Cleavage of the Carbon–Carbon Double Bond over Zeolites using Hydrogen Peroxide

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Zeolite molecular sieves catalyse the cleavage of carbon–carbon double bonds of various alkenes in the presence of aqueous hydrogen peroxide as an oxidant; titanium silicate molecular sieves, TS-1 and TS-2 exhibit very high activity in the conversion of α-methylstyrene into acetophenone.

Potassium permanganate has been reported to catalyse the cleavage of carbon–carbon double bonds of various organic molecules[1,2] in aqueous solutions. But the major disadvantage associated with this reaction is the low solubility of organic substrates in the aqueous system. Phase-transfer catalysts[3] and cyclic polyethers[4] have been used to overcome these problems. Tercio *et al.*[5] have reported this reaction over potassium permanganate supported on silica gel under mild conditions. Acetylacetonato- or cyclopentadienyl-rhodium complexes, allylrhodium systems and $(Ph_3P)_3RhCl$ also have been used to cleave carbon–carbon double bonds using molecular oxygen.[6] In this communication, we report for the first time, the use of zeolite catalysts in the cleavage of carbon–carbon double bonds using hydrogen peroxide.

TS-1,[7a] TS-2,[7b] Ga-MEL[7c] and Ga-TS-2[7d] are synthesized according to literature procedures. In a typical reaction, α-methylstyrene (1.0 g) in acetonitrile (10 ml) solvent is added to the catalyst (0.2 g; 200–300 mesh size). The reaction mixture is heated to 353 K. Then, 26 wt% aqueous hydrogen peroxide solution (0.56 g) is added. The products are analysed using HP 5880A series gas chromatograph (50 m long 0.2 mm i.d. silicon gum capillary column).

The activity and selectivity of various reactants over mordenite are reported in Table 1. Styrene and stilbene

Table 1 Activity of various reactants with hydrogen peroxide over mordenite[a]

Reactant	Alkene convn. (wt%)[b]	Product distribution, wt% Epoxide[c]	>C = O[d]	Diol[e]	Others
Styrene	39.0	7.1	72.7	10.1	10.1
α-Methylstyrene	40.6	5.6	54.5	35.6	4.3
Oct-1-ene	9.2	32.6	21.7	*f*	45.7
Stilbene	29.0	*f*	72.4	*f*	27.6

[a] *Reaction conditions*: Catalyst wt = 0.2 g; T/K = 353; Reactant: H_2O_2 (mol) = 2.0; Reaction time (h) = 5. Large port synthetic H-Mordenite supplied by PQ-zeolites, Holland (SiO_2/Al_2O_3 = 30). [b] (Alkene conversion/theoretically possible alkene conversion) × 100. [c] Epoxide of corresponding alkene. [d] Product of the cleavage of carbon–carbon double bond alkene. [e] Diol of corresponding alkene. [f] Not identified.

Table 2 Effect of various zeolite catalysts on reaction of α-methylstyrene with H_2O_2[a,e]

Catalyst				Product distribution, wt%			
Name	Si/Me[b]	Si/Ti	Alkene convn. (% Theor.)	Epoxide	>C=O	Diol	Others[c]
H-Y[d]	10	—	43.6	16.0	51.6	20.2	12.2
H-Mordenite[d]	30	—	40.6	5.6	54.5	35.6	4.3
H-Al-MFI	42	—	35.0	1.7	80.0	11.4	6.9
Alumina	—	—	38.6	7.8	53.4	24.4	14.5
Fumed silica	—	—	37.0	6.5	62.7	21.6	9.2
Silicalite-2	—	—	60.0	6.3	59.0	19.7	15.0
H-Al-MEL	37	—	52.8	7.6	52.3	27.7	12.0
H-Ga-MEL	35	—	68.4	5.1	54.1	26.4	14.4
H-Ga-TS-2	35	85	95.8	4.0	54.9	30.9	10.2
TS-2	—	29	100.0	9.1	42.9	37.9	10.1
TS-2	—	29	83.0	13.3	66.3	10.2	10.2
TS-1	—	24	97.0	15.2	48.0	24.6	12.2

[a] Catalyst wt = 0.2 g; *T*/K = 353; α-methylstyrene: H_2O_2 (mol) = 2; Reaction time (h) = 20. [b] M = Al or Ga. [c] β-Phenylpropionaldehyde, β-phenylpropionic acid and some unidentified compounds. [d] Y zeolite was supplied by Linde, USA and large pore synthetic mordenite was supplied by PQ-zeolites, Holland. [e] Also see Table 1.

showed very good selectivity (~80%) for the cleavage of C=C bond, whereas oct-1-ene exhibited very low selectivity. When styrene oxide was treated under the same conditions, benzaldehyde and styrenediol were the major products. It was expected that benzaldehyde is formed from styrenediol. However, when styrenediol was treated similarly, the reaction did not occur indicating that benzaldehyde (product from the cleavage of C=C bond of styrene) is formed directly from styrene epoxide. Similar activity and selectivity of the as-synthesized form of titanium silicate, TS-2 compared with its calcined form indicates that the reaction is taking place at the surface of the zeolite crystals. This cannot explain the lower activity of bulky molecules like stilbene compared with smaller molecules. However, in the case of stilbene the steric factors cannot be excluded. The lower activity of oct-1-ene also suggests that not only the diffusional and steric factors but the electronic distribution on the C=C bond also affects the activity.

The results obtained in the conversion of α-methylstyrene into acetophenone over different zeolite catalysts are reported in Table 2. Acetophenone, α-methylstyrene epoxide and α-methylstyrenediol were the major products. Some unidentified products including 2-phenylpropionaldehyde are also present. Formaldehyde, the second product of C–C bond cleavage was also identified, but the exact quantity was not determined. Similar products have been reported by Bönnemann *et al.*[6] in the oxidation of 2,3-dimethylbut-2-ene using acetylacetonatorhodium as the catalyst. In the epoxidation of styrene over TS-1, Neri *et al.*[8] have reported about 85% selectivity for phenylacetaldehyde. These results are contrary to the results obtained in this study. TS-1 exhibited slightly better selectivity for the epoxide than TS-2, but in both the cases, the overall selectivity was found to be high towards C=C bond cleavage. When Ti is incorporated into the zeolite framework the activity is increased very sharply. TS-2 (titanium silicate analogue of MEL) exhibited better selectivity for epoxide compared with Ga-MEL and Ga-TS-2 (gallotitanium-silicate analogues of MEL). The presence of acid sites in Ga-MEL and Ga-TS-2 may cause the ring cleavage of epoxide resulting in lower selectivities. Higher activity of TS-2 (Si/Ti = 75) and Ga-TS-2 (Si/Ti = 85; Si/Ga = 35) compared with Ga-MEL (Si/Ga = 39) indicates that the Ti^{4+} ions, substituted into the zeolitic framework play a significant role in this reaction.

The detailed studies indicated that a small amount of catalyst can significantly catalyse this reaction. When the reaction is carried out over TS-2 at 300 K instead of 353 K, selectivity for C=C bond cleavage is increased from 43 to 67%; the conversion being similar. Acetonitrile, *tert*-butyl alcohol and water are good solvents for C=C bond cleavage whereas, acetone seems to be a good solvent for the formation of epoxide.

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