Epoxidation of Styrene on a Novel Titanium–Silica Catalyst Prepared by Ion Beam Implantation

Qihua Yang, Can Li,[1] Shandong Yuan, Jian Li, Pinliang Ying, Qin Xin, and Weidong Shi*

*State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023,China; and * State Key Laboratory of Materials Modification by Laser, Ion and Electron Beams, Dalian University of Technology, Dalian 116023, China*

A Ti–SiO$_2$ catalyst with highly isolated titanium ions was prepared by ion beam implantation. The catalyst was tested for the epoxidation of styrene using dilute H$_2$O$_2$ (30%) as the oxidizing agent. Two kinds of product were formed: epoxide and benzaldehyde. The selectivity for epoxide approaches 100% at 298 K and decreases at elevated reaction temperatures. A turnover frequency for styrene up to 11.7 h^{-1} was observed. The activity and selectivity for epoxide decreased when the catalyst was calcined at higher temperatures. It is proposed that there are at least two types of active sites on the catalyst: Ti(α) (isolated Ti^{3+} and Ti^{4+}) for the selective formation of epoxide and Ti(β) (TiO$_2$ clusters) for the formation of benzaldehyde.

© 1999 Academic Press

Epoxides are important intermediates in organic synthesis of fine chemicals and pharmaceuticals. The direct epoxidation of alkenes has been the main process for preparing the epoxides. Epoxidation has traditionally been carried out using peracids, and the procedures are very costly and usually produce huge amounts of pollutants. It is highly desirable to replace the conventional process with an environmentally benign procedure. One possibility is titanium silicalite-1 (TS-1) which shows unique catalytic activity and selectivity in the oxidation of a large number of organic substrates, such as alkenes, alcohols, aromatics, phenols, and alkanes (1–5), using H$_2$O$_2$ as oxidant under mild reaction conditions. The high activity and selectivity of TS-1 catalyst are attributed to its framework titanium sites which are isolated monoatomic sites. But the small pore size, 0.5–0.6 nm, of this zeolite limits its applications to the epoxidation of small molecules (6). Many efforts have been made to find alternative catalysts with highly isolated titanium sites. The preparation of such catalysts has focused mainly on using chemical methods, such as the impregnation of silica with titanium-containing precursors (7), a sol–gel procedure followed by supercritical drying (8), and different approaches to zeolite synthesis (9).

---

[1] To whom correspondence should be addressed. Fax: 86–0411–4694447. E-mail: canli@ms.dicp.ac.cn.

In this paper we report for the first time a novel titanium–silica catalyst prepared by a physical method, ion beam implantation, and the epoxidation of styrene as a test reaction for this new catalyst. It is found that the Ti–SiO$_2$ catalyst prepared by ion beam implantation shows quite good activity and selectivity in the epoxidation of styrene.

Ion beam implantation has been widely used to modify materials (10, 11), but no work has been reported on its use in preparing catalysts for selective oxidation. Principally, ion beam implantation is an effective method for preparing isolated atoms on a solid surface. In this work, the titanium atom is ionized first, then the ionized titanium beam is accelerated under a high voltage and the titanium ion beam is implanted at high speeds in a support (silica in this work). The titanium ions implanted in the support are highly isolated because the ion density of the beam is very small and the ions are repelled from each other in the beam. These highly isolated titanium sites may resemble the titanium sites in TS-1 zeolites.

The ion implantation was carried out in a Mevva 80-10 ion implantation system at 573 K with a dose of 3×10^{18} ions cm^{-2} at 40 keV. The vacuum system during the implantation was maintained at 1.07×10^{-3} N m^{-2}. Silica powder of 40–60 mesh and with a BET surface area of ca. 300 m^2 g^{-1} was used as the support. The silica powder was kept rotating in a vessel during the implantation to ensure a uniform distribution of the titanium ions on the silica surface. Titanium metal with a purity of 99.9% was used as the titanium source. The catalyst prepared by the ion beam implantation is referred to as Ti–SiO$_2$(298). The titanium content of the Ti–SiO$_2$(298) catalyst was measured to be 0.28 wt% by ICP-AES. The catalyst was calcined at 573, 673, and 773 K in air for 2 h before use. The samples calcined at these different temperatures are referred to as Ti–SiO$_2$(573), Ti–SiO$_2$(673), and Ti–SiO$_2$(773), respectively.

