Catalysis Letters Vol. 103, Nos. 1–2, September 2005 (© 2005)
DOI: 10.1007/s10562-005-6526-2

Influence of Pt–Pd/TS-1 catalyst preparation on epoxidation of olefins with hydrogen peroxide

Qingfa Wang, Li Wang*, and Zhentao Mi*

Key Laboratory for Green Chemical Technology of the Ministry of Education of China, School of chemical Engineering & Technology, Tianjin University, Tianjin, 300072, P. R. China

Received 20 April 2005; accepted 4 May 2005

The catalytic performance of the platinum–palladium/titanium silicalite, which was a common catalyst for the direct epoxidation of olefins with hydrogen and oxygen, was tested by epoxidation of allyl chloride with hydrogen peroxide. The epoxidation capacity of the TS-1catalyst was reduced after loading palladium and platinum on it. Ti leaching and crystallinity decrease were observed by XRD and FT-IR. The decomposition of hydrogen peroxide was accelerated by the supported Pd and Pt. These contributed to the loss of epoxidation capacity of TS-1. Ti leaching and crystallinity decrease were probably main causes. We propose that the Ti leaching had the most important influence on the loss of epoxidation capacity

KEY WORDS: epoxidation; olefins; hydrogen peroxide; platinum–palladium/titanium silicalite; Ti leaching.

1. Introduction

The oxidation of propylene by a H_2–O_2 mixture over a precious metal containing titanium silicalite was a particularly interesting approach and attracted many researchers [1–10]. Such catalytic systems have also been tested for the oxidation of alkanes, for the hydroxylation of benzene to phenol and for the oxidation of phenol [11]. During the reaction Hydrogen peroxide, directly formed from H_2 and O_2 at the precious metal sites of the bifunctional catalyst, diffused to the isolated Ti site and consumed as oxidant at the Ti-sites in TS-1. Proper design and synthesis of this catalyst was very important. The catalyst preparation by simple impregnation of $[Pd(NH_3)_4](NO_3)_2$ and $[Pd(NH_3)_4]Cl_2$ on TS-1 and reduction of the $[Pd(NH_3)_4](NO_3)_2$ and $[Pd(NH_3)_4]Cl_2$ precursors in nitrogen at 150 °C is a suitable technique[12]. In case of the epoxidation of propylene with a H_2-O_2 mixture on Pd/TS-1 catalyst, Sato [13] and Mueller [14] had found that the conversions of propylene was too low ($<2\%$) and the selectivity also suffered from the hydrogenation of propylene to propane. It was discovered that the in situ generation of hydrogen peroxide at the precious metal site is the rate-determining step in this reaction [15]. Although significant effort has been given to establish the reactivity of these supported TS-1 catalyst, relatively little attention has been given to the stability of these materials. Enhancing the catalytic performance of the catalyst must therefore focus on the impregnation and reduction procedure. Hoelderich and his coworkers [16] had reported that the catalytic performance was affected by some reduction methods and the addition of salt to the reaction and considered that the epoxidation reactivity of TS-1 decreased by ammonia blocking the Ti site. However this influence on epoxidation capacity of TS-1 could be eliminated by calcining at high temperature.

In this work, the epoxidation of allyl chloride with hydrogen peroxide was taken as a probe reaction to test the epoxidation capacity of TS-1. We investigated how the preparation of a Pt-Pd/TS-1 catalyst affects the synthesis of epichlorohydrin with hydrogen peroxide. The objective of this study is to discuss the causes of the loss of epoxidation capacity of the TS-1 catalyst.

2. Experimental

The TS-1 catalyst was prepared according to the procedure described in Ref [17]; 300 g of tetraethylorthosilicate were stirred under a N_2 atmosphere and 9 g of tetraethyltitanate were added followed by dropwise addition of 480 g 25 wt% solution of tetrapropylammonium hydroxide. After the alcohol had been destilled off at 80 °C, 526 g of distilled water were added to the solution. The mixture was transferred to an autoclave, heated at 170 °C under autogenous pressure for three days. After cooling down to room temperature, the crystaline product was separated from the liquid by centrifugation, washed with water, dried for 12 h at 120 °C, and finally calcined for 6 h at 550 °C in air.

