Epoxidation of alkenes over new amorphous materials containing different acidic functions

D. Trong On, M. P. Kapoor and S. Kaliaguine*

Department of Chemical Engineering, Laval University, Québec, Canada G1K 7P4

Titania–silica mixed oxides with different trivalent cations, such as B^{3+} or Al^{3+}, are synthesized using a simple route; these catalysts are very active in epoxidation of alkenes and selective in α-diol formation.

Ti-containing zeolites (TS-1 and TS-2) are effective catalysts for the selective oxidation of alkanes, alcohols and the epoxidation of alkenes in the presence of hydrogen peroxide.[1] Recently, Hutchings and Lee[2] achieved the controlled selective epoxidation of allyl alcohol with H_2O_2 by controlling the acidity of TS-1. Jacobs and coworkers[3] have also shown that the epoxidation of cycloalkenes can be achieved using zeolite-encapsulated manganese(II) complexes, followed by acid-catalysed ring opening and carbon–carbon bond cleavage. However, owing to the relatively small pore size of the host framework, the application range is limited, because the large and bulky substrates cannot penetrate into the narrow pores of zeolites. Recently, large pore zeolites such as Ti-β[4] and especially Ti-MCM-41[5] were synthesized and they are more active than TS-1 in the epoxidation of bulky alkenes.

By contrast, as compared to zeolites, titania–silica amorphous mixed oxides of homogeneous composition can be synthesized with a wide variety of surface areas and pore structures by controlling the hydrolysis conditions, *e.g.* pH, temperature, concentration, stirring and dropping rate *etc.*, and the drying procedure.[6] These materials were found to show selective catalytic activity towards the epoxidation of bulky cycloalkenes in the presence of H_2O_2.[7,8]

In the present communication, we report a relatively simple and effective route to synthesize highly dispersed titania–silica mixed oxides containing a trivalent cation such as B^{3+} or Al^{3+} in the silica matrix. These solids can actively catalyse the epoxidation of bulky alkenes. Epoxidation of oct-1-ene is followed by acid-catalysed epoxy-ring opening and formation of the corresponding diol with a degree of selectivity which depends on the nature of the trivalent cation.

The Ti–Si mixed oxides with B^{3+} or Al^{3+} were prepared by simultaneous hydrolysis and condensation of the metal alkoxides by controlling the rate of water addition. Gels with the following molar chemical composition were prepared: $SiO_2 : 0.02\ TiO_2 : 0.015\ M_2O_3$ (M = B, Al). A typical synthesis procedure of Ti–Si mixed oxides sample was performed as follows: 20.8 g of tetraethylorthosilicate (TEOS) (Aldrich 99%) and 0.568 g of $Ti(OPr^i)_4$ (Aldrich 97%) were added to 100 ml of propan-2-ol at room temp. with continuous stirring. Then, 10 ml of deionized water was injected at a constant low rate over 30 min. The solvent was allowed to slowly evaporate from the well agitated system at room temperature. A white amorphous powder then obtained was further dried at 373 K overnight and calcined at 773 K for 5 h under a continuous air flow. The Ti–Si mixed oxides with B^{3+} or Al^{3+} and pure SiO_2 samples were prepared in a similar manner. 0.564 g of $B(OPr^i)_3$ (Aldrich 98%) and 0.613 g of $Al(OPr^i)_3$ (Aldrich 98%) were used for B–Ti–Si and Al–Ti–Si mixed oxides respectively. For comparison, Na-free Ti-β and titanium borosilicalite (TBS-1) were also synthesized as reported previously.[4,12] The detailed compositions of the samples are given in the Table 1.

Fig. 1 shows the diffuse reflectance UV–VIS spectra of calcined samples. The single strong band at *ca.* 230 nm indicates an electronic transition localized on a structure containing all titanium in essentially tetrahedral coordination. Moreover, the Ti K-edge (XANES) and Ti $2p_{3/2}$ (XPS) spectra (not shown) of the dehydrated Ti–Si amorphous mixed oxide (Table 1) also confirm that titanium is only present as tetrahedral $[TiO_4]$ units, supporting previous XANES and EXAFS results.[9] The XPS data are in agreement with those reported by Stakheev *et al.* for similar samples.[11] As compared

Table 1 Chemical composition (atomic ratios) and BET surface areas

Sample	Si/Ti	Si/B	Si/Al	Surface area/ $m^2\ g^{-1}$
SiO_2	—	—	—	245
Ti–Si	48	—	—	210
B–Ti–Si	50	34	—	205
Al–Ti–Si	47	—	32	185
TBS-1[a]	75	35	—	415
Ti-β[a]	52	—	45	n.d.[b]

[a] Ti-β and titanium borosilicalite (TBS-1) were obtained following the procedures given in refs. 4 and 12 respectively. [b] n.d. = Not determined.