Table 1 gives the results of the epoxidation of styrene at 333 K on the implanted Ti–SiO$_2$ catalyst calcined at different temperatures. Two types of products are formed: the epoxide and benzaldehyde. For the uncalcined catalyst, Ti–SiO$_2$(298), the turnover frequency (TOF) is estimated to

128

TABLE 1

Epoxidation of Styrene on Ti–SiO₂ Catalyst Calcined at Different Temperatures

Catalyst	TOF^a (h⁻¹)	Conv$_{styrene}$ (mol%)	Eff$_{H_2O_2}$ ^{b} (%)	Selectivity (mol%)			
				Epoxide	Benzaldehyde	Phenylacetaldehyde	Others
Ti–SiO₂(298)	12.3	4.8	37.8	55.5	44.5	0	0
Ti–SiO₂(573)	11.7	4.5	36.3	52.5	47.5	0	0
Ti–SiO₂(673)	4.4	1.7	11.5	53.1	46.9	0	0
Ti–SiO₂(773)	3.1	1.2	8.5	0	100	0	0
TS-1^c	5.9	35.4		2.0	22.8	74.2	1.0

Note. Catalyst, 0.4 g; styrene, 18 mmol; H₂O₂, 18 mmol; solvent CH₃CN, 4 ml; reaction temperature, 338 K; reaction time, 3 h. The products were separated from the catalyst and analyzed using gas chromatography (50 m × 0.2 mm i.d. capillary column).

^{a} TOF = moles of styrene converted per mole of Ti in the catalyst per hour. All titaniums ions are assumed to be on the surface of the catalyst. One gram of Ti–SiO₂ contains 5.8×10^{-5} mol of Ti.

^{b} Peroxide efficiency is defined as millimoles of substrate converted per millimole of hydrogen peroxide consumed.

^{c} From Ref. (12); the reaction temperature was 333 K.

be at least two times larger than that of TS-1 (12). The selectivity for epoxide is more than 50% for the implanted Ti–SiO₂ while TS-1 produced mainly phenylacetaldehyde, the isomeric product of the epoxide. This indicates that the isolated titanium ions in the implanted catalyst possess very high activity and selectivity in the epoxidation of styrene.

The results in Table 1 show that the calcination temperature has a large effect on activity and selectivity. The activity and selectivity decrease when the catalyst is calcined at higher temperatures. When the catalyst was calcined at 773 K, no epoxide product was detected. This implies that the nature of the active sites in the catalyst was significantly changed with the calcination treatment.

The effect of reaction temperature on styrene conversion and product selectivity is summarized in Table 2. As expected, by increasing the reaction temperature from 298 to 358 K, the conversion of styrene increased from 1.8 to 6.7%. The selectivity for epoxide is 100% at 298 K, but decreases dramatically at higher temperatures, while the selectivity for benzaldehyde increased at the cost of the epoxide. It

TABLE 2

Dependence of Catalytic Activity and Selectivity on Reaction Temperature for Ti–SiO₂(298) Catalyst

T (K)	TOF^a (h⁻¹)	Conv$_{styrene}$ (mol%)	Selectivity (mol%)	
			Epoxide	Benzaldehyde
298	4.7	1.8	100	0
338	12.3	4.8	55.5	44.5
358	17.5	6.7	16.0	84.0

Note. Catalyst, 0.4 g; styrene, 18 mmol; H₂O₂, 18 mmol; solvent CH₃CN, 4 ml; reaction time, 3 h.

