Available online at www.sciencedirect.com
SCIENCE DIRECT®
ELSEVIER
Journal of Catalysis 227 (2004) 257–261
JOURNAL OF CATALYSIS
www.elsevier.com/locate/jcat

Research Note

$MnO_4{}^{-1}$ exchanged Mg–Al hydrotalcite: a stable and reusable/environmental-friendly catalyst for selective oxidation by oxygen of ethylbenzene to acetophenone and diphenylmethane to benzophenone

Vasant R. Choudhary [*], Jayant R. Indurkar, Vijay S. Narkhede, Rani Jha

Chemical Engineering and Process Development Division, National Chemical Laboratory, Pune-411008, India

Received 27 February 2004; revised 9 July 2004; accepted 16 July 2004

Abstract

The liquid-phase selective oxidation of a methylene group attached to an aromatic ring by molecular oxygen to a carbonyl group, using $MnO_4{}^{-1}$-exchanged Mg–Al hydrotalcite ($Mg/Al = 2–10$) has been investigated in the absence of solvent. The methylene-to-carbonyl group oxidation activity of the $MnO_4{}^{-1}$-exchanged hydrotalcite, as well as the H_2O_2 decomposition activity and basicity of Mg–Al hydrotalcite increased with increasing Mg/Al ratio of the catalyst. The $MnO_4{}^{-1}$-exchanged Mg–Al–hydrotalcite is a highly active and selective, stable, and reusable catalyst for the oxidation of ethylbenzene to acetophenone and diphenylmethane to benzophenone by molecular oxygen in the absence of solvent. The reaction catalyzed by this environmental-friendly catalyst is truly heterogeneous, without leaching of the active component(s) from the catalyst. The catalyst showed better performance after its first use in the oxidation of both ethylbenzene and diphenylmethane.

Keywords: Oxidation of ethylbenzene/diphenylmethane; Hydrotalcite catalyst; Acetophenone; Benzophenone

1. Introduction

Aromatic ketones, such as acetophenone and benzophenone, are important intermediates for perfumes, drugs, and pharmaceuticals. Production of these aromatic ketones by Friedel–Crafts acylation of aromatic compound by acid halide or acid anhydride, using a stoichiometric amount of anhydrous aluminum chloride or of a homogeneous acid catalyst, leads to the formation of a large volume of highly toxic and corrosive waste [1–3]. In the past, efforts have been made to produce aromatic ketones by oxidizing the methylene group attached to an aromatic ring using stoichiometric quantities of oxidizing agents, e.g., the oxidation of ethylbenzene to acetophenone by $KMnO_4$ [4], the oxidation of diphenylmethane to benzophenone by $KMnO_4$ [5], SeO_2 [6], or CrO_3–SiO_2 [7], and the oxidation of alkylarenes by $KMnO_4$ supported on Mont-K10 [8]. However, in these stoichiometric oxidation reactions, the waste produced is very large and, moreover, the separation of reactants and products from the reaction mixture is difficult. Acetophenone can also be produced by the liquid-phase oxidation of ethylbenzene by oxygen or air using homogeneous transition metal (viz. Co, Mn, Cu, or Fe) compounds as catalyst [2,9]. Although the metal compound in this process is used in catalytic amounts, the reaction conditions are harsh, the product selectivity is poor, often corrosive promoters like bromide anions are used along with the catalyst, the separation of catalyst from the reaction mixture is difficult, the catalyst cannot be reused, and also a lot of tarry waste is produced. It is, therefore, of great practical interest to develop a more efficient, easily separable, reusable, and environmental-friendly catalyst for the production of aromatic ketones. Processes

---

[*] Corresponding author. Fax: +91 20 25893041/25893355.
E-mail addresses: vrc@ems.ncl.res.in, vrc@che.ncl.res.in (V.R. Choudhary).

0021-9517/$ – see front matter © 2004 Elsevier Inc. All rights reserved.
doi:10.1016/j.jcat.2004.07.017

based on hydrocarbon oxidation particularly using molecular oxygen as an oxidizing agent are desirable [10].

