Reduction of benzaldehyde on alkaline earth metal oxides

A. Saadi [a,*], Z. Rassoul [a], M.M. Bettahar [b,1]

[a] *Laboratoire de Chimie du Gaz Naturel, Faculté de Chimie, USTHB, BP32 El-Alia, 16111 Bab-Ezzouar, Algeria*
[b] *Laboratoire de Catalyse Hétérogène, UMR-CNRS 7565, Université Henri Poincaré, Nancy-I, Faculté des Sciences,*
BP 239, 54506, Vandoeuvre-lès-Nancy-Cedex, France

Abstract

Benzaldehyde reduction was studied over alkaline earth metal oxide catalysts and carried out in a nitrogen or a dihydrogen atmosphere at the 100–350 °C of the range reaction temperature. The results show that benzyl alcohol is produced by the Cannizzaro reaction under nitrogen flow on MgO oxide and by direct hydrogenation under dihydrogen on irreducible oxides such as CaO, BaO and SrO. The Cannizzaro reaction involves the basic hydroxyl groups and is followed by the reduction of benzoate species by H_2 to benzaldehyde. Toluene and benzene were produced at high reaction temperature under N_2 flow over alkaline earth oxides from a reaction involving benzylate species. Under H_2 flow, toluene and benzene were also formed by means of consecutive reduction reactions.

The present work deals with the acid–base properties of alkaline earth metal oxide catalysts (MgO, CaO, BaO, SrO) and benzaldehyde reduction was used as probe reaction for characterizing the surface properties.
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Keywords: Reduction; Alkaline earth metal oxide; Benzaldehyde; Acid–base properties; Benzyl alcohol; Toluene; Benzene

1. Introduction

In the past few years, various reduction reactions in the gas or the liquid phases have been studied to synthesize valuable intermediate products or fine chemicals [1–5]. Benzaldehyde reduction is one of these reactions which can provide information about nature and properties of surface centers [1–13]. A large number of papers have been published concerning the transformation of benzaldehyde on oxide catalysts [2,4,6,11,14]. Alkaline earth metal oxides, which were reported to have basic properties on the surface [14], were used as catalysts.

It is well known that benzaldehyde is reduced to benzyl alcohol or toluene on metal oxides by two main process [2,6,15]: the first one seems to be the formation of the reduced compounds, at the absence of dihydrogen flow, by the Cannizzaro reaction accompanied by that of oxygenated products such as benzoate species and the active sites are mobile hydroxyl groups [2]. In the second process, the presence of dihydrogen flow pro-

vokes the direct hydrogenation of benzaldehyde. In this case, the presence of surface adsorbed hydrogen over alkali earth metal oxides has been proved [16]. The experimental evidence that the low-coordination sites are responsible for H_2 dissociation has also been confirmed by theoretical investigations [17]. The presence of a totally dehydration surface is therefore necessary for both heterolytic dissociative hydrogen adsorption [16]. As to metal oxides as catalysts, one of us have shown that their catalytic properties in the hydrogenation of benzaldehyde to benzyl alcohol depends on their reducibility and, also, on their surface acid–base properties [2]. Toluene and benzene by-products arose from benzyl alcohol and benzaldehyde hydrogenolysis, respectively [1,2,7,11,18,19].

Adsorption studies of benzaldehyde over several metal oxides [20] strengthen the hypothesis of the contribution of the acid–base properties of the SiO_2 or Al_2O_3 supports. Indeed, an IRTF study [20] showed that the adsorption of benzaldehyde on silica occurs through a hydrogen bond of the oxygen atom of the C=O group to the surface silanol groups whereas for the rather basic alumina it involves a nucleophilic attack at the carbonyl center by surface oxygen (or hydroxyl), producing surface benzoate species [21]. Moreover, stable surface oxygenated intermediates have also been detected in the hydrogenation of CO

* Corresponding author. Fax: +213 21 24 73 11.
E-mail addresses: adel_saadi@yahoo.fr (A. Saadi),
bettahar@lcah.u-nancy.fr (M.M. Bettahar).
[1] Fax: +33 3 83 912181.

on nickel-based catalysts [22]. They were identified as methoxy species on the alumina support but not found on the silica support [23–26].

Benzaldehyde can be used as, model reaction by the characterization of metal oxide surfaces [2,6]. Therefore, comparison of benzaldehyde conversion on metal oxide catalysts, in the presence or absence of dihydrogen atmosphere would allow the classification of the metal oxides according to their hydroxyl mobility (basicity).

The present paper reports the correlation between the catalytic activity and the surface property, the nature of active sites and the reaction mechanism.

2. Experimental

2.1. Catalysts preparation, activation and characterization

The metal oxides used are reported in Table 1. CaO, BaO and SrO oxides were prepared by calcinating the carbonate precursors (MCO_3: M = Ca, Ba, Sr) at 1200 °C for 3 h in air, whereas MgO oxide was prepared from the hydroxide precursor ($Mg(OH)_2$) by thermal decomposition (Table 1).

The specific area measurements and average pore radius were performed by the classical BET method on a Coultronics 2100E apparatus. The data were interpreted using the BET equation and an effective cross-sectional area of 16.2 Å for N_2. The standard pre-treatment consisted of heating the sample under dynamic vacuum at 300 °C for 3 h in order to remove adsorbed water and other impurities. The measurement was then made at liquid nitrogen temperature with nitrogen as adsorbate.

