Titanium Silicate Molecular Sieve (TS-1)/H_2O_2 induced Triphase Catalysis in the Oxidation of Hydrophobic Organic Compounds with Significant Enhancement of Activity and *Para*-Selectivity

Asim Bhaumik and Rajiv Kumar*

Catalysis Division, National Chemical Laboratory, Pune-411 008, India

Triphasic conditions (solid and two immiscible liquid reactants) when compared with more commonly employed biphasic ones (solid and immiscible liquids along with a cosolvent), significantly enhance the catalytic activity and *para* selectivity in the hydroxylation/oxidation of various hydrophobic organic compounds (*viz.* toluene, anisole, benzyl alcohol, cyclohexanol *etc.*) over crystalline, microporous, titanium silicate, TS-1, using dilute H_2O_2 (30 mass%, aq.).

In heterogeneous liquid-phase reactions using a solid catalyst and two immiscible reactants a cosolvent is generally used to homogenize the liquid phase with the aim of accelerating the interaction of reactants with the catalyst. However, in such biphasic conditions the solvent plays an important role in influencing both activity and selectivity. Further, the separation of product(s) from solvent/reaction mixture is a cumbersome process. Regen[1] introduced a concept of triphase catalysis in heterogeneous systems, where a solid catalyst and two immiscible liquid reactant phases are present. Such studies were made using polymer supported resins,[1] quaternary ammonium salts[2] or aluminas.[3] Recently, crystalline, microporous titanium silicate molecular sieves, such as TS-1 (MFI type with pore dimensions: 0.54 × 0.56 nm straight channels and 0.51 × 0.55 nm sinusoidal channels), TS-2 (MEL type with pore dimension: 0.56 × 0.54 nm straight channels) *etc*, have been found to be excellent catalysts for the oxidation of various organic compounds.[4–8] However, in most of the cases, the catalytic reactions were conducted under biphasic conditions using a cosolvent.[6,8] Now we report, for the first time, TS-1/H_2O_2 catalysed oxidation of some water immiscible (hydrophobic) organic compounds under triphasic conditions (solid catalyst with two immiscible liquids) compared to that under biphasic conditions. A significant enhancement in the activity and *para* selectivity is observed under triphasic conditions in the absence of any solvent.

The catalyst, TS-1 (Si/Ti = 27) was synthesized according to known procedures,[5] and characterized through techniques such as XRD, IR, UV–VIS, adsorption and catalytic test reactions, which ascertained that the catalyst is free from impurities; such details have been given earlier.[4–7] The liquid-phase catalytic reactions were conducted in a glass batch reactor. In a typical reaction, 10 mmol of the substrate and 10 mmol of H_2O_2 were reacted over the catalyst (TS-1, 20 mass% with respect to the substrate) in the presence of acetonitrile as solvent (biphase) or water (triphase). The substrate : acetonitrile or substrate : water ratio was kept at 1 : 10 (m/m) so that the total volume of the reaction mixture remains same in both bi- and tri-phasic conditions. The products were analysed by high resolution capillary gas chromatograph (HP, 5880 using FID).

In Table 1, the results of the hydroxylation of toluene **1**, anisole **2**, *m*-cresol **3** and oxidation of benzyl alcohol **4** and cyclohexanol **5** over TS-1/H_2O_2 (30 mass%, aq.) are reported. In all the cases two sets of experiments, one in a biphasic system using acetonitrile (a commonly used solvent in TS-1/H_2O_2 catalysis) as solvent and a triphasic system in the absence of any organic solvent were carried out under similar reaction conditions.

It is quite clear from Table 1, that in all the cases the conversion as well as reaction rates are considerably increased under triphasic conditions. Further, in triphasic conditions during hydroxylation of the aromatic ring in toluene **1**, anisole **2** and *m*-cesol **3**, high regioselectivity for the *para*-hydroxy product is observed, while the biphasic system (using acetonitrile solvent) exhibits more selectivity for *ortho*-hydroxy products.

For example, in the hydroxylation of toluene **1** the molar ratio of *o*-cresol **1x** to *p*-cresol **1y** exhibited under bi- and tri-phasic conditions was 2.45 : 1 and 0.75 : 1, respectively. Similarly, during hydroxylation of anisole **2** the ratio of 2-hydroxyanisole **2x** to 4-hydroxyanisole **2y** was 2.22 : 1 and 0.35 : 1 in bi- and triphase systems, respectively. This is an interesting illustration of the reversal of regioselectivity. During hydroxylation of *m*-cresol **3** all the isomers of dihydroxytoluene were obtained. Although, the relative distribution of 3,4-dihydroxytoluene **3x** was comparable in both the bi- and triphasic conditions, the distribution of 2,3- **3y** and 2,5- **3z** isomers was found to be completely reversed. Whereas the 2,3-isomer (*ortho* to both OH and Me) was predominant in the biphasic system, the 2,5-isomer (*ortho* to Me and *para* to OH) of dihydroxytoluene was most favoured under triphasic conditions.

