

Solvent-free oxidation of benzyl alcohol to benzaldehyde by *tert*-butyl hydroperoxide using transition metal containing layered double hydroxides and/or mixed hydroxides

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Abstract

Performance of Mn–Al, Co–Al, Ni–Al, Zn–Al, Mg–Fe, Mn–Fe, Co–Fe, Ni–Fe, Mn–Cr, Co–Cr, Ni–Cr, Cu–Cr, and Zn–Cr layered double hydroxides (LDH) and/or mixed hydroxides (HD) solid catalysts has been evaluated for the liquid phase oxidation of benzyl alcohol to benzaldehyde using TBHP as an oxidizing agent in the absence of any solvent. The Mn, Cu, and Co containing LDH solids show good catalytic activity in the oxidation and hence these are promising catalysts for the solvent-free oxidation of benzyl alcohol to benzaldehyde. © 2004 Elsevier B.V. All rights reserved.

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1. Introduction

Catalytic vapor phase oxidation of benzyl alcohol to benzaldehyde [1–8] is a widely investigated reaction as it provides chlorine-free benzaldehyde required in perfumery and pharmaceutical industries. However, because of the formation of carbon-oxides causing very appreciable carbon loss in the vapor phase reaction, it is preferable to produce benzaldehyde more selectively by catalytic liquid phase oxidation of benzyl alcohol. A few studies on liquid phase oxidation of benzyl alcohol using supported palladium [9,10], heteropolyacid [11] and Ni–Al–hydrotalcite [12] catalysts and molecular O₂ or aqueous H₂O₂ as the oxidant have been reported earlier.

In the earlier studies [12], Ni–Al–hydrotalcite showed good activity in the benzyl alcohol-to-benzaldehyde oxidation by O₂ in the presence of a solvent. It is of both scientific and practical interests to explore the possibility of using different hydrotalcite clay-like materials such as layered double hydroxides (LDH) containing different transition metals for the liquid phase oxidation of benzyl

alcohol using different oxidizing agents such as hydrogen peroxide and organic hydroperoxides.

The present work was undertaken with the objective of investigating the liquid phase oxidation of benzyl alcohol in the absence of any solvent using a number of synthetic hydrotalcite like materials LDHs containing one or two different transition elements (viz. Ni, Co, Zn, Cu, Fe, Mn, and Cr) and *tert*-butyl hydroperoxide (TBHP) as an oxidizing agent. Since the LDHs containing transition elements showed very high H₂O₂ decomposition activity at the oxidation conditions, TBHP was chosen as the oxidizing agent in the present studies.

2. Experimental

The layered double hydroxides and/or mixed hydroxides (HD) containing different divalent [M(II)] and trivalent [M(III)] metallic elements with M(II)/M(III) mole ratio of 3.0 but having same anions [CO₃²⁻], given in Tables 1 and 2, were prepared as follows: two aqueous solutions, one containing mixed nitrates of the divalent and trivalent metals (with a M(II)/M(III) ratio of 3.0) and second containing potassium hydroxide and potassium carbonate, are added drop wise into a flask containing deionized water under vigorous stirring at 40 °C, while maintaining a constant pH

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Table 1

Characterization of layered double hydroxide (LDH) and mixed metal hydroxide catalysts containing different divalent [M(II)] and trivalent [M(III)] metals [M(II)/M(III) = 3.0]

M(II)	M(III)	XRD phase(s)	d (001) spacing (nm)	CO ₃ ²⁻ content (mmol g ⁻¹)	pH of water slurry ^a	Surface area (m ² g ⁻¹)	t _{1/2} for H ₂ O ₂ decomposition (min)
Mn	Al	Mn(OH) ₂ , MnCO ₃ , Al(OH) ₃	–	0.33	7.1	73	0.4
Co	Al	Pure HT	0.756	1.1	7.8	66	4.4
Ni	Al	Pure HT	0.784	1.07	8.0	119	7% ^b
Zn	Al	Pure HT, Zn(OH) ₂ , Al(OH) ₃	0.751	0.71	7.5	46	n.d. ^c
Mg	Fe	Pure HT	0.769	1.19	9.6	58	15.8
Mn	Fe	Mn(OH) ₂ , MnCO ₃ , Fe(OH) ₂	–	0.38	7.0	55	0.2
Co	Fe	Pure HT	0.760	0.57	7.4	75	0.8
Ni	Fe	Pure HT	0.775	0.66	7.0	60	22% ^b
Mn	Cr	HT, Cr(OH) ₃ ·H ₂ O, Mn(OH) ₂ , MnCO ₃	0.748	0.09	6.3	96	0.9
Co	Cr	Pure HT	0.781	0.92	7.3	108	3.0
Ni	Cr	Pure HT	0.701	1.1	8.7	60	22% ^b
Zn	Cr	HT, Zn(OH) ₂ , ZnCO ₃	0.762	0.47	7.1	85	15% ^b
Cu	Cr	HT, Cu(OH) ₂ , CuCO ₃	0.748	0.98	7.4	111	9.7

