# Reduction of Benzaldehyde on Metal Oxides

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The study of benzaldehyde reduction over simple metal oxides was carried out at 300°C in a helium or dihydrogen atmosphere. The results obtained show that benzyl alcohol is produced by the Cannizzaro reaction under helium and by direct hydrogenation under dihydrogen on reducible oxides such as ZnO and Cr<sub>2</sub>O<sub>3</sub>. Over slightly reducible oxides such as ZrO<sub>2</sub>, both reactions occur under H<sub>2</sub>: the Cannizzaro reaction involves the most basic OH groups and is followed by the reduction of benzoate species by H<sub>2</sub> to benzaldehyde, regenerating the active hydroxyl groups. Toluene is formed under He on the most acidic oxides (Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>) from a reaction involving benzyl alcoholate species, and under H<sub>2</sub> on reducible oxides (Fe<sub>2</sub>O<sub>3</sub>) by means of consecutive reduction reactions. The present study shows that the benzaldehyde transformation via the Cannizzaro reaction is a good test for determining the mobility of surface hydroxyl groups on metal oxides, whereas its direct reduction under H<sub>2</sub> characterizes the metal oxide redox properties. © 1997 Academic Press

## INTRODUCTION

The transformation of benzaldehyde into reduced compounds such as benzyl alcohol or toluene can occur on metal oxides (1–3). Two main processes seem to be involved depending on whether or not the formation of the reduced compounds is accompanied by that of oxygenated products such as benzoate. In the former case (Cannizzaro reaction) the active sites are mobile hydroxyl groups, whereas in the latter case, which requires the presence of hydrogen, reduced sites are certainly involved (4).

Therefore comparison of benzaldehyde conversion on metal oxides, in the presence or absence of hydrogen, would allow the classification of the metal oxides according to their hydroxyl mobility (basicity) and reducibility. This paper deals with the conversion of benzaldehyde under helium or under hydrogen over a large number of metal oxides:

 $\begin{array}{l} MgO, ZnO, Al_{2}O_{3}, V_{2}O_{3}, Cr_{2}O_{3}, Fe_{2}O_{3},\\ SiO_{2}, TiO_{2}, ZrO_{2}, CeO_{2}, V_{2}O_{5}. \end{array}$ 

These oxides possess very distinctive acid/base and redox properties. MgO,  $Al_2O_3$ , and  $SiO_2$  are fixed valence oxides

Transition metal oxides are more difficult to characterise. The properties depend a priori on their positions in the periodic table and the oxidation state of the ion. For a given oxidation state, reducing ability and basicity of these oxides increase in a given column from top to bottom and in a period from right to left. Numerous analysis techniques allow these tendencies to be confirmed: titration (5), microcalorimetry (6), or use of IR with probe molecules (7). In particular: pyridine and carbon monoxide adsorption demonstrate the presence of Lewis acidic sites on all samples tested; Brönsted acidity is also detected, especially on  $V_2O_5$  (8); CO<sub>2</sub> adsorption reveals no notable basicity on  $V_2O_5$  and SiO<sub>2</sub> (8, 9); and the presence of strongly basic hydroxydes has only been described for a few samples such as MgO, ZrO<sub>2</sub>, and CeO<sub>2</sub> (4).

#### **EXPERIMENTAL**

The metal oxides used are reported in Table 1. Some are commercial, the others were prepared by hydrolysis of the corresponding isopropylate, followed by calcination at  $550^{\circ}$ C (10).

Before the reaction, a current of either helium (denoted as N, like the neutral pretreatment) or dihydrogen (denoted as R, like the reducing pretreatment) was passed over the oxides (100 mg) for 2 h at  $350^{\circ}$ C.

The benzaldehyde transformation was performed in helium atmosphere (N process) or in dihydrogen atmosphere (R process) in a quartz microflow reactor at atmospheric pressure and 300°C. The flow rate was 40 ml/min, and the space velocity was W/F = 0.21 kg mol<sup>-1</sup> h<sup>-1</sup>.

The reaction mixture was analysed on line by gas chromatography equipped with a FID detector, the first analysis being performed after a reaction time of 21 min.

# REDUCTION OF BENZALDEHYDE IN A HELIUM ATMOSPHERE

# 1. Results

## Influence of the Nature of Metal Oxides

In helium atmosphere, the reactivity decreased with time on flow (Fig. 1), generally tending to zero or to a very low

considered to be basic, amphoteric, and weakly acidic, respectively.

