

Synthesis, characterization, and catalytic properties of chromium-containing hexagonal mesoporous aluminophosphate molecular sieves

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Chromium-containing hexagonal mesoporous aluminophosphate molecular sieve materials were synthesized, characterized and evaluated for the oxidation of cyclohexane under mild conditions. The catalysts showed remarkable activity for the chosen reaction with very high substrate conversion and excellent product selectivity. In addition, recycling studies over the spent catalysts as well as studies on quenched solutions under the reaction conditions indicated no or very meager loss in activity; thus, the materials behaved truly as heterogeneous catalysts. This observation was well supported by ICP–AES analysis of the filtrates obtained from the washed catalysts where no leaching of active chromium species was detected. Furthermore, the reaction carried out using these filtrates confirmed the absence of active metal ions as it exhibited only a marginal activity.

KEY WORDS: (Cr)HMA; mesoporous; aluminophosphates; cyclohexane oxidation; cyclohexanol; cyclohexanone.

1. Introduction

The selective oxidation of hydrocarbons is one of the major commercial processes, as the reaction products are important themselves or as precursors of other chemicals. Among the numerous reactions of interest, the liquid-phase oxidation of cyclohexane has attracted much attention owing to the importance of the products, i.e., cyclohexanol and cyclohexanone, which are key intermediates in the production caprolactam (a monomer in the manufacture of nylon-6) and adipic acid (a building block for a number of polyamide fibers; e.g., nylon-66 and polyurethane resins) [1]. However, the cyclohexane oxidation process is a relatively difficult one, since the desired products, i.e., cyclohexanol and cyclohexanone, are intermediates in a sequence of reactions, and over-oxidation easily results in a series of undesired by-products (mostly diacids). Traditional processes involving stoichiometric amounts of inorganic oxidants produce very large amounts of environmentally unacceptable wastes [2,3] and hence catalytic oxidation in the liquid phase is increasingly important. However, the use of soluble salts or transition metal complexes as catalysts in combination with eco-friendly oxidants, e.g., O_2 , H_2O_2 , RO_2 (R = alkyl or aryl), results in a mixture of products. Furthermore, the process also leads to several other problems, such as the difficulty in separation, recovery and recycling of

the catalysts after reaction, and the disposal of liquid and solid wastes, deactivation complications, etc., make it highly unattractive [3–5]. In particular, highly active chromium-based catalysts are increasingly prohibited owing to the toxic nature of the spent catalysts. Hence, attempts have been made to develop chromium-based heterogeneous catalysts by incorporation of active metal ions/complexes on a variety of solid matrices including microporous materials such as (Cr)S-1 [6], (Cr)APO-5 [6], (Cr)SAPO-37 [7], silica gels, e.g., (Cr)- SiO_2 [8], mesoporous (Cr)MCM-41 [9], etc. All these catalysts have shown promise for the cyclohexane oxidation reaction. However, in most cases, extreme reaction conditions such as high pressures and high temperatures in conjunction with low activity make the process undesirable. Moreover, they are often susceptible to solvolysis by polar molecules such as water, diols and acids present in the oxidation mixtures resulting in extensive leaching of active species metal ions under the reaction conditions [10]. In addition, the catalysts are persistently deactivated by strong interaction of such polar solvents thereby preventing diffusion of the reactants to the active sites. Thus, the development of highly efficient processes/catalysts that generate small amounts of residues/by-products with good activity is one of the main challenges to the scientific community.

Recently, we have reported several transition metal-based mesoporous silicate and aluminophosphate molecular sieves, which show promise for a variety of industrially relevant organic transformations [11–18]. However, in the present context, the chromium-containing MCM-41 and MCM-48 structures are interesting