Recently, $K_2Cr_2O_7$ supported on alumina [11] and Cr-MCM-41 or 48 [11] have been employed as heterogeneous catalysts for the oxidation by oxygen of ethylbenzene to acetophenone [12–14] and diphenylmethane to benzophenone [11]. However, the leaching of chromium from the catalyst during the reaction, the lengthy induction periods, and the rapid deactivation of the reused catalyst are serious problems [14–16]. For developing an environmental-friendly/green process for the production of aromatic ketones, it is necessary to have a nontoxic and reusable solid catalyst, which shows high activity and selectivity in the oxidation of ethylbenzene to acetophenone and diphenylmethane to benzophenone by molecular oxygen in the absence of any solvent and also without significant leaching of its components in the liquid reaction mixture. We report here that this goal can be achieved by using a MnO_4^{-1}-exchanged Mg–Al–hydrotalcite catalyst. This catalyst has high activity and selectivity and also has an excellent stability and reusability in the process. Moreover, the oxidation process catalyzed by this catalyst is solvent-free and also a truly heterogeneous one.

2. Experimental

The MnO_4^{-1}-exchanged Mg–Al hydrotalcite catalysts ($Mg/Al = 2–10$ and a MnO_4^{-1} loading of 0.41 ± 0.01 mmol/g) were prepared as follows. Mg–Al hydrotalcite ($Mg/Al = 2.0$, 3.0, 5.0, and 10), synthesized by a procedure similar to that described earlier [17], was powdered and calcined at 600 °C for 4 h. The calcined mass (10 g) was then treated under stirring with a 100 ml aqueous solution of $KMnO_4$ (1.22 g) at 80 °C for 24 h. The exchanged mass was filtered and washed with hot deionized water and then dried at 80 °C under vacuum. All the MnO_4^{-1} ions from the solution were utilized in the exchange for all the hydrotalcite samples. The other anions present in the exchanged hydrotalcites were mainly hydroxyl anions. Before use, the MnO_4^{-1}-exchanged Mg–Al hydrotalcite was heated in an air oven at 200 °C for 2 h. The hydrotalcite structure of the catalyst was confirmed by XRD. The basicity of the catalysts and hydrotalcites was studied by titrating them with nonaqueous benzoic acid using a phenolphthalein indicator ($pK_a = 9.3$) [18] and/or by measuring the pH of their suspension in water (0.15 g solid particles in 10 ml deionized water at 27 °C), as well as by thermal analysis and infrared spectroscopy.

The oxidation of the methylene group attached to the aromatic ring (viz. ethylbenzene, diphenylmethane, and propylbenzene) by pure O_2 in the absence of solvent was carried out in a magnetically stirred glass reactor (capacity $= 25\ cm^3$), provided with a mercury thermometer and reflux condenser, under the following reaction conditions: reaction mixture = 6 ml aromatic substrate +0.6 g catalyst, at a total pressure of 148 kPa, 130 °C, and a reaction time of 1 to 20 h. The concentration of Mn in the catalysts was the same and the exact loading of Mn per mole of substrate in the reaction was 0.005, 0.0057, and 0.0068 mol per mole of ethylbenzene, propylbenzene, and diphenylmethane, respectively. The reaction products were analyzed by gas chromatography with a thermal conductivity detector, using a SE-30 column (3 mm × 4 m) and hydrogen as carrier gas. Toluene was used as an internal standard and the mass balance in the reaction was above 95%.

The H_2O_2 decomposition over the catalysts was studied in a magnetically stirred glass reactor ($25\ cm^3$ capacity) at 27 °C by introducing 1 ml of 30% H_2O_2 aqueous solution in the reactor containing 0.1 g catalyst and 10 ml deionized water and measuring quantitatively the amount of O_2 evolved in the H_2O_2 decomposition reaction ($2H_2O_2 \rightarrow 2H_2O + O_2$), as a function of time.