^a 0.15 g catalyst in 10 ml distilled water.

^b Actual H₂O₂ decomposition in 45 min.

^c n.d.: Not determined.

of 11–12, following the procedure similar that to describes earlier [13]. The resulting gel-like material was aged for 0.5 h and then filtered, thoroughly washed and dried at 80 °C in vacuum oven and then further heated in air oven at 200 °C for 12 h.

The LDH and HD solid materials were characterized for their crystalline phase(s) by XRD (using a Phillips Diffractometer (1730 series) and Cu K α radiations), for their surface area by the single point N₂ adsorption method (using a Surface Area Analyser; Quanta Chrome, USA) and also for their basicity by measuring the pH of their suspension in water (0.15 g catalyst in 10 ml deionized water at room temperature) and also for their CO₃²⁻ content (by treating the catalyst with 4.0 M HNO₃ and measuring quantitatively

the CO₂ evolved). Before carrying out the surface area measurements, the catalyst (0.1–0.5 g) was pretreated in situ in an U-shaped sample cell in a flow of moisture-free N₂–He (1:3) gas mixture (30 cm³ g⁻¹) at 200 °C for 2 h.

The LDH and HD solid catalysts were also characterized for their H₂O₂ decomposition activity by determining the time required for half the H₂O₂ decomposition. The H₂O₂ decomposition over the LDHs was carried out in a magnetically stirred glass reactor (capacity 25 cm³) at 27 °C by injecting 1.0 ml of aqueous H₂O₂ (30%) solution in the reactor containing 10 ml distilled water and 0.1 g catalyst and measuring quantitatively the amount of oxygen evolved in the decomposition (H₂O₂ → 0.5O₂ + H₂O) using constant pressure gas collector [14].

Table 2

Results of the liquid phase oxidation of benzyl alcohol to benzaldehyde over different layered double hydroxides (LDH) and mixed hydroxides (HD)

Catalyst	Conversion of benzyl alcohol (%)	Selectivity (%)			Conversion of TBHP (%)
		Benzaldehyde	Benzoic acid	Benzyl benzoate	
Mg–Al–HT	20.2	99.3	0.0	0.7	19.7
Mn–Al–HD	46.7	91.3	7.7	0.97	99.7
Co–Al–LDH	56.7	77.4	17.5	5.0	92.8
Ni–Al–LDH	15.9	100	0.0	0.0	14.4
Zn–Al–LDH/HD	10.5	100	0.0	0.0	8.2
Mg–Fe–LDH	19.4	97.7	0.1	2.2	21.6
Mn–Fe–HD	53.9	70.6	27.5	1.9	96.7
Co–Fe–LDH	52.5	79.2	17.9	2.9	97.3
Ni–Fe–LDH	17.0	100	0.0	0.0	16.5
Mn–Cr–LDH/HD	49.8	83.5	15.2	1.3	95.4
Co–Cr–LDH	59.5	70.0	24.0	6.0	98.9
Ni–Cr–LDH	15.0	100	0.0	0.0	15.4
Cu–Cr–LDH/HD	51.3	74.9	6.6	18.5	99.8
Zn–Cr–LDH/HD	41.9	91.5	6.5	2.0	73.6
Without catalyst	14.3	98.0	1.5	0.5	13.5

Reaction conditions: reaction mixture: 52 mmol benzyl alcohol; 68 mmol TBHP; 0.5 g catalyst [M(II)/M(III) = 3.0]; temperature: under reflux (bath temperature, 94 ± 1 °C); reaction period: 5 h.

