

# Selectivity Problems in the Catalytic Deoxygenation of Benzoic Acid

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The oxides of Mg, Pb, Cr, La, Pr, Yb, Mn, Fe, Co, Zn, Zr, and Ce were studied as catalysts for the reactions of benzoic acid in the temperature range 523–723 K. All experiments were performed in a continuous flow apparatus, at a total pressure of about one bar, with hydrogen as the reductant. The oxides studied could be subdivided into several groups according to their product pattern. The groups indicate the prevailing mechanism. The two basic mechanisms are: (i) Mars and van Krevelen (selective to benzaldehyde) and (ii) radical-like decomposition of benzoate. The highest yield of benzaldehyde can be obtained with oxides of high metal–oxygen bond strength. © 1997 Academic Press

## INTRODUCTION

Due to the increasing demand for aromatic aldehydes (used as fragrances and, for example, the synthesis of pyrethroid insecticides), there is also increasing interest in information on the selective production of aldehydes from aromatic carboxylic acids. The direct hydrogenation of carboxylic acids by using suitable catalysts is a very convenient method for synthesis of aldehydes. By this method, aldehydes would be synthesized effectively without producing undesirable by-products that can pollute the environment. Therefore, much attention has been paid to exploring new catalysts with high activities and a selectivity to aldehydes, suitable for industrial processes. These are usually oxidic catalysts (1–11).

A long list of available patents (not all are quoted here) documents the growing interest in practical applications, but an inspection of scientific and patent literature reveals that only very little is known about the fundamentals of the reactions and the function of the catalysts. It is, for example, still impossible to predict which catalysts should be suitable for which substrate (aliphatic vs aromatic acid; benzoic vs substituted acids) and why. The mechanism and the factors determining the selectivity, etc., have yet to be discovered. This study will concentrate mainly on the last of the above-mentioned areas.

A glance at the patent literature (1–11) would reveal that a large portion of the elements of the periodic table has already been suggested for use in their oxidic form as catalysts (or catalysts' component) for selective deoxygenation. Among them are alkali earth, transition metal, and rare-earth oxides. From the patent literature the differences between the oxides are unclear as is the role of the individual components, when a multicomponent catalyst is used.

As far as aliphatic carboxylic acids are concerned, much more is known about the mechanism and the role of various oxides as catalysts or components of catalysts. This information will be used in the discussion (12, 13).

This paper reports catalytic properties of various oxides in the deoxygenation of benzoic acid. The main aim was to determine whether all oxides behave uniformly or whether different categories of oxides, each characterized by a certain, common mechanism, can be distinguished. This approach may perhaps lead to a more rational design of new catalysts.

## EXPERIMENTAL

### Methods and Data Collection

All experiments reported in this paper were performed with a glass continuous-flow apparatus. The schematic view of the apparatus is shown in Fig. 1. The whole apparatus is kept at a temperature higher than 473 K by heating tapes and infrared irradiation. Helium, when applied as the carrier gas, and H<sub>2</sub> (as a reactant) enter the apparatus through valves A and B, respectively. Gases are purified in the BTS catalyst column (D) and the molecular sieve column (E) and then passed through a vessel containing liquid benzoic acid. The saturator temperature is maintained at around 450 K. The partial pressure of benzoic acid, fed into the reactor, is controlled by a condenser (G) which is kept at a desired (lower) temperature. The reactor H is typically filled with ca 0.3 g of catalyst. The unreacted reactants and products are condensed in a trap tube (K) at liquid nitrogen temperature and can be used for analysis.

The product mixture is analyzed by a gas liquid chromatograph (GLC). The sample of the product mixture (ca 5 ml) is

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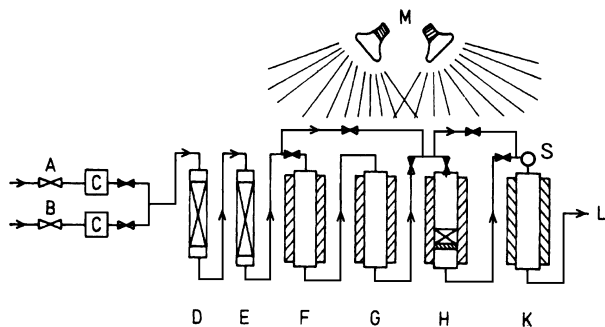


FIG. 1. Schematic view of the flow apparatus used in this work: A, He; B, H<sub>2</sub>; C, mass flow controller; D, a column with BTS catalyst; E, a column with a molecular sieve; F, saturator with benzoic acid; G, condenser for benzoic acid; H, reactor; K, second condenser; L, flow meter at the exit of the second condenser; M, infrared lamp for heating; S, the position of the sampling port.

taken as gas from the sampling port (S) by a special syringe that is kept at 473 K during sample collection and injection into the gas chromatograph. The sample of the condensed phase in the condenser (K) can be analyzed by GLC as well. A HP 5890 II GC, equipped with flame ionization detector, was used for the analysis; the data were collected and evaluated by a HP-Chem.Station. Separation of the compounds in the product mixture is achieved by means of a 25 m wide-bore CP-Sil 13 column (Chrompack, NL).

In a standard experiment, benzoic acid was added at 35 Pa and a flow rate of 28 ml/min; pure hydrogen was added to give a total pressure of one bar.

The conversion  $\alpha$  is defined as

$$\alpha = \frac{A_{BA}^{\circ} - A_{BA}}{A_{BA}^{\circ}} \quad [1]$$

The selectivity to a component “*i*” is calculated in terms of the carbon atom balance using the following equation:

$$S_i = \frac{A_i}{\sum A_i - A_{BA}} \quad [2]$$

In both these equations,  $A$  is the integrated peak intensity of the FID corresponding to the gas mixture component, indicated by the index, the index BA indicates benzoic acid, and  $A_{BA}^{\circ}$  is the signal of the feed.