The enhancement in the converson of benzyl alcohol **4** during its oxidation to benzaldehyde **4x** and benzoic acid **4y**, was dramatically high in the triphase system, exhibiting a nearly seven-fold increase in activity compared to that obtained in the biphasic system (Table 1). In the oxidation of cyclohexanol **5** to

Table 1 Oxidation/hydroxylation of various substrates over TS-1[a]

Substrate	Phase	Conv. (mole%)	*t*/h[b]	TON (h^{-1})[c]	Product sel. (%)			
					x	y	z	Other[d]
Toluene **1**	Biphase	5.5	12	0.42	69.7	28.4	—	1.9
	Triphase	14.8	6	2.28	41.4	55.9	—	2.7
Anisole **2**	Biphase	42.2	16	2.07	66.6	30.3	—	3.1
	Triphase	66.5	8	6.54	25.6	72.3	—	2.1
m-Cresol **3**	Biphase	10.7	14	0.60	38.2	39.4	18.5	3.9
	Triphase	26.5	14	1.49	35.6	20.3	40.4	3.7
Benzyl alcohol **4**	Biphase	12.5	18	0.55	86.0	14.0	—	—
	Triphase	89.6	18	3.92	73.5	25.6	—	0.9
Cyclohexanol **5**	Biphase	12.8	18	0.60	98.5	—	—	1.5
	Triphase	36.4	12	2.58	96.2	—	—	3.8

[a] Reaction temperature = 353 K. [b] Time required to obtain maximum conversion of the substrate. [c] Moles of substrate converted per mole of Ti in TS-1 per h. [d] Some higher boiling, unidentified products.

cyclohexanone **5x**, an approximately three-fold increase in conversion was observed under triphasic conditions. The selectivity for benzoic acid, a further oxidation product of primarily formed benzaldehyde, was also quite high in the triphasic system, which may be a consequence of high conversion levels.

Significantly higher *para* selectivity obtained in triphasic conditions indicates that the reaction takes place inside the zeolite channels. However, in the biphasic system, low conversion as well as very high *ortho* selectivity probably indicate that the reaction takes place significantly on the external surface of the catalyst.

Although, it is clear that more work is required to explain these above mentioned interesting results, one can speculate that under biphasic conditions, the solvent may be competing with reactant for diffusion in the channels and adsorption at the active sites of TS-1 catalyst. This point is further supported by the fact that when *tert*-butanol, which is too bulky to enter in TS-1 (MFI topology) pores, was used as solvent in place of acetonitrile, very high *para* selectivity (*o*/*p* = 0.2; conv. = 28%) was obtained in the hydroxylation of anisole. Since titanium silicate molecular sieves are relatively hydrophobic in nature[5] reactant may be competing more favourably with water for diffusion and adsorption under triphasic conditions resulting in the higher conversion and shape selectivity.

In summary, it has been demonstrated that using a triphasic system (solid–liquid–liquid), in the absence of any cosolvent, considerable increase in the conversion of water-immiscible organic compounds during their oxidation by TS-1/H_2O_2 (30% aq.) system can be achieved along with very high *para* selectivity (*vis-á-vis* biphasic conditions). In addition to better activity and *para* selectivity, the present triphase system offers a distinct advantage in product separation.

A. B. thanks CSIR, New Delhi for providing a research fellowship.

Received, 14th November 1994; Com. 4/06933A

References

1 S. L. Regen, *J. Am. Chem. Soc.*, 1975, **97**, 5956; *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 421.
2 H. Molinari, F. Monttanari, S. Quici and P. Tundo, *J. Am. Chem. Soc.*, 1979, **101**, 3920.
3 S. Quici and S. L. Regen, *J. Org. Chem.*, 1979, **44**, 3436.
4 B. Notari, *Stud. Surf. Sci. Catal.*, 1987, **37**, 413.
5 A. Thangaraj, R. Kumar, S. P. Mirajkar and P. Ratnasamy, *J. Catal.*, 1991, **130**, 1.
6 A. Thangaraj, R. Kumar and P. Ratnasamy, *J. Catal.*, 1991, **131**, 294.
7 M. S. Rigutto and H. Van Bekkum, *Appl. Catal.*, 1991, **68**, L-1.
8 A. Bhaumik, R. Kumar and P. Ratnasamy, *Stud. Surf. Sci. Catal.*, 1994, **84C**, 1883.