

Solvent-free oxidation of aldehydes to acids by TBHP using environmental-friendly MnO_4^{-1} -exchanged Mg-Al hydrotalcite catalyst

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Abstract. A number of hydrotalcite (Mg–Al, Mn–Al, Co–Al, Ni–Al, Mg–Fe, Mg–Cr and Cu–Al) catalysts, with or without MnO_4^{-1} -exchange, were evaluated for their performance in the solvent-free oxidation of benzaldehyde to benzoic acid by tert-butyl hydroperoxide under reflux in the absence of any solvent. The MnO_4^{-1} -exchanged Mg–Al-hydrotalcite (Mg/Al = 10) showed high activity in the oxidation of different aromatic and aliphatic aldehydes to their corresponding acids and also showed excellent reusability in the oxidation process which is environmental-friendly.

Keywords. Aldehyde; acid; oxidation; TBHP; MnO_4^{-1} -exchanged Mg–Al-hydrotalcite catalyst.

1. Introduction

Oxidation of aldehyde to acid is one of the frequently used transformations in organic synthesis. It is one of the most important steps in the synthesis of pharmaceutically important compounds like α -arylpropionic acids e.g., ibuprofen, flurbiprofen, etc. These are known to be good antiinflammatory agents.¹

Aldehydes can be oxidized to carboxylic acids by atmospheric oxygen but with very low product yield.² Several oxidizing reagents have been reported for obtaining good product yields in the oxidation of aldehydes. However, the commonly used oxidants like chromic acid, potassium permanganate in acidic, basic and neutral solution, bromine and nitric acid are not suitable for the large scale preparation of carboxylic acid because of the formation of hazardous waste. Balicki Roman³ achieved mild oxidation of aromatic and heteroaromatic aldehydes to the corresponding acids using urea hydrogen peroxide in formic acid. Howarth⁴ reported the oxidation of aromatic aldehydes, containing both electron donating and electron withdrawing substituents at *para* position by oxygen at atmospheric pressure using the $[\text{Ni}(\text{ace})_2]$ catalyst in an ionic liquid. A few studies have been reported on the oxidation of benzaldehyde using homogeneous or heterogeneous catalysts, such as $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$,⁵ Amberlite IR-120(acidic form)⁶ and cerium(IV) sulfate in aqueous sulfuric acid.⁷ A number of studies

have also been reported on the oxidation of benzaldehyde by quaternary ammonium permanganate,⁸ KMnO_4 in aqueous solutions of surfactant⁹ and basic permanganate¹⁰ in stoichiometric amounts. The stoichiometric reactions have severe limitations, such as the formation of large amounts of liquid and solid wastes and the corrosive nature of the reaction medium. It is practically very interesting and important to use permanganate in catalytic amounts for the oxidation of different aldehydes to their corresponding acids without using any solvent to make the aldehyde oxidation environmentally benign. We report here that different aromatic and aliphatic aldehydes can be selectively oxidized to their corresponding acid with high yields by tert-butyl hydroperoxide (TBHP) using MnO_4^{-1} -exchanged-hydrotalcite as a catalyst in the absence of any solvent. The catalyst can be easily separated by simple filtration and reused in the reaction several times.

2. Experimental

The hydrotalcite catalysts were characterized for their crystalline structure by XRD (using a Philips 1730 series) diffractometer and CuK_α radiations), 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 cat-

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alyst with 4N HNO₃ and measuring quantitatively the evolved CO₂).

2.1 General procedure for catalyst preparation

The 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, drop-wise 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.¹¹ 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 preparation and characterization of other hydrotalcites containing different divalent [M (II)] and trivalent [M (III)] metallic elements (viz. Mn–Al, Co–Al, Ni–Al, Mg–Fe, Mg–Cr and Cu–Al) were described earlier and their crystal structure as hydrotalcite was confirmed by XRD.^{11–13} In these hydrotalcites, MnO₄^{−1} anions were incorporated by the procedure described earlier.^{11,14}

2.2 General procedure for oxidation reaction

The catalytic oxidation of benzaldehyde was carried out in a magnetically stirred round bottom flask (capacity: 25 cm³), provided with a mercury thermometer for measuring the reaction temperature, in the absence of any solvent, at the following reaction conditions: reaction mixture = 10 mmol aldehyde + 15 mmol TBHP (70% TBHP in water) + 0.1 g catalyst, temperature = under reflux (bath temperature of 97°C), reaction time = 1–10 h. The reaction was monitored by TLC. After completion of the reaction, the product was isolated and purified using column chromatography. The oxidation of substituted aromatic and aliphatic aldehyde was also carried out as above. All the products were known compounds and were characterized by their melting point and/or NMR spectroscopy.

