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Solvent-free selective oxidation of benzyl alcohol and benzaldehyde by *tert*-butyl hydroperoxide using MnO_4^--exchanged Mg–Al–hydrotalcite catalysts

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MnO_4^- (0.4 mmol/g)-exchanged Mg–Al–hydrotalcite is an active and highly selective catalyst for the oxidation of benzyl alcohol to benzaldehyde by *tert*-butyl hydroperoxide under reflux in the absence of solvent. It also shows high activity for the oxidation of benzaldehyde to benzoic acid. The higher the Mg/Al ratio, the higher is the catalytic activity (in both the reactions) and basicity of the hydrotalcite catalyst.

KEY WORDS: oxidation; benzyl alcohol; benzaldehyde; MnO_4^--exchanged Mg–Al–hydrotalcite.

1. Introduction

Selective oxidation of benzyl alcohol to benzaldehyde is a practically important reaction for the production of chlorine-free benzaldehyde required in the perfumery and pharmaceutical industries. Several studies have been reported on the catalytic vapor-phase oxidation of benzyl alcohol to benzaldehyde [1]. However, in the vapor-phase oxidation, carbon oxides are also formed, leading to very significant carbon loss. Liquid-phase oxidation of benzyl alcohol to benzaldehyde is therefore preferable. A few studies have been reported on the liquid-phase oxidation of benzyl alcohol by oxygen or aqueous H_2O_2 in the presence of different solvents, using Pd/C [2], Pd–Ag/pumice [3], heteropoly acid [4] and Ni–Al–hydrotalcite [5] catalysts.

Recently, Kotai *et al.* [6] reported the formation of benzaldehyde, ammonia and MnO_2 by the stoichiometric reaction between ammonium permanganate and benzyl alcohol at room temperature. The oxidation of benzyl alcohol to benzaldehyde and benzoic acid using stoichiometric or excess amounts of potassium permanganate in aqueous acidic medium has also been reported [7]. These stoichiometric reactions have severe limitations, such as the formation of large amounts of liquid and solid wastes and the corrosive nature of the acidic reaction medium. It is of both scientific and practical interest to use permanganate in catalytic amounts for the oxidation of benzyl alcohol to benzaldehyde, using an oxidizing agent such as H_2O_2 or organic hydroperoxides. We report here that benzyl alcohol can be selectively oxidized to benzaldehyde by *tert*-butyl hydroperoxide (TBHP) without any solvent using an MnO_4^--exchanged Mg–Al–hydrotalcite catalyst, which can be separated by simple filtration and reused in the reaction several times. This catalyst is also useful for the selective oxidation of benzaldehyde to benzoic acid.

2. Experimental

The MnO_4^--exchanged Mg–Al–hydrotalcite catalysts [with Mg/Al ratios of 2, 3, 5 and 10 but same MnO_4^- loading (0.42 ± 0.01 mmol/g)] were prepared as follows. Mg–Al–hydrotalcite was synthesized by adding two aqueous solutions, one containing magnesium nitrate and aluminum nitrate with the required Mg/Al ratio and the other containing potassium hydroxide and potassium carbonate, dropwise into a flask containing deionized water under vigorous stirring at 40 °C, while maintaining a constant pH of 11–12, by a procedure similar to that described earlier [8]. The resulting white gel was aged for 0.5 h and then filtered, thoroughly washed and dried at 80 °C in a vacuum oven for 12 h. The surface area of the resulting Mg–Al–hydrotalcite with Mg/Al ratios of 2, 3, 5 and 10 was 60.3, 57.8, 76.8 and 70.7 m^2/g, respectively. The crystal structure of these materials as hydrotalcite was confirmed by XRD. In these hydrotalcites, MnO_4^- anions were incorporated as follows. The resulting Mg–Al–hydrotalcite was powdered and calcined at 600 °C for 4 h. The calcined mass (13 g) was then treated under stirring with an aqueous solution of $KMnO_4$ (1.58 g in 100 ml of water) at 80 °C for 24 h. The resulting MnO_4^--exchanged Mg–Al–hydrotalcite was filtered and washed with hot deionized water and then dried at 80 °C in a vacuum

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oven. The amount of MnO_4^- exchanged was determined by measuring the amount of $KMnO_4$ present in the filtrate and washings. Before use, the MnO_4^--exchanged Mg–Al–hydrotalcite catalysts were heated in an air oven at 200 °C for 2 h. The Mg–Al–hydrotalcites and MnO_4^--exchanged Mg-Al-hydrotalcite catalysts were characterized for their crystalline structure by XRD (using a Philips 1730 series) diffractometer and Cu Kα radiation), for their surface area by the single-point N_2 adsorption method (using a surface area analyzer; Quanta Chrome, USA) and for their basicity by measuring the pH of their suspension in water (0.15 g of catalyst in 10 ml of deionized water at room temperature) and also for their concentration of carbonate anions (by treating the catalyst with 4 N HNO_3 and measuring quantitatively the CO_2 evolved).

