Deoxygenation of benzoic acid on metal oxides
1. The selective pathway to benzaldehyde

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Abstract

The mechanism of the selective deoxygenation of benzoic acid to benzaldehyde was studied on ZnO and ZrO_2. The results show conclusively that the reaction proceeds as a reverse type of Mars and van Krevelen mechanism consisting of two steps: hydrogen activates the oxide by reduction resulting in the formation of oxygen vacancies. Subsequent re-oxidation of these vacancy sites by benzoic acid yields benzaldehyde. Inhibition of the deoxygenation reaction can be achieved by addition of suitable polar compounds with a high affinity for the oxygen vacancy sites such as carbon dioxide or water. Differences in the catalytic activity and selectivity of ZnO and ZrO_2 can be attributed to differences in hydrogen activation, redox properties and extent of benzoic acid coverage. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Deoxygenation; Benzoic acid; Benzaldehyde; ZnO; ZrO_2; Mars and van Krevelen mechanism

1. Introduction

Aromatic aldehydes constitute an important group of fine chemicals that are used as intermediates in the production of pharmaceuticals such as analgetics, antipyrethics and antispasmodics and in the production of agrochemicals, in particular pyrethroid-based insecticides. Aromatic aldehydes can be produced in a variety of ways such as oxidation of alkylaromatics, halogenation of alkylaromatics followed by hydrolysis or halogenation of aromatic acids followed by hydrogenation, the so-called Rosenmund reduction. There are, however, serious drawbacks to these technologies. The yield of aldehydes is often unsatisfactory. For example, in the case of toluene oxidation a mixture of benzaldehyde, benzoic acid and benzylalcohol

is formed which has to be separated. Benzoic acid can be used to produce phenol but the added value of this process is rather small. Other processes require the use of corrosive reactants, which poses problems. Moreover, the production of waste in stoichiometric amounts, as in the case of the Rosenmund reduction, is undesirable because of its impact on the environment. An alternative method of preparing aromatic aldehydes is the selective deoxygenation of aromatic acids:

$$C_6H_5COOH + H_2 \rightarrow C_6H_5CHO + H_2O$$
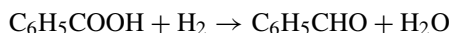
With a suitable catalyst high aldehyde yields can be achieved in a one-step process while the formation of environmentally damaging waste is minimised. Another advantage of this process is that aromatic acids are a cheap feedstock that is more easily produced by oxidation of alkylaromatics than the less oxygenated aldehyde. For this reason the selective deoxygenation

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of benzoic acid has received much attention in industry as an alternative method for preparing aldehydes, as can be inferred from the large volume of patents (primarily on metal oxides) that has appeared over the last 20 years [1–18]. In contrast relatively few studies [19–23] exist in open literature and, moreover, those relevant publications provide conflicting views on the mechanism of this reaction. Obviously determining the mechanism of the reaction is of paramount importance in the design of new catalytic materials. The deoxygenation of aromatic acids is described by Yokoyama et al. [19] as a reaction between dissociatively adsorbed benzoic acid (which forms a symmetric benzoate species upon adsorption) and adsorbed hydrogen to produce benzaldehyde. Several types of ZrO_2 were tested and a correlation was found between the acid–base characteristics of the catalysts and their activity and selectivity. Other studies [21–23] stress the importance of redox properties. Koutstaal et al. [21] studied the deoxygenation of benzoic acid to benzaldehyde on group IV oxides and found that the benzaldehyde selectivity decreased in the order Hf > Zr > Ti, as does the metal–oxygen bond strength. This was taken as an indication that the reaction follows a two-step reverse type of Mars and van Krevelen mechanism with participation of lattice oxygen: hydrogen reduces the surface and creates an oxygen vacancy. Subsequently benzoic acid re-oxidises the surface and desorbs as benzaldehyde. Sakata et al. [22] who tested a great number of metal oxides also found a correlation between reducibility and catalytic behaviour.

The aim of this study is to determine which mechanism operates in the selective deoxygenation of aromatic acids to aldehydes. This knowledge will enable us to develop new catalysts for this reaction [24]. This paper is the first of a series of two. The second publication [25] will focus on the entire reaction network and the factors that control the formation of by-products. Two metal oxides with high selectivity for this reaction were chosen. The effectiveness of ZrO_2 is well documented and forms the basis for a series of patents [3–7]. Recently comparable high selectivity has been obtained with a ZnO catalyst [22]. These two catalysts were tested here under steady-state conditions and also the behaviour of corresponding benzoates forming an adsorption layer was studied. In addition the impact of oxygen vacancies on the reaction was monitored by adsorption of carbon dioxide, a suitable probe molecule with specific affinity for oxygen vacancies [26–30].