3. Results and discussion

Results showed the performance of the different hydrotalcite (with or without MnO₄^{−1}-exchange) catalysts in the oxidation of benzaldehyde to benzoic acid by

Table 1. Performance of different catalysts in the oxidation of benzaldehyde to benzoic acid by TBHP (reaction conditions: benzaldehyde = 10 mmol, TBHP = 15 mmol, catalyst = 0.1 g, bath temperature = 97°C).

No.	Catalyst	Reaction time (h)	Conversion of benzaldehyde (%)
1	MnO ₄ ^{−1} (1.55 mmol/g) / Ni-Al HT (Ni/Al = 3)	5	90.5
2	MnO ₄ ^{−1} (0.94 mmol/g) / Ni-Al HT (Ni/Al = 10)	3	92.7
3	MnO ₄ ^{−1} (0.42 mmol/g) / Cu-Al HT (Cu/Al = 3)	4	81.0
4	MnO ₄ ^{−1} (0.77 mmol/g) / Mn-Al HT (Mn/Al = 3)	4	90.4
5	MnO ₄ ^{−1} (0.23 mmol/g) / Co-Al HT (Co/Al = 3)	4	90.6
6	MnO ₄ ^{−1} (0.14 mmol/g) / Co-Al HT (Co/Al = 10)	4	95.5
7	MnO ₄ ^{−1} (2.11 mmol/g) / Mg-Cr HT (Mg/Cr = 3)	4	90.9
8	MnO ₄ ^{−1} (0.77 mmol/g) / Mg-Fe HT (Mg/Fe = 3)	4	87.8
9	MnO ₄ ^{−1} (0.71 mmol/g) / Mg-Fe HT (Mg/Fe = 10)	4	99.0
10	MnO ₄ ^{−1} (0.80 mmol/g) / Mg-Al HT (Mg/Al = 3)	3	94.2
11	MnO ₄ ^{−1} (0.40 mmol/g) / Mg-Al HT (Mg/Al = 10)	3	99.9
12	Mg-Al-HT (Mg/Al = 10)	4	11
13	Ni-Al-HT (Ni/Al = 10)	4	20
14	Co-Al-HT (Co/Al = 10)	4	23
15	Mg-Fe-HT (Mg/Fe = 10)	4	12
16	Co-Al-HT (Co/Al = 3)	4	19
17	nil	4	11
18	MnO ₄ ^{−1} (0.40 mmol/g) / Mg-Al HT (Mg/Al = 10) ^a	3	99.5
19	MnO ₄ ^{−1} (0.40 mmol/g) / Mg-Al HT (Mg/Al = 10)	10	60 ^b
20	KMnO ₄ ^c	3	50.5

^a5th reuse of the catalyst. ^bWhen O₂ was used as the oxidizing agent, ^cAmount used was equivalent to that of MnO₄^{−1} (0.40 mmol/g) / Mg-Al HT (Mg/Al = 10) catalyst

TBHP in the absence of any solvent (table 1). No product other than benzoic acid was observed. The MnO_4^- -exchanged hydrotalcites were characterized for their XRD phases, $d(001)$ spacing and pH of water slurry (table 2). The characterization of the hydrotalcite catalysts before their MnO_4^- -exchange was reported in our earlier studies.^{11–14} From these results, the following important observations are made.

- (i) The hydrotalcites without MnO_4^- -exchange showed very poor catalytic activity in the oxidation. However, after the MnO_4^- -exchange, their activity was drastically increased (from 11–23% to 81–99.9% conversion).
- (ii) The Mg–Al–HT (Mg/Al = 10) showed a little or no activity in the oxidation (the benzaldehyde conversion is almost the same as that observed in the absence of any catalyst). However, after the MnO_4^- -exchange, it showed highest activity (99.9% conversion) in the oxidation. The catalyst also showed excellent reusability in the reaction; after its fifth reuse, it showed no significant loss in its activity (entry no. 18). Other MnO_4^- -exchanged hydrotalcites with Ni/Al, Co/Al and Mg/Fe = 10 (entry nos. 2, 6 and 9) also showed good activity (92.7, 95.5 and 99.0%, respectively). It is interesting to note that all these MnO_4^- -exchanged hydrotalcites showed better activity when their divalent/trivalent metal ratio was higher. This may be attributed to their higher basicity.^{11–14}
- (iii) When KMnO_4 [equivalent to the MnO_4^- ions present in the MnO_4^- -exchanged Mg–Al–HT (Mg/Al = 10)] was used as a homogeneous catalyst in the reaction, the conversion under the similar reaction conditions was 50.5%; which is much lower than that obtained using the different MnO_4^- -exchanged hydrotalcites. This reveals that the catalytic activity of MnO_4^- ions increases appreciably after their immobilization in the hydro-

talcsites. Because of the immobilization of the active catalyst component, the separation/removal of the catalyst from the reaction mixture is easy, simply by filtration. Moreover, the catalyst can be reused in the reaction several times without a significant loss in its activity.

