Sn-exchanged hydrotalcites as catalysts for clean and selective Baeyer–Villiger oxidation of ketones using hydrogen peroxide

Unnikrishnan R. Pillai, Endalkachew Sahle-Demessie*

National Risk Management Research Laboratory, Sustainable Technology Division MS-443, US Environmental Protection Agency, Cincinnati, OH 45268, USA

Abstract

A Sn-doped hydrotalcite (Sn/HT) catalyst prepared by ion-exchange technique is found to be an active and selective catalyst for the liquid phase Baeyer–Villiger (BV) oxidation of cyclic ketones in acetonitrile using hydrogen peroxide (H_2O_2) as oxidant. Different reaction parameters such as effect of solvent, Sn content, reaction temperature and catalyst-to-substrate ratio are studied. The activity of the catalyst for the selective BV oxidation of ketones is attributed to the presence of active Sn sites in the interstitial position of hydrotalcite support. Sn sites activate the carbonyl group of ketones followed by a nucleophilic attack by the active peroxide species (peroxycarboximidic acid by reaction of acetonitrile and H_2O_2) to form a Criegee adduct that rearranges to give the lactone.
© 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

Baeyer–Villiger (BV) oxidation was first reported by Baeyer and Villiger in 1899 when they converted cyclic ketones, like menthone, carvone and camphor to the corresponding lactones by an oxidative transformation using Caro's acid (mixture of persulfate and concentrated sulphuric acid) [1]. The application of this generally stereoselective reaction has grown tremendously in organic synthesis such as synthesis of natural compounds [2,3]. BV oxidation is traditionally carried out using peracids oxidants, like trifluoroperacetic acid, perbenzoic acid and *m*-chloro perbenzoic acid (*m*-CPBA) in more than stoichiometric quantities

in buffered solutions, which eventually produce large amount of waste [3–6]. In addition, the preparation of these reagents requires hazardous concentration levels of hydrogen peroxide (H_2O_2). There have been a plethora of activities exploring a variety of alternative reagents, oxidants and catalysts, which can versatalize this reaction to include a variety of linear ketones as well as aldehydes. These activities can be summarized into two groups. The first approach to this is to develop new catalysts that activate H_2O_2 as a clean oxidant by increasing its nucleophilicity and facilitates attack by the oxidizing species on the carbonyl carbon atom. [7]. Different catalyst systems reported for this include heterogeneous catalysts based on solid acids [8], zeolites [9], titanium silicalite [10], Se [11], As [12] and homogeneous catalyst based on Pt [13], Zr [14], Re [15], Se [16], As [17] and Mo [18]. The second approach is oxidation with molecular oxygen

* Corresponding author. Fax: 513-569-7677.
E-mail address: sahle-demessie.endalkachew@epa.gov
(E. Sahle-Demessie).

catalyzed by either metal complexes or supported metal complexes using aldehydes as co-oxidants [19]. Most of these processes, however, suffer from some disadvantages like low activity or selectivity and expensive catalyst or the need for anhydrous H_2O_2. For example, homogeneous Mo [18] and Re [20] complexes showed low turnover numbers (TON <20) and low selectivity. Silica-supported Ni complexes also showed low activities (conversions ≤20%) [19]. Heterogeneous catalysts like titanium silicate (TS-1) [19], zeolites (H-β and USY) [9] and supported Pt-complexes [21] also showed limited activity and selectivity.

A novel approach to address the problem of selectivity has been shown by Corma et al. [22] to oxidize the substrate by activating the –C=O group of the ketone instead of activating H_2O_2. They used a novel Sn/zeolite-β heterogeneous catalyst containing 1.6% Sn in the zeolite framework, for the chemoselective BV oxidation in an efficient manner. They followed this study with Sn incorporated MCM-41 as another potential catalyst for this reaction [23].

