Catalysis Letters 10 (1991) 259–262

Shape selectivity as a function of pore size in epoxidation of alkenes with supported titanium catalysts

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Received 10 May 1991; accepted 7 July 1991

Reactant shape selectivity of supported titanium catalysts for epoxidation of cyclohexene and 2-hexene has an excellent correlation with the pore diameter of the catalysts. With titanosilicate the preference to cis isomer epoxidation is small compared to TiO_2-SiO_2 probably because of the restriction of its diffusion imposed by the zeolite micropore structure.

Keywords: Shape selectivity; epoxidation of alkenes; titanium catalyst; catalyst pore size; titanosilicate catalyst

Titanium supported on silica has been reported to catalyse the epoxidation of alkenes with organic hydroperoxides [1]. TiO_2 as such is inactive for the epoxidation and hence the catalysts containing titanium chemically bonded to siloxane ligands are considered to be active. Recently, titanosilicate, in which titanium atoms are incorporated in a zeolite framework and surrounded by the siloxane ligands, has been found to catalyse the epoxidation of alkenes as well as hydroxylation of aromatics with H_2O_2 [2]. We have already reported the remarkable shape selectivity in the epoxidation of alkenes catalysed by titanosilicate; cycloalkenes failed to be oxidized in contrast to linear alkenes [3]. We have also found that titanosilicate is able to catalyse the oxidation of alkanes with similar shape selectivity [4]. Here we report a remarkable change in shape selectivity in epoxidation of C_6 alkenes with pore size of supported titanium catalysts.

Titanosilicate (Si/Ti = 60) was prepared from $Ti(OC_2H_5)_4$, $Si(OC_2H_5)_4$, and $(C_3H_7)_4NOH$ according to a method in a patent [5]. Hydrolysis of a mixture of $Ti(OC_2H_5)_4$ and $Si(OC_2H_5)_4$ followed by drying and calcination at 550 °C gave rise to amorphous TiO_2-SiO_2 with pores widely ranging from 5 to 2000 nm.

Table 1
Epoxidation of cyclohexene and 2-hexene catalysed by supported titanium

Catalyst	Pore diameter (nm)	Turnover (mol-epoxide/mol-Ti) [a]		Ratio of epoxidation rate cyclohexene/2-hexene
		cyclohexene	2-hexene	
Titanosilicate	0.54×0.56, 0.52×0.58	0 [b,c]	3.6 [b]	0
Ti/silicalite	0.54×0.56, 0.52×0.58 [d]	0 [b,c]	0.74 [c]	0
Ti/Na-mordenite	0.67×0.70 [d]	0 [b,c]	0.015 [c]	0
Ti/dealuminated USY	0.74 [d]	0.006 [b]	0.018 [b]	0.33
Ti/SiO_2(RD)	2.2 [d]	0.052 [c]	0.078 [c]	0.67
Ti/SiO_2(ID)	12 [e]	2.9 [c]	0.89 [c]	3.2
TiO_2-SiO_2	300 [e]	3.0 [c]	0.90 [c]	3.3

[a] Conditions: catalyst (Si/Ti = 15–60) 0.5 g, alkene 10 cm^3, 323 K, 2 h.
[b] Oxidant: H_2O_2 (30%) 10 cm^3.
[c] Oxidant: *tert*-butyl hydroperoxide 10 cm^3.
[d] Pore diameter before introduction of Ti.
[e] Measured by the Hg intrusion method.

Other titanium catalysts supported on SiO_2 or zeolites, silicalite, Na-mordenite and dealuminated ultrastable Y, were prepared by allowing the supports to react with $TiCl_4$ vapor, followed by contact with air resulting in hydrolysis, and calcination at 500 °C. Dealuminated ultrastable Y ($SiO_2/Al_2O_3 = 270$) was prepared by allowing ultrastable Y ($SiO_2/Al_2O_3 = 11$ Tosoh Corp.) to react with 1 N HCl. For all zeolite catalysts good crystallinity was retained after the introduction of Ti. Two types of SiO_2 were employed: Fuji Davison ID silica gel with an average pore diameter of 14 nm and RD SiO_2 with an average pore diameter of 2.2 nm. A typical oxidation run used 1.0 g of a catalyst in 10 cm^3 of alkenes in a round-bottom flask, to which was added 10 cm^3 of *tert*-butyl hydroperoxide or 30% aqueous solution of H_2O_2. The resulting mixture was stirred for 2 h at 50 °C. Catalysts were filtered off and products were subjected to gas chromatographic analysis.

