

## Highly Selective Epoxidation of 1-Pentene with H<sub>2</sub>O<sub>2</sub> over TS-1

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The study of epoxidation with H<sub>2</sub>O<sub>2</sub> is an attractive topic in catalysis, because epoxides are extremely important intermediates for the chemical industry and H<sub>2</sub>O<sub>2</sub> is a green oxidant. Since the invention of TS-1, a titanium-containing silicalite with the MFI structure by Taramasso *et al.*<sup>1</sup> 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<sub>2</sub>O<sub>2</sub>. 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.<sup>2</sup> This new material has been found to be effective in the mild oxidation of a number of organic substrates using dilute H<sub>2</sub>O<sub>2</sub>, *i.e.*, hydroxylation of aromatic compounds<sup>3</sup>, epoxidation of olefins<sup>1</sup>, oxidation of paraffins<sup>5,6</sup> and oxidation of alcohols and amines.<sup>7</sup>

The epoxidation of C<sub>3</sub>-C<sub>8</sub> linear and cyclic olefins is an important application for the system of H<sub>2</sub>O<sub>2</sub>-Ti-zeolite.<sup>8-11</sup> 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<sub>2</sub>O<sub>2</sub> has not been reported. We now communicate a preliminary results of 1-pentene epoxidation with H<sub>2</sub>O<sub>2</sub> on TS-1 under mild conditions.

### Experimental Section

TS-1 was synthesized as described by Thangaraj *et al.*<sup>12</sup> 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<sub>2</sub>O<sub>2</sub> (44 mmole), 98% methanol (65 mL) and TS-1 (0.3 g) were charged to the reactor. Air was removed by purging with N<sub>2</sub> under vigorous stirring. The slurry was stirred at 18 °C under atmospheric N<sub>2</sub>. Analyses were performed by titration with a standard KMnO<sub>4</sub> solution and by GC.

**Table 1.** 1-pentene epoxidation with H<sub>2</sub>O<sub>2</sub> over TS-1 at 18 °C

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

<sup>a</sup>This work, <sup>b</sup>TS-1 4.1 g/L, <sup>c</sup>TS-1 6.2 g/L, <sup>d</sup>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<sub>2</sub>O<sub>2</sub> 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<sub>2</sub>O<sub>2</sub> was set to 1 : 1, the conversions of both H<sub>2</sub>O<sub>2</sub> 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<sub>2</sub>O<sub>2</sub> = 5.75 : 1 was used, the conversion of H<sub>2</sub>O<sub>2</sub> 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.*<sup>13</sup> reported that TS-1 started to deactivate after 2 h of propylene epoxidation. The deactivation 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<sub>2</sub>O<sub>2</sub> and TS-1 was reported by Clerici *et al.*<sup>9</sup> In an atmospheric batch reaction system with a molar ratio of 1-pentene : H<sub>2</sub>O<sub>2</sub> = 5 : 1, H<sub>2</sub>O<sub>2</sub> conversion of 94% was achieved with a 1-pentene oxide selectivity of 91% based on H<sub>2</sub>O<sub>2</sub> over TS-1 within 1 h of reaction at 25 °C. 1-pentene glycol 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.<sup>14,15</sup> 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.<sup>16</sup> By-product formation is mainly due to sites with high acidity.<sup>13</sup> These sites are independent of the catalytic site for epoxidation and are probably silanol groups at crystal defect sites.<sup>13</sup> 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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