloride, which step is followed by hydrogenation of the chloride to the aldehyde, with the use of a suitable heterogeneous catalyst (Rosenmund-reduction) [1]. However, this method has various disadvantages, such as a low yield

and production of useless and harmful by-products in stoichiometric amounts.

A direct gas-phase reduction of carboxylic acids to aldehydes is, when using suitable catalysts, another possible method. It is a very advantageous method, if the catalyst exhibits a sufficient activity and selectivity. There are already several patents on this subject, dealing with effective catalysts and technology of the whole process [2–10]. Recent patents and papers show that ZrO₂ and the metal-ion promoted ZrO₂ exhibit excellent catalytic performances in the reduction of those carboxylic acids which have no α -hydrogen (such as benzoic or vibaric acid) to the corresponding aldehydes [4–7]. There are already some ideas about the functioning of these catalysts [11,12]. We have also been investigating the selective reduction of aliphatic and aromatic carboxylic acids to the corre-

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sponding aldehyde over various oxide catalysts from the mechanistic point of view [13–18]. For aliphatic carboxylic acids, it has been confirmed that an oxygen vacancy in the surface acts in activating the carboxylic acid. The carboxylic acid deoxygenates with the help of the oxygen vacancy to form a bound acylium ion (oxidation of the catalyst in the Mars and van Krevelen mechanism [19]) and this intermediate is consequently hydrogenated to aldehyde. Hydrogen adsorption (the extent and the dynamics thereof) is also related to the activity and selectivity of the catalyst. Thus, a good catalyst should induce the first step of the Mars and van Krevelen mechanism, the deoxygenation, in the right extent and, possess good propensity to adsorb hydrogen without, however, enabling an attack of hydrogen on the ring.

Our previous study revealed that the oxide catalysts can be divided into several categories, according to their catalytic behaviour [17,18]. Two kinds of mechanism can be postulated: one is a radical-like mechanism of the thermal decomposition of surface benzoate (on oxides with basic character), the other is a mechanism of direct deoxygenation of benzoic acid, in a framework of an oxidation–reduction cycle. The latter mechanism is mainly observed with oxides catalysts that can sustain a continuous formation of active oxygen vacancies. The steady-state concentration of active oxygen vacancies under a running reaction is one of the most important factor controlling the selectivity of benzoic acid reduction to benzaldehyde [18]. Among the various oxides, CeO_2 showed a particularly high activity, selectivity, and other properties which lead to the present study.

In this paper, we have studied the catalytic property of various CeO_2 catalysts in reduction of benzoic acid. The catalytic behaviour was monitored when changing the reaction conditions discontinuously and by using a temperature-programmed regime of reaction. Furthermore, we have investigated the effects of various metal oxides as additives to CeO_2 .

2. Methods

2.1. Catalyst preparation

The pure CeO_2 catalyst used in this work was prepared by calcination of $\text{Ce}(\text{OH})_3$. The latter oxide

was obtained by precipitation of $\text{Ce}(\text{NO}_3)_3$ (Merck) with NH_4OH at $\text{pH} = 9$, and calcination in air at 773 K for 15 h. Various metal-ion modified CeO_2 catalysts were prepared by calcination of coprecipitates of the homogeneously mixed hydroxides, obtained from hydrolysis in the $\text{Ce}(\text{NO}_3)_3$ solution mixed with the corresponding metal nitrate, in desired ratio. Precipitation was performed with NH_4OH at $\text{pH} = 9$ and the final step calcination in air at 773 K for 15 h. The nitrates used in the present work are $\text{Al}(\text{NO}_3)_3$ (Aldrich), $\text{Cr}(\text{NO}_3)_3$ (Fluka), $\text{Mn}(\text{NO}_3)_2$ (Alpha-products), $\text{Fe}(\text{NO}_3)_2$ (Fluka), $\text{Ga}(\text{NO}_3)_3$ (Aldrich), $\text{ZrO}(\text{NO}_3)_3$ (Aldrich), $\text{In}(\text{NO}_3)_3$ (Aldrich) and $\text{Pd}(\text{NO}_3)_2$ (Merck). All metal compounds were added at their 5 at.-% of the cation, relative to the Ce ion concentration in the catalyst. The catalyst (0.3 g) was loaded in the reactor and in a standard experiment kept first in a He flow at 725 K, for 1 h.

2.2. Experimental procedure

All the experiments mentioned below were carried out in a continuous flow apparatus, equipped with a benzoic acid saturator. A heating system kept the whole apparatus at temperatures above 373 K. For other details see our previous paper [18].

The product mixtures were analyzed by a gas-liquid chromatograph (GLC). A sample (ca. 5 ml) of reactor effluent containing products and unreacted benzoic acid, was extracted from the system behind the reactor, by a special syringe, heated to 473 K during the entire procedure of transfer and injection into GLC. The mixtures of the products and of unreacted benzoic acid could also be condensed in a condenser before the exit from the system and, this condensate could be thereafter analyzed by GLC. A Hewlett Packard 5890, series II, gaschromatograph, equipped with FID detector and wide-bore CP-Sil 13 column (Chrompack, NL) was used for separating and determining the products. The data were stored and evaluated by HP-Chem. station [18].

In a standard experiment, the reaction was carried out under 1 bar total pressure of H_2 and benzoic acid (BA). The flow rate was 28 ml/min, and partial pressure of BA was 35 Pa. The monitoring of reaction started at 523 K and thereafter, the reaction temperature was increased stepwise (by 25 K) up to 725 K. The partial pressure of benzoic acid was controlled by

changing the temperature of the condenser with BA. The products were analyzed every 30 min and, after achieving a steady state of the reaction, the reaction temperature was increased or the reaction condition were changed, as desired.

