Gas-phase epoxidation of propylene by molecular oxygen over Ag/BaCO₃ catalysts: Effect of preparation conditions

Qing Zhang, Yanglong Guo*, Wangcheng Zhan, Yun Guo, Li Wang, Yunsong Wang, Guanzhong Lu*

Key Laboratory for Advanced Materials, Research Institute of Industrial Catalysis, East China University of Science and Technology, Shanghai 200237, PR China

ARTICLE INFO

ABSTRACT

Ag/BaCO₃ catalysts with different Ag crystallite sizes, prepared by the reduction-deposition method, were developed for gas-phase epoxidation of propylene to propylene oxide (PO) by molecular oxygen. Effects of preparation conditions, such as pretreatment of organic amines of BaCO₃ support, pretreatment way of ethylene diamine, reduction temperature of HCHO and calcination temperature, on the catalytic performance and Ag crystallite size of Ag/BaCO₃ catalyst were investigated. Ag/BaCO₃* catalyst, with pretreatment of BaCO₃ support by ethylene diamine and prepared at the reduction temperature of HCHO of $10\,^{\circ}C$ and the calcination temperature of $250\,^{\circ}C$, exhibited better catalytic performance and good durability, in which 12.5% of propylene conversion and 36.9% of PO selectivity were achieved under the reaction conditions of $20\%C_3H_6-10\%O_2-70\%N_2$, $200\,^{\circ}C$, 0.1 MPa and GHSV of $3000\,h^{-1}$. Both lower reduction temperature of HCHO and lower calcination temperature can get smaller Ag crystallite sizes, which is more effective for epoxidation of propylene over Ag/BaCO₃* catalyst. The catalytic reaction mechanism of Ag/BaCO₃* catalyst for epoxidation of propylene is that propylene in the gas phase reacts with molecular oxygen species adsorbed on the catalyst surface to produce PO and follows Rideal–Eley mechanism.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Epoxidation of propylene to propylene oxide (PO) is one of the most important reactions in the chemical industry because PO is an important bulk chemical and widely used for production of propylene glycols, polyether polyols, polyurethane, surfactants and other commercial products. PO is produced mainly by the chlorohydrin process, the Halcon process and the hydroperoxide process, however, which have several shortcomings. The chlorohydrin process is not environmentally friendly and produces a large number of chlorinated by-products. The Halcon process generates the equimolar coproducts which values depend on their demands in the market [1]. The hydroperoxide process needs construction of large-scale production equipments and its commercialization has been hindered largely by the expense of H_2O_2 [2]. The Au-based catalysts can produce PO from epoxidation of propylene by the in-situ production of H_2O_2 from H_2-O_2 mixture with a high selectivity [3–10]. However, H_2 must be used as a sacrificial coreactant and its effi-ciency is usually low. Gas-phase epoxidation of propylene to PO by molecular oxygen is a one-step green chemical process, which has attracted much attention in recent years. Ag nanoparticles of 2–5 nm supported on WO_3 nanorods could get 15.5% of propylene conversion with 83% of PO selectivity [11]. Dissociation of O_2 at the interface between Ag aggregates and Al_2O_3 support could account for high catalytic activity for epoxidation of propylene over Ag_{19}/Al_2O_3 catalyst [12]. $TiCuO_x$ mixed oxide catalyst with highly dispersed and stabilized active sites of Cu^+ could get 69% of PO selectivity [13]. A strong synergistic effect between CuO_x and RuO_x was found to be responsible for PO formation over RuO_x-CuO_x/SiO_2 catalyst [14]. $SnO_2-CuO-NaCl/SiO_2$ catalyst [15] and NaCl–Cu–Mn mixed metal oxide catalyst [16] were also found to be effective for epoxidation of propylene by molecular oxygen. Strong interaction between Cs^+ and CuO_x nanoparticles favored the selective formation of PO over Cs^+-CuO_x/SiO_2 catalyst [17] and Cu^I was thought to be active sites for PO formation [17,18]. The light-induced reduction of Cu catalysts could increase PO selectivity [19] and Cu_2O rhombic dodecahedra exposing (1 1 1) crystal planes were found to be most effective for PO formation among Cu_2O catalysts with different morphologies [20]. The unsupported AgCu bimetallic catalyst