The catalytic oxidation of benzyl alcohol over the LDH and HD catalysts was carried out in a magnetically stirred round bottom flask (capacity: 25 cm³), provided with a mercury thermometer for measuring the reaction temperature and reflux condenser, at the following reaction conditions. Reaction mixture: 52 mmol benzyl alcohol; 68 mmol TBHP (70% TBHP in water); 0.5 g catalyst; temperature, under reflux (bath temperature = 94 ± 1 °C); and reaction time, 0.5–5 h. After the reaction the catalyst was removed from the reaction mixture by filtration and the reaction products and unconverted reactants were analyzed by gas chromatograph with flame ionization detector, using a SE-30 column and N₂ as a carrier gas. For measuring the catalysts performance for the oxidation as function of time, liquid samples were removed time-to-time from the reaction mixture by syringe and analyzed by GC.

3. Results and discussion

The LDH and HD catalysts have been characterized for their crystalline phases and spacing between hydroxide layers [d (001) spacing] by XRD, CO₃²⁻ content, basicity (in terms of pH of LDH-water slurry), surface area and also for their H₂O₂ decomposition activity (in terms of the time required for half the H₂O₂ decomposition at 27 °C). The results of the characterization of the LDH catalysts are presented in Table 1.

The Mn containing catalysts (viz. Mn–Al, Mn–Fe, Mn–Cr hydroxides) do not show the presence of HT phase; these catalysts contain Mn-carbonate and Mn and other metal hydroxide phases.

The Zn–Al, Cu–Cr, and Zn–Cr containing catalysts do not contain only HT phase but these have mixed HT and metal hydroxide/carbonate phases, as shown in Table 1. However the other catalysts (viz. Co–Al–LDH, Ni–Al–LDH, Mg–Fe–LDH, Co–Fe–LDH, Ni–Fe–LDH, Co–Cr–LDH, and Ni–Cr–LDH) have pure HT phase.

The CO₂ content is varied from catalyst to catalyst, depending upon the presence of HT phase and/or the transition elements present in the catalysts. It is very low for the Mn–Cr, Mn–Al, and Mn–Fe–hydroxides because of the absence of HT phase; consequently these catalysts do not have exchangeable CO₃²⁻ anions.

The basicity (measured in terms of the pH of catalysts-water slurry) of the Mn containing catalysts is very poor (pH ≤ 7.0). This is consistent with the fact that these catalysts do not contain HT phase. Earlier, Valente et al. [15] have found that the basicity of hydrotalcites is controlled by the electronegativity of their components and also changed by their chemical composition.

A comparison of the CO₃²⁻ content and the pH data for the catalysts shows that there is a relationship between the two; Fig. 1 shows that in general the pH (or the basicity) is increased with increasing the CO₃²⁻ content.

There is a large variation in the surface area of the catalysts, depending upon their composition. The surface area does not show any dependence on the presence or absence of HT phase in the catalysts.

The catalysts differ very widely in their H₂O₂ decomposition activity (at 27 °C). The Mn containing catalysts have a very high H₂O₂ decomposition activity (the *t*_{1/2} for the Mn–Al, Mn–Fe, and Mn–Cr–hydroxides are 0.4, 0.2, and 0.9 min, respectively). The Co–Fe–LDH also has very