In a standard experiment, the reaction was started at 523 K, and the temperature was increased in steps of 25 K, up to 723 K. The products were analyzed every 30 min, and when the steady state of the reaction was reached at a given temperature, the reaction temperature was increased.

### Catalysts

Several oxides used in this study were prepared in our laboratory but commercially available oxides were also used. MgO (surface area 91 m<sup>2</sup>/g) was prepared by calcining mag-

nesium hydroxide at 815 K. La<sub>2</sub>O<sub>3</sub> (surface area 3 m<sup>2</sup>/g) was prepared by calcining La(NO<sub>3</sub>)<sub>3</sub> (Merck) in air at 975 K for 10 h.  $\alpha$ -Mn<sub>3</sub>O<sub>4</sub> (surface area of  $\alpha$ -Mn<sub>3</sub>O<sub>4</sub> was 26 m<sup>2</sup>/g), MnO<sub>2</sub>, ZrO<sub>2</sub> (26 m<sup>2</sup>/g), and CeO<sub>2</sub> (50 m<sup>2</sup>/g) were prepared by calcining the corresponding hydroxides, obtained by precipitation of Mn(NO<sub>3</sub>)<sub>2</sub>, ZrO(NO<sub>3</sub>)<sub>2</sub> (Aldrich), and Ce(NO<sub>3</sub>)<sub>3</sub> (Merck) with NH<sub>4</sub>OH at pH = 9 and calcination in air at 400 K for  $\alpha$ -Mn<sub>3</sub>O<sub>4</sub> and 773 K for the other oxides for 10 h. PbO (Aldrich) (1 m<sup>2</sup>/g), Fe<sub>2</sub>O<sub>3</sub> (7 m<sup>2</sup>/g surface area), Pr<sub>6</sub>O<sub>11</sub>, Yb<sub>2</sub>O<sub>3</sub> (Fluka), Cr<sub>2</sub>O<sub>3</sub> (3 m<sup>2</sup>/g), CO<sub>3</sub>O<sub>4</sub> (10 m<sup>2</sup>/g), and ZnO (5 m<sup>2</sup>/g) (British Drug House) were purchased. ZnMn<sub>2</sub>O<sub>4</sub> (23 m<sup>2</sup>/g) was prepared by calcining the coprecipitate of corresponding hydroxides, obtained by the same procedure as, for example, Mn<sub>3</sub>O<sub>4</sub>, at 400 K. The oxides were kept *in situ* at 523 or 723 K, under He flow, for 1 h before the reaction was initiated. The crystallographic structure and phase purity was measured by XRD for all oxides, where this was relevant (ZrO<sub>2</sub>, Mn-oxides, Co<sub>3</sub>O<sub>4</sub>, CeO<sub>2</sub>). Values of the surface area are shown above to indicate, rather the dispersion of oxides before the reaction than the number of active sites under the running reaction.

## RESULTS

Results obtained with various oxides, i.e., the conversion and selectivity to the main products, both as a function of temperature, are shown in Figs. 2 to 6. As we shall see later, there are reasons for subdividing the oxides in this way. Different oxides produce a different spectrum of products, and this gives some indication of the prevailing mechanism and the factors controlling the selectivity. In addition to the benzaldehyde production, the production of toluene and benzene (the ratio of these two) is particularly important.

### Group 1

The results obtained with Group-1 oxides are shown in Fig. 2.

MgO. The conversion increases with increasing reaction temperature, but is low (below 20%) in the whole temperature range up to 723 K. In the experiment represented in Fig. 2 the reaction was first carried out below 573 K for more than 10 h. Thereafter the reaction temperature was increased to 598 K, i.e., above the melting point of magnesium benzoate (melting of the catalyst was visible), and monitoring of the reaction was continued. This suggests that MgO probably reacted with benzoic acid to form magnesium-benzoate, which has a low melting point.

The selectivity to benzaldehyde (BALD) which is the desired product, is very low (below 35%). It is interesting that at low conversions, as much as 40% phenol ( $\Phi$ -OH) can be formed. Another important feature is that benzene is formed while the production of toluene ( $\Phi$ -CH<sub>3</sub>) is low.