2. Experimental

2.1. Experimental setup and procedures

The catalytic measurements were carried out at atmospheric pressure in a continuous flow apparatus. A carrier gas (hydrogen or nitrogen) was used to transport benzoic acid from the saturator to the reactor. After the reactor products were dissolved in ethanol by passing ethanol and the product stream simultaneously through a long capillary tube. This mixture was collected in two condensers cooled by water (15°C) and liquid nitrogen, respectively. The connections between saturator and reactor and between reactor and the capillary tube were wrapped in heating tape and held at a temperature of at least 200°C to avoid condensation of benzoic acid. The diameter of the reactor was 5 mm and the length of the reactor bed 10–15 mm. In each run 500 mg of catalyst was used with particle sizes between 300 and 500 μm. Smaller particles were used in a test reaction and similar product distributions were obtained indicating that intraparticle diffusion limitations did not hamper the reactions in the standard sized catalysts. Product distribution was determined by injecting a sample of the solution collected in the condensers into a Varian 3700 gas chromatograph equipped with a 25 m wide-bore CP-Sil 13 column (Chrompack NL). The mass balance was always better than 90%.

Two modes of operation were utilised. In reaction mode the flow of reactants is constant and the following reaction conditions were applied: catalyst loading 500 mg, hydrogen flow rate 40 ml/min, benzoic acid partial pressure 13 mbar which corresponds to a W/F ratio of 0.39 kg/mol h. In temperature-programmed (TPR) mode first a pretreatment was carried out with N_2 or H_2 at a flow rate of 40 ml/min at 430°C for 1 h, also using 500 mg catalyst. Then the catalyst was cooled in nitrogen to 250°C at which temperature a feed consisting of 30 mbar benzoic acid in nitrogen at a flow rate of 40 ml/min was led over the catalyst for 1 h at 250°C, allowing for the chemisorption of benzoic acid. At this temperature the two catalysts are not active in any reaction. The reactor with catalyst was

then heated up in nitrogen and the desorption of products (from the decomposition of benzoates formed upon adsorption) was followed. Every 25 min the reactor temperature was increased 25°C, a condensate was collected over this period and analysed simultaneously. In one experiment catalyst pretreatment in H_2 was followed by a treatment in carbon dioxide at 250°C for 1 h at a flow rate of 40 ml/min and then the standard benzoic acid adsorption–decomposition procedure outlined above was carried out.

The effect of water on the catalytic activity was studied using another continuous flow setup, also operating at atmospheric pressure. The layout of the system differed with respect to the product collection as gaseous samples of the products leaving the reactor were taken directly with a specially constructed heated syringe and manually injected into a HP 5890 II gas chromatograph also equipped with a 25 m wide-bore CP-Sil 13 column (Chrompack NL). The water pulses were generated by injecting water into the heated (200°C) flow system at a point after the saturator just before the reactor. In these reactions 200 mg of catalyst was used, the hydrogen flow rate was 28 ml/min and the benzoic acid partial pressure 5 mbar which corresponds to a contact time of 0.58 kg/mol h.

The temperature-programmed reduction experiment was carried out in a quartz tube of similar dimensions and catalyst loading as in the main flow system. A quadrupole mass spectrometer (Balzers) was used to detect hydrogen and water evolution. Sample pretreatment consisted of a oxygen flow at 350°C. The reduction was carried out with a 5% H_2/Ar mixture flowing at 20 ml/h, starting at room temperature and increasing the temperature 10°C/min.

Conversion (%), selectivity (%) and yield (%) are calculated in terms of the carbon atom balance and defined as follows:

$$X = \frac{A_{R,0} - A_R}{A_{R,0}} \times 100$$

$$S_p = \frac{A_p}{\sum A_p} \times 100$$

$$Y_p = \frac{A_p}{A_{R,0}} \times 100$$

where A_p is the integrated FID peak intensity of selected product, A_R the integrated FID peak intensity

of benzoic acid and $A_{R,0}$ is the integrated FID peak intensity of benzoic acid in the feed.

