

Liquid phase selective oxidation of alcohols over modified molecular sieves[☆]

N. Srinivas, V. Radha Rani, M. Radha Kishan,
S.J. Kulkarni*, K.V. Raghavan

Catalysis Group, Indian Institute of Chemical Technology, Hyderabad - 500007, India

Received 3 November 1999; received in revised form 8 December 1999; accepted 10 February 2000

Abstract

FeZSM-5 has been found to be an efficient catalyst for oxidation of cinnamyl alcohol and primary alcohols with high yields and selectivity. Catalyst was reused for several times and was confirmed to be stable without leaching any metal percent into the solvent. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Zeolites; Oxidation; Selective epoxidation; Cinnamyl alcohol

1. Introduction

The possibility to manipulate active site microenvironment, in zeolites, offers an opportunity to create a redox metal center in molecular sieves by incorporating certain transition metals, e.g. Fe, Ti, V, etc. It enables us to carry out selective oxidation reactions on these catalytically active sites [1–14]. Most of the oxidation reactions using aqueous H₂O₂ or *t*-butylhydroperoxide (*t*-BHP) over molecular sieves have been carried out with those substrates having one functional group. The discovery of the titanium zeolites (e.g. TS-1) has enabled remarkable progress to be made in oxidation of olefins, diolefins and allylic alcohols [15,16]. Not much attention has been paid to the oxidation of the substrates having two active functional groups. In this paper, we report the results of

chemoselective competitive oxidation of alcohols over the modified HZSM-5 (30) and MCM-41 catalysts.

2. Experimental

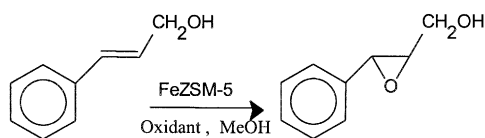
HZSM-5 (Si/Al=30) was obtained from Conteka, Sweden. MCM-41 mesoporous molecular sieve was synthesized [17] using 0.38 g aluminum isopropoxide, 0.3 g sodium hydroxide, 9.26 g Ludox (colloidal) silica, 9.26 g tetra ethyl ammonium hydroxide and 10.55 g hexadecyl trimethyl ammonium bromide in water at 100°C for 24 h and initial pH 12.0. The organic template and surfactant were removed by calcining at 500°C for 10 h. HZSM-5 was further modified by Ti, Cr, Fe and Co (1 wt.%, 5 wt.%) using conventional impregnation method by using nitrates as their corresponding precursors. The reaction was carried out taking 20 ml solvent methanol, 1 g of reactant and 0.5 g of catalyst in a round bottom flask. The reaction was carried out with stirring under reflux conditions for 20 h with reactant to oxidant molar ratio 1:2. The

[☆] IICT Communication No. 4417

* Corresponding author. Tel.: +91-40-673-387;

fax: +91-40-717-3387.

E-mail address: sjkulkarni@iict.ap.nic.in (S.J. Kulkarni).



Scheme 1.

products were analyzed by GC, GC-Mass, IR and were confirmed with authentic samples.

3. Results and discussion

An active catalyst can be prepared by incorporating transition metal cations into zeolites, as they usually possess very high surface area. The XRD patterns of calcined HZSM-5 and MCM-41 and for those modified by transition metals were found to be highly crystalline.

The liquid-phase oxidation of cinnamyl alcohol was carried out using methanol as a solvent and H_2O_2 or *t*-butyl hydroperoxide as an oxidant under reflux conditions. The yields of phenyl glycidol were 88.0 and 72.6 wt.% at 96.8 and 83.4% conversion over FeZSM-5 (1 wt.% Fe) and CrZSM-5 (1 wt.% Cr), respectively, as given in Scheme 1 and Table 1. This shows that in case of such allylic alcohols having internal C=C bond or branching adjacent to C=C bond, the oxidative dehydrogenation of $-\text{CH}_2\text{OH}$ group competes favorably with epoxidation, thus suppresses high chemoselectivity for epoxidation. When there is terminal C=C bond in allylic alcohols, the epoxidation is the major process [16]. When oxidation was

carried out in the presence of molecular sieves, whose pore dimensions are much larger, greater number of catalytic sites are available for the reactants resulting in fast formation of the expected product with lower selectivity because of the unavoidable occurrence of undesired side-reactions [18]. As the product functional group chemoselectivity is influenced by both electronic and steric effect, the suppression of epoxidation is more prominent when a much bulkier oxidant, *t*-BHP was used and the results are given in Table 2. The low reactivity of methanol towards this system allows its use as a solvent.