Phase analysis and crystallite size of the samples were performed by X-ray powder diffraction employing a PW1710 Philips diffractometer. Patterns were using Ni-filtered copper radiation ($\lambda = 1.5406$ Å) at a scanning rate of 2° at 2θ/min. The average size of the metal particle was calculated from the linewidth at half height of the MO (M = Mg, Ca, Sr, Ba) peaks using the Scherrer equation with Warren's correction for instrumental line broadening [27].

2.2. Catalyst testing

Benzaldehyde (Aldrich, 99.88%) was degassed under nitrogen purge before use. H_2 and N_2 (Air liquid) were passed through Supelco molecular sieve traps oxytraps (Altech).

The catalytic performances were carried out in the same reactor with 0.2 g samples at atmospheric pressure and a total flow rate of 50 cm^3 min^{-1}.

Before testing, the oxides were in situ pre-treated for 2 h at 350 °C in a current of dihydrogen (H_2) or in a current of nitrogen (N_2) with a flow rate of 20 cm^3 min^{-1}.

Benzaldehyde transformation was performed in dihydrogen atmosphere or in nitrogen atmosphere at atmospheric pressure and in the whole range of reaction temperature 100–350 °C. Gaseous benzaldehyde (3.2 Torr) was obtained by bubbling N_2 (250 Torr) in liquid benzaldehyde maintained at constant temperature (50 °C) in a suitable saturator.

The gaseous reactant and products were heated up-stream and outstream in order to avoid their condensation and analyzed on line by a FID gas chromatograph (Delsi IGC 121 ML) equipped with a CP-Sil8CB/Chromosorb WAW column.

3. Results

3.1. BET and XRD characterizations

The characteristics of alkaline earth metal oxides are reported in Table 1. The calcined simple at 1200 °C showed a very small surface areas in the range 7.0–15.0 m^2 g^{-1} and the pore volume (V_P) decreased with the decrease of the specific surface area. These results indicate that high thermal treatment process strongly affected the microstructure of the alkaline earth metal oxides.

On the other hand, the XRD spectra showed the characteristic intense bands of the different oxides and, the characteristic weak bands of the corresponding carbonates ($CaCO_3$, $SrCO_3$, $BaCO_3$) or hydroxide ($Mg(OH)_2$) phases. The pattern was that of crystallized materials with well-defined bands and high degree of crystallinity of the diffraction lines. The metal phase was of 'CFC' structure for all the oxides. Calculations showed that the mean crystallite size of metal oxide was not the same, and vary in the range of 60–150 nm (Table 1).

3.2. Catalytic activity

3.2.1. Benzaldehyde reduction under nitrogen atmosphere (N_2)

Before reaction under N_2 flow, all oxides were pre-treated for 2 h at 350 °C in a current of the same gas (N_2). Fig. 1 reports activity results with time on stream in the whole range of reaction temperature. It can be noted in this figure that benzaldehyde reactivity decreased with time on flow at all reaction temperatures, generally tending to zero ($T_R < 250$ °C) or to a low residual value ($T_R > 250$ °C). In this case, benzaldehyde was reduced stoichiometrically in the range of temperature to benzyl alco-

Table 1
Characteristics of alkaline earth metal oxide catalysts

Oxide	Origin	S_{BET} (m^2 g^{-1})	V_P (cm^3 g^{-1})	XRD species identification	Crystallite size[a] (nm)	$E^{\circ}_{2 \rightarrow 0}$ (Volt)
MgO	Fluka	15.0	0.073	MgO, $Mg(OH)_2$	65	−1.86
CaO	Fluka	11.0	0.045	CaO, $CaCO_3$	77	−2.26
SrO	Fluka	10.0	0.039	SrO, $SrCO_3$	108	−2.59
BaO	Fluka	7.0	0.032	BaO, $BaCO_3$	139	−1.59

