

Selective Oxidation of Cycloalkanes over Iron-substituted Hexagonal Mesoporous Aluminophosphate Molecular Sieves

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(Received November 22, 2003; CL-031136)

Iron-substituted hexagonal mesoporous aluminophosphate (FeHMA) molecular sieves oxidize cycloalkanes into cycloalkanol and cycloalkanone with excellent yield in the presence of molecular oxygen or air under mild reaction conditions. The catalyst showed higher activity as compared to mesoporous FeMCM-41 as well as microporous FeS-1 and FeAPO-5 molecular sieves, and that FeHMA can be recycled without much loss in activity.

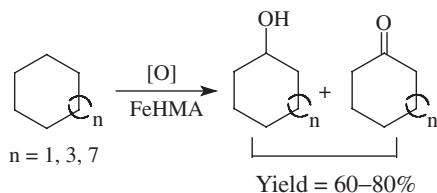
The development of environmentally benign catalytic oxidation process with eco-friendly oxidants, e.g., hydrogen peroxide (H_2O_2), molecular oxygen (O_2) and air, under mild reaction conditions is of immense industrial importance.¹ In recent years, several groups have put forward a number of promising heterogeneous catalysts for the oxidation of cyclohexane.² However, till date, no such advancement has been made for the oxidation of bulky cycloalkanes such as cyclooctane and cyclododecane. On the other hand, a number of homogeneous catalysts have been reported for the oxidation of these bulky cycloalkanes. However, low yields, longer reaction periods, deactivation of the catalysts by oxidative degradation of ligands, separation difficulties, production of hazardous by-products, etc. have made these routes extremely unattractive.³ In order to overcome many of these problems, heterogeneous catalysts as well as few other attractive processes have been proposed but the obtained yield is significantly low ($\approx 40\%$).^{4,5} Hence, in this investigation, we employed trivalent iron-substituted hexagonal mesoporous aluminophosphate (FeHMA) molecular sieves for the selective oxidation of cycloalkanes in the presence of O_2 and air under mild reaction conditions (Scheme 1).

The synthesis and characterization of the FeHMA catalyst having 2.3 wt % iron was carried out as per the procedure reported elsewhere.⁶ For a comparison, FeMCM-41 (2.10 wt % Fe), FeAPO-5 (1.95 wt % Fe) and FeS-1 (1.90 wt % Fe) were also prepared according to the literature procedures.⁷ The oxidation of cyclohexane (18 mmol) was carried out using 10 mL of solvent (acetic acid), 5 mmol of initiator (methyl ethyl ketone; MEK), 50 mg of the catalyst with O_2 or air (40 mL/min flow) as oxidant at 373 K for 12 h under atmospheric pressure. The oxidation of cyclooctane (18 mmol) and cyclododecane (12 mmol)

were carried out under similar reaction conditions of cyclohexane except that mixed solvents (5 mL acetic acid + 5 mL dichloromethane) were used to make a homogeneous reaction mixture. After the reaction, the catalyst was separated and the products were extracted with ether and analyzed by means of gas chromatography (GC; Nucon) with Carbowax column. Further, the oxidation products were confirmed by GC-MS (Hewlett Packard G 1800A) equipped with HP-5 capillary column. While the separated catalyst was washed with distilled water for three-times, dried in an air-oven and then activated at 773 K for 6 h. The regenerated catalyst was then used for the subsequent recycling studies.

Table 1 summarizes the results of cycloalkanes oxidation over FeHMA. It can be seen from this table that the mesoporous catalyst successfully transforms the substrate molecules into desired products with good conversion under mild reaction conditions. Further, the reactions predominantly give cycloalkanol and cycloalkanone as the major products along with a small amount of secondary reaction product, viz., cycloalkyl acetates. It can also be seen from this table that the catalyst exhibits high TON, which clearly reflects the efficiency of FeHMA. At this juncture, it is noteworthy that in the presence of iron-free HMA catalyst as well as without the use of catalyst (blank reaction), the reaction showed meager activity ($<5\%$ conversion). Thus, the high activity of FeHMA for the chosen reactions could be accounted primarily to the isolated trivalent iron present in the framework structure of HMA.