- (iv) The MnO_4^- -exchanged Mg–Al–HT (Mg/Al = 10) also showed good oxidation activity when molecular oxygen is used as the oxidizing agent (entry no.19). However, in this case, the reaction was found to be relatively quite slow.

The XRD analysis of all the catalysts (entry nos. 1–16 in table 1) showed the presence of pure hydrotalcite phase in all the catalysts except for the MnO_4^- -exchanged Cu–Al–HT (which was found to contain hydrotalcite phase along with copper hydroxide and aluminum hydroxide phases).

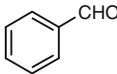
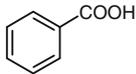
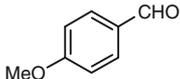
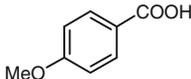
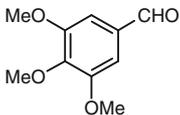
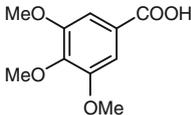
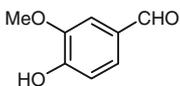
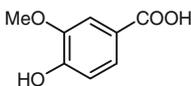
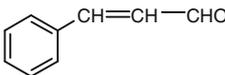
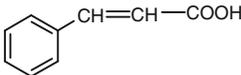
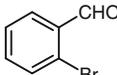
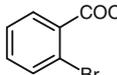
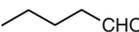
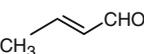
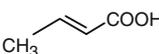
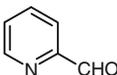
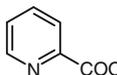
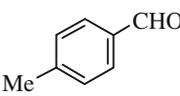
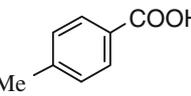
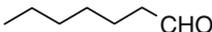
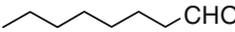
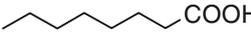
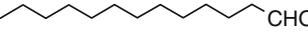
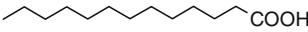
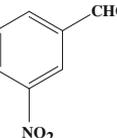
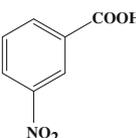
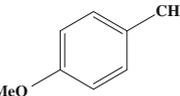
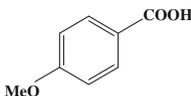
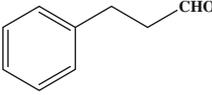
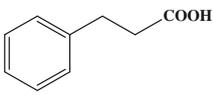
The surface area of the catalyst before use was $26\text{ m}^2/\text{g}$. After the use in the oxidation (entry no.18), the surface area of the catalyst remained almost the same. Also the concentration of Mn in the catalyst (0.40 mmol/g) was not changed. Moreover, the XRD spectra for the MnO_4^- -exchanged Mg–Al–HT (before and after its 5th reuse in the benzaldehyde oxidation reaction) were found to be almost similar. These facts revealed that, after its 5th use in the oxidation, the catalyst retained its hydrotalcite structure and also had high stability during the oxidation.

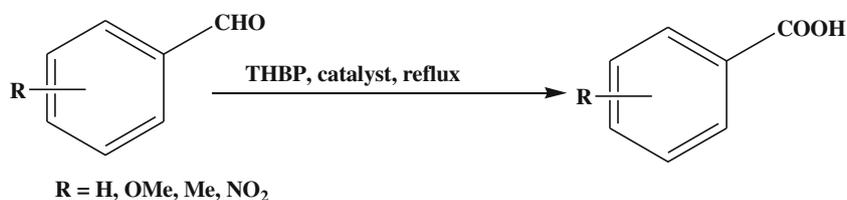
Since the MnO_4^- -exchanged Mg–Al–HT (Mg/Al = 10) showed the best performance in the benzaldehyde to benzoic acid oxidation, further work on the oxidation of other aromatic and aliphatic aldehydes by TBHP to their corresponding acids (scheme 1) in the absence of any solvent was carried out using this catalyst. The results are presented in table 3. In this case, the product was isolated from the reaction mixture and purified using column chromatography. The results in table 3 reveal that the catalyst shows high activity even in the

Table 2. Characterization of different MnO_4^- -exchanged hydrotalcite catalysts.