* Corresponding authors. Fax: +86 21 64252923.
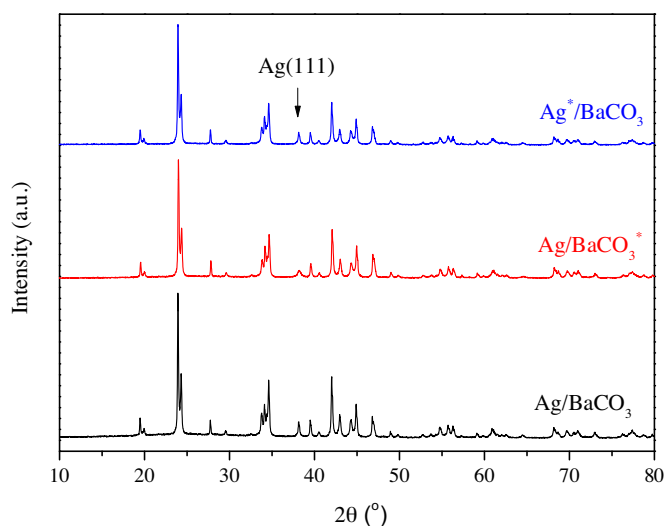 *E-mail addresses:* ylguo@ecust.edu.cn (Y. Guo), gzhlu@ecust.edu.cn (G. Lu).

Fig. 1. XRD patterns of Ag/BaCO$_3$, Ag/BaCO$_3$* and Ag*/BaCO$_3$ catalysts.
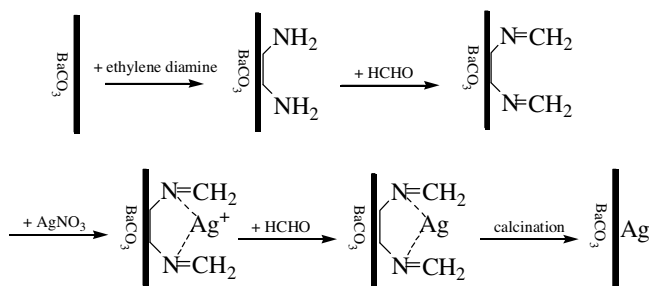

Fig. 2. Schematic diagram of the preparation process of Ag/BaCO$_3$* catalyst.

was more stable than unsupported Cu catalyst for epoxidation of propylene [21].

Epoxidation of ethylene by molecular oxygen over Ag-based catalysts has been commercialized for several decades, in which 83–95% of selectivity of ethylene oxide is obtained [22–24]. Ag-based catalysts have also been investigated for epoxidation of propylene by molecular oxygen. However, PO selectivity is low over unpromoted Ag catalysts, because propylene has the active α-H atoms and α-H atoms can easily react with oxygen to result in combustion of propylene to CO$_2$ and H$_2$O. Therefore, various attempts have been made to modify Ag catalysts for epoxidation of propylene. NaCl, CuCl, Y$_2$O$_3$, K$_2$O and MoO$_3$ have been used as promoters to enhance PO selectivity [25–30]. These Ag-based catalysts were effective for epoxidation of propylene, but they were high Ag loading or heavily promoted. AgCu bimetallic catalyst with low loadings of Ag and Cu, could get PO selectivity of 55.1% at propylene conversion of 3.6% [31].