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 TABLE 1

 Origin and Surface Area of the Different Metal Oxides Used

Oxide	Origin	Surface area (m <sup>2</sup> /g)
MgO	Merck	54
ZnO	Asturienne des mines	40
$Al_2O_3$	ex-isopropylate	179
$V_2O_3$	Merck	24
$Cr_2O_3$	Rhône-Poulenc	42
Fe <sub>2</sub> O <sub>3</sub>	Rhône-Poulenc	12
SiO <sub>2</sub>	Degussa	200
TiO <sub>2</sub>	ex-isopropylate	70
$ZrO_2$	ex-isopropylate	50
CeO <sub>2</sub>	Rhône-Poulenc	120
$V_2O_5$	Merck	8

residual value. After three on flow, all oxides were inactive with the exception of TiO\_2 (0.1% T).

The benzaldehyde conversions f after 21 min of reaction are reported in Fig. 2. Reaction products were benzyl alcohol (A), toluene (T), and benzene (B).

Activities and selectivities depend on the metal oxide used. The reactivity of benzaldehyde decreases in the following order:

$$\begin{split} MgO \gg TiO_2 \approx ZrO_2 > Al_2O_3 > Cr_2O_3 > CeO_2 \\ \approx V_2O_3 \approx Fe_2O_3 > ZnO = SiO_2 = V_2O_5 = 0. \end{split}$$

# Influence of the N Pretreatment Temperature

Previous work showed some influence of the pretreatment temperature on benzaldehyde reduction on the basic oxides MgO,  $ZrO_2$ , and ZnO (4). Thus, for MgO, after 21 min of reaction, the conversion of benzaldehyde decreased from 12.7 to 3.5% when the pretreatment temperature increased from 350 to 450°C. Similary, on  $ZrO_2$ ,



FIG. 1. Benzaldehyde conversion versus time on flow on metal oxides in a helium atmosphere at  $300^{\circ}$ C.



**FIG. 2.** Benzaldehyde conversion on metal oxides in a helium atmosphere at 300°C after 21 min under flow: B, benzene; T, toluene; A, benzyl alcohol.

the conversion of benzaldehyde decreased from 2.2 to 0%, whereas ZnO remained inactive. No change was observed in the selectivities.

## Influence of the R Pretreatment in a Dihydrogen Atmosphere

The same oxides (MgO,  $ZrO_2$ , and ZnO) were pretreated by molecular hydrogen at 350°C. The MgO activity was not affected (12.9% A);  $ZrO_2$  became totally inactive, and no change was observed in the case of ZnO which remained inactive.

## Influence of Water Pretreatment

After the R pretreatment at  $350^{\circ}$ C, a mixture of water (P=10 Torr) in helium was passed over the oxide samples for 10 min at  $300^{\circ}$ C (<u>RW</u> pretreatment); thereafter the benzaldehyde-helium mixture was passed over the samples (<u>RW</u>N process).

In relation to the <u>NN</u> process (pretreatment and reaction in a helium atmosphere), the influence of water depended on the metal oxide used. The results show that the zirconia activity was not only re-established but, moreover, enhanced, since the conversion of aldehyde to benzyl alcohol increased from 2.2 to 6.1%. A positive effect was also observed for cerium, vanadium (V<sub>2</sub>O<sub>3</sub>) and iron oxides which became slightly active ( $\approx$ 0.3–0.5% conversion). Cerium oxide produced some benzyl alcohol (selectivity: 33% A + 67% B), in contrast to vanadium oxide (100% T) or iron oxide (67% T + 33% B). No effect was observed in the case of ZnO, Cr<sub>2</sub>O<sub>3</sub>, and TiO<sub>2</sub>.

Conversely, the conversion of benzaldehyde to benzyl alcohol decreased from 12.7 to 4.5% A on magnesia. The same feature was observed for alumina, since the toluene production decreased from 1.2 to 0.1% T.

## 2. Discussion

Under helium atmosphere, benzyl alcohol is selectively formed on MgO,  $ZrO_2$ , and  $CeO_2$ , whereas toluene is obtained on  $Al_2O_3$ ,  $V_2O_3$ ,  $TiO_2$ , and  $Fe_2O_3$ . Small amounts of benzene were also found in the case of  $Cr_2O_3$  and  $TiO_2$ .

