Deoxygenation of benzoic acid on metal oxides
2. Formation of byproducts

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Abstract

Benzene, benzophenone, toluene and benzylalcohol are byproducts in the selective deoxygenation of benzoic acid to benzaldehyde on ZnO and ZrO$_2$. In this paper, the pathways to the byproducts are discussed and a complete overview of the reaction network is presented. Benzene and benzophenone are products of the decomposition of the strongly adsorbed benzoic acid at elevated temperature. Toluene is formed by the deoxygenation of benzaldehyde at oxygen vacancy sites. Direct hydrogenation of benzaldehyde yields benzylalcohol. Selectivity to byproducts is not only determined by the reaction temperature, but also by the degree of surface reduction and the difference in adsorption strength between reactant and product. At temperatures <360° benzoic acid forms a strongly benzoate layer which is stable and prevents readsorption of benzaldehyde. Reduction of the catalyst by hydrogen leads to a small number of oxygen vacancy sites which deoxygenate benzoic acid to benzaldehyde and as a result selectivity to benzaldehyde is very high (>95%). Higher temperatures induce decomposition of the benzoate layer into benzene and more importantly enhance the degree of reduction of the catalyst, which results in the formation of toluene from benzaldehyde. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Benzoic acid; Benzaldehyde; Deoxygenation; Benzylalcohol; ZnO, ZrO$_2$

1. Introduction

The selective deoxygenation of aromatic acids to aldehydes is an example of "green" technology and an alternative to current aldehyde synthesis methods which are characterised by low yields and/or high amounts of waste formation [1]. Part 1 [2] focussed on the mechanism of the formation of benzaldehyde. It was determined that the deoxygenation proceeds in two steps involving lattice oxygen, i.e. a type of Mars–Van Krevelen mechanism operates. In the first step, hydrogen removes a lattice oxygen atom, in the second step benzoic acid is deoxygenated to benzaldehyde by replenishing the oxygen vacancy. In this paper, the reactions that produce byproducts will be investigated. The main byproducts are benzene, toluene and benzylalcohol. Formation of benzene and toluene is undesirable, but a mixture of benzaldehyde and benzylalcohol can be of commercial interest. It is not clear how these compounds are produced and how the selectivity can be manipulated by changing the reaction conditions. Hence, the main objective of this paper is to provide a network mapping the different reactions and to attain a proper understanding of influence of the reaction conditions. This knowledge will make it possible to optimise the catalysts performance and aid the development of new catalytic systems.

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The same catalysts as in the previous publication [2], i.e. ZnO and ZrO$_2$ will be studied. At low conversions the byproduct formation is very small so reaction conditions have to be set at which specifically the selective reaction to benzaldehyde is unfavourable. This is done by operating at different temperatures, partial pressures of the reactants, working at different flow rates, by using byproducts as reactants and by manipulating the concentration of active sites, i.e. oxygen vacancies.

2. Experimental

The experiments were carried out with a continuous flow apparatus operating at atmospheric pressure. A hydrogen or nitrogen flow passed through a saturator containing the reactant and this feed was fed to the reactor. The product stream leaving the reactor was dissolved in ethanol and collected in two condensers. The condensate was injected into a Varian 3700 gas chromatograph equipped with a 25 m wide-bore CP-Sil 13 column (Chrompack NL) for product analysis. The set-up is described in more detail in Part 1 [1].

In most experiments, samples were acquired every 25 min and the reaction conditions were only changed when several samples taken under the same conditions produced identical results. Exceptions were made for experiments where there was a transient effect occurring. In those instances, it should be emphasised that the results are the average of what was collected in the condenser over a 25 min period.

The partial pressure of benzoic acid was varied by changing the temperature of the saturator containing the reactant. The partial pressure of hydrogen was altered by diluting hydrogen with nitrogen. Contact times were varied by changing the flow rates of the carrier gas.

The definitions of the carbon atom-based conversion per unit weight catalyst, yield and selectivity are the same as in Part 1.

The same batch of ZnO and ZrO$_2$ was used as Part 1 and details of the preparation procedure can be found there. The BET surface areas of the catalysts before reaction were 50 and 96 m^2/g for ZnO and ZrO$_2$, respectively.

3. Results

The catalytic behaviour of ZnO and ZrO$_2$ in the deoxygenation of benzoic acid as a function of temperature was reported in our previous paper [2]. In short, at 360 °C the selectivity to benzaldehyde is very high (>95%) on both catalysts with some benzylalcohol formed on ZnO which is the more active of the two catalysts. At higher temperatures (>400 °C) conversion of benzoic acid is complete and considerable amounts of toluene and benzene are formed.

