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Shape Selective Epoxidation of Alkenes Catalyzed by Titanosilicate

Takashi TATSUMI,* Makoto NAKAMURA, Kensei YUASA, and Hiro-o TOMINAGA
Department of Synthetic Chemistry, Faculty of Engineering,
The University of Tokyo, Hongo, Tokyo 113

Epoxidation of 1- and 2-hexenes with H_2O_2 was catalyzed by titanosilicate whereas cyclohexene failed to be oxidized by this catalyst system. This shape selectivity was ascribed to the molecular sieving action of titanosilicate. The rates for epoxidation of linear alkenes decreased with increasing the chain length.

Zeolites have channels and cages, which are accessible to those molecules with dimensions and shape that permit their passage through the host structure. Shape selective effects have been frequently observed with such reactions catalyzed by inherent acidic sites as hydrocarbon cracking and alcohol dehydration.[1)] Their use as shape selective oxidation catalysts, however, has not been well developed. Catalytic epoxidation of alkenes has been mainly carried out by soluble metal complexes containing Ti, V, Mo, or W.[2)] Shell developed a heterogeneous Ti/SiO_2 catalyst for the epoxidation of alkenes with alkyl hydro-peroxides.[2)] Recently ENI researchers have found that titanosilicate, zeolite containing the same chemical element as the Shell catalyst and having pentasil structure, catalyzes the oxidation of a variety of substrates with aqueous solution of H_2O_2.[3)] Since this material contains the active Ti atoms in a zeolite framework, oxidation can be constrained in such a shape-selective environment. Here we report the shape selective epoxidation of alkenes by the titanosilicate catalyst.

Titanosilicate (Ti/Si = 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.[4)] A typical oxidation run used 0.05 g of a catalyst in 10 cm^3 of alkenes in a round-bottom flask, to which was added 10 cm^3 of 30% aqueous solution of H_2O_2. The resulting mixture was stirred for 3 h at 50 °C. Catalysts were filtered off and both the organic and aqueous phases were subjected to gaschromatographic analysis. Adsorption characteristics of C_6 alkenes on titanosilicate were investigated by elution chromatography[5)] at 150 °C with an FID monitor.

As is evident from Fig. 1, epoxides were formed from 2-hexene (cis/trans = 0.6) in a considerable yield, whereas no products were obtained from cyclohexene. This remarkable substrate selectivity presumably arose from the molecular sieving action of titanosilicate, which was revealed by elution chromatography. As shown in Fig. 2, cyclohexene (bp 83 °C) was eluted from titanosilicate instantly and much faster than 2-hexenes (bp 69 °C), suggesting the sorption of cyclohexene was restricted because of its molecular dimensions. The favorable epoxidation of 2-hexene compared to 1-hexene is in agreement with the observation for conventional

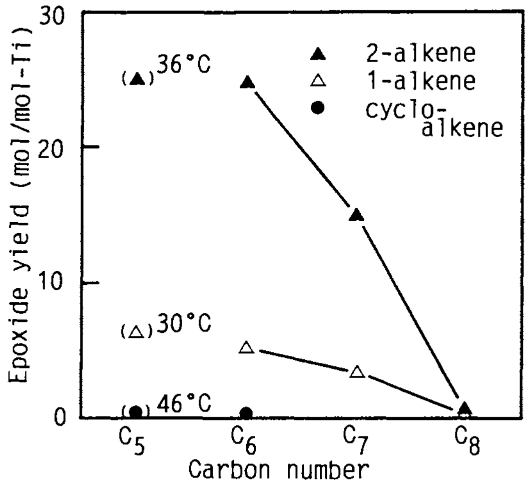

Fig. 1. Epoxidation of alkenes catalyzed by titanosilicate.

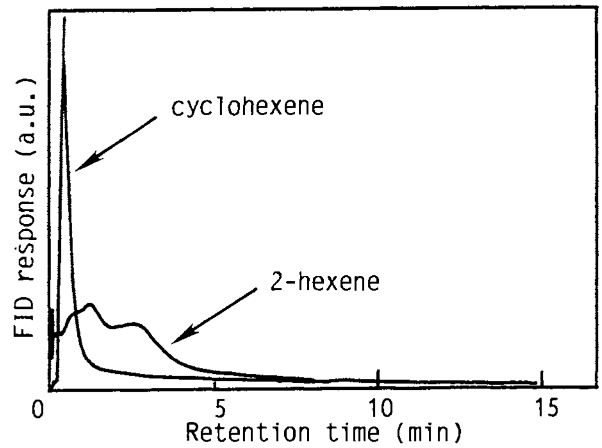

Fig. 2. Elution chromatograms on titanosilicate (0.1 g) at 150 °C. N_2 carrier, 60 ml/min; pulse size, 1 μl.

metal-catalyzed epoxidations[2] and adequately explained by an electrophilic nature of the attack of active oxygen species against alkene double bonds. Amorphous TiO_2-SiO_2 prepared from the same Ti and Si sources as the titanosilicate failed to epoxidize alkenes with H_2O_2.

Investigation of the time-course of the oxidation of 2-hexene revealed that formation of the product epoxides was levelled off 2-3 h after the start of the run. However, the recovered catalyst exhibited its initial activity after calcination at 550 °C. Hence we believe the levelling-off of turnover is not due to catalyst destruction but due to a pore blocking mechanism. Figure 1 also shows that the rates for epoxidation of linear alkenes were decreased with increasing the chain length. This is consistent with the observed large decrease in diffusivity with increasing the chain length,[1,6] suggesting oxidation is precluded by restrictions of transport of reactants and/or products through the crystalline channels.

Stereoselectivity was observed with the titanosilicate catalysts. With 2-hexene (cis/trans = 0.6) as substrate the ratio of cis to trans epoxides was 0.82. By using the mixtures of 2-hexenes with three different cis/trans ratios, the relative rate constants of stereochemical retention (trans-hexene to trans-epoxide and cis to cis) and stereochemical interconversion (trans-hexene to cis-epoxide and cis to trans) were calculated. If the rate constant of trans to trans was taken as unity, that of cis to cis proved was 1.4. The rate constants of stereochemical interconversion were negligible, suggesting that the reaction proceeded by a non-radical mechanism involving active species such as Ti-O-O-H.

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