#### Benzyl Alcohol Formation

Analogous to results obtained in homogeneous medium (11), benzyl alcohol should be produced by the Cannizzaro reaction, formally:

$$2 \text{ PhCHO} + \text{OH}^{-} \rightarrow \text{PhCOO}^{-} + \text{PhCH}_2\text{OH}.$$
 [1]

The mechanism on oxide surfaces can be written as follows (4):



The first step is the nucleophilic addition of the hydroxyl group to the first aldehyde molecule. The second step is the nucleophilic addition of the intermediate hydride species on the second aldehyde molecule. Such a scheme involves the disappearance of surface basic hydroxyls and the formation of adsorbed benzoate species. Stoichiometrically, the formation of one benzyl alcohol molecule consumes one surface hydroxyl group, thus explaining the decrease in reactivity with time.

The observed activities MgO (12.7%)  $\gg$  ZrO<sub>2</sub> (2.2%)  $\gg$  CeO<sub>2</sub> (0.05%) > ZnO (0%) mean that the number of active hydroxyls varies in the same way. This order is surprising and not in agreement with the bulk basicity (PIES) in the Parks scale (5):

MgO (12.4) > ZnO (8.9) > CeO<sub>2</sub> (6.8) 
$$\approx$$
 ZrO<sub>2</sub> (6.7).

However, the strength of basic sites, estimated from the adsorption of Hammett indicators is different (12):  $H_{0, MAX}$  (ZrO<sub>2</sub>) = 9.5  $\gg$   $H_{0, MAX}$  (ZnO) = 6.4. Thus the observed activity would only depend on the number of strong basic hydroxyls.

The effects of different pretreatments as well as complementary results corroborate such a conclusion. The pretreatment of the oxides modifies their surface properties and, especially for a given oxide, the strength and number of the surface hydroxyl groups:

(i) The increase in the MgO activation temperature leads to the decrease in the number of the hydroxyl surface species and, consequently, in benzaldehyde conversion. The number of active sites can be estimated tentatively for the most active oxide: MgO, from the extrapolation to  $t \rightarrow 0$  of the curve "activity versus time." However, Fig. 1 shows that the determination of the initial activity is imprecise; it was estimated tentatively as 20  $\mu$ mol/m<sup>2</sup>h. Taking into account the amount of benzyl alcohol formed with time, we can deduce that the number of hydroxyl groups *n*(OH), which were consumed after two of reactions, are approximately

$$n(OH) = 20 \ \mu \text{mol/m}^2 = 12 \ OH/n \text{m}^2$$
.

This OH number may be different from the total number of hydroxyl groups present on the surface.

(ii) In infrared studies of partially dehydroxylated metal oxides, several types of the OH group were detected. The most basic, referred to as type I, is a terminal OH coordinated to one metal cation (M-OH). It corresponds to the highest v (OH) wave number in the IR spectrum. Such species give rise to a very strong absorption band on MgO, a weaker band on  $ZrO_2$ , and the weakest band on ZnO (4). In the case of CeO<sub>2</sub>, which was not very active in the considered reaction, it has been shown that type-I OH groups are thermally unstable, explaining the poor activity of this oxide (13). The presence of basic OH groups was proven by the formation of hydrogen carbonate species with the adsorption  $CO_2$  (14) or by  $CS_2$  and COS hydrolysis (15). The latter test confirms the low basicity of the ZnO surface OH groups and, on the other hand, the efficiency of those on ZrO<sub>2</sub> (16).

(iii) The pretreatment in a  $H_2$  atmosphere is expected to reduce the oxide surfaces and to affect the hydroxyls. The activity of the irreducible magnesia was not modified by the <u>R</u>N process; on the contrary, in the case of the slightly reducible zirconia (17), the  $H_2$  pretreatment drastically inhibited the Cannizzaro reaction; no conversion was observed. One infers that this activation mode provokes the modification of hydroxyl groups and, as a result, the total inhibition of the dismutation reaction. The mechanism of dehydroxylation is probably complex. At 350°C, dihydrogen produced some oxygen vacancies by moderate reduction of the surface and altered the surface structure (monoclinic to quadratic) (18). No change was observed on ZnO, because it does not possess active hydroxyl groups and, thus, remains inactive after pre-reduction.