[a] Determined after calcination step by XR diffraction using Debby-Scherrer equation.
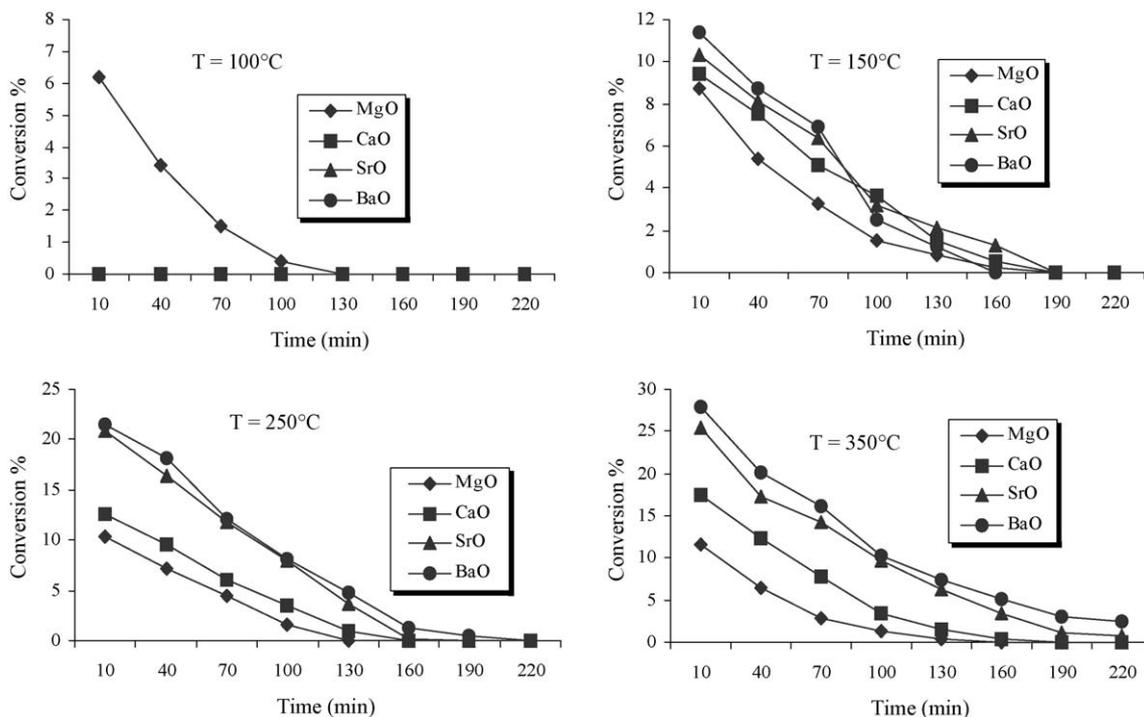
Fig. 1. Benzaldehyde conversion vs. time on stream on alkaline earth metal oxides under a nitrogen atmosphere. Range of reaction temperature 100–350 °C. Pre-treatment: N$_2$/350 °C.

hol, toluene and benzene. At low reaction temperature (100 °C) and after 10 min on nitrogen flow, all oxides were inactive with exception of MgO (6.2%).

Generally, the conversion of benzaldehyde after 10 min of reaction shows that the reactivity increases as function of reaction temperature on the following order (Fig. 2): MgO < CaO < SrO < BaO. On the other hand, and at given reaction temperature, the inspection of the Fig. 2 shows that the benzaldehyde conversion increased with the basicity character of metal oxide and the increase being more pronounced in SrO and BaO oxides at 250 °C and 350 °C. A gap of activity was observed between 250 °C and 350 °C in the case of CaO, SrO and BaO oxides; a conversion of which were multiplied by 1.4 (Table 2).

The reaction products were benzyl alcohol, toluene and benzene. No aromatic ring hydrogenation was observed:
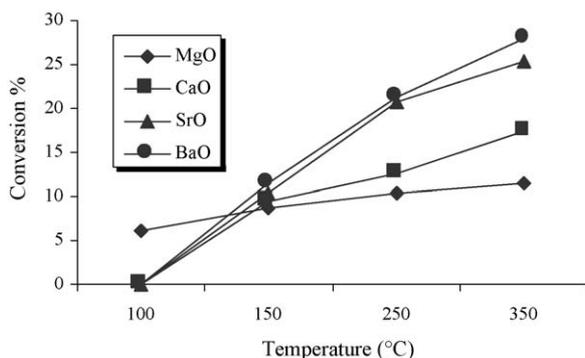
Fig. 2. Benzaldehyde conversion vs. reaction temperature on metal oxides in a nitrogen atmosphere after 10 min under flow.

- Benzyl alcohol was appeared only on the MgO oxide in the whole range of reaction temperature 100–350 °C (Table 2). The results were showed that benzyl alcohol decreased progressively as a function of the reaction temperature for to reach at 350 °C a value of 92.6%. In the whole range of the reaction temperature 100–350 °C, benzyl alcohol was

Table 2
Catalytic results for benzaldehyde reduction under nitrogen flow after 10 min of stream over alkali earth metal oxides

Oxide	$T_{reaction}$ (°C)	Conv (%)[a]	Pre-treatment/N$_2$/350 °C, reaction/PhCHO/N$_2$/$T_{reaction}$ °C, selectivity %		
			Benzyl alcohol	Toluene	Benzene
MgO	100	6.2	**100**	0	0
	150	8.7	**100**	0	0
	250	10.3	**95.9**	0	4.1
	350	11.5	**92.6**	0	7.4
CaO	100	0	0	0	0
	150	9.4	0	28.1	71.9
	250	12.6	0	19.5	80.5
	350	17.5	0	6.2	93.8
SrO	100	0	0	0	0
	150	10.4	0	0	100
	250	20.8	0	0	100
	350	25.4	0	0	100
BaO	100	0	0	0	0
	150	11.4	0	0	100
	250	21.3	0	0	100
	350	27.9	0	0	100

Pre-treatment: 350 °C/N$_2$.
[a] After 10 min of reaction.
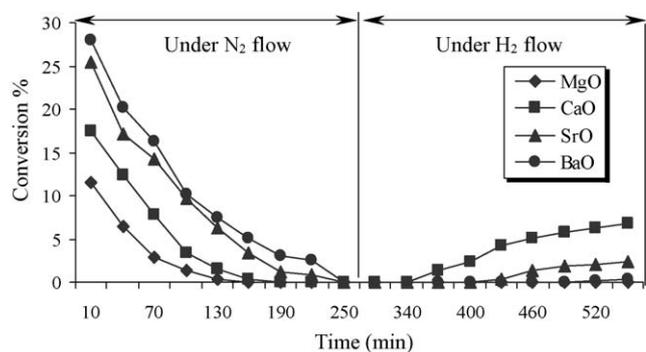
Fig. 3. Influence of the nitrogen replacement by dihydrogen as gas carrier on benzaldehyde conversion at 350 °C.

obtained as a result of the Cannizzaro reaction only for the MgO oxide.
- Toluene was obtained only on the CaO oxide and the same feature was observed, since the toluene production decreased from 28.1% (at 150 °C) to 6.2% (at 350 °C).
- In contrast, benzene was produced with all the oxides and the yield was higher to raised temperature.