Hydrotalcites are high surface area, homogeneous, basic, mixed hydroxides with a layered structure bearing the formula $Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$ [24]. Hydrotalcite-like materials are especially active in base-catalyzed reactions like Knovenagel [25], Micheal [26] and Claisen–Schmidt [27], epoxidation [28] and aldolizations [29] reactions. Metal containing hydrotalcites are found to be very useful in many important industrial reactions like selective hydrogenation of aromatics as well as selective oxidation reactions [30,31]. Kaneda and co-workers [32] have shown that hydrotalcites are also active in the BV oxidation of ketones using O_2. The basic sites of hydrotalcites are proposed to be involved in this oxidation mechanism [32]. However, these methods involve the use of *m*-CPBA as the oxidant and in some cases employ aldehydes as sacrificial co-oxidants, which eventually form undesired industrial waste. However, incorporating a Lewis acid site like Sn in the interstitial positions can enhance the chemoselectivity of the process besides avoiding the use of other co-oxidants like aldehydes. Herein, we report a selective BV oxidation of ketones using Sn-doped hydrotalcite (Sn/HT) as catalyst and a clean oxidant, viz. H_2O_2.

2. Experimental

All the substrate materials, $Mg(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ were obtained from Aldrich Chemicals and used as such without any further purification. $SnCl_2 \cdot 2H_2O$ was obtained from Fischer Chemicals.

Magnesium aluminum hydroxycarbonate (hydrotalcite) was prepared by co-precipitation technique at a constant pH of 8 from a 0.5 M solution of $Mg(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ in de-ionized water using a mixture of NaOH and Na_2CO_3 as the precipitants according to the procedure described elsewhere [24,31]. After the precipitation, the solid was filtered and washed several times with de-ionized water and dried in an oven at 100 °C overnight. The dried material was calcined in air at 400 °C for 5 h and cooled to room temperature. Ion-exchange and wet impregnation methods were used to load Sn onto the hydrotalcite support. Sn/HT containing 0.4, 1.5 and 3 wt.% Sn were prepared by ion-exchange method as follows. The calcined hydrotalcites was refluxed at 80 °C for 24 h with a solution of appropriate amount of $SnCl_2 \cdot 2H_2O$ in a mixture (1:1 ratio) of methanol and de-ionized water taken in a 500 ml round-bottomed flask equipped with a reflux condenser and a magnetic stirrer. After the ion-exchange, the material was filtered, washed with de-ionized water followed by methanol and dried at 110 °C overnight. It was then calcined at 400 °C for 5 h and cooled to room temperature. The structure of hydrotalcite was confirmed by X-ray diffraction analysis of the dried material, which showed characteristic peaks at 2θ values of around 11.5. The Sn content in the dried catalysts was determined by inductively coupled argon plasma–atomic emission spectrophotometry (ICAP–AES) elemental analysis technique using a Perkin-Elmer (Optima 3300DV) ICAP–AES spectrophotometer.

A 1.5% Sn/HT (w/w) catalyst was also prepared by wet impregnation of the calcined hydrotalcite with a solution (0.02 M) of $SnCl_2 \cdot 2H_2O$ in 1:1 ratio of methanol–water mixture. After the impregnation step, the catalyst was dried and calcined as described earlier.

Single point BET surface areas of the catalysts were determined using N_2 adsorption at 77 K using a micromeritics Gemini physical adsorption analyzer.

X-ray diffraction analysis of the catalyst samples were carried out by Siemens D5000 diffractometer

with a Cu Kα radiation running at 40 KV per 30 mA in the 2θ range of 10–80° with a step size of 0.05°.

Oxidation of ketone was conducted in liquid phase in a 100 ml round-bottomed flask equipped with a reflux condenser and a magnetic stirrer. In a typical reaction procedure, 0.25 g catalyst was mixed with 12.5 mmol of the substrate and 10 ml of the solvent. To this mixture, 50 mmol of 30% H_2O_2 was added and the mixture was heated to the reaction temperature with stirring. Samples were collected at different reaction times and the organic layer was extracted with ether and analyzed by a Hewlett-Packard 6890 gas chromatograph using a HP-5 of 5% phenyl methyl siloxane capillary column (30 m × 320 μm × 0.25 μm) and a quadruple mass filter equipped HP 5973 mass selective detector. Samples were analyzed in duplicate with an injection volume of 1 μl. Quantification of the oxygenated products was obtained using a multi-point calibration curve for each product. The aqueous phase was also analyzed for detecting any acid formation using a HPLC (Finniganmat-LCQ) system using a Supelcogel^{TM} H 59346 column (25 cm × 4.6 mm) with a water–phosphoric acid solution as the eluent. The aqueous phase was also analyzed by ICAP–AES for determining the quantity of leached Sn at the end of the reaction, which showed a Sn concentration in the range of 10–30 ppm.