The effect of contact time on selectivity is shown in Fig. 1. At short contact times benzaldehyde is highly favoured. It appears that byproducts emerge only when all of the benzoic acid has been completely converted into benzaldehyde. Toluene is the main byproduct whereas a small amount of benzene is formed at very long contact times. Benzylalcohol formation is very small at this temperature, regardless of contact time. The pattern of byproduct formation appears the same for ZnO as for the ZrO$_2$ catalysts, but the ZnO catalyst is much more active in the formation of both benzaldehyde and byproducts. This experiment suggests that consecutive reactions involving benzaldehyde play an important role in the formation of byproducts. Therefore, experiments were undertaken with benzaldehyde as a feedstock replacing benzoic acid. The results are shown in Fig. 2.

At low temperature benzaldehyde is hydrogenated to benzylalcohol. At elevated temperature toluene is the main product. A small amount of benzene is also detected at 430 °C. The yield of these two products is higher with benzaldehyde as the reactant than with benzoic acid. Just as in the previous experiment (Fig. 1) the behaviour of the ZrO$_2$ catalyst resembles that of the ZnO catalyst but the ZnO catalyst is more active in the formation of all three products.

Additional information regarding the reaction network was gathered by reacting benzylalcohol over the catalysts (Fig. 3). Benzylalcohol is rapidly converted into benzaldehyde, i.e. a dehydrogenation takes place despite the fact that the catalyst is operating in a hydrogen atmosphere. At longer contact times toluene is formed, but both figures indicate that this is the result of the deoxygenation of benzaldehyde and not of the hydrogenolysis of the C–OH bond in benzylalcohol.

Fig. 4 shows the effect of an increase of the partial pressure of benzoic acid on the selectivity. An increase
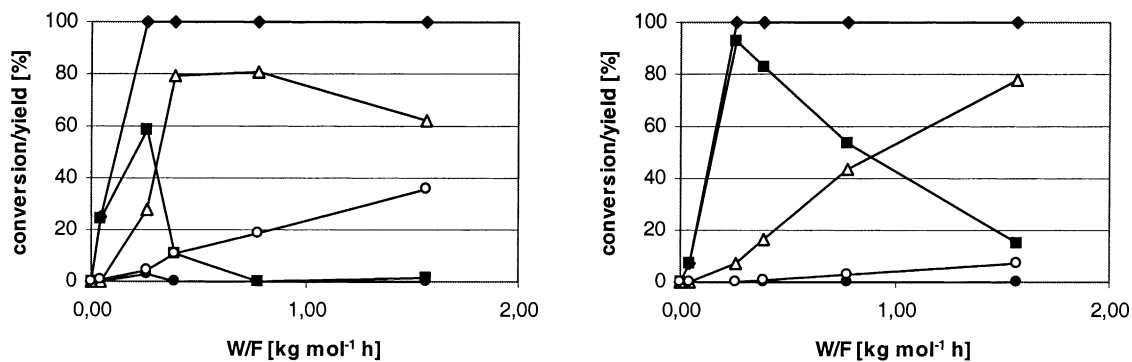
Fig. 1. Deoxygenation of benzoic acid at 400 °C on ZnO (left) and ZrO₂ (right) as a function of contact time. Symbols: (◆) benzoic acid conversion; (■) benzaldehyde yield; (●) benzylalcohol yield; (△) toluene yield; (○) benzene yield. Reaction conditions: catalyst, 500 mg; hydrogen flow rate, 10–60 ml/min; benzoic acid partial pressure, 13 mbar.
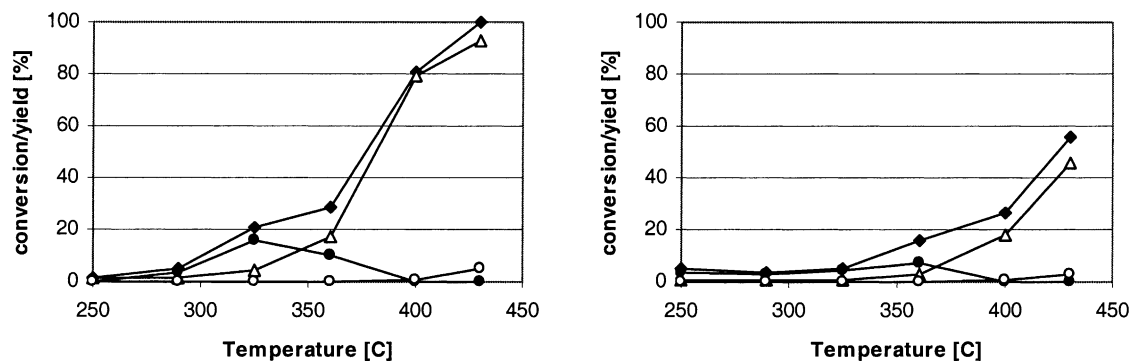