The temperature dependence of the reactivity of adsorbed benzoic acid was also examined in the absence of BA in the feed. In these experiments, the adsorption of BA took place at 473 K, upon exposing the catalyst to benzoic acid vapor carried in He, until the unadsorbed benzoic acid was detected in the condenser placed before the exit of the apparatus. After adsorption of benzoic acid, the catalyst was kept in the He flow for 1 h at the same temperature, to desorb the physically adsorbed benzoic acid. The test of reactivity was then carried out in the flow under 1 bar H₂. Such an experiment started at 523 K and the desorbed products were analyzed at every 25 K, up to 723 K.

The parameters used in this paper are the carbon atom based conversion (α) per weight unit catalyst, and the selectivity (S). These parameters were defined in the same way as in our previous paper [18].

3. Results

3.1. Catalytic behaviour of CeO₂ in the reduction of benzoic acid

Temperature dependence of reaction parameters, as obtained with the benzoic acid hydrogen mixtures lead over pure CeO₂, is shown in Fig. 1. Fig. 1(A) shows the conversion, Fig. 1(B) – the selectivity. The conversion increased with the increase of the reaction temperature and achieved a value above 90% at 623 K, as can be seen in Fig. 1(A). The selectivity to benzaldehyde stayed above 90% up to 648 K and then decreased markedly, while the selectivity to toluene and benzene increased.

It can be noticed from Fig. 1(B), that the selectivity to benzene was larger than that to toluene at temperatures above 648 K. Toluene is probably formed by a too deep deoxygenation (both oxygen atoms removed) of the adsorbed benzoic acid, while benzene is likely produced by decarboxylation (hydrogenolysis) of the surface benzoate [18].

The dependence of the activity and selectivity on the partial pressure of benzoic acid in the reactant flow is shown in Fig. 2. Fig. 2(A) shows this dependence at 598 K, when the conversion of benzoic acid is around 50%. Fig. 2(B) shows the same for a reaction at 673 K, when the conversion is nearly 100% (under otherwise standard experimental conditions). When the partial pressure of benzoic acid was increased at 598 K, (Fig. 2(A)) the conversion of benzoic acid decreased monotonically with increasing pressure of benzoic acid vapor, while the selectivity to benzaldehyde stayed high, above 95%. On the other hand, when the partial pressure of benzoic acid was increased at 673 K, the conversion reached nearly 100%, irrespective the partial pressure of benzoic acid. However, an important change in the selectivity was still observed. The selectivity to benzaldehyde increased with increasing the partial pressure of benzoic acid and it achieved values higher than 90%, while the selectivity to other products correspondingly decreased. In particular, the selectivity to toluene considerably decreased, below 1%.

The reactivity of adsorbed benzoic acid in the H₂ flow was also investigated at various temperatures. The catalyst was first reduced in H₂ flow at 723 K for 1 h and after this pretreatment the benzoic acid was adsorbed at 473 K. After the pretreatment, the colour of the catalyst was blue-purple and when benzoic acid was adsorbed on this surface the colour immediately changed to yellow-white. The first colour corresponds to CeO_{2-y}, the yellow one to CeO₂, itself. This means that benzoic acid acts as an oxidant and reoxidizes the partially reduced CeO₂ by filling the oxygen vacancies in CeO₂. These visible changes demonstrate clearly the operation of the Mars and van Krevelen mechanism.

The reaction of the adsorbed benzoic acid in the flow of hydrogen is shown in Fig. 3. Fig. 3(A) shows the total amount of desorbed products (total 'carbon') as a function of temperature, and Fig. 3(B) shows the selectivity to various desorbed products. In Fig. 3(A), two peaks at 573 and 673 K respectively, are observed. The selectivity to various desorbed compounds is different at the two peaks; the selectivity to benzaldehyde is more than 95% during the first peak at about 573 K, but toluene and benzene are produced with a high selectivity during the second peak (at and around 673 K).

