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Catalysis Today 87 (2003) 153–162

CATALYSIS TODAY

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Partial oxidation of ethylene to ethylene oxide over nanosized Ag/α-Al_2O_3 catalysts

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Abstract

Ethylene oxide is an important raw material in manufacturing processes of ethylene glycol, acrylonitrile and nonionic surfactants, etc. In general, commercial scaled ethylene oxide is synthesized over Ag catalysts.

In this work, a series of α-Al_2O_3 supported Ag catalysts were prepared by several methods, i.e., precipitation, modified precipitation, water–alcohol, and micro emulsion methods. Particle sizes of the supported Ag were analyzed by TEM and XRD, and the TPD/TPR profiles were compared to investigate the state of adsorbed oxygen in view of the elucidation of the active oxygen species.

The Ag particles of about 30 nm showed enhanced stability and higher activity than the particles less than 15 nm. The activities for the ethylene oxide of the catalysts prepared by water–alcohol method were higher than those of the catalysts prepared by micro emulsion method. It seems due to the larger particle sizes as well as the easier desorption of molecular oxygen from the catalysts. An unique TPD/TPR peak of the molecular oxygen was observed at about 400 °C in the catalysts prepared by water–alcohol method. However, the desorption peaks of the molecular and the atomic oxygens were observed at about 400 and 650 °C, respectively, in the micro emulsion prepared catalysts.

Keywords: Oxidation of ethylene; Nanosized silver catalysts; Preparation method; TPD/TPR

1. Introduction

Ethylene oxide from the partial oxidation of ethylene is an important intermediate material for the manufacturing of many useful petrochemicals, such as anti-freezer, detergents, surfactants, solvents, lubricants, plasticizers, and ethylene glycol as a raw material for synthetic fibers and explosives, etc. Commercial production of ethylene oxide is known to be a gas phase reaction of ethylene over Ag catalysts [1]. Since the first patent on the ethylene oxide manufacturing with Ag catalyst by Lefort in 1931 [2], many studies have been done to improve the catalytic activities. Goncharova [3] and Campbell [4] reported that small amount addition of promoters like Cl increased the ethylene oxide selectivity. Twigg [5] reported the reaction mechanism of the ethylene oxide. Harriott studied the distribution of the Ag supported on

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doi:10.1016/j.cattod.2003.09.012

alumina [6] and reported that the silver particles of 30–70 Å on alumina or silica showed higher activities in ethylene oxide production [7]. Many other works have been carried out to investigate the effects of the particle sizes and shapes, the surface structures, and the support types on the catalytic activities [8–11]. Sajkowski and Boudart [12], and Campbell [13] studied the effect of the silver particle sizes. They explained the enhanced yield as the result of the mobility of the small silver particles on the catalyst surface, due to the metal–support interaction. Ruckenstein and Lee [14] studied the mobilities of the silver particles as well as the shape effect of the silver clusters on the catalytic activities in mild reaction conditions. They observed changes in the size distribution according to the calcination conditions and reported that the size of the silver particles affected the rate of the reaction.

The special selectivity of the silver catalyst in the partial oxidation of ethylene has been ascribed to its adsorption characteristics for the oxygen. Three types of oxygens, i.e., the molecular, the atomic, and the lattice oxygens, are generally accepted, although the adsorbed states have been reported differently depending on the experimental conditions, such as the types of catalyst and/or support, surface structure, adsorption temperature and pressure, etc. The active oxygen species have been regarded as participating in the ethylene oxide formation step via either one of the two procedures. One is the molecular mechanism, in which the ethylene oxide is believed to be formed by molecularly adsorbed oxygen. The other is the atomic mechanism, where the ethylene oxide is explained to be formed by atomically adsorbed oxygen. Which one is the case, however, is not fully elucidated yet. The desorption temperatures of the molecular, the atomic, and the lattice oxygens have been reported as 150–470, 550–650, and above 750 °C, respectively [15–17]. On the other hand, the molecular, the atomic, and the lattice oxygens were reported to be reduced in TPR at 410, 500, and 870 °C, respectively [18].

In this study, the effect of the particle size on the catalytic activities depending on the preparation method were considered and the TPD/TPR results were compared with the catalytic activities in view of the role of the adsorbed oxygen species.

