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Research Note

Highly efficient epoxidation of propylene to propylene oxide over TS-1 using urea + hydrogen peroxide as oxidizing agent

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Abstract

We compared the efficacies of urea + hydrogen peroxide (U+HP) and hydrogen peroxide (HP) as an oxidizing agent in the epoxidation of propylene catalyzed by a titanium silicate-1 (TS-1) molecular sieve. The TS-1 catalyst exhibited good performance and stability in the TS-1/(U+HP) system. EPR results showed that more active Ti-superoxo species led to better performance of TS-1 in the TS-1/(U+HP) system than in the TS-1/HP system.

Keywords: Epoxidation; Propylene; Propylene oxide; Urea; Hydrogen peroxide; Titanium silicate-1; Electron paramagnetic resonance

1. Introduction

Propylene oxide (PO) is an important industrial chemical; based on volume of production, it is among the top 50 chemicals produced worldwide [1]. PO is used to produce a wide range of commercial and industrial products, including polyether polyols, propylene glycols, propylene glycol ethers, flame retardants, modified carbohydrates (starches), synthetic lubricants, and oilfield drilling chemicals. Current routes for manufacturing PO include the chlorohydrin process and the Halcon process. Both of these processes have disadvantages [2]; the chlorohydrin process produces environmentally unfriendly chlorinated byproducts, whereas the Halcon process produces large amounts of side product (*t*-butyl alcohol or styrene). There is an urgent need to create a novel, clean process for producing PO to replace the current industrial processes. Although much recent research has been focused on the direct epoxidation of propylene by molecular oxygen [3–8], direct epoxidation routes cannot yet be commercialized because the current available catalysts are not sufficiently active, stable, or selective.

This environmentally benign hydroperoxide process uses titanium silicalite-1 (TS-1) as the catalyst. High yields of PO can be obtained over TS-1 using H_2O_2 (HP) as an oxidant and CH_3OH as a solvent during the epoxidation of propylene [9–14]. This innovative process technology has several advantages over conventional routes, being more economical, environmentally friendly and flexible in terms of locating new plants. Furthermore, a worldwide hydrogen peroxide-to-propylene oxide (HPPO) process based on TS-1 is scheduled for commercialization [15]. But the epoxidation of propylene produces wastewater containing at least 2–4% monomethyl ethers. Monomethyl ethers and water can form azeotropic mixtures. An important problem in the industrial process is that the separation of azeotropic mixture is impossible by ordinary distillation; usually benzene is added into azeotropic mixture to allow its separation into pure components [16,17]. Benzene is a poisonous chemical that may cause environmental problems. Based on "green" chemical principles, the use of additional solvents should be avoided to the greatest extent possible in chemical processes [18]; on the other hand, large investments and high energy costs are inevitable.

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In an attempt to circumvent this problem, urea–hydrogen peroxide adduct (UHP), which slowly releases anhydrous H_2O_2 into solution [19], has been successfully used in the epoxidation of substituted allylic alcohols [20] and styrene [21,22], with TS-1 as a redox catalyst, with excellent epoxide yields produced. The addition of urea has a significant effect on the epoxide. This has motivated us to carry out the epoxidation of propylene by adding urea to the reaction system.

This paper reports our study on the epoxidation of propylene using TS-1 as the solid redox catalyst, and HP and U+HP (urea and aqueous H_2O_2) as the oxidizing agents. It also describes different structural properties of the TS-1/U+HP system and reports on a comparison between that system and the TS-1/HP system done using EPR spectroscopy.