$$\text{conversion (\%)} = \frac{\text{moles of reactant consumed}}{\text{initial moles of the reactant}} \times 100 \tag{1}$$

$$\begin{aligned}\text{selectivity of a product } (P, \text{ \%}) \\ = \frac{\text{percentage formation of the product } (P)}{\text{percentage of total conversion}} \times 100\end{aligned} \tag{2}$$

$$\begin{aligned}\text{turnover number (TON)} \\ = \frac{\text{number of moles of the reactant consumed}}{\text{total number of metal sites}}\end{aligned} \tag{3}$$

3. Results and discussion

The selective BV oxidation of cyclohexanone to ε-caprolactone was conducted at 70 °C over a 1.5% of Sn-exchanged hydrotalcite catalyst using H_2O_2 as oxidant in acetonitrile medium. The observed conversions/yield as well as the calculated TON are given in Table 1. TONs as high as 229 could be achieved which is comparatively better than most of the earlier catalyst systems for this oxidation, except the Sn/zeolite-β [22]. A maximum of 58% ketone conversion was obtained with 100% selectivity to the desired lactone. No other reaction products such as acid formation were observed. Increasing the reaction time from 4 to 24 h also increased the conversion. There was no significant increase in the conversion with further increase in the reaction time. The linearity of the logarithm of the cyclohexanone concentration against time at 70 °C, as shown in Fig. 1, implies that the reaction is first order with respect to the ketone concentration. The conversion or the reaction rate increased steadily with increase in the ketone concentration, where the maximum conversion or TON was obtained using 10 ml solvent (entries 1, 5 and 6, Table 1). The rate of the reaction increased linearly with ketone concentrations. However, reactant concentrations or the solvent quantity appears to have no influence on the product selectivity.

Table 1 also shows that the reaction works only in acetonitrile medium. Other solvents such as dioxane, methanol, methyl tertiary butyl ether (MTBE), dimethyl sulfoxide (DMSO) and ethylene glycol (EG) have also been examined but do not seem to effect the reaction. Acetonitrile is known to activate H_2O_2
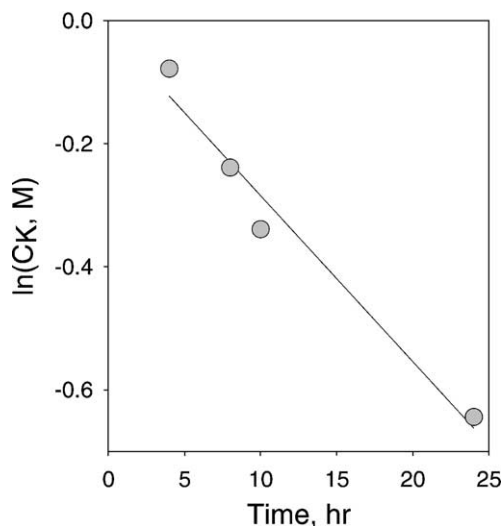

Fig. 1. Plot of logarithm of cyclohexanone concentration against time at 70 °C for the initial concentration of 1.25 M.

Table 1

Baeyer–Villiger oxidation of cyclohexanone over 1.5% Sn-doped hydrotalcite (Sn/HT) as catalyst using H_2O_2 as oxidant[a]

Entry	Solvent (ml)	Catalyst (g)	Duration (h)	Conversion/ Yield (%)	Turnover number (TON)	ε-Caprolactone selectivity (%)
1	MeCN (10)	0.25	4	26	103	>95
2	MeCN (10)	0.25	8	37	146	>95
3	MeCN (10)	0.25	10	43	170	>95
4	MeCN (10)	0.25	24	58	229	>95
5	MeCN (20)	0.25	4	20	79	>95
6	MeCN (30)	0.25	4	10	40	>95
7	MeCN (10)	0.10	4	14	139	>95
8	MeCN (10)	0.50	4	33	66	>95
9	MeCN (10)	0.50	8	42	83	>95
10	MeCN (10)	0.50	24	58	115	>95
11	Dioxane (10)	0.50	4	0	0	0
12	MeOH (10)	0.50	4	0	0	0
13	MTBE (10)	0.50	4	0	0	0
14	DMSO (10)	0.50	4	0	0	0
15	EG (10)	0.50	4	0	0	0
16[b]	MeCN (10)	0.25	4	0	0	0
17[c]	MeCN (10)	0.25	4	0	0	0
18[d]	MeCN (10)	0.25	4	14	55	>95

[a] Reaction conditions: 12.5 mmol ketone, 0.25 g catalyst, 50 mmol 30% of H_2O_2, 10 ml acetonitrile, 4 h, 70 °C.