2. Experimental

2.1. Preparation of the catalysts

The surface area of the α-Al_2O_3 (Saint Gobain Co. USA) used as a supporting material in this work was 0.75 m^2/g. It was crushed into 18–35 mesh size and dried at 120 °C for 1 h before using. The silver precursor used in the preparation of the catalysts was silver nitrate (99.8% pure, Next Chem. S. Africa) and the surfactant was AOT (95%, Poole, BH15 1TD, UK), which was able to form the micro emulsion in the wide range of its concentration without using other surfactants. Ethyl alcohol (99.5% pure, Dae-Jung Chem. Co., Korea) and *n*-heptane (98% pure, Yakuri Pure Chem., Japan) were used as solvents. The preparation procedures were as follows.

2.1.1. Precipitation method (catalyst A)

The solution of potassium oxalate monohydrate ($(COOK)_2\cdot H_2O$) as a precipitator was slowly added and agitated to the solution of silver nitrate. Powder type silver oxalate was obtained after mixing, filtering, and drying procedures. This powder was dissolved into ethanol amine, then α-Al_2O_3 was added and mixed into the solution. After drying the slurry, catalyst A was obtained by calcining it at 300 °C for 2 h.

2.1.2. Modified precipitation method (catalyst B)

Ammonium hydroxide solution and ethanol as precipitators were added and agitated to the silver nitrate solution to obtain silver hydroxide. Other procedures were the same as those in the precipitation of the catalyst A.

2.1.3. Water–alcohol method (catalyst C)

The accurate amount of silver nitrate was thoroughly dissolved in the mixture of distilled water and alcohol for 1 h. Then α-Al_2O_3 was added and this solution was rotary evaporated at constant temperature of 80 °C. The resulting slurry was dried at 100 °C for 12 h, then was calcined at 300 °C for 2 h under air condition.

2.1.4. Micro emulsion method (catalyst D)

The accurate amount of silver nitrate dissolved in distilled water was emulsified by the surfactant

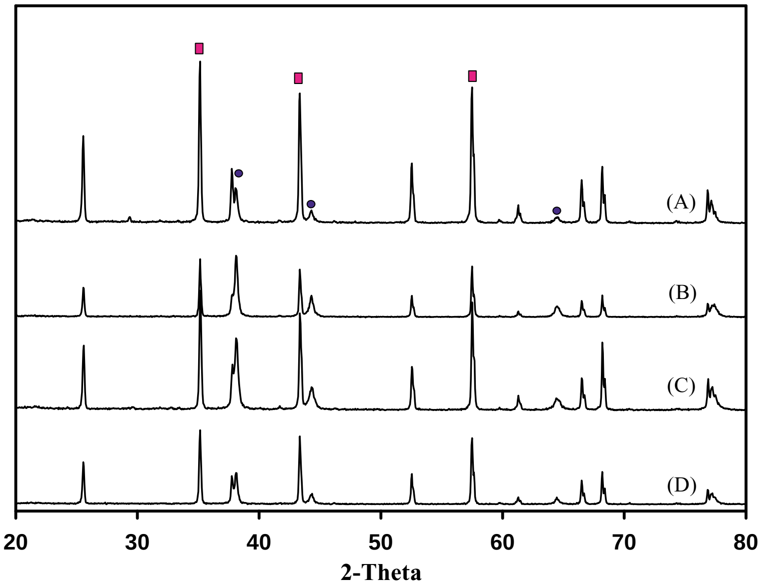

Fig. 1. XRD patterns of Ag/α-Al_2O_3 catalysts (Al_2O_3, ■: g, ●). (A) precipitation method (cat. A); (B) modified precipitation method (cat. B); (C) water–alcohol method (cat. C); (D) micro emulsion method (cat. D).

dissolved in *n*-heptane. α-Al_2O_3 was added and mixed to this emulsified solution, which was maintained at the constant pH 9 by ammonium hydroxide. The liquid was slowly evaporated to prepare the supported silver catalyst. Repeated washing by acetone was taken to remove the surfactants which might remain in the catalyst. It was then dried at 100 °C for 12 h and calcined at 300 °C for 2 h under air condition.

