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Effect of solvent on the propylene epoxidation over TS-1 catalyst

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Abstract

The effect of solvent on the epoxidation of propylene with H_2O_2 over TS-1 has been investigated, and the spent catalysts were characterized by TG analysis and FT-IR spectra. The results show that both the activity and the selectivity of TS-1 decrease with the length of carbon chain of the alcohol solvent; TS-1 exhibits high selectivity with low activity in aprotic solvent; using H_2O as the solvent, both the activity and the selectivity of TS-1 are quite low. The differences in the depositing amount and the depositing species in the spent catalysts show that, the nature of the solvent plays an important role in the propylene epoxidation. The formed by-products mainly depend on the nature of solvent besides the Brönsted acid site of the catalyst.

Keywords: TS-1; Propylene; Epoxidation; Solvent effect

1. Introduction

The synthesis of titanium silicalite (TS-1) was first reported by Taramasso et al. [1] in 1983. Over the last decade, the literature has reflected a high activity and selectivity of H_2O_2 on TS-1 as catalysts for mild oxidation reactions with H_2O_2 used as the oxidant, such as phenol hydroxylation [2], olefins epoxidation [3], cyclohexanone ammoximation [4], alkane oxidation [5], oxidation of ammonia to hydroxylamine [6], secondary amines to dialkylhydroxylamines [7]. The epoxidation of propylene has been investigated in some detail [3] and offers a clean and economically viable alternative to existing processes for propylene oxide (PO). In the reaction, TS-1 catalytic process is advantageous from the environmental point of view as the aqueous hydrogen peroxide, which turn into water, and the reaction, open in liquid phase under mild conditions, show very high selectivity and yields reducing problems and costs of by-product treatment. It is a promising method and will be commercialized in the future.

It has been found that the solvent has an important influence on the catalytic properties of TS-1 for olefins epoxidation [3]. The catalyst exhibits higher catalytic activity, when the molecular of solvent is small enough to get into the pore of TS-1, such as methanol and other protic solvents, which was explained according to the five-membered cyclic structure mechanism [8,9], in which the protic molecule, ROH, coordinates with the Ti centers and stabilizes the Ti-peroxo complex through hydrogen bonding.

In this paper, the influence of the nature of solvents on the catalytic properties of TS-1 in the epoxidation of propylene with diluted H_2O_2 as an oxidant is investigated. For the purpose, we have selected seven solvents having different polarities including five protic molecules: methanol, ethanol, *i*-propanol, *t*-butyl alcohol, and H_2O; two aprotic solvents: acetone, acetonitrile. The solvents were chosen because they form a single phase with the propylene and hydrogen peroxide solution, so mass transfer problems associated to the presence of different phase were avoided. Spent catalysts reacted in different solvents were characterized by TG analysis and FT-IR. The amount and the nature of the deposit species in spent catalysts have been studied.

2. Experimental

2.1. Catalyst preparation

Titanium silicalite was prepared according to the literature [10]. Colloidal silica (30%) and tetra-butyl-orthotitanate (TBOT) were used as silicon and titanium source, respectively. Tetrapropylammonium bromide (TPABr) was used as

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the template. TS-1 samples crystallized from gels with the following molar composition:

SiO_2-$a \times TiO_2$-$b \times n$-butylamine-$c \times$ TPABr-$d \times H_2O$

where $0 < a < 0.03$, $0 < b < 1.0$, $0 < c < 0.1$, $20 < d < 100$. The gel was transferred into the autoclave and crystallized for 2–10 days at 150–190 °C. The solid obtained was filtered, washed with distilled water, dried at 100 °C in static air for 12 h and finally calcined at 540 °C for 5 h. Thus, the powdery TS-1 was obtained.

2.2. Catalyst characterization

FT-IR spectra were recorded on a Nicolet FT-5DX spectrophotometer using KBr wafer technique. TG analysis was performed in a thermogravimetric analyzer (Mettler-Toledo TGA/SDTA851^e) with nitrogen flow rate of 40 ml/min. The temperature was increased from ambient temperature up to 600 °C with a heating rate of 20 °C/min. TPD–MS of the products presented in the spent catalysts was carried out by flowing 20 ml/min of He while the sample was heated at 10 °C/min. Around 15 mg of the sample was loaded in a *U*-shaped quartz reactor connected on line with a quadrupole mass spectrometer (OMNISTARS QMS 200) that allows the analysis of the reactor outlet.

