Gas-phase propylene epoxidation over Ag/TS-1 prepared in W/O microemulsion: effects of the molar ratio of water to surfactant and the reaction temperature

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Ag/TS-1 was prepared by microemulsion method in which dioctyl sulfosuccinate sodium salt (AOT) was used as the surfactant and *n*-heptane as the organic solvent. The synthesized Ag/TS-1 was characterized by UV–Vis and TEM and its catalytic properties in gas-phase propylene epoxidation were carried out in a fixed bed reactor. The results show that Ag is highly dispersed on TS-1 and the crystal size can be adjusted through the adjusting of the molar ratio of water to surfactant ($[H_2O]/[\text{surfactant}] = R$). The catalyst prepared with $R = 4.74$ exhibits the highest catalytic activity for propylene epoxidation in gas-phase, the optimal reaction temperature scope is between 363 and 383 K. Over the catalyst prepared with $R = 4.11$, propylene conversion and the selectivity to propylene oxide (PO) are 1.1% and 91.0%, respectively.

KEY WORDS: Ag/TS-1; microemulsion; *R*-value; propylene; epoxidation.

1. Introduction

Propylene oxide (PO) is one kind of very important chemical feedstock in basic organic chemical industry. Up to now, the commercial scale production of PO is chlorohydrin and Halcon methods. However, the chlorohydrin method generates lots of chlorinated by-products, mainly dichloropropane and $CaCl_2$; and the Halcon method needs great equipments investment. Moreover, the sales fluctuation of the by-product, namely *tert*-butyl alcohol or styrene, greatly affects the economy of PO. Another promising method for PO production is the selective oxidation of propylene with hydrogen peroxide as the oxidant over TS-1 [1,2]. DOW chemical company and BASF are joining forces in this ecologically friendly hydrogen peroxide for propylene oxide (HPPO) technology, and the process "would allow the production of PO without co-products and is expected to significantly lower capital costs, compared to currently practiced technologies"; they are targeting start-up of a world-scale plant as early as 2006 [3].

Recently, propylene epoxidation in gas-phase to PO attracts much interest for its cleanness and low cost. Lu *et al.* [4] found that over NaCl promoted Ag catalyst 12.4% propylene conversion and 31.6% PO selectivity is obtained. Haruta and co-workers [5] reported that when Au particles are in the range of 2–4 nm, Au/Ti-MCM-41 exhibits high catalytic properties, and 3.2% propylene conversion with more than 90% PO selectivity is obtained at 373 K. Jenzer *et al.* [6] used Pd-Pt/TS-1 as catalyst to *in situ* generate hydrogen peroxide and 99% PO selectivity at 3.5% propylene conversion is obtained at the beginning of the reaction. Wang *et al.* [7] reported that Ag/TS-1 exhibits high selectivity to PO in the gas-phase propylene epoxidation, 0.92% propylene conversion with 91.2% selectivity to PO can be obtained at 423 K.

The catalyst preparation method has great effect on the catalytic performance in the gas-phase epoxidation of propylene. Haruta *et al.* [8] once investigated the preparation of Au/TiO_2 catalyst by methods of impregnation (IMP), chemical vapor deposition (CVD), deposition–precipitation (DP) and sol–gel. He found that only DP was the most ideal method. Oliveira *et al.* [9] also tested the performance of Ag/TiO_2 prepared by IMP, CVD, DP and sol–gel, and also found that the catalyst prepared by DP exhibited high catalytic activity for propylene epoxidation. However, there is no report on propylene epoxidation over the catalyst prepared by microemulsion method.