The catalytic oxidation of benzyl alcohol was carried out in a magnetically stirred round-bottomed flask (capacity 25 cm^3), provided with a mercury thermometer for measuring the reaction temperature and reflux condenser, under the following reaction conditions: reaction mixture, 52 mmol benzyl alcohol + 78 mmol TBHP (70% TBHP in water) + 0.5 g catalyst; temperature, 92–95 °C (under reflux at a bath temperature of 97 ° C); and reaction time, 1–10 h. The reaction products were analyzed by gas chromatography with flame ionization detection, using an SE-30 column and N_2 as carrier gas.

3. Results and discussion

3.1. Catalyst characterization

Data on the characterization of the MnO_4^--exchanged Mg–Al–hydrotalcite catalysts with different Mg/Al ratios are presented in table 1. The large amount of CO_2 evolved in the acidification of the catalysts indicates that the anions present in the hydrotalcite catalysts other than MnO_4^- anions are carbonated anions. The pH (>7.0) of the catalyst–water suspension is indicative of the basic nature of the catalysts. The increase in pH with increasing Mg/Al ratio suggests that the basicity of the catalyst is increased with increasing of Mg/Al ratio. The surface area of the catalyst, however, decreases with increasing Mg/Al ratio.

3.2. Oxidation of benzyl alcohol

Results showing the performance of the MnO_4^--exchanged Mg–Al–hydrotalcite catalysts in the oxidation of benzyl alcohol to benzaldehyde by TBHP are given in table 2 and figures 1 and 2. From these results, the following important observations can be made.

MnO_4^--exchanged Mg–Al–hydrotalcite is an active catalyst for the selective oxidation of benzyl alcohol to benzaldehyde in the absence of solvent. Its catalytic activity and selectivity are much higher than those of $KMnO_4$ alone (i.e. when $KMnO_4$ in the form of fine particles was used instead of the hydrotalcite catalyst). This is as expected, mostly because of the highly dispersed MnO_4^- anions in the hydrotalcite catalysts.

It is interesting that, although the concentrations of MnO_4^- anions in the hydrotalcite catalysts are nearly the same, the activity of the catalyst showed a strong dependence upon its Mg/Al ratio: the activity increased with increasing Mg/Al ratio. This may be attributed to the different basicities of the hydrotalcite catalysts; the higher the basicity, the higher is the catalytic activity (tables 1 and 2). It is also interesting that the conversion of benzyl alcohol in the absence of catalyst is higher (14.3%) than that (4.7%) in the presence of the Mg–Al–hydrotalcite (Mg/Al = 10) without containing MnO_4^- anions. Thus, in the absence of MnO_4^- anions, the hydrotalcite inhibits the oxidation reaction, probably because of the termination of radical intermediates (formed in the homogeneous oxidation) by the hydrotalcites.

From the observed products, the consecutive reactions involved in the benzyl alcohol oxidation are as follows:

$$\text{Ph-CH}_2\text{OH} \xrightarrow{\text{TBHP}} \text{Ph-CHO} \xrightarrow{\text{TBHP}} \text{Ph-COOH} \xrightarrow{\text{Ph-CH}_2\text{OH}} \text{Ph-COOCH}_2\text{-Ph} \qquad (1)$$

where Ph = C_6H_5.

Table 1
Characterization of MnO_4^--exchanged Mg–Al–hydrotalcite catalysts with different Mg/Al ratios

Mg/Al ratio	Concentration of MnO_4^- anions (mmol/g)	XRD phase[a]	Surface area (m^2/g)	CO_2 evolved in the acid treatment (mmol/g)	pH of the suspension of catalyst in water
2.0	0.42	HT	36.3	2.15	9.3
3.0	0.40	HT	31.5	1.74	9.8
5.0	0.41	HT	29.1	1.29	10.0
10.0	0.40	HT	25.9	0.84	10.4

[a] HT = hydrotalcite phase.

