SUPPORTING INFORMATIONS

Characterization, and catalytic performance of deactivated and regenerated TS-1 extrudates in a pilot plant of propene epoxidation

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1. Characterization of the externally regenerated TS-1 extrudates

Figure S.1 shows the XRD patterns of the externally regenerated TS-1 extrudates (samples 6-9) and of fresh TS-1 (sample 5). All samples show the five characteristic peaks of MFI topology; meaning that regeneration by calcination did not destroy the framework of the zeolites. However, the relative crystallinity of the samples decreased after regeneration, due to the high temperature of calcination [S.1, S.2], but was still higher than that of the fresh TS-1 (Table S.1).

The FT-IR spectra of the regenerated TS-1 extrudates are shown in Fig. S.2. The intensity of the characteristic band at 550 cm-1, which is considered to be characteristic for the MFI topology, became stronger after regeneration due to the clearance of the pores. The intensity of the band at 960 cm-1 also increased because of the exposure of stretching vibration of [SiO_4] units in the neighborhood of titanium ions [S.3].

The UV-Vis spectra of the regenerated TS-1 are shown in Fig. S.3. Although, according to the elemental analysis, the amount of Ti decreased, the UV-Vis bands of the four regenerated samples show little difference from the fresh one, thus the catalytic activity should not be influenced by the loss of a small amount of titanium.

2. Characterization of the in situ regenerated TS-1 extrudates

There was no clear difference between the characteristic peaks of the MFI framework in the XRD patterns of samples 4, 5, 10, and 11 (Fig. S.4). The relative crystallinity decreased after in-situ regeneration from 92% to 79% for samples 10 and to 75% for sample 11, but was still higher than that of fresh TS-1, which was similar to the crystallinity obtained after external regeneration.

The intensity of the band at 960 cm-1 in the FT-IR spectra of samples 10, and 11 became stronger after regeneration (cf. Fig. S.5), because of the clearance of the channels and the resulting exposure of the active tetrahedrally coordinated titanium. The intensity of the bands at about 590 and 630 cm^{-1}, which are considered to be characteristic of anatase TiO_2 [S.4], increase. This indicates that the amount of anatase TiO_2 increase after in-situ regeneration.

The UV-Vis spectra of samples 4, 5, 10, and 11 (Fig. S.6) show that the amount of non-framework Ti (~250 nm) and anatase TiO_2 (~310 nm) increased after regeneration, while the amount of framework Ti, with a characteristic band at ~210 nm, decreased a little. This means that the framework Ti transforms to non-framework Ti or anatase TiO_2 by the washing of H_2O_2 at high temperature. Therefore, if in-situ regeneration were adopted in industry, long time washing by H_2O_2 at high temperature should be used prudently.

The BET surface area and pore volume of sample 4 were both lower than the fresh sample 5 (Table S.2). After regeneration, the pore volume recovered, and the surface area were even larger than the fresh TS-1, due to the leaching of amorphous silica.

3. References

S.1) Y.F. Chen, C.Y. Lee, M.Y. Yeng, H.T. Chiu, J. Cryst. Growth 247 (2003) 363-370.

S.2) W.D. Bai, B. Qu, Z.L. Sun, L.J. Song, X.T. Zhang, Petrochem. Tech. Appl. 28 (2010) 286-288.

S.3) X.W. Liu, X.S. Wang, X.W. Guo, G. Li, H.S. Yan, Catal. Lett. 97 (2004) 223-229.

S.4) M.G. Knözinger, in: G. Ertl, H. Knözinger, J. Weitkamp (Eds.), Handbook of heterogeneous catalysis, Weinheim, 1997, pp. 539-574.

Table S.1 The relative crystallinity of the deactivated, regenerated, and fresh TS-1 extrudates.

Cat.	Relative crystallinity (%)	Cat.	Relative crystallinity (%)
1	99	7	74
2	99	8	72
3	95	9	66
4	92	10	79
5	64	11	75
6	84		

Table S.2 The surface area and pore volume of the deactivated, fresh, and regenerated TS-1.