^{a} TOF = moles of styrene converted per mole of Ti in the catalyst per hour. All titanium ions are assumed to be on the surface of the catalyst. One gram of Ti–SiO₂ contains 5.8×10^{-5} mol of Ti.

seems that benzaldehyde is formed mainly via the further oxidation of the epoxide, and the higher reaction temperature favors the oxidation of epoxide.

The excellent activity and selectivity in the epoxidation of styrene on the Ti–SiO₂ catalyst can be explained in terms of the unique active sites derived by ion beam implantation. Since the Ti content of Ti–SiO₂ is only 0.28% and the surface area of SiO₂ is more than 200 m² g⁻¹, the possibility of aggregated titanium ions is small. Therefore most of the titanium ions are in a well-isolated form on the silica. XPS failed to determine the valence state of the titanium ions in Ti–SiO₂ because the titanium content is far below the detection limit. A sharp EPR signal at a g value of 2.003 was observed for Ti–SiO₂(298). This EPR signal is tentatively assigned to the isolated Ti^{3+} species (13) and/or a trapped single electron, implying that some Ti^{3+} may be stabilized in the SiO₂ substrate. The EPR signal gradually weakens when the calcination temperature is increased, and disappears when the sample is calcined at 773 K in air. The disappearance of the EPR signal is possibly due to the oxidation of Ti^{3+} to Ti^{4+} because this signal is maintained for the calcination in N₂. The titanium sites on the Ti–SiO₂ catalyst can be grouped into at least two kinds of species: isolated Ti^{3+} and Ti^{4+} ions, referred to as Ti(α); and small oxide clusters, $(TiO_2)_n$ ($n > 1$), referred to as Ti(β). It is suggested that the surface titanium ions, either Ti^{3+} or Ti^{4+} on the SiO₂ support, are stabilized in the form of oxide species, i.e., $TiO_{1.5}(Ti^{3+})$ and $TiO_2(Ti^{4+})$. Other Ti^+ and Ti^{2+} ions are quite unstable and easily oxidized into Ti^{3+} or Ti^{4+} and their concentrations in the Ti–SiO₂ catalyst will be extremely small, especially when the sample is calcined in air at high temperature. Therefore the $TiO_{1.5}(Ti^{3+})$ and $TiO_2(Ti^{4+})$ species should predominate on the catalyst surface. In addition, some aggregated oxide clusters $(TiO_2)_n$ ($n > 1$) may be formed in air during calcination at high temperature. According to the correlation between the catalytic data and calcination

temperature, we assume that Ti(α) sites contribute to the high activity and selectivity for the epoxide, while Ti(β) sites contribute mainly to the formation of benzaldehyde. The lower activity of the catalyst calcined at higher temperatures is due to the decrease in Ti(α) sites.

To confirm the stability of Ti^{3+} sites under calcination at high temperature, Ti–SiO$_2$ was heated in N$_2$ instead of air at 773 K for 2 h and cooled down to room temperature in N$_2$. This catalyst shows a conversion of styrene of 7.2% and a selectivity to epoxide of 66.8% which is even higher than that of Ti–SiO$_2$(298). The catalyst also shows an EPR signal at $g = 2.003$. This strongly suggests that the Ti^{3+} sites are quite stable and can be oxidized to Ti^{4+} only in air at elevated temperatures. The higher conversion and epoxide selectivity are partly due to the fact that the isolated Ti^{3+} and Ti^{4+} sites in the bulk of the silica move to the surface when the catalyst is calcined.

The following epoxidation routes of styrene are proposed:
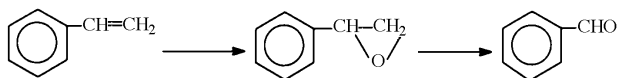
It seems that the successive reactions are catalyzed respectively by two types of active sites, Ti(α) and Ti(β). The epoxidation may take place mainly on Ti(α) sites while the cleavage of the carbon–carbon bond takes place mainly on Ti(β) sites because the selectivity to benzaldehyde is increased for the Ti–SiO$_2$ catalyst calcined at high temperature where more Ti(β) species are produced. When the reaction temperature is increased, the epoxide produced is further oxidized on Ti(β) sites. Accordingly, the selectivity of epoxide depends on both reaction temperature and concentration of surface Ti(α) sites.

