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Selective oxidation of cyclohexane over TS-2, a titanium silicate molecular sieve

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The selective oxidation of cyclohexane to cyclohexanol and cyclohexanone using hydrogen peroxide has been studied over TS-2, a titanium silicate molecular sieve with a MEL structure. The reaction is found to be catalyzed by the Ti present in the framework structure, the activity being proportional to the Ti content.

Keywords: TS-2; titanium silicates; oxidation over TS-2; cyclohexane oxidation; oxidation using hydrogen peroxide

1. Introduction

TS-1 a medium pore titanium silicate molecular sieve [1] with MFI structure [2] has been found to catalyze the oxidation of many organic compounds with hydrogen peroxide [3–5].

Recently, Huybrechts et al. [6] and Tatsumi et al. [7] have shown that TS-1 is capable of catalyzing the oxyfunctionalization of even highly inert organic compounds like normal alkanes by hydrogen peroxide. Among the alkane oxidation reactions, the conversion of cyclohexane and cyclohexanone is industrially very important. At present, the above reaction is carried out over transition metal catalysts with low conversions and poor selectivities [8]. Tatsumi et al. [7] have shown that TS-1 catalyzes the conversion of cyclohexane into cyclohexanol and cyclohexanone.

Reddy et al. [9] have reported the synthesis of another medium pore titanium silicate, designated as TS-2, having a MEL structure. They have found that TS-2 also catalyzes many of the reactions like ammoximation [10] and hydroxylation [11] of hydrocarbons which have been reported to take place over TS-1 [4]. In this paper we report the oxyfunctionalization of cyclohexane with hydrogen peroxide in moderate yields using the newer titanium silicate TS-2. The present studies could open up a new commercial route to the manufacture of cyclohexanol and cyclohexanone from cyclohexane.

2. Experimental

The titanium silicate, TS-2 was synthesized according to published procedures [9]. The confirmation for the incorporation of Ti in the lattice was obtained from the increase in unit cell parameters (when compared to the corresponding silicalite) [12] and the presence of an IR absorption band and around 960 cm^{-1} attributed to tetrahedral Si-O-Ti linkages [1]. The as synthesized zeolites were washed, dried in an inert gas atmosphere and calcined in dry air at 773 K to remove the organics.

The catalytic reactions were carried out in stirred autoclaves (Parr Instrument company, Illinois, USA) of 300 ml capacity at temperatures between 353 and 393 K under autogeneous pressure, using different mole ratios of hydrogen peroxide (aqueous solution) and cyclohexane. In order to get a single liquid phase, acetone was used as a solvent. Typically 1 g of the catalyst was used as a fine powder (300–400 mesh). The duration of the runs was 5 h. The analysis of the products was carried out in a gas chromatograph (HP 5880 A) using a capillary column (HP1; 50 m × 0.5 mm) and an FID detector.

3. Results and discussions

The results of the reaction of cyclohexane with hydrogen peroxide in the presence of TS-2 are presented in table 1. In all the experiments the major products were cyclohexanol and cyclohexanone. Small amounts of compounds with more than one functional group and lactones were also detected. These compounds have not been estimated in detail. Increasing the temperature of the reaction increases cyclohexane conversion. Higher temperatures also favour the formation of cyclohexanone. For example, the cyclohexanone to cyclohexanol (mole) ratio is 0.45 at 353 K, while it is 1.32 at 393 K (table 1). Again, another factor that affects the relative yields of cyclohexanone and cyclohexanol is the amount of H_2O_2 used in the reaction. When the H_2O_2: cyclohexane mole ratios are 1.0 and 0.20, the cyclohexanone/cyclohexanol ratios are 1.02 and 0.48. It is found from table 1 that the H_2O_2 selectivity (% of H_2O_2 usefully consumed) and product selectivity (selectivity for cyclohexanol and cyclohexanone) increases with temperature. Similarly, they increase with a decrease in H_2O_2 concentration.