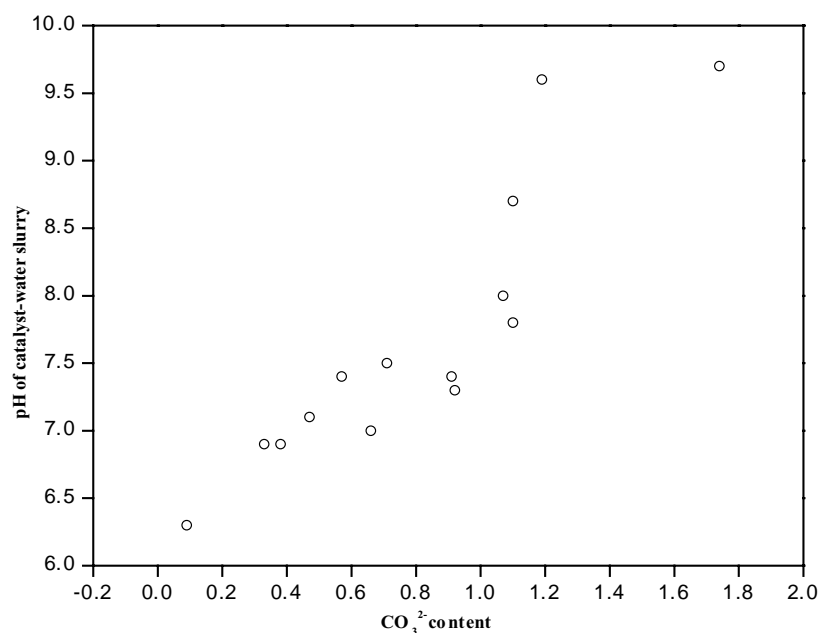


Fig. 1. Correlation between CO₃²⁻ content and the pH for various transition metal containing LDH and HD catalysts.

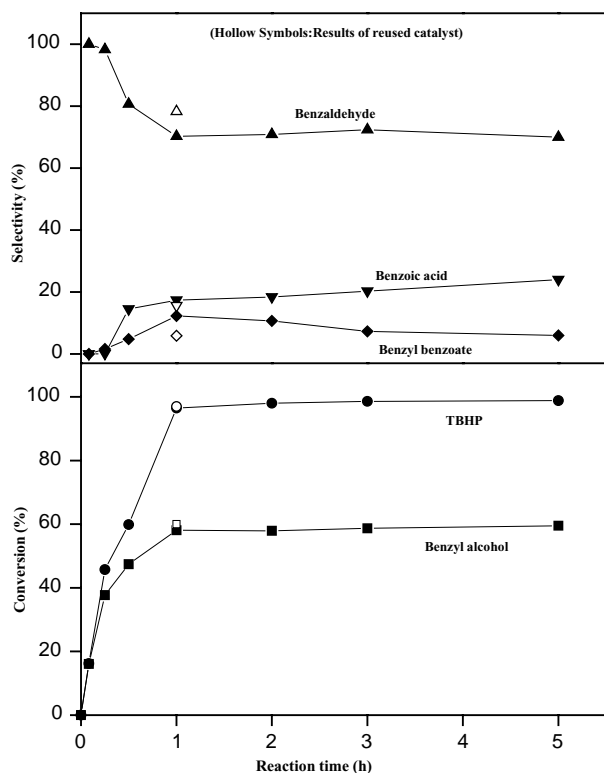


Fig. 2. Variation with the reaction time of the conversion and product selectivity in the oxidation of benzaldehyde over the Co-Cr-LDH (under reflux).

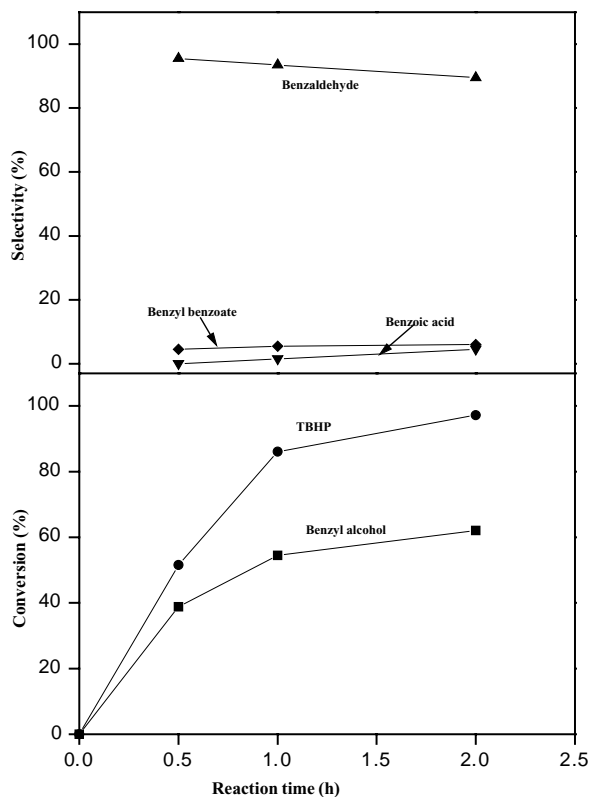


Fig. 3. Variation with the reaction time of the conversion and product selectivity in the oxidation of benzaldehyde over the Co-Cr-LDH (at 70°C).