2.3. Catalyst test

Propylene epoxidation tests were performed in a laboratory scale stirred autoclave reactor. The experiment was carried out under the following reaction conditions: reaction temperature 60 °C, propylene pressure 0.4 MPa, reaction time 1.5 h, catalyst 0.4 g, solvent 32 ml, H_2O_2 (30 wt.%) 2 ml. After the reaction, the spent catalysts were recovered by centrifugation and dried at 60 °C by exposure to the ambient air.

The residual H_2O_2 was measured by iodometric titration. The products were analyzed by GC (equipped with a FID detector and PEG-20M capillary). Propylene oxide was the main product. Propylene glycol and its monoalkyl ether (MAE) were the by-products. The result of the reaction was given using these criteria:

$$X_{H_2O_2} = \frac{n^0_{H_2O_2} - n_{H_2O_2}}{n^0_{H_2O_2}} \times 100\% \qquad S_{PO} = \frac{n_{PO}}{n_{PO} + n_{MAE} + n_{PG}} \times 100\%$$

$X_{H_2O_2}$ and S_{PO} stand for the conversion of H_2O_2 and the selectivity to PO, respectively. The n_{PO}, n_{MAE} and n_{PG} stand for the number of moles of PO, MAE and PG, respectively. The $n^0_{H_2O_2}$ and $n_{H_2O_2}$ stand for the initial mole content and the final mole content of H_2O_2, respectively.

Table 1
The catalytic performances of TS-1 in different solvents during propylene epoxidation

Protic solvent	$X_{H_2O_2}$ (%)	S_{PO} (%)	Aprotic solvent	$X_{H_2O_2}$ (%)	S_{PO} (%)
MeOH	96.9	94.6	MeCOMe	71.0	98.1
EtOH	93.2	90.6	MeCN	66.2	100
i-PrOH	85.6	69.2			
t-BuOH	49.8	–			
H_2O	41.7	21.3			

Reaction conditions: temperature 60 °C; propylene pressure 0.4 MPa; time 1.5 h; catalyst 0.4 g; solvent 32 ml; H_2O_2 (30 wt.%) 2 ml.

3. Results and discussion

Table 1 shows the effect of solvent on the reactivity of propylene epoxidation over TS-1. In the case of protic solvents, it can be seen that the activity decreases in the order of MeOH, EtOH, *i*-PrOH, *t*-BuOH as a result of decreasing electrophilicity and increasing steric constraints of five-membered cyclic species. The selectivity to PO decreases with the increasing size of the alcohol, due to the nature of solvents and its diffusion rate out of the pore. Although the donor properties of water are lower than that of alcohol, it may form five-membered cyclic structure (H substitutes R). However, its concentration in TS-1 pore will be quite low because of hydrophobicity of TS-1. Therefore, much lower reactivity of TS-1 is obtained when using water as the solvent. Using aprotic solvents, they cannot form the five-membered cyclic active species with TS-1; the activities of catalyst are similar when MeCOMe and MeCN are used as solvents, which cannot yet be explained.

In order to identify what are the products occluded in the spent catalysts, TS-1 was impregnated with the products (PO and its by-products, MME and PG), and were labeled as PO/TS-1, MME/TS-1 and PG/TS-1, respectively. The obtained catalysts were dried at the boiling point of the impregnating materials in order to remove physisorption of the species.

Fig. 1 shows the DTG curves of the catalysts impregnated with the products. It can be seen from Fig. 1 that

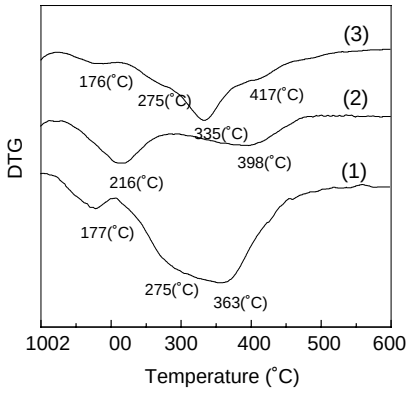

Fig. 1. The DTG curves of TS-1 impregnated with the products: (1) PO/TS-1; (2) MME/TS-1; (3) PG/TS-1.