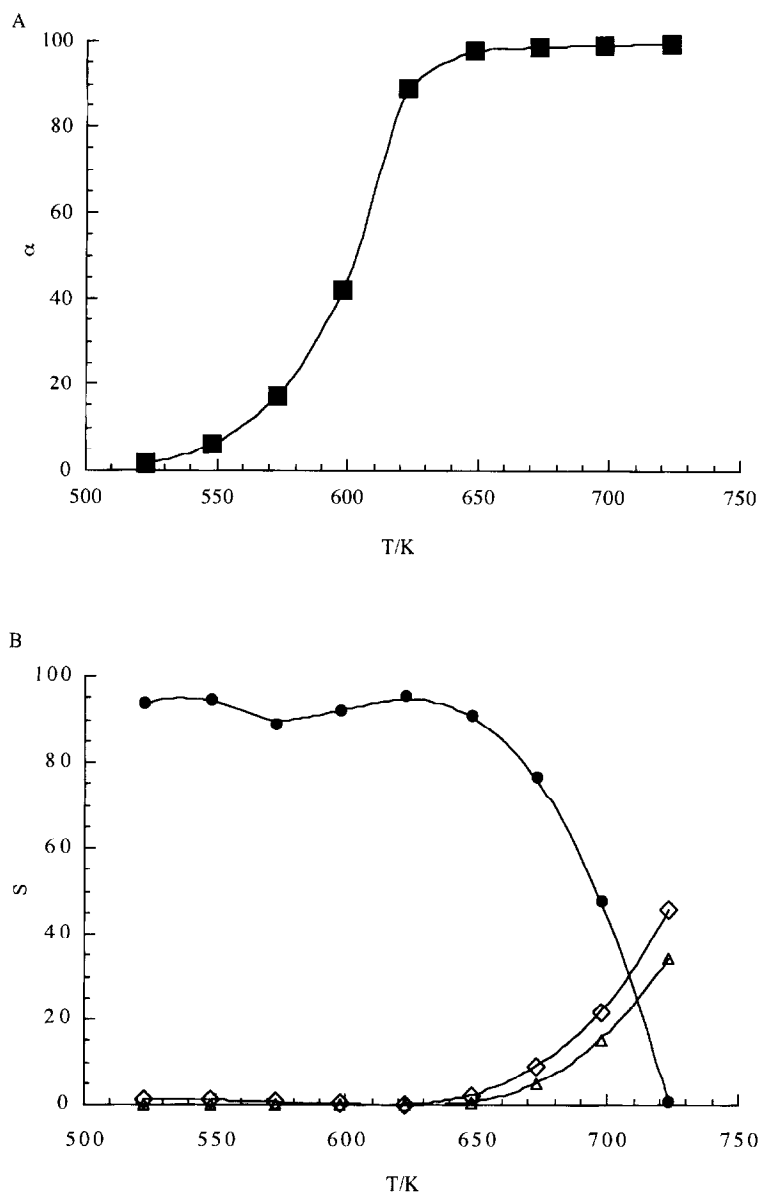


Fig. 1. Reduction of benzoic acid on CeO₂, temperature dependence of catalytic activity and selectivity. A: conversion; and B: selectivity. Symbols: ■: conversion; ◇: selectivity to benzene; △: selectivity to toluene; ●: selectivity to benzaldehyde.

3.2. The additives – Al, Ga and In oxides

Fig. 4 shows the effects of Al, Ga and In oxides, added to the CeO₂ catalysts. Fig. 4(A) shows the conversion of benzoic acid as a function of the reaction temperature for pure CeO₂ and for the modified metal compounds CeO₂. The Fig. 4(B–D) show the corresponding relation for the selectivities. As can be

seen in Fig. 4(A), the effect on the activity varied with the additive. Compared to CeO₂, the conversion decreased by adding Al compound, but was nearly the same after adding Ga oxide. It was enhanced considerably by introducing the In compound into the CeO₂ catalyst.

The selectivity of the catalyst with Al (oxide) additive, was similar to that of CeO₂, as shown in

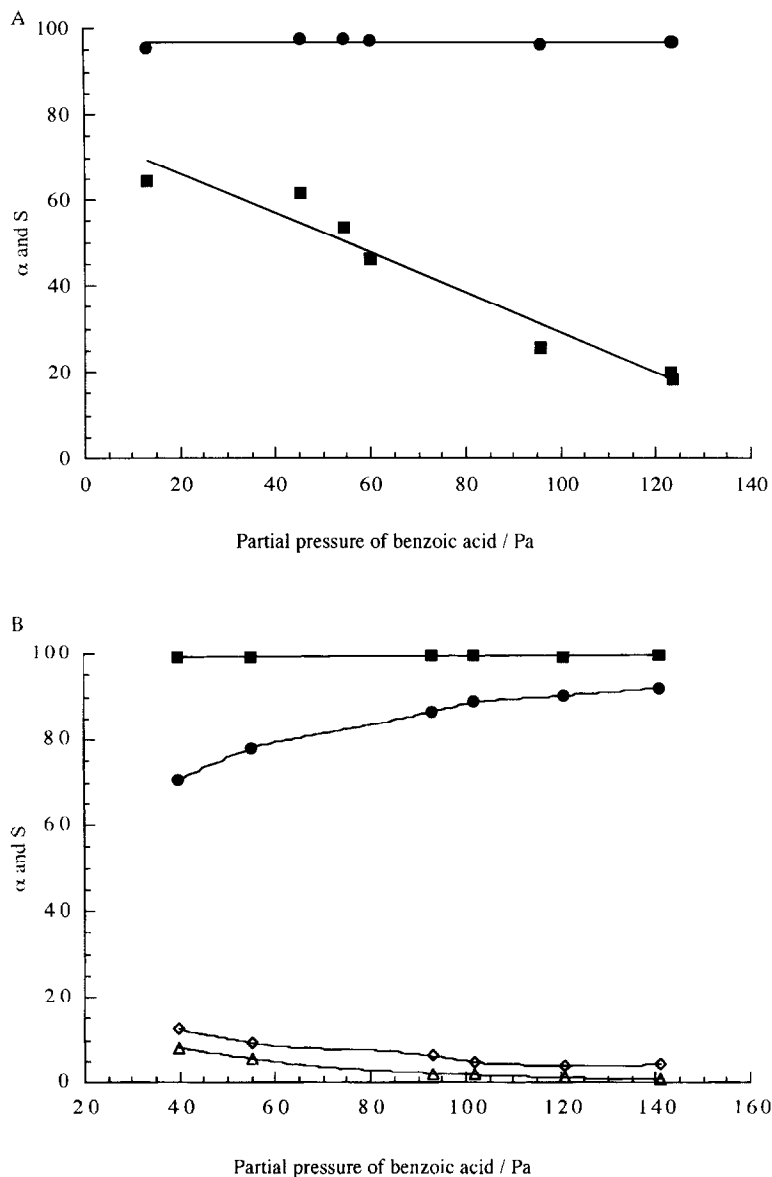


Fig. 2. Activity and selectivity of CeO_2 as a function of the partial pressure of benzoic acid in the reactant mixture at A: 598 K; and B: 673 K; Symbols as in Fig. 1.