The activity and product selectivity increase with increasing Ti-content (decreasing Si/Ti ratios) suggesting that Ti ions are the active centers. The activities (at 373 K) of the three samples with Si/Ti ratios of 29, 48 and 124, respectively, expressed as turn over numbers (TON = number of molecules of cyclohexane converted per Ti atom per second) are respectively 1.57×10^{-3}, 1.92×10^{-3} and 3.66×10^{-3}. Keeping the cyclohexane/H_2O_2 (mole) ratios constant at 3, the studies on the influence of catalyst amount were carried out at

Table 1
Oxidation of cyclohexane with H_2O_2 over TS-2 [a]

Si/Ti ratio	Catalyst amount (g)	Temp. (K)	H_2O_2 [b] (moles)	Cyclohexane conversion (mole %)	TON [c] ($\times 10^{-3}$)	H_2O_2 selectivity [d]	Product composition (mole %)		Others [g]
							CH-OL [e]	CH-ONE [f]	
29	1.0	373	0.038	13.0	1.50	42.2	60	34	6
48	1.0	373	0.038	9.8	1.92	30.4	62	31	7
124	1.0	373	0.038	7.0	3.66	20.0	65	25	10
29	1.0	353	0.038	5.8	0.67	23.1	64	29	7
29	1.0	393	0.038	15.8	1.82	59.3	41	54	5
29	1.0	373	0.102	27.8	3.21	31.4	44	45	11
29	1.0	373	0.024	7.3	0.84	70.0	64	31	5
29	0.2	373	0.038	7.5	4.51	20.3	40	29	31
29	0.5	373	0.038	11.7	2.82	36.3	52	35	13
22 [h]	1.0	373	0.038	17.5	1.60	60.0	58	38	4

[a] Duration of run = 5 h.

[b] Cyclohexane = 0.1190 moles; solvent = 0.43 moles.

[c] TON = turn over number; no. of molecules of cyclohexane converted per Ti atom per sec.

[d] H_2O_2 selectivity = (H_2O_2 consumed for cyclohexanol and cyclohexanone formation/Total H_2O_2 consumed) × 100.

[e] CH-OL = cyclohexanol;

[f] CH-ONE = cyclohexanone.

[g] Oxygenates like lactones and compounds and compounds with more than one functional group.

[h] Catalyst = TS-1.

three different catalyst levels, viz., 0.2, 0.5 and 1.0 g. The H_2O_2 content was kept intentionally low to achieve better H_2O_2 selectivities. Increasing the catalyst content increases the cyclohexane conversion as well as product selectivity. Further the turn over number (TON, defined earlier) decreases when the catalyst amount is increased; TON $= 4.51 \times 10^{-3}$, 2.82×10^{-3} and 1.57×10^{-3} for 0.2, 0.5 and 1.0 g catalyst loadings, respectively. As expected for a medium pore system, shape-selectivity in the oxidation of alkanes has been observed in the case of TS-2. For example, when a mixture (50 : 50 mole%) of n-hexane and cyclohexane is used as the feed, the conversion of n-hexane and cyclohexane are 12.3 and 1.8 wt% [10]. The activity of TS-1 for the oxidation of cyclohexane under similar conditions is also reported in table 1. It is found that the activities of TS-1 and TS-2 are comparable.

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References

[1] M. Taramasso and B. Notari, U.S. Pat (1983) 4, 410, 501.

[2] W.M. Meir and D.H. Olson, *Atlas of Zeolite Structure Types*, 2nd ed. (Butterworths, London, 1987).

[3] W. Hölderich, M. Hesse and F. Näumann, Angew. Chem. Int. Ed. Engl. 27 (1988) 226.

[4] B. Notari, in: *Innovation in Zeolite Material Science* (Stud. Surf. Sci. and Catal., Vol. 37), eds. P.J. Grobet, W.J. Mortier, E.F. Vansant and G. Schulz-Eklosf (Elsevier, Amsterdam, 1989) p. 413.

[5] W.F. Hölderich, in: *Zeolites as Catalysts, Sorbents and Detergent Builders* (Stud. Surf. Sci. and Catal., Vol. 46), eds. H.G. Karge and J. Weitkamp (Elsevier, Amsterdam, 1989) p. 194.

[6] D.R.C. Huybrechts, L. De. Bruycker and P.A. Jacobs, Nature 345 (1990) 240.

[7] T. Tatsumi, M. Nakamura, S. Negishi and H-O. Tominaga, J. Chem. Soc., Chem. Commun. (1990) 476.

[8] Kirk-Othmer, *Encyclopaedia of Chemical Technology*, 3rd ed., Vol. 18 (John Wiley and Sons, New York, 1978) p. 425.

[9] J.S. Reddy, R. Kumar and P. Ratnasamy, Appl. Catal. 58 (1990) L1.

[10] J.S. Reddy, S. Sivasanker and P. Ratnasamy, J. Mol. Catal., in press.

[11] J.S. Reddy and S. Sivasanker, unpublished results.

[12] J.S. Reddy and R. Kumar, J. Catal. 130 (1991) 440.