After the benzaldehyde reaction under a current of nitrogen, the latter was replaced by dihydrogen flow. Previous work showed some influence of the gas reaction on benzaldehyde reduction on the alkaline earth metal oxides. Thus, after a total disappearance of catalytic activity under nitrogen atmosphere, Fig. 3 shows that the benzaldehyde conversion increased pro-

gressively with time on stream after introduction of dihydrogen over CaO, SrO and BaO, whereas, MgO oxide remained completely inactive.

After 8 h of the beginning of the reaction, CaO, SrO and BaO oxides exhibited various activities. In relation to the reaction under nitrogen atmosphere, the influence of dihydrogen atmosphere depended on metal oxide used (Fig. 3). Comparatively to the reaction under nitrogen flow, the results show that the magnesia activity was not re-established and conversely, the benzaldehyde conversion was relatively lowest on CaO, SrO and BaO. No change was observed in the selectivities.

3.2.2. Benzaldehyde reduction under dihydrogen atmosphere (H_2)

Before testing under a dihydrogen flow, the oxides were in situ activated for 2 h at 350 °C in a current of H_2. Fig. 4 shows that benzaldehyde was reduced catalytically in the whole range of reaction temperature. The alkaline earth metal oxides exhibited initial activation before the steady state was established and the duration (1–3 h) of activation depended on the nature of metal oxide and reaction temperature.

For all oxides, the inspection of Fig. 4 shows the increase of the steady state activity with the reaction temperature. The level and order of activities depended on both reaction temperature and nature of oxide. The activity results with time of stream showed that MgO oxide was remained inactive in benzaldehyde hydrogenation in all temperature reaction. The SrO and BaO oxide were inactive at 100 °C and the activity increased with the increasing of reaction temperature. On the other hand, the
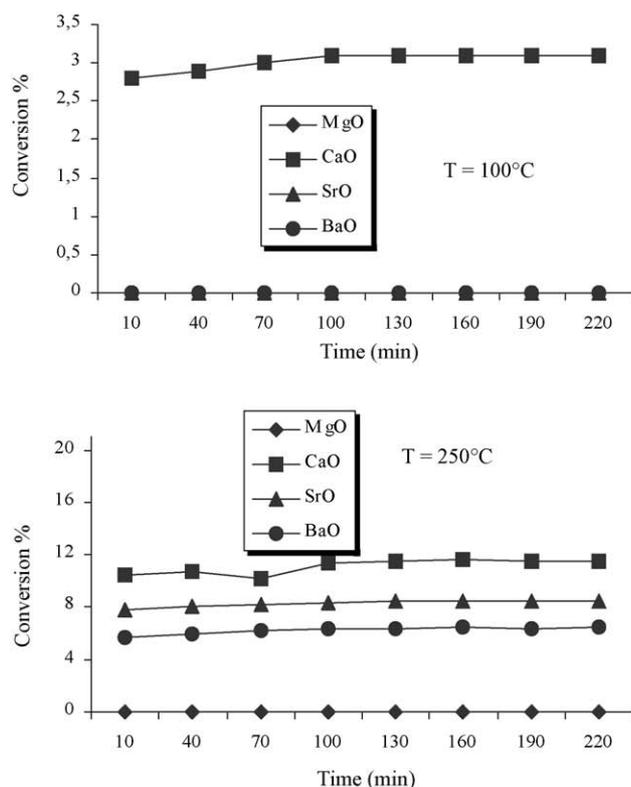
Fig. 4. Benzaldehyde conversion vs. time on stream on alkaline earth metal oxides under a dihydrogen atmosphere. Range of reaction temperature 100–350 °C. Pre-treatment: $H_2/350$ °C.
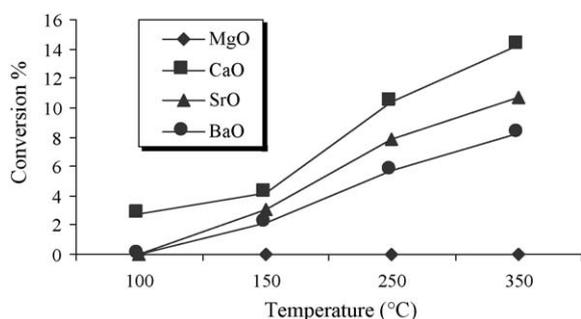
Fig. 5. Benzaldehyde conversion vs. reaction temperature on metal oxides in a dihydrogen atmosphere after 10 min under flow.

Fig. 6. Influence of the dihydrogen replacement by nitrogen as gas carrier on benzaldehyde conversion at 350 °C.

maximum of conversion was obtained at 350 °C for CaO oxide (14.3%), whereas it reached lower values (<11%) for SrO and BaO oxides. Strikingly, a similar gap of activity was observed for the CaO, SrO and BaO oxides between 150 °C and 250 °C: the activity was multiplied by 2.4 for CaO, 2.5 for SrO and 2.7 for BaO (Table 3, Fig. 5).