2.2. Characterization of the catalysts and the reaction experiments

The amount of the supported silver was measured by a wet titration method in which the dissolved silver in nitric acid was titrated by ammonium thiocyanate solution with the ferric sulfate indicator. Powdered XRD technique (MAC Science Co., Model M18XHF) was used to determine the particle sizes of the supported silver clusters depending on the preparation method. Particle sizes were determined from the width of the XRD peaks by the Debye–Scherrer equation. They were confirmed by the transmission electron microscope (TEM, JEOL, JEN-2000FXII) with LaB6 filament under 220 kV acceleration voltage condition.

The XRD patterns and the characteristics of the catalysts prepared in this work are found in Fig. 1 and Table 1, respectively.

Pulse ChemiSorb 2705 Micromerities (USA) was used to measure the TPD profiles of oxygen (O_2-TPD) and the TPR profiles of hydrogen (H_2-TPR).

The reaction was carried out in a fixed bed flow reactor under atmospheric pressure. The reactants

Table 1
Characteristics of the Ag/α-Al_2O_3 catalysts used in this work

Catalysts	Preparation method	Loading amount of silver (wt.%)	Particle size (nm)	Reaction temperature (°C)	Yield (%)
A	Precipitation	7.5	15.4	280	1.93
B	Modified precipitation	8.6	29.0	250	3.98
C	Water–alcohol	8.6	29.3	335	4.65
D	Micro emulsion	7.6	15.4	381	1.48

and products were analyzed by a gas chromatography (GC-8A, Schimadzu Co., Japan). The reaction temperature was between 180 and 350 °C, the molar ratio of the reactants was $C_2H_4:O_2 = 27:7$ and *W/F* was 422.6 g cat. min/mol.

3. Results and discussion

3.1. Reaction activities depending on the preparation methods

The conversion of ethylene and the selectivity of ethylene oxide according to the preparation methods were shown in Figs. 2 and 3, respectively. The yields and the particle sizes are listed in Table 1.

In Fig. 2, the catalyst A and the catalyst B seem to show similar trends, in that the equilibrium conversion was obtained at 240–270 °C. For the case of the catalyst C prepared by alcohol emulsifier, the conversion was increased rapidly at about 250 °C to reach equilibrium conversion at about 350 °C. For catalyst D which was prepared by micro emulsion method, the conversion was remained negligible until 310 °C, then started to increase to reach about 4% at 350 °C. In Fig. 3, the selectivity of ethylene oxide was slowly decreased with conversion for catalysts A, B and C. For the catalyst D, however, the selectivity of ethylene oxide was rapidly decreased as the low conversion.

3.2. Size of the silver particles and the reaction activity

Fig. 4 shows the TEM photographs of the catalyst C and D which were used to measure the particle sizes of the supported silver. The sizes obtained from TEM analysis were in good agreement with those obtained from the equation based on XRD. As can be seen in Table 1, the average size of the silver particles for both the catalysts A and D were 15.4 nm. While those of the catalysts B and C were 29.0 and 29.4 nm, respectively. The yields for the larger particle catalysts were more than twice of those for the smaller particled ones.

Fig. 5 shows a presentation of the ethylene oxide selectivity and particle size of Ag with 6–7 and 11–12% in ethylene conversion, respectively. When the