The 1 wt%Pd/TS-1(IM) catalyst were prepared according to a former procedure[12,15]. For the 0.01 wt.%Pt-1 wt.%Pd/TS-1(IM) sample, the 3 mmol/L $[Pt(NH_3)_4]Cl_4$ aqueous solution was added in the impregnation process. In DP method, $PdCl_2$ was

---

* To whom correspondence should be addressed.
E-mail: zhtmi@tju.edu.cn

1011-372X/05/0900–0161/0

dissolve in HCl aqueous solution. Palladium hydroxide was exclusively precipitated on the surface of TS-1 by slow addition of 0.5 M Na_2CO_3 solution into the PdCl2 solution heated at 70 °C with continuous stirring. The PH value of the solution was maintained at 9∼10 for 1 h. Solid were recovered by filtration and were washed to neutral. All the samples were dried at 120 °C for 2 h and calcined at 400 °C for 2 h. Reduction was carried out with 5 vol% H_2+ 95 vol% N_2 at a heating rate of 1 K /min from room temperature to 150 °C, and kept for 2 h under this temperature.

Epoxidation reaction was performed as batch reactions in a 100 ml glass reactor. In the typical run, 0.2 g TS-1, 13.4 g methanol, 3.4 g aqueous 30 wt%H_2O_2 solution and 2.3 g allyl chloride were charged into the reactor and stirred at 40 °C for 2 h. A sample was withdrawn over a filter and mixed with a defined amount of iso-Butanol, which acted as internal standard. GC analysis was performed on a HP4890 gas chromatograph (FID detector and HP-5 capillary column). The decomposition reaction of H_2O_2 was carried out similar to epoxidition reaction except that no allyl chloride was charged into the reactor. Hydrogen peroxide was determined by iodiometric titration.

X-ray diffraction patterns were recorded on a D/mass-2500 diffractometer using nickel-filtered Cu K_α radiation($\lambda = 0.154056$ nm). Bragg angles between 5° and 50° were scanned with 0.02° step. FT-IR spectra of the samples in the framework region (400–4000 cm^{-1}) were recorded at room temperature with a MAGNA-IR 560 spectrometer. KBr pellet technique was used.

3. Results and disscussion

Figure 1 shows the XRD patterns of the catalysts supported noble metal and fresh TS-1. The same patterns indicated that the MFI structure of the support TS-1 catalyst had little change and the preparation conditions had no effect on the crystal structure. But notably, the peak intensities decreased comparing the supported catalyst with fresh TS-1. The crystallinity of the samples was calculated according to the method described in Ref. [18]. The results (listed in Table 1) indicated that the crystal defect in TS-1 was caused to some extent during the catalyst preparation. And the destruction was irreversible. In the XRD patterns of supported catalysts, the peak of PdO phase (d = 0.264 nm and 0.267 nm) did not appeared. It also could be obtained that the supported Pd was unsformly dispersed on the surface of TS-1.

All the samples showed six prominent features in the FT-IR spectra (as shown in Fig. 2). The main maxima are observed at 1230, 1104, 960, 804, 550 and 450 cm^{-1}, which agreed with the FT-IR skeletal spectra of TS-1 reported in the literature [18,19]. These results indicated that the framework of TS-1 had no change with the process of supporting noble metal, which is consistent with the results of XRD.

The intensity of the 960 cm^{-1} band in the IR spectrum is a useful guide to the extent of lattice incorporation, probably assignable to the Si–O or Si–O–M stretch of an $(Si–O)_3SiOM$ grouping, where M is a heteroatom such

Table 1
The XRD and FT-IR results of different catalyst samples

Entry	Samples	Crystallinity (%)	FT-IR 960/550 cm^{-1} band ratio
1	Fresh TS-1	100	0.752
2	1% Pd/TS-1 (IM)	90	0.743
3	0.01%Pt-1%Pd/TS-1 (IM)	87	0.728
4	1%Pd/TS-1 (DP)	82	0.722