Under dihydrogen atmosphere, the reaction products obtained are the same as those obtained for the transformation under nitrogen flow: benzyl alcohol, toluene, benzene and traces of condensed products (not analyzed). Of course, the selectivities are different:

- Benzyl alcohol was produced between 100 °C and 150 °C on CaO oxide and only at 150 °C on SrO and BaO oxides (Table 3). The elevation of reaction temperature is not favorable to benzyl alcohol formation. Indeed, after 150 °C this product was totally disappeared.
- In the range of reaction temperature, low selectivity values to toluene (<11%) was observed for the CaO and BaO oxides

except SrO who produced the toluene with high amount at only 150 °C reaction temperature (Table 3). On the other hand, the increase of reaction temperature leads to the decrease of toluene selectivity.

- High selectivity to benzene was observed for the SrO (100% at 350 °C), CaO (99.7% at 350 °C) and BaO (98.9% at 350 °C). In contrast to benzyl alcohol and toluene, the benzene selectivity increased with the reaction temperature and the maximum of selectivity (100%) was obtained at a high reaction temperature (Table 3). On SrO oxide, only benzene formation was observed in the range 250–350 °C.

After 4 h of reaction under dihydrogen flow, the same gas was substituted by the nitrogen gas. Fig. 6 shows that benzaldehyde conversion decreased with time on stream and after 8 h of reaction, all oxides became totally inactive.

4. Discussion

4.1. Benzaldehyde reduction under nitrogen atmosphere (N₂)

4.1.1. Activity

In the discussion of the results of benzaldehyde reduction under nitrogen flow, we have to bear in mind the nature of active sites and organic molecules. Let us then discuss in more detail the obtained results in this study. We first consider the results obtained in the reduction of benzaldehyde under N_2 flow because they give useful information on acid–base properties of the catalysts.

The correlation of the basicity of the alkaline earth metal oxides with the activity and the increase in activity with atomic number seem to indicate that the active sites are mainly basic. In the whole range of the reaction temperature, the observed activities: MgO < CaO < SrO < BaO mean that this order is in good agreement with the bulk basicity in the periodic table.

It was reported by several workers that the basic site is a surface lattice oxygen O^{2-} [28–30] but the only presence of basic sites was not sufficient for activated the C=O bond. Indeed, Tanabe and Saito [14] were showed that the use of the solids NaOH/SiO₂, SrO₂ and BaO₂, which exhibited only basic property with phenolphthalein, does not show any catalytic activity

Table 3
Catalytic results for benzaldehyde hydrogenation under H₂ flow after 10 min of stream over alkali earth metal oxides

Oxide	$T_{reaction}$ (°C)	Conv (%)[a]	Pre-treatment/H₂/350 °C, reaction/PhCHO/H₂/$T_{reaction}$ °C, selectivity %		
			Benzyl alcohol	Toluene	Benzene
MgO	100	0	0	0	0
	150	0	0	0	0
	250	0	0	0	0
	350	0	0	0	0
CaO	100	2.8	**100**	0	0
	150	4.2	**100**	0	0
	250	10.4	0	10.7	89.3
	350	14.3	0	0.7	99.3
SrO	100	0	0	0	0
	150	3.1	**100**	0	0
	250	7.8	0	9.4	90.6
	350	10.7	0	1.3	98.7
BaO	100	0	0	0	0
	150	2.1	**56.7**	43.3	0
	250	5.7	0	0	100
	350	8.3	0	0	100

Pre-treatment: 350 °C/H₂.

[a] After 10 min of reaction.

and the catalytic activity of MgO and CaO was lost by the addition of pyridine. These results were suggested that the Lewis acid site (metal ions of MgO and CaO) is considered to be also important as an active site. The active species formed by the reaction of benzaldehyde with basic and acidic sites were benzylate and benzoate species and their existence on MgO and CaO oxides was confirmed by infrared study [14,31–33]. The raise of the reaction temperature increased the intensity bands of surface benzoates and decreased the intensity bands of surface benzylates, suggesting that the benzylate species change to benzoate species [14,33].

After total inhibition of reaction with time on flow, the replacement of nitrogen by dihydrogen as the carrier gas entailed the progressively apparition of the activity on CaO, SrO and BaO oxides, whereas MgO oxide was completely inactive. However, although the raise of the activity with reaction time has been observed, one notices that the initial activity gotten under current of nitrogen was not recovered. This result suggests that the regeneration of active species such as basic hydroxyl groups ($OH_{surface}$) or others intermediate species are probably more difficult.

4.1.2. Selectivity
4.1.2.1. Benzyl alcohol selectivity.
After N_2 pretreatment, benzyl alcohol was selectively obtained only on MgO oxide in the whole range of reaction temperature (Table 2). It was also obtained like only reaction product at $T_R < 250\,°C$ and the reactivity decreased with time on flow (Fig. 1), tending to zero order. Analogous to results obtained in homogeneous medium [21],

In this process, the obtained results reflect the surface mobility (or nucleophilicity) of the hydroxyl groups on MgO oxide [2,6,19] and the formation of one benzyl alcohol molecule consumes one surface hydroxyl group, thus explaining the decrease in reactivity with time. This result involves the disappearance of surface basic hydroxyl groups and the formation of adsorbed benzoate species. The number of active sites can be estimated tentatively for MgO oxide from extrapolation to $t \to 0$ of the curve conversion versus time (Fig. 1). Taking into account the amount of benzyl alcohol formed with time, we can deduced the number of hydroxyl groups reacts with benzaldehyde.