Fig. 1(B). The selectivity profile $S(T)$ marginally shifted by approximately 25 K, compared with CeO_2 . The analogous $S(T)$ curve for benzaldehyde did not shift, when Ga was added. However, at higher temperatures, the selectivity to toluene was higher than that observed with pure CeO_2 . After adding In oxide, the selectivity to benzaldehyde (Fig. 4(B)) was at higher temperatures lower than that of pure

CeO_2 , but the overall conversion and the selectivities to benzylalcohol and toluene, increased by this additive.

3.3. The additives – Cr, Mn and Fe oxides

The effects of Cr, Mn and Fe oxides additives are shown in Fig. 5. Fig. 5(A) shows the relation between

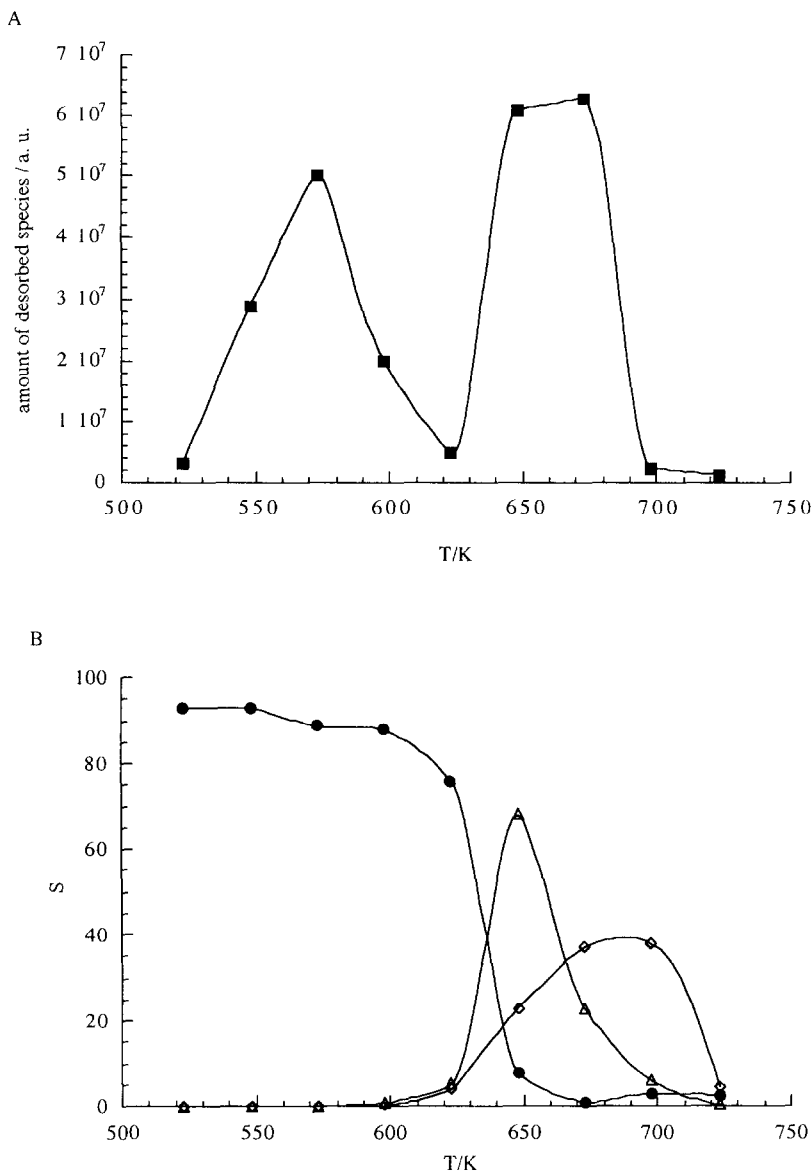


Fig. 3. Temperature programmed reaction of adsorbed benzoic acid in H_2 flow. A: total amount of desorbed compounds (total carbon) and B: selectivity to various compounds. Symbols as in Fig. 1.

the total conversion of benzoic acid and the reaction temperature, for pure CeO_2 and for the catalysts with the indicated additive to CeO_2 . The Fig. 5(B–D) show the relation between the product selectivities and the reaction temperature for Cr, Mn and Fe oxides added, respectively. Fig. 5(A) shows that the activity varies when various additives are used. The conversion is decreased by adding Cr oxide, stays nearly the same

when adding Fe oxide and it is improved considerably when adding Mn oxide.

The temperature dependence of the product selectivities obtained with the Cr oxide as modifier of CeO_2 , is nearly the same as that with unmodified CeO_2 (Fig. 5(B)). The selectivity to benzaldehyde showed values above 90% but only up to 648 K; the selectivity to toluene and benzene increased, while