2. Experimental

TS-1 was hydrothermally synthesized as described previously [23]. In a typical preparation, 50 g of colloidal silica (30 wt%) was added to 33 g of distilled water under vigorous stirring for 0.5 h. This was followed by dropwise addition of 0.95 g of titanium tetrachloride dissolved in 3.65 g of dry isopropanol under vigorous stirring. The solution was stirred for 1 h. Then 10 g of TPABr, 16.7 g of ethylamine, and 1.5 g of seeds were added very slowly under vigorous stirring, which continued for 0.5 h. This was followed by the addition of 33.5 g of distilled water under vigorous stirring. The final solution was stirred for 0.5 h. The reaction mixture gave a mole composition of 1.00 Si:0.02 Ti:0.15 TPABr:0.96 C_2H_5N:24.00 H_2O.

The crystallization of the sample was carried out in a stainless-steel autoclave at 170 °C for 40 h. After crystallization, the solid product was washed with deionized water, dried at 120 °C for 4 h, and calcined at 540 °C in air for 5 h. The mole ratio of Si/Ti determined by XRF analysis was 45.7 in the solid final TS-1 catalyst. DR UV-Vis analysis demonstrated that this TS-1 had fewer external framework Ti sites attributed to TiO_2 nanoparticles. Scanning electron microscopy of TS-1 revealed a particle size of about 1 μm.

The catalysts were characterized by electron paramagnetic resonance (EPR) spectroscopy. The EPR spectra of the samples were recorded on a JES-FEIXG EPR spectrometer operating at X-band frequency and 100 kHz field modulation. EPR spectra of 77 K were observed using a liquid Nitrogen Dewar. The signals of g_3 and g_4 of Mn^{2+} in MnO powder were used as the standard sample.

The epoxidation of propylene in autoclave was carried out in a stainless steel reactor that was immersed in a bath controlled at the required temperature. In a typical run, 0.4 g of calcined catalyst, 2.0 g of 30 wt% H_2O_2, 32 ml of distilled water, and 1.06 g of urea were fed into the reactor, then propylene was charged at constant pressure (0.4 MPa). The epoxidation reaction was conducted at 60 °C under stirring. After completion of the reaction, the residual H_2O_2 was checked by iodometric titration, and products of the reaction were analyzed on a 1102 gas chromatograph with a flame ionization detector and a capillary column (30 m × 0.25 mm, polyethylene glycol 20 M). PO was the main product; propylene glycol (PG) was the byproduct. The result of the reaction was given using the following criteria:

$$X_{H_2O_2} = \frac{n^0_{H_2O_2} - n_{H_2O_2}}{n^0_{H_2O_2}}, \qquad U_{H_2O_2} = \frac{n_{PO} + n_{PG}}{n^0_{H_2O_2} X_{H_2O_2}},$$

$$S_{PO} = \frac{n_{PO}}{n_{PO} + n_{PG}}, \qquad S_{PG} = \frac{n_{PG}}{n_{PO} + n_{PG}}.$$

The experimental errors of the H_2O_2 conversion and PO selectivity were within 1 and 2%, respectively.

Table 1
Effect of different oxidants on propylene epoxidation over TS-1[a]

Run	Oxidant	TOF (h^{-1})[e]	$X_{H_2O_2}$ (%)	S_{PO} (%)	S_{PG} (%)	$U_{H_2O_2}$ (%)
1	HP[b]	42.0	56.0	83.5	16.5	54.1
2	U+HP	86.6	63.2	98.1	1.9	98.9
3	U+HP (0.5:1)[c]	58.0	59.7	90.4	9.6	70.1
4	U+HP (2:1)	60.1	71.1	96.6	3.4	61.0
5	U+HP (3:1)	56.1	73.3	97.5	2.5	55.2
6	U+HP (5:1)	44.2	90.4	97.2	2.8	35.3
7	U+HP (0.35)[d]	57.1	80.5	98.5	1.5	98.0
8	U+HP (0.18)	31.2	86.9	96.6	3.5	96.4
9	U+HP (0.10)	17.8	90.0	95.5	4.5	95.7
10	U+HP (0.08)	14.6	90.6	96.4	3.6	97.5

[a] Reaction conditions: reaction temperature, 60 °C; propylene pressure, 0.4 MPa; catalyst concentration, 11.9 g/l; reaction time, 60 min.