Fig. 2. Hydrogenation of benzaldehyde on ZnO (left) and ZrO₂ (right) as a function of temperature. Symbols: (◆) benzaldehyde conversion; (●) benzylalcohol yield; (△) toluene yield; (○) benzene yield. Reaction conditions: hydrogen flow rate, 40 ml/min; benzaldehyde partial pressure, 13 mbar; benzaldehyde W/F, 0.39 kg mol⁻¹ h.
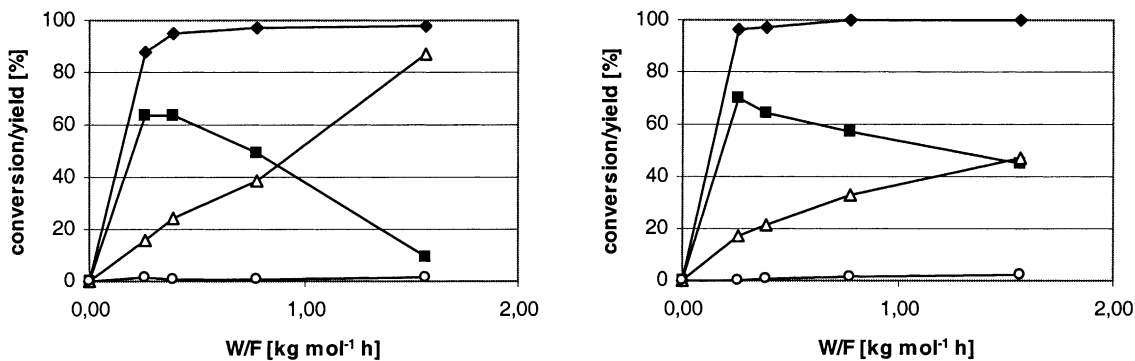

Fig. 3. Reactions of benzylalcohol in hydrogen at 400 °C on ZnO (left) and ZrO₂ (right) as a function of contact time. Symbols: (◆) benzylalcohol conversion; (■) benzaldehyde yield; (△) toluene yield; (○) benzene yield. Reaction conditions: catalyst, 500 mg; hydrogen flow rate, 10–60 ml/min; benzylalcohol partial pressure, 13 mbar.
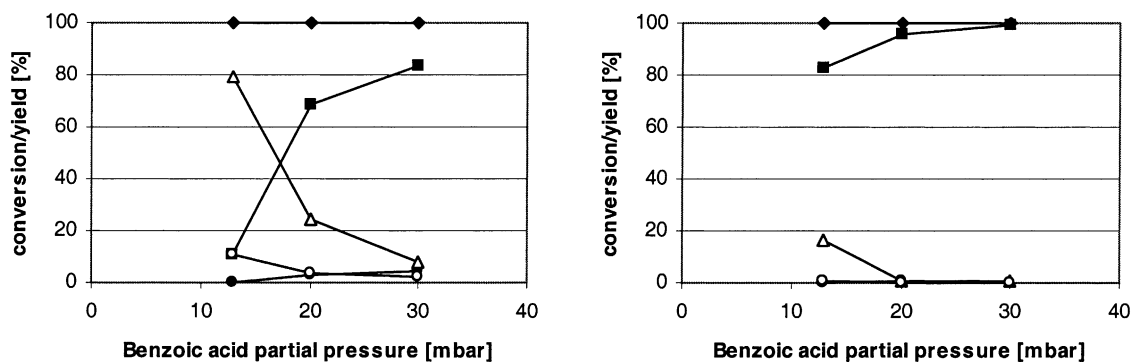
Fig. 4. Deoxygenation of benzoic acid at 400 °C on ZnO (left) and ZrO_2 (right) as a function of benzoic acid partial pressure. Symbols: (◆) benzoic acid conversion; (■) benzaldehyde yield; (●) benzylalcohol yield; (△) toluene yield; (○) benzene yield. Reaction conditions: catalyst, 500 mg; hydrogen flow rate, 40 ml/min.

in the partial pressure leads to a substantial reduction in the selectivity towards toluene on both catalysts. On ZnO the yield of toluene decreases from 79 to 8% when the benzoic acid partial pressure is raised from 13 to 30 mbar. The effect on the formation of benzene and benzylalcohol is small, indicating a different origin.