However, the analysis results show that the increase in the reaction temperature leads to the increase the number of the surface active hydroxyl species. At $100\,°C$, the number of hydroxyl groups, which were consumed after reaction are approximately $18\,OH/nm^2$ and this number increased to $25\,OH/nm^2$ at $150\,°C$. Haffad et al. [2] were showed that the determined OH number not reflects the real basicity of surface metal oxide and may be different from the total number of hydroxyl groups present on the surface. The observed activity to benzyl alcohol would only depend on the number of strong basic hydroxyls, referred to as type I, is a terminal OH coordinated to one metal cation (M—OH). It corresponds to the highest wave number in the IR spectrum. The presence of basic OH groups was proven by the formation of hydrogen carbonate species with the adsorption CO_2 [34] or by CS_2 and COS hydrolysis [35].

On the other hand, on the basis of the basic and acidic nature of alkaline earth metal oxides and the kinetic results [14], it is inferred that benzylate and benzoate species are formed over CaO oxide:

benzyl alcohol should be produced by the Cannizzaro reaction:

$$2PhCHO + OH^- \to PhCOO^- + PhCH_2OH$$

The decrease of the benzyl alcohol formation with the time on flow leads to the decrease in the number of the hydroxyl surface species and consequently, in benzaldehyde conversion. The Cannizzaro reaction stoichiometrically consumes surface hydroxyl groups (OH_{surf}) then ends up. The mechanism on oxide surfaces can be written as follows:

$$PhCHO_g + OH_{surf} \leftrightarrows PhCH(OH)O_{ads}$$
$$\xrightarrow{PhCHO_g} PhCOO_{surf} + PhCH_2OH_g$$

Benzaldehyde reacts with basic sites O^{2-} of CaO oxide to form an intermediate (I), while it reacts with Lewis acid sites Ca^{2+} to form an intermediate (II). Calcium benzoate (III) and benzylate (IV) are formed by the hydride ion transfer form (I) to (II). Benzyl alcohol is considered to be formed by a proton transfer of surface hydroxyl group to benzylate (IV).

On CaO, SrO and BaO oxides, no benzaldehyde conversion at $100\,°C$ and no benzyl alcohol formation above $100\,°C$ are probably due to the strong adsorption of benzylate species formed on the surface oxide, and the increase in the reaction temperature changes the surface benzylate species to benzoate species [14]. Benzaldehyde is known to dissociatively adsorb as ben-

zoate and benzylate species on basic oxides [2,20,21,36] and subsequent heating leads to the disproportionation to toluene [15], or to the decomposition of these species to benzene [20,37–38].

4.1.2.2. Toluene selectivity. In such conditions, only CaO oxide produced selectively the toluene (Table 2). It appears in the range 150–350 °C and decreases progressively with a reaction temperature. Formally, toluene formation requires two hydrogen atoms from benzaldehyde and four hydrogen atoms if water appears [2]. In the absence of dihydrogen flow, hydrogen comes from surface hydroxyl or aldehydic groups. Sreekumar and Pillai [15] showed that toluene product is formed by disproportionation from benzyl alcohol:

$$2PhCH_2OH \rightarrow PhCH_3 + PhCHO + H_2O$$

On CaO oxide, no trace of benzyl alcohol was detected in the reaction mixture, suggesting that alkoxy species do not desorb (reaction 2) and probably react directly by a new surface step to toluene [2]. By analogous to Sreekumar and Pillai reaction, toluene may arise from successive reactions.

Benzaldehyde dismutation to surface benzylate species (Cannizzaro reaction):

$$2PhCHO_g \rightarrow PhCOO_{ads} + PhCH_2O_{ads}$$

and the presence of two nearby benzylate species could transformation to toluene (Pillai reaction):

$$2PhCH_2O_{ads} + 2H_{ads} \rightarrow PhCH_3 + PhCHO_g + H_2O_g \qquad (1)$$

or a benzylate species and a benzaldehyde molecule (reaction 2):

$$PhCH_2O_{ads} + PhCHO_g \rightarrow PhCH_3 + PhCOO_{ads} \qquad (2)$$

To differentiate mechanisms (1) and (2), we had recourse to TCD detector in GC analysis. The results reveal the totally absence of the water formation and the presence in the reaction mixture the concomitant formation of CO_2. These results confirm the high benzene selectivity obtained on CaO oxide, and suggest that mechanism (2) prevails.

4.1.2.3. Benzene selectivity. Some benzene appears on all alkaline earth metal oxides and the rate increase with the increasing of basicity in order: MgO < CaO < SrO < BaO (Table 2). Over SrO and BaO oxides, the high selectivity to benzene (100%) between 150 °C and 350 °C, and the increased benzaldehyde conversion to benzene with the increasing reaction temperature suggests that the final product should be dependant only the acidic or redox surface properties [2]. Benzene is usually considered to be the result of the decomposition of surface benzoate species with carbon dioxide formation [37]:

$$C_6H_5COO_{ads} + H_{ads} \rightarrow C_6H_{6g} + CO_{2g}$$

The high activity and benzene selectivity over SrO and BaO suggest that a subsequent heating leads to the decomposition of the benzoate species into benzene and CO_2. On CaO oxide, the

toluene formation is accompanied to benzoate species. The elevation of reaction temperature decomposed the benzoate species to benzene and CO_2.