(iv) Conversely, the hydration of the reduced samples (<u>RW</u>N process) is expected to re-establish or even increase the number of surface hydroxyls and, consequently, the Cannizzaro reaction. This is notably the case on zirconia and, to a lesser extent, on ceria. No detectable effect was observed on ZnO, whereas a negative effect was noted on magnesia. Water molecules should inhibit some active hydroxyl groups on magnesia by means of a nondissociative (coordinative) adsorption (19).

In summary, benzaldehyde reduction to benzyl alcohol on oxides in helium atmosphere is the result of the Cannizzaro dismutation. The reaction requires basic hydroxyl groups. The observed conversions depend only on the initial number and strength of these entities.

## Reduction to Toluene

Toluene is produced selectively on amphoteric or acidic oxides (mainly  $TiO_2$  and  $Al_2O_3$  and, to a lesser extent, on  $V_2O_3$  and  $Fe_2O_3$ ). Formally, this reaction requires two hydrogen atoms to produce toluene from benzaldehyde and four hydrogen atoms if water appears. In a helium atmosphere, if no coking occurs, hydrogen comes from surface hydroxyl or aldehydic groups.

Sreekumar and Pillai (20) showed that benzyl alcohol undergoes disproportionation to toluene, benzaldehyde, and water over alumina at 300°C:

$$2 C_6H_5CH_2OH \rightarrow C_6H_5CH_3 + C_6H_5CHO + H_2O.$$

This result suggests that toluene may arise from successive reactions: benzaldehyde dismutation to benzyl alcohol (Cannizzaro reaction) and then benzyl alcohol transformation to toluene (Pillai reaction). However, on the metal oxides which produce toluene, no trace of benzyl alcohol was detected in the reaction mixture, suggesting that alkoxy species do not desorb (reaction [2]) and react directly by a new surface step to toluene:

$$2 PhCHO + OH_{ads} \rightarrow PhCOO_{ads} + PhCH_2O_{ads} + H_{ads}$$
 [2]

The mechanism could involve either two nearby alkoxy species according to Sreekumars and Pillai's suggestion (reaction [3]):

$$2 PhCH_2O_{ads} + 2 H_{ads} \rightarrow PhCH_3 + PhCHO + H_2O$$
 [3]



or an alkoxy species and a benzaldehyde molecule (reaction [4]):

$$PhCH_2O_{ads} + PhCHO \rightarrow PhCH_3 + PhCOO_{ads}$$
 [4]



To differentiate mechanisms [3] and [4], small amounts of benzyl alcohol were added to the benzaldehyde flow during the transformation. Alcohol addition leads to an increase in toluene formation and has little influence on the quantity of benzaldehyde detected which is slightly diminished. These results suggest that mechanism [4] prevails. Thus, it seems to us that reaction [4] better reflects the experimental conditions, especially the presence of benzaldehyde in the gas phase and the participation of Brönsted acid sites.

It appears therefore that, whatever the reaction products formed (benzyl alcohol or toluene), the surface-active sites (basic hydroxyls) involved in the first step (formation of benzyl alcohol or alkoxy species) are the same.

The benzaldehyde conversion to toluene decreases in the order:

$$\begin{split} \text{TiO}_2 > \text{Al}_2\text{O}_3 \gg \text{V}_2\text{O}_3 \approx \text{Fe}_2\text{O}_3 > \text{Cr}_2\text{O}_3 \\ = \text{SiO}_2 = \text{V}_2\text{O}_5 = 0. \end{split}$$

This should reflect the relative abundance of the basic hydroxyls on these metal oxides.

Titania appears to be nearly as active as zirconia (2.2% A) after 21 min on flow, but its selectivity is quite different. We observed that both oxides are active in COS hydrolysis which also involves basic hydroxyl groups (21). In addition, on TiO<sub>2</sub>, a slight residual activity ( $\approx 0.1\%$  T) persists even after a very long time on flow. This formation, considered to be nearly catalytic, requires the regeneration of some basic hydroxyls and the continuous disappearance of surface benzoate species, explaining the presence of benzene traces in the products formed. However, the weak activity and the use of a FID detector in GC analysis do not allow us to prove the concomitant formation of CO<sub>2</sub>, as would be from [5], reported below.