FeZSM-5 was found to be a potential catalyst for epoxidation with high selectivity, it was used for epoxidation of allyl alcohol, olefins and oxidation of primary alcohols, aldehydes. Table 3 shows the elemental composition (atomic wt.%) of FeZSM-5(30). The composition was recalculated from the individual elemental analysis of the elements silicon, aluminum and iron obtained as wt.%. The oxygen content is not included in this calculation. The sum of the elemental analysis was never 100%, but typically 98%. The systematic error can be due to rapid sorption of water during sample preparation.

Typical thermogravimetric analysis of FeZSM-5 before and after the reaction is given in Fig. 1. The weight loss of the catalyst after the reaction was about 12.58 wt.%. The weight loss is in the temperature range of 200°C to 400°C, indicating the presence of adsorbed organic substrates in the channels of the zeolite.

The catalyzed liquid phase epoxidation of olefins with the terminal C=C is faster as the increased

Table 1

Epoxidation of cinnamyl alcohol with H_2O_2 : variation of catalyst

Reactant: Cinnamyl alcohol (0.5 g); Solvent: Methanol (20 ml); Oxidant=hydrogen peroxide (30 w/v); Molar ratio=Cinnamyl alcohol:Oxidant=1:2; Catalyst weight=0.5 g; Temperature=80°C; Duration=20 h.

S. No.	Catalyst	% Conversion of cinnamyl alcohol	Liquid product distribution (wt.%)			
			Phenyl glycidol	Cinnamaldehyde	Benzaldehyde	Others
1	FeZSM-5 (1 wt.% Fe)	96.8	88.0	–	1.9	6.9
2	CrZSM-5 (1 wt.% Cr)	83.4	72.6	–	4.7	6.1
3	CoZSM-5 (1 wt.% Co)	24.6	15.4	1.9	3.6	3.7
4	TiZSM-5 (1 wt.% Ti)	19.0	10.0	3.0	1.5	4.5
5	CrZSM-5 (5 wt.% Cr)	45.5	37.3	–	2.8	5.4
6	FeMCM-41 (1 wt.% Fe)	80.8	40.8	4.2	12.0	23.8
7	CrMCM-41 (1 wt.% Cr)	50.1	5.0	–	19.1	26.0

Table 2

Epoxidation of cinnamyl alcohol with *t*-butylhydroperoxide (*t*-BHP): variation of catalyst Reactant: Cinnamyl alcohol (0.5 g); Solvent: Methanol (20 ml); Duration=20 h; Molar ratio=Cinnamyl alcohol:Oxidant=1:2; Catalyst weight=0.5 g; Temperature=80°C.

S. No.	Catalyst	% Conversion of cinnamyl alcohol	Liquid product distribution (wt.%)			
			Phenyl glycidol	Cinnamaldehyde	Benzaldehyde	Others
1	FeZSM-5 (1 wt.% Fe)	69.0	44.2	15.0	3.6	6.2
2	CrZSM-5 (1 wt.% Cr)	72.9	36.5	15.2	9.2	12.1
3	CoZSM-5 (1 wt.% Co)	58.0	9.6	11.9	30.7	5.8
4	CrZSM-5 (5 wt.% Cr)	58.7	11.9	22.9	9.3	14.6
5	FeMCM-41 (1 wt.% Fe)	50.6	3.1	23.7	8.8	15.0
6	CrMCM-41 (1 wt.% Cr)	49.7	3.6	10.0	16.0	20.1

Table 3

Chemical analysis (EDAX)

Catalyst	Elemental composition (wt.%)			SEM morphology
	Si	Al	Fe	
HZSM-5(30)	30.31	1.31		
FeZSM-5(30)	32.01	2.28	0.55	Snow ball like 6 μm

diffusional resistance experienced by longer chain with olefin to reach the active site is believed to be the main reason for the observed (1-hexene>1-octene>1-decene) shape selective epoxidation (Table 4). This is consistent with the fact that epoxidation rate decreases

with the increase in chain length of olefins [16]. Along with this certain cleaved products of epoxide such as corresponding diols are obtained along with minor amounts of other high boiling unidentified products.