[b] HP, Hydrogen peroxide (30 wt%); U+HP = urea and hydrogen peroxide mixture (1:1, mole ratio); the H_2O_2 concentration in reaction mixture, 0.67 mol/l.

[c] The number in parentheses is molar ratio of urea to H_2O_2.

[d] The number in parentheses is the H_2O_2 concentration in reaction mixture (mol/l).

[e] Turnover frequency (TOF) = moles of H_2O_2 converted for producing propylene oxide + byproduct per mole of Ti per hour.

3. Results and discussion

The effect of different sources of oxidizing agent (H_2O_2) on the performance of TS-1 is characterized in Table 1. It can be seen that the H_2O_2 conversion, PO selectivity, and H_2O_2 utilization were very low in TS-1/HP system (run 1). For the TS-1/(U+HP) system (run 2), in which urea and aqueous hydrogen peroxide solution were added, all of these values were increased, especially the H_2O_2 utilization, which grew from 54.1 to 98.9%. Urea may act as a buffer for the TS-1/(U+HP) system, which can release H_2O_2 in a controlled manner [21,22] and make most of the H_2O_2 form active Ti species.

Because the addition of urea was found to have a significant effect on PO selectivity and H_2O_2 utilization, we further investigated the effect of the urea/HP molar ratio. The H_2O_2 conversion, PO selectivity, and H_2O_2 utilization showed differing tendencies to change with increasing amounts of urea (runs 2–6). The H_2O_2 conversion increased steadily with increasing molar ratio of urea to H_2O_2. The PO selectivity increased from 90.4 to 98.1% as the molar ratio of urea to H_2O_2 increased from 0.5 to 1 (runs 2 and 3), and then remained stable on further increases (runs 4–6). The H_2O_2 utilization first increased as the urea/H_2O_2 molar ratio went from 0.5 to 1 (runs 2 and 3), reached a maximum level at a molar ratio of 1 (run 2), and then

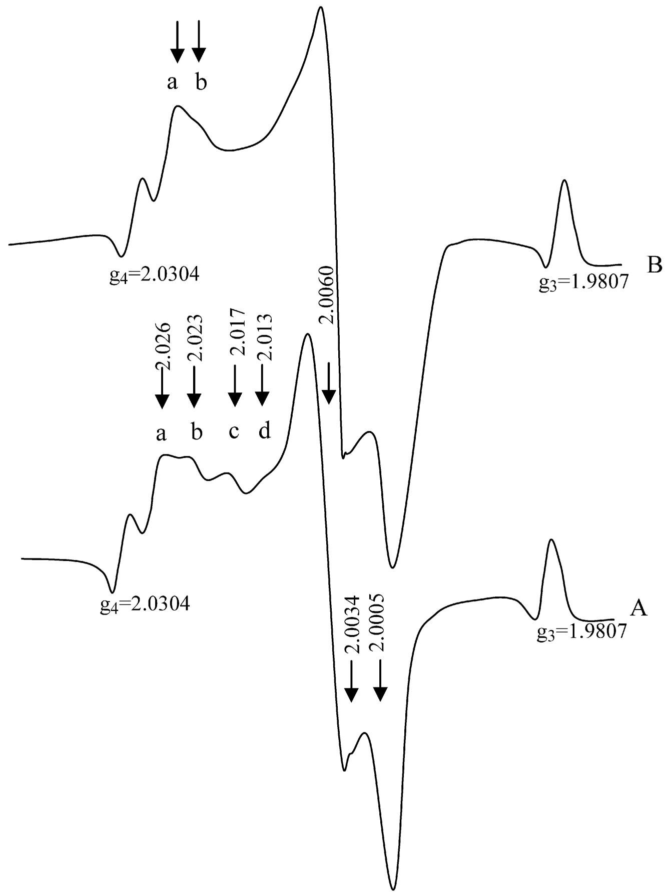

Fig. 1. EPR spectra of TS-1 + urea + aqueous H_2O_2 (A) and TS-1 + aqueous H_2O_2 (B). (The signal of g_3 (1.9807) and g_4 (2.0304) were one of Mn^{2+} in MnO powder.)