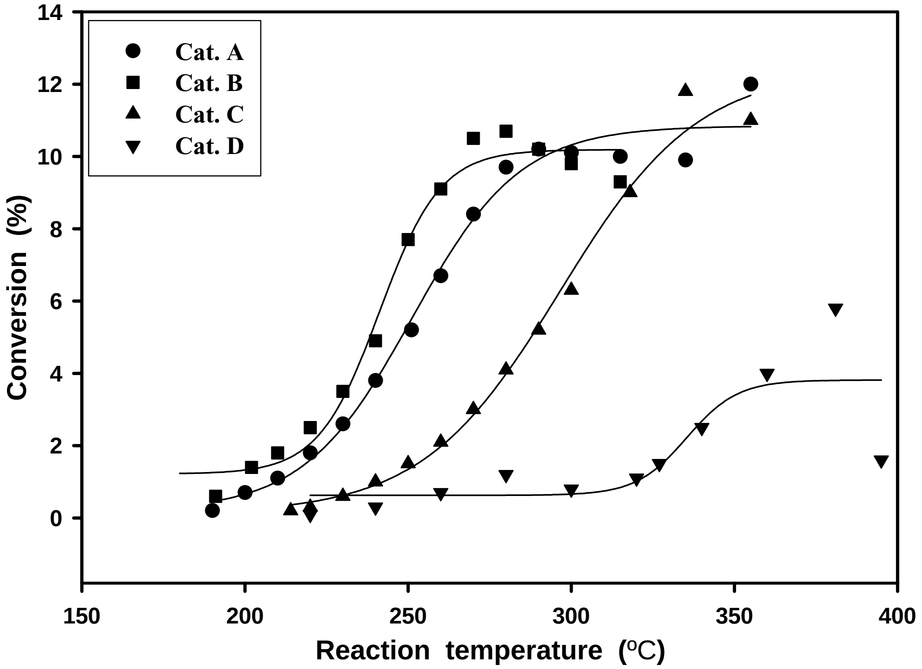

Fig. 2. Conversion of ethylene with different preparation method of catalysts.

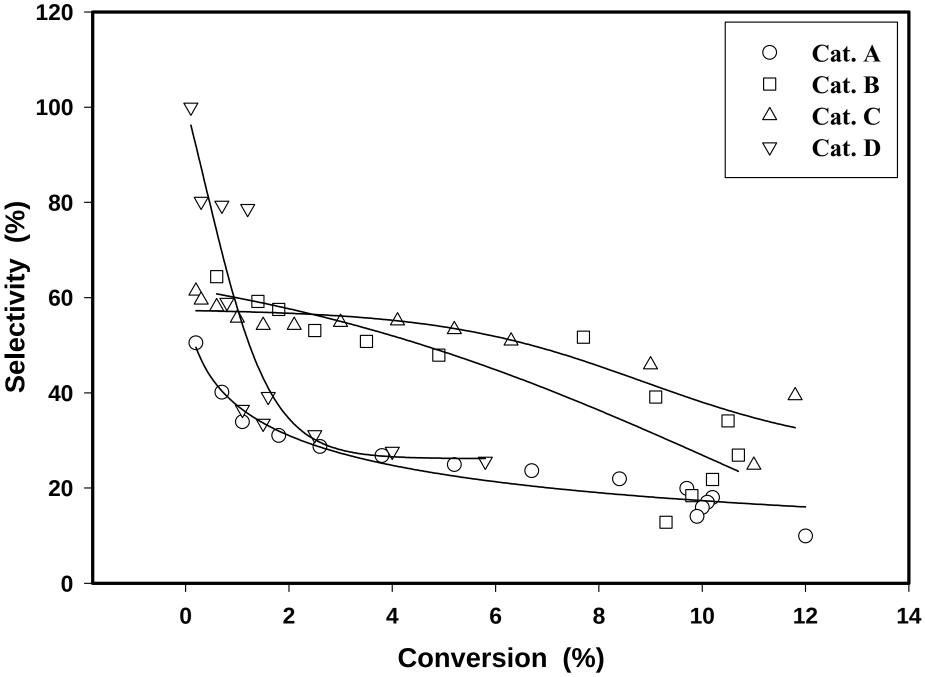

Fig. 3. Selectivity and conversion of ethylene oxide with different preparation method of catalysts.

ethylene conversion was 6–7%. As the particle size was increased, the ethylene oxide selectivity was increased to 15–52% dramatically, but the ethylene conversion was 11–12%. As the particle size was increased, the ethylene oxide selectivity was concentrated between 38 and 50% generally. Consequently, the catalysts with 11–12% on the ethylene conversion remain rather stable on the ethylene oxide selectivity and can get higher yield compared to the lower ethylene conversion catalysts throughout the particle size of Ag.