It is also important to mention here that the use of air as oxidant shows lower TON as compared to molecular O_2 . The reaction may proceed through radical path, as evidenced for the oxidation of cyclohexane over FeAPO-5,^{2a} and that direct attack of O_2 on cycloalkanes is endothermic process, and hence the use of carbonyls as reaction initiator is inevitable. Further, the oxidation of cyclooctane showed high TON as compared to the inert cyclohexane and the highly steric cyclododecane. On the other hand, the conversion of cyclooctane and cyclododecane can be



Scheme 1. Oxidation of cycloalkanes (C₆, C₈, and C₁₂).

Table 1. Oxidation of cycloalkanes over FeHMA

Substrate	Oxidant	Conv. /wt %	TON ^a	Selectivity/wt %		
				-ol	-one	Others ^b
Cyclohexane	O_2	62.7	564	62.2	34.0	3.8
	Air	46.0	414	67.8	31.2	1.0
Cyclooctane	O_2	74.6	671	52.5	46.0	3.5
	Air	52.5	472	55.0	43.2	1.8
Cyclododecane	O_2	82.5	492	50.0	47.3	2.7
	Air	55.8	335	55.6	43.0	1.4

^aTurn over number = number of moles of cycloalkanes converted per mole of iron. ^bMainly cycloalkyl acetate is obtained as chain-terminating product.

enhanced to 92 and 95%, respectively using H_2O_2 (30%) as oxidant, however, with the formation of excess quantities (≈ 8 –10%) of secondary chain-terminating products such as cycloalkyl acetates. While the use of TBHP (70%) gave 72 and 68% conversion of cyclooctane and cyclododecane, respectively. The lower activity could be attributed to the deactivation of the catalyst as a result of the formation of *t*-butanol as a consequence of TBHP decomposition under the reaction conditions.

For a comparison, the cyclododecane reaction was carried out over mesoporous FeMCM-41 as well as microporous FeAPO-5 and FeS-1 catalysts, and the results are presented along with FeHMA in Figure 1. It can be seen from this figure that both the microporous catalysts show much lower activity as compared to their mesoporous analogues, viz., FeHMA and FeMCM-41. The lower activity of both FeAPO-5 and FeS-1 could largely be attributed to the small pore openings and thereby hinder the diffusion of bulky molecules, viz., cyclododecane, inside the pore aperture. On the other hand, the lower activity of FeMCM-41 as compared to FeHMA could be explained on the basis of higher pore wall thickness of the former than the latter (see Table 2), which suggests that low amount of active species exposed for the substrate molecules.⁸

In order to check the reusability of the various catalysts, recycling experiments were executed for the oxidation of cyclododecane with O_2 , and the results are illustrated in Figure 1. It is interesting to note from this figure that the activity remains nearly intact even after three recyclings (4th run). This is well sup-

ported by the ICP–AES analysis where no change in iron content was noticed for the reused catalysts. In addition, it may also be noted here that the mesoporous catalysts keep their structure intact and porosity intact even after three cycling procedures. It is, however, important to note that, unlike FeHMA, the activity of FeMCM-41 decreases upon recycling owing to leaching of active iron (12%) under reactions conditions. This could be attributed to the lower stability of trivalent iron in the silicate matrix.^{6,7a}

In conclusion, in the present investigation, it was demonstrated that FeHMA is an efficient and novel heterogeneous catalyst for the selective oxidation of cycloalkanes with molecular oxygen or air as oxidant. The catalyst showed better activity than many other catalyst systems reported so far, and thus opens up a new possibility as a potential catalyst for the synthesis of fine chemicals.