The hydration of the samples after pretreatment under dihydrogen (<u>RW</u>N process) induces various effects. As in the case of magnesia, the activity on the irreducible alumina clearly decreases, water inhibiting the reaction through a possible nondissociative adsorption. No detectable effect appears on titania, whereas the reactivity of benzaldehyde is enhanced on  $V_2O_3$  and  $Fe_2O_3$  as observed above in the case of ceria. Note that the reduction of such transition metal oxides could increase their surface basicity (22).

In conclusion, benzaldehyde reduction to toluene on metal oxides is the result of two consecutive reactions, the Cannizzaro dismutation leading to adsorbed alkoxy species which form toluene by hydrogen transfer. This transformation requires amphoteric oxides with basic hydroxyl groups to trigger the first step and with acidic sites to avoid benzyl alcohol desorption.

#### Benzene Formation

Some benzene appears in the case of chromia and titania:  $Cr_2O_3$  (0.1%) > TiO<sub>2</sub> (0.05%). Benzene is usually considered to be the result of the decomposition of surface benzoate species with carbon dioxide formation (23):

$$C_6H_5COO_{ads} + H_{ads} \rightarrow C_6H_6 + CO_2.$$
 [5]

Over TiO<sub>2</sub>, benzoate and alkoxy species are formed via the Cannizzaro reaction. Over  $Cr_2O_3$ , the high selectivity (100%) and the low activity to benzene suggests a reduction in the  $Cr_2O_3$  surface by the benzaldehyde molecule. Let us recall that the  $Cr_2O_3$  surface is readily reduced (24).

All results strongly suggest that benzoate surface species always appear during the formation of benzyl alcohol, toluene, or benzene. A possible intermediate is a hemiacetal specie Ph–CH(OH)O<sub>ads</sub> (25). It may be regarded as a hydride producer for reductions (via alkoxy species) or a benzene precursor. The final products should be dependent only on the acidic or redox surface properties.

## HYDROGENATION IN A DIHYDROGEN ATMOSPHERE

## 1. Results

#### Influence of the Metal Oxide Nature

The benzaldehyde reduction was carried out under a dihydrogen flow after the total disappearance of strong basic hydroxyls by pretreatment and reaction in a helium atmosphere: (<u>N</u>NR process). Dihydrogen replaced the helium flow 5 h after the test was started. Under such conditions, the oxide surface was partially covered with carboxylate species and all metal oxides were inactive before introducing H<sub>2</sub> (with the exception of  $TiO_2 \approx 0.1\%$  T under He).

The activity and selectivity of the various metal oxides used are reported in Fig. 3. The reported data describe the stationary conditions, no deactivation being observed in this case.

The reaction is catalytic and the products obtained are the same as those obtained for the transformation under



**FIG. 3.** Benzaldehyde conversion on metal oxides in a dihydrogen atmosphere at 300°C after 3 h under flow.



FIG. 4. Influence of the dihydrogen pressure on benzaldehyde conversion at 300°C.

helium: benzyl alcohol, toluene, benzene, and traces of condensed products (not analysed). Of course, the activities and selectivities are different.

The irreducible oxides (magnesia, alumina, and silica) remained almost inactive after dihydrogen introduction. In contrast, all transition metal oxides exhibited various activities:

(i) ZnO gave rise to large amounts of benzyl alcohol and some toluene.

(ii) The metal oxides of the fourth period, with three as the oxidation number, became active, and the benzalde-hyde conversion increased with the atomic number ( $V_2O_3 < Cr_2O_3 < Fe_2O_3$ ). The selectivities differed considerably from one oxide to the other (100% toluene on  $V_2O_3$  and  $Fe_2O_3$ ; 88% alcohol and 12% toluene on chromia).

(iii) As for the metal oxides of the fourth column, zirconia displayed the same activity and selectivity as at the beginning of the reaction under He (Cannizzaro reaction), whereas the activity of titania was weaker. Ceria became slightly active ( $\approx 0.5\%$ ) under hydrogen flow, giving rise mainly to benzyl alcohol and to very small amounts of toluene and benzene.

#### Influence of the Dihydrogen Partial Pressure

The effects of the partial pressure of dihydrogen on benzaldehyde hydrogenation are reported in Fig. 4.