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[11–14]. Although these catalysts exhibit excellent activity under mild conditions, they also show a considerable initial loss of activity due to leaching of non-framework chromium ions. In this communication, we report, for the first time, the catalytic activity of novel chromium-substituted hexagonal mesoporous aluminophosphates, designated as (Cr)HMA, as highly selective and non-leaching or marginally leaching heterogeneous catalysts for the oxidation of cyclohexane under mild reaction conditions. It is also worth mentioning here that unlike many other chromium-based heterogeneous catalysts [6–8,19], the mesoporous silicates and aluminophosphates stabilize chromium ions in the matrix, which do not leach under the reaction conditions, albeit with an initial loss in the case of the former [12,14], and hence they can act as true heterogeneous catalysts. (Cr)HMA is a novel mesoporous molecular sieve material [20], analogous to mesoporous chromosilicate, (Cr)MCM-41 [11–14], having one-dimensional pores with high surface area and large pore openings. Realizing the importance of cyclohexane oxidation and the urgent need to develop true chromium-based heterogeneous catalysts, in this investigation an attempt was made to synthesize, characterize and explore the catalytic properties of CrHMA. Further, the performance of the catalysts were compared with microporous (Cr)APO-5, (Cr)S-1 and (Cr)- β as well as mesoporous (Cr)MCM-41 materials.

2. Experimental

2.1. Synthesis

The synthesis of (Cr)HMA was carried out hydrothermally as per the following procedure. Phosphoric acid (85%; Qualigens) was diluted with water, and to this aluminum isopropoxide (97%; Merck) was added under constant stirring followed by the addition of an aqueous solution of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (98.5%; Alfa). The resulting mixture was stirred at 343 K for 1 h and then tetramethylammonium hydroxide (TMAOH; 25 wt% in water; Aldrich) was added drop-wise. After a few hours of stirring, cetyltrimethylammonium chloride (CTAC; 25 wt% in water; Aldrich) was added dropwise and the stirring was continued for another 12 h. The pH of the gel was maintained at 10. The final gel having a molar composition of $\text{Al}_2\text{O}_3 : \text{P}_2\text{O}_5 : 0.04 \text{Cr}_2\text{O}_3 : \text{CTAC} : 2.8 \text{TMAOH} : 70 \text{H}_2\text{O}$ ($[\text{Al} + \text{P}]/\text{Cr} = 50$) was kept in a Teflon-lined autoclave and heated in an air oven at 373 K for 72 h for crystallization. The resultant solid product was washed repeatedly with distilled water, filtered and dried at 243 K for 12 h. Calcination was performed at 823 K for 1 h in a flow of N_2 , followed by 2 h in O_2 . Since the results of the present investigation are compared with certain potential redox catalysts, i.e., mesoporous (Cr)MCM-41 as well as certain microporous catalysts such as (Cr)APO-5,

(Cr)- β and (Cr)S-1, they were also synthesized and characterized. The (Cr)MCM-41 catalyst was prepared as per the procedure outlined elsewhere [12] with a final gel molar composition of 1 $\text{SiO}_2 : 0.27 \text{CTAB} : 0.26 \text{NaOH} : 0.26 \text{TMAOH} : 60 \text{H}_2\text{O} : 0.02 \text{Cr}_2\text{O}_3$ ($\text{Si}/\text{Cr} = 50$ and ∞). Likewise, (Cr)S-1 ($\text{Si}/\text{Cr} = 50$) [6], (Cr)APO-5 ($[\text{Al} + \text{P}]/\text{Cr} = 50$) [6] and (Cr)- β ($[\text{Si} + \text{Al}]/\text{Cr} = 50$) [19,21] were prepared and characterized as per the earlier reports.

2.2. Characterization

All samples were systematically characterized by various analytical and spectroscopic techniques. Powder X-ray diffraction (XRD) patterns were recorded using a Rigaku-miniflex diffractometer with nickel-filtered $\text{CuK}\alpha$ radiation and a step size of 0.02° . Transmission electron microscopy (TEM) images were recorded using a Philips 200 microscope operated at 160 kV. Surface area analysis was performed using a Sorptomatic-1990 instrument. Before measurement, the calcined sample was evacuated at 523 K for 12 h under vacuum (10^{-3} torr). The surface area was estimated using the Brunauer–Emmett–Teller (BET) method and the pore size was calculated by the Horvath–Kawazoe (H–K) approach. The pore volume was determined from the amount of N_2 adsorbed at $P/P_0 = 0.5$. Diffuse reflectance ultraviolet and visible (DRUV–vis) spectra were recorded using a UV-260 Shimadzu spectrophotometer with Whatman-40 filter paper as standard. Electron spin resonance (ESR; Varian E-112) spectra were recorded both at room temperature and liquid N_2 temperature. Inductively coupled plasma–atomic emission spectrometry (ICP–AES; Labtam Plasma Lab 8440) analysis was used to determine the percentage of metal in the catalysts.