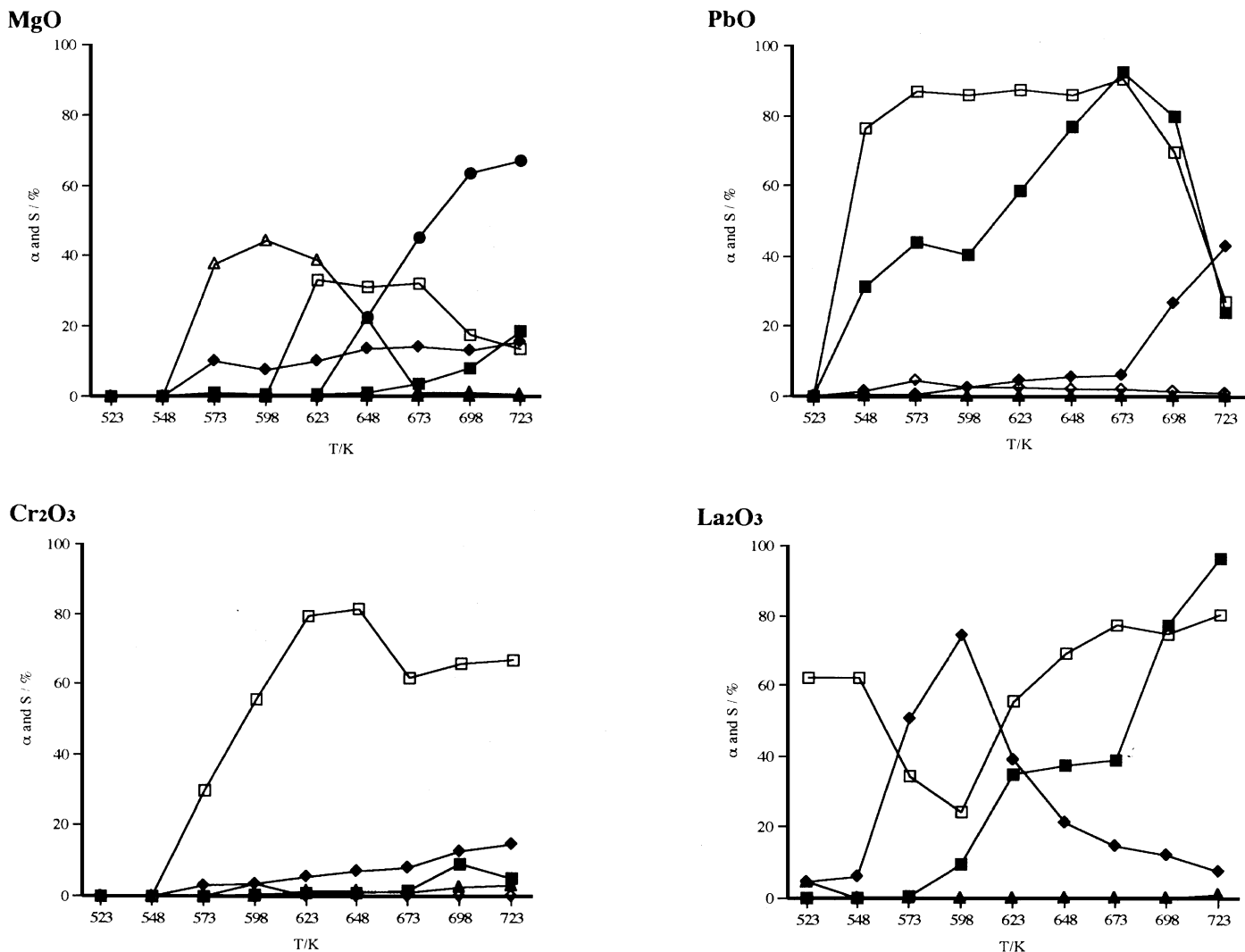


FIG. 2. Reaction profiles of benzoic acid under H<sub>2</sub> over MgO, PbO, Cr<sub>2</sub>O<sub>3</sub>, and La<sub>2</sub>O<sub>3</sub>: ■, conversion; ◆, benzene; ▲, toluene; □, benzaldehyde; ◇, benzylalcohol; △, phenol; ●, benzphenon.

The rather high selectivity to acetophenone is remarkable. This product can be considered as an analogue of ketones formed from aliphatic acids (e.g., acetone from acetic acid). Ketonization of aliphatic acid is known to proceed by two different mechanisms (14–16) of which only one, not requiring the alpha-hydrogen, would be possible here. We shall return to this point in the “Discussion.”

**PbO.** The conversion of benzoic acid reached a maximum value at 673 K. This value is rather high (ca 90%). The selectivity to the most desired product (BALD) was rather high (80–90%), too. Benzene was produced but the production of toluene was very low. The selectivity to benzene increased while the selectivity to BALD as well as the total conversion decreased above 673 K. The latter is probably caused by a partial reduction of the oxide under the running reaction.

**Cr<sub>2</sub>O<sub>3</sub>.** This oxide exhibited a very low activity in the whole temperature range. The product formation was seen above 548 K. At very low conversion, there was some selectivity to benzaldehyde (ca 80% at around 623 K). Again, the production of benzene is clearly higher than that of toluene. In the low temperature range, a relatively rather high formation of products of destructive reactions, such as low molecular weight hydrocarbons and alcohols (not shown in the figure), was observed (absolutely, in small amounts).

**La<sub>2</sub>O<sub>3</sub>.** The conversion to the various products was very low, below 600 K, but a value of more than 95% at 723 K was reached. As can be seen in the corresponding figure, the selectivity to benzaldehyde does not vary with increasing temperatures in a monotonic way. The dip in S<sub>BALD</sub> is accompanied by a marked increase in benzene selectivity. The production of toluene was, as in all cases mentioned

up to now, lower than that of benzene.  $\text{Pr}_6\text{O}_{11}$  and  $\text{Yb}_2\text{O}_3$  behaved similarly as  $\text{La}_2\text{O}_3$ .

### Group 2

The results obtained with Group-2 oxides are shown in Fig. 3. This group is formed by different manganese based oxides. Two of the these oxides ( $\alpha\text{-Mn}_3\text{O}_4$  and  $\text{ZnMn}_2\text{O}_4$ ) are A(II)B(III) $_2\text{O}_4$  spinels, with A(II) being either Mn or Zn.

$\text{MnO}_2$ . The conversion of benzoic acid was low below 600 K. It increased with increasing temperature up to 648 K. However, it decreased again at 673 K and achieved a very high value at still higher temperatures. The selectivity to benzaldehyde increased with increasing reaction temperature to around 95%, and then, it decreased as temperature rose above 673 K. The selectivity to other products, such as benzene and toluene, were low below 673 K,

but the selectivity of toluene increased markedly above 673 K.