In another experiment, the partial pressure of hydrogen was varied. The results are depicted in Fig. 5 for the ZnO catalyst and Fig. 6 for the ZrO_2 catalyst. Selectivity to toluene is >90% on ZnO at 430 °C if hydrogen is the only carrier gas. Reducing the hydrogen partial pressure (by diluting with nitrogen) lowers the selectivity to toluene significantly. If 75%

of the hydrogen has been replaced by nitrogen the selectivity to toluene has dropped to 15% and meanwhile the selectivity to benzaldehyde has increased to 81%. In total absence of hydrogen in the feed, mainly benzene is produced with some minor benzophenone formation. Upon re-introducing hydrogen to the feed immediately the formation of these two byproducts drops and benzaldehyde returns as the main product. At high hydrogen partial pressure the high selectivity to toluene reappears. On ZrO_2 to some extent the same behaviour can be observed. Lowering the hydrogen partial pressure results in a decrease in toluene selectivity in favour of benzaldehyde. However, in the absence of hydrogen
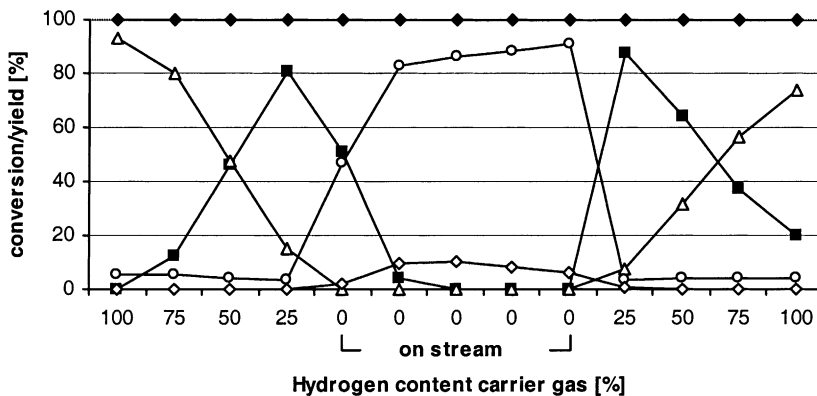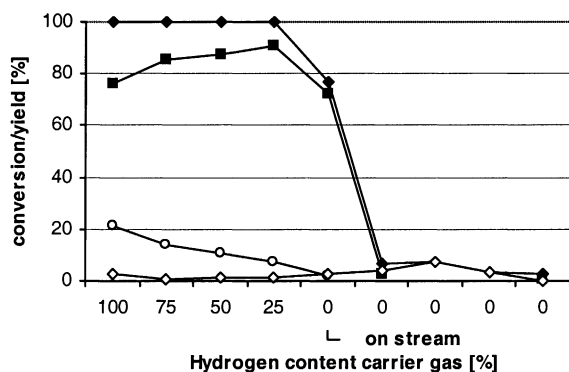

Fig. 5. Deoxygenation of benzoic acid at 430 °C on ZnO as a function of hydrogen partial pressure. Symbols: (◆) benzoic acid conversion; (■) benzaldehyde yield; (●) benzylalcohol yield; (△) toluene yield; (○) benzene yield. Reaction conditions: carrier gas ($H_2 + N_2$) flow rate, 40 ml/min; benzoic acid partial pressure, 13 mbar; benzoic acid W/F, 0.39 kg mol^{-1} h.

Fig. 6. Deoxygenation of benzoic acid at 430 °C on ZrO$_2$ as a function of hydrogen partial pressure. Symbols: (◆) benzoic acid conversion; (■) benzaldehyde yield; (●) benzylalcohol yield; (△) toluene yield; (○) benzene yield. Reaction conditions: catalyst, 500 mg; carrier gas (H$_2$ + N$_2$) flow rate, 40 ml/min; benzoic acid partial pressure, 13 mbar; benzoic acid W/F, 0.39 kg mol^{-1} h.

benzene formation is only very small in contrast to ZnO.

In Part 1, carbon dioxide was used as a probe molecule with specific affinity for oxygen vacancies. As such it could, in principle, also be added to the feed with the objective to decrease the amount of oxygen vacancies as active sites under steady state conditions. Carbon dioxide was introduced into the feed at 360 °C at which temperature benzaldehyde is predominantly formed and at 430 °C when selectivity to toluene is high. In Table 1, the results of the former experiment are presented. The effect of adding carbon dioxide to the feed is hardly noticeable at 360 °C. At 420 °C, on the other hand, the effect is quite dramatic (Table 2). Toluene formation is largely suppressed by the presence of carbon dioxide, while the benzaldehyde yield increases almost three-fold.