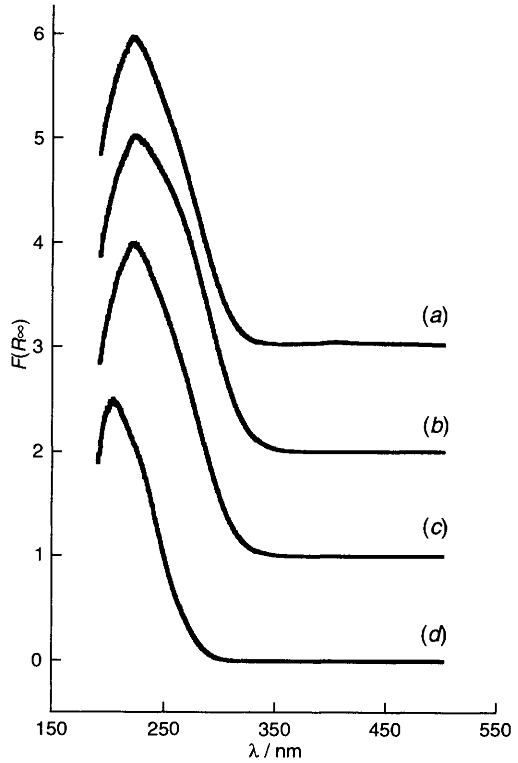

Fig. 1 Diffuse reflectance UV–VIS spectra of: (*a*) Al–Ti–Si, (*b*) B–Ti–Si, (*c*) Ti–Si amorphous oxide and (*d*) TS-1 (Ti/Si = 1.5%)

to a TS-1 sample (Ti/Si = 1.5%),[10] known to contain only tetrahedral Ti species [UV band at *ca.* 200 nm, Fig. 1(*d*)], the red shift (*ca.* 30 nm) can be related to a difference in Ti–O–Si bond angle. The Ti sites in an amorphous titania–silica matrix are therefore believed to display smaller bond angles. Moreover, as discussed earlier,[10] this also indicates that the so-called closed sites, $Ti(OSi)_4$, are mostly present in the amorphous silica matrix, whereas the opened sites, $Ti(OH)(OSi)_3$ are predominant in TS-1. The specific BET surface areas determined by nitrogen physisorption at 77 K, varied in the range of 180–240 $m^2 g^{-1}$ (Table 1). The FTIR spectra of pyridine adsorbed on the mixed oxides show a weak band at 1455 cm^{-1} which can be assigned to Lewis-acid sites. This band disappeared after evacuation at 423 K. No band was observed at 1545 cm^{-1} which is specifically attributed to Brønsted-acid sites. The characteristic bands observed at 1441 and 1600 cm^{-1} were due to physisorbed pyridine. Their intensity decreased sharply upon evacuation at elevated temperatures. For TBS-1 and Ti-β, the bands at 1455 and 1545 cm^{-1} were still observed, even after evacuation at 573 K. This reveals that the mixed oxides are of much lower acidity, as compared to TBS-1 and Ti-β. The order of the acid strength was $SiO_2 \approx$ Ti–Si < B–Ti–Si < Al–Ti–Si ≪ TBS-1 < Ti-β.

Concerning the catalyst activity for hydrocarbon oxidation, these mixed oxides have been used as catalysts in the epoxidation of oct-1-ene with aqueous hydrogen peroxide. In a typical catalyst evaluation reaction procedure, a mixture of oct-1-ene (0.089 mol), catalyst (0.250 g) and 30% H_2O_2 (0.044 mol) in ethanol (5 g) was continuously stirred at 328 K in a glass batch reactor at reflux for 5 h. Aliquots were taken at selected reactions times and analysed using a GC equipped with a capillary column and FID detector. All experiments were conducted under identical conditions. Typical results and reaction conditions are summarized in Table 2.

Table 2 Epoxidation of oct-1-ene by H_2O_2 over titania–silica mixed oxide catalysts containing different acidic functions, in comparison with titanium zeolites

Sample	t/*h*	Conv. /mol%	Product distribution/mol%			H_2O_2/mol%	
			Epoxide[a]	Diol[b]	Other[c]	Conv.	Select.
SiO_2	5	0.0	0	0	0	8.3	—
Ti–Si	1	1.9	100	0	0	11.2	45
	3	4.0	100	0	0	18.7	56
	5	6.7	100	0	0	27.5	64
B–Ti–Si	1	1.8	73	27	0	11.0	42
	3	3.0	74	26	0	17.2	46
	5	6.0	71	29	0	27.0	58
Al–Ti–Si	1	1.7	92	8	0	10.0	44
	3	2.9	74	26	0	16.4	47
	5	5.3	47	53	0	26.4	52
TBS-1	5	5.2	13	24	63	19.8	69
Ti-β	5	7.0	8	21	71	25.2	73

Reaction conditions: catalyst = 0.250 g, oct-1-ene = 0.089 mol, H_2O_2 (30%) = 0.044 mol, solvent (ethanol) = 5 g, reaction temperature = 55 °C, reaction duration = 5 h. [a] 1,2-Epoxyoctane. [b] Octane-1,2-diol. [c] Aldehyde and 1-hydroxyoctan-2-one.