The particle size of metal catalyst plays an important role in chemical reaction. For most of reactions, only when the size was in an appropriate scope can the catalyst exhibit the highest activity. The application of W/O microemulsion in the preparation of metal catalysts is very attractive for its special capability to partially control the particle size through the adjusting

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of the molar ratio of water to surfactant, which was noted as R in literature, and other factors [10–15]. The W/O microemulsion contains spherical reversed micelles (or water droplets) surrounded by surfactant molecules on the surface, which, like microreactors, provide an excellent environment for the growth of nano-particles and eventually limit the size of particles to some extent. That is the reason why this method attracts much interest in the field of nanoparticles preparation. In this experiment, AOT (dioctyl sulfosuccinate sodium salt, Acros) is used as surfactant, which can be easily solved in *n*-heptane and form W/O microemulsion at high water concentration. For example, in *n*-heptane, a 0.1 mol dm^{-3} solution of AOT can solubilize up to 10% water [16]. In this paper, we prepared a series of Ag/TS-1 with various R values and investigated their performance in gas-phase propylene epoxidation. The optimal temperature scope of the reaction over the catalyst was also investigated.

2. Experimental

2.1. Catalyst preparation

TS-1 was prepared according to the literature and the molar ratio of Si to Ti is 64 [17]. The Ag was supported on TS-1 by mixing microemulsion A, B and TS-1. In a typical experiment, the catalyst with $R = 4.74$ was prepared as the following: First of all, two identical AOT solutions were prepared by adding 2.6 g AOT to 10 mL *n*-heptane. After the complete dissolution of AOT, 0.5 mL $AgNO_3$ aqueous solutions (0.3 mol dm^{-3}) was added to one of the AOT solutions to form microemulsion A, and 0.5 mL K_2CO_3 aqueous solution (0.15 mol dm^{-3}) was added to another AOT solution to form microemulsion B. After that, the microemulsion A was slowly dropped into the mixture of microemulsion B and 0.81 g TS-1 with continuous moderate stirring. After the mixing of the two microemulsion, the mud-like catalyst precursor was separated in a centrifuge and washed by 40 mL ethanol, dried at 90 °C for 3 h. Finally, the precursor was heated to 450 °C with a heating rate of 1 °C per minute and maintained at 450 °C for 5 h and then cooled to room temperature for use. The R value was calculated by the following equation:

$$R = \frac{\text{mole of water added in microemulsion system}}{\text{mole of AOD added in microemulsion system}}$$

Catalysts with different R-value were acquired by adjusting the amount of AOT added in microemulsion system while maintaining the volume of $AgNO_3$ (0.3 mol dm^{-3}) and K_2CO_3 (0.15 mol dm^{-3}) aqueous solution added in microemulsion and AOT concentration in *n*-heptane. In our experiment, to ensure 2% Ag loaded on TS-1, the volume of $AgNO_3$ (0.3 mol dm^{-3}) and K_2CO_3 (0.15 mol dm^{-3}) aqueous solution were kept at 0.5 mL, and the concentration of AOT in *n*-heptane is 0.51 mol dm^{-3}.

2.2. Catalyst Characterization

TEM images were acquired on a TECNAI $G^2$20 transmission electron microscope with acceleration voltage of 200 kV. UV–Vis spectra were obtained on Jasco V-550 spectrophotometer.