During the test, the carrier gas was a helium–hydrogen mixture, the dihydrogen pressure being increased in 25% steps from 0 to 100 kPa. It is shown that the conversion increased with dihydrogen pressure. If we consider the plug flow reactor to be differential, the apparent reaction order in the dihydrogen pressure,  $\alpha$ , can be determined; it depends on the metal oxide used and is not clearly defined on Fe<sub>2</sub>O<sub>3</sub>:

$$\alpha(\text{Cr}_2\text{O}_3) \approx 2.5, \quad \alpha(\text{ZrO}_2) \approx 2, \quad \alpha(\text{TiO}_2) \approx 0.5,$$
  
 $\alpha(\text{Fe}_2\text{O}_3) = \text{unspecified (nearly 2)}.$ 

## Influence of the Pretreatment Conditions

A series of experiments was performed on the same metal oxides pretreated at 350°C for 2 h in dihydrogen and then water. After the benzaldehyde reaction under helium, the latter was replaced by hydrogen (<u>RW</u>NR process). Very similar activities were observed, as after the <u>N</u>NR process, with the exception of iron and zirconium oxides. The conversion of benzaldehyde was very high on the former (99% T + 1% B), whereas on the latter it doubled from 2.2 to 4.3% A.

#### 2. Discussion

The replacement of helium by dihydrogen as the carrier gas can provoke not only the direct hydrogenation of benzaldehyde but it can also modify the surface properties: the basicity may increase due to surface reduction and regeneration of surface hydroxyls may occur. Under the experimental conditions, the hydrogen molecules could be activated by the transition metal oxides but not by the irreducible oxides. However, the observed activities were not related directly to the reducibility of the metal oxides. The order of activity over the set of oxides ( $\mathbf{ZnO} \gg \operatorname{Fe}_2\operatorname{O}_3 \approx \mathbf{ZrO}_2 > \operatorname{Cr}_2\operatorname{O}_3 > \operatorname{TiO}_2 \gg \mathbf{CeO}_2 > \operatorname{V}_2\operatorname{O}_3 \gg \approx \operatorname{MgO} = \operatorname{SiO}_2 = 0$ ) is different from the order of the standard potentials redox  $\operatorname{E}_0$  (Ox/Red) (26):

$$\begin{split} \mathbf{E_0}(\mathbf{CeO_2}/\mathbf{Ce_2O_3}) &> \mathbf{E_0}(\mathrm{Fe_2O_3}/\mathrm{Fe_3O_4}) > \mathbf{E_0}(\mathrm{Fe_2O_3}/\mathrm{FeO}) \\ &> \mathbf{0} > \mathbf{E_0}(\mathrm{Cr_2O_3}/\mathrm{CrO}) \approx \mathbf{E_0}(\mathbf{ZnO}/\mathbf{Zn}) \approx \mathbf{E_0}(\mathrm{TiO_2}/\mathrm{Ti_2O_5}) \\ &\approx \mathbf{E_0}(\mathbf{V_2O_3}/\mathbf{V_2O_2}) > -\mathbf{0.6} > E_0(Si\,O_2/Si) \\ &\gg \mathbf{E_0}(\mathbf{ZrO_2}/\mathbf{Zr}) \approx E_0(Al_2\,O_3/Al) > E_0(Mg\,O/Mg). \end{split}$$

Nevertheless, not all  $E_0$  values are known, in particular for partly reduced or nonstabilised forms such as  $Zr_2O_3$ or nonstoichiometric phases. The lack of data makes comparison incompete. However, all transition oxides (including  $ZrO_2$ ) present semiconducting properties. By partial reduction under dihydrogen, some oxygens of the lattice will be eliminated, while some cations pass to a lower oxidation state. Thus, some reactions, particularly hydrogen or carbon monoxide addition, are best explained by radicals such as neutral intermediate species on metals and semiconducting oxides (27). Moreover, the occurrence of oxygen vacancies or mobile oxygen over the surface might favor deoxygenating–oxygenation reactions.

Taking these data into account, the most striking results are observed with zinc and zirconium oxides, which show substantial activity despite their low reducibility.

(i) Zinc oxide was the only inactive transition metal oxide in the Cannizzaro reaction. Thus, a basic hydroxyl regeneration under dihydrogen is not the cause of its activity under  $H_2$ . ZnO is not considered to be an easily re-

ducible oxide, but it presents *n*-type semiconductivity due to its tendency to include some interstitial Zn atoms or  $Zn^+$  ions in the lattice. Therefore, IR studies on such an oxide have shown heterolytic and homolytic dissociation of dihydrogen (28). Therefore, hydrogen surface species may be considered as active intermediates for the direct hydrogenation of benzaldehyde to benzyl alcohol. Subsequently, the reaction can continue to toluene and possibly benzene:

$$\begin{array}{c} \text{PhCHO} \xrightarrow{H_2} \text{PhCH}_2\text{OH} \\ \xrightarrow{H_2} \text{PhCH}_3 + H_2\text{O}\big( \xrightarrow{H_2} C_6H_6 + \text{CH}_4 \big). \end{array} [6]$$

The first step may take place as follows:



It is worth noting that ZnO, which is considered to be strongly basic, mainly produces benzyl alcohol (91%), a small amount of toluene (9%), and no benzene.