2.3. Reaction procedure

The liquid-phase oxidation of cyclohexane was carried out at 373 K using 50 mg of catalyst, 18 mmol of cyclohexane (99.5%; Merck), 5 mmol of 2-butanone (99.5%; S.D. fine chemicals) and 18 mmol aq. H_2O_2 (30 wt%; S.D. fine chemicals) in 10 ml of acetic acid (99.9%; SISCO) for 12 h under ambient pressure. The reaction products were analyzed by gas chromatography (GC; Nucon 5700) using a Carbowax column.

2.4. Quenching studies

In order to check the leaching of chromium ions (under reaction conditions) from the mesoporous matrix, several recycling and quenching experiments were carried out on both calcined and washed catalysts. The quenching experiments were carried out by separating catalyst from the reaction mixture under the reaction conditions and the reaction was followed on the quenched solution.

2.5. Recycling and washing studies

In order to check the recyclability of the catalyst four reaction runs were carried out. For this purpose, after each reaction, the catalyst was separated from the reaction mixture by filtration and washed with acetone followed by drying at 353 K. Then in order to remove the adsorbed molecules, the catalyst was activated at 723 K for 6 h in air. The washed catalyst was prepared as per the following procedure. About 100 mg of the calcined catalyst was washed with 1 M ammonium acetate (30 ml) solution under constant stirring for 12 h at room temperature. It was then filtered and activated in the same way as that for the recycled catalyst, i.e., heat treatment at 723 K in air for 6 h. The reaction was then carried out on the recycled as well as the washed catalysts.

3. Results and discussion

The XRD of as-synthesized (Cr)HMA (figure 1(a)) showed the typical pattern of MCM-41-type structure [22–25] with an average unit cell parameter (a_0) of 47.6 Å. The main four reflections are reasonably resolved, and indexed on the basis of a hexagonal lattice. On the other hand, the diffraction pattern of calcined (Cr)HMA (figure 1(b)) showed a single broad reflection with an a_0 value of 40.8 Å, characteristic of a disordered (hexagonal) mesoporous structure [25,26]. Further, the main reflection is shifted as compared to the as-synthesized sample (figure 1(a)), i.e., a shift toward higher 2θ values (lower d values), which is in accordance with literature reports for mesoporous materials. This

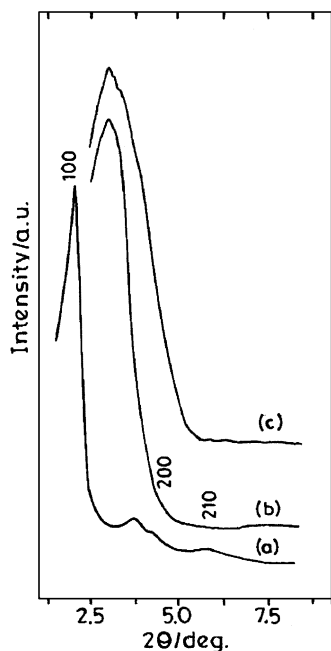


Figure 1. XRD patterns of (Cr)HMA: (a) as-synthesized, (b) calcined and (c) recycled.



Figure 2. TEM image of calcined (Cr)HMA catalyst.

observation is further confirmed by the TEM image (figure 2), and the profile is in good agreement with the disordered FeHMA structure [16]. The BET surface area and pore volume of the calcined (Cr)HMA were $760 \text{ m}^2 \text{ g}^{-1}$ and $0.40 \text{ cm}^3 \text{ g}^{-1}$, respectively, with an average H–K pore size of 28 Å indicating the mesoporous nature of the sample. The ICP–AES analysis of calcined (Cr)HMA gave 1.1 wt% of chromium. The as-synthesized samples were green in color and changed to yellow upon calcination. The former is due to the presence of trivalent chromium ions and the latter is due to the presence of higher-valent chromium ions, i.e., chromate, dichromate and/or polychromates. These observations are in good agreement with our earlier reports on (Cr)MCM-41 and (Cr)MCM-48 [12–14]. Figure 3 depicts the XRD patterns of (Cr)MCM-41. The distinct profiles are typical of MCM-41 structure [14,24,26]. The main four reflections are very well resolved, and are indexed on the basis of a hexagonal lattice. As expected, the reflections are shifted for the calcined sample (figure 3(b)) over the as-synthesized one (figure 3(a)), i.e., a shift toward higher 2θ values (lower d values), which is generally observed for mesoporous systems. On the other hand, the observed slight broadening and shifting of the reflections to lower 2θ values (higher d values) for the recycled catalyst (figure 3(c)) as compared to the calcined catalyst (figure 3(b)) can be accounted for by a possible deformation of the pore walls, which may take place as a consequence of filling of the pores by chromium species [14].