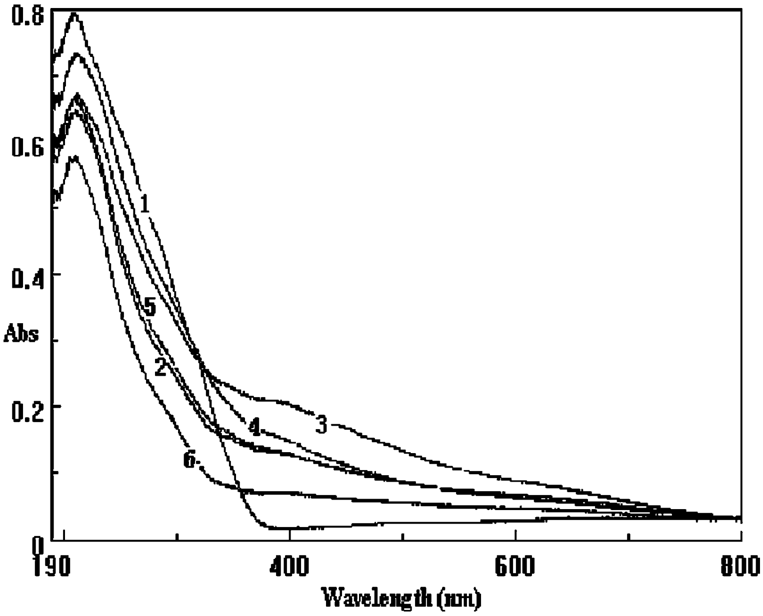

Figure 1. UV–Vis spectra of catalysts with different R. TS-1 without Ag loading (1); Ag/TS-1 of $R = 4.53$ (2); $R = 4.11$ (3); $R = 4.74$ (4); $R = 4.94$ (5) and $R = 6.17$ (6), respectively.