Table 2

Oxidation of benzyl alcohol to benzaldehyde by TBHP over MnO_4^--exchanged Mg–Al–hydrotalcite with different Mg/Al ratios and $KMnO_4$ [reaction conditions: reaction mixture, 52 mmol benzyl alcohol + 78 mmol TBHP + 0.5 g catalyst; temperature, under reflux (bath temperature, 97 °C); reaction time, 5 h]

Mg/Al ratio	Conversion of benzyl alcohol (%)	Selectivity (%)		
		Benzaldehyde	Benzoic acid	Benzyl benzoate
2	35.2	99.8	0.2	0.0
3	37.4	98.6	0.1	1.3
3[a]	29.5	99.5	0.05	0.5
5	45.3	98.4	0.04	1.5
10	50.2	99.7	0.3	0.0
10[b]	4.7	100	0.0	0.0
$KMnO_4$[c]	28.5	84.4	14.4	1.2
No catalyst	14.3[d]	99.0	1.0	0.0

[a] MnO_4^--exchanged Mg–Al–hydrotalcite (Mg/Al = 3) was obtained by directly exchanging the Mg–Al–hydrotalcite with $KMnO_4$ solution under identical conditions (amount of MnO_4^- exchanged = 0.104 mmol/g).

[b] Mg–Al–hydrotalcite (Mg/Al = 10) without MnO_4^- anions.

[c] Fine particles of $KMnO_4$ equivalent to that present in the MnO_4^--exchanged Mg–Al–hydrotalcite catalysts (the reaction mixture was colorless).

[d] Conversion due to non-catalytic homogeneous reaction.

It is also interesting (see table 2) that the direct exchange of MnO_4^- anions with Mg–Al–hydrotalcite leads to a less active catalyst than that obtained from the thermally decomposed hydrotalcite (table 2), using its memory effect [9].

The results in figure 1 clearly show that the benzyl alcohol oxidation reaction is a heterogeneous reaction catalyzed by the solid catalyst. In the presence of the hydrotalcite solid catalyst the benzyl alcohol conversion is increased continuously without a significant change in the product selectivity with increasing reaction period. However, when the solid catalyst was removed from the reaction mixture after a reaction period of 1 h, the increase in conversion with reaction time was very small but there was a significant decrease and increase in the selectivity for benzaldehyde and benzoic acid, respectively. The small increase in the benzyl alcohol conversion is as expected because of the non-catalytic oxidation.

In order to test the catalyst reusability, the hydrotalcite catalyst (Mg/Al = 10) was reused in the benzyl alcohol oxidation several times. The results showing the reusability of the catalyst are presented in figure 2. It is interesting that the catalyst performance, particularly the benzyl alcohol conversion, is increased significantly after the first use of the catalyst. Further work is necessary to understand why this is so.

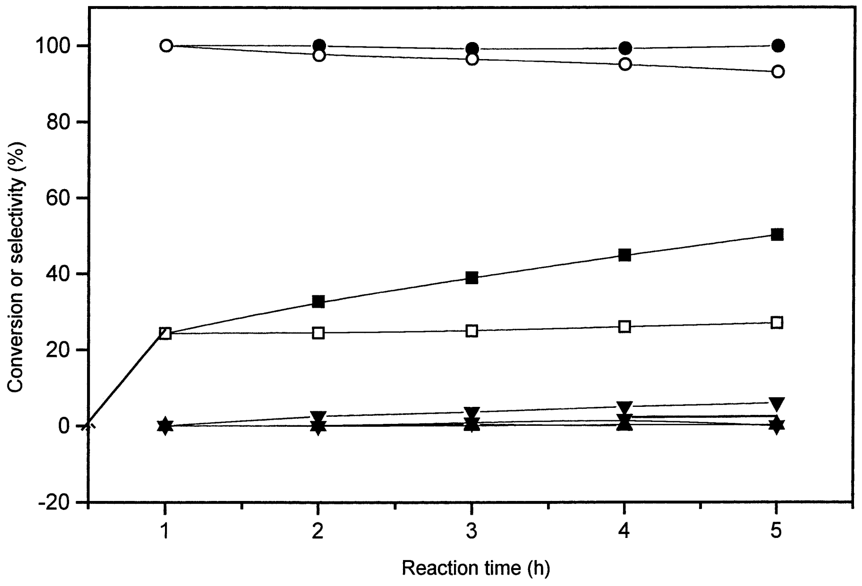

Figure 1. Variation of conversion and product selectivity with the reaction time in the oxidation of benzyl alcohol over MnO_4^--exchanged Mg–Al–hydrotalcite (Mg/Al = 10) catalyst. Solid symbols, data in the presence of solid catalyst throughout the reaction for 5 h; open symbols, data when the solid catalyst was removed from the reaction mixture after the reaction period of 1 h. ■, □, conversion of benzyl alcohol; ●, ○, selectivity for benzaldehyde; ▲, selectivity for benzoic acid; ▼, selectivity for benzyl benzoate.