2.2. Catalyst preparation

ZnO was prepared by decomposing zinc basic carbonate (British Drug House, nominal composition $ZnCO_3 \cdot 2ZnO \cdot 3H_2O$) in nitrogen. The heating cycle was almost identical to the one reported by King and Nix [31]. The carbonate was first heated to 250°C at 10°C/min, held at this temperature for 4 h and then heated up to 400°C at 10°C/min with a dwell time of 6 min. The catalyst has the wurtzite structure and the BET surface of the fresh catalyst was 50 m²/g. ZrO_2 was prepared by calcining $Zr(OH)_4$ for 3 h at 600°C in nitrogen using a ramp of 10°C/min from ambient temperature to 600°C. The catalyst thus obtained had a monoclinic crystal structure and a BET surface area of 96 m²/g.

3. Results

3.1. Steady-state reactions

The activity and selectivity of the ZnO and ZrO_2 catalyst is shown in Fig. 1. Both catalysts are very selective to benzaldehyde. In fact by-product formation becomes only significant at elevated temperatures when the conversion of benzoic acid into benzaldehyde is almost complete. The ZnO catalyst is more active than the ZrO_2 catalyst, however, not only with respect to the selective reaction but also with respect to the by-products. Toluene is the main by-product for both catalysts. Benzylalcohol is only found in small quantities on both catalysts. Benzene formation is small and only significant at 430°C.

3.2. Reactions of adsorbed benzoates

In Figs. 2–4 experiments are depicted in the so-called temperature-programmed mode using the ZnO catalyst. Fig. 2 shows the results of an experiment in which first the catalyst was pretreated in a flow of hydrogen at 430°C for 1 h followed by a period of benzoic acid adsorption at 250°C. Then the sample was heated in nitrogen and the desorption of products from the surface was monitored.
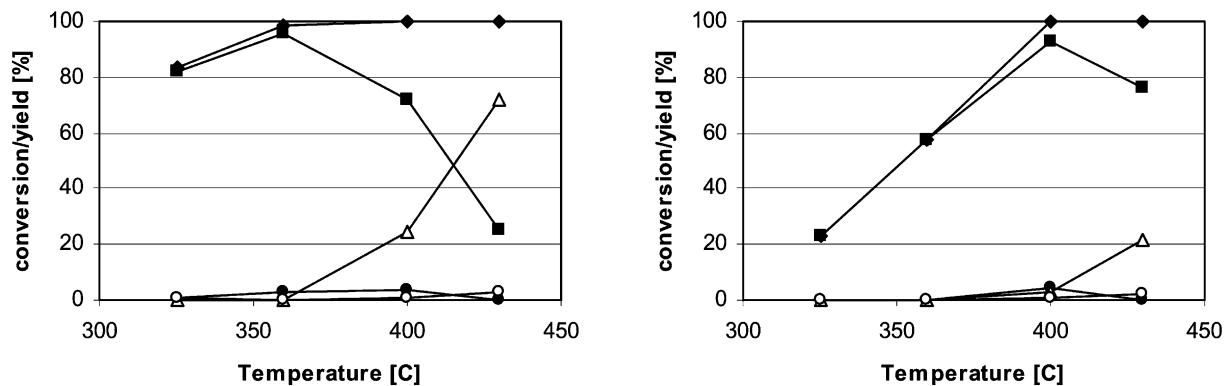
Fig. 1. Product distribution in the deoxygenation of benzoic acid over ZnO (left) and ZrO_2 (right) as a function of temperature. Symbols: (◆) benzoic acid conversion; (■) benzaldehyde yield; (●) benzylalcohol yield; (△) toluene yield; (○) benzene yield. Reaction conditions: H_2 flow rate 40 ml/min; benzoic acid partial pressure 13 mbar; benzoic acid $W/F = 0.39$ kg/mol h.
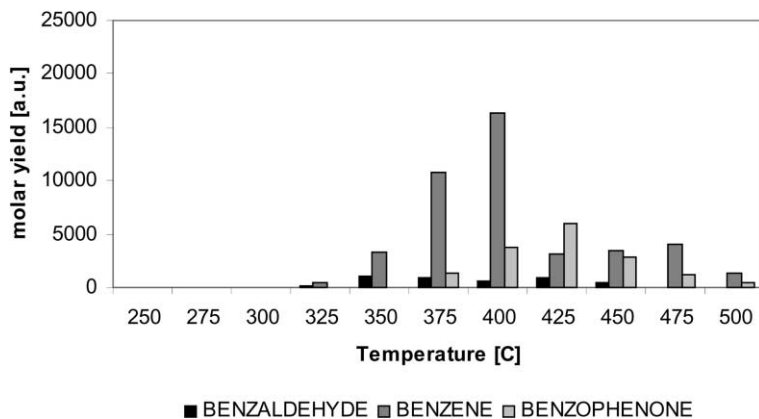