3.3. TPD/TPR analysis

Figs. 6 and 7 show O_2-TPD profiles for the catalysts C and D, respectively. As mentioned before, the desorption temperatures of the molecular, atomic, and lattice oxygen were known as 150–470, 550–650, and above 750 °C, respectively. A single desorption peak due to the molecularly adsorbed oxygen is observed at about 400 °C in Fig. 6. The amount of desorbed oxygen increased with the silver loading. On the other hand, both the peaks due to molecularly and atomically adsorbed oxygens are observable at about 400 and 650 °C, respectively, in Fig. 7. As in Fig. 6, the amount of desorbed oxygen increased with the silver loading. When the silver loading was increased to 11.1%, molecularly adsorbed band became very strong. One thing interesting here is the almost constant maximum desorption temperatures regardless of the silver loading, i.e., 400 °C for the catalysts prepared by water–alcohol method (Fig. 6), while 400 and 650 °C for the catalysts prepared by micro emulsion method (Fig. 7). Depending on the adsorbed oxygen species which participate in the step of ethylene oxide formation, the reaction has been claimed to be either a molecular or an atomic mechanism. Recently, the oxygens which were adsorbed in O_2^- state have been reported to participate in the partial oxidation of ethylene with some experimental evidences provided by electron spin resonance (ESR) and infrared spectroscopy [19].

Although the catalyst C had molecularly adsorbed oxygen only as shown in Fig. 6, it showed higher activity than the catalyst D from which a little of molecularly adsorbed oxygen was desorbed when the

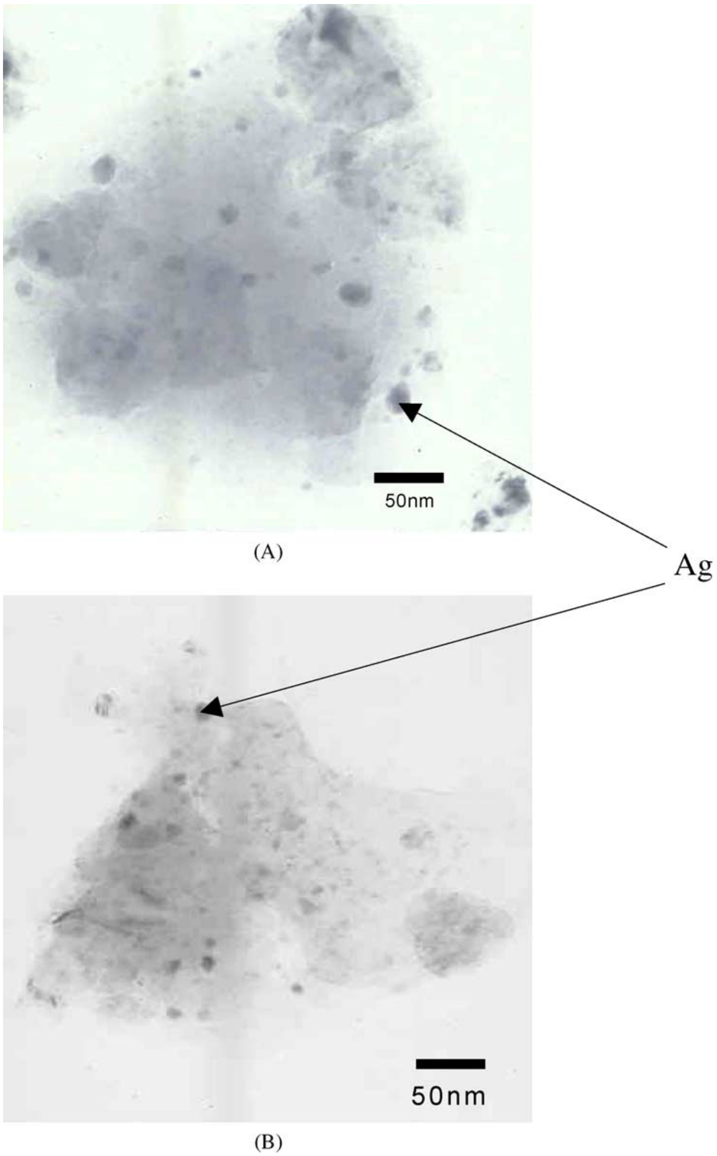

Fig. 4. TEM photographs of Ag/α-Al_2O_3 prepared by different methods: (A) water–alcohol method (cat. C); (B) micro emulsion method (cat. D).

atomically adsorbed oxygen was desorbed a lot. This seems to suggest that the molecularly adsorbed oxygen is the active surface species to contribute directly in the formation of ethylene oxide in the partial oxidation of ethylene. The fact that the production of ethylene oxides decreased in spite of the increased active oxygen species with the silver loading, might be explained by the further oxidations of the already formed ethylene oxides.

