EFFECT OF ADDITIVE IN FEEDSTOCK ON PERFORMANCE OF Ag-MoO$_3$/ZrO$_2$ CATALYST FOR PROPYLENE EPOXIDATION BY MOLECULAR OXYGEN

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Abstract

The performance of the Ag-MoO$_3$/ZrO$_2$ catalyst for propylene epoxidation by molecular oxygen is influenced obviously by the composition of feedstock. As an additive in feedstock, the presence of organic chloride, CO$_2$, NO$_x$ or H$_2$ at a suitable concentration can improve the catalytic performance of Ag-MoO$_3$/ZrO$_2$ catalyst for the propylene epoxidation.

Keywords: Propylene epoxidation, silver-molybdena catalyst, molecular oxygen, additive

INTRODUCTION

Propylene oxide (PO) is an important chemical intermediate in producing resins (such as polyurethane), and is produced commercially by the chlorohydrin and Halcon methods, but these processes above have the disadvantages of environment pollution and co-product, respectively. The epoxidation of propylene with H$_2$O$_2$ over TS-1 zeolite catalyst has a high conversion and selectivity to PO under the mild conditions, but the cost of this process catalyzed

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by TS-1 is very high due to using expensive H₂O₂ oxidant and TS-1 catalyst, compared with the cheaper product PO [1], which is uncompetitive commercially with the conventional methods. For the epoxidation of propylene with O₂ and H₂ over Au/TiO₂ [2] or Pd-Pt/TS-1 [3], the selectivity to PO is higher than 90% and propylene conversion is 1-2%, however, this process consumes large quantities of H₂ and careful handling is strictly required for the explosive mixture of H₂-O₂. In view of economy and green chemistry, the direct epoxidation of propylene by molecular oxygen over a solid catalyst should be the most ideal process to produce PO. Lu et al. [4] and Lu et al. [5] reported that the NaCl-modified Ag catalyst exhibited a good performance for the propylene epoxidation by air, and 54.0% propylene conversion and 26.3% selectivity to PO were achieved [4]. ARCO chemists reported that a propylene conversion of 1.5% and selectivity to PO of 64% were achieved over the modified Ag/CaCO₃ catalyst by using oxygen as an oxidant and an additive of EtCl, NO or CO₂ [6].

When oxygen adsorbs on silver surface, transfer of electrons from silver to adsorbed oxygen makes the latter electronegative [7,8]. The mechanism of propylene oxidation on the silver surface has been studied by Nakatsuji and co-workers [9,10], they think that the formation of PO is initiated by a reaction of olefinic carbon (-C=C-) and adsorbed oxygen, and the combustion reaction of propylene is initiated by abstraction of allylic hydrogen (α-H) by adsorbed oxygen. Therefore, lowering the electron density of adsorbed oxygen on the silver sites to restrict the reaction between adsorbed oxygen and allylic H is an important way to improve selectivity to PO. Based on the above idea, we have developed Ag-MoO₃ and Ag-MoO₃/ZrO₂ catalysts for the propylene epoxidation [11-15]. Herein, we report an effective method of improving the performance of the Ag-MoO₃/ZrO₂ catalyst for propylene epoxidation with molecular oxygen, in which an inhibitor (or additive) is added in feedstock. The effects of concentration of different additive on the catalytic epoxidation of propylene are studied, and the role of additive is discussed.

EXPERIMENTAL

Preparation of catalyst

The 20%Ag-4%MnO₃/ZrO₂ catalyst was used as a model catalyst and prepared by an impregnation method. AgNO₃ (12.5 g) was solved in distilled water (12.5 mL) to form AgNO₃ aqueous solution. ZrO₂ (30.0 g) was slowly added into this AgNO₃ aqueous solution to form a slurry under ultrasonic vigorous stirring at room temperature and the slurry was heated at 80°C to nearly waterless, and then dried at 110°C for 4 h and calcined at 450°C for 4 h to form the precursor. After this the precursor was impregnated with an aqueous solution (12.5 mL) of (NH₄)₆Mo₇O₂₄·4H₂O (1.95 g), dried at 110°C for 4 h and calcined at 300°C for 4 h to get the 20%Ag-4%MnO₃/ZrO₂ catalyst.