The DRUV–vis spectra of as-synthesized (Cr)HMA (not reproduced here) showed distinctive absorption bands at ~ 642 , 445 and 290 nm corresponding to ${}^4\text{A}_{2g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$, ${}^4\text{A}_{2g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{F})$ and ${}^4\text{A}_{2g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$ transitions, respectively, typical of trivalent

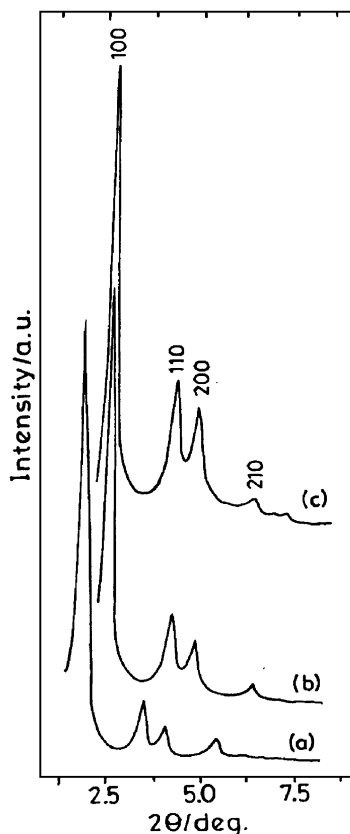


Figure 3. XRD patterns of (Cr)MCM-41: (a) as-synthesized, (b) calcined and (c) recycled.

chromium in octahedral coordination. On the other hand, the DRUV-vis spectrum of calcined (Cr)HMA (figure 4(a)) showed a strong charge transfer ($O \rightarrow Cr$) band at 375 nm ($1t_1 \rightarrow 2e$ symmetry allowed) along with a weak shoulder at 445 nm ($1t_1 \rightarrow 2e$ symmetry forbidden) assigned to chromate and polychromate species, respectively [27,28]. It is interesting to note that

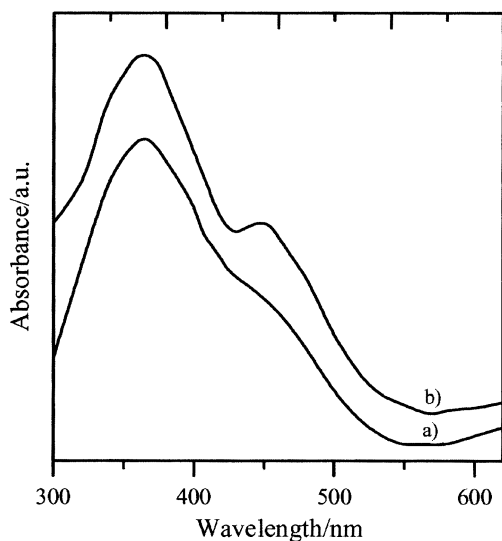


Figure 4. DRUV-vis spectra of (a) calcined (Cr)HMA and (b) calcined (Cr)MCM-41.

only a very small amount of polychromate species was observed for (Cr)HMA as compared to (Cr)MCM-41 (see figure 4(b)) indicating that chromium species are well isolated in the case of the former. It is worth noting here that a similar observation of isolated chromate-type species was also reported for carefully prepared (Cr)MCM-41 [13]. The ESR spectra (not reproduced here) of as-synthesized (Cr)HMA showed a broad spectrum with $g_{\text{eff}} = 1.98$ indicating the presence of trivalent chromium in octahedral coordination, while for the calcined samples a sharp signal appeared at $g_{\text{eff}} = 1.97$, which is characteristic of pentavalent chromium in tetrahedral coordination [13,27,28].