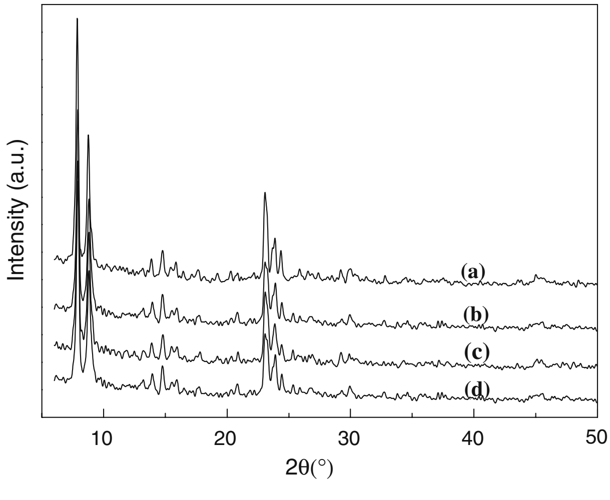

Figure 1. The XRD spectra of fresh TS-1 and supported TS-1.a) Fresh TS-1; b) 1%Pd/TS-1 (IM); c) 0.01%Pt-1%Pd/TS-1 (IM); d) 1%Pd/TS-1 (DP).

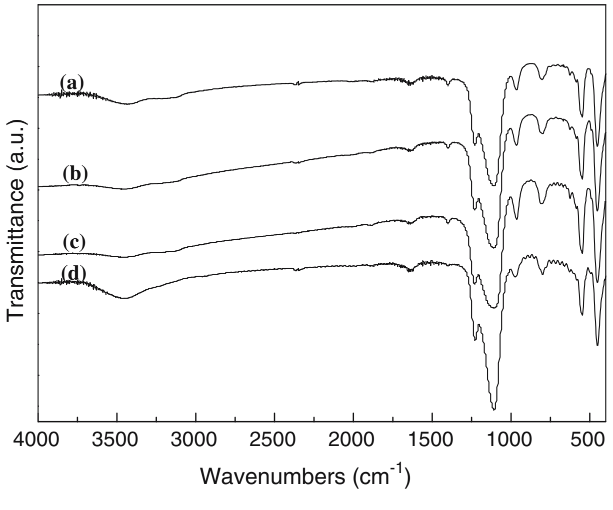

Figure 2. FT-IR spectra of TS-1 catalysts supported with precious metal. a) Fresh TS-1; (b) 1%Pd/TS-1 (IM); (c) 0.01%Pt-1%Pd/TS-1 (IM); d) 1%Pd/TS-1.

Table 2
Epoxidation of allyl chloride with hydrogen peroxide catalyzed by Pt-Pd/TS-1 catalysts

Entry	Samples	ALC conversion [a](%)	ECH [b]	
			Yield (%)	Selectivity (%)
1	TS-1	80.4	76.1	94.7
2	1%Pd/TS-1 (IM)	87.9	57.2	65.1
3	0.01%Pt-1%Pd/TS-1 (IM)	86.9	60.8	70.0
4	1%Pd/TS-1 (DP)	70.0	40.0	57.2

[a] ALC: allyl chloride. [b] ECH: epichlorohydrin. The yield and selectivity were calculated based on ally chloride.

as Ti [18, 20]. As a semi-quantitative measurement, the intensity of this band is expressed as a ratio to that of the 550 cm^{-1} band, which is characteristic of MFI and similar pentasil structures [21]. The ratio values of the intensities of 960 cm^{-1} band to 550 cm^{-1} band were listed in Table 1. The FT-IR spectra of the supported catalysts show that the level of titanium in the lattice decreases with the addition of Pt and the difference of preparation methods. In the preparation process of impregnation (IM), the support TS-1 was treated with alkaline solution because of the weak alkaline of impregnation precursors. Ti leaching occurred in the process and the level of Ti in the lattice of TS-1 decreased. In the Pt–Pd/TS-1 preparation, the basicity of Pd precursor solution became stronger with the addition of Pt precursor, the $[Pt(NH_3)_4]Cl_4$ solution, and the preparation time was also prolonged. The much lower level of Ti in the lattice of TS-1 catalyst was observed. In the preparation process of deposition–precipitation (DP), the Ti leaching rate was enhanced by treatment with strong acid and stirring during the neutrality process with Na_2CO_3 solution. And at the end of this process, TS-1 was also treated by alkaline solution. So the 1 wt%Pd/TS-1 (DP) sample had much more Ti leaching. The results in the Table 1 indicated that Ti leaching was occurred in the preparation process and the preparation method had much more effects on the Ti leaching.