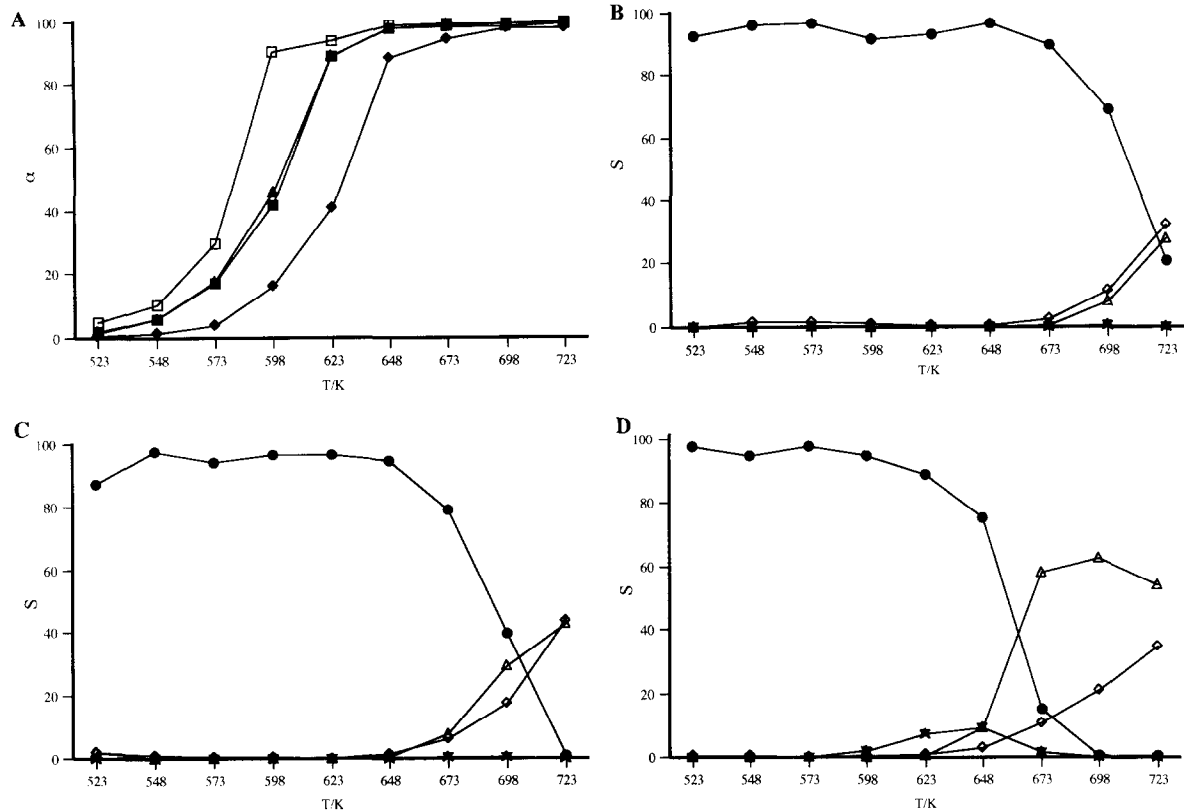


Fig. 4. Activity and selectivities, as a function of temperature; Al, Ga and In added to CeO_2 . A: a comparison of the conversion of benzoic acid. ■: pure CeO_2 ; ◆: Al added to CeO_2 ; ◇: Ga added to CeO_2 ; □: In added to CeO_2 . B: temperature dependence of selectivities to various products; Al added to CeO_2 . C: Ga added to CeO_2 . D: In added to CeO_2 . Symbols: ◇: benzene; △: toluene; ●: benzaldehyde; ★: benzylalcohol.

that to benzaldehyde decreased, when Mn additive was introduced into CeO_2 . The selectivity to toluene was always higher than that to benzene. The selectivity to benzaldehyde was higher than 90% up to 598 K. When adding iron oxide to the CeO_2 catalyst, the selectivities to benzylalcohol, to toluene and benzene increased all above 598 K, while that to benzaldehyde decreased. Particularly, the selectivity to toluene increased considerably above 623 K.

3.4. Zirconium oxide as an additive

The effects of Zr oxide on the catalytic properties of CeO_2 in reduction of benzoic acid are shown in Fig. 6. Fig. 6(A) shows the relation between the conversion of benzoic acid and the reaction temperature, for CeO_2 and for CeO_2 with Zr oxide as additive. Fig. 6(B)

shows the relation between the product selectivities and the reaction temperature. It can also be observed from Fig. 6(A), that the activity at low temperatures is considerably improved by adding Zr oxide. The total conversion was higher than 90% even at 598 K, while the value for pure CeO_2 was at this temperature only 40% (see more about the comparison in the discussion).

The temperature dependence of the selectivities, shown in Fig. 6(B), has the following features. The selectivity to benzaldehyde was higher than 90% up to 623 K and then, gradually decreased with increasing the temperature up to 673 K. Simultaneously, the selectivity to toluene increased. Above 673 K, the selectivity to benzaldehyde markedly decreased, while that to toluene and benzene increased. The selectivity to toluene is much higher than that to