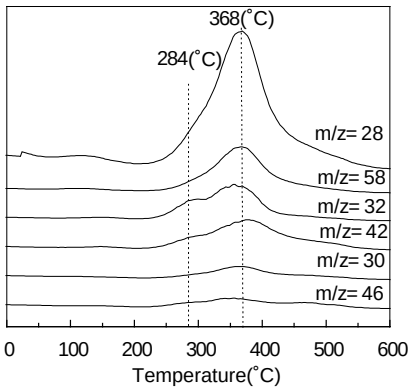

Fig. 2. The TPD–MS curves of PO/TS-1 catalyst.

the main desorption peak of PO/TS-1 is centered at 177, 275 and 363 °C, respectively; the peak of MME/TS-1 is mainly centered at 216 and 398 °C, respectively, and that of PG/TS-1 is centered at 176, 275, 335 and 417 °C, respectively. It can also be seen that similar deposit species are existed in both PO/TS-1 and PG/TS-1 samples. The TPD–MS curves of PO/TS-1 catalyst are shown in Fig. 2. The following *m*/*z* fragments were recorded by quadrupole MS: 28, 30, 32, 42, 46, and 58. The desorbed temperature of these fragments is accord with DTG of PO/TS-1. No fragments were detected around 176 °C. This means that the amount of this species is quite small, whose peak may be attributed to PG. Other peaks may be attributed to the oligomers of PO or PG. Likewise, the peaks centered at 216 and 398 °C in MME/TS-1 may be attributed to the dimmers and oligomers of MME.

TG–DTG curves of the spent catalysts reacted in the propylene epoxidation using different solvents are shown in Fig. 3. It can be seen from Fig. 3 that solvent has a great effect on the distribution of deposits on TS-1. In the case of protic solvent, with the carbon chain of alcohol increasing, the weight loss of the spent catalyst increases significantly in TG curves. When H_2O or aprotic solvents were used in the reaction, the weight loss of the spent catalysts is high. In DTG curves, when alcohol was used as the solvent, the main weight loss appeared at around 135 °C becomes obvious with carbon chain increasing and that centered around 210 °C decreases gradually. Moreover, the peak attributed to the polymers (centered around 330 °C) appears and its intensity is quite strong. When using H_2O as the solvent, the peak is similar to that of PO/TS-1. It is surprised that when using aprotic molecules as the solvents, there is a strong peak centered around 110 °C. Maybe it is due to chemisorption of PO [11].

The main weight loss data of the impregnated catalysts in TG analysis is summarized in Table 2. It can be seen that when TS-1 was impregnated using pure PO, MME or PG, large quantity of the deposits are polymers. It indicates that the products are prone to polymerize over TS-1 without solvent. The steric effect of bulk molecule polymers is quite obvious because the diffusion of polymers out of the pore of TS-1 is difficult without solvent.

Table 3 summarizes the main weight loss of the spent catalysts reacted in different solvents in TG analysis.

It can be seen from Table 3 that when alcohol was used as the solvent, the amount of the deposit which attributed to monoalkyl ethers increases obviously with longer carbon chain, the amount of which makes up half of the total deposits and the amount of polymers (centered around 330 °C) is very low. When using H_2O as the solvent, half of the deposits are attributed to PG. Because TS-1 is hydrophobic, the diffusion of PO is restricted. Thus, most of PO hydrolyzes to form PG and oligomers of PO. With aprotic solvents, the amount of the deposit in the range of 80–220 °C becomes obvious. It indicates that polymerization of PO is evidently weakened in the presence of solvent. With carbon chain increasing, steric effect of alcohol increases, and the diffusion rate of PO from TS-1 pore decreases accordingly. The formation of by-products increases in protic solvent because of the ring opening reaction of PO with the solvent. In the case of aprotic solvent, with PO concentration increasing in the reaction process, the chemisorption amount of PO on TS-1 also increases, as the nature of aprotic solvent and the capacity of polymerization of PO are restricted in the presence of a large amount of solvent.