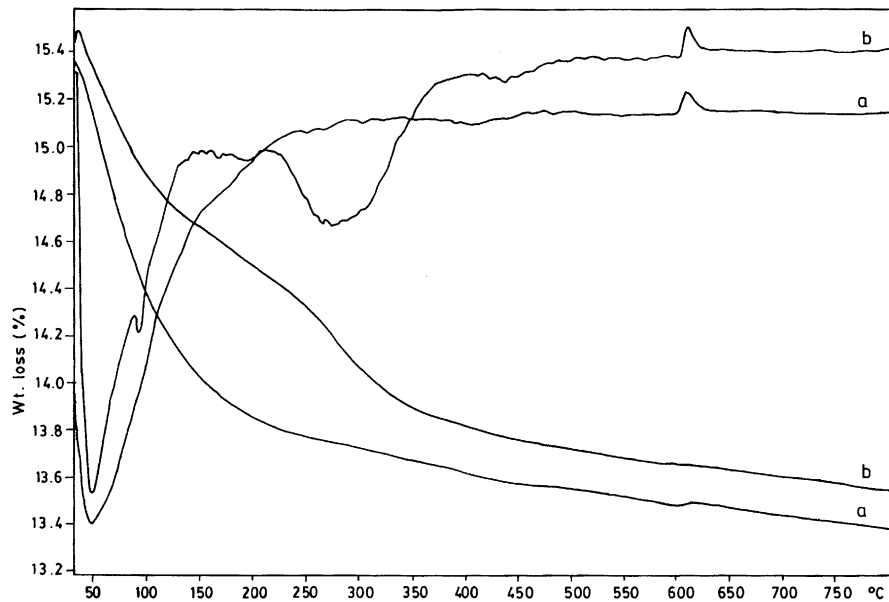


Fig. 1. TG/DTA curves of Fe-ZSM5 (a) before reaction, (b) after reaction.

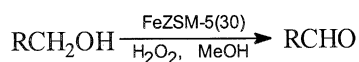
Table 4

Epoxidation of terminal alkenes: reactants variation

Catalyst=1% FeZSM-5 (0.5 g); Solvent: Methanol; Oxidant=H₂O₂; Molar ratio=Reactant:Oxidant=1:2; Temperature=80°C.

S. No.	Reactant	% Conversion	Liquid product distribution (wt.%)		
			Epoxide	1,2-Diol	Others
1	1-Hexene	82.6	47.0	34.0	1.6
2	1-Octene	89.5	46.6	11.6	31.3
3	1-Decene	Traces	Traces		

Similarly, the oxidation of terminal alcohols also faces increased resistance to reach the active site as the chain length increases. As seen from Scheme 2



Scheme 2.

(Table 5), the yields of butyraldehyde, valeraldehyde and hexanaldehyde are 99.4, 97.6 and 94.7 wt.% at 99.9% conversion, by the oxidation of the corresponding alcohols.

Several experiments of oxidation of cinnamyl alcohol, in which the catalyst was filtered and the mother liquor was allowed to react further, were also made. After removal of the catalyst, no further reaction was evidenced. No traces of metal was observed in the

mother liquor when analyzed by ICP-MS. Further, the reaction was carried out three to four times over the same catalyst after activation for 2 h and got same yields repetitively; the results are given in Table 6. The reaction of cinnamyl alcohol was also carried out in presence of Fe(NO₃)₃, without FeZSM-5 under identical conditions about 20% various products including ~4% phenyl glycidol were obtained.

The catalytic oxidation using hydrogen peroxide as oxidizing agent depends on two types of H₂O₂ cleavage/activation: (I) heterolytic (ionic) and (II) homolytic (radical). In general, heterolytic mechanism predominates in the case of those catalysts involving metal ions having low redox potential [16] (difficult redox transition Mⁿ⁺ → M⁽ⁿ⁻¹⁾⁺), while radical mechanism is operative in cases where redox potentials are high with easy redox transition Mⁿ⁺ → M⁽ⁿ⁻¹⁾. The

Table 5

Oxidation of alcohols: reactants variation

Catalyst=1% FeZSM-5 (0.5 g); Solvent: Methanol; Oxidant=H₂O₂; Molar ratio=Reactant:Oxidant=1:2; Temperature=80°C.