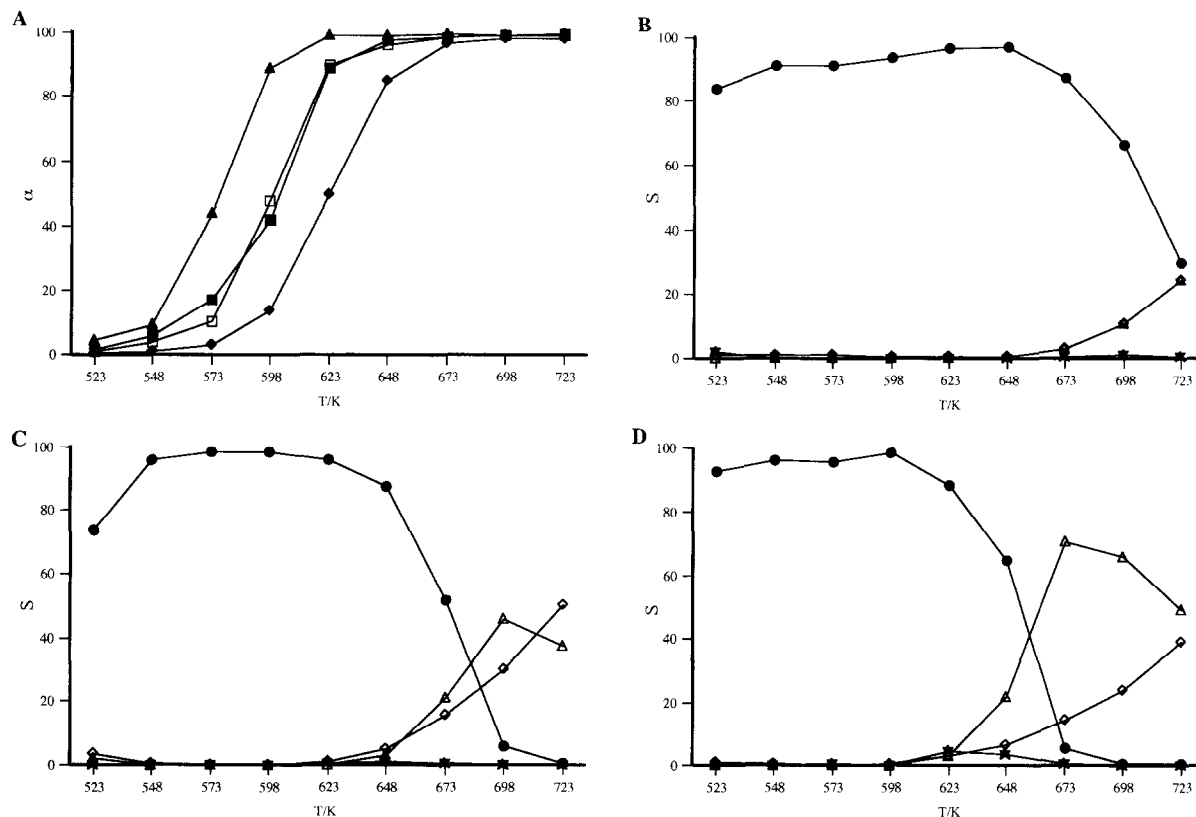


Fig. 5. Temperature dependence of activity and selectivity. Cr, Mn and Fe added to CeO₂. A: a comparison of the conversion of benzoic acid on different catalysts at various temperatures. ■: CeO₂; ◆: Cr added to CeO₂; ◇: Mn added to CeO₂; □: Fe added to CeO₂. Temperature dependence of selectivities. Cr added to CeO₂ (B); Mn added to CeO₂ (C); Fe added to CeO₂ (D). Symbols: ◇: benzene; △: toluene; ●: benzaldehyde; ★: benzylalcohol.

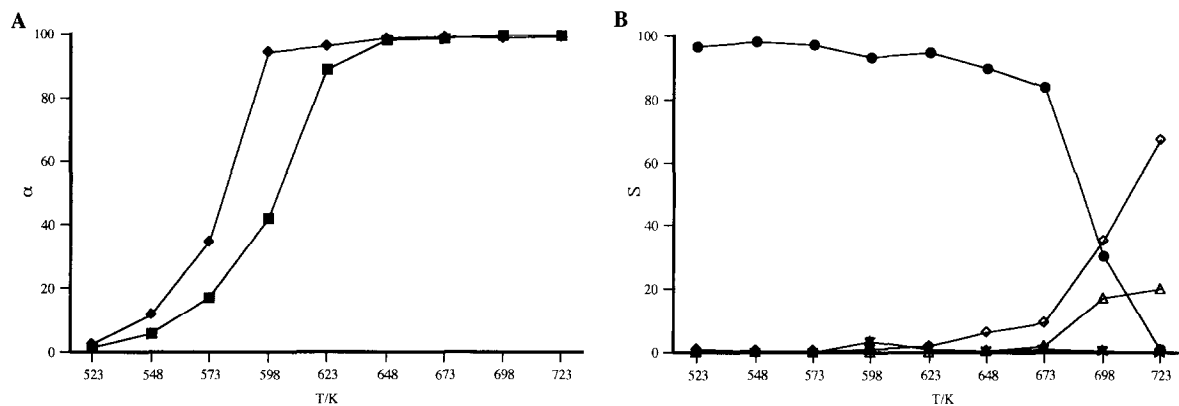


Fig. 6. Temperature dependence of activity and selectivity. Zr added to CeO₂. A: comparison of the conversion of benzoic acid. Zr added to CeO₂ and unmodified CeO₂, at various temperatures. ■: CeO₂; ◐: Zr added to CeO₂. B: temperature dependence of selectivities of Zr added to CeO₂ catalysts. Symbols: ◇: benzene; △: toluene; ●: benzaldehyde; ★: benzylalcohol.