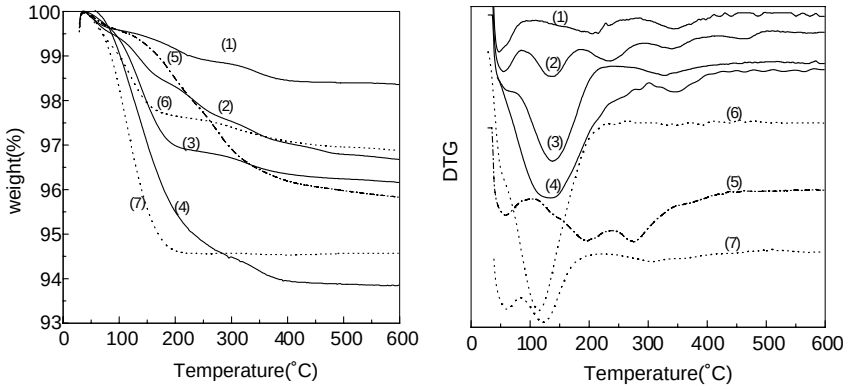

Fig. 3. TG–DTG curves of spent TS-1 after reaction in different solvents: (1) MeOH; (2) EtOH; (3) *i*-PrOH; (4) *t*-BuOH; (5) H_2O; (6) MeCOMe; (7) MeCN.

Table 2
Weight loss in the TG analysis of the impregnated catalysts

Catalyst	Weight loss of spent TS-1 (%)		Total weight loss (%)
PO/TS-1	0.27 (105, 203 (176) °C)	4.66 (203, 500 (275, 363) °C)	4.93
MME/TS-1	1.39 (127, 286 (216) °C)	1.29 (286, 480 (398) °C)	2.68
PG/TS-1	0.47 (121, 212 (176) °C)	3.40 (212, 526 (275, 335, 409) °C)	3.87

Table 3
Weight loss of the spent catalysts reacted in different solvents in TG analysis

Spent catalyst	Weight loss of spent TS-1 (%)			Total (%)
MeOH	0.39 (38, 90 (46) °C)	0.77 (90, 288 (209) °C)	0.43 (288, 462 (347) °C)	1.59
EtOH	0.50 (35, 86 (54) °C)	1.08 (86, 184 (135) °C) 0.89 (184, 300 (236) °C)	0.49 (300, 400 (342) °C)	2.96
i-PrOH	0.34 (30, 80 (54) °C)	3.22 (80, 230 (137) °C)	0.64 (230, 500 (332) °C)	4.20
t-BuOH		5.51 (50, 300 (133) °C)	0.58 (300, 433 (366) °C)	6.09
H_2O	0.44 (30, 103 (58) °C)	1.77 (103, 245 (194) °C) 1.33 (245, 349 (277) °C)	0.40 (349, 453 (400) °C)	3.94
MeCN	0.72 (37, 86 (59) °C)	1.65 (86, 211 (122) °C)	0.67 (211, 500 (309) °C)	3.04
MeCOMe	0.58 (35, 74 (57) °C)	4.84 (74, 226 (114) °C)		5.42

Fig. 4 shows the FT-IR spectra of the impregnated catalysts and the fresh TS-1 zeolite. Fresh TS-1 zeolite presents a band near 960 cm^{-1}, which is commonly assigned in the literature to the stretching vibration of [SiO_4] units linked to Ti atoms, confirming that the Ti atoms are linked to the zeolite framework. Its intensity is correlated with the amount of framework titanium [12]. From Fig. 4 it can be seen that the band near 1637 cm^{-1} assigned to the adsorption of H_2O occurs, which is in consistent with the results of TG analysis. The band near 3430 cm^{-1} is assigned to the vibration of OH group, which is brought about by the deposit in the spent catalysts including small amount H_2O. The intensity of the band near 960 cm^{-1} of the impregnated catalysts becomes weak, in which that of PO/TS-1 is the weakest. Moreover, the position of this band is shifted to higher wave number obviously, which appears at 962.5 cm^{-1} (PO/TS-1), 968.6 cm^{-1} (MME/TS-1) and 965.4 cm^{-1} (PG/TS-1), respectively. Compared with Table 2 it can be concluded that intensity of the bands near 960 and 3400 cm^{-1} of the spent catalysts is resulted from its polymers, and these species adsorbed in TS-1 resulted in the shift of the band near 960 cm^{-1}. There are two shoulders near 2974 cm^{-1} of PO/TS-1 catalyst, which are assigned to $-CH_3$, and $-CH_2$ group. It is proposed that there exists the physisorption of PO, which deeply decreases the intensity of the band near 960 cm^{-1}, but has little effect on its position. It is the reason that there is a little difference in PO/TS-1 and PG/TS-1, though their deposits are similar.