high H_2O_2 decomposition activity ($t_{1/2} = 0.8$ min). The other catalysts except the Mg-Al-HT, Zn-Al-LDH/HD, and Ni-Al-LDH catalysts show relatively a very poor H_2O_2 decomposition activity. The other catalysts show intermediate to high activity for the H_2O_2 decomposition.

It may be noted that even the Mg-Al-HT (Table 2) shows little or no H_2O_2 decomposition activity at 27°C, but very high H_2O_2 decomposition activity at the temperature at which the benzyl alcohol oxidation reaction is carried out. Hence, it is not possible to use H_2O_2 as an oxidizing agent for the oxidation reaction over the catalysts used in the present studies.

Results showing the performance of the various transition metals containing LDH and HD catalysts in the solvent-free oxidation of benzyl alcohol to benzaldehyde by TBHP are presented in Table 2 and Figs. 2–8.

The Mn-, Co-, and Cu-containing catalysts and Zn-Cr-LDH/HD catalysts showed much higher benzyl alcohol conversion (41.9–59.5%) than the pure Mg-Al-HT (20.2%) and different Ni-containing LDH catalysts (15–17%). Among the various bimetallic transition metal-containing LDH catalysts, the best performance in terms of highest catalytic activity ($\geq 52.5\%$) with good selectivity to ben-

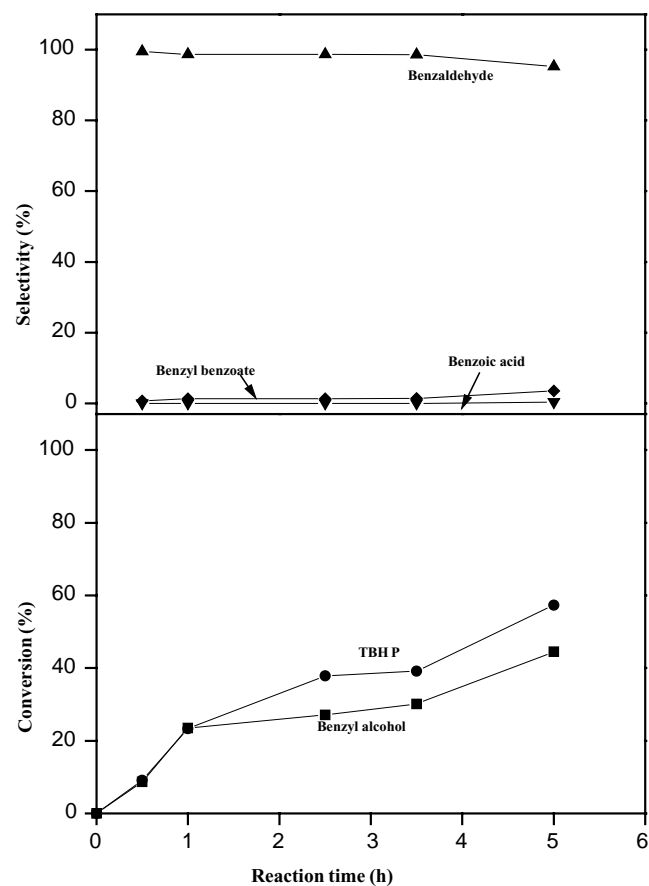


Fig. 4. Variation with the reaction time of the conversion and product selectivity in the oxidation of benzaldehyde over the Co-Cr-LDH (at 50°C).