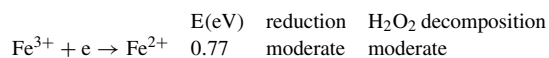
S. No.	Reactant	% Conversion	Liquid product distribution (wt.%)	
			Aldehyde	Others
1	Butanol	99.9	99.4	0.5
2	Pentanol	99.9	97.6	2.3
3	Hexanol	99.5	94.7	4.8
4	Decanol	99.9	62.0	37.9
5	Crotyl alcohol	99.9	95.4	4.5

Table 6

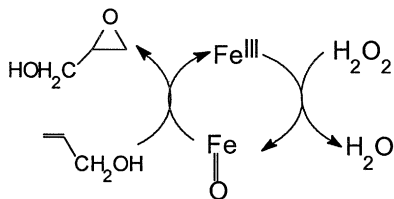
Reusability of the catalyst Reactant: Cinnamyl alcohol (0.5 g); Solvent: Methanol (20 ml); Oxidant=hydrogen peroxide (30 w/v), Molar ratio=Cinnamyl alcohol:Oxidant=1:2; Catalyst weight=0.5 g; Temperature=80°C; Duration=20 h.

Run	Conversion of cinnamyl alcohol (wt.%)	Conversion of H ₂ O ₂ (wt.%)	Selectivity of H ₂ O ₂ (%)	Liquid product distribution(wt.%)	
				Phenyl glycidol	Others
1	99.0	99.0	49.6	88.0	8.8
2	97.3	99.0	49.5	88.1	9.2
3	96.8	99.0	49.6	89.2	7.6

redox potential of:



The possible mechanism [19]:



The extent of H₂O₂ decomposition was estimated by iodometric titrations, which was around 99% and given in Table 6. This indicates that more than the stoichiometric ratio of H₂O₂ to the reactant is being utilized during the reaction. This excess amount of H₂O₂ decomposition may be attributed to the non-selective thermal decomposition of H₂O₂ to O₂ and H₂O [20].

4. Conclusion

The substantial amounts of epoxidation product or aldehydes were formed in the liquid phase oxidation of α,β unsaturated alcohol or primary alcohol over ferric impregnated (redox) molecular sieves.

Acknowledgements

We are thankful to the Department of Science and Technology, India. The project No. SP/S1/H07/97.

NS is thankful to UGC, India for Senior Research Fellowship.

References

- [1] R.A. Sheldon, *J. Mol. Catal. A: Chem* 107 (1996) 75–83.
- [2] I.W.C.E. Arends, R.A. Sheldon, M. Wallau, U. Schuchardt, *Angew. Chem., Int. Ed. Engl.* 36 (1997) 1144.
- [3] W. Holderich, M. Hesse, F. Naumann, *Angew. Chem., Int. Ed. Engl.* 27 (1988) 226.
- [4] C.B. Dartt, M.E. Davis, *Catal. Today* 19 (1994) 151.
- [5] A. Corma, *Chem. Rev.* 97 (1997) 2373.
- [6] T. Maschmeyer, F. Rey, G. Sanker, J.M. Thomas, *Nature* 378 (1995) 159.
- [7] A. Corma, P. Esteve, A. Matinez, S. Valencia, *J. Catal.* 152 (1995) 18.
- [8] T. Blasco, A. Corma, M.T. Navarro, J. Perez Pariente, *J. Catal.* 156 (1995) 65.
- [9] J.S. Reddy, R. Kumar, *J. Catal.* 130 (1991) 440.
- [10] W. Zhang, M. Froba, J. Wang, P.T. Tanev, J. Wong, T.J. Pinnavaia, *J. Am. Chem. Soc.* 118 (1996) 9164.
- [11] R.D. Oldroyd, J.M. Thomas, T. Maschmeyer, P.A. MacFaul, D.W. Snelgrove, K.U. Ingold, D.D.M. Wayner, *Angew. Chem., Int. Ed. Engl.* 35 (1996) 2787.
- [12] W.A. Carvalho, P.B. Varaldo, M. Wallau, U. Schuchardt, *Zeolites* 18 (1997) 408.
- [13] S. Gontier, A. Tuel, *J. Catal.* 157 (1995) 124.
- [14] Z.R. Tian, W. Tong, J.Y. Wang, N.G. Duan, V.V. Krishnan, S.L. Suib, *Science* 276 (1997) 926.
- [15] R.A. Sheldon, *J. Mol. Catal.* 7 (1980) 107.
- [16] P. Kumar, R. Kumar, B. Pandey, *Synlett* (1995) 289.
- [17] C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli, J.S. Beck, *Nature* 359 (1992) 710.
- [18] L. Palombi, F. Bonadies, A. Scettri, *J. Mol. Catal.* 140 (1999) 47.
- [19] A.B. Boricha, H.M. Modi, A. Das, H.C. Bajaj, *Appl. Catal., A* 179 (1999) 5.
- [20] V.I. Paruvulescu, D. Dumitriu, G. Poncelet, *J. Mol. Catal.* 140 (1999) 91.