Table 1 summarizes the results of cyclohexane oxidation over different catalysts. It can be seen that (Cr)HMA is highly active for the chosen reaction, with cyclohexanol (Cy-ol) and cyclohexanone (Cy-one) as the major and minor products, respectively. The observed high conversion and selectivity of the catalyst is explained on the basis of coordination environment and oxidation states of Cr ions in the matrix. Thus, under the reaction conditions, the pentavalent/hexavalent chromium in a tetrahedral environment present in the matrix may interact with the oxidant (hydrogen peroxide) to form a catalytically active peroxy complex. Subsequently, the substrate molecules react with this active intermediate species to give the final products. It is to be noted here that the reaction performed over chromium-free HMA or blank (no catalyst) reaction did not show any significant activity indicating that the presence of chromium ions in the aluminophosphate framework influences the activity greatly. It can also be seen from table 1 that the calcined catalyst showed high activity, while a considerable decrease in activity was noticed, first time, for the recycled samples owing to leaching of active (non-framework) chromium ions under the reaction conditions. On the other hand, the activity remains nearly the same in the subsequent cycles. The lower conversion during recycling experiments of (Cr)MCM-41 could, however, be attributed to lower chromium content (0.75 wt%). Interestingly, the washed (Cr)MCM-41 catalyst (0.72 wt%) also showed a similar result. This observation of loss of chromium content upon recycling/washing treatments is well supported by DRUV-vis studies where the initial decrease in absorption band intensity was noted for the calcined (Cr)MCM-41. However, the spectra remain nearly the same for the washed and recycled samples [12–14]. Further, the results are corroborated by the filtrate as well as the quenching studies carried out on washed catalysts (see table 1), which are in line with the above findings.

Further, the reaction was carried out in the absence of catalyst or initiator or with chromium-free HMA as well as MCM-41. In all these cases, a low conversion was noted. Thus, it is clear from all these studies that the amount of chromium ions present in the mesoporous matrix plays an important role in the reaction. Unlike

Table 1
Oxidation of cyclohexane over chromium-containing mesoporous molecular sieves

Catalyst	Conversion (wt%)	Cr content ^a (wt%)	Selectivity (wt%)		
			Cy-ol	Cy-one	Cy-oAc
(Cr)HMA					
Calcined	93.5	1.10	96.3	3.7	–
Filtrate	12.4	0.11	84.0	2.3	13.7
Quenched solution	11.0	0.10	89.2	3.4	7.4
Recycled ^b	85.8	0.96	95.5	4.5	–
Washed	87.5	0.98	97.6	1.6	0.8
HMA	9.8	–	82.8	1.3	15.9
(Cr)MCM-41					
Calcined	95.6	1.25	93.4	4.5	2.1
Filtrate	30.2	0.52	85.6	4.6	9.8
Quenched solution	25.1	0.48	87.2	5.8	7.0
Recycled ^b	72.8	0.75	90.5	2.7	6.8
Washed	73.5	0.72	89.6	6.4	4.0
MCM-41	11.6	–	96.4	–	3.6
Blank	9.0	–	78.1	–	21.9

^a From ICP–AES analysis.

^b Third recycle or fourth run.

the analogous FeHMA system [16], where a considerable distribution of the products (66% Cy-ol, 27% Cy-one) is noticed, the (Cr)HMA catalyst is exceptionally selective toward cyclohexanol (>95%). Furthermore, it is also worth noting that, unlike many other chromium-based catalysts, (Cr)HMA produces no or a negligible amount of the undesired product, i.e., cyclohexyl acetate (Cy-oAc). A similar observation was also noted for CoHMA [18]. Several recycling, washing and quenching experiments were performed under the reaction conditions so as to check the classically encountered problems of active metal ion leaching as well as the stability of the chromium ions in the (Cr)HMA matrix. It is interesting to note that, unlike many other chromium-based catalysts, in particular (Cr)MCM-41, only a marginal loss in activity was noticed for (Cr)HMA in the first recycling (or second run) due to very little leaching of the active species from the matrix. This is very well supported by the results for the washed catalysts where no loss in activity upon recycling was noticed (see table 1), thus indicating that the chromium ions are intact in the mesoporous framework structure.