Figs. 8 and 9 show the H_2-TPR profiles depending on the silver loading for the catalysts C and D, respectively. The molecular, the atomic, and the lattice oxygen have been reported to be removed by the reduction in TPR at 410, 500, and 870 °C, respectively.

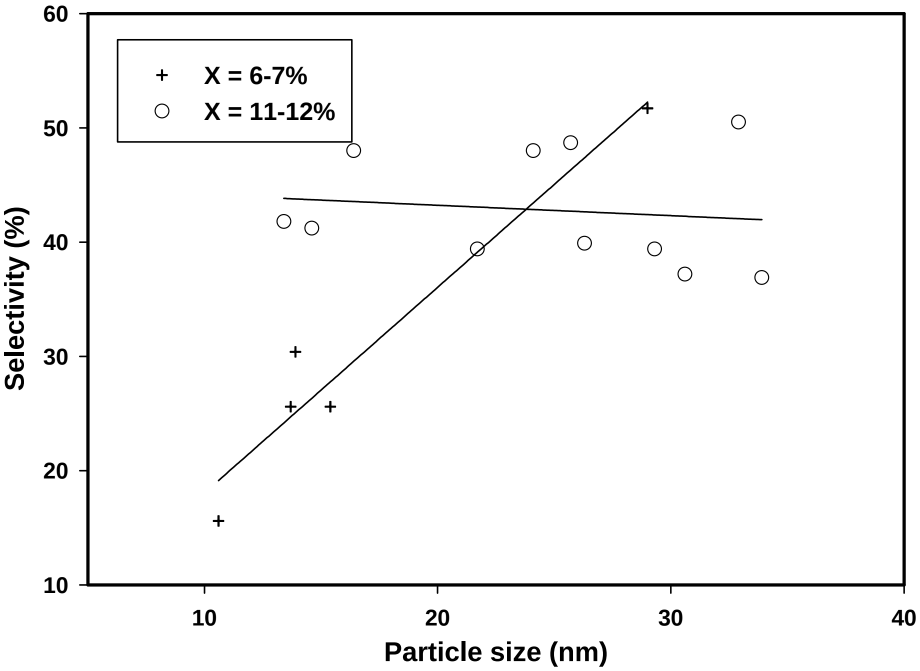

Fig. 5. Selectivity vs. particle size on the conversion (*X*, %) of catalysts.

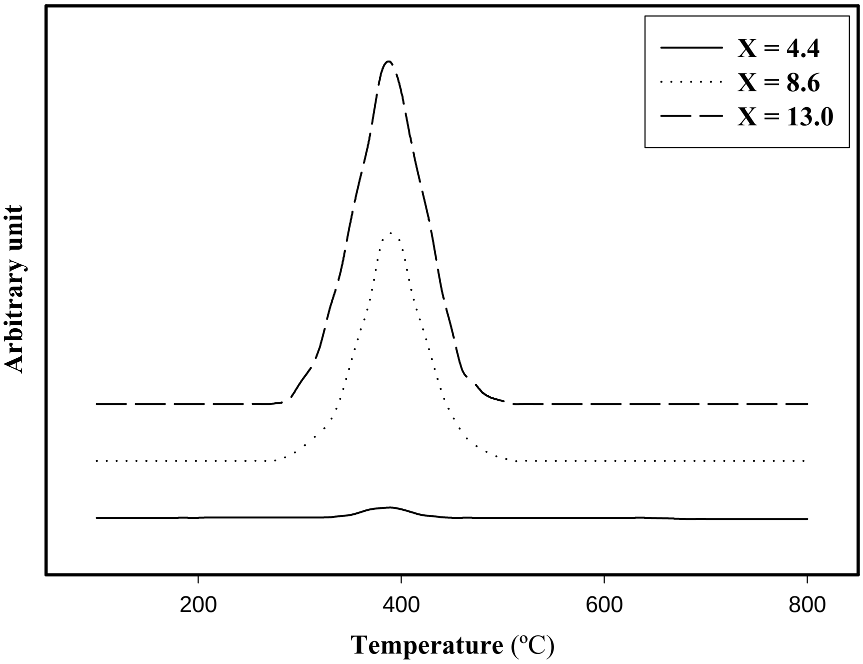

Fig. 6. TPD profiles on the loading amount (*X*, wt.%) of Ag in Ag/α-Al_2O_3. Catalyst prepared by water–alcohol method.