$\alpha\text{-Mn}_3\text{O}_4$ . The behavior was similar to that of  $\text{MnO}_2$ , but the corresponding curves shifted slightly to a lower temperature. The conversion of benzoic acid showed a non-monotonic variation with the temperature, as can be seen in Fig. 3 at 650 K. It achieved a high value (around 95%) at 700 K. The selectivity to benzaldehyde remained high, being more than 90% in the reaction temperature range from 550 to 673 K; thereafter it decreased. The selectivities to other products were low; only the selectivity to toluene increased markedly above 673 K, similarly as with  $\text{MnO}_2$ .

$\text{ZnMn}_2\text{O}_4$ . The conversion of benzoic acid increased monotonically with increasing reaction temperature and reached a very high value above 648 K. This tendency is slightly different from the tendency of manganese oxides mentioned above. The selectivity to benzaldehyde was over 95% between 573 K and 648 K. However, above 648 K, the

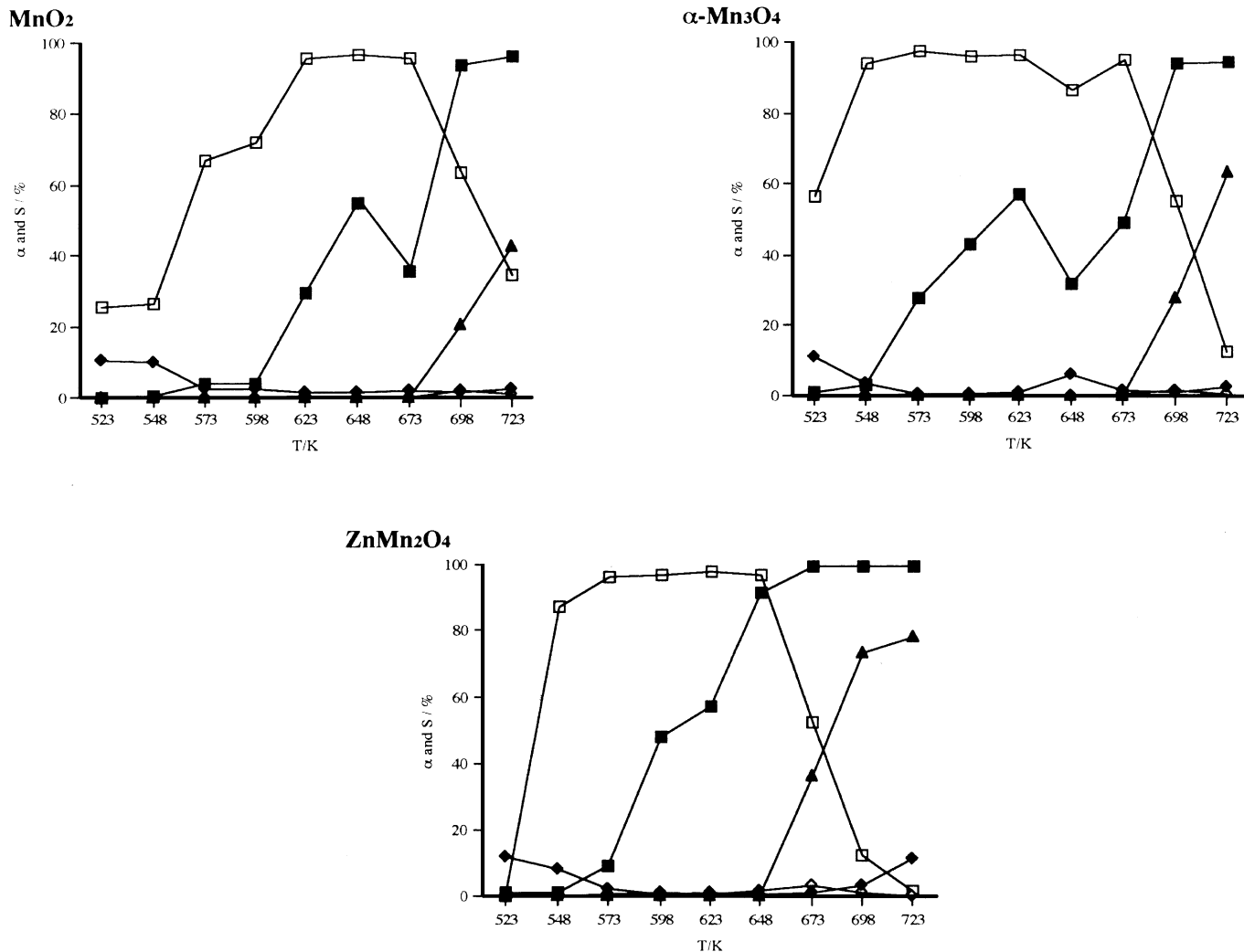


FIG. 3. Reaction profiles of benzoic acid under  $\text{H}_2$  over  $\text{MnO}_2$ ,  $\alpha\text{-Mn}_3\text{O}_4$ , and  $\text{ZnMn}_2\text{O}_4$ : ■, conversion; ◆, benzene; ▲, toluene; □, benzaldehyde.

deoxygenation of benzoic acid proceeded further by the formation of toluene. The selectivity to toluene increased with increasing of reaction temperature, while that to benzaldehyde decreased. The main difference in the catalytic behavior as compared to  $\alpha$ - $\text{Mn}_3\text{O}_4$  and  $\text{MnO}_2$  was that the conversion increased monotonically with increasing in the reaction temperature. It is noteworthy that with all the catalysts in this group, the production of toluene was always clearly higher than that of benzene (in contrast to the Group 1 catalysts, for example).