The reusability of the catalyst is reported in Table 3. No obvious loss of activity and selectivity is observed after the catalyst is reused five times. This result confirms that the leaching of the titanium ions from the Ti–SiO$_2$ catalyst is negligible, at least the first several times. This may be due to the chemical bonding of TiO$_x$ and (TiO$_2$)$_n$ with SiO$_2$.

In summary, a titanium–silica catalyst prepared by ion beam implantation shows high catalytic activity and selectivity for the epoxidation of styrene using dilute H$_2$O$_2$

(30%) as oxidizing agent. The high activity and selectivity are attributed to the highly isolated titanium sites on the implanted silica surface. It is proposed that there are two types of active sites, on the catalyst, Ti(α) (isolated Ti^{3+} and Ti^{4+}) and Ti(β) (TiO$_2$ clusters), and the formation of epoxide and benzaldehyde is catalyzed by the two kinds of active sites, respectively.

TABLE 3

Reusability of Ti–SiO$_2$(573) in Epoxidation of Styrene

No. of times used	TOF^a (h^{-1})	Conv$_{styrene}$ (mol%)	Selectivity (mol%)	
			Epoxide	Benzaldehyde
1	11.7	4.5	52.5	47.5
2	11.7	4.5	50.9	49.1
3	11.9	4.6	52.8	47.2
4	11.2	4.3	50.7	49.3
5	11.4	4.4	49.6	50.4

Note. Catalyst, 0.4 g; styrene, 18 mmol; H$_2$O$_2$, 18 mmol; solvent CH$_3$CN, 4 ml; reaction temperature, 338 K; reaction time, 3 h.

^{a} TOF = moles of styrene converted per mole of Ti in the catalyst per hour. All titanium ions are assumed to be on the surface of the catalyst. One gram of Ti–SiO$_2$ contains 5.8×10^{-5} mol of Ti. The solid catalyst was filtered after reaction, washed with water, and dried at 393 K for 6 h and finally calcined in air at 573 K for 2 h.

REFERENCES

1. Epsosito, A., Taramasso, M., and Buonomo, F., U.S. Patent 2,116,974 (1985).
2. Neri, C., Esposito, A., Anfossi, B., and Buonomo, F., European Patent Appl. 100,119 (1984).
3. Esposito, A., Neri, C., and Buonomo, F., U.S. Patent 4,480,135 (1984).
4. Tatsumi, T., Nakamura, M., Negishi, S., and Tominage, H., *J. Chem. Soc. Chem. Commun.*, 476 (1990).
5. Huybrechts, D. R. C., De Bruycker, L., and Jacobs, P. A., *Nature* **345**, 240 (1990).
6. Kochkar, H., and Figueras, F., *J. Catal.* **171**, 420 (1997).
7. Neumann, R., and Levin-Elad, M., *J. Catal.* **166**, 206 (1997).
8. Fraile, J. M., Garcia, J. I., Mayoral, J. A., der Menorval, L. C., and Rachdi, F., *J. Chem. Soc. Chem. Commun.*, 539 (1995).
9. Van der Waal, J. C., Rigutto, M. S., and van Bekkum, H., *Appl. Catal. A* **167**, 331 (1998).
10. Leon Shohet, J., *IEEE Trans. Plasma Sci.* **19**, 725 (1991).
11. Coates, D. M., and Kaplan, S. L., *MRS Bull.*, 43 (1996).
12. Kumar, S. B., Mirajkar, S. P., Pais, Godwin, C. G., Kumar, P., and Kumar, R., *J. Catal.* **156**, 163 (1995).
13. Brintzinger, H. H., *J. Am. Chem. Soc.* **89**, 6871 (1967).