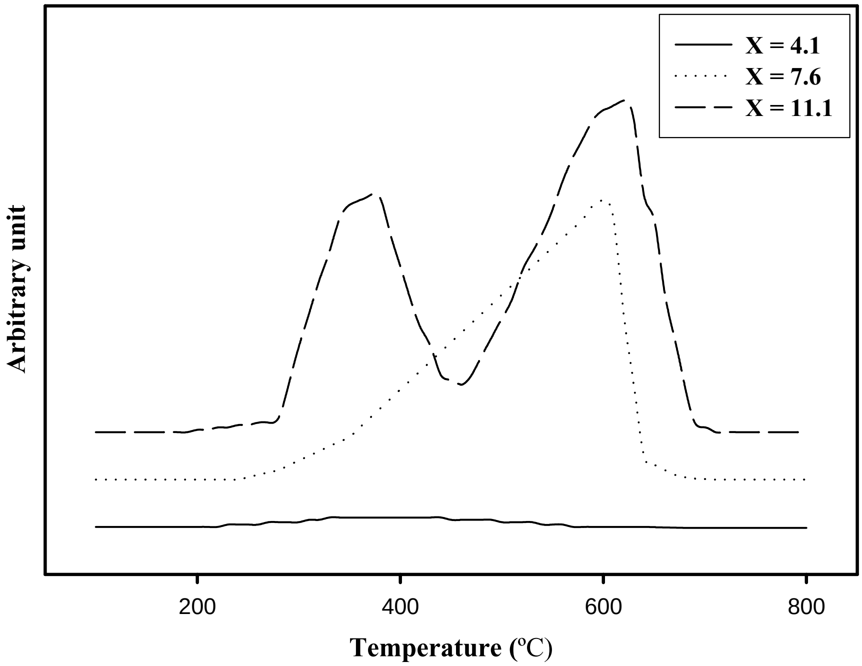

Fig. 7. TPD profiles on the loading amount (*X*, wt.%) of Ag in Ag/α-Al_2O_3. Catalyst prepared by micro emulsion method.

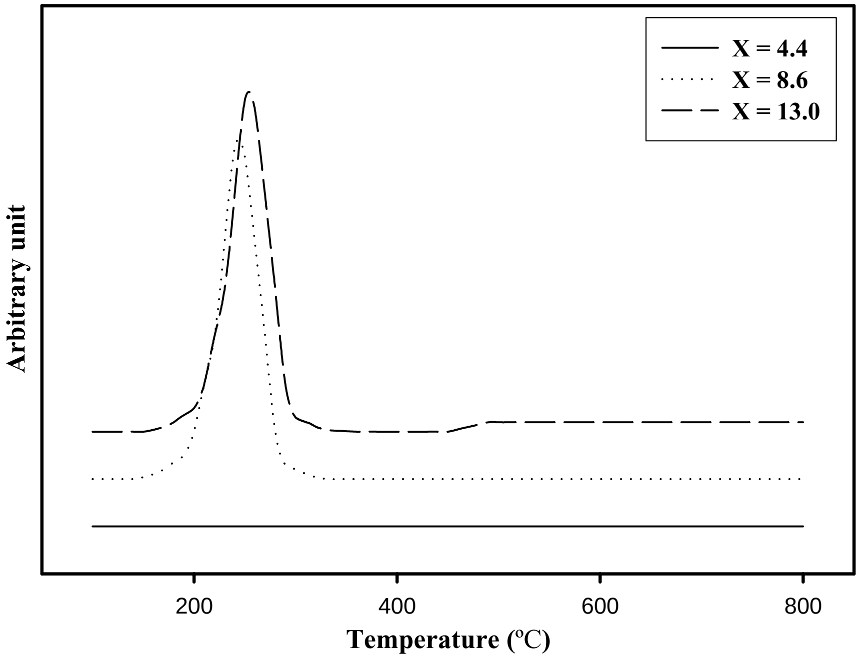

Fig. 8. TPR profiles on the loading amount (*X*, wt.%) of Ag in Ag/α-Al_2O_3. Catalyst prepared by water–alcohol method.