### Group 3

The results obtained with the Group-3 oxides are shown in Fig. 4. The oxides are  $\text{Co}_3\text{O}_4$ ,  $\text{Fe}_2\text{O}_3$ , and  $\text{Fe}_3\text{O}_4$ , the latter prepared by reducing  $\text{Fe}_2\text{O}_3$  with hydrogen at 673 K for 2 h.

$\text{Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$ . The conversion of benzoic acid was rather low at reaction temperatures below 623 K, but

reached 90% above 648 K. The selectivity to benzaldehyde was high below 623 K, where, however, the conversion was low (see Fig. 4). The selectivity to toluene increased while that to benzaldehyde decreased above 623 K. The selectivity to benzene increased with increasing temperature. It is clear that catalytic behavior changes markedly at reaction temperatures above 623 K. It appears that the change is somehow related to the reduction of  $\text{Fe}_2\text{O}_3$  by the reaction mixture. Therefore,  $\text{Fe}_2\text{O}_3$  was prereduced at 673 K and converted by that into a  $\text{Fe}_3\text{O}_4/400$  sample (see Fig. 4). Prereduction clearly increased the conversion which reached a value of more than 95% already at 598 K. The selectivity to benzaldehyde can be very high at low conversion, but it decreases with increasing conversion. The selectivity to toluene increased again as the selectivity to benzaldehyde decreased. The selectivity to benzene increased with temperature but was lower than for toluene.

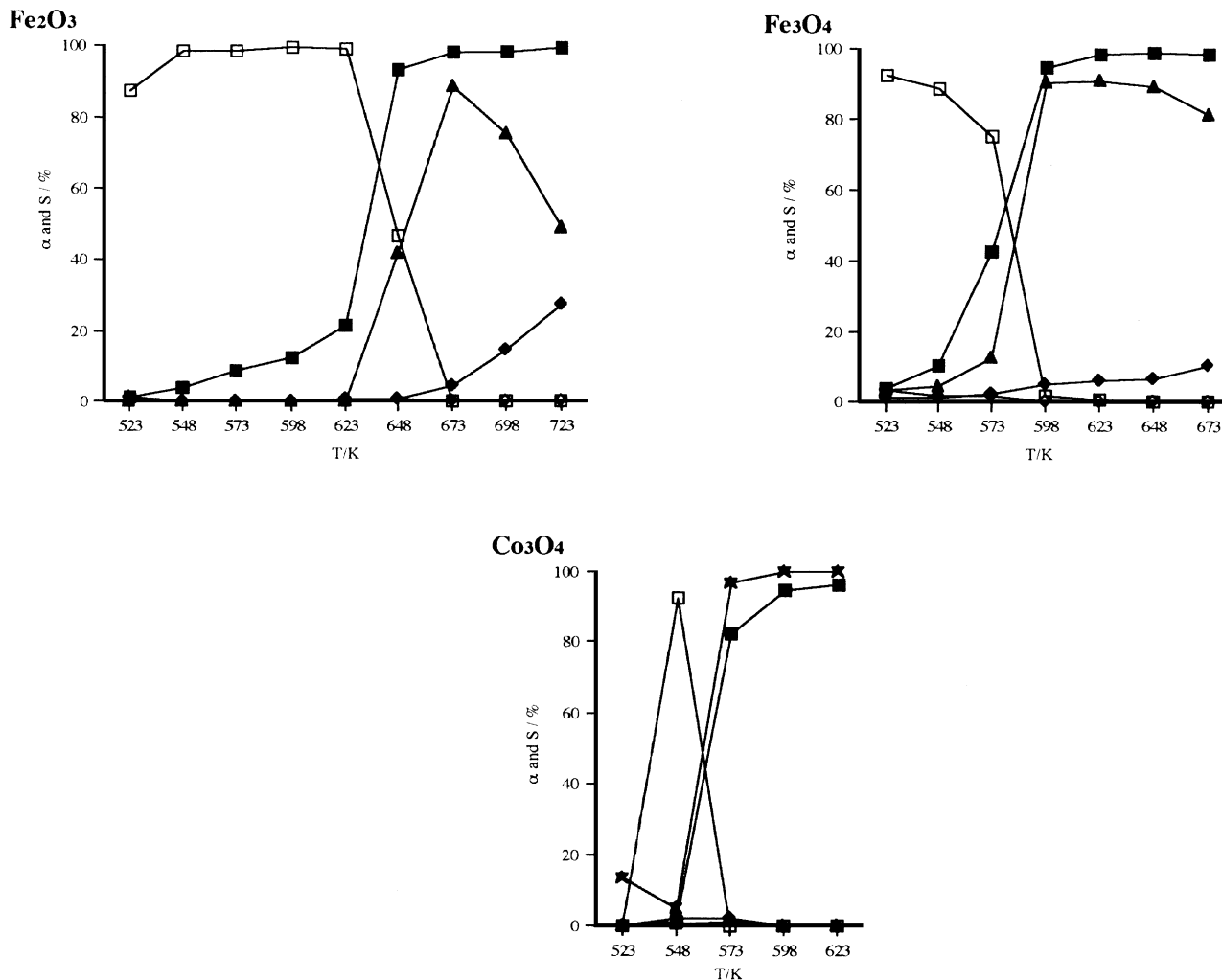


FIG. 4. Reaction profiles of benzoic acid under  $\text{H}_2$  over  $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$ , and  $\text{Co}_3\text{O}_4$ : ■, conversion; ◆, benzene; ▲, toluene; □, benzaldehyde; ★, methane.