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$_{ads}$ [39]. It may be regarded as a hydride producer for reductions (via benzylate species) or a benzene precursor.

4.2. Benzaldehyde reduction under dihydrogen atmosphere (H₂)

4.2.1. Activity

The use dihydrogen flow, as the carrier gas can provokes not only the direct hydrogenation of benzaldehyde but it can also modify the surface properties [2]. Indeed, the comparison of the obtained results with the two reaction processes revealed that, in the range reaction temperature, the activity was the most weak under atmosphere hydrogen. Thus, the dihydrogen pretreatment is expected to affect the hydroxyl groups. The dihydrogen produced some oxygen vacancies by moderate reduction of the surface [2,24].

However, the activity of the irreducible alkaline earth metal oxides was modified by the dihydrogen atmosphere process and decrease in the order: CaO > SrO > BaO > MgO = 0 (Table 3). In the whole temperature reaction, no conversion was observed over the irreducible magnesia and the H_2 pretreatment drastically inhibited the Cannizzaro reaction. One infers that this activation mode provokes the modification of hydroxyl groups and, as a result, the total inhibition of the dismutation reaction and mechanism of dehydroxylation is probably complex. On the other hand, the observed activities were not related directly to the reducibility of the metal oxides. The order of the standard potentials redox E_0 (ox/red) [40]:

$$BaO/Ba(-1.59\,V) > MgO/Mg(-1.86\,V)$$

$$> CaO/Ca(-2.26\,V) > SrO/Sr(-2.59\,V)$$
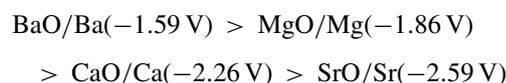
is different from the order of activity of the alkaline earth metal oxides. Under the experimental conditions, probably the hydrogen molecules could be not activated by the irreducible MgO oxide because of its small crystallite size, whereas CaO, SrO, BaO oxides that exhibits thick crystallite size can probably encourage the activation of hydrogen molecules (Table 1). This result was confirmed when the dihydrogen was replaced by the nitrogen as carrier gas. The benzaldehyde conversion decreased with time on stream until the total reaction inhibition on all oxides, what shows that the reaction is become stoichiometric and the presence of a nondissociative or dissociative hydrogen adsorption on the surface oxides has been completely consumed.

4.2.2. Selectivity

The fact that the aromatic nucleus is unreactive while the carbonyl group undergoes hydrogenation and hydrogenolysis suggest that the aromatic aldehyde reacts principally with the catalyst via carbonyl function [19]. In such case, the adsorbed hydrogen preferably attack the carbonyl group due to the energy barriers [18,41,42].

4.2.2.1. Benzyl alcohol selectivity. At low reaction temperature (<250 °C), benzyl alcohol was produced with high selectivity at low conversion on CaO (100%), SrO (100%) and BaO (56.7%) oxides. The elevation of reaction temperature seems to indicate that benzyl alcohol disappeared progressively with the increase of benzaldehyde conversion. This result reveals that the benzyl alcohol is favored only at low benzaldehyde conversion.

In such conditions, benzyl alcohol is the primary product during the gas-phase hydrogenation of benzaldehyde over alkaline earth metal oxides. In the presence of dihydrogen flow, these oxides favored the carbonyl reduction compound to the corresponding alcohol, even at low conversion. As to the chemical process of benzyl alcohol formation, it can be supposed to be 1–2 nucleophilic addition, with a high polarization of the transition state, as in the case of the hydrogenation of conjugated carbonyl compounds [41–44]:

$$Ph-CH=O_g \xrightarrow[H^{\delta-}-M^{\delta+}]{} Ph-CH_2-O-M \xrightarrow{H_2} Ph-CH_2-OH_g +$$
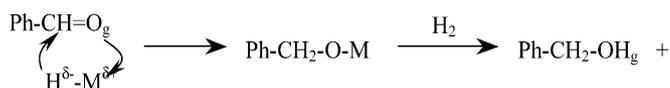
Therefore, hydrogen surface species may be considered as active intermediates for the direct hydrogenation of benzaldehyde to benzyl alcohol [2,5,19,45]. It was reported by several workers that the infrared studies have shown on different oxides, the heterolytic and homolytic dissociation of dihydrogen [45]. The surface oxide has been totally dehydrated prior by H_2 adsorption and the OH group is likely to originate from the dissociative adsorption of the hydrogen molecule occurring on the thoroughly dehydrated oxide [16].

It is worth noting that MgO bare oxide, which is considered to be basic, no benzyl alcohol was observed in the exit gas probably because, more strongly held on the oxide surface or the hydroxyl groups, active in the Cannizzaro reaction, has been removed by the dihydrogen pretreatment.

