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Short communication

Direct epoxidation of propylene to propylene oxide with molecular oxygen over Ag–Mo–W/ZrO_2 catalysts

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ABSTRACT

A series of Ag–(x)Mo–(5–x)W/ZrO_2 (x = 5, 3.75, 2.50, 1.25, and 0) catalysts with different molybdenum content (x, wt%) were prepared by a slurry method. They were then applied to the direct epoxidation of propylene to propylene oxide with molecular oxygen. Selectivity for propylene oxide showed a volcano-shaped trend with respect to molybdenum content. This result was well correlated with the binding energy shift of Ag $3d_{5/2}$ of the catalysts. Among the catalysts, Ag–(3.75)Mo–(1.25)W/ZrO_2 catalyst with the highest binding energy shift of Ag $3d_{5/2}$ showed the best catalytic performance. Furthermore, Ag–(3.75)Mo–(1.25)W/ZrO_2 catalyst was reusable in the direct epoxidation of propylene.

1. Introduction

Propylene oxide (PO) is an important intermediate because it is used as a precursor for various chemicals such as polyester resin, propylene glycol, and polyurethane. Propylene oxide is commercially produced by Halcon process, chlorohydrin process, and HPPO (hydrogen peroxide-propylene oxide) process [1–3]. However, these processes involve many drawbacks in economical and environmental viewpoints. In order to overcome these problems, direct synthesis of propylene oxide from propylene and molecular oxygen has attracted much attention as a cheap and green chemical process.

Silver catalyst supported on α-alumina is well known to be the most efficient catalyst in the direct epoxidation of ethylene to ethylene oxide [4]. However, this catalyst shows a very low catalytic activity in the direct epoxidation of propylene to propylene oxide. It has been reported that allylic C—H bond energy (77 kcal/mol) in propylene is lower than vinylic C—H bond energy (112 kcal/mol) in ethylene [5]. This means that total oxidation of adsorbed molecular oxygen and C—H bond in propylene is more preferable than that in ethylene. As a consequence, H_2O and CO_2 rather than propylene oxide are mainly produced in the direct epoxidation of propylene [6].

Oxidation of propylene follows two reaction pathways; total oxidation and partial oxidation [7,8]. Total oxidation to H_2O and CO_2 occurs by the reaction of adsorbed molecular oxygen with allylic hydrogen (C—H) in propylene, whereas partial oxidation to propylene oxide occurs by the reaction of oxygen adsorbed on the silver active site with C═C π bond in propylene. This means that less nucleophilic property of adsorbed molecular oxygen is more favorable to enhance the reaction possibility between C═C π bond in propylene and adsorbed oxygen on the silver active site [7–9]. Therefore, modification of silver catalyst and change of electronic property of adsorbed oxygen can be a good strategy to enhance the selectivity for propylene oxide. In an attempt to improve the selectivity for propylene oxide in the direct epoxidation of propylene, introduction of various promotors such as alkali (earth), chlorine, and transition metals has been investigated [9–12].

In this work, a series of Ag–(x)Mo–(5–x)W/ZrO_2 catalysts were prepared by a slurry method with a variation of molybdenum content (x, wt%), and they were applied to the direct epoxidation of propylene to propylene oxide with molecular oxygen. The effect of molybdenum content on the physicochemical properties and catalytic activities was investigated.

2. Experimental

2.1. Catalyst preparation

A series of Ag–(x)Mo–(5–x)W/ZrO_2 catalysts were prepared by a slurry method. In short, 1.63 g of oxalic acid ($C_2H_2O_4$, Junsei) and 0.9 ml of ethylene diamine ($C_2H_8N_2$, Sigma-Aldrich) were dissolved in distilled water (6 ml). After it was stirred for a few minutes, 1 g of silver oxide (Ag_2O, Sigma-Aldrich) was dissolved in the solution. Known amounts of ammonium molybdate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, Samchon) and ammonium (para) tungstate hydrate ($(NH_4)_{10}H_2(W_2O_7)_6\cdot xH_2O$,

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Sigma-Aldrich) were then added into the solution. After stirring the solution for 1 h, 3.54 g of zirconium oxide (ZrO_2, Sigma-Aldrich) was slowly added into the solution to form a slurry. After vigorous stirring the mixed slurry at 70 °C, it was evaporated to obtain a solid. The product was then dried at 120 °C in a convection oven for 1 day. The resultant was grinded and calcined at 460 °C for 3 h to obtain Ag–(x)Mo–(5–x)W/ZrO_2 catalysts. The prepared catalysts were denoted as Ag–(x)Mo–(5–x)W/ZrO_2 (x = 5, 3.75, 2.50, 1.25, and 0), where x represented wt% of molybdenum in the catalysts. Silver content in all the Ag–(x)Mo–(5–x)W/ZrO_2 catalysts was fixed at 20 wt%.