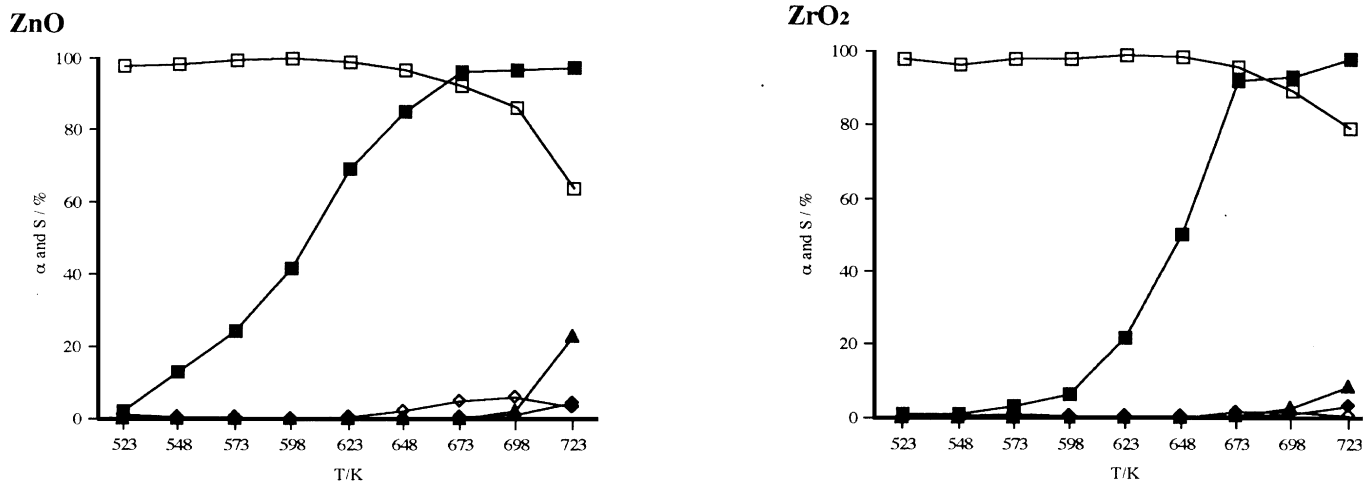


FIG. 5. Reaction profiles of benzoic acid under  $H_2$  over  $ZnO$  and  $ZrO_2$ : ■, conversion; ◆, benzene; ▲, toluene; □, benzaldehyde; ◇, benzylalcohol.

$Co_3O_4$ . The conversion is low below 548 K, but reached a value of more than 90% at 598 K. The selectivity to benzaldehyde is ca 90%, but only at 548 K when the conversion is still very low. The selectivity to methane is very high at reaction temperatures over 573 K (in this temperature region one observes also decomposition to methane of the adsorbed benzoic acid), while the selectivity to other products is low. However, formation of toluene (as a possible intermediate product) is clearly observable.

#### Group 4

The results obtained with these oxides are shown in the Figs. 5 and 6.

$ZnO$ . The conversion of benzoic acid reached a value of more than 90% at 673 K. The selectivity to benzaldehyde was high, ca 98%, at reaction temperatures below

648 K. The selectivity to benzaldehyde decreased gradually with increasing reaction temperature, while the selectivity to other products, such as benzyl alcohol, toluene, and benzene, gradually increased at temperatures above 648 K. Selectivity to toluene increased at 723 K.

$ZrO_2$ . The catalytic behaviour was nearly the same as that of  $ZnO$  (see Fig. 5). This oxide was a very good catalyst, as also reported in the patent literature (18). The conversion above 90% can be achieved with selectivity to benzaldehyde higher than 90% at 673 K. The main by-products are toluene and benzene and their formation increases with increasing temperatures. The selectivity to toluene is always higher than that to benzene (note the difference with Group-2 oxides). Let us add that  $ZrO_2$  is very similar to  $TiO_2$  and  $HfO_2$ .

$CeO_2$ . The results obtained with  $CeO_2$  are presented in Fig. 6. The conversion could be as high as 95% at 648 K. The selectivity to benzaldehyde was more than 90% up to 648 K. It decreased markedly above 648 K. The main by-products were benzene and toluene, and their selectivities increased with increasing reaction temperature above 673 K. The selectivity to benzene is higher than that to toluene, and although  $CeO_2$  is otherwise very similar to the other oxides of Group 4, it is different in this respect.

#### DISCUSSION

Before discussing the catalytic behavior of oxides as reported in this paper, information on the reactions of carboxylic acids from the literature will be summarised: (i) Aliphatic acids react in hydrogen-free or hydrogen-lean mixtures to ketones; the existence of two mechanisms of ketonization have been proven (14–16): one involves the  $\alpha$ -hydrogen of the hydrocarbon chain, and the other can be characterized as a radical-like decomposition of carboxylates. Obviously, benzoic acid cannot react by the first

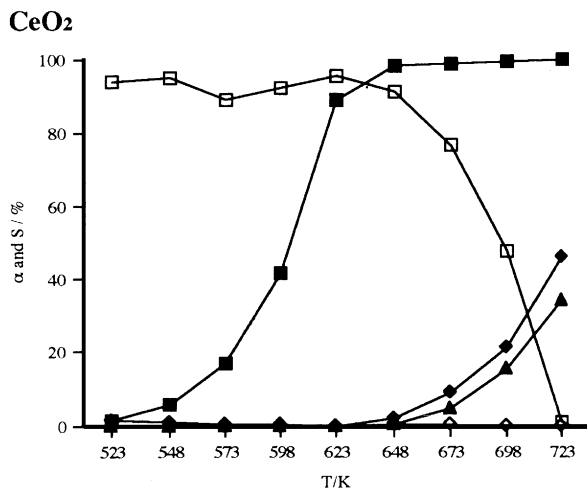


FIG. 6. Reaction profiles of benzoic acid under  $H_2$  over  $CeO_2$ : ■, conversion; ◆, benzene; ▲, toluene; □, benzaldehyde; ◇, benzylalcohol.