[b] Hydrotalcite.

[c] $SnCl_2 \cdot 2H_2O$.

[d] 2% Sn/HT-impregnated catalyst.

by forming a perhydroxyl anion (OOH^-), which nucleophilically attacks the nitrile to generate a peroxycarboximidic acid intermediate (Scheme 1, **I**) [33]. This intermediate is a good oxygen transfer agent. In addition, acetonitrile has a comparatively good solubility power for both the organic substrate as well as the aqueous H_2O_2.

The TON increased with increase in the catalyst-to-substrate ratio during the initial reaction time. However, the effect was not apparent at longer reaction
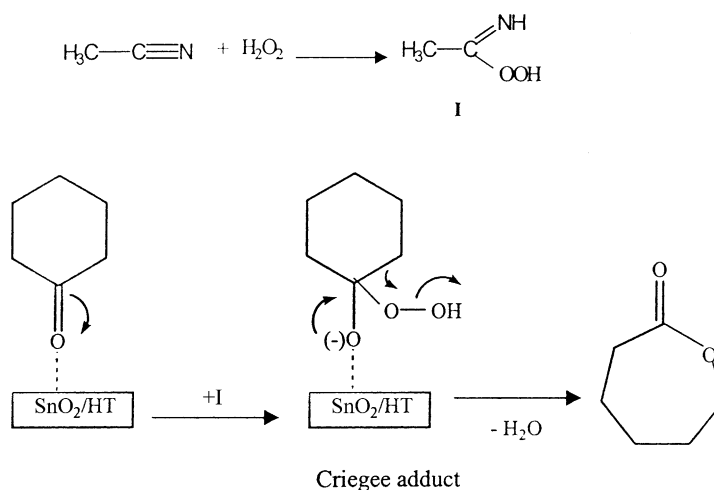
Scheme 1.

Table 2

BET surface areas of various Sn-doped hydrotalcite (Sn/HT) catalysts

Catalyst	BET surface area ($m^2 g_{cat}^{-1}$)
Hydrotalcite (HT)	180
1.5% Sn/HT (ion-exchanged)	186
1.5% Sn/HT (impregnated)	177

time. This indicates an apparent non-linear influence of the catalyst amount on the reaction rate. Table 1 also shows that a 1.5% of Sn/HT prepared by impregnation technique was not as active as the catalyst prepared by ion-exchange method indicating that the dispersion and position of Sn in the hydrotalcite structure is important in providing an effective active site. In the case of impregnated catalyst, the metal is usually present on the surface of the support in a relatively less dispersed state (bigger catalyst particle size). On the other hand, in the ion-exchanged catalyst, Sn may be present in a highly dispersed state and also in the interstitial positions acting as Lewis acid centers, which are understood to be the active site for the reaction [22]. This is also evident from the increase in the surface areas of the Sn-exchanged hydrotalcite catalysts (Table 2). The lower surface area obtained for the impregnated Sn-hydrotalcite catalyst may be attributed to the blocking of the catalyst pores by Sn particles. This, however, has not happened for the Sn-exchanged hydrotalcites. Control runs showed that the reaction did not take place in the absence of the catalyst and also in the presence of simple hydrotalcite without any Sn or with only $SnCl_2 \cdot 2H_2O$ as catalysts under similar reaction conditions. It was also confirmed that the reaction was not catalyzed by leached Sn as another experiment in which the catalyst was separated by filtration after 2 h reaction and 15% conversion did not show

any further raise in the conversion value. These experiments further suggest that the Sn exchanged to the hydrotalcite interstitial positions is responsible for the reaction.