Catalyst	XRD phases	$d(001)$ spacing (nm)	pH of water slurry
MnO_4^- (1.55 mmol/g)/ Ni-Al HT (Ni/Al = 3)	Pure HT	0.780	8.0
MnO_4^- (0.94 mmol/g)/ Ni-Al HT (Ni/Al = 10)	Pure HT	0.784	8.0
MnO_4^- (0.23 mmol/g)/ Co-Al HT (Co/Al = 3)	Pure HT	0.752	7.8
MnO_4^- (0.14 mmol/g)/ Co-Al HT (Co/Al = 10)	Pure HT	0.756	7.8
MnO_4^- (0.77 mmol/g)/ Mg-Fe HT (Mg/Fe = 3)	Pure HT	0.764	9.6
MnO_4^- (0.71 mmol/g)/ Mg-Fe HT (Mg/Fe = 10)	Pure HT	0.769	9.6
MnO_4^- (0.80 mmol/g)/ Mg-Al HT (Mg/Al = 3)	Pure HT	0.765	9.7
MnO_4^- (0.40 mmol/g)/ Mg-Al HT (Mg/Al = 10)	Pure HT	0.767	10.5

Table 3. Performance of the MnO_4^- -exchanged Mg-Al-hydrotalcite catalyst in the oxidation of various aldehydes to corresponding acids by TBHP (reaction conditions: aldehyde = 10 mmol, TBHP = 15 mmol, catalyst = 0.1 g, bath temperature = 97°C).

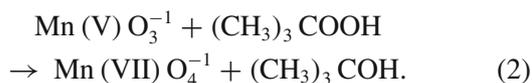
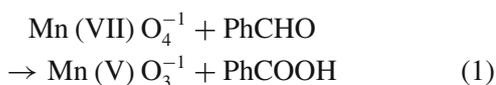
Entry	Aldehyde	Reaction time (h)	Product	Melting point of product ($^\circ\text{C}$)	Isolated product yield (%)
1		3		121	95
2		3		183	87
3		3		170	87
4		3		212	86
5		4		133	90
6		5		150	80
7	$\text{CH}_3\text{.CH}_2\text{.CHO}$	1	$\text{CH}_3\text{.CH}_2\text{.COOH}$	Liq.	87
8		2		Liq	87
9		1		73	86
10		3		192	80
11		2		172	88
12		2		Liq	85
13		2		Liq	86
14		2		Liq	85
15		5		138	79
16		2		182	85
17		4		Liq	85



Scheme 1. Oxidation of various aldehydes to acids.

oxidation of different aromatic and aliphatic aldehydes to their corresponding acids in the absence of any solvent. A small decrease in the product yield is, however, observed because of the substitution in aromatic ring of the aromatic aldehydes.

When benzaldehyde was refluxed with the MnO_4^- -exchanged hydrotalcites catalyst under N_2 atmosphere (in the absence of TBHP and air), an appreciable amount of benzoic acid was formed. This indicates that the catalytic aldehyde to acid oxidation by TBHP mostly involves a redox mechanism with following redox reactions:



A side reaction involving a catalytic decomposition of TBHP to *t*-butanol and oxygen is also expected to occur simultaneously with the redox reactions. Reaction (1) is, however, expected to be the rate-limiting step in the aldehyde oxidation.

4. Conclusions

Both the hydrotalcites (viz. Mg–Al–HT, Ni–Al–HT, Cu–Al–HT, Co–Al–HT, Mn–Al–HT, Mg–Cr–HT and Mg–Fe–HT) and KMnO_4 alone show poor catalytic activity in the solvent-free oxidation of benzaldehyde to benzoic acid by TBHP. However, when the MnO_4^- anions are immobilized in the hydrotalcites through anion exchange, the resulting MnO_4^- -exchanged hydrotalcites show high catalytic activity in the oxidation. The MnO_4^- -exchanged Mg–Al–HT (Mg/Al = 10) showed highest activity in the oxi-

dation. It also showed high activity for the solvent-free oxidation of different aromatic and aliphatic aldehydes to their corresponding acids. This catalyst is environmental-friendly because of its excellent reusability in the oxidation and operation in the absence of any solvent. The oxidation over this catalyst most probably involves redox mechanism.

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