Partial oxidation of ethylene to ethylene oxide
over Ag/α-Al₂O₃ catalysts prepared water–alcohol method

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Abstract

Partial oxidation of ethylene to ethylene oxide was studied over Ag/α-Al₂O₃ catalysts. To elucidate the effect of particle size on selectivity, the Ag/α-Al₂O₃ catalysts were prepared by water–alcohol methods and then calcined by changing calcination temperature, time and atmospheric conditions. BET surface areas of catalysts before and after the reaction were characterized by N₂ physisorption and the particle size of Ag was measured by TEM and XRD analysis. It was found that the Ag/α-Al₂O₃ catalyst calcined at 673 K for 2 h in air atmosphere showed higher activity than the other catalysts. It was also found that the Ag/α-Al₂O₃ catalysts with Ag particle of about 30 nm were more stable and better active than the other catalysts.

Introduction

Ethylene oxide is a very important raw material in the chemical process, especially, in the manufacturing process of ethylene glycol, acrylonitrile and nonionic surfactants. It has been reported that the ethylene oxide is commercially synthesized over Ag–catalysts[1]. Generally, the selectivity of ethylene oxide has been reported to be related to the surface area of active silver species[1–4]. Reviews for active oxygen species, promoter effects and reaction mechanism on the silver catalysts have
frequently been reported[1-6]. But the relationship between characteristics of catalysts and selectivity of ethylene oxide has not been reported in detailed. In this work, to elucidate the effect of particle size and the calcinations effects, Ag/a-Al₂O₃ catalysts were prepared by water-alcohol methods and then calcined by changing calcination temperature, time and conditions, and characterized by N₂ physisorption, TEM and XRD analysis.

Experimental

The catalytic performance for partial oxidation of ethylene over Ag/a-Al₂O₃ catalysts was investigated in a fixed bed reactor system.

The Ag/a-Al₂O₃ catalysts were prepared by water-alcohol methods. A solution of potassium oxalate monohydrate((COOK)₂·H₂O) was added to a solution of AgNO₃ and then it was stirred with rotary evaporation. The prepared materials were calcined by changing calcinations temperature, time and atmospheric conditions to produce Ag/a-Al₂O₃ catalysts with different Ag particle size.

X-ray diffraction patterns were used to obtain information on the structure of prepared catalysts and the particle size of silver species. The size of Ag particle was also checked by transmission electron micrograph (TEM) using JEM-2000FXII, and the specific surface area was measured by N₂ physisorption.

Results and discussion

To identify Ag peak (2θ=38.2) in XRD analysis, Ag/Al₂O₃ catalysts with different calcination temperatures of 150, 250, 280, 320 and 350 ºC were prepared. It was found that the Ag peak was detected over catalysts calcined over 280 ºC. This result means that the calcinations temperature of the Ag/Al₂O₃ catalyst is reasonable over 280 ºC, at least, to measure the particle size of catalyst by XRD analysis. The particle sizes of Ag at 280, 320 and 380 ºC were 33.4, 30.8, 32.9 nm, respectively.

Figure 1 shows the effect of calcinations temperature on the conversion of ethylene over Ag/Al₂O₃ catalysts. It was found that the conversion of ethylene in partial oxidation of ethylene is dependent on the calcination temperature and reaction temperature. It was also found that the Ag/Al₂O₃ catalyst calcined at 400 ºC showed higher conversion than the other catalysts. The yield of ethylene oxide over catalyst B calcined 400 ºC was obtained about 5.31%, while the yields over catalyst A and catalyst C was 4.63% and 4.15%, respectively.

Figure 2 shows that the effect of calcinations time on the conversion of ethylene over Ag/Al₂O₃ catalysts. The catalyst calcined for 2 h showed higher conversion than
5 h or 10 h, which were obtained 13.6%, 11.7-11.8% at 330 °C (reaction temperature) respectively. It was found that the catalytic activity decreased with increasing calcinations time.

Figure 3 shows the effect of atmospheric gas in calcination on conversion of ethylene oxide over Ag/α-Al₂O₃ catalyst. The catalyst calcined in the air atmosphere showed higher conversion than the other. Figure 4 shows the effect of atmospheric gas in calcination on particle size with calcination temperature. This results might be interpreted that the activity of Ag/α-Al₂O₃ catalyst in the partial oxidation of ethylene was correlated with the morphology and Ag particle size of the catalyst calcined in air atmosphere. More detailed research on the characterization of morphology of catalyst are needed in the future.

Reference

1. Yukio Sakai, *Catalysis Surveys from Japan*, 1, 247 (1997)

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Table 1. Ag/α-Al₂O₃ catalysts.
Fig. 1. Effect of calcination temperature on conversion of ethylene over \( \text{Ag/} \alpha-\text{Al}_2\text{O}_3 \) catalyst.

Fig. 2. Effect of the calcination time on conversion of ethylene over \( \text{Ag/} \alpha-\text{Al}_2\text{O}_3 \) catalyst.

Fig. 3. Effect of atmospheric gas in calcinations on conversion of ethylene over \( \text{Ag/} \alpha-\text{Al}_2\text{O}_3 \) catalyst.

Fig. 4. Effect of atmospheric gas in calcination on particle size with calcination temperature.