Table 2
Repeated tests of TS-1 catalyst in the system of TS-1/(U+HP)[a]

Run	$X_{H_2O_2}$ (%)	S_{PO} (%)	S_{PG} (%)	$U_{H_2O_2}$ (%)
1	90.0	95.5	4.5	95.7
2	89.8	95.3	4.7	96.9
3	90.3	95.1	4.9	95.3
4	89.1	95.2	4.8	95.5
5	90.6	95.9	4.1	96.4

[a] Reaction conditions: reaction temperature, 60 °C; propylene pressure, 0.4 MPa; catalyst concentration, 11.9 g/l; reaction time, 60 min; the H_2O_2 concentration in reaction mixture, 0.10 mol/l; $CO(NH_2)_2$: H_2O_2 (molar ratios) = 1:1.

decreased with further increases (runs 4–6). The proper amount of urea, which can facilitate the formation of active Ti species, can make most of the H_2O_2 react with propylene and prevent further PO hydrolysis. But excessive urea addition will cause the decomposition of H_2O_2.

We also found that in the TS-1/(U+HP) system, the concentration of H_2O_2 had a significant effect on H_2O_2 conversion (runs 2, 7–10). A decrease in H_2O_2 concentration led to an increase in H_2O_2 conversion (runs 2, 7–9) before the concentration of H_2O_2 reached 0.10 mol/l. H_2O_2 conversion remained stable with further decreases in H_2O_2 concentration (run 10). At H_2O_2 concentration of 0.10 mol/l, the H_2O_2 conversion was 90.0%, PO selectivity was 95.5%, and H_2O_2 utilization was 95.7%. As expected, with high H_2O_2 concentrations in the TS-1/(U+HP) system, the concentration of Ti–superoxo complex was low, and thus propylene epoxidation was slow. With a decreasing H_2O_2 concentration, the concentration of Ti–superoxo complex increased, facilitating the formation of desired PO inside the zeolitic pore.

EPR spectroscopy was used to characterize the interaction between TS-1 and HP. Fig. 1 shows the different Ti–superoxo complexes appearing in the EPR spectra. The *g* values of the two curves are in good agreement with those reported previously for the superoxide radical ion stabilized on Ti(IV) centers of TS-1 interacting with HP or U+HP [21,22]. The Ti–superoxo species in the TS-1/(U+HP) system differ from those in the TS-1/HP system. The presence of three different Ti–superoxo species (a, b, and c) in curve A indicates the existence of different Ti^{4+} sites in the original TS-1 [24] and/or generated during reactions with HP and urea [21,22]. Free superoxo radicals weakly attached to lattice silicon represent species "d." In curve B, the dominant Ti–superoxo species is "a," indicating that other coordination sites of Ti are occupied by water. But water molecules cannot fill vacant coordination sites of Ti in the case of curve A.

It is generally accepted that the active Ti species are responsible for the epoxidation of propylene when H_2O_2 is used as an oxidant. The catalytic performance of TS-1 is strongly dependent on the number of Ti–superoxo species. The active Ti–superoxo species b [25], which has pentacoordination, is not accessible to water molecules. The TS-1/(U+HP) system contains more active Ti species b than the TS-1/HP system, because some Ti sites are occupied by water in the TS-1/HP system. Consequently, TS-1 exhibits higher activity in the TS-1/(U+HP) system. Because most of the H_2O_2 can form Ti–superoxo species b through the interaction between TS-1 and HP, H_2O_2 utilization is very high in the TS-1/(U+HP) system. Less H_2O_2 can form Ti–superoxo species b in the TS-1/HP system; much of the H_2O_2 that cannot form Ti–superoxo species b decomposes during the reaction. Consequently, H_2O_2 utilization is very low in the TS-1/HP system.

