Titanium-substituted Zeolite Beta(Ti-Al-β)-catalysed Epoxidation of Oct-1-ene with *tert*-Butyl Hydroperoxide(TBHP)

Takashi Sato, Jihad Dakka and Roger A. Sheldon*

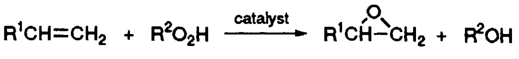
Laboratory of Organic Chemistry and Catalysis, Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands

Titanium substituted zeolite beta(Ti-Al-β) catalyses the epoxidation of oct-1-ene with TBHP; high selectivities to epoxide (92–100%) are observed when the Brønsted acid sites are neutralized by ion exchange with alkali or alkaline earth metal ions.

The catalytic epoxidation of propylene with alkyl hydroperoxide (Scheme 1; R^1 = Me) accounts for more than 1 million tons annual production of propylene oxide worldwide. Both homogeneous (molybdenum compounds) and heterogeneous [titanium(IV)/silica] catalysts are used in the ARCO[1] and Shell[2] processes, respectively.

Neither of these catalysts is effective with hydrogen peroxide as the oxidant owing to severe inhibition of the catalyst by water.[3] More recently Enichem workers showed[4] that titanium(IV) silicalite (TS-1) is an effective catalyst for the epoxidation of lower olefins, such as propylene, with 30% aqueous hydrogen peroxide, under mild conditions (40 °C) in MeOH as solvent. The success of TS-1 can be attributed to the hydrophobic nature of the pores of silicalite, which favours the diffusion of the nonpolar olefin substrate to the active site.

On the other hand, TS-1 does not catalyse epoxidation with alkyl hydroperoxides, such as TBHP, owing to the limited size of the silicalite pores (5.6 × 5.3 Å). Similarly, pore size restrictions render TS-1 ineffective for the epoxidation of branched and cyclic olefins, such as cyclohexene.[4] Consequently, there is considerable interest in the incorporation of titanium(IV) into large pore molecular sieves. Recently, the synthesis of titanium-containing zeolite beta (pore size 7.6 × 6.4 Å) was reported.[5] Ti-Al-β was shown to catalyse the oxidation of hex-1-ene with aqueous hydrogen peroxide in MeOH as a solvent, albeit with a lower activity than TS-1. The major product was, however, the corresponding diol derivative, presumably formed by ring opening of the intermediate epoxide catalysed by the Brønsted acid sites in the Ti-Al-β. The lower activity of Ti-Al-β, compared to TS-1, is presumably due to the more hydrophilic character of the pores of the former, resulting from the presence of aluminium.



$$R^1CH{=}CH_2 + R^2O_2H \xrightarrow{\text{catalyst}} R^1\overset{O}{CH{-}CH_2} + R^2OH$$

Scheme 1 *Reagents*: Catalyst: Mo^{VI} (homogeneous) or Ti^{IV}/SiO_2 (heterogeneous) R^2=Bu^t or Ph(Me)CH–

We now report that when the Brønsted sites in Ti-Al-β are neutralized by alkali metal exchange the resulting material is an efficient catalyst for the epoxidation of oct-1-ene (Scheme 1; $R^1 = C_6H_{13}$) with TBHP.

Ti-Al-β was synthesized by a slightly modified version of the published procedure.[5] Titanium tetraethoxide (1.60 g; 7.0 mmol) was added dropwise with stirring to a 22.4% (m/m) aqueous solution of tetraethylammonium hydroxide (31.81 g; 216 mmol) at 20 °C. Aerosil 200 silica (23.65 g; 394 mmol) was subsequently added during 10 min to give a clear solution which was stirred for 2 h at 20 °C. A solution of aluminium nitrate (0.25 g; 0.67 mmol) in water (1 ml) was added and the mixture transferred to a 200 ml Teflon bottle, which was put in a stainless steel autoclave. The autoclave was rotated (600 rpm) at 135 °C for 10 days after which time the solid material was separated by centrifuging, washed four times with hot water and dried at 65 °C in a vacuum oven. This material was then calcined at 550 °C for 24 h. X-Ray powder diffraction and IR spectra of the crystals were in agreement with published data.[5] Inductively coupled plasma-atomic emission spectrometric (ICP-AES) analysis showed Si/Ti and Si/Al molar ratios to be 41 and 46, respectively. Alkali metal exchange was carried out by treating the catalyst twice with 0.5% (m/m) aqueous metal acetate at 70–85 °C followed by washing with water(2 x) and methanol(2 x), drying at 120 °C and calcining at 530 °C. X-Ray diffraction analysis confirmed that the catalyst had the BEA topology and elemental analysis using inductively coupled plasma (ICP) spectrometry indicated a titanium content of 2.5%. In common with TS-1, Ti-Al-β exhibits a characteristic IR band at 960 cm^{-1}.