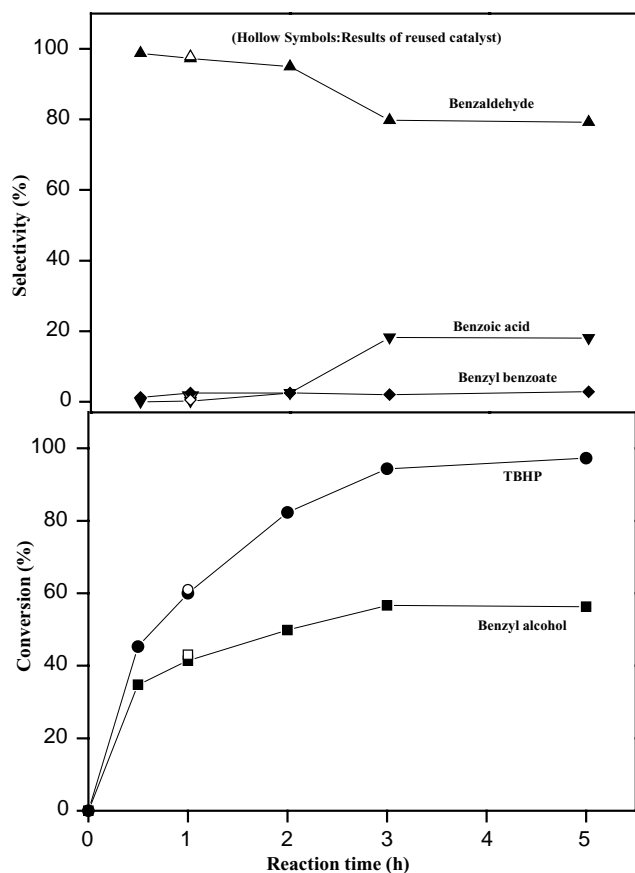


Fig. 5. Dependence on the reaction time of the conversion and product selectivity in the oxidation of benzaldehyde over the Co-Fe-LDH (under reflux).

zaldehyde ($\geq 70\%$) was observed over Co-containing LDH. It is interesting to note that the results achieved using Ni-containing catalysts are very close to the benzyl alcohol conversion (14.3%) achieved in the absence of any catalyst. With the Zn-Al-LDH/HD catalyst, the conversion was even less than that obtained in the absence of any catalyst indicating reaction inhibition due to the catalyst. A similar catalyst inhibition was also observed when the oxidation of benzyl alcohol by TBHP [16] and molecular oxygen [17] was performed over Mg-Al-HT (Mg/Al = 10) and Ni containing hydrotalcite-like solid catalyst, respectively.

Bijlani and Chandalia [9] have also reported very poor performance for Pd/C catalyst when the oxidation of benzyl alcohol by air was performed under solvent-free conditions. It is also reported earlier [12] that, in the presence of non-polar solvent (such as toluene) Ni-Al-hydrotalcite (Ni/Al = 2:1) shows an excellent performance in the oxidation by molecular oxygen of substituted benzyl alcohols to their corresponding aldehydes. However, in the present case, LDH and/or HD based catalysts showed both high activity and selectivity in the oxidation of benzyl alcohol in the absence of any solvent (Table 2 and Figs. 2–8). The solvent-free oxidation is practically very important to have environmentally more benign process. The catalysts could

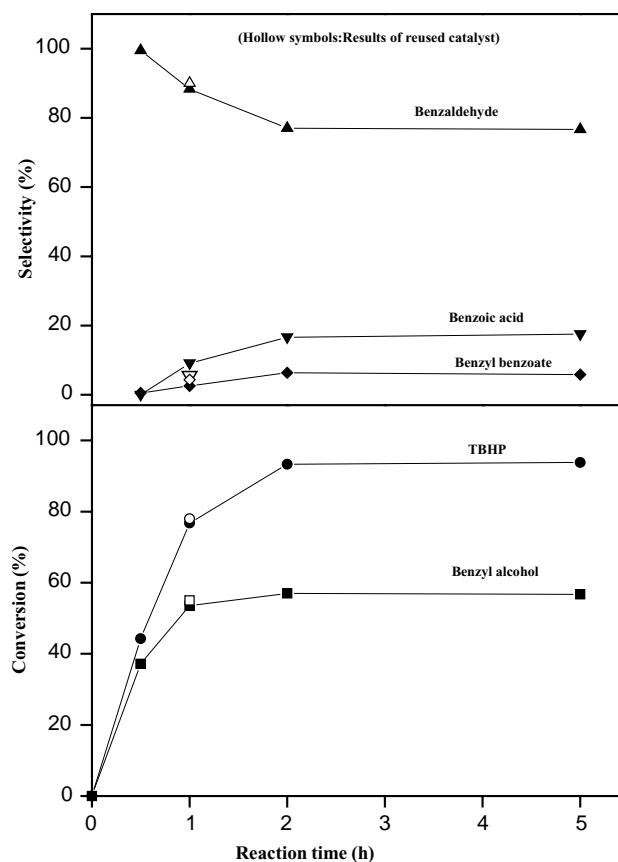
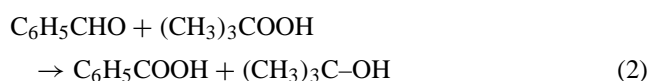
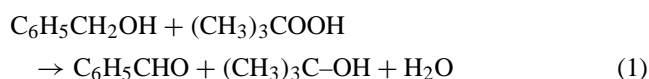