In the epoxidation of olefins with hydrogen and oxygen, the Pt–Pd/TS-1 actually plays two roles. The noble metal was the active center, on which hydrogen peroxide was generated from hydrogen and oxygen. TS-1 acts as the component for epoxidation reaction of olefins with hydrogen peroxide. From the results of XRD and FT-IR, it can be known that the epoxidation capacity of Pt–Pd/TS-1 was certainly affected by the preparation process. The epoxidation capacity of supported catalysts in Table 2 had significant decrease, which may be contributed by three factors observed from the experiments. The first one is Ti leaching in the preparation process. Ti in TS-1 catalyst is the active center for epoxidation of olefins and in the epoxidation the intermediates of epoxide from olefins and hydrogen peroxide were formed on it. The second one is the decrease of crystallinity. The higher the crystallinity was, the better performance the TS-1 sample had [22,23]. The third one was the decomposition of H_2O_2 on noble metal supported on the surface of TS-1. In order to investigate this influence, the decomposition of hydrogen peroxide over Pd/TS-1 was carried out. The results were shown in Fig. 3. The supported Pd had apparent promote on the decomposition of H_2O_2, which was consistent with the results of Ref. [16]. Pt had almost the same catalytic performance for the decomposition of hydrogen peroxide as Pd metal, while its effect could be neglected because of little loading. In epoxidation, however, the decomposition of H_2O_2 was not so vigorous from the results of epoxidation of allyl chloride in Table 2. Compared the 1 wt%Pd/TS-1 (IM) and 1 wt%Pd/TS-1 (DP) samples, it can be obtained that the former two parameters were main causes for the decrease of epoxidation capacity. Compared the 1 wt%Pd/TS-1 (IM) and 0.01 wt%Pt-1 wt%Pd/TS-1 (IM) sample, it could be observed that Pt ingredient also improved the epoxidation of allyl chloride with hydrogen peroxide catalyzed by Ti-catalysts. This phenomenon had not been discovered before. The mechanism of the Pt influence on epoxidation process would be very interesting work to investigate. In view of the epoxidation

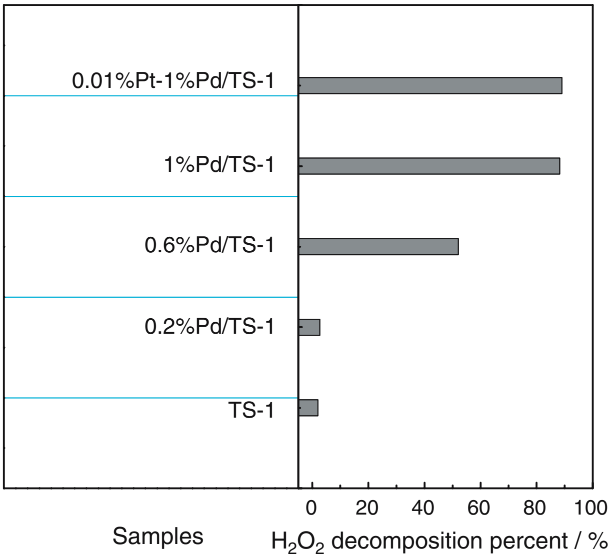

Figure 3. Decomposition of hydrogen peroxide over various Pt-Pd/TS-1 catalysts.

mechanism reported by Clerici [24], Ti leaching was the most important cause for the decrease of epoxidation capacity of Pt-Pd/TS-1 catalyst.

