

Copper-based efficient catalysts for propylene epoxidation by molecular oxygen

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Abstract

Among a series of SBA-15-supported transition metal oxides with and without modification, the CuO_x/SBA-15 after K⁺ modification exhibited the best catalytic performance for the epoxidation of propylene by molecular oxygen. Potassium was the best modifier among various alkali and alkaline earth metal ions examined, and potassium acetate was a superior precursor of K⁺ for propylene oxide formation. The highest propylene oxide selectivity was obtained over a catalyst with copper content of 1 wt.% and K/Cu molar ratio of 0.7. Kinetic studies reveal that the allylic oxidation mainly proceeds over the CuO_x/SBA-15 providing acrolein as the main partial oxidation product, and the K⁺ modification switches the main reaction route from allylic oxidation to epoxidation. The characterizations suggest that copper species with content of ≤5 wt.% are located in the mesoporous channels of SBA-15 existing mainly as CuO_x clusters and Cu²⁺ ions, and there exists an interaction between K⁺ and the copper species. This interaction is proposed to play pivotal roles in epoxidation of propylene. As compared with other reported Cu-based catalysts for propylene epoxidation, the present catalyst possesses several distinct features.

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1. Introduction

Propylene oxide (PO) is an important synthetic intermediate. In the current chemical industry, PO is mainly produced by the chlorohydrin and the organic hydroperoxide processes, but both processes have caused the production of a large amount of waste water or organic by-products, which have brought about serious environmental problems, and thus are not atomically economic [1]. Therefore, it becomes urgent to establish a direct and green epoxidation route for PO production. Many studies have been contributed to the direct C₃H₆ epoxidation using a proper catalyst combined with an appropriate oxidant. The use of H₂O₂ [2–4], O₂–H₂ gas mixture [5–8], and N₂O [9–14] as the oxidant can provide excellent PO selectivities at reasonable C₃H₆ conversions if a proper catalyst is used, but these oxidants are still expensive. Oxygen or air is the most ideal oxidant for selective oxidation. The epoxidation of ethylene by O₂ has been commercialized for several decades using Ag-based catalysts,

but the epoxidation of propylene by O₂ is not successful [15]. Ag- and Cu-based catalysts have mainly been reported so far for this reaction, but PO selectivity can hardly exceed 50% even at a lower propylene conversion [16–21]. The epoxidation of C₃H₆ by O₂ remains one of the most challenging targets in catalysis.

The existence of the allylic C–H bonds, which are much more active toward oxidation than the vinyl C–H bonds in C₂H₄, is believed to cause the lower selectivity in C₃H₆ epoxidation. It is known that the nucleophilic oxygen such as lattice oxygen species will attack preferentially the reactive allylic hydrogen atoms and cause the allylic oxidation, while the epoxidation needs the electrophilic oxygen. Therefore, our approach is to suppress the reactivity of lattice oxygen species, and to generate electrophilic oxygen species. Moreover, the site isolation may overcome the problem of consecutive oxidation of PO. Thus, the catalysts with highly dispersed active sites may be promising. Recently, we reported that a KCl-modified FeO_x/SBA-15 could work as a highly selective C₃H₆ epoxidation catalyst when N₂O was used as an oxidant [11]. It was elucidated that the highly dispersed Fe³⁺ (or Fe²⁺ generated in situ during the reaction) sites located in mesoporous channels

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of a mesoporous silica, e.g., SBA-15, were responsible for the activation of N_2O , and KCl modifier could enhance the electrophilicity of the active oxygen species derived from N_2O [12,13]. However, unfortunately this iron-based catalyst cannot catalyze the epoxidation of C_3H_6 by O_2 [14]. Nevertheless, it is still reasonable to think that the combination of an alkali metal modifier with other dispersed transition metal oxides or ions possibly capable of activating O_2 may be promising.

In the present paper, we report our recent investigations on the possibility of potassium-modified various transition metal oxides dispersed on SBA-15 for C_3H_6 epoxidation by O_2 and the details of catalytic behaviors of the modified copper-based catalysts, which have shown superior catalytic performances for PO formation as reported previously in a short paper [22].