3. Results and discussion

3.1. Catalyst characterization

XRD spectra of the Mg–Al–hydrotalcite catalyst, before and after the MnO_4^{-1} exchange, and also of the MnO_4^{-1}-exchanged Mg–Al–HT catalyst after the oxidation reactions are given in Fig. 1. After the MnO_4^{-1} exchange, the hydrotalcite structure remained intact (Figs. 1a and b). It even remained intact after the oxidation reaction (Figs. 1b–d).

The appearance of an IR band in the region 890–920 cm^{-1} after exchanging the hydrotalcite with aqueous $KMnO_4$ indicated the presence of MnO_4^{-1} anions in the MnO_4^{-1}-exchanged hydrotalcite catalysts [19]. When the MnO_4^{-1}-exchanged hydrotalcites were treated with an aqueous sodium carbonate solution, a quantitative replacement of the exchanged MnO_4^{-1} anions by carbonate anions was observed. These observations clearly show that, in the MnO_4^{-1}-exchanged hydrotalcite catalysts; the MnO_4^{-1} anions are located at the anion-exchange positions in the hydrotalcite catalysts.

The hydrotalcites ($Mg/Al = 2–10$), before and after MnO_4^{-1} exchange, were also characterized by thermal analysis. After the exchange, the DTG/DTA peak for all the Mg–Al–hydrotalcites is shifted toward higher temperatures (from 400 to 416, 395 to 447, 367 to 422, and 366 to 392 °C, for the hydrotalcites with a Mg/Al ratio of 2, 3, 5, and 10, respectively), indicating an increase in the thermal stability of the hydrotalcite due to the presence of MnO_4^{-1} anions at anion-exchange sites. The surface areas of the MnO_4^{-1}-exchanged Mg–Al–hydrotalcites with Mg/Al ratios of 2, 3, 5, and 10 was 36.3, 31.5, 29.1, and 25.9 $m^2\ g^{-1}$, respectively.

The hydrotalcite catalysts were also characterized for their basicity and H_2O_2 decomposition activity. The results in Fig. 2 show the influence of the Mg/Al ratio on the number of basic sites (obtained by the nonaqueous benzoic acid

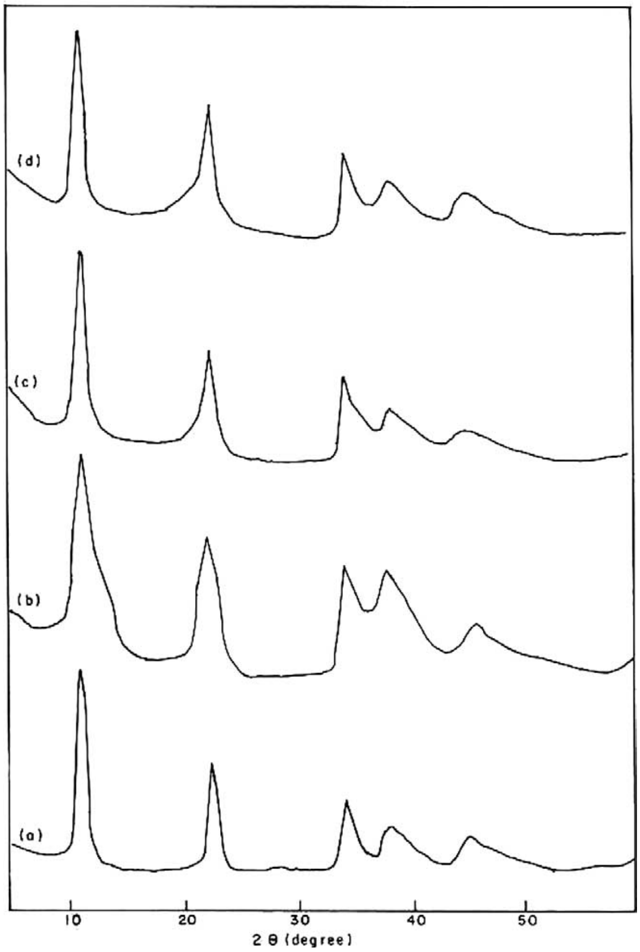

Fig. 1. XRD spectra of (a) Mg–Al hydrotalcite (Mg/Al = 3), (b) $MnO_4{}^{-1}$–Mg–Al–HT (before the oxidation reaction), (c) $MnO_4{}^{-1}$–Mg–Al–HT after the ethylbenzene oxidation, and (d) $MnO_4{}^{-1}$–Mg–Al–HT after the diphenylmethane oxidation.