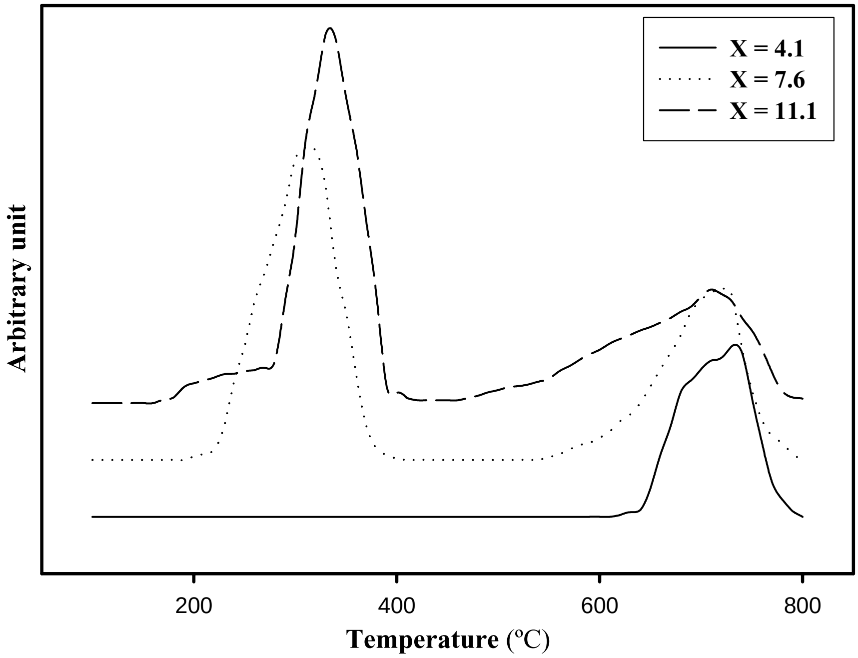

Fig. 9. TPR profiles on the loading amount (X, wt.%) of Ag in Ag/α-Al_2O_3. Catalyst prepared by micro emulsion method.

A band at around 250 °C in the catalyst C represent the amount of hydrogen which was consumed in the reduction of the molecular oxygen at surface. It appeared at around 320 °C for the catalyst D, while the band at around 720 °C is believed to represent the consumed hydrogen in the reduction of the atomic oxygen. In the TPR of the catalyst C, only a band which resulted from the molecularly adsorbed oxygen can be observed (Fig. 8). However, the band due to the molecular oxygen became dominant in the TPR of the catalyst D even at the silver loading of 7.6%. It was unobservable in TPD of the same catalyst (Fig. 7).

4. Conclusions

The results of the partial oxidation of ethylene over silver catalysts can be summarized as follows:

(1) The average sizes of the supported silver particles were about 15 nm for both the catalysts prepared by precipitation and micro emulsion methods. Those for both the catalysts prepared by modified precipitation and water–alcohol methods were about 30 nm. The catalysts with larger particles showed higher and more stable activities.

(2) The catalyst prepared by water–alcohol method showed only one desorption peak due to the molecularly adsorbed oxygens at around 400 °C. However, the catalyst prepared by micro emulsion method showed two desorption peaks, for the molecularly adsorbed oxygens at around 400 °C and the atomically adsorbed ones at around 650 °C.

(3) From the TPD/TPR profiles, molecularly adsorbed oxygens seem to be the active surface species to contribute the formation of the ethylene oxide directly. However, further oxidations of ethylene are believed to result in the decreased yield of ethylene oxide in spite of the increased active oxygens with the silver loading.

Acknowledgements

This study was financially supported by Chonnam National University in the program, 2001.

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