Hydrogenation of benzaldehyde to benzylalcohol might proceed via a Cannizzaro-type mechanism. The

Table 1
Effect of the addition of carbon dioxide on product yield on ZnO at 360 °C[a]

Carrier gas composition	Conversion (%)	Benzaldehyde yield (%)
H$_2$:N$_2$ 4/1	100	99
H$_2$:CO$_2$ 4/1	99	98

[a] Reaction conditions: carrier gas flow rate, 40 ml/min; benzoic acid partial pressure, 13 mbar; benzoic acid W/F, 0.39 kg mol^{-1} h.

Table 2
Effect of the addition of carbon dioxide on product yield on ZnO at 420 °C[a]

Carrier gas composition	Conversion (%)	Toluene yield (%)	Benzaldehyde yield (%)
H$_2$:N$_2$ 4/1	100	64	29
H$_2$:CO$_2$ 4/1	100	22	75

[a] Reaction conditions: carrier gas flow rate, 40 ml/min; benzoic acid partial pressure, 13 mbar; benzoic acid W/F, 0.39 kg mol^{-1} h.

formal equation for this reaction is:

$$2C_6H_5CHO + OH^- \rightarrow C_6H_5CH_2OH + C_6H_5COO^- \quad (1)$$
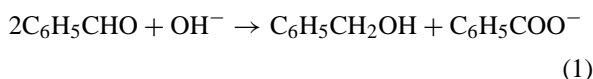
This reaction takes place when the OH groups are the only source of O as the oxidising agent. To check for this reaction the catalyst was hydrated by passing water vapour over the catalyst followed by a feed of benzaldehyde in nitrogen. A small amount (2%) of benzylalcohol was formed on the ZrO$_2$ catalyst which decayed to zero over time, but not on the ZnO catalyst. The formation of benzylalcohol was higher (9%) when a mixture of benzaldehyde and hydrogen was led over non-hydrated ZrO$_2$.

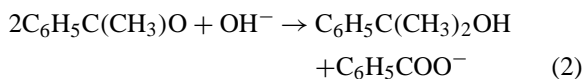As a test reaction, the hydrogenation of acetophenone was also studied. The analogue of Eq. (1) for this reactant is

$$2C_6H_5C(CH_3)O + OH^- \rightarrow C_6H_5C(CH_3)_2OH \\ +C_6H_5COO^- \quad (2)$$

Table 3
Acetophenone hydrogenation on ZnO and ZrO$_2$ at 360 °C[a]

Catalyst	Conversion (%)	Yield (%)			
		Benzene	Ethylbenzene/styrene	Benzaldehyde	Heavy products
ZnO	90	3	77	4	5
ZrO$_2$	78	9	43	7	17

[a] Reaction conditions: hydrogen flow rate, 40 ml/min; acetophenone partial pressure, 13 mbar; acetophenone W/F, 0.39 kg mol^{-1} h.

Thus, if 2-phenyl-2-propanol is formed, this would provide evidence of a concerted Cannizzarro-type mechanism. However, this was not observed. Instead the main product of this reaction was either ethylbenzene or styrene (see Table 3). These two compounds gave practically identical retention times in the gas chromatogram of the GC used and so, unfortunately, no distinction could be made.

4. Discussion

There are two main pathways in the selective deoxygenation of benzoic acid, as discussed in Part 1:

1. A selective pathway in which benzaldehyde is formed. This reaction proceeds via a reverse type of Mars–Van Krevelen mechanism. Hydrogen reduces the catalyst so that oxygen vacancies are produced which deoxygenate benzoic acid to benzaldehyde.
2. A non-selective pathway in which benzene and benzophenone are formed preferentially. These products are formed via the slow decomposition of strongly bound benzoates.

First, the reactions that produce toluene, benzylalcohol, benzene and benzophenone will be reviewed. At the end of the discussion an overall picture of the reaction network is presented.
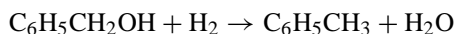
4.1. Toluene formation

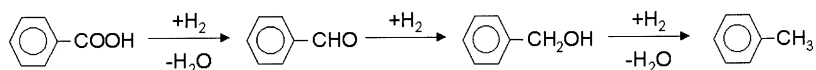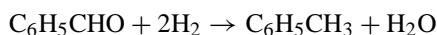There are three potential reaction pathways for the formation of toluene:

1. direct reduction of benzoic acid

   $$C_6H_5COOH + 3H_2 \rightarrow C_6H_5CH_3 + 2H_2O$$
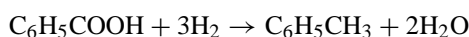
2. hydrogenation or hydrogenolysis of benzylalcohol

   $$C_6H_5CH_2OH + H_2 \rightarrow C_6H_5CH_3 + H_2O$$

3. hydrogenation (deoxygenation) of benzaldehyde

   $$C_6H_5CHO + 2H_2 \rightarrow C_6H_5CH_3 + H_2O$$

Reaction (1) can be excluded on ZnO and ZrO$_2$. At short contact times toluene is not seen among the primary products (Fig. 1). Furthermore, toluene formation was also absent in the temperature programmed reactions shown in Part 1. Reaction (2) seems plausible considering the reduction sequence shown in Scheme 1 suggested by Yokoyama et al. [3].

However, when benzylalcohol is led over the catalyst, benzaldehyde is formed initially (Fig. 3). Clearly toluene is a secondary product formed from benzaldehyde. Furthermore, at long contact time benzaldehyde selectivity drops and toluene selectivity rises (Fig. 1).

It was shown in Part 1 that oxygen vacancies are present on the catalyst during benzoic acid deoxygenation so this must also be the case during the experiments with the benzaldehyde feed with identical hydrogen pressure. If these reactive defect sites are able to deoxygenate benzoic acid it is fair to expect that they can deoxygenate benzaldehyde to toluene as well. Ample evidence for this deduction, that reaction (3) proceeds via a reverse type of Mars–Van Krevelen mechanism and is the main source of toluene, can be gathered from the experiments. First, the concentration of oxygen vacancies depends on the ratio of oxidant and reductant. If this ratio is increased (by either increasing the partial pressure of benzoic acid or lowering the partial pressure of hydrogen) the concentration of oxygen vacancies will be small which means that few of those sites are available for benzaldehyde re-adsorption and deoxygenation. Consequently, the selectivity to toluene will drop and this is indeed observed (Figs. 4 and 5). Moreover, another method of decreasing the concentration of oxygen vacancies is by the adding another oxygen donor to the feed, in our case carbon dioxide [4–8]. This results in a drop in toluene selectivity as well. It is possible that the formation of toluene proceeds without desorption and re-adsorption of benzaldehyde. In that case, the adsorbed benzoic acid loses both its oxygen atoms at, e.g. adjacent oxygen vacancy sites during a single sojourn on the surface. In the temperature-programmed reactions of adsorbed benzoates reported in Part 1, toluene was not found among the products. It is,

Scheme 1.

therefore, probable that most of the toluene is indeed formed indirectly, via desorption and re-adsorption of benzaldehyde.

So benzoic acid and benzaldehyde compete for the same sites, namely, the oxygen vacancies. Still under the right conditions, the selectivity to benzaldehyde is extremely high (>98%). The implication is that benzoic acid must adsorb much more strongly than benzaldehyde. This is not really surprising since it is common knowledge that carboxylates benzoates are far better ligands than aldehydes. Moreover, in the reverse reaction, the oxidation of benzaldehyde to benzoic acid, Sachtler et al. [9] observed a negative reaction order in benzoic acid, which implies product inhibition and strong adsorption. It is obviously a tremendous advantage of such deoxygenation reaction that the product also having an oxygen atom is not as reactive as the reactant. A drop in selectivity due to consecutive reactions is only observed at high benzoic acid conversion.

The strong adsorption of benzoic acid is also illustrated by the carbon dioxide experiment. While adding carbon dioxide lowers the deoxygenation of benzaldehyde to toluene, it does not reduce the rate of deoxygenation of benzoic acid to benzaldehyde. This means that the relative adsorption strength on the oxygen vacancy sites must be in the following order $C_6H_5COOH > CO_2 > C_6H_5CHO$. This is also in agreement with results obtained by King and Strojny [10]. They observed that yttrium oxide covered by benzoates did not convert carbon dioxide to CO, but high conversion was resumed after removal of the benzoate by air oxidation.

The mechanism suggested above also offers an explanation for the observed difference in toluene selectivity between the ZnO and the ZrO_2 catalyst. Selectivity to toluene is much higher on the ZnO catalyst because oxygen vacancies are more easily created. The activity in deoxygenation of benzaldehyde deoxygenation resembles the activity in benzoic acid deoxygenation (compare Tables 3 and 4 with Fig. 2). The main difference between the two reactions is that the latter reaction requires a slightly higher reaction temperature. This is probably related to the fact that in benzaldehyde a C=O *double* bond must be broken whereas in benzoic acid the C–O bond order is formally like 1.5 and in the transition state even lower, between 1 and 1.5.