2.2. Catalyst characterization

N_2 adsorption-desorption measurements were carried out to examine the textural properties of Ag–(x)Mo–(5–x)W/ZrO_2 catalysts with a BELSORP-mini II (BEL Japan) instrument. Metal contents in the catalysts were determined by ICP-AES (Shimadz, ICP-1000IV) analyses. Crystalline structures of the catalysts were investigated by X-ray diffraction (XRD) measurements (D-Max2500-PC, Rigaku). Surface morphologies of the catalysts were examined by high resolution-transmission electron microscopy (HR-TEM) analysis (Jeol, JEM-3010). SEM analyses (Jeol, JSM-6700F) were conducted with energy dispersed X-ray spectroscopy (EDX) mapping to confirm the distribution of metal species. X-ray photoelectron spectroscopy (XPS) analyses (Sigma probe) were carried out to measure the binding energies of silver (Ag $3d_{5/2}$ and Ag $3d_{3/2}$) in the catalysts. All the XPS spectra were calibrated using **C** 1s peak (284.5 eV) as a reference.

2.3. Direct epoxidation of propylene to propylene oxide

Direct epoxidation of propylene to propylene oxide with molecular oxygen was tested in a continuous flow fixed-bed quartz reactor at 460 °C under atmosphere pressure. Each catalyst (0.3 g) was thermally treated at 460 °C in a stream of nitrogen prior to the catalytic reaction. After treating the reactor with nitrogen for 30 min, propylene and oxygen were continuously supplied into the reactor with a nitrogen carrier. Feed composition was fixed at propylene:oxygen:nitrogen = 1.5:1:9. Total feed rate with respect to catalyst weight was maintained at 3000 ml/h g_{cat}. Reaction products were periodically sampled and analyzed with gas chromatographs (Younglin, ACME 6100) equipped with a thermal conductivity detector (Molsieve 5A and Porapak N columns) and a flame ionization detector (DB-1 column).

3. Results and discussion

3.1. Characterization of Ag–(x)Mo–(5–x)W/ZrO_2 catalysts

Detailed textural properties of Ag–(x)Mo–(5–x)W/ZrO_2 (x = 5, 3.75, 2.50, 1.25, and 0) catalysts determined by N_2 adsorption-desorption measurements are listed in Table 1. All the catalysts exhibited very low surface area (<10 m^2/g) and small pore volume (<0.02 cm^3/g), indicating that they existed in the form of bulk-type catalysts. These textural properties are advantageous for propylene epoxidation, because well-developed porosity and high surface area are known to cause total oxidation of propylene [13]. Actual silver, molybdenum, and tungsten contents in the Ag–(x)Mo–(5–x)W/ZrO_2 catalysts were similar to the designed values.

Crystalline structures of Ag–(x)Mo–(5–x)W/ZrO_2 (x = 5, 3.75, 2.50, 1.25, and 0) catalysts were investigated by XRD measurements as shown in Fig. 1. All the catalysts showed four characteristic diffraction peaks (2θ = 38°, 44°, 64°, and 77°) which were ascribed to the crystal faces of silver (111), (200), (220), and (311). All the catalysts also showed diffraction peaks of tetragonal ZrO_2 (2θ = 34° and 49°) and monoclinic ZrO_2 (2θ = 28° and 31°), in good agreement with the previous result [14]. Diffraction peaks of molybdenum oxide and tungsten oxide were also observed at 2θ = 27° and 2θ = 29°, respectively. This means that Ag–(x)Mo–(5–x)W/ZrO_2 catalysts were successfully prepared as attempted in this work.

