

Highly Effective Propylene Epoxidation over TS-1/SiO₂ Hydrothermally Treated

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Abstract: The propylene epoxidation over TS-1/SiO₂ catalyst hydrothermally treated was investigated. It was found by EPR characterization that two types of Ti (IV)-superoxide radicals, A ($g_z=2.0271$; $g_y=2.0074$; $g_x=2.0010$) and B ($g_z=2.0247$; $g_y=2.0074$; $g_x=2.0010$), were observed for TS-1/SiO₂. The superoxo species A converted to B after TS-1/SiO₂ catalyst was hydrothermally treated. The results show that over TS-1/SiO₂ catalyst hydrothermally treated at 170°C, about 95% conversion of H₂O₂ with above 94% PO selectivity is obtained during continuous running for 300 h under the conditions of reaction temperature 45°C, 0.5 h⁻¹WHSV of propylene.

Keywords: Hydrothermal, TS-1/SiO₂, propylene epoxidation, EPR, radical.

A global research effort is under way to replace environmentally problematic liquid or halide-containing solid acids with environmentally friendly oxides. Propylene oxide (PO) is an important chemical product. The conventional route for epoxidation of propylene involving the use of chlorine and lime produces much pollution. A large amount of side products such as *t*-butyl alcohol or styrene were coproduced in the process developed by Halcon for the manufacture of PO.

The invention of titanium silicalite-1 (TS-1) offers a clean and economically viable alternative to existing processes. Almost quantitative yields of PO are produced at near room temperature, with dilute methanol solutions of hydrogen peroxide¹. TS-1 synthesized with less expensive tetrapropylammonium bromide (TPABr) as the template exhibits good performance in propylene epoxidation using hydrogen peroxide as the oxidant²⁻⁴. Industrial catalysts, which are used in fixed-bed, must be formed with binder into pellets or extrudates. However, the performance of the extruded catalyst is not satisfied. It is known that hydrothermal treatment is an effective method to tailor catalytic properties. The TS-1/SiO₂ catalyst obtained in this way has not been reported in propylene epoxidation. The present paper reports the performance of TS-1/SiO₂ catalyst hydrothermally treated in propylene epoxidation with hydrogen peroxide.

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Experimental

TS-1 was synthesized according to the literature⁵. The TS-1/SiO₂ catalyst was prepared through mixing TS-1 with colloidal silica, extruding, drying and calcining. 15 g TS-1/SiO₂ catalyst was added into 50 mL deionizing water and sealed in an autoclave, then heated in an oven at 170 °C for 4 h. *Prior to* reaction, the sample was calcined at 540 °C for 4 h. The samples before and after hydrothermal treatment were designated as HT-0 and HT-170, respectively. UV-Vis measurements were performed on a Jasco V-550. The EPR spectra of 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 $g_3(1.9807)$ and $g_4(2.0304)$ of Mn²⁺ in MgO powder (see **Figure 2**) were used as standard sample.

The catalytic reaction was carried out in a small stainless-steel fixed-bed reactor at the pressure of 3.0 MPa. Diluted H₂O₂ and propylene were introduced into the fixed-bed reactor by two measuring pumps respectively. The products were trapped in a refrigerator. The residual H₂O₂ was checked by iodometric titration. The products of the reaction were analyzed on a 1102 gas chromatograph.

Results and Discussion

A comparison of catalytic performance with TS-1/SiO₂ catalysts before and after hydrothermal treatment

Table 1 Performance of TS-1/SiO₂ before and after hydrothermal treatment

Sample	X _{H₂O₂} (%)	S _{PO} (%)	U _{H₂O₂} (%)
HT-0	90.48	95.78	81.22
HT-170	95.99	91.83	91.35

Reaction condition: reaction temperature 60 °C, space velocity of propylene 0.5 h⁻¹, propylene pressure 3.0 MPa, n(C₃H₆) / n(H₂O₂) = 3/1
 X_{H₂O₂}; conversion of H₂O₂, S_{PO}; PO selectivity, U_{H₂O₂}; utilization of H₂O₂.

The activities of TS-1/SiO₂ before and after hydrothermal treatment were showed in **Table 1**. The TS-1/SiO₂ catalyst hydrothermally treated had higher catalytic activity than TS-1/SiO₂. **Figure 1** (a) and (b) show the UV-Vis spectra of TS-1/SiO₂ catalyst and hydrothermally treated TS-1/SiO₂ catalyst absorbed aqueous H₂O₂, respectively. In **Figure 1**, absorption band at 210 nm is assigned to charge transfer transition of tetrahedrally coordinated titanium in the silicalite framework and some absorption in the 250 to 300 nm region is assigned to solvent molecules to coordinated Ti centers. The presence of a continuous absorption band (300-500 nm) of two catalysts indicates the formation of different Ti–superoxide complexes, though there is no remarkable difference between curves a and b. **Figure 2** (a) and (b) show the EPR spectra of TS-1/SiO₂ catalyst and hydrothermally treated TS-1/SiO₂ catalyst absorbed aqueous H₂O₂, respectively. Activation of H₂O₂ by isolated Ti centers form three types of