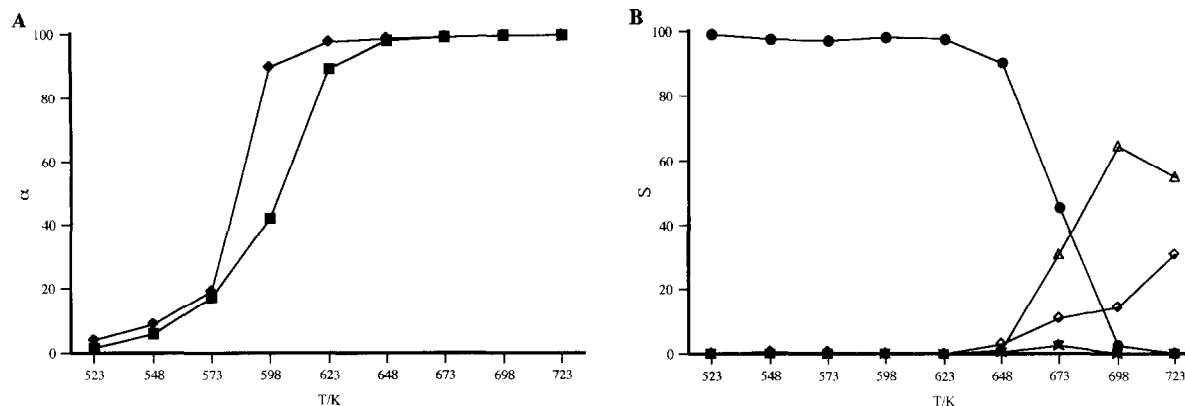


Fig. 7. Temperature dependence of activity and selectivity. Pb added to CeO₂. A: comparison of the conversion of benzoic acid. Pb added to CeO₂ and unmodified CeO₂, at various temperatures. ■: CeO₂; □: Pd added to CeO₂. B: temperature dependence of selectivities. Pb added to CeO₂ catalysts. Symbols: ◇: benzene; △: toluene; ●: benzaldehyde; ★: benzylalcohol.

benzene. When compared with the results obtained with pure CeO₂ (as shown in Fig. 1(B)), the corresponding curves are different for unmodified CeO₂ and CeO₂ modified by the Zr oxide.

3.5. Additive containing Pb oxide

The effects of Pb-additive to the CeO₂ catalyst are shown in Fig. 7. Fig. 7(A) shows the total conversion of benzoic acid as a function of temperature for CeO₂ and for the Pb-modified CeO₂. Fig. 7(B) shows the relation between the product selectivities and the reaction temperature. In Fig. 7(A), the temperature dependence of the total conversion with the modified CeO₂ was nearly the same as that with pure CeO₂ up to 573 K, but the conversion improved markedly above 573 K. The conversion achieved values above 90% at 598 K. The positive effect of the Pb addition on the conversion of benzoic acid appeared only above 573 K. In Fig. 7(B) the selectivity to benzaldehyde was higher than 95% up to 623 K and then markedly decreased above 648 K, while the selectivities to toluene and benzene increased. In this case the selectivity to toluene was much higher than that to benzene.

4. Discussion

In an earlier paper [18], catalytic properties of various oxides have been studied in the reduction of benzoic acid. Several regularities in the catalytic

properties of various oxides could have been established. The reaction of benzoic acid proceeds by two basic mechanisms: one is a radical-like thermal decomposition (decarboxylation, hydrogenolysis) of benzoate formed by adsorption of benzoic acid and the other is an oxidation–reduction cycle (Mars and van Krevelen mechanism [19], with benzoic acid as a donor and the active center (oxygen vacancy) on the catalyst as the acceptor of oxygen atom. Only the second mechanism is the basis of a high selectivity to benzaldehyde.

The CeO₂ oxide is well known as being easily reduced to form a non-stoichiometric oxide with oxygen vacancies, in a – basically – fluorite structure. The oxidation–reduction properties have been investigated elsewhere [20–23]. According to these investigations, the degree of reduction can be controlled by changing the reaction conditions, such as the temperature and the composition of the feed. Once the vacancy is produced on the surface, it acts as a strong reductant, being able to convert H₂O into H₂ [24,25] and SO₂ into elemental S [26]. The CeO₂ oxide is very promising as a catalyst for the reduction of benzoic acid just on the basis of these redox properties [18].

The catalytic behaviour of CeO₂ in the reduction of benzoic acid, will be discussed separately for two regions of temperatures. The first region is below 648 K, and the second above it. In the first region, the conversion of benzoic acid increased with increasing the reaction temperature and the selectivity of benzoic acids could exceed 95%. Under these condi-

tions, oxygen vacancies are produced by hydrogen and then are refilled by oxygen from benzoic acid, just to a level ensuring a high selectivity with the removal of only one oxygen atom.

At temperatures higher than 648 K, benzaldehyde selectivity decreased with increasing reaction temperature, while the selectivity to toluene and benzene increased. In this region the conversion of benzoic acid was almost 100%. In this temperature region the reduction of CeO₂ proceeds to a higher degree and excessive amount of oxygen vacancies is formed in the surface. This causes a further deoxygenation of the intermediate acylium ion and mainly toluene (with perhaps some benzene) is formed. In Fig. 2(B), the increase in the selectivity to benzaldehyde with the increase of partial pressure of benzoic acid can be seen, with a corresponding decrease of selectivities to other products, in particular to toluene. This confirms the picture of the redox mechanism and the role of vacancies in the desired selectivity.

Selectivity to benzene does not decrease with increasing benzoic acid pressure so strongly as that to toluene. This is because there are two routes to benzene. One is the decarboxylation in the form of hydrogenolysis of an intermediate which is the same as for toluene and, the other route is a direct decarboxylation–decomposition of adsorbed benzoic acid (benzoate). If benzene were produced only by the former route, the production of benzene would be suppressed by the increase of partial pressure of benzoic acid in a similar way, like with toluene. Since the benzene formation behaves differently from that of toluene, we can conclude that benzene formation proceeds preferentially by the latter route and, the formation of toluene by the former one. To learn more about the reaction the reactivity of preadsorbed benzoic acid (temperature programmed reaction) was also studied (Fig. 3).

The results in Fig. 3 clearly show the contribution by two different surface species to the overall reaction. The surface species that desorb under 623 K (produced over say, A-site) induce the selective deoxygenation of benzoic acid to benzaldehyde and the reaction proceeds here by the selective redox (MvK) mechanism. However, benzene is produced mainly on the B-site from the species which is relatively stable on the surface (like expected for a benzoate) up to higher temperatures. For instance, toluene is

even produced at 648 K, while benzene at 673 K at B-sites. Thus, two kinds of overall hydrogenolyses can be proposed for benzoic acid adsorbed on the surface: one via the acylium species and the other via benzoate which produces benzene directly. The direct decomposition to benzene occurs at higher temperatures. The selectivity seems to depend then on the strength of the interaction between the B-site and benzoic acid.