mechanism, since for that the presence of  $\alpha$ -hydrogen in the molecule is required and the potential products of the decomposition of the surface benzoate (or bulk benzoate, as in the case with magnesium) are benzene (de-carboxylation), phenol, benzophenone, and some secondary products. It is not clear whether some benzaldehyde may also be a product of such a reaction network. (ii) Selective deoxygenation of aliphatic acids to the corresponding aldehydes is probably a reaction of the Mars and van Krevelen (Kröger) type (17, 18). It means that an oxidic catalyst offers an oxygen vacancy to the adsorbate, one of the oxygens of the (benzoic) acid enters it, and subsequently one carbon–oxygen bond is broken. Hydrogen, from the OH groups in the surroundings of the fragment, hydrogenates the fragment to an aldehyde. The deposited oxygen is subsequently removed by hydrogen from the reaction mixture. There are several factors which strongly suggest that such a mechanism is in operation (13, 19): the effect of hydrogen/acid ratio, the effect of the prereluction of the oxide on its activity and selectivity and the existence of an “optimal” metal–oxygen bond strength, corresponding to the highest activity in the deoxygenation. The IR spectra of adsorbed acetic acid also support this idea (20). For chemically related reactions, the deoxygenation of nitrobenzene to nitrosobenzene (and the reversed reaction), evidence for the Mars and van Krevelen mechanism exists, based on the results of experiments with isotopically labeled molecules (21). Other results also support this conclusion (22).

In this paper we divide the oxide catalysts into four groups according to their catalytic behavior in the deoxygenation of benzoic acid, whereby the most principal difference is between Group 1 on one side and Groups 2, 3, and 4 on the other. The differences emerging from a comparison of the results in Figs. 2 to 6 are most likely a consequence of different contributions of various mechanisms of benzoic acid conversion. Within each group of oxides, the relative contributions by the “basic” mechanisms, seem to be similar. Taking the points (i) and (ii) into account, the activity and selectivity patterns, shown in Figs. 2 to 6, can be rationalized as follows.

The oxides belonging to Group 1, such as MgO and the lanthanide oxides, generally show *basic* properties. With the basic magnesium and rare-earth oxides the prevailing mechanism is the decomposition of the benzoate. Benzoate species have been observed by means of infrared spectroscopy (23). The layered structure (24–26) of carboxylates makes an intermolecular transfer of groups possible.

To support this we monitored the decomposition of benzoic acid, preadsorbed on La<sub>2</sub>O<sub>3</sub>, in pure H<sub>2</sub> atmosphere. Decomposition of the benzoate started at 598 K, the maximum amount of products was obtained at 648 K and almost all preadsorbed species decomposed or desorbed at 723 K. The distribution of desorbed products was similar to that observed with the reaction mixture: benzene, ben-

zaldehyde, and ketones were produced along with a small amount of toluene. This indicates that the reaction with the reaction mixtures simulates the thermal decomposition and hydrogenolysis of benzoate. Hydrogen is needed to form benzaldehyde and benzene. However, low production of toluene and benzylalcohol shows that stepwise consecutive hydrogenation hardly takes place on these surfaces.

These may be the mechanisms by which phenol is formed at low temperatures. It is known that phenol is formed in the presence of water and oxygen (27–30) and that water is produced upon the formation of the benzoate, benzaldehyde, and other species.

Different contributions by different mechanisms can be observed with Groups 2 and 3 oxides. These oxides can form nonstoichiometric oxides, and they tolerate active oxygen vacancies on their surfaces. It has been established that both the selective deoxygenation of nitrobenzene to nitrosobenzene (22) and the selective reduction of aliphatic carboxylic acids to the corresponding aldehyde can take place on Fe<sub>3</sub>O<sub>4</sub> (31). With this catalyst it has been confirmed that the oxygen vacancies in the surface play an important role in the selective reduction of aliphatic acids (13, 19, 31), and the overall mechanism of aliphatic acid reactions is similar to mechanism (ii) described above with benzoic acid. The catalytic behavior of MnO<sub>2</sub> was nearly the same as that of  $\alpha$ -Mn<sub>3</sub>O<sub>4</sub>. The latter oxide showed better catalytic performance at lower reaction temperatures. MnO<sub>2</sub> must probably be first prerelucted to become active in deoxygenation (see a similar situation in (22)). None of these oxides, however, was catalytically stable. The catalytic behaviour of both oxides changed dramatically between 648 K and 673 K. In this temperature region the oxides are probably overreduced and a high concentration of oxygen vacancies renders a *loss of both oxygen atoms*, subsequently toluene is formed. It is not a consecutive hydrogenation (for example, no dependence on the flow rate, as observed with  $\Phi$ NO<sub>2</sub>, where overreduction leads to aniline formation), but overhydrogenation during one sojourn of the molecule on the surface.

In an attempt to stabilize the Mn oxide against overreduction a zinc manganese spinel was prepared and the reaction monitored with it. As shown in Fig. 2, the conversion reached a value higher than 90% with a selectivity to benzaldehyde of ca 97%. However, above 673 K, the selectivity to toluene increased.