Fig. 6. Dependence on the reaction time of the conversion and product selectivity in the oxidation of benzaldehyde over the Co-Al-LDH (under reflux).

be reused without a significant loss in their activity and selectivity (Figs. 2, 5–8).

Recently, Farkas et al. [18] have reported selective oxidation of benzylic alcohols to aldehydes by metallic nitrates as an oxidizing agent, using solid acid catalysts. In this case, although the aldehyde yields are higher than that obtained in the present case, the use of bismuth nitrate as an oxidizing agent in stoichiometric quantities and benzene as a solvent lead to production of undesirable waste.

Results showing the influence of reaction time on the conversion of benzyl alcohol and TBHP and product selectivity in the oxidation over the catalysts (viz. Co-Cr-LDH, Co-Al-LDH, Mn-Cr-LDH/HD, and Mn-Fe-HD) showing good performance are presented in Figs. 2–8. With increasing the reaction time, the selectivity for benzaldehyde is decreased while the conversion of both benzyl alcohol and selectivity for benzoic acid and benzyl benzoate are increased. The consecutive reactions involved in the catalytic process are as follows:



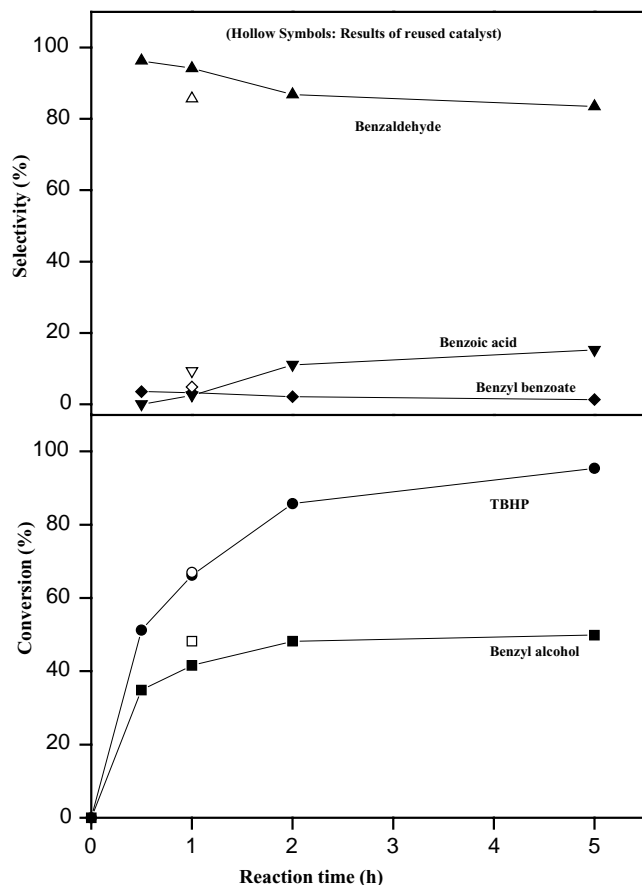
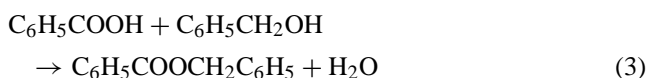


Fig. 7. Dependence on the reaction time of the conversion and product selectivity in the oxidation of benzaldehyde over the Mn-Cr-LDH/HD (under reflux).