We have seen earlier, the role of the reaction mechanism (redox mechanism vs. thermal decomposition) in the selectivity and the detrimental role (in the redox mechanism) of excessive amounts of oxygen vacancies. The vacancies are created by hydrogen, the adsorption of which is necessary for both the vacancy creation and the desorption of intermediates.

Let us discuss now the influence that additives can have on the performance of CeO₂. Obviously, the goal is not only to achieve a higher total conversion at low temperatures, but more importantly, to achieve a high selectivity at the highest conversion. Very little is known about the principles of the promotion of oxidic catalysts in general and, practically nothing is known about the specific promotion effects in deoxygenation reactions. Therefore, an explorative research was necessary.

The desirable effects on deoxygenation, potentially achievable by the use of promoters, are: (i) setting the steady-state number of active vacancies on a right level and (ii) creating the most suitable (for the reaction to aldehyde) concentration of surface bound hydrogen. This concentration must be high enough to fulfill condition (i), but it must not lead to the adsorption through, and an attack on, the phenyl ring. It should be noted that metallic additives (Pt, Cu) do just that [18].

The first group of additives tested comprises those containing Al, Ga or In; from them only the In; additive showed a positive effect on the activity, but this was counteracted by the negative selectivity effects at higher temperatures. At 598 K the main by-product was benzyl-alcohol, which is likely a product of consecutive secondary hydrogenation of benzaldehyde. It is known that In oxide (and other similar oxides) is a promoter of hydrogenation of aldehydes by metals [27], or a mild hydrogenation catalyst, itself. The negative effect on the selectivity at still higher temperatures is probably related to the increase (by In) in the steady state degree of CeO₂

reduction. This effect has been observed earlier [28,29], upon studies of syngas reactions. For these reactions an increase in the steady state concentration of Ce^{3+} (i.e. also in the concentration of oxygen vacancies) was beneficial and lead to an enhanced olefin production.

The addition of 'redox' oxides, such as Cr, Mn, and Fe oxides, changed the catalytic behaviour of CeO_2 in the direction of the catalytic behaviour of pure oxides of these elements [18]. Among these oxides, Mn oxide has positive effects on the catalytic activity and the selectivity to benzaldehyde. Compared to the effects of In oxide (benzaldehyde hydrogenated up to benzylalcohol and toluene excessively formed) addition of Mn oxide improved the activity in a way, as if it added new active centers for the primary deoxygenation (acylium formation).

The addition of Zr oxide has also positive effects on the catalytic behaviour and the effect is very similar to that of Mn oxide addition. An interesting case is the promotion by the Pb oxide: an improvement in the total activity can be achieved, but this is mainly observable at temperatures higher than 573 K. This might be related to the reduction degree of Pb oxide.

Results shown in the Figs. 4–7 were not gathered on basis of a proper kinetic study. Nevertheless, it is tempting to pass the limit of a pure phenomenology and to speculate on the effect of promoters. First, the conversion-temperature curve ($\alpha(T)$) in the temperature range between 510 and 560 K can be better described by a reaction of first order than by a reaction of zero order. The apparent first order constants evaluated from the $\alpha(T)$ curves, show that the main effect of the promoters of Al, Fe (a negative effect) and of In and Zr (a positive effect) is on the pre-exponential factor. The effect on activation energy is within the experimental errors of this rough evaluation. In contrast with it, the effect of Pb is more complicated and the decrease in the activation energy seems to be larger than the experimental errors. The ratio of the pre-exponential reaction constants (promoted to unpromoted catalysts) is 2.3 for Mn, 1.5 for Zr, 1.8 for In, and 2.5 for Pb promoted CeO_2 . The ratio of surface areas (promoted to unpromoted) is 1.2 for Mn, 1.3 for Zr, 1.3 for In, and 1.2 for Pb promoted CeO_2 . It is difficult to go beyond this statements, because the total surface areas are formed by CeO_2 and the additive. The additive is in some cases rather a

co-catalyst than a promoter, which taken alone is inactive.

5. Conclusions

In this paper, the catalytic properties of pure CeO_2 and of additives containing CeO_2 have been studied in the reduction of benzoic acid, in a temperature range between 523 and 723 K. The following conclusions can be formulated on basis of results and discussion.

1. The reaction proceeds up to 623 K through the redox (MvK) mechanism. Under these conditions, the selectivity to benzaldehyde is more than 95% and the activity is controlled by the number of oxygen vacancies which are produced under the reaction condition.
2. In the reaction occurring above 648 K, the conversion of benzoic acid is almost 100%. However, the reaction proceeds further, up to toluene and benzene is also formed. The decrease in benzaldehyde selectivity is due to a very high concentration of oxygen vacancies and a parallel running direct decarboxylation/decomposition.
3. Two kinds of adsorption site (A- and B-site) exist the surface. The A-site is involved in the redox mechanism and manifests itself already at low temperatures. The B-site is involved in the thermal decomposition/decarboxylation of the adsorbed benzoic acid. On the A-site, adsorbed benzoic acid can be selectively converted to benzaldehyde.
4. A moderate enhancement of the low temperature activity of CeO_2 (i.e. the activity accompanied with a high selectivity to benzaldehyde) can be achieved by addition of the 'redox'-oxide promoters.
5. In oxide enhances the low temperature activity, but mainly towards the hydrogenation (benzaldehyde is reduced up to benzylalcohol). This might also be desirable in some special cases.

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