Surface morphologies and distributions of silver, molybdenum, tungsten, and zirconium species in the Ag–(3.75)Mo–(1.25)W/ZrO_2 catalyst were confirmed by HR-TEM and SEM-EDX analyses as shown in Fig. 2. In the HR-TEM and SEM images (black and white), the catalyst existed in the form of bulk-type particles (100–300 nm). It is noticeable that silver atom (blue dot), molybdenum atom (purple dot), tungsten atom (red dot), and zirconium atom (yellow dot) were co-presented in the bulk particle domain of Ag–(3.75)Mo–(1.25)W/ZrO_2 catalyst. This result supports that silver, molybdenum, tungsten, and zirconium species were finely dispersed in the Ag–(3.75)Mo–(1.25)W/ZrO_2 catalyst.

SEM-EDX mapping images of reused Ag–(3.75)Mo–(1.25)W/ZrO_2 catalyst were examined (Fig. S1 of Supporting information). Reused Ag–(3.75)Mo–(1.25)W/ZrO_2 catalyst showed no great difference in distribution of metal species compared to fresh Ag–3.75)Mo–(1.25)W/ZrO_2 catalyst. In particular, no significant silver sintering was found after the reaction. Thus, Ag–(3.75)Mo–(1.25)W/ZrO_2 catalyst served as a stable catalyst in the direct epoxidation of propylene.

Electronic state of silver species in the Ag–(x)Mo–(5–x)W/ZrO_2 (x = 5, 3.75, 2.50, 1.25, and 0) catalysts was confirmed by XPS analyses as shown in Fig. 3. For comparison, XPS analysis of Ag/ZrO_2 catalyst was also conducted (not shown in Fig. 3). All the Ag–(x)Mo–(5–x)W/ZrO_2 catalysts with molybdenum and/or tungsten promotor exhibited higher binding energies of Ag $3d_{5/2}$ and Ag $3d_{3/2}$ than Ag/ZrO_2 catalyst (368.1 eV (Ag $3d_{5/2}$) and 374.1 eV (Ag $3d_{3/2}$)). This result indicates that addition of promotor causes high binding energy of silver due to electron transfer from silver atom to promotor species. Binding energies of Ag $3d_{5/2}$ and Ag $3d_{3/2}$ were different with a variation of molybdenum content. Detailed binding energies of Ag $3d_{5/2}$ and Ag $3d_{3/2}$ of the catalysts are summarized in Table 1. The binding energy of Ag 3d increased in the order of Ag–(5)W/ZrO_2 < Ag–(5)Mo/ZrO_2 < Ag–(1.25)Mo–(3.75)W/ZrO_2 < Ag–(2.50)Mo–(2.50)W/ZrO_2 < Ag–(3.75)Mo–(1.25)W/ZrO_2. Among the catalysts, Ag–(3.75)Mo–(1.25)W/ZrO_2 catalyst showed the highest binding energy shift of Ag 3d.

According to the dipped adcluster model (DAM) theory [15], movement of electron occurs from silver atom to adsorbed oxygen when molecular oxygen is adsorbed on the silver surface. This movement of electron leads to total oxidation reaction between allylic hydrogen in

Table 1
Physicochemical properties and XPS results of Ag–(x)Mo–(5–x)W/ZrO_2 (x = 5, 3.75, 2.50, 1.25, and 0) catalysts.

Sample	Ag content (wt%)[a]	Mo content (wt%)[a]	W content (wt%)[a]	Surface area (m^2/g)[b]	Pore volume (cm^3/g)[c]	Binding energy (eV)	
						Ag $3d_{5/2}$	Ag $3d_{3/2}$
Ag–(5)Mo/ZrO_2	18.7	4.7	–	8.3	0.02	368.6	374.6
Ag–(3.75)Mo–(1.25)W/ZrO_2	19.5	3.61	1.37	6.0	0.02	369.2	375.3
Ag–(2.50)Mo–(2.50)W/ZrO_2	21.3	2.56	2.53	7.3	0.02	369.1	375.2
Ag–(1.25)Mo–(3.75)W/ZrO_2	20.4	1.23	3.42	7.0	0.02	368.9	375.0
Ag–(5)W/ZrO_2	19.4	–	5.1	6.7	0.02	368.4	374.3

[a] Determined by ICP-AES measurement.
[b] Calculated by the BET (Brunauer–Emmett–Teller) equation.
[c] Total pore volume at $P/P_0 = 0.99$.