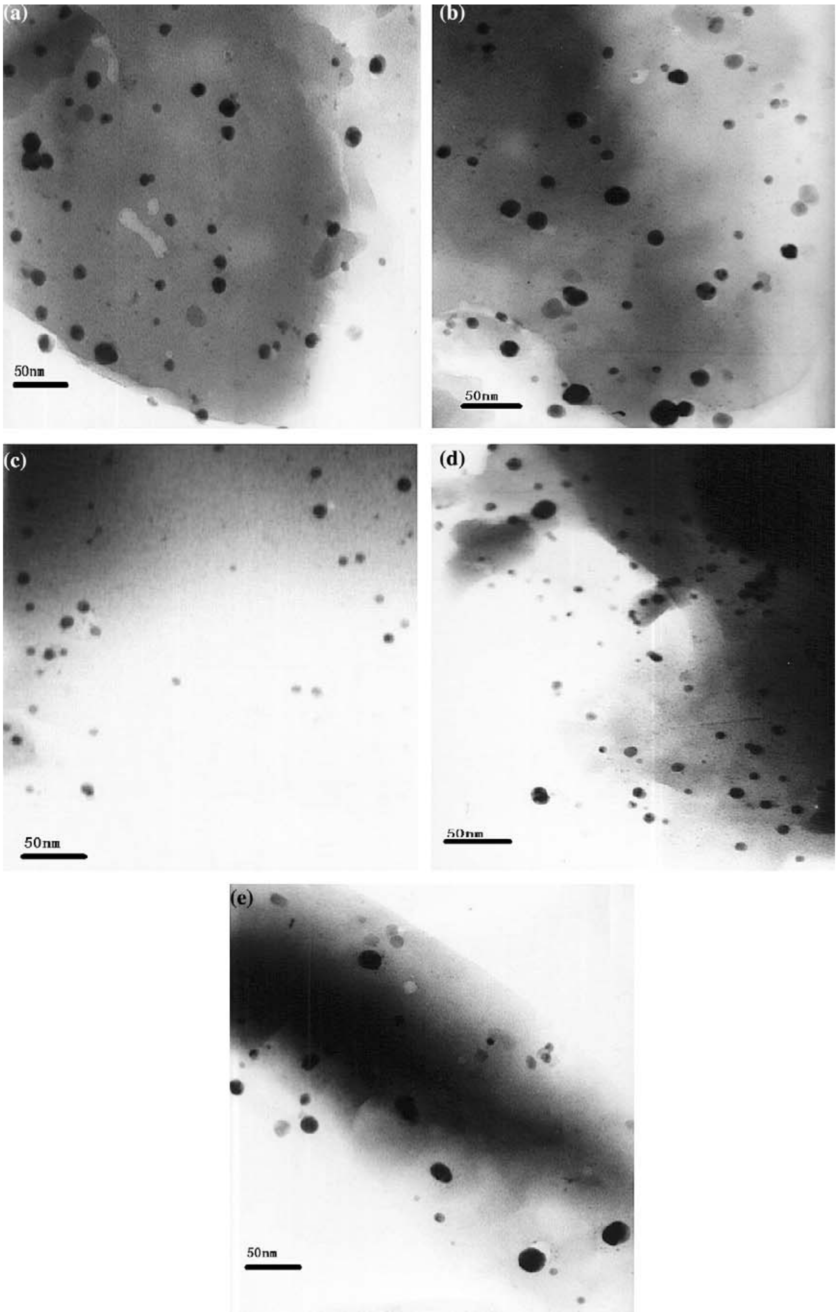

Figure 2. TEM images of catalysts with different R: $R = 3.53$ (a); 4.11 (b); 4.74 (c); 4.94 (d); 6.17 (e) respectively.

2.3. Catalytic tests

Gas-phase propylene epoxidation was carried out in a fixed bed, quartz down-flow reactor of 8 mm inner diameter. About 0.6 g Ag/TS-1 (20–40 mesh) was placed between quartz beads. The typical reaction conditions were as follows: 373 K, $V_{O_2} : V_{C_3H_6} : V_{H_2} : V_{N_2} = 1 : 0.57 : 1.5 : 7.7$, space velocity 4000 h^{-1}. Analysis of the products was carried out by GC–MS (HP6890 GC/5973MSD) and GC (GC 7890F equipped with an FID with 50 m × 0.25 mm × 0.4 μm PEG20M capillary column and SRI 8610C equipped with a TCD with 2.5 m × 3 mm GDX-101 packed column). The activity of the catalyst was calculated on the basis of carbon balance [18].

3. Results and discussion

3.1. Effect of R-value

During the preparation process of catalyst by microemulsion method, the molar ratio of water to surfactant (R) is an important factor to control the crystal size of metal particles. Hence, the effect of R is first investigated.

3.1.1. Characterization of catalysts with different R

Figure 1 is the UV–Vis spectra of the catalysts with different R, respectively. It can be seen that there is an absorption signal shoulder between 380 and 420 nm, which was assigned to metallic Ag [19, 20].

Typical TEM images of catalysts with different R were shown in figure 2. It can be seen that the variation of R values can really result in different Ag particle size. Of all the samples, the crystal of $R = 4.74$ has the smallest particles and more uniform shape. While, in other samples, more or less, some irregularly bigger particles coexist with the small ones, especially in the case of $R = 6.17$.

Average particles size (figure 3) of the catalysts was acquired by statistics from images taken at random. As can be seen from the figure, the catalyst of $R = 4.74$ has the smallest particles. The catalysts of R lower or higher than 4.74 all lead to larger particles.

Theoretically, the decrease of R will lead to smaller water droplets [16,21]. The particle size, which much depends on the size of reversed micelles, will decrease accordingly. However, in our experiment, when R is lower than 4.74, the average particle size does not seem to decrease any more with the decrease of R. In other words, the average silver particle of 7.6 nm is the smallest particle that can be acquired in this way.

Figure 4 are the size distribution of the catalysts of different R values, $R = 3.53$, $R = 4.11$, $R = 4.74$, $R = 4.94$ and $R = 6.17$, respectively. The increase of R leads to the widening of size distribution of Ag particles. The possible reason is: the interface of micells turns incompact with the increase of R, and so the happening of interface penetration between different micelles become more easily. Accordingly, the reaction of the reagents contained in micelles quickens, which leads to the widening of size distribution [22].