Cat.	S_{BET} (m^2/g)	Pore volume (cc/g)	$S_{BET,micro}$ (m^2/g)	Pore $volume_{micro}$ (cc/g)
4	338.3	0.276	152.4	0.095
5	375.0	0.346	263.9	0.111
9	393.2	0.340	270.8	0.115
10	405.8	0.346	328.4	0.125
11	412.2	0.352	333.0	0.124

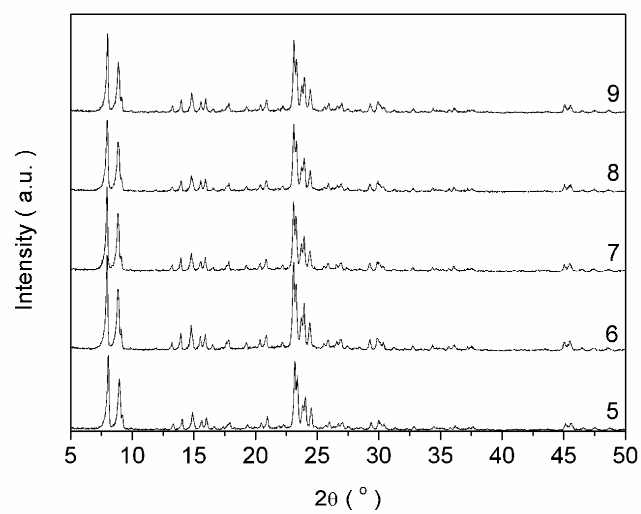

Figure S.1. The XRD patterns of the TS-1 extrudates: (5) the fresh TS-1 extrudates; (6) - (9) the externally regenerated TS-1 extrudates from the bottom to the top of the pilot plant fixed-bed reactor.

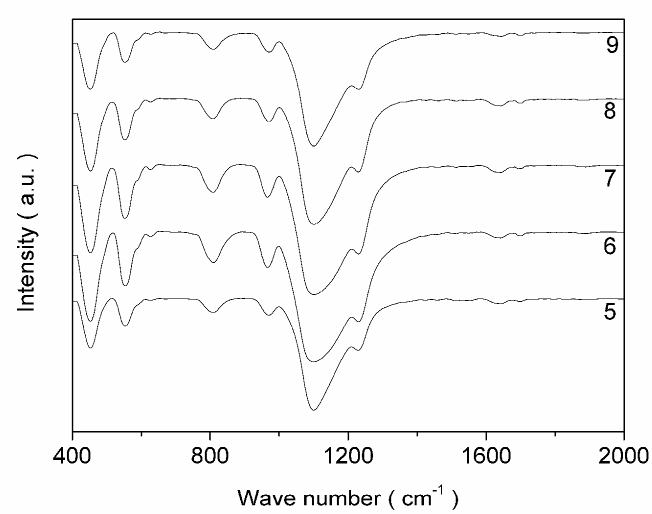

Figure S.2. The FT-IR spectra of the TS-1 extrudates. For sample notation, see Caption to Fig. S.1.

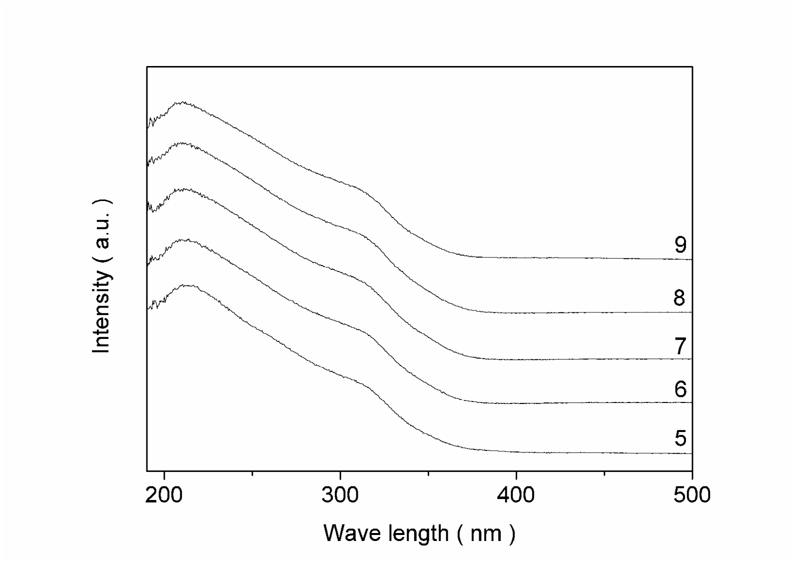

Figure S.3. The UV-Vis spectra of the TS-1 extrudates. For sample notation, see Caption to Fig. S.1.