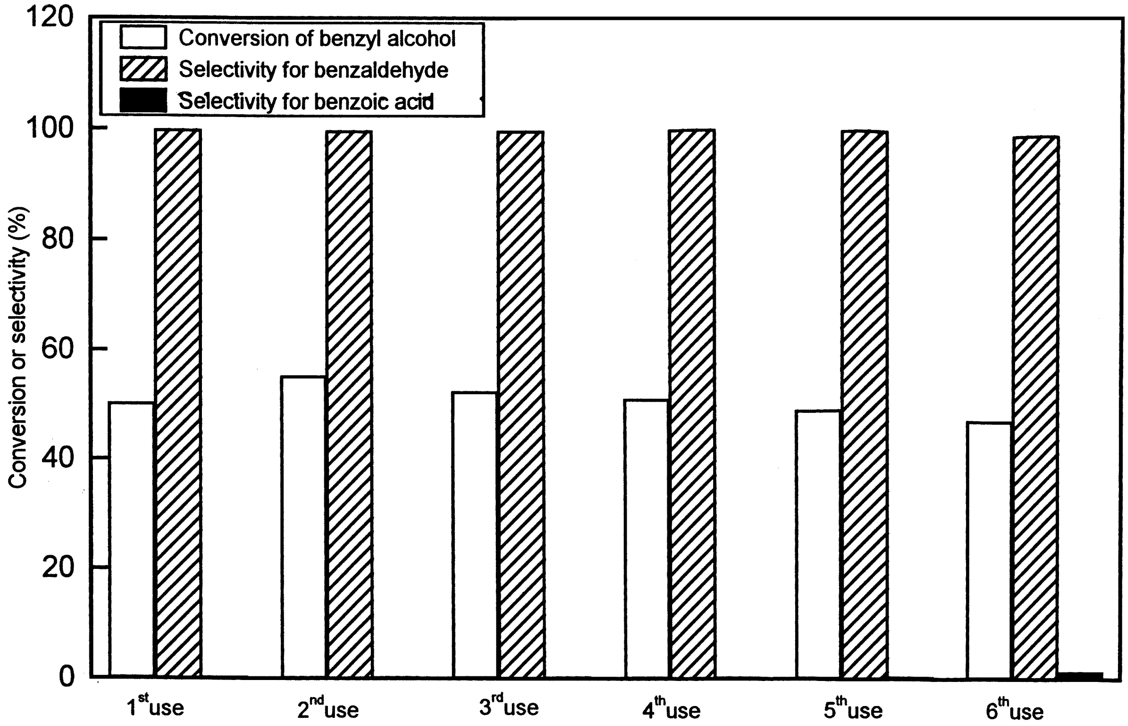

Figure 2. Reusability of the MnO_4^--exchanged Mg–Al–hydrotalcite (Mg/Al = 10) catalyst in the oxidation of benzyl alcohol. Reaction period = 5 h.

3.3. Oxidation of benzaldehyde

Results showing the selective oxidation of benzaldehyde to benzoic acid by TBHP over the MnO_4^--exchanged hydrotalcites with different Mg/Al ratios are given in table 3. As in benzyl alcohol oxidation, in this case also the conversion is increased with increasing Mg/Al ratio, and there was no formation of products other than benzoic acid. The hydrotalcite catalyst, particularly that with Mg/Al = 10, shows high activity for the selective oxidation of benzaldehyde to benzoic acid.