The effect of the catalyst Sn content on the activity (TON) and product selectivity of cyclohexanone oxidation is as shown in Table 3. There was no significant variation in the conversion with increase in Sn-content from 0.4 to 3 wt.%. On the other hand, the TON decreased by a factor of 6 from 297 to 46, with increase in Sn content from 0.4 to 3% (w/w). This may be attributed to the decrease in the Sn dispersion with increase in its concentration. The Sn dispersion would be higher at lower Sn concentration. However, the X-ray diffractogram showed very broad peaks of Sn(IV) for all the catalyst samples, suggesting the amorphous nature of the dispersed Sn. No other Sn phases could be identified.

The selectivity to the lactone was almost 100% irrespective of the Sn concentration with no formation of any side-products. Effect of the reaction temperature is as shown in Table 4. Conversion and TON increased as the reaction temperature was increased from 30 to 70 °C. Dependence of the logarithm of the reaction rate versus the inverse of the temperature is as shown in Fig. 2. The straight line represents the linear fit of the data points and the estimated activation energy is 12 KJ mol^{-1}. There was no significant gain in the conversion with further raise in the temperature of the bath above the boiling point of the solvent.

Catalyst re-cyclability was tested by filtering off the catalyst from one batch and subsequently using it for another batch of experiment under identical conditions. The activity of the used catalyst was found to be lower than the fresh catalyst. Nevertheless, almost the same conversion was obtained by using the spent catalyst after calcining it in air at 400 °C for

Table 3

Effect of Sn concentration on the Baeyer–Villiger oxidation of cyclohexanone over Sn-doped hydrotalcite (Sn/HT) as catalyst using H_2O_2 as oxidant[a]

Entry	Sn (wt.%) in Sn/HT	Conversion/yield (%)	Turnover number (TON)	ε-Caprolactone selectivity (%)
1	0.4	20	297	>95
2	1.5	26	103	>95
3	3.0	23	46	>95

[a] Reaction conditions: 12.5 mmol cyclohexanone, 0.25 g catalyst, 50 mmol 30% of H_2O_2, 10 ml acetonitrile, 4 h, 70 °C.

Table 4
Effect of reaction temperature on the Baeyer–Villiger oxidation of cyclohexanone over 1.5% of Sn-doped hydrotalcite (Sn/HT) as catalyst using H_2O_2 as oxidant[a]

Entry	Temperature (°C)	Conversion/yield (%)	Turnover number (TON)	ε-Caprolactone selectivity (%)
1	30	12	47	>95
2	50	20	79	>95
3	70	26	103	>95
4	80	30	119	>95

[a] Reaction conditions: 12.5 mmol cyclohexanone, 0.25 g catalyst, 50 mmol 30% of H_2O_2, 10 ml acetonitrile, 4 h.

2 h. This suggests that the reduction in activity is due to the poisoning of the active sites by adsorption of the reaction products or intermediates during the reaction.

Further oxidation experiments of various other ketones using 1.5% Sn/HT catalyst at 70 °C shows that Sn/HTs are active and highly selective for the BV oxidation of a variety of cyclic ketones (Table 5). The TONs obtained are generally encouraging. However, the catalyst, apparently, was not active for the oxidation of aliphatic and acyclic ketones like 2-hexanone and acetophenone. This is not unexpected as the methyl group has the lowest migrating ability [34]. Also, as hydrotalcite is a very good epoxidation catalyst [28,33], the Sn/HT catalyst system was not selective for the lactone formation in the case of olefinic ketones. Nevertheless, this oxidation protocol is promising for cyclic ketones and much cleaner than the traditional BV oxidation as it gives relatively higher TON and involves no use of peracids, which would produce many undesired by-products. The catalyst preparation is also relatively simple and does not involve the use of any expensive precursor materials or organic templates.