titration method [18]) of the hydrotalcite (without $MnO_4{}^{-1}$ exchange), on the basicity of the hydrotalcite before and after the $MnO_4{}^{-1}$ exchange (measured in terms of the pH of the hydrotalcite or $MnO_4{}^{-1}$-exchanged hydrotalcite–water slurry) and also on the H_2O_2 decomposition activity (at 27 °C) of the $MnO_4{}^{-1}$-exchanged hydrotalcite. The hydrotalcites without $MnO_4{}^{-1}$ exchange showed no H_2O_2 decomposition activity under the same conditions. The H_2O_2 decomposition activity and basicity of the hydrotalcite catalyst increased with increasing Mg/Al ratio.

3.2. *Oxidation of the methylene group of aromatic compounds*

Results of the oxidation of different aromatic hydrocarbons that contain a methylene group (viz. ethylbenzene, diphenylmethane, and *n*-propylbenzene) by molecular oxygen over the $MnO_4{}^{-1}$-exchanged hydrotalcite catalysts are presented in Tables 1 and 2 and Figs. 3 and 4.

A comparison of the oxidation of the methylene group from the different aromatic hydrocarbons (Table 1) indi-

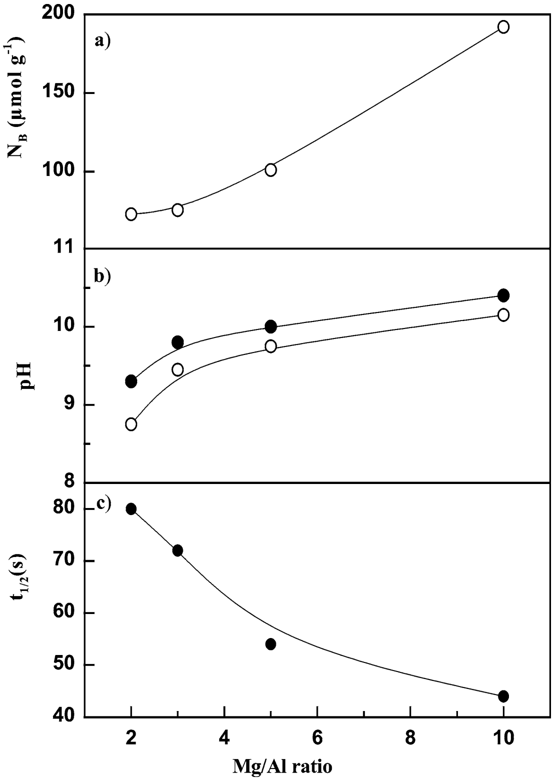

Fig. 2. Variation with the Mg/Al ratio of (a) number of basic sites of Mg–Al hydrotalcite (N_B), (b) pH of aqueous slurry of Mg–Al hydrotalcite before (○) and after (●) the $MnO_4{}^{-1}$ exchange of the hydrotalcite, and (c) time required for half the H_2O_2 decomposition reaction at 27 °C ($t_{1/2}$).

Table 1
Solvent-free oxidation by O_2 of different aromatic compounds containing a methylene group over $MnO_4{}^{-1}$-exchanged Mg–Al hydrotalcite (Mg/Al = 10) (reaction time: 5 h)

Ethylbenzene	Conversion (%)	Selectivity for carbonyl compound (%)	TOF[a] (h^{-1})
Ethylbenzene	22.6	98.4	9.0
Diphenylmethane	27.4	100	8.0
n-Propylbenzene	10.3	90.5	3.6

[a] Turnover frequency (number of substrate molecules converted per permanganate anion per hour).