Fig. 2. Temperature-programmed reactions of benzoic acid adsorbed on ZnO after a pretreatment in hydrogen.
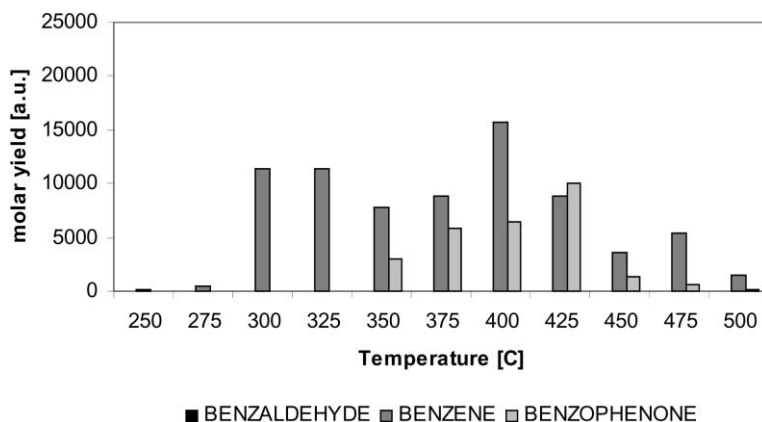

Fig. 3. Temperature-programmed reactions of benzoic acid adsorbed on ZnO after a pretreatment in nitrogen.
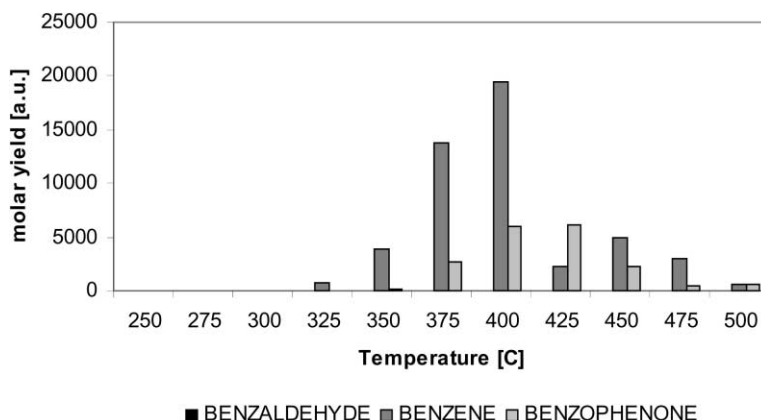
Fig. 4. Temperature-programmed reactions of benzoic acid adsorbed on ZnO after a pretreatment in hydrogen followed by a treatment in carbon dioxide.

The main product observed is benzene. At increased temperature the condensation product benzophenone is also detected. Benzaldehyde formation is observed but only in small quantities.

The experimental procedure of which the results are shown in Fig. 3 is the same as the procedure leading to Fig. 2 but now the ZnO catalyst is pretreated in nitrogen instead of hydrogen. Again benzene and benzophenone are the major products desorbing from the catalyst. However, in this experiment benzaldehyde formation is absent.

The hydrogen pretreatment might give rise to the formation of oxygen vacancies. If that indeed is the case a subsequent admission of carbon dioxide (which possesses specific affinity for these defect sites

[26–30]) should reduce the amount of oxygen vacancies. Fig. 4 shows the results of such an experiment. First the catalyst was subjected to a pretreatment in hydrogen. Next a flow of carbon dioxide was passed over the reactor at $250°C$ for 1 h. Finally, a feed of benzoic acid in nitrogen was led into the system. The results thus obtained are similar to the results obtained when the catalyst was pretreated in nitrogen (Fig. 3). No benzaldehyde is detected, only benzene and benzophenone are found.