Fig. 5 shows the FT-IR spectra of the spent catalysts reacted in different solvents. It can be seen that the intensity of the band near 960 cm^{-1} of the spent catalysts has an obvious difference, compared with that of fresh TS-1. When using alcohols as solvent, with longer carbon chain the intensity

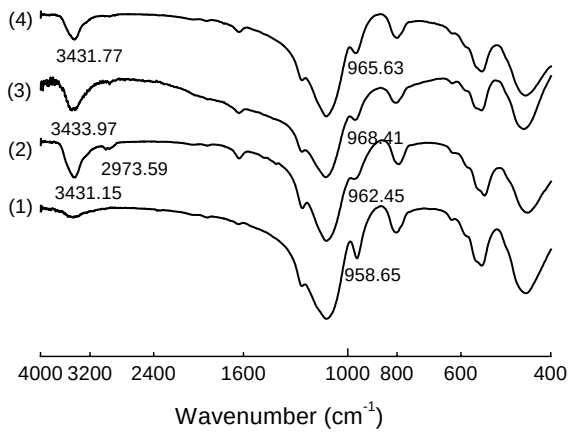

Fig. 4. FT-IR spectra of the impregnated TS-1 catalysts: (1) fresh TS-1; (2) PO/TS-1; (3) MME/TS-1; (4) PG/TS-1.

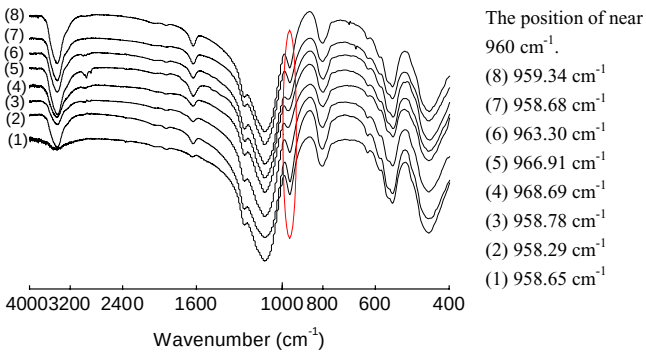

Fig. 5. FT-IR spectra of the spent TS-1 reacted in different protic solvents: (1) fresh TS-1; (2) MeOH; (3) EtOH; (4) *i*-PrOH; (5) *t*-BuOH; (6) H_2O; (7) MeCOMe; (8) MeCN.

of the band decreases obviously, which is in consistent with the results shown in Table 3. Compared with the impregnated catalysts, it can be seen that the effect of solvent on the deposits becomes stronger and stronger with longer carbon chain. Though the polymerization of products is restricted, the amount of the by-products that remained inside the pore of TS-1 zeolite increases because of its steric effect, which affects the intensity and position of the band near 960 cm^{-1}. When H_2O was used as the solvent, the FT-IR spectra of spent catalyst are similar to those of PO/TS-1 and PG/TS-1 catalysts. Using aprotic solvents, the intensity of the band near 960 cm^{-1} has a little decrease and has no shift in the position of this band. It is noteworthy that the band assigned to physisorption of PO at 2973 cm^{-1} does not occur. It further indicates that the deposit (the desorption peak mainly centered at 120 °C) may be the chemisorption of PO.

4. Conclusions

The nature of solvents has an important effect not only on the activity and selectivity of TS-1, but also on the kind and amount of deposited species in the spent catalysts. When alcohol was used as the solvent, the deposited species in the spent catalysts is similar, which mainly include monoalkyl ether of PG and small polymers of PO. While H_2O was used as solvent, there remained PG and oligomers of PO in the spent catalyst. However, when aprotic molecule was used as the solvent, the deposited species in the spent catalyst mainly includes the chemisorption of PO. The different deposits in the spent catalysts have a slight effect on framework titanium. The difference in the amount of deposit is determined by the diffusion effect and nature of the solvent.

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