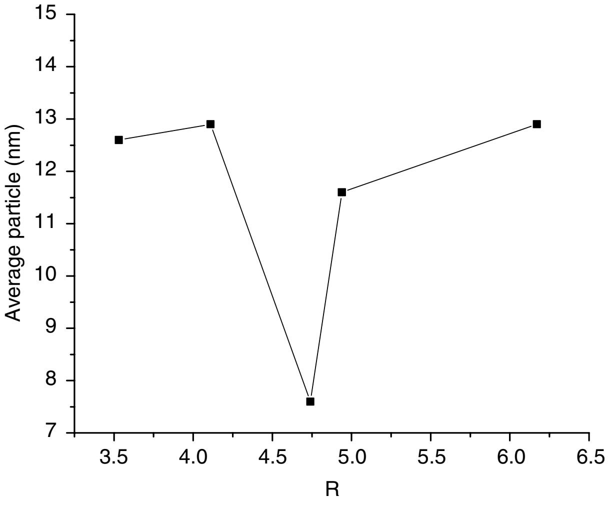

Figure 3. Relationship between average particle size and R.

3.1.2. Effect of R on propylene conversion and PO selectivity

The effect of different R or different Ag particle size on the conversion of propylene and PO selectivity at 373 K is shown in figure 5. It can be seen that the catalyst of $R = 4.74$ exhibited the highest activity of about 1.3% propylene conversion at 30 min during the reaction; however, its selectivity to PO is the lowest among the five catalysts and could reach 80% at the end of the reaction. And the catalyst of $R = 3.53$ and 6.17 showed the lowest activity. Combined with the TEM images in figure 3, it can be postulated that the catalyst with smaller Ag particles shows higher activity and lower selectivity to PO. The catalyst with larger Ag particles is less active for propylene conversion because of less active site exposed at the particle surface and gives higher selectivity to PO. Only the catalyst with appropriate particle size can exhibit both high conversion and high selectivity to PO.

3.2. Investigation of the optimal reaction temperature

To investigate the optimal reaction temperature of propylene epoxidation over the catalyst prepared by microemulsion method, the epoxidation of propylene was carried out at different temperatures of 323, 343, 363, 383, 403 and 443 K. The catalyst was prepared with $R = 4.74$ and the results of 30 min are shown in table 1. It can be seen that the conversion of propylene increases with the increase in the reaction temperature, especially when the temperature is above 383 K, the conversion of propylene sharply increased to about 10% at the beginning of the reaction. It is due to the emergence of lots of CO_2. Greenen et al. [23] had reported that the active energy of propylene complete oxidation to CO_2 is lower than that of propylene selective oxidation to PO over Ag catalyst. The increase of reaction temperature does not favor the formation of PO. Moreover, the heat produced locally from propylene deep oxidation to CO_2 at high temperature also further accelerates the formation of CO_2 and other by-products. It can be seen from table 1 that the propylene conversion 1.1% and the selectivity to PO is 91.0% when the reaction is carried out at 363 K. Haruta and co-workers [24] once reported that the optimal reaction temperature is 323 K over Au/TS-1 prepared by DP. While Wang et al. [25] reported that the optimal reaction temperature is 423 K over Ag/TS-1 by DP. While the optimal reaction temperature is 363 K over Ag/TS-1 prepared by microemulsion method, the optimal reaction temperature decreases about 60 K. The reason is still in study.

4. Conclusion

The catalyst prepared in microemulsion with $R = 4.74$ exhibited the highest activity in the gas-phase