In a previous paper (31), it was established that an oxidation–reduction property of the active center and a sufficient production of activated hydrogen are the two key factors in the selective reduction of aliphatic carboxylic acids to the corresponding aldehydes. It has also been reported that highly reduced Fe<sub>2</sub>O<sub>3</sub>, which exposes the surface of Fe<sub>3</sub>O<sub>4</sub> mixed with Fe metal (31) or a platinumized Fe<sub>3</sub>O<sub>4</sub> (19), shows a good catalytic performance in the selective reduction of acetic acid to acetaldehyde. In this study we used the same Fe<sub>3</sub>O<sub>4</sub> catalyst for the reduction of benzoic acid. However,

at higher temperatures, the production of toluene was high, as with the reduced manganese oxides.

Obviously, the steady state degree of cobalt oxide reduction is too high (most likely, metallic cobalt is present at higher temperatures). The catalyst contains then too many sites on which oxygen can be deposited and the metallic cobalt is a good catalyst for hydrogenolysis up to methane. The reducibility of transition metal oxides, discussed up to this point, follows the order  $Mn < Fe < Co$ , which is the order of decreasing selectivity to benzaldehyde, a molecule which is formed by a selective loss of only one oxygen atom of the benzoic acid. Because of the very poor catalytic performance of cobalt oxide in the desired reaction, this oxide was not studied any further. However, it can be remarked that methane can be also formed from CO ex benzaldehyde, etc.

Good catalytic performance and a highly selective reduction of benzoic acid to benzaldehyde was observed over  $ZrO_2$  and  $ZnO$ , which represent Group 4 (our numbering) oxides. A previous paper reported the catalytic performance of  $TiO_2$ ,  $ZrO_2$ , and  $HfO_2$ , with results similar to those reported here for  $ZrO_2$ . Although these oxides are relatively stable and have a relative high M–O bond energy, they all ( $TiO_2$ ,  $ZrO_2$ ,  $HfO_2$ ) can tolerate some oxygen vacancies in their surface (32). However, the concentration of the vacancies remains low, these oxides are much less reducible than the Mn, Fe, and Co oxides, which obviously suppresses toluene formation (33). In this study only  $ZrO_2$  was studied as a catalyst representative of the Group 4 elements, but the results are in good agreement with those of Ref. (33).

With the  $TiO_2$ ,  $ZrO_2$ , and  $HfO_2$  oxides, the activity varied as  $Ti > Zr > Hf$ , while the selectivity followed the reversed order  $Hf > Zr > Ti$  (33). The order of the metal–oxygen bond strength is also  $Hf > Zr > Ti$ . The main by-product with these oxides is toluene, and its production could be suppressed by water in the feed. The activity/selectivity pattern and the effect of water strongly suggest that, when the surface concentration of oxygen vacancies increases, toluene formation (both oxygens are lost) increases, too, while that of benzaldehyde decreases (only one oxygen is removed in the latter reaction). When the vacancies are blocked by oxygen from water, the selectivity to benzaldehyde increases. Zinc oxide is very similar to this group oxides, although zinc oxide is not a transition metal oxide.

Cerium dioxide is slightly different from other oxides of Group 4. Cerium dioxide is, with its chemical properties, close to the series of lanthanide oxides, but as well as basic properties it also shows oxidation–reduction properties (34–37). In particular, a nonstoichiometric oxide lattice can easily be formed under a reducing atmosphere, and the average valency of the oxide changes by changing the atmospheric condition. A rather high metal–oxygen bond strength which is, nevertheless, accompanied by a certain re-

ducibility of the oxide, is responsible for the beneficial catalytic properties in the reaction. However, it is observed that the selectivity to both benzene and toluene increases with increasing temperature, whereby the selectivity to benzene is higher than that to toluene. It seems that, in the behavior of  $CeO_2$ , the properties of the Group 4-oxides are combined with those of basic oxides (Group 1). The reaction may proceed by the prevailing mechanism of type (i) at lower reaction temperatures and both mechanisms (i.e., types (i) and (ii)) operate simultaneously at higher temperatures. A number of other oxides, not mentioned explicitly up to now, also show a behaviour which can be considered as arising from a combination of the mechanisms (i) and (ii) above.

At this point we can make the following conclusion. Oxides of Group 1 manifest mainly their *basic* properties; an easy formation of benzoate and subsequent reactions to this formation. Group-2 oxides, the various oxides of manganese, show the (expected) *redox* properties. A high conversion and a high selectivity to benzaldehyde can be achieved at rather low temperature. Oxides (Group 3) with redox properties, but a higher reducibility than manganese oxide (Fe, Co), remove nonselectively both oxygen atoms from the benzoic acid. Redox oxides (Group 4) with a high metal–oxygen bond strength (low reducibility) show a higher selectivity. The selectivity to benzaldehyde at higher conversions follows the order:  $Hf > Zr > Ti$  (33)  $> Mn > Fe > Co$ .

## CONCLUSIONS

The oxides can be divided into several categories, each being characterized by the product pattern and/or prevailing mechanism. The categories are as follow:

(1) Group 1, for which the *radical-like mechanism* clearly prevails. Phenol is among the products (mainly those formed at low temperature), and benzene formation is higher than that of toluene.

(2) Groups 2, 3, and 4 oxides all have some *redox properties*, and the selectivity of deoxygenation to benzaldehyde is controlled by the concentration of oxygen vacancies. In other words, the selectivity is determined by the degree of reduction of the oxide in the steady state of the catalytic reactions. Group 4 represents the best catalysts.

(3)  $CeO_2$  also shows a very good catalytic performance in the selective deoxygenation of benzoic acid, but both the redox and the radical-like mechanisms operate here simultaneously.

(4) Oxides of Group 4 are most promising as catalysts for selective deoxygenation of benzoic acid.

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