Since, benzaldehyde is an intermediate product in the oxidation process, its selectivity is decreased with increasing the reaction time (Figs. 2–8) depending upon the reaction temperature (Figs. 2–4). At the lower temperature, the benzaldehyde selectivity is higher.

The observed higher conversion of TBHP as compared to that of benzyl alcohol is due to the catalytic decomposition of TBHP $[(\text{CH}_3)_3\text{COOH} \rightarrow (\text{CH}_3)_3\text{C-OH} + 0.5\text{O}_2]$ and the formation of benzoic acid in Eq. (2) (Figs. 2, 5–8).

A comparison of the catalytic performance (Table 2 and Figs. 2–8) with surface properties (Table 1) of the catalysts indicates that there is no direct relationship between their catalytic activity/selectivity in the oxidation and their surface area or basicity (measured in terms of the pH of water slurry). However, a direct correlation existed between the catalytic performance of the transition metal containing LDHs and/or HDs and their H_2O_2 decomposition activity (Table 1); in general the catalysts showing high H_2O_2 decomposition activity gave better performance in the selective oxidation of benzyl alcohol to benzaldehyde. The basic sites of the catalysts may be responsible for the activation

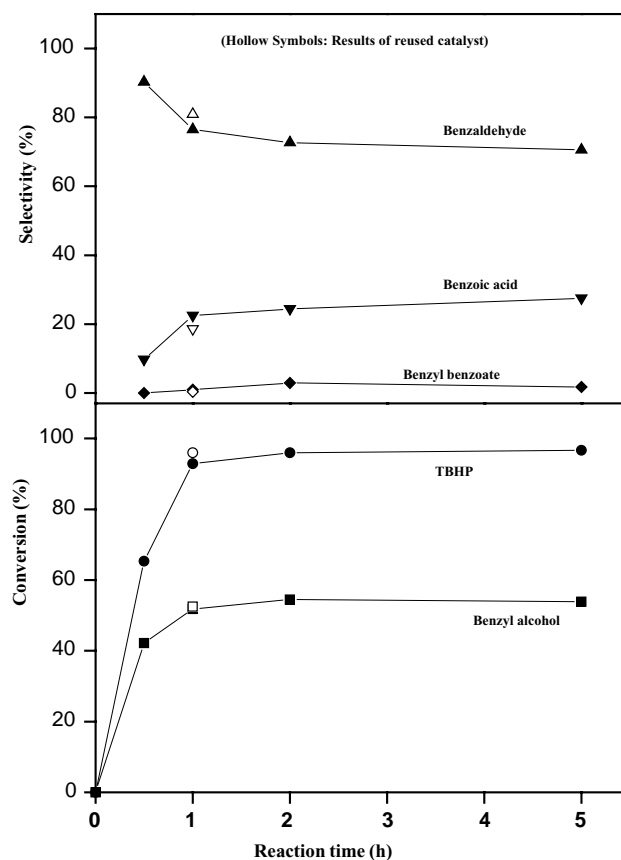
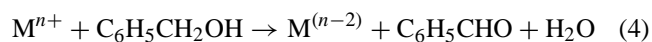


Fig. 8. Dependence on the reaction time of the conversion and product selectivity in the oxidation of benzaldehyde over the Mn-Fe-HD (under reflux).

of benzyl alcohol and/or TBHP. However, the oxidation of benzyl alcohol by TBHP over the transition metal containing LDH and/or HD catalysts is expected to involve a redox mechanism, similar to that described earlier [16], involving following two reactions:



where, M = transition metal (e.g. Mn, Cr, Co, etc.) in the catalyst.

The Eq. (4) is expected to be the rate-controlling step in the oxidation.

4. Conclusions

Among the transition metal (Co-Al, Ni-Al, Zn-Al, Mg-Fe, Mn-Fe, Co-Fe, Ni-Fe, Zn-Fe, Mg-Cr, Mn-Cr, Co-Cr, Ni-Cr, Zn-Cr, and Cu-Cr) containing layered double hydroxides and/or mixed hydroxides, the Mn, Co, Cu, and Zn-Cr containing LDH and/or HD are promising the solvent-free liquid-phase oxidation of benzyl alcohol to benzaldehyde. The Co containing LDH catalysts, however, show higher activity but lower benzaldehyde selectivity.

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