oxo-titanium species viz. Ti (IV)-peroxide, hydroperoxide and superoxide which are found to be active in oxidations catalyzed by titanosilicates. Among these, Ti (IV)-superoxide species is detected in EPR due to its paramagnetic nature and is also said to bring about the epoxidation reactions^{6,7}. In **Figure 2**, there is a striking difference between the EPR spectra of these two samples. Two types of Ti (IV)-superoxide radicals: A and B (curve a) are observed for TS-1/SiO₂ while, only one type of Ti (IV)-superoxide radical B is seen for TS-1/SiO₂ hydrothermally treated. Species A and B differ only in g_z parameter (for A: $g_z=2.0271$; $g_y=2.0074$; $g_x=2.0010$ and for species B: $g_z=2.0247$; $g_y=2.0074$; $g_x=2.0010$) while in case of curve b, species A is totally absent with EPR parameters as ($g_z=2.0271$; $g_y=2.0074$; $g_x=2.0010$). Difference of EPR signals of TS-1/SiO₂ before and after hydrothermal treatment could establish that superoxo species A has converted to B which leads to a higher activity.

Figure 1 UV-Vis spectra of TS-1/SiO₂ (a) and hydrothermally treated TS-1/SiO₂ (b) absorbed aqueous H₂O₂

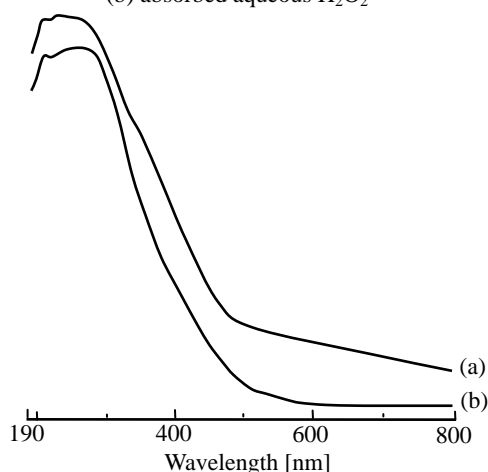
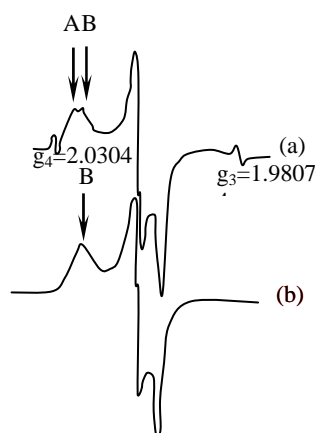
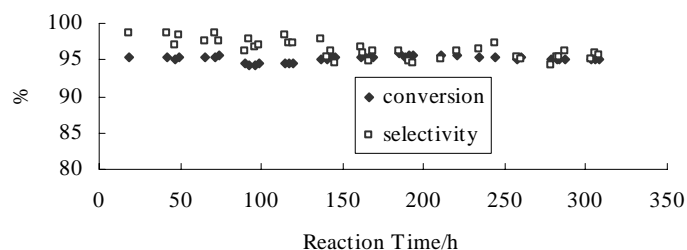


Figure 2 EPR spectra of TS-1/SiO₂ (a) and hydrothermally treated TS-1/SiO₂ (b) absorbed aqueous H₂O₂



Stability of TS-1/SiO₂ hydrothermally treated

Figure 3 The stability of TS-1/SiO₂ catalyst hydrothermally treated at 170 °C in propylene epoxidation



From the results shown in **Figure 3**, it can be seen that TS-1/SiO₂ catalyst hydrothermally treated at 170 °C has very high activity and stability in propylene epoxidation. Under follow reaction condition: reaction temperature 45 °C, space velocity of propylene 0.5 h⁻¹, propylene pressure 3.0 MPa, C₃H₆/H₂O₂ =3/1, it displays no decrease of conversion of H₂O₂ after 300 h continuous running. The conversion of H₂O₂ maintains about 95% during the reaction course. Meanwhile, the catalyst has very high initial PO selectivity and displays slightly slow decrease of PO selectivity in the reaction course. But the PO selectivity maintains above 94% all the time.

Conclusion

The TS-1/SiO₂ catalyst hydrothermally treated exhibits higher activity than TS-1/SiO₂. Using TS-1/SiO₂ catalyst hydrothermally treated at 170 °C as catalyst at the reaction temperature of 45 °C and 0.5 h⁻¹WHSV of propylene, about 95% conversion of H₂O₂ with above 94% PO selectivity is obtained during 300 h continuous running. An EPR study of TS-1/SiO₂ catalyst before and after hydrothermal treatment could show that the existence of superoxo species B ($g_z = 2.0247$; $g_y = 2.0074$; $g_x = 2.0010$) leads to a higher activity.

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