4.2. Benzylalcohol formation

The results of Fig. 2 demonstrate that benzylalcohol is also a secondary product from benzaldehyde:

$$C_6H_5CHO + H_2 \rightarrow C_6H_5CH_2OH$$
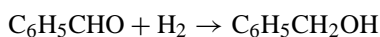
Benzylalcohol is only formed at temperatures <360°. The fact that benzylalcohol rapidly dehydrogenates at 400 °C (Fig. 3) signifies that the equilibrium of reaction lies to the left hand side of the equation. Only at lower temperatures benzylalcohol can be formed in appreciable amounts. But at lower temperatures (a) not all benzoic is converted into benzaldehyde and (b) the surface is covered by strongly bound benzoates. This explains why the benzylalcohol yield from the benzaldehyde feed is considerably higher than when benzoic acid is the reactant.

There are two probable routes from benzaldehyde to benzylalcohol:

1. a reaction between adsorbed hydrogen and benzaldehyde molecules (a reaction which easily occurs on metals);
2. a Cannizzaro mechanism between two benzaldehyde molecules at a basic OH site (see Eq. (1)).

On hydrated ZrO_2, some benzylalcohol is formed in the absence of hydrogen. This might provide an

Table 4
Product distribution in the deoxygenation of benzoic acid at 360 °C[a]

Catalyst	Conversion (%)	Yield (%)			
		Benzaldehyde	Benzylalcohol	Toluene	Benzene
ZnO	98	95	3	0	0
ZrO_2	58	58	0	0	0

[a] Reaction conditions: hydrogen flow rate, 40 ml/min; benzoic acid partial pressure, 13 mbar; benzoic acid W/F, 0.39 kg mol^{-1} h.

Table 5
Product distribution in the deoxygenation of benzoic acid at 430 °C[a]

Catalyst	Conversion (%)	Yield (%)			
		Benzaldehyde	Benzylalcohol	Toluene	Benzene
ZnO	100	25	0	72	3
ZrO_2	100	76	0	22	2

[a] Reaction conditions: hydrogen flow rate, 40 ml/min; benzoic acid partial pressure, 13 mbar; benzoic acid W/F, 0.39 kg mol^{-1} h.

indication that indeed a Cannizzaro mechanism is operating as suggested in literature [11,12]. However, the amount is small compared to the benzylalcohol yield obtained in a flow of benzaldehyde and hydrogen. Furthermore, when the H of the aldehydes group is exchanged for a methylgroup, i.e. by using acetophenone no 2-phenyl-2-propanol is formed as would have been expected on the basis of the Cannizaro mechanism, although this does not prove the absence of the Cannizaro reaction on ZrO_2, it provides an indication. Infrared studies of benzaldehyde and acetophenone adsorption do not provide any support for a Cannizzaro mechanism either [13]. The benzylalcohol that is observed on hydrated ZrO_2 in the absence of hydrogen, could also be formed via the recombination of benzaldehyde and adsorbed hydrogen instead. Some adsorbed hydrogen will always be present on the surface since part of the benzaldehyde adsorbs dissociatively Table 5.

Although the presence of a Cannizzaro mechanism cannot be completely excluded on ZrO_2 the contribution is likely to be small. Reaction (1), the direct hydrogenation of benzaldehyde, is therefore the main pathway to benzylalcohol formation. This reaction occurs more easily on ZnO, which is known to be a better hydrogenation catalyst.

4.3. Formation of benzene and benzophenone

Decarboxylation of benzoates to benzene and benzophenone was observed in the temperature-programmed reactions reported in Part 1. In the experiments shown here, with continuous flow of reactants and at high hydrogen pressure, benzene is formed in small amounts and benzophenone is not even detected. Benzene and benzophenone are formed in significant amounts only when hydrogen is not present in the feed (Figs. 5 and 6). Apparently decarboxylation of

benzoic acid is a much slower process than deoxygenation to benzaldehyde or toluene.

Decarboxylation of metal benzoates to benzene probably proceeds via a radical mechanism: a benzyloxyradical is formed via homolytic cleavage of the RCO_2-M. The benzyloxyradical rapidly decarboxylates to a benzylradical and the radical chain is terminated by reaction with a H atom [14]. For the ketonisation of aromatic acids on oxidic catalysts different reaction mechanisms have been proposed. Kwart and King suggested a concerted reaction between two carboxylate groups bound to one metal cation [15]. Lee and Spinks proposed a polar mechanism involving acylonium (R–C$^+$=O) species [16]. Given the relative stability of the benzylradical (due to resonance) the radical-chain mechanism put forward by Bell and Reed [17,18] might also be a valid mechanism. Ketonisation is absent in steady state reactions. Under these conditions the amount of adsorbed H is much higher than in the temperature-programmed reactions because hydrogen is present in the feed. The benzyl radical will then react rapidly with a proton to benzene. In the temperature-programmed reactions and in the reaction of benzoic acid in the absence of hydrogen (Fig. 5), the H coverage is low so the benzylradical might react with another carboxylate group to benzophenone.