Five cycles of the same process were conducted to evaluate the stability of the TS-1 catalyst (Table 2). The findings indicate that catalyst can be reused up to 5 times with little degradation in its performance in propylene epoxidation. Taken together, our findings indicate that the good TS-1 performance and simple chemical process make the TS-1/(U+HP) system suitable for use in the industrial manufacture of PO.

4. Conclusion

A significant improvement in the performance of TS-1 was achieved when urea and HP were used as oxidant in the epoxidation of propylene, compared with the traditional use of HP only. Under optimal conditions, H_2O_2 conversion was 90.0%, PO selectivity was 95.5%, and H_2O_2 utilization was 95.7% in the TS-1/(U+HP) system. The TS-1 catalyst can be reused up to 5 times without reduction. EPR results showed that the more active Ti–superoxo species in the TS-1/(U+HP) system led to better TS-1 performance compared with that seen in the TS-1/HP system.

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References

[1] http://www.dow.com/propyleneoxide/about/index.htm.

[2] D.L. Trent, Kirk–Othmer Encyclopedia Chem. Technol., vol. 20, The Dow Chemical Company, 1996, p. 271.

[3] A. Palermo, A. Husain, M.S. Tikov, R.M. Lambert, J. Catal. 207 (2002) 331.

[4] O.P.H. Vaughan, G. Kyriakou, N. Macleod, M. Tikhov, R.L. Lambert, J. Catal. 236 (2005) 401.

[5] J. Lu, M. Luo, H. Lei, X. Bao, C. Li, J. Catal. 211 (2002) 552.

[6] J. Lu, J.J. Bravo-Suarez, A. Takahashi, M. Haruta, S.T. Oyama, J. Catal. 232 (2005) 85.

[7] H. Chu, L. Yang, Q. Zhang, Y. Wang, J. Catal. 241 (2006) 225.

[8] B.S. Uphade, T. Akita, T. Nakamura, M. Haruta, J. Catal. 209 (2002) 331.

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

[10] W. Panyaburapa, T. Nanok, J. Limtrakul, J. Phys. Chem. C 111 (2007) 3433.

[11] W. Cheng, X. Wang, G. Li, X. Guo, B. Du, Catal. Lett. 95 (2004) 185.

[12] X. Liu, X. Wang, X. Guo, G. Li, Catal. Today 93–95 (2004) 505.

[13] D. Wells, W. Delgass, K. Thomson, J. Am. Chem. Soc. 126 (2004) 2956.

[14] G. Langhendries, D. De Vos, G. Baron, P. Jacobs, J. Catal. 187 (1999) 453.

[15] B. Ford, Chem. Mark. Rep. 269 (2006) 24.

[16] S. Wang, S. Zhang, Y. Li, H. Guo, Petrochem. Technol. 31 (2002) 973.

[17] S. Wang, S. Zhang, Y. Li, H. Guo, J. Dalian Univ. Technol. 42 (2002) 419.

[18] P. Anastas, J. Warner, Nature 398 (1999) 33.

[19] A. Gonsalves, R. Johnstone, M. Pereira, J. Shaw, J. Chem. Res. Synop. (1991) 208.

[20] W. Adam, R. Kumar, T. Reddy, M. Renz, Angew. Chem. Int. Ed. Engl. 35 (1996) 880.

[21] S. Laha, R. Kumar, J. Catal. 204 (2001) 64.

[22] S. Laha, R. Kumar, J. Catal. 208 (2002) 339.

[23] X. Wang, Y. Zhang, X. Guo, G. Li, Appl. 01145256.0 (2001), to Dalian University of Technology.

[24] A. Tuel, Y. Taârit, Appl. Catal. A 110 (1994) 137.

[25] K. Chaudhari, D. Srinivas, P. Ratnasamyl, J. Catal. 203 (2001) 25.