In summary, our work has demonstrated that the epoxidation capacity of Pt–Pd/TS-1 catalyst, which generally used as catalyst for the direct epoxiation of olefins with hydrogen and oxygen, was affected by the catalyst preparation and this influence was discussed. The Ti leaching and crystallinity decrease occurred in the Pt–Pd/TS-1 preparation process. These parameters and the decomposition of H_2O_2 by the supported Pd and Pt contributed to the epoxidation capacity of Pt–Pd/TS-1 catalyst. The former two factors were the main causes. Ti was the active center for epoxidation reaction of olefins with hydrogen peroxide. The Ti leaching was considered as the uppermost cause for the decrease of epoxidation capacity of Pt–Pd/TS-1 catalyst.

Acknowledgments

This work was funded by the National Natural Science Foundation of China (Granted No. 20446003) and the PhD Specific Foundation of the Ministry of Education (Granted No. 20030056035).

References

[1] W. Laufer and W.F. Hoelderich, Appl. Catal. A: Gen. 213 (2001) 163.

[2] G. Jenser, T. Mallal, M. Mueciejewski, F. Eigenmann and A. Baiker, Appl. Catal. A: Gen. 208 (2001) 125.

[3] B. Notari, Adv. Catal. 41 (1996) 253.

[4] X. Guo, R. Wang, X. Wang and J. Hao, Catal. Today 93-95 (2004) 211.

[5] R. Wang, X. Guo, X. Wang, J. Hao, G. Li and J. Xiu, Appl. Catal. A: Gen. 261 (2004) 7.

[6] C. Wang, X. Guo, X. Wang, R. Wang and J. Hao, Catal. Lett. 96 (2004) 79.

[7] N. Yap, R.P. Andres and W.N. Delgass, J. Catal. 226 (2004) 156.

[8] T.A. Nijhuis, B.J. Huizinga, M. Makkee and J.A. Moulijn, Ind. Eng. Chem. Res. 38 (1999) 884.

[9] C.X. Qi, T. Akita, M. Okumura and M. Haruta, Appl. Catal. A: Gen. 218 (2001) 81.

[10] G. Grosch, U. Muller, M. Schulz, N. Rieber, and H. Wurz, WO 9,747,386 (1997); G.R. Bowman, J.J. Maj, W.H. Clark, WO 9,800,414 (1998); W.H. Clark, J.J. Maj, G.R. Bowman, WO 9,800,415 (1998).

[11] P. Ingallina, M.G. Clerici, L. Rossi, and and G. Belussi, Stud. Surf. Sci. Catal. 92 (1995) 31; T. Tatsumi, K. Yuasa, and H.J. Tominaga, J. Chem. Soc., Chem. Commun. 19 (1992) 1446.

[12] R. Meiers, U. Diagerdissen and W.F. Hoelderich, J. Catal. 176 (1998) 376.

[13] A. Sato, and T. Miyake, JP 4,352,771, (1992); A. Sato, M. Oguri, M. Tokumaru, and T. Miyake, JP 2,690,309, (1996).

[14] U. Muller, P. Lingelbach, P. Babler, W. Harder, E. Karsten, “V. Kohl, J. Dembowski, N. Rieber, and M. Fischer, DE 4,425,672 (1996).

[15] R. Meiers and W. Holderich, Catal. Lett. 59 (1999) 161.

[16] W. Laufer, R. Meiers and W. Holderich, J. Mol. Catal. A: Chem. 141 (1999) 215.

[17] M. Taramasso, G. Perego, B. Notari, US 4,410,501 (1983).

[18] E. Astorino, J.B. Peri, R.J. Willey and G. Busca, J. Catal. 157 (1995) 482.

[19] T. Armaroli, F. Milella, B. Notari, R.J. Willey and G. Busca, Top. Catal. 15 (2001) 63.

[20] K.S. Smirnov and B. van de Graaf, Micropor. Mater. 7 (1996) 133.

[21] A. Thangaraj, R. Kumar, S.P. Mirajkar and P. Ratnasamy, J. Catal. 130 (1991) 1.

[22] A. Tuel and Y. Ben Taârit, Zeolites 13 (1993) 357.

[23] C.S. Cundy and J.O. Forrest, Micro. Mes. Mat. 72 (2004) 67.

[24] M.G. Clerici, G. Bellussi and U. Romano, J. Catal. 129 (1991) 159.