Gas-phase epoxidation of propylene by molecular oxygen over Ag-based catalysts is a structure-sensitive reaction, but opinions are different. Zemichael et al. [27] found that Ag/CaCO$_3$ catalyst with Ag nanoparticles of 20–40 nm exhibited better catalytic performance. Lu et al. [32] showed that large Ag nanoparticles favored ethylene epoxidation by 3–5 fold at 473–493 K, whereas Ag particle size did not have a large effect on propylene epoxidation over Ag/CaCO$_3$ catalyst. Molina et al. [33] found that Ag/Al$_2$O$_3$ catalyst with Ag nanoparticles of 23.3 nm was more selective towards PO formation. Lei et al. [34] found that size-selected Ag$_3$ clusters and Ag nanoparticles of ∼3.5 nm on alumina supports could catalyze epoxidation of propylene by molecular oxygen with high PO selectivity at low temperature. Ghosh et al. [11] found that Ag/WO$_3$ catalyst with 2–5 nm Ag particle size was much more effective than those

with 15–20 nm or 30–50 nm Ag particle size for epoxidation of propylene by molecular oxygen at high pressure. DFT calculations showed that CO$_2$ was the main product for epoxidation of propylene by O$_2$ or H$_2$–O$_2$ mixtures irrespective of the silver particle size [35].

In this paper, unpromoted Ag/BaCO$_3$ catalysts with low Ag loading were prepared by the reduction-deposition method and investigated for gas-phase epoxidation of propylene by molecular oxygen at atmospheric pressure. Effects of preparation conditions, such as pretreatment of organic amines of BaCO$_3$ support, pretreatment way of ethylene diamine, calcination temperature and reduction temperature of HCHO, on the catalytic performance and Ag crystallite size of Ag/BaCO$_3$ catalyst were investigated, and the catalytic reaction mechanism for epoxidation of propylene was proposed.

2. Experimental

2.1. Preparation of catalysts

Ag/BaCO$_3$ catalyst was prepared by the reduction-deposition method. At room temperature, 2 g of formaldehyde (HCHO) was dissolved in 40 mL of deionized water as the reductant, into which 8 g of BaCO$_3$ support was added to form a slurry. After stirring for 20 min, 0.6 g of AgNO$_3$ dissolved in 40 mL of deionized water was added dropwise into the above slurry, then the solid was filtered and washed with deionized water and ethanol for several times. The solid was dried overnight at room temperature and then calcined in N$_2$ atmosphere at 450 °C for 4 h. The similar procedure was used to prepare Ag*/BaCO$_3$ catalyst except that AgNO$_3$ was firstly dissolved in deionized water and then ethylene diamine was added until the solution became clear. Ag/BaCO$_3$* catalyst was prepared by the similar method to Ag/BaCO$_3$ catalyst except that BaCO$_3$ support was firstly immersed into ethylene diamine aqueous solution for 12 h and then dried under vacuum at 60 °C for 4.5 h.

2.2. Epoxidation of propylene

Epoxidation of propylene was carried out in a fixed-bed quartz reactor under the reaction conditions of 0.6 g catalyst, 200 °C, 0.1 MPa and GHSV of 3000 h^{-1}. The feed gas consisted of 20% propylene, 10% O$_2$ and balance N$_2$. Reaction products were analyzed by two on-line gas chromatographs equipped with a two packed columns (G.D.X.-401 and Porapak Q) with FID and TCD detectors. All lines between the reactor exit and the gas chromatographs were heated to 120 °C to prevent condensation of the products. PO selectivity and propylene conversion were calculated on a carbon balance basis.

2.3. Characterization of catalysts

Elemental analysis was done by inductively coupled-plasma atomic emission spectroscopy (ICP-AES) using a TJA IRIS ADVANTAG 1000 instrument.

XRD patterns were performed on a Bruker AXS D8 Focus diffractometer operated at 40 kV, 40 mA (Cu Kα radiation, λ = 0.15406 nm).

TEM images were recorded on a JEM-1400 transmission electron microscope. The sample was ultrasonically suspended in the ethanol solvent, and one drop of this slurry was deposited on a copper grid. The liquid phase was evaporated before the grid was loaded into the microscope.

XPS spectra were recorded on a Thermo ESCALAB 250 spectrometer with a monochromatized AlKα X-ray source (1486.6 eV), and a passing energy of 20 eV. C1s (binding energy of 284.6 eV) of adventitious carbon was used as the reference.