These experiments were also performed with the ZrO_2 catalyst and the results with regard to the benzaldehyde formation were similar. Benzaldehyde was only found after a reductive pretreatment and not after a pretreatment in nitrogen. The main difference with
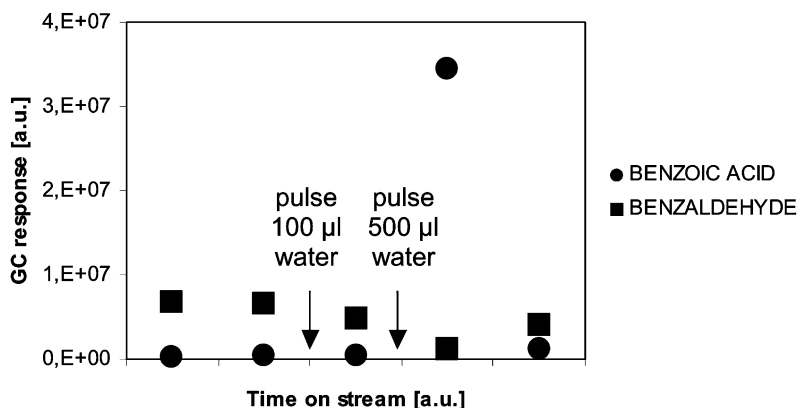

Fig. 5. Effect of water pulses on the deoxygenation of benzoic acid over ZnO.
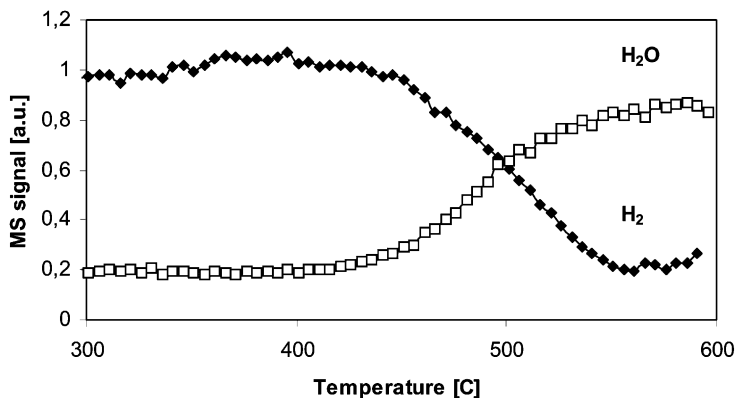
Fig. 6. TPR spectrum of ZnO.

the ZnO catalyst was that the amount of benzophenone formed was very small. Benzene accounted for more than 85% of the products (excluding benzaldehyde) desorbing from the catalyst.

3.3. Effect of water

One experiment was done in which under steady-state conditions pulses of water were injected into the feed in order to determine the effect of water on the performance of the catalyst (Fig. 5). The water is responsible for a temporary dip in activity while at the same time a large quantity of benzoic acid desorbs from the surface. The effect is not irreversible and after a while the catalyst returns to the original state.

3.4. Temperature-programmed reduction

A temperature-programmed reduction experiment was carried out on the ZnO catalyst, the results of which are shown in Fig. 6. The process of hydrogen consumption and water production starts around 430°C and is not complete at 600°C when the experiment was terminated.

4. Discussion

Benzaldehyde is produced in very high yields (>95%) on both the ZnO and ZrO$_2$ catalysts under steady-state conditions with a high partial pressure of hydrogen. However, no conclusions with regard to the

mechanism of the reaction can be drawn solely based on these results. A detailed picture of the mechanism of benzaldehyde formation can be obtained from the temperature-programmed reactions that, therefore, will be discussed first.

From the temperature-programmed reactions (Figs. 2–4) it is clear that the adsorption of benzoic acid and the reactivity of the benzoate depend on the type of pretreatment. After a pretreatment in nitrogen the benzoate species that is formed will decompose into benzene and benzophenone. Obviously this benzoate species cannot be deoxygenated to benzaldehyde. The same benzoate species is also present after a pretreatment in hydrogen but in this experiment next to the aforementioned decomposition products benzaldehyde is observed as well. This means that the active site for deoxygenation has been created during pretreatment in hydrogen. The benzoic acid adsorbed at this site will desorb as benzaldehyde upon heating. Thus, hydrogen is not only a reactant in the overall reaction, it also plays an essential role in activating the oxide, during the pretreatment before the temperature-programmed reaction and, more importantly, during the steady-state reaction as well. The TPR experiment shows that during pretreatment at 430°C a slight reduction of the metal oxide takes place. In this process some oxygen vacancies must have been created. It appears that the benzoic acid that adsorbs on these defect sites will deoxygenate to benzaldehyde. So the following picture emerges (Fig. 7).