(ii)  $ZrO_2$  is a nearly irreducible oxide, although partial surface reduction has been reported. Recent conductivity measurements showed that zirconia can show a weak *n*-type semiconductivity (29). However, neither EPR (30) nor IR studies (31) clearly confirm the occurrence of  $Zr^{3+}$ cations when reducing zirconia. The assignment of an IR  $\nu$ (CO) wave number near 2120 cm<sup>-1</sup> when adsorbing CO is nuclear, since CO adsorption on basic sites, giving rise to carbonite and ketene species, seems more likely than CO adsorption on  $Zr^{3+}$  sites. On the other hand, stabilization of the superoxide radical ion on H<sub>2</sub> treated zirconia may provide indirect evidence of its reducive properties (32). Hydrogen molecule dissociation was also found on zirconia, after activation under conditions different from those used in the present study (33).

Zirconium oxide was active under Cannizzaro reaction conditions. Therefore, carboxylate species covered the oxide surface when dihydrogen was introduced. The conversion in the steady state observed under H<sub>2</sub> (2.2% A) is of the same magnitude as that found in a helium atmosphere (2.3% A) after 21 min of reaction (Figs. 2 and 3). Thus, hydroxyl groups may play an important role in benzaldehyde hydrogenation over  $ZrO_2$ . As shown previously (4), some surface benzoate species on  $ZrO_2$  react with hydrogen at 300°C, leading back to benzaldehyde. This result suggests the regeneration of active species such as basic hydroxyls (OH<sub>ads</sub>) or intermediate species (C<sub>6</sub>H<sub>5</sub>CH(OH)O<sub>ads</sub>) and the reactions:

$$H_{2} + C_{6}H_{5}COO_{ads} \rightarrow C_{6}H_{5}CHO + OH_{ads}$$
[7]  

$$C_{6}H_{5}CHO + OH_{ads} \rightarrow C_{6}H_{5}CH(OH)O_{ads}$$
  

$$C_{6}H_{5}CH(OH)O_{ads} + C_{6}H_{5}CHO$$
  

$$\rightarrow C_{6}H_{5}COO_{ads} + C_{6}H_{5}CH_{2}OH$$
  

$$H_{2} + C_{6}H_{5}CHO \rightarrow C_{6}H_{5}CH_{2}OH$$

or, when Cannizzaro steps (full line) are introduced near the regenerative steps (dotted line):



To check such a mechanism, we investigated the effect of the dihydrogen pressure, at a given pressure of benzaldehyde, on the reaction rate. Figure 4 shows that the reaction increases with  $p(H_2)$  but that the variation is not linear. To explain the surprising second-order  $\alpha(\text{ZrO}_2) \approx 2$ , we assume that the hydrogenation of benzoate species [7] is the rate determining step:  $r = k[C_6H_5COO_{act}] p(H_2)$  in which  $[C_6H_5COO_{act.}]$  is the surface concentration of active benzoate intermediate species in the benzylalcohol formation. According to mechanism [8] these intermediate species are reduced by H<sub>2</sub> and the apparent second order can be explained by considering their number to be proportional to  $p(H_2)$ :  $r = k p(H_2)^2$ . In addition, benzyl alcohol production is directly related to his number of active sites:  $p(A) \propto$  $[C_6H_5COO_{act.}]$  and  $r = k'' p(A) p(H_2)$ . Figure 5 shows that the product  $p(A) p(H_2)$  is indeed linear in conversion. Strict proportionality is obtained at high  $p(H_2)$ , confirming the previous assumption. Conversely, when  $p(H_2)$  is low, the rate-determining step may be different, implying a change in the oxide surface according to the dihydrogen pressure.