The titania–silica mixed oxide catalyst is highly selective for epoxidation and no other reaction products have been detected. The incorporation of B^{3+} or Al^{3+} in the matrix of titania–silica mixed oxides slightly lowers the total oct-1-ene conversion, but significantly affects the product distribution. The selectivity towards the α-diol, however, depends on the nature of trivalent ions. As compared to boron the aluminium containing titania–silica mixed oxide favours the hydrolysis of epoxide to the α-diol. The partial conversion of H_2O_2 due to decomposition is essentially the same in pure SiO_2 ($x_3 = 0.0083$) and in mixed-oxide catalysts ($x_3 = 0.0088$–0.0110) after 5 h, suggesting that the presence of Ti, Al and B in the silica matrix does not affect significantly decomposition of H_2O_2. For comparison, the results obtained with Ti–borosilicate (TBS-1) and Ti-β are also included in Table 2. Ti-β shows a comparatively higher conversion (7.0 mol%) as compared to TBS-1 (5.2%) after 5 h of reaction. This is probably due to the large pore size of Ti-β. The product distribution also differs from mixed oxide catalysts and indicates that epoxidation of oct-1-ene is followed by acid-catalysed ring opening (hydrolysis) with further oxidation of octane-1,2-diol to corresponding aldehydes and/or 1-hydroxyoctan-2-one.

Therefore, a direct conclusion is that mixed oxides behave like Ti-substituted large-pore molecular sieves. The titania–silica mixed oxide catalysts incorporated with boron or aluminium yield good selectivities for the diol formation and their acid strength is low enough to prevent secondary oxidation. It is also remarkable that these mixed oxides are easy to synthesize with a variety of surface areas and pore diameters and have therefore a potential in the fine chemical industry, for the conversion of bulky alkenes.

References

1 M. G. Clerici and P. Ingallina, *J. Catal.*, 1993, **140**, 71.
2 G. H. Hutchings and D. F. Lee, *J. Chem. Soc., Chem. Commun.*, 1994, 1095.
3 P. P. Knops-Gerrits, D. De Vos, F. Thibault-Starzyk and P. A. Jacobs, *Nature*, 1994, **369**, 543.
4 M. A. Camblor, A. Corma and J. Perez-Pariente, *Zeolites*, 1993, **13**, 82.
5 A. Corma, M. T. Navarro and J. Pérez-Pariente, *J. Chem. Soc., Chem. Commun.*, 1994, 147.
6 E. I. Ko, *Chemtech*, April, 1993, 31; J. A. Schwarz, C. Contescu and A. Contescu, *Chem. Rev.*, 1995, **95**, 477.
7 H. P. Wulff, *US Pat.*, 3923843, 1975; H. P. Wulff and F. Wattimena, *US Pat.*, 4367342, 1983.
8 R. Hutter, D. C. Dutoit, T. Mallat, M. Schneider and A. Baiker, *J. Chem. Soc., Chem. Commun.*, 1995, 163; R. Hutter, T. Mallat and A. Baiker, *J. Catal.*, 1995, **157**, 665; R. Hutter, T. Mallat and A. Baiker, *J. Chem. Soc., Chem. Commun.*, 1995, 2487; A. Keshavaraja, V. Ramaswamy, H. S. Soni, A. V. Ramaswamy and P. Ratnasamy, *J. Catal.*, 1995, **157**, 501.
9 Z. Liu and R. Davis, *J. Phys. Chem.*, 1994, **98**, 1253.
10 D. Trong On, L. Le Noc and L. Bonneviot, *Chem. Commun.*, 1996, 299.
11 A. Yu. Stakheev, E. S. Shpiro and J. Apijok, *J. Phys. Chem.*, 1993, **97**, 5668.
12 D. Trong On, S. Kaliaguine and L.Bonneviot, *J. Catal.*, 1995, **157**, 235; D. Trong On, M. P. Kapoor, L. Bonneviot, S. Kaliaguine and Z. Gabelica, *J. Chem. Soc., Faraday Trans.*, 1996, **92**, 1031.

Received, 8th February 1996; Com. 6/00933F