After a pretreatment in nitrogen benzoic acid adsorbs dissociatively and forms a symmetrical benzoate
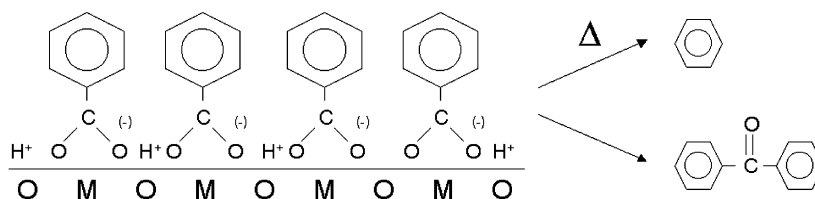
Fig. 7. Reaction model of benzoic acid adsorbed on a catalyst pretreated in nitrogen.

and an adsorbed hydrogen species. Infrared studies suggest that either a bidentate or bridging coordination is likely [19,20,32,33]. Upon heating in nitrogen this benzoate will decompose into benzene and benzophenone. After a pretreatment in hydrogen two different types of site will be available for benzoic acid adsorption, a non-reduced site and a reduced defect site (Fig. 8).

The benzoic acid that adsorbs on a non-reduced site will decarboxylate into the products indicated on the left-hand side. The benzoic acid that adsorbs on the oxygen vacancy sites created during hydrogen pretreatment will be deoxygenated and effectively re-oxidise the surface. The temperature-programmed reduction experiment (Fig. 6) shows that the reduction of the surface is far from complete and only a small number of oxygen vacancies are formed. It is well known that surface reduction occurs at temperatures much lower than for bulk reduction [34,35]. This explains why the amount of benzaldehyde formed in the temperature-programmed reaction is just a fraction (ca. 7%) of the total amount of products (Fig. 2).

The presence of oxygen vacancies is further illustrated by the experiment with carbon dioxide. Fig. 4 shows nothing more than the selective poisoning of the active site, i.e. the oxygen vacancy, by carbon dioxide. It cannot be inferred from our results in what

way the carbon dioxide interacts with the defect site on ZnO. Two different types of interaction have been proposed [26–30]. There could be a carbonate species formed which blocks the adsorption of benzoic acid. The carbon dioxide might also re-oxidise the surface under the release of CO so that no reduced sites are available. Unfortunately, the gas chromatography setup as used here did not permit the detection of small molecules such as CO so the type of interaction remains unknown. Nevertheless the important point is made that the active site involves an oxygen vacancy that can be selectively poisoned by carbon dioxide.

This experiment is of great importance for our discussion. If the reaction would proceed via a Langmuir–Hinshelwood mechanism between adsorbed hydrogen and benzoic acid species one would expect some benzaldehyde formed in the temperature-programmed experiment shown in Fig. 4 since it is improbable that the adsorption of carbon dioxide removes all the hydrogen adsorbed, given the different nature of the two adsorbates (hydrogen and carbon dioxide).

Hence, we conclude that a redox mechanism operates in the selective deoxygenation of benzoic acid as suggested by Koutstaal and co-workers [21,22] and Sakata and Ponec [23]. For the deoxygenation of aliphatic acids, an analogous reaction, this
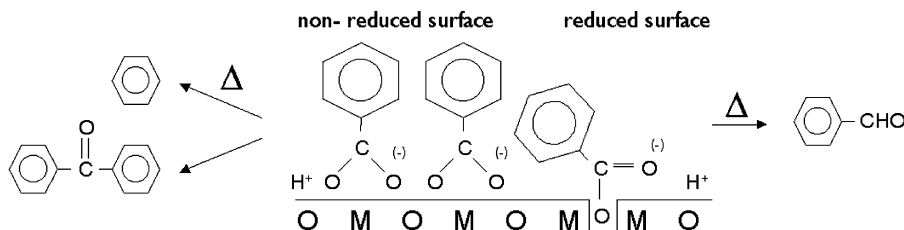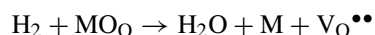