The high lactone selectivity obtained is attributed to the operation of a different mechanism of oxidation when compared to the traditional peroxide catalyzed oxidations. Corma et al. [22,23] have proposed a carbonyl group activation mechanism for this reaction over Sn/zeolite-β and Sn-MCM-41 catalysts. A similar mechanism is also expected in this case. The carbonyl group of the ketone is activated by co-ordination with the Lewis acid center (Sn) on the catalyst forming an electrophilic carbonyl carbon as shown in Scheme 1. This is followed by a nucleophilic attack by the active peroxide species (peroxycarboximidic acid in this case) to form a Criegee adduct which rearranges to give a lactone. Corma et al. [22] have confirmed this by carrying out in situ IR experiments where a shift of the carbonyl band towards lower wave numbers ($48 \, cm^{-1}$) was observed and the ketone remained co-ordinated even at 100 °C. That the reaction requires a modest Lewis acid site like Sn was further confirmed by carrying out the reaction using a 1.5% Sn-doped Montmorillonite K-10 catalyst. Montmorillonite K-10 is an acidic material containing predominantly Brönsted acid centers [35]. This catalyst also gave about the same ketone conversion (19% after 4 h) but only 13% yield of lactone, the balance being over oxidation products like acids, which is due to a Brönsted acid catalyzed reaction mechanism [36].
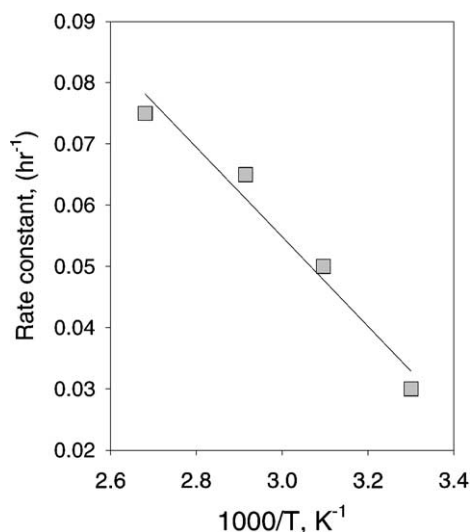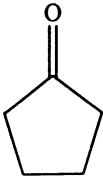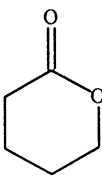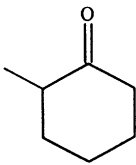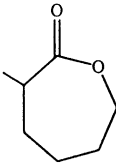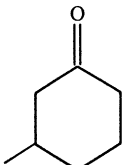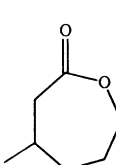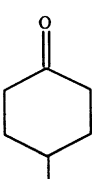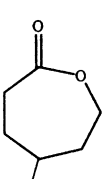

Fig. 2. Plot of logarithm of reaction rate constants vs. the reaction temperatures.

Table 5
Baeyer–Villiger oxidation of ketones over 1.5% of Sn-doped hydrotalcite (Sn/HT) as catalyst using H_2O_2 as oxidant[a]

Entry	Ketone	Product (%)	Yield/selectivity (%)	Turnover number (TON)
1			16/100	63
2[b]			42/100	166
3[b]			32/100	127
4[b]			26/100	103

[a] Reaction conditions: 12.5 mmol ketone, 0.25 g catalyst, 50 mmol 30% of H_2O_2, 10 ml acetonitrile, 4 h, 70 °C.
[b] Stereo isomers were not identified by GC–MS analysis.

4. Conclusions

This study reveals that Sn-exchanged hydrotalcites are efficient and relatively cheap catalysts for the BV oxidation reactions using the environmentally benign oxidant, H_2O_2. The mechanism of oxidation is tentatively explained as due to the carbonyl group activation of ketone by Sn present in the interstitial positions of hydrotalcite followed by subsequent oxygen transfer from the active peroxide species to form lactone as the final product. This offers an efficient protocol for this important oxidative transformation without the use of harmful organic peroxides and, hence makes the process cleaner.

Acknowledgements

References

[1] A. Baeyer, V. Villiger, Ber. Dtsch. Chem. Ges. 32 (1899) 3625.
[2] M. Renz, B. Meunier, Eur. J. Org. Chem. 64 (1999) 737.
[3] G.R. Krow, Org. React. 43 (1993) 251.

[4] B.M. Trost, Science 254 (1991) 1471.

[5] W.F. Sager, A. Duckworth, J. Am. Chem. Soc. 77 (1955) 188.

[6] S.L. Friess, N. Farnham, J. Am. Chem. Soc. 72 (1950) 5518.

[7] G. Strukul, Angew. Chem. Int. Ed. 37 (1998) 1198.