Reactant shape selectivity of a variety of titanium catalysts was tested. With zeolite-supported catalysts both H_2O_2 and *tert*-butyl hydroperoxide were utilizable as oxidants. However, with TiO_2-SiO_2 and SiO_2-supported ones only *tert*-butyl hydroperoxide was effective in oxidizing the substrates. Table 1 compares the results of epoxidation of 2-hexane (*cis/trans* = 0.6) and cyclohexene. Contrasting strikingly with titanosilicate, amorphous TiO_2-SiO_2, where all chemistry must occur on the non-shape-selective surface, showed activity for epoxidation of cyclohexene with *tert*-butyl hydroperoxide. It exhibited moderate activity, a quarter of the activity of titanosilicate, for the epoxidation of 2-hexene. Obviously cyclohexene vs. 2-hexene shape selectivity has an excellent correlation with the pore diameter of the catalysts. No reaction of cyclohexene occurred on the catalysts supported on silicalite and Na-mordenite, the pore size of which are less than 0.7 nm. On the catalysts with larger pore size, cyclohexene was converted to its epoxide. With increasing pore size the ratio of epoxycyclohexane yield to 2,3-epoxyhexane yield increased. Ti supported on ID silica gel having large pores is virtually equal to TiO_2-SiO_2 in the ratio, indicating the absence of control by the structure of the solid framework. The activities in terms of turnover number of epoxidation of 2-hexene on the small-pore RD SiO_2- or zeolite-supported catalysts were considerably lower than those on titanosilicate and TiO_2-SiO_2. This might be attributed to poor dispersion of titanium and/or difficult accessibility of the active sites inside the micropores to the reactant [6].

Titanosilicate and TiO_2-SiO_2 were significantly different in the stereospecificity of epoxidation. With 2-hexene (*cis*/*trans* = 0.6) as substrate the ratio of *cis* epoxides to *trans* epoxides was 0.82 for the titanosilicate whereas TiO_2-SiO_2 yielded a ratio of 3.2. By changing the *cis*/*trans* ratio of the substrate the relative rate of epoxidation was estimated. The rate was assumed to be 1st order of the concentration of reactant, which was added in excess and therefore constant at the initial concentration. The reaction was stereoselective; the rates of stereochemical interconversion (*cis*-alkene to *trans*-epoxide and *trans*-alkene to *cis*-epoxide) were negligible. If the rate of epoxidation of *trans*-2-hexene to trans-2,3-epoxyhexane was taken as unity, then the rate of *cis* to *cis* was 1.4 for the titanosilicate whereas it proved 4.5 for the TiO_2-SiO_2. It seems that the epoxidation of cyclohexene (exclusively *cis*) in preference to 2-hexene (*cis*/*trans* = 0.6) in the absence of restriction imposed by the steric environment is partly due to this higher reactivity of *cis* isomer.

Preferential epoxidation of *cis* isomer is usually observed with homogeneous oxidation systems [7]. It is known that *trans*-2-butene diffuses 200-fold faster than *cis*-2-butene in CaA zeolite micropores [8]. Hence the decreased preference to oxidation of *cis*-isomer with titanosilicate compared to TiO_2-SiO_2 could be another consequence of the zeolite interior structure.

References

[1] R.A. Sheldon, J. Mol. Catal. 7 (1980) 107.
[2] B. Notari, Stud. Surf. Sci. Catal. 37 (1988) 413.
[3] T. Tatsumi, M. Nakamura, K. Yuasa and H. Tominaga, Chem. Lett. (1990) 297.
[4] T. Tatsumi, M. Nakamura, S. Negishi and H. Tominaga, J. Chem. Soc., Chem. Commun. (1990) 476.
[5] UK Patent Application GB 2071071.
[6] N. Herron, G.D. Stucky and C.A. Tolman, J. Chem. Soc., Chem. Commun. (1986) 1521.
[7] J. Sobczak and J.J. Ziolkowski, J. Mol. Catal. 13 (1981) 11;
J.T. Groves and T.E. Nemo, J. Am. Chem. Soc. 105 (1983) 5786.
[8] N.Y. Chen and P.B. Weisz, Eng. Prog. Symp. Ser. 63 (1967) 86.