Table 2
Results showing reusability of the $MnO_4{}^{-1}$-exchanged Mg–Al hydrotalcite (Mg/Al = 10) in the oxidation of ethylbenzene to acetophenone and diphenylmethane to benzophenone (reaction time = 5 h)

No. of uses of the catalyst	Ethylbenzene oxidation		Diphenylmethane oxidation	
	Conversion (%)	Selectivity for acetophenone (%)	Conversion (%)	Selectivity for benzophenone (%)
First	22.7	98.0	26.1	98.2
Second	32.5	98.0	32.3	98.4
Third	34.6	97.7	38.2	98.1
Fourth	34.6	98.0	38.0	98.3

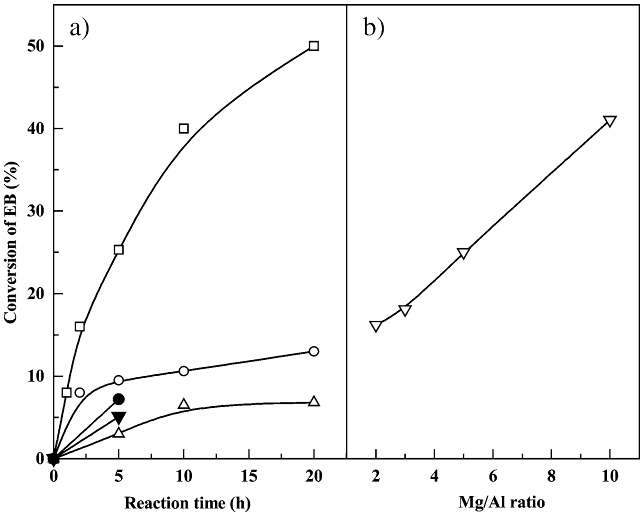

Fig. 3. Oxidation of ethylbenzene to acetophenone over $MnO_4{}^{-1}$-exchanged Mg–Al hydrotalcite. (a) Effect of the reaction time on the conversion of ethylbenzene (EB) for the catalyst with Mg/Al = 10 (□), when the catalyst was removed after 1.0 h (○), in the absence of catalyst (△), the hydrotalcite without $MnO_4{}^{-1}$ anions (▼), and in the presence of equivalent amount of $KMnO_4$ (●). (b) Effect of the Mg/Al ratio of the catalyst on the conversion (reaction time = 10 h) (▽). Selectivity for acetophenone for all the catalysts = 97 ± 2%.

cates that, in the oxidation, the reactivity of the methylene group attached to the aromatic ring depends strongly on the other group (viz. methyl, ethyl, and phenyl) attached to the methylene group. The order for TOF in the oxidation is ethylbenzene > diphenylmethane > *n*-propylbenzene.

From the results in Figs. 3 and 4, the following important observations can be made:

- The $MnO_4{}^{-1}$-exchanged Mg–Al–hydrotalcite catalyst with a Mg/Al ratio of 10 showed high activity and selectivity (above 95%) for the oxidation by O_2 of ethylbenzene to acetophenone and diphenylmethane to benzophenone (Figs. 3a and 4a). In both cases, the activity increases with increasing Mg/Al ratio in the catalyst (Figs. 3b and 4b) and there is no induction period. This is consistent with earlier observations in the oxidation of benzyl alcohol and benzaldehyde [20].
- The oxidation reactions also occur in the absence of catalyst, but very slowly (Fig. 3a).
- In the presence of an amount of $KMnO_4$, equivalent to the $MnO_4{}^{-1}$ anions present in the catalyst, the reaction also occurs but at a much slower rate than in the presence of the catalyst (Fig. 3a).
- After the removal by filtration of the catalyst from the reaction mixture while hot, the reaction rate is drastically reduced and the reaction proceeds at a very slow rate (Fig. 3a).

These observations reveal that the catalytic activity of $KMnO_4$ is drastically increased by the immobilization of $MnO_4{}^{-1}$ anions at anionic exchange sites in the hydrotalcite and that the oxidation reaction catalyzed by the solid catalyst is truly heterogeneous. No leaching of permanganate from the catalyst was observed in the reactions.