Fig. 8. Reaction model of benzoic acid adsorbed on a catalyst pretreated in hydrogen.

mechanism has been proposed too [36]. The mechanism consists of two steps:

1. Activation of the catalyst by hydrogen:

$$H_2 + MO_O \rightarrow H_2O + M + V_O^{\bullet\bullet}$$

2. Re-oxidation of the catalyst by benzoic acid yielding benzaldehyde:

$$C_6H_5\text{–}COOH + V_O^{\bullet\bullet} + M \rightarrow MO_O + C_6H_5\text{–}CHO$$

The fact that during the steady-state experiments the selectivity to benzaldehyde is much higher than after a reductive pretreatment when decomposition products prevail is clarified as follows. During steady-state reactions hydrogen is constantly supplied and oxygen vacancies are continuously created. The benzoic acid reacts much more readily with the oxygen vacancies than that the benzoates decompose into benzene and benzophenone. Moreover, the majority of benzoates are strongly bonded and do not decompose at the temperatures at which selective deoxygenation occurs. So although this strongly bonded benzoate is easily observed in infrared spectroscopy its role is more that of a spectator than of an intermediate.

More evidence that under steady-state conditions an extended layer of benzoates covers the surface comes from the experiment where water was added to the feed (Fig. 5). Upon the addition of water a large amount of benzoic acid is released from the surface. This has also been observed in the reverse reaction, i.e. the oxidation of benzaldehyde to benzoic acid [37,38]. In this reaction water increases the reaction rate. It was suggested [37,38] that the addition of water increases the population of hydroxyl groups on the oxide surface thereby facilitating the reaction between the strongly bound surface benzoate and surface hydroxyls. Without water the desorption of benzoic acid is very slow. In the deoxygenation reaction another effect next to the desorption of benzoic acid is observed: the formation of benzaldehyde drops. Water, just as carbon dioxide, has a high affinity for oxygen vacancies [39,40]. Adsorption of water at these active sites lowers the rate of deoxygenation.

There are two important differences between the ZnO and the ZrO$_2$ catalyst. First the deoxygenation proceeds much slower on ZrO$_2$. Yokoyama et al. [19] state that the activation of hydrogen is related to the rate-determining step and this was confirmed by some elementary kinetic experiments. It was found that the reaction orders varied between 0.6 and 0.9 with respect to hydrogen and between 0.0 and 0.1 with respect to benzoic acid. Studies show that hydrogen activation is much more difficult on ZrO$_2$ than on ZnO [41]. The energy barrier for the formation of an oxygen vacancy on ZrO$_2$ is much higher than on ZnO because of the difference in metal–oxygen bond strength. In fact ZrO$_2$ is often considered to be an irreducible oxide but recent research has shown that defect sites can be found on ZrO$_2$ albeit at very low concentrations [35,42–44]. Thus, under steady-state conditions at identical temperatures the concentration of oxygen vacancies will be higher on ZnO than on ZrO$_2$. A second difference between the oxides is the low yield of benzophenone found with ZrO$_2$ in the temperature-programmed mode. This is due to the low lattice stability of ZnO. Carboxylic acid coverage is high on basic and alkaline oxides such as ZnO. Such an extended carboxylate layer makes an intermolecular exchange of groups during decomposition possible and thus favours, amongst others, the formation of ketones [45–47]. On ZrO$_2$ the benzoic acid coverage is lower because it is a less basic oxide. The benzoates are more isolated and the decomposition takes place monomolecularly.

5. Conclusions

The selective deoxygenation of benzoic acid to benzaldehyde was studied on ZnO and ZrO$_2$. The results can be adequately explained by the operation of a reverse Mars and van Krevelen mechanism in which hydrogen reduces the metal oxides upon which re-oxidation by benzoic acid follows. The oxygen vacancy sites at which the deoxygenation reaction proceeds can be effectively poisoned by carbon dioxide or water. Under reaction conditions the surface of the catalyst is covered by an extended layer of benzoates that can decompose at elevated temperatures into benzene and benzophenone. In the presence of hydrogen, however, the selective pathway is much faster than the non-selective route. This model applies to both ZnO and ZrO$_2$. ZnO is more easily reducible, which results in more surface defects and is therefore the more active catalyst.

Acknowledgements

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