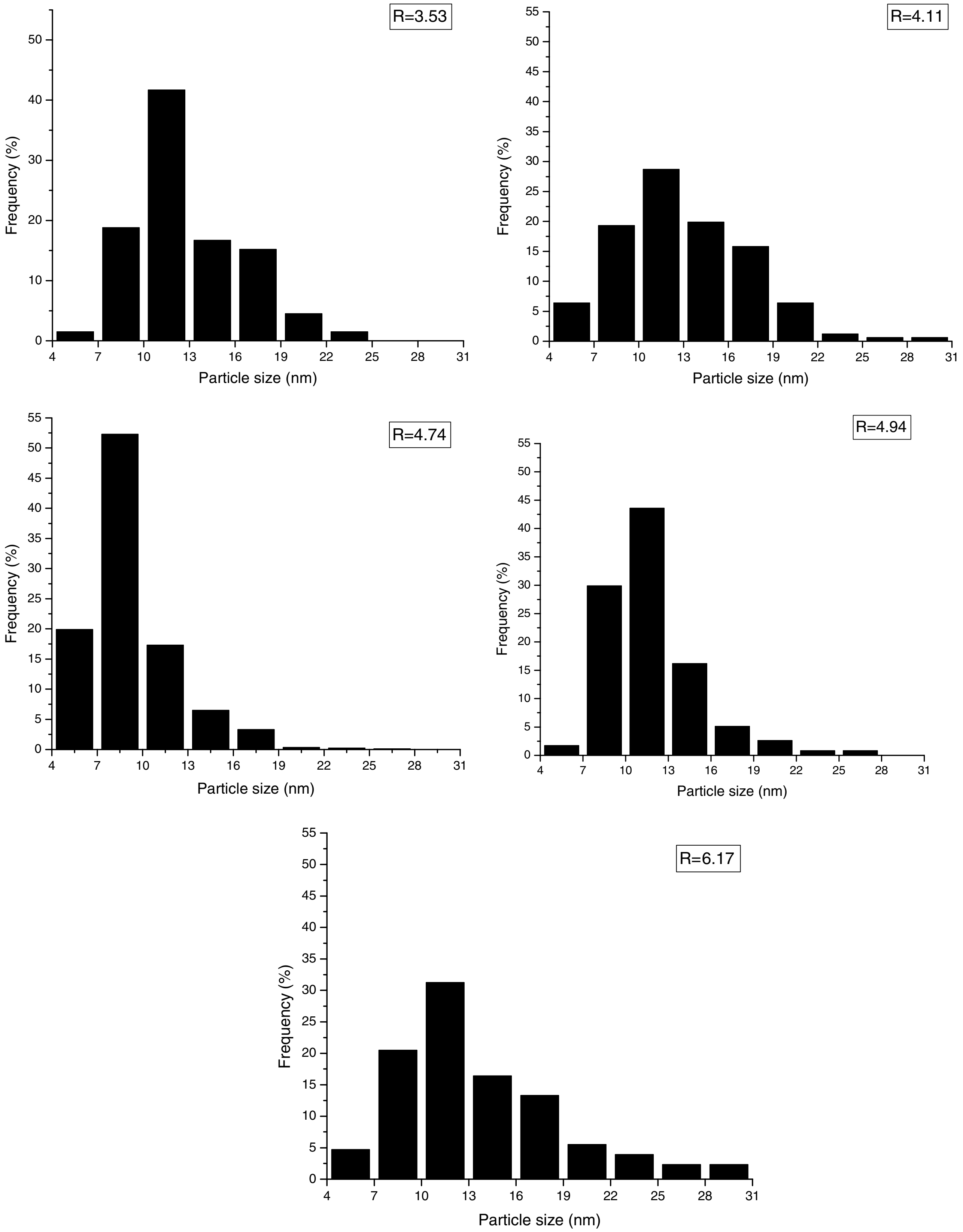

Figure 4. Effects of *R* on the particle size distribution.

propylene oxidation. The Ag particle of about 8 nm in size supported on TS-1 is thought to be the optimal size. The optimal temperature scope is between 363 and 383 K. 91.0% selectivity to PO and 1.1% propylene conversion were obtained over Ag/TS-1 prepared in microemulsion when the reaction temperature is 363 K.