It appears, therefore, that the behavior of ZnO and  $ZrO_2$ is quite different, both producing mainly benzyl alcohol from benzaldehyde reduction but in different ways, depending on the metal oxide reducibility and/or the occurrence of active surface basic OH groups. The behavior of the other oxides appears to be even more complicated, but is considered to imply both mechanisms [6] and [8]. They can be regarded as limiting cases; their relative occurrence depends on the oxide properties.

Therefore, the reducible, rather acidic  $Fe_2O_3$  oxide may produce toluene mainly via the direct consecutive hydrogenation route (mechanism [6]). An interesting feature is the pre-reduction effect of  $Fe_2O_3$ , which dramatically



FIG. 5. Benzaldehyde conversion on  $ZrO_2$  under dihydrogen at  $300^{\circ}C$ . The influence of the dihydrogen pressure.

increases its activity in benzaldehyde hydrogenolysis to toluene and benzene. A similar result was also found for the hydrogenolysis of methyl benzoate and acetic acid. In the latter case, iron oxide was prereduced at 450°C, a temperature sufficiently high to give rise to metal iron detectable by XRD (34).

As Fe<sub>2</sub>O<sub>3</sub>, V<sub>2</sub>O<sub>3</sub>, and Cr<sub>2</sub>O<sub>3</sub> are only slightly active under helium atmosphere, therefore, mechanism [6] probably most often occurs, although these oxides are less reducible than Fe<sub>2</sub>O<sub>3</sub>. However, the observed selectivities, **88%** of benzyl alcohol on chromia and 100% of toluene on vanadium oxide, are quite different. The latter result may be due to the occurrence of a partially oxided phase over the vanadium sesquioxide used. V<sub>2</sub>O<sub>4</sub>, detected by X-ray analysis, is more acidic than V<sub>2</sub>O<sub>3</sub> which could favor toluene over benzaldehyde formation.

Titanium, zirconium, and cerium are three elements of the fourth column in the periodic table. Contrary to TiO<sub>2</sub> and ZrO<sub>2</sub>, ceria appears to be almost inactive or slightly active in benzaldehyde conversion both in a helium and in a dihydrogen atmosphere, although it is partially reduced by dihydrogen at 300°C. High selectivities in benzene or light products were observed at 300°C (15%) and 350°C (97%); these results are probably related to the occurrence of highly stable benzoate species due to the high basicity of ceria or coking which could hinder the benzaldehyde conversion. TiO<sub>2</sub>-expropylate is active in the Cannizzaro reaction, although it is generally classified as a weakly acidic metal oxide. Titania can also generate a reducing property (an electron donating property): according to ESR studies, titanium oxide is reduced to form  $Ti^{3+}$  (35), and this cation can go back to Ti<sup>4+</sup> and an electron which may lead to an anion radical with an electrophilic molecule such as benzaldehyde (36). The latter is a possible intermediate for the hydrogen transfer reaction and may participate in mechanism [6]. Under H<sub>2</sub>, the rehydroxylation via mechanism [8], would be different for the reduced surfaces and, thus, mechanism [6] would be predominant on reducible  $TiO_2$ .

## CONCLUSION

This study shows that benzaldehyde reduction at  $300^{\circ}$ C is a sensitive test reaction for determining the surface properties of metal oxides. When transformation occurs under helium, the active sites are basic hydroxyl groups. On irreducible basic oxides such as MgO, benzyl alcohol is obtained selectively, whereas on irreducible amphoteric oxides (Al<sub>2</sub>O<sub>3</sub>) toluene is usually formed. Under such conditions, the conversion decreases with time on-stream up to the final consumption of the active hydroxyls.

Under  $H_2$ , a stationary state is reached and most of the active metal oxides are ZnO,  $Cr_2O_3$ , and  $Fe_2O_3$ , which are known to be reducible, whereas  $Al_2O_3$  and MgO are inactive.

A special case is constituted by  $ZrO_2$  and, to lesser extent, by TiO<sub>2</sub>, both being active whatever the nature (He or H<sub>2</sub>) of the flow gas used. This is explained by an auto-catalytic mechanism involving the Cannizzaro reaction in the first stage, the benzoate species thus formed being reduced to benzaldehyde, leading to the regeneration of the active hydroxyl sites. Those metal oxides have both properties: they are slightly (TiO<sub>2</sub>) or moderately (ZrO<sub>2</sub>) basic and slightly (ZrO<sub>2</sub>) or moderately (TiO<sub>2</sub>) reducible.

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