In a typical reaction procedure 3.36 g (30 mmol) of oct-1-ene, 0.54 g (6 mmol) of TBHP, 0.2 g of catalyst (0.0104 mmol Ti) and 30 ml of solvent were heated for 100 min with

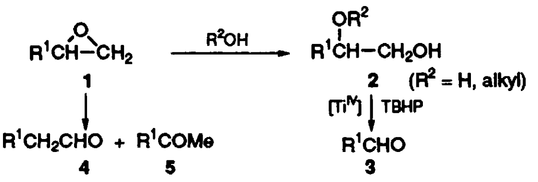
Table 1 Ti-Al-β catalysed epoxidation of oct-1-ene with TBHP: solvent effects. Reaction conditions; oct-1-ene (30 mmol), TBHP (6 mmol 70% soln in H_2O), 0.2 g (0.0104 mmol) catalyst, solv. 30 ml, 90 °C, 100 min

	Conv. (%)		Selectivity (%)[a]				
Solvent	TBHP	Oct-1-ene	**1**	**2**	**3**	**4/5**	TBHP efficiency (%)[b]
H_2O	26	25	0	0	50	50	96
$MeOH/H_2O$ (2:1)	16	13	0	51	8	40	83
MeOH	13	13	0	47	0	53	100
MeOH(H_2O free)	10	8	54	12	5	30	83
Bu^tOH	0.3	0.2	23	00	10	44	100
CF_3CH_2OH	58	47	38	39	2	20	82
MeCN	14	14	80	0	2	18	100
MeCN(H_2O free)	25	25	80	0	3	17	100
PhCl[c]	11	0	0	0	0	0	0
Oct-1-ene[d]	86	7	0	0	100	0	15

[a] Selectivity on oct-1-ene converted. [b] Efficiency of TBHP conversion to oxidation products of substrate. [c] TBHP in chlorobenzene was used, the mixture was dried by $MgSO_4$. After filtration, it was stored with 3A zeolite. [d] Oct-1-ene was used as a solvent, the mixture was dried by $MgSO_4$. After filtration, it was stored with 3A zeolite.

Table 2 Ti-Al-β catalysed epoxidation of oct-1-ene with TBHP: effect of ion exchange. Reaction conditions; oct-1-ene (30 mmol), TBHP (6 mmol; 70% soln in H_2O), 0.2 g (0.0104 mmol) catalyst, 30 ml TFE, 90 °C, 100 min

Metal ion	Conv. (%) TBHP	Conv. (%) Oct-1-ene	Epoxide sel. (%) on TBHP	Epoxide sel. (%) on Oct-1-ene	TBHP efficiency (%)
H^+	58	47	30	38	82
Li^+	40	38	95	100	95
Na^+	15	13	86	99	87
K^+	28	22	77	98	78
Mg^{+2}	37	29	72	92	78
Ba^{+2}	27	26	95	99	96



Scheme 2

vigorous stirring at 90 °C in a Teflon lined stainless steel autoclave. TBHP conversion was determined by iodometric titration and product yields by GLC analysis.

In initial experiments we examined the effect of solvent (see Table 1) on the epoxidation of oct-1-ene with TBHP in the presence of Ti-Al-β (H-form). In addition to the epoxide **1** the corresponding diol derivative **2** was observed together with heptanal **3** from oxidative cleavage of the diol and the epoxide rearrangement products, octanal **4** and octan-2-one **5** as depicted in Scheme 2.

In water or aqueous MeOH no epoxide was observed. The major product was **2** (R=H or Me) formed by acid-catalysed ring opening of the intermediate epoxide. When the MeOH and TBHP were rigorously dried the epoxide was formed in 54% selectivity. In *tert*-butyl alcohol 23% epoxide was observed together with the rearranged products (44%) and the heptanal (10%). The highest selectivity to epoxide (80%) was observed in MeCN as solvent. Presumably the weakly basic acetonitrile preferentially coordinates to the Brønsted acid sites in the catalyst, thus preventing acid-catalysed ring opening/rearrangement of the epoxide. The highest activity (58% conversion) was observed in 2,2,2-trifluoroethanol(TFE) as solvent. We also confirmed that no oxidation of the latter to trifluoroacetic acid had taken place. In chlorobenzene no conversion of oct-1-ene was observed. In oct-1-ene itself as solvent substantial (86%) TBHP decomposition was observed but little (7%) substrate was converted. We attribute the poor results observed in chlorobenzene and oct-1-ene to inefficient extraction of the hydrophobic oct-1-ene from the non polar environment of the bulk solvent into the relatively hydrophilic cavity of Ti-Al-β (see Table 1).

Others[6,7] have also found that the nature of the solvent can have a dramatic effect on both activity and selectivity in liquid phase reactions catalysed by molecular sieves.

Since the highest activity was observed in TFE we elected to study the effect of alkali metal exchange in this solvent. As shown in Table 2 this resulted in a dramatic increase in epoxide selectivity. The most dramatic increase was observed with the Li-exchanged catalyst: 100% compared to 38% with the untreated catalyst. The conversion was slightly lower than with the untreated (H-form) catalyst (40% *vs*. 58%).

Showa Denko K. K. Japan and Solvay Interox are gratefully acknowledged for financial support.

Received, 14th April 1994; Com. 4/02231I

References

1 R. Landau, G. A. Sullivan and D. Brown, *Chem. Tech.*, 1979, 602.
2 R. A. Sheldon, in *Aspects of Homogeneous Catalysis*, ed. R. Ugo, Reidel, Dordrecht, vol. 4, 1981, p. 3.
3 R. A. Sheldon, *J. Mol. Catal.*, 1980, **7**, 107.
4 M. G. Clerici and P. Ingallina, *J. Catal.*, 1993, **140**, 71.
5 M. A. Camblor, A. Corma and J. Pérez-Pariente, SP Pat. 9,101,798, 1991.
6 T. Tatsumi, M. Nakamura, S. Nigishi and H. Tominaga, *J. Chem. Soc., Chem. Commun.*, 1990, 476.
7 L. Gilbert and C. Mercier, *Stud. Surf. Sci. Catal.*, 1993, **78**, 51.