However, as illustrated in figure 5, a continuous leaching and therefore decrease in activity is noticed for the microporous-based catalysts, i.e., (Cr)APO-5, (Cr)- β and (Cr)S-1, which is in good agreement with the results of Lempers and Sheldon [6]. It can also be seen from figure 5 that all the microporous catalysts showed much lower activity than the mesoporous (Cr)MCM-41 and (Cr)HMA. The observed loss in activity for (Cr)MCM-41 is attributed to the leaching of active chromium ions (0.52 wt%), which is very well supported by the filtrate experiments (under reaction conditions) where the washed chromium ions showed substantial activity. On the other hand, for (Cr)HMA only a very

small amount of leaching of chromium ions (0.11 wt%) was noted. It is also worth noting that the ICP–AES analysis of the filtrates obtained from the washed catalysts showed no leaching of active chromium species. Furthermore, the reaction carried out using these filtrates confirms the absence of active metal ions and hence displays only a marginal activity. It is also interesting to note that both these catalysts, i.e., (Cr)HMA and (Cr)MCM-41, do not lose crystallinity significantly even after recycling or washing treatments, thus behaving truly as heterogeneous catalysts. This is clearly reflected in the XRD patterns (see figures 1(c) and 3(c)) where the catalysts, before and after reaction, show the prominent reflections characteristic of disordered (HMA) and

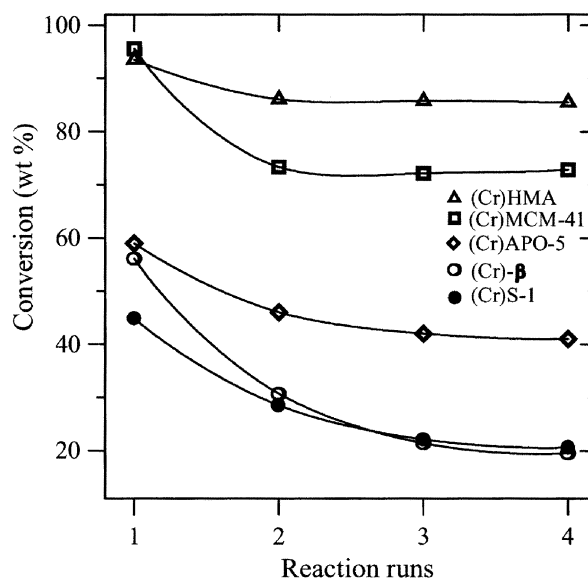


Figure 5. Cyclohexane conversion as a function of recycling runs over various chromium-based mesoporous and microporous catalysts.

ordered (MCM-41) structures. However, a slight broadening-cum-shift of the reflections can be noticed, which may possibly be due to the finer particle size and/or a small loss in crystallinity of the catalyst generated upon cycling. At this juncture, it is also worth noting that, unlike the (Cr)MCM-41 catalyst prepared using tetradecyltrimethylammonium (TDTMA) cationic surfactant [14], the (Cr)MCM-41 catalyst used in the present investigation was prepared using hexadecyltrimethylammonium or cetyltrimethylammonium (CTA) cationic surfactant as well as TMAOH as an organic base. The use of both CTA and TMAOH for the synthesis of (Cr)MCM-41 led to much higher stability and crystallinity, which are clearly evidenced from the XRD patterns.

4. Conclusions

For the first time we report here a superior chromium-based mesoporous aluminophosphate catalyst, (Cr)HMA, for the oxidation of cyclohexane. The catalyst exhibits excellent activity, i.e., a conversion of >95% with a combined cyclohexanol and cyclohexanone selectivity of nearly 100%. More importantly, the leaching of active chromium ions from the matrix is minimal as compared to almost all the chromium-based heterogeneous catalysts reported so far. Thus, this opens up new possibilities as a potential heterogeneous catalyst and the application of these catalysts can further be extended for the oxidation of bulkier molecules.