3.4. Redox reaction mechanism

When a mixture of 0.2 ml of benzyl alcohol, 6 ml of toluene (solvent) and 1.0 g of MnO_4^--exchanged hydrotalcite (Mg/Al = 10) catalyst was refluxed in the absence of O_2 and TBHP for 5 h, there was a significant conversion of benzyl alcohol (7.5%) to benzaldehyde. This conversion is expected mainly owing to the stoichiometric liquid–solid reaction between the MnO_4^- anions of the catalyst and the substrate (benzyl alcohol). This indicates a high possibility of the operation of a redox mechanism in the above oxidation reactions in the presence of TBHP, involving the following redox reactions:

$$\mathrm{Mn(VII)O_4^-} + \mathrm{C_6H_5CH_2OH} \longrightarrow \mathrm{Mn(V)O_3^-} + \mathrm{C_6H_5CHO} + \mathrm{H_2O} \quad (2)$$

$$\mathrm{Mn(V)O_3^-} + \mathrm{(CH_3)_3COOH} \longrightarrow \mathrm{Mn(VII)O_4^-} + \mathrm{(CH_3)_3COH}. \quad (3)$$

Reaction (2) is expected to be the rate-limiting step in the oxidation. The basic sites of the catalyst may be responsible for the activation of benzyl alcohol through partial abstraction of H from its $-CH_2-$ group. Further detailed study is necessary to understand the oxidation reaction mechanism.

Table 3
Oxidation of benzaldehyde to benzoic acid by TBHP over MnO_4^--exchanged Mg–Al–hydrotalcite with different Mg/Al ratios [reaction conditions: reaction mixture, 50 mmol benzaldehyde + 78 mmol TBHP + 0.5 g catalyst; temperature, under reflux (bath temperature, 97 °C); reaction time, 5 h]

Mg/Al ratio	Conversion of benzaldehyde (%)	Selectivity for benzoic acid (%)
2	84.2	100
3	92.7	100
5	94.5	100
10	99.4	100

4. Conclusions

MnO_4^--exchanged Mg–Al–hydrotalcites (Mg/Al = 2–10) show high activity and selectivity in the oxidations of benzyl alcohol to benzaldehyde and benzaldehyde to benzoic acid by TBHP in the absence of solvent. The oxidation involves both non-catalytic (homogeneous) and catalytic reactions. The catalytic reactions are confirmed to be heterogeneous and their contribution to the oxidation is much higher than that of the homogeneous non-catalytic oxidation reaction. A redox mechanism involving reduction of Mn(VII) to Mn(V) and oxidation of Mn(V) to Mn(VII) by TBHP seems to be operative in the catalytic oxidation process.

References

[1] (a) S. Tsuruya, Y. Okamoto and T. Kuwada, J. Catal. 56 (1979) 52; (b) S. Tsuruya, H. Miyamoto, T. Sakae and M. Masai, J. Catal. 64 (1980) 260; (c) S.J. Kulkarni, R. Ramachandra Rao, M. Subrahmanyam, A.V. Rama Rao, A. Sarkany and L Guczi, Appl. Catal. A 139 (1996) 59; (d) M. Arai, S. Nishiyama, S. Tsuruya and M. Masai, J. Chem. Soc., Faraday Trans. 92 (1996) 2631; (e) H. Hayashibara, S. Nishiyama, S. Tsuruya and M. Masai, J. Catal. 153 (1995) 254; (f) S. Sueto, S. Nishiyama, S. Tsuruya and M. Masai, J. Chem. Soc., Faraday Trans. 93 (1997) 659; (g) R. Sumathi, K. Johnson, B. Vishwanathan and T.K. Varadarajan, Appl. Catal. A 172 (1998) 15; (h) N. Idaka, S. Nishiyama and S. Tsuruya, Phys. Chem. Chem. Phys. 3 (2001) 1918.

[2] N.S. Bijlani and S.B. Chandalia, Indian Chem. Eng. 23 (1981) 44.

[3] L.F. Liotta, A.M. Venezia, G. Deganello, A. Longo, A. Martorana, Z. Schay and L. Guczi, Catal. Today 66 (2001) 271.

[4] G.D. Yadav and C.K. Mistry, J. Mol. Catal. A 172 (2001) 135.

[5] B.M. Choudary, M. Lakshmi Kantam, A. Rahman, Ch. Venkat Reddy and K. Koteswara Rao, Angew. Chem., Int. Ed. Engl. 40 (2001) 763.

[6] L. Kotai, B. Kazinczy, A. Keszler, H. Sandor, I. Gacs and K. Banerji, Z. Naturforsch., Teil B 56 (2001) 823.

[7] A. Corma, V. Lambies, F.V. Melo and J. Palou, Ann. Quim. Ser. A 76 (1980) 304.

[8] E. Lopez-Salinas, M. Garcia-Sanchez, M.L. Ramon-Garcia and I. Schifter, J. Porous Mater. 3(1996) 169.

[9] F. Cavani, F. Trifiro and A. Vaccari, Catal. Today 11 (1991) 173.