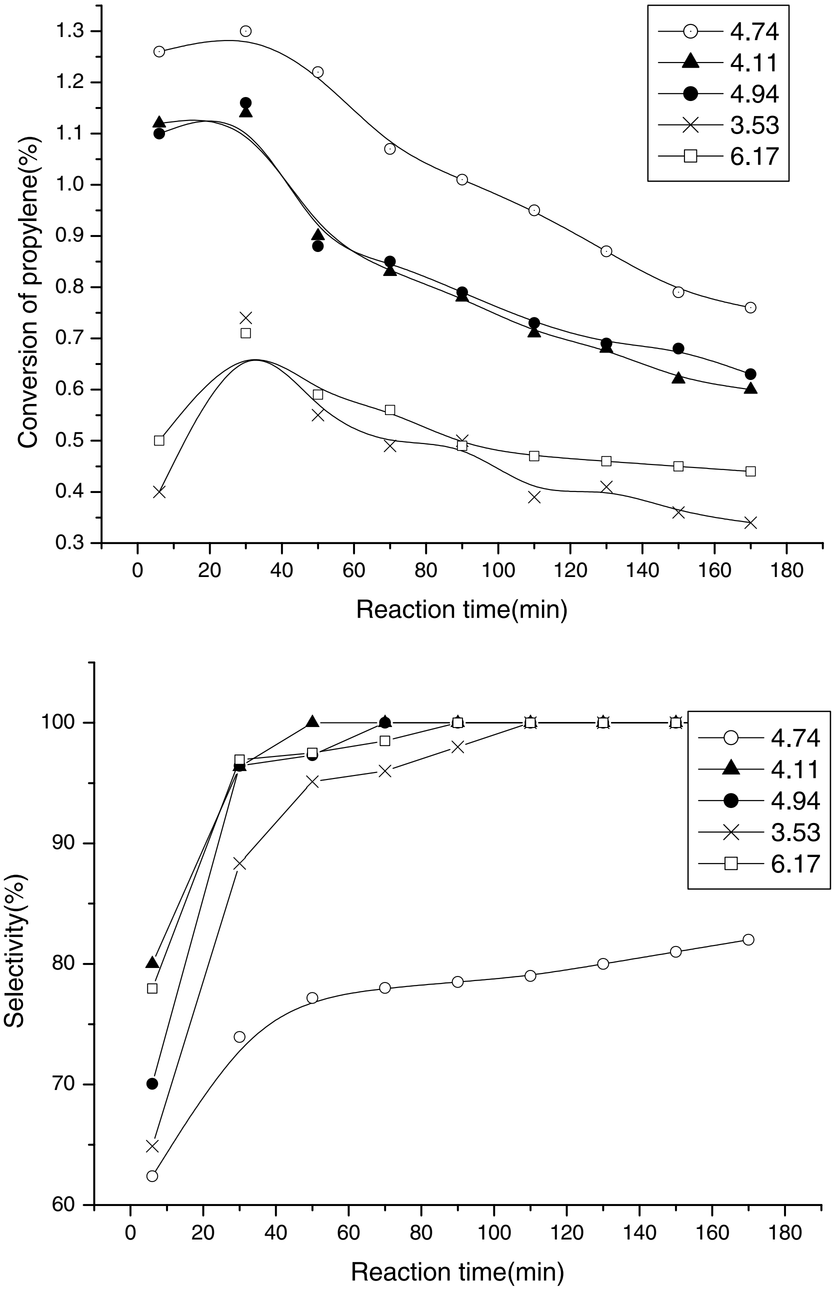

Figure 5. Effect of *R* on propylene conversion and PO selectivity.

Table 1
Effect of reaction temperature on propylene epoxidation

T (K)	Propylene conversion (%)	Selectivity for products (%)					
		CO_2	PO	Acetone	Acrolein	Acetaldehyde	Propionaldehyde
323	0.02	0.00	100	0.00	0.00	0.00	0.00
343	0.12	0.00	100	0.00	0.00	0.00	0.00
363	1.1	3.52	91.0	0.00	0.00	5.58	0.00
383	1.16	9.15	84.3	0.00	0.00	5.51	1.04
403	9.78	84.7	0.15	1.24	5.71	3.40	4.70
443	9.55	89.2	0.00	1.08	3.62	1.35	4.75

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