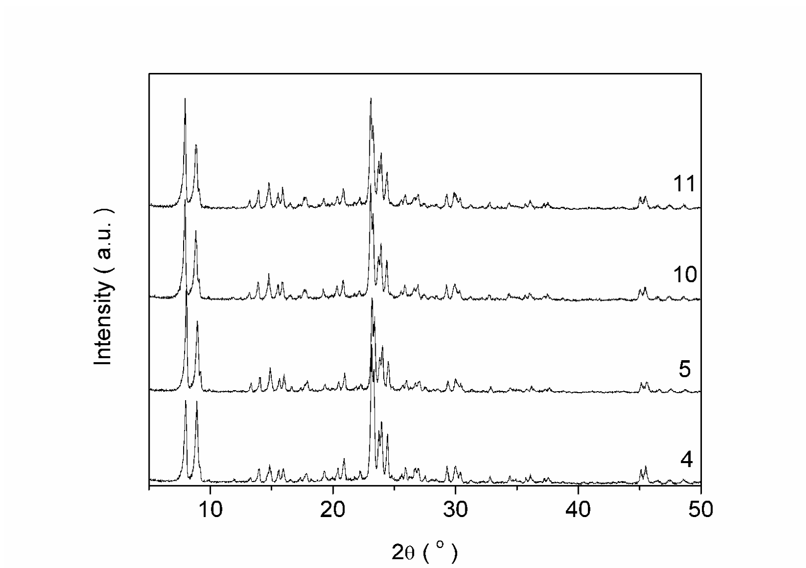

Figure S.4. The XRD patterns of the TS-1 extrudates: (4) the deactivated TS-1 extrudates in the top of the fixed-bed reactor; (5) the fresh TS-1 extrudates; (10) the in-situ regenerated TS-1 by using 5 wt% H_2O_2 at 80 °C for 12 h; (11) the in-situ regenerated TS-1 by using 1.5 wt% H_2O_2 at 80 °C for 24 h.

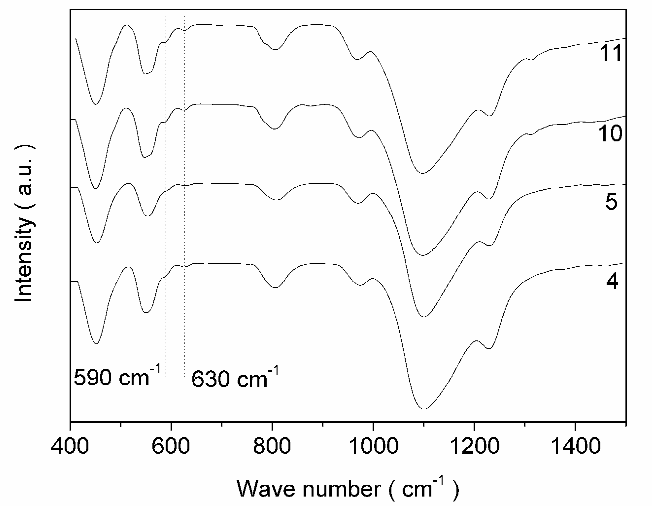

Figure S.5. The FT-IR spectra of the TS-1 extrudates. For sample notation, see Caption to Fig. S.4.

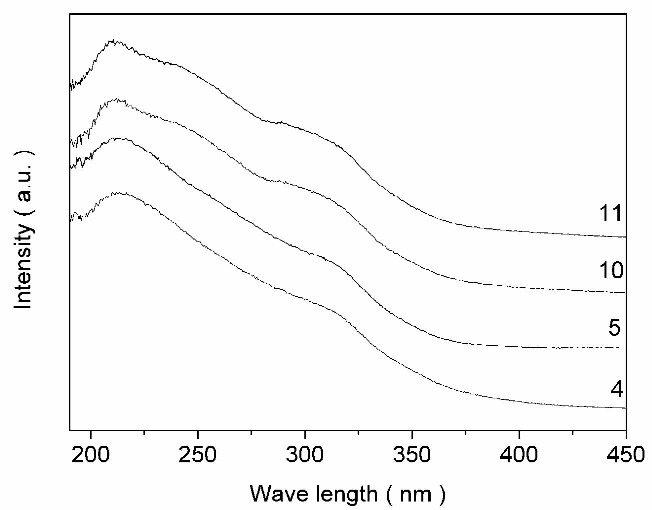

Figure S.6. The UV-Vis spectra of the TS-1 extrudates. For sample notation, see Caption to Fig. S.4.