4.2.2.2. Toluene selectivity. It is generally considered that toluene is the product of a consecutive reaction of hydrogenolysis of benzyl alcohol [1,2,19,46]. Indeed, flowing the CaO, SrO, and BaO oxides with the benzyl alcohol instead of benzaldehyde, selectively led to toluene production. In a parallel experiment, replacing benzaldehyde by benzylalcohol in the reactant flow showed the formation of toluene with a selectivity of 100%. However, benzyl alcohol is a complex molecule possessing several active centers such as the acidic proton and basic oxygen of the O–H function and the reductive hydrogen of the C–H exocyclic function. All these centers may interact with the oxide surface or dihydrogen molecule [19]. Also several pathways can be envisaged for toluene formation.

- In the case of the CaO and SrO oxides, the totally disappearance of benzyl alcohol product and the appearance of toluene product with low selectivity in the mixture reaction supposed that the hydrogenation of benzaldehyde to benzyl alcohol can continue to toluene. In such a case, the activity in toluene should reflect the aptitude of the surface oxide to both adsorb the alcohol and dissociate H_2. The toluene formation probably resulted in the protonation of the alcohol

function on a Brönsted acid site (H–O–M_{surf}) followed by hydrogenolysis of the protonated specie on a adjacent metal site (M–H):

$$Ph-CH_2-O^{\delta-}-H \xrightarrow{H_2} Ph-CH_3 + H_2O$$
$$H^{\delta-}-M^{\delta+} \qquad\qquad H^{\delta-}-M^{\delta+}$$
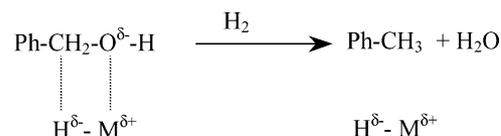
- In the case of BaO oxide, during the steady-state setting-up at low reaction temperature (150 °C), toluene appeared as a secondary product. The presence of benzyl alcohol and toluene products in the reaction mixture suggests the existence of another reaction path than that described above. This path probably involves very active sites on which toluene is fastly formed in the early stages of the reaction where the partial pressure of both reactants and products were low. These sites were then poisoned at higher conversion by the one or the other reactant molecule, even water. The possible route would be the benzylalcohol dismutation to toluene, benzaldehyde and water on the support [47–49]:

$$Ph-CH_2 ----H-CH-Ph \xrightarrow{H_2} Ph-CH_3 + Ph-CHO + H_2O$$
$$M-O^{\delta-}--H^{\delta}O \quad H^{\delta+}-O^{\delta-}---M \qquad M^{\delta+}O^{\delta-} \qquad M-OH$$
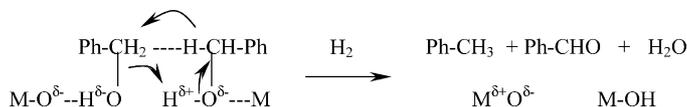
4.2.2.3. Benzene selectivity. In the present case, Benzene is formed only at high reaction temperature (>250 °C) on CaO (>89%), SrO (>90%) and BaO (100%) oxides. It is believed to be the product of the hydrogenolysis of the external C(aryl)–C bond of benzaldehyde [18,19]. Vannice and Poondi [1] were showed that benzene formation was produced directly from the reactant molecule and not from the alcohol or toluene intermediates. Carbon monoxide was identified as co-product of benzene [1]. However, Herskowitz [46] was showed that benzene is the sequential product of the consecutive hydrogenation of the alcohol to toluene; it appears only when essentially all aldehyde has disappeared.

In our study, using of TCD detector in GC analysis has shown that no CH_4 was detected. The results were revealed in the reaction mixture the presence of carbon monoxide as co-product benzene. These results confirm the high benzene selectivity obtained on CaO, SrO and BaO oxides. In the following sequence, we can be simplified the benzaldehyde hydrogenolysis to benzene:

$$C_6H_5CHOg \rightarrow C_6H_6 + CO_{ads}$$
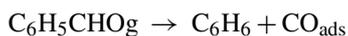
The exact nature of the reaction paths of benzaldehyde hydrogenolysis to benzene and carbon monoxide is not yet reported to our best knowledge. It probably implies a bifunctional site: the adsorption of the reactant molecule on an acidic/cationic site then dissociation of the aldehydic C–H bond on a metal site. Further work is needed to obtain more information's on the real involved reaction paths.

5. Conclusion

Reduction of benzaldehyde has been chosen as a model reaction for determining the surface properties of alkaline earth

metal oxides. Under nitrogen atmosphere, the results show that the active sites are basic hydroxyl groups. Only MgO oxide produced selectively the benzyl alcohol, whereas toluene and benzene are usually formed at high reaction temperature on CaO, SrO and BaO oxides. On MgO, the mechanism suggests that benzaldehyde reduction to benzyl alcohol 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.

Under dihydrogen flow, a stationary state is reached on CaO, BaO and SrO, whereas MgO is inactive. The presence of H_2 flow not affects the benzyl alcohol formation on CaO oxide. This result suggests that the presence of totally dehydrated surface is probably necessary for both dissociative and nondissociative adsorption of dihydrogen, as consequence, benzaldehyde is directly reduced to benzyl alcohol. Toluene product arose from the hydrogenolysis of benzyl alcohol on probably bifunctional sites involving metal hydride species. As to benzene, it resulted from benzaldehyde hydrogenolysis probably through a surface hydrogenate specie. Useful information on the surface properties of the alkaline earth metal oxides and the reaction course were given by comparing the transformations of bnezaldehyde under N_2 or H_2 atmosphere.

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