The authors thank Sophisticated Analytical Instrumentation Facility, IIT-Bombay for ICP–AES and GC–MS analyses.

References

- 1 a) R. A. Sheldon and J. K. Kochi, "Metal-Catalyzed Oxidations of Organic Compounds," Academic Press, New York (1981). b) C. L. Hill, "Activation and Functionalization of Alkanes," Wiley, New York (1989).
- 2 a) R. Raja, G. Sankar, and J. M. Thomas, *J. Am. Chem. Soc.*, **121**, 11926 (1999). b) M. Nowotny, L. N. Pedersen, U. Hanefeld, and T. Maschmeyer, *Chem.—Eur. J.*, **8**, 3724 (2002). c) A. Sakthivel and P. Selvam, *J. Catal.*, **211**, 134 (2002). d) S. E. Dapurkar, A. Sakthivel, and P. Selvam, *New J. Chem.*, **27**, 1184 (2003). e) S. K. Mohapatra and P. Selvam, *Top. Catal.*, **22**, 17 (2003).
- 3 a) D. H. R. Barton, E. Csuhai, and N. Ozbalik, *Tetrahedron Lett.*, **46**, 3743 (1990). b) U. Schuchardt, D. Mandelli, and G. B. Shul'pin, *Tetrahedron Lett.*, **37**, 6487 (1996). c) J.-H. In, S.-E. Park, R. Song, and W. Nam, *Inorg. Chim. Acta*, **343**, 373 (2003).
- 4 a) R. Neumann and A. K. Khenkin, *Chem. Commun.*, **1996**, 2643. b) K. Yamaguchi and N. Mizuno, *New J. Chem.*, **26**, 972 (2002). c) U. R. Pillai and E. Sahle-Demessie, *New J. Chem.*, **27**, 525 (2003).
- 5 N. Theysen and W. Leitner, *Chem. Commun.*, **2002**, 410.
- 6 S. K. Mohapatra, B. Sahoo, W. Keune, and P. Selvam, *Chem. Commun.*, **2002**, 1466.
- 7 a) S. K. Badamali and P. Selvam, *Stud. Surf. Sci. Catal.*, **113**, 749 (1998). b) J. Das, C. V. V. Satyanaryana, D. K. Chakrabarty, S. N. Piramanayagam, and S. N. Shringi, *J. Chem. Soc., Faraday Trans.*, **88**, 3255 (1992). c) R. Szostak, V. Nair, and T. L. Thomas, *J. Chem. Soc., Faraday Trans. 1*, **83**, 487 (1987).
- 8 a) W. Zhang, J. Wang, P. T. Tanev, and T. J. Pinnavaia, *Chem. Commun.*, **1996**, 979. b) S. K. Mohapatra, F. Hussain, and P. Selvam, *Catal. Commun.*, **4**, 57 (2003).

Table 2. Structural data of calcined FeHMA and FeMCM-41

Catalyst	S_{BET} /m ² g ⁻¹	Pore volume /ml g ⁻¹	H-K pore diameter/Å	FWT /Å ^a
FeHMA	923	0.48	28	8.8
FeHMA ^b	890	0.46	28	9.2
FeMCM-41	637	0.50	33	18.2

^a Framework wall thickness (FWT) = a_0 – H-K pore diameter

^b Used catalyst (cyclododecane oxidation) – after 3rd recycling (or 4th run).

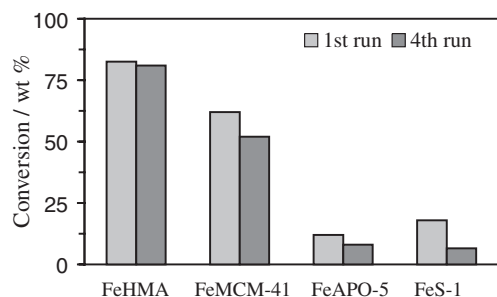


Figure 1. Recycling studies of cyclododecane oxidation over various iron-containing molecular sieves.