[8] (a) A. Lambert, D.J. Macquarrie, G. Carr, J.H. Clark, New J. Chem. 24 (2000) 485;
(b) A. Berkessel, M.R.M. Andrae, Tetrahedron Lett. 42 (2001) 2293.

[9] J. Fischer, W.F. Holderich, Appl. Catal. Part A. Gen. 180 (1999) 435.

[10] A. Bhaumik, P. Kumar, R. Kumar, Catal. Lett. 40 (1996) 47.

[11] R.T. Taylor, L.A. Flood, J. Org. Chem. 48 (1983) 5160.

[12] S.E. Jacobson, F. Mares, P.M. Zambri, J. Am. Chem. Soc. 101 (1979) 6938.

[13] R. Gavagnin, M. Cataldo, F. Pinna, G. Strukul, Organometallics 17 (1998) 661.

[14] C. Bolm, O. Beckmann, Chirality 12 (2000) 523.

[15] A.M. Phillips, C. Romao, Eur. J. Org. Chem. 64 (1999) 1767.

[16] G.J.T. Brink, J.M. Vis, I.W.C.E. Arends, R.A. Sheldon, J. Org. Chem. 66 (2001) 2429.

[17] T. Miyauchi, H. Kurata, Japanese Patent 7109284A2 (1993).

[18] S.E. Jacobson, R. Tang, F.J. Mares, J. Chem. Soc., Chem. Commun. (1978) 888.

[19] I.C. Chisem, J. Chisem, J.H. Clark, New J. Chem. 22 (1998) 81.

[20] W.A. Hermann, R.W. Fischer, J.D.G. Correia, J. Mol. Catal. 94 (1994) 213.

[21] C. Palazzi, F. Pinna, G. Strukul, J. Mol. Catal. Part A. Chem. 151 (2000) 245.

[22] A. Corma, L.T. Nemeth, M. Renz, S. Valencia, Nature 412 (2001) 423.

[23] A. Corma, M.T. Navarro, L. Nemeth, M. Renz, Chem. Commun. (2001) 2190.

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

[25] M.L. Kantam, B.M. Choudary, Ch.V. Reddy, K.K. Rao, F. Figueras, Chem. Commun. (1998) 1033.

[26] B.M. Choudary, M.L. Kantam, Ch.V. Reddy, K.K. Rao, F. Figueras, J. Mol. Catal. Part A. Chem. 146 (1999) 279.

[27] E. Suzuki, Y. Ono, Bull. Chem. Soc. Jpn. 61 (1988) 1008.

[28] B.M. Choudary, M.L. Kantam, B. Kavitha, Ch.V. Reddy, K.K. Rao, F. Figueras, Tetrahedron Lett. 39 (1998) 3555.

[29] K. Yamaguchi, K. Mori, T. Mizugaki, K. Ebitani, K. Kaneda, J. Org. Chem. 65 (2000) 6897.

[30] S. Narayanan, K. Krishna, J. Chem. Soc., Chem. Commun. (1997) 1991.

[31] R. Unnikrishnan, S. Narayanan, J. Mol. Catal. Part A. Chem. 144 (1999) 173.

[32] S. Ueno, K. Ebitani, A. Ookubo, K. Kaneda, Appl. Surf. Sci. 121/122 (1997) 366.

[33] (a) S. Ueno, K. Yamaguchi, K. Yoshida, K. Ebitani, K. Kaneda, Chem. Commun. (1998) 295;
(b) K. Yamaguchi, K. Ebitani, K. Kaneda, J. Org. Chem. 64 (1999) 2966;
(c) K. Yamaguchi, K. Mori, T. Mizugaki, K. Ebitani, K. Kaneda, J. Org. Chem. 65 (2000) 6897;
(d) U.R. Pillai, E. Sahle-Demessie, R.S. Varma, Tetrahedron Lett. 43 (2002) 2909.

[34] M.B. Smith, J. March, March's Advanced Organic Chemistry: Reactions, Mechanisms and Structure, 5th Edition, Wiley, New York, 2001, Chapter 18, 1417 pp.

[35] J.M. Thomas, in: M.S. Whittingham, A.J. Jacobsons (Eds.), Intercalation Chemistry, Academic Press, New York, 1982, p. 55.

[36] K. Neimann, R. Neumann, Org. Lett. 2 (2000) 2861.