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References

- [1] W.B. Fisher, J.F. Vanpappen and A.S. Inc, in: *Kirk-Othmer Encyclopedia of Chemical Technology*, Vol. 7, eds. M. Howe-Grant and J.I. Kroschwitz (Wiley, New York, 1992) p. 851.
- [2] R.A. Sheldon and J.K. Kochi, *Metal Catalyzed Oxidation of Organic Compounds* (Academic Press, New York, 1981).
- [3] G.W. Parshall and S.D. Ittel, *Homogeneous Catalysis* (John Wiley, New York, 1992).
- [4] R.A. Sheldon and R.A. van Santen, eds., *Catalytic Oxidation: Principles and Applications* (World Scientific, Singapore, 1995).
- [5] U. Schuchardt, D. Cardoso, R. Sercheli, R. Pereira, R.S. da Cruz, M.C. Guerreiro, D. Mandelli, E.V. Spinace and E.L. Pires, *Appl. Catal. A* 211 (2001) 1.
- [6] H.E.B. Lempers and R.A. Sheldon, *J. Catal.* 62 (1998) 175.
- [7] E.V. Spinacé, U. Schuchardt and D. Cardoso, *Appl. Catal. A* 185 (1999) L193.
- [8] R.S. da Cruz, J.M.D.S. e Silva, U. Arnol and U. Schuchardt, *J. Mol. Catal. A* 171 (2001) 251.
- [9] W.A. Carvalho, P.B. Varaldo, M. Wallau and U. Schuchardt, *Zeolites* 18 (1997) 408.
- [10] R.A. Sheldon, M. Wallau, I.W.C.E. Arends and U. Schuchardt, *Acc. Chem. Res.* 31 (1998) 485.
- [11] R.J. Mahalingam, S.K. Badamali and P. Selvam, *Chem. Lett.* (1999) 1141.
- [12] A. Sakthivel, S.E. Dapurkar and P. Selvam, *Catal. Lett.* 77 (2001) 155.
- [13] A. Sakthivel, S.K. Badamali and P. Selvam, *Catal. Lett.* 80 (2002) 73.
- [14] A. Sakthivel and P. Selvam, *J. Catal.* 211 (2002) 134.
- [15] A. Sakthivel, S.E. Dapurkar and P. Selvam, in: *Advances in Environmental Materials, Vol. I. Pollution Control Materials*, eds. T. White and D. Sun (Materials Research Society, Singapore, 2001) p. 67.
- [16] S.K. Mohapatra, B. Sahoo, W. Keune and P. Selvam, *Chem. Commun.* (2002) 1466.
- [17] S.K. Mohapatra, S.U. Sonavane, R.V. Jayaram and P. Selvam, *Tetrahedron Lett.* 43 (2002) 8527.
- [18] S.K. Mohapatra and P. Selvam, *Top. Catal.* 22 (2003) 17.
- [19] A. Sakthivel, S.K. Badamali and P. Selvam, in: *Recent Trends in Catalysis*, eds. V. Murugesan, B. Arabindoo and M. Palanichamy (Narosa, New Delhi, 1999) p. 96.
- [20] C. Subrahmanyam, B. Louis, R. Fabio, B. Viswanathan, A. Renken and T.K. Varadarajan, *Catal. Commun.* 3 (2002) 45.
- [21] S. Yuvaraj, M. Palanichamy and V. Krishnasamy, *Chem. Commun.* (1996) 2707.
- [22] T. Kimura, Y. Sugahara and K. Kuroda, *Chem. Lett.* (1997) 983.
- [23] Z. Luan and L. Kevan, *Chem. Commun.* (1997) 1009.
- [24] C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli and J.S. Beck, *Nature* 359 (1992) 710.
- [25] P. Selvam, S.K. Bhatia and C.G. Sonwane, *Ind. Eng. Chem. Res.* 40 (2001) 3237.
- [26] Y.J. Khimyak and J. Klinowski, *Phys. Chem. Chem. Phys.* 2 (2000) 5275.
- [27] B.M. Weckhuysen, A.A. Verberckmoes, A.R. De Baets and R.A. Schoonheydt, *J. Catal.* 166 (1997) 160.
- [28] Z. Zhu, Z. Chang and L. Kevan, *J. Phys. Chem. B* 103 (1999) 2680.