Fig. 2 shows that some benzene can also be formed from benzaldehyde. This decarboxylation might proceed as a CO-elimination reaction at metal cationic sites, but it is also possible that benzaldehyde is oxidised to a benzoate that decomposes. Either way, the yield of benzene from benzaldehyde is rather small which indicates that the main source of benzene is the direct decarboxylation pathway.

Figs. 5 and 6 show a distinct difference between ZnO and ZrO_2 in terms of benzene formation. Benzoic acid is easily decarboxylated on ZnO in the absence of

hydrogen, but on ZrO_2 the amount of benzene formed is much smaller. This can be related to the fact that carboxylic acids have a higher affinity for metal oxides which are more basic or in which the lattice oxygen is less strongly bound [19,20]. On such oxides, including ZnO, the formation of an extended carboxylate layer(s) can be observed [21]. Decomposition of these strongly bound carboxylates is the main source of benzene. The yield of benzene on ZrO_2 is low probably because the low basicity and the relatively high strength of the Zr–O bond prevent the formation of such an extended carboxylate layer.

4.4. Reaction model

Based on the discussion above, the reaction network shown in Scheme 2 can be schematically drawn.

This reaction network can be clarified by looking at Fig. 5. In this figure, almost all reactions are represented. Benzylalcohol is not observed at this temperature due to thermodynamical constraints.

At 430 °C and at a high partial pressure of hydrogen conditions for surface reduction are favourable. So the concentration of oxygen vacancies is high and first benzoic acid is deoxygenated to benzaldehyde and subsequently benzaldehyde is deoxygenated to toluene or benzoic acid reacts through to toluene directly. If the hydrogen partial pressure is decreased the concentration of oxygen vacancies drops which means that neighbouring oxygen vacancies are rare and, moreover, that benzaldehyde cannot readsorb on a defect site. So the selectivity to toluene drops and to benzaldehyde increases. If hydrogen is completely excluded from the feed benzoic acid will oxidise the

surface and eventually no oxygen vacancies will be available for its adsorption. Under these conditions no deoxygenations can take place and, thus, the slower parallel running reactions to benzene and benzophenone can take over. Upon re-introduction of hydrogen the original situation leading to benzaldehyde is restored.

5. Conclusions

The reactions that lead to byproduct formation have been described and the conditions under which they occur are specified. They can be summarised as follows:

1. The deoxygenation of benzoic acid to benzaldehyde and the decarboxylation to benzene are two parallel running reactions, but the latter reaction is much slower and is only prominent in the absence of hydrogen, on highly oxidised surfaces.
2. Toluene and benzylalcohol are formed via secondary reactions of benzaldehyde, but since benzoic acid adsorbs much more strongly than benzaldehyde these two products are only observed when benzoic acid conversion is nearly complete.
3. The formation of toluene proceeds via a reverse type of Mars–Van Krevelen mechanism. Therefore, both the deoxygenation of benzoic acid to benzaldehyde and the deoxygenation of benzaldehyde to toluene occur at oxygen vacancy sites.
4. A Cannizzaro mechanism is unlikely in the conversion of benzaldehyde to benzylalcohol.
5. The oxygen vacancy concentration is an important parameter determining the selectivity.
6. All reactions are faster on ZnO than on ZrO_2 because hydrogen is more easily activated on ZnO and also because the higher basicity of ZnO favours the build-up of an extended carboxylate layer which decomposes at elevated temperatures.
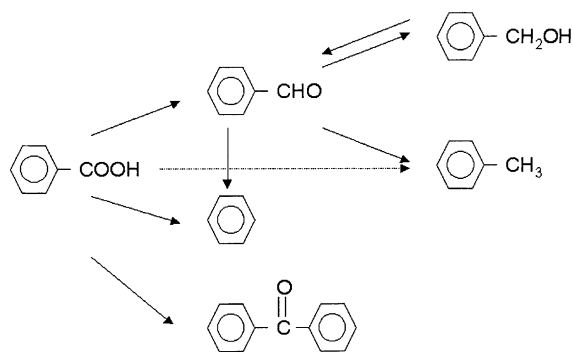
Scheme 2.

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