A comparison of the results in Figs. 3b and 4b with those in Fig. 2 indicates a good correlation of the catalytic activity

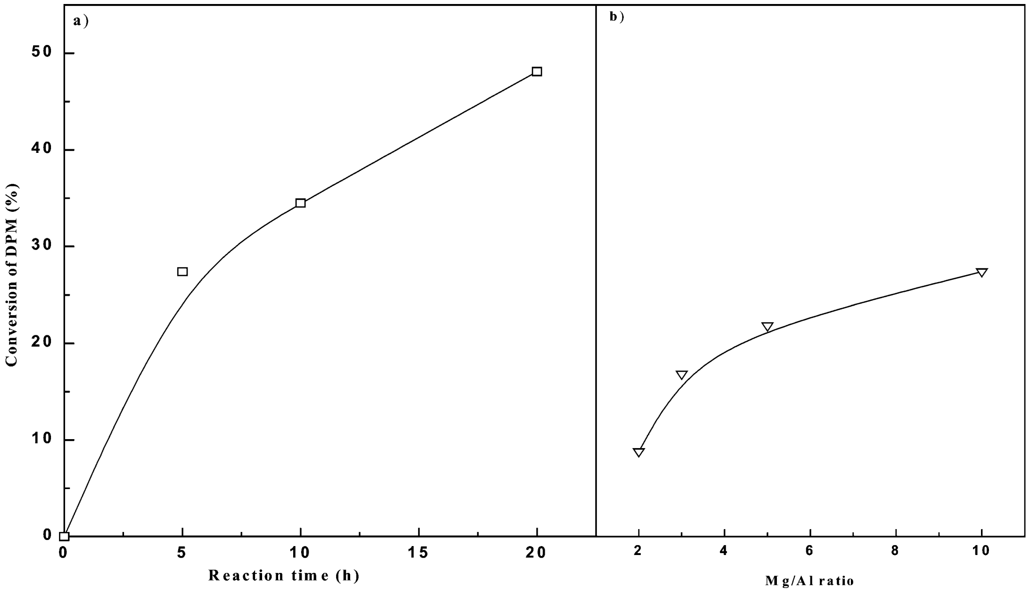

Fig. 4. Oxidation of diphenylmethane to benzophenone over $MnO_4{}^{-1}$-exchanged Mg–Al–hydrotalcite. (a) Effect of the reaction time on the conversion of diphenylmethane (DPM) for the catalyst with Mg/Al = 10. (b) Effect of the Mg/Al ratio of the catalyst on the conversion (reaction time = 5 h). Selectivity for benzophenone for all the catalysts = 99 ± 1%.

for both the ethylbenzene and the diphenylmethane oxidation reactions with the H_2O_2 decomposition activity of the catalyst (Fig. 2a), with the pH of the catalyst (when it is slurred in pure water) (Fig. 2b) or with the basicity of the hydrotalcite used for the catalyst. Like the catalytic oxidation activity, the H_2O_2 decomposition activity and pH of the catalyst and the basicity are increased with increasing Mg/Al ratio (Fig. 2). However, the basicity has little or no effect on the product selectivity.

The catalyst ($Mg/Al = 10$) also showed excellent reusability in both oxidation reactions (Table 2). Interestingly, the catalytic activity is found to increase after its use in both the oxidation reactions (Table 2). This may be due to the removal of strongly adsorbed water from the catalyst during the first and subsequent use of the catalyst. The selectivity also remained high ($> 95\%$) in the reuse of the catalyst in both cases.

A comparison of the XRD spectra of the catalyst before and after use in the oxidation reactions (Figs. 1b–d) reveals that the hydrotalcite structure of the catalyst is not changed during reaction. The surface area of the catalyst was also not changed significantly after the reaction.

The oxidation reaction is expected to involve a mechanism similar to that described by Bukharkina and Digurov [21] for manganese-catalyzed ethylbenzene oxidation by molecular oxygen in nonpolar media. It is initiated by the direct interaction of the hydrocarbon with oxygen, leading to the formation of an intermediate hydroperoxide species, which is subsequently decomposed to the corresponding carbonyl compound and water. The presence of hydroperoxide in the reaction products was, however, not observed, most probably because of its fast catalytic decomposition; the catalyst has very high peroxide decomposition activity (Fig. 2c).

