Highly Selective Epoxidation of 1-Pentene with H_2O_2 over TS-1

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The study of epoxidation with H_2O_2 is an attractive topic in catalysis, because epoxides are extremely important intermediates for the chemical industry and H_2O_2 is a green oxidant. Since the invention of TS-1, a titanium-containing silicalite with the MFI structure by Taramasso *et al.*[1] in 1983, much research has been focused on its synthesis as well as on its application as oxidation catalysts in a wide range of oxygenations with H_2O_2. The selective catalytic capacity of TS-1 lies in a possession of isolated tetrahedrally coordinated titanium atoms in a silicate structure with a hydrophobic and acid-free defined environment.[2] This new material has been found to be effective in the mild oxidation of a number of organic substrates using dilute H_2O_2, *i.e.*, hydroxylation of aromatic compounds[3], epoxidation of olefins[4], oxidation of paraffins[5,6] and oxidation of alcohols and amines.[7]

The epoxidation of C_3~C_8 linear and cyclic olefins is an important application for the system of H_2O_2-Ti-zeolite.[8-11] TS-1 is one of the most popular catalysts for the oxidation of small organic molecules. Up to date, a systematic study on the pentene oxidation by H_2O_2 has not been reported. We now communicate a preliminary results of 1-pentene epoxidation with H_2O_2 on TS-1 under mild conditions.

Experimental Section

TS-1 was synthesized as described by Thangaraj *et al.*[12] The epoxidation of 1-pentene was carried out in a glass batch reactor at 18 °C. In a typical experiment, 1-pentene (43 mmole), 30% H_2O_2 (44 mmole), 98% methanol (65 mL) and TS-1 (0.3 g) were charged to the reactor. Air was removed by purging with N_2 under vigorous stirring. The slurry was stirred at 18 °C under atmospheric N_2. Analyses were performed by titration with a standard $KMnO_4$ solution and by GC.

Table 1. 1-pentene epoxidation with H_2O_2 over TS-1 at 18 °C

No	[1-pentene] (M)	[H_2O_2] (M)	Reaction Time (h)	H_2O_2 conv. (%)	1-pentene conv. (%)	Epoxide sel. (%)
1[a,b]	0.59	0.60	1	45	45	100
2[a,b]	0.59	0.60	12	59	59	100
3[a,c]	0.92	0.16	1	87	16	100
4[a,c]	0.92	0.16	5	88	16	100
5[a,c]	0.92	0.16	12	88	16	100
6[d]	0.90	0.18	1	94	-	91

[a]This work. [b]TS-1 4.1 g/L. [c]TS-1 6.2 g/L. [d]Clerici, M. G.; Ingallina, P. *J. Catal.* **1993**, *140*, 71. TS-1 6.2 g/L.

Results and Discussion

Table 1 shows the results of 1-pentene epoxidation with H_2O_2 over TS-1. TS-1 was observed to be a very active and selective catalyst for this reaction under mild conditions. When the molar ratio of 1-pentene to H_2O_2 was set to 1 : 1, the conversions of both H_2O_2 and 1-pentene show 45% with a 1-pentene oxide selectivity of 100% after 1 h reaction. Extended reaction enhances the conversions up to 59% without yielding any by-product. When the molar ratio of 1-pentene : H_2O_2 = 5.75 : 1 was used, the conversion of H_2O_2 reaches 87% and that of 1-pentene is 16% with a 1-pentene oxide selectivity of 100%. The 1-pentene oxide concentration remains basically unchanged during the extended reaction. Since no by-products were detected throughout the reaction in both cases, the TS-1 catalyst was stable and caused no side-reactions.

It is noteworthy that the catalytic stability of TS-1 is a critical problem toward the practical production of epoxides. Thiele *et al.*[13] reported that TS-1 started to deactivate after 2 h of propylene epoxidation. The deactivtion of TS-1 usually results in the formation of epoxide oligomers within the zeolite micropores. The only study involving the epoxidation of pentene with H_2O_2 and TS-1 was reported by Clerici *et al.*[9] In an atmospheric batch reaction system with a molar ratio of 1-pentene : H_2O_2 = 5 : 1, H_2O_2 conversion of 94% was achieved with a 1-pentene oxide selectivity of 91% based on H_2O_2 over TS-1 within 1 h of reaction at 25 °C. 1-pentene gylcol and its monomethyl ethers were the principal by-products. This result implies that there is more or less formation of by-products, whereas the main product is predominant during the reaction. However, there was no description on the observations of a prolonged reaction and the deactivation of TS-1 in this paper. It is known that the presence of acidic sites inside zeolites favors the addition of methanol and water to epoxides to form glycols and glycol ethers.[14,15] Although titanium silicalite catalyzed oxidation reactions have been investigated by a number of laboratories, there are significant differences among results described which are mainly attributed to different characteristics of catalysts used.[16] By-product formation is mainly due to sites with high acidity.[13] These sites are independent of the catalytic site for epoxidation and are probably silanol groups at crystal defect sites.[13] The absence of by-products such as 1-pentene oxide glycol and methoxy-pentanol in the present study suggests that the TS-1 catalyst used has fairly hydrophobic and acid-free properties that can prevent the deactivation by

water and the occurrence of undesirable side-reactions.

This short report presents a successful application of TS-1 as a highly effective catalyst in the epoxidation of 1-pentene. On the other hand, the observations of high activity and selectivity to 1-pentene oxide during prolonged reaction may prove that the synthesis of TS-1 with specific structural and chemical characters is qualified.

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