Thus, a stoichiometric $KMnO_4$ reagent, commonly employed for oxidations, can be transformed into a highly active, stable, easily separable, and reusable environmental-friendly catalyst for the oxidation of ethylbenzene to acetophenone, diphenylmethane to benzophenone, or similar reactions by immobilizing MnO_4^{-1} anions in highly basic Mg–Al–hydrotalcite at its anion-exchange sites. The activity of this catalyst can be further improved by optimizing the catalyst composition parameters and removing continuously the water formed in the reaction, using a Dean Stark trap for the reaction water.

Acknowledgment

R.J. is grateful to CSIR, New Delhi (India), for the award of Senior Research Fellowship (SRF).

References

[1] P.H. Groggins, R.H. Nagel, Ind. Eng. Chem. 26 (1934) 1313.

[2] H.J. Sanders, H.F. Keag, H.S. McCullough, Ind. Eng. Chem. 45 (1953) 2.

[3] G.A. Olah, Friedel–Crafts and Related Reactions, Wiley–Interscience, New York, 1963.

[4] C.F. Cullis, J.W. Ladbury, J. Chem. Soc. (1955) 2850.

[5] R. Gopalan, R.W. Sugumar, Indian J. Chem. 16A (1978) 198.

[6] N.D. Valechha, A. Pradhan, J. Indian Chem. Soc. 61 (1984) 909.

[7] S.D. Borkar, B.M. Khadilkar, Synth. Commun. 29 (1999) 4295.

[8] A. Shaabani, A. Bazgir, F. Teimouri, D.G. Lee, Tet. Lett. 43 (2002) 5165.

[9] (a) B.B. Wentzel, M.P.J. Donners, P.L. Alsters, M.C. Feiters, R.J.M. Nolte, Tetrahedron 56 (2000) 7797;
(b) V.F. Gaevskii, N.P. Evmenenko, Ukr. Khim. Zh. (Russ. Ed.) 48 (1982) 160;
(c) S.N. Vyas, S.R. Patwardhan, T.N. Pal, Indian Chem. Eng. 28 (1986) 44;
(d) G.B. Shul'pin, M.M. Kats, React. Kinet. Catal. Lett. 41 (1990) 239;
(e) J.H. Clark, S. Evans, J.R.L. Smith, Spec. Publ.-R. Soc. Chem. 216 (1998) 187.

[10] Y. Ishii, S. Sakaguchi, T. Iwahama, Adv. Synth. Catal. 343 (2001) 393, and references cited therein.

[11] J.H. Clark, A.P. Kybett, P. London, D.J. Macquarrie, K. Martin, J. Chem. Soc., Chem. Commun. (1989) 1355.

[12] A. Sakthivel, S.E. Dapurkar, P. Selvam, Catal. Lett. 77 (2001) 155.

[13] J.H. Clark, P. London, S.J. Barlow, C.V.A. Duke, K. Martin, Chem. Ind. (1991) 800.

[14] I.C. Chisem, K. Martin, M.T. Shieh, J. Chisen, J.H. Clark, R. Jachuck, D.J. Macquarrie, J. Rafelt, C. Ramshaw, K. Scott, Org. Process Res. Dev. 1 (1997) 365.

[15] H.E.B. Lempers, R.A. Sheldon, J. Catal. 175 (1998) 62.

[16] I.W.C.E. Arends, R.A. Sheldon, Appl. Catal. A 212 (2001) 175.

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

[18] F.M.P.R. Van Laar, D.E. de Vos, F. Pierard, A. Kirsch-De Mesmaeker, L. Fiermans, P.A. Jacobs, J. Catal. 197 (2001) 139.

[19] C.N.R. Rao, in: Chemical Application of Infrared Spectroscopy, Academic Press, New York, 1963, p. 337.

[20] V.R. Choudhary, D.K. Dumbre, V.S. Narkhede, S.K. Jana, Catal. Lett. 86 (2003) 229.

[21] T.V. Bukharina, N.G. Digurov, Org. Proc. Res. Dev. 8 (2004) 320.