2. Experimental

2.1. Catalyst preparation

SBA-15 was prepared using the method reported previously [23]. Typically, a homogeneous mixture composed of poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) triblock copolymer (P123, $EO_{20}PO_{70}EO_{20}$) as the template and tetraethyl orthosilicate (TEOS) as the source of silicon in hydrochloric acid was stirred at 313 K for 20 h, and the obtained milky suspension was further treated in autoclave at 373 K for 24 h. The resultant solid product was recovered by filtration followed by washing with deionized water and drying at 313 K in vacuum. The organic template was finally removed via calcination in air by heating from ambient temperature to 823 K at a rate of 1 K/min and keeping at 823 K for 6 h.

Copper as well as other transition metal ions or oxide clusters was introduced into SBA-15 by an impregnation method. Powdery SBA-15 after calcination was added into the aqueous solution of various transition metal salts such as $Cu(NO_3)_2$. The mixture was stirred for 10 h and was then allowed to rest overnight at ambient temperature. Subsequently, the slurry was evaporated to dryness at 343 K with continuous stirring. The powdery sample was calcined in air at 823 K for 6 h to obtain the $MO_x/SBA-15$ (M = transition metal). The alkali or alkaline earth metal ion-modified $MO_x/SBA-15$ samples were prepared by impregnation of the calcined $MO_x/SBA-15$ with an aqueous solution of alkali or alkaline earth metal salt followed by drying and calcination with the same procedure described above. Alkali or alkaline earth metal acetates were used as the precursors, unless otherwise stated.

2.2. Characterization

The structures of catalysts were characterized by Powder X-ray diffraction (XRD), N_2 -physisorption, transmission electron microscopy (TEM), and H_2 -temperature programmed reduction (H_2 -TPR). XRD measurements were performed with a Panalytical X'Pert Pro Super X-ray diffractometer with $Cu-K\alpha$ radiation (40 kV, 30 mA). N_2 -physisorption at 77 K was carried out with a Micromeritics TriStar 3000 surface area and porosimetry analyzer. The sample was pretreated at 573 K in

vacuum for 3 h before N_2 adsorption measurements. TEM observations were carried out with a FEI Tecnai 30 electron microscope (Phillips FEI) operated at an acceleration voltage of 300 kV. The sample for TEM observations was suspended in ethanol and ultrasonically dispersed, and then drops of suspensions were applied on a copper grid coated with carbon. H_2 -TPR and NH_3 -TPD were performed using a Micromeritics AutoChem II 2920 instrument. Typically, the sample (100 or 200 mg) was first pretreated in a quartz reactor with a gas flow containing O_2 and N_2 at 823 K for 1 h followed by purging with high-purity N_2 . For H_2 -TPR, after the sample was cooled to 323 K, a H_2 -Ar (5 vol.% H_2) gas flow was introduced into the reactor, and the temperature was raised to 1173 K at a rate of 10 K/min. The consumption of H_2 was monitored by a thermal conductivity detector. For NH_3 -TPD, the adsorption of NH_3 was performed at 393 K in an NH_3 -He (10 vol.% NH_3) mixture for 1 h, and the remaining or weakly adsorbed NH_3 was purged by high-purity He. TPD was performed in He flow by raising the temperature to 973 K at a rate of 10 K min^{-1} . The desorbed NH_3 was detected with a mass spectrometer (ThermoStar GSD 301 T2) by monitoring the signal of $m/e = 16$.

2.3. Catalytic reaction

The epoxidation of C_3H_6 was carried out using a fixed-bed reactor operated at atmospheric pressure. The catalyst (typically 0.2 g) was pretreated with a gas flow containing He and O_2 at 823 K for 30 min followed by purging with He for another 30 min. After the temperature was decreased to the desired reaction temperature (typically 573 K), the reactant gas mixture of C_3H_6 and O_2 diluted with He was introduced to start the reaction. The products were analyzed by on-line gas chromatography. All the lines and valves between the exit of the reactor and the gas chromatograph were heated to 393 K to prevent the condensation of the products.

3. Results and discussion

3.1. Unique catalytic behaviors of modified $CuO_x/SBA-15$ catalyst

Fig. 1 shows the catalytic performances of various transition metal oxides (content, 1 wt.%) dispersed on SBA-15 with and without K^+ modification for the oxidation of C_3H_6 by O_2 . No C_3H_6 conversion can be detected over SBA-15 either with or without K^+ modification. In the absence of K^+ modifier (Fig. 1A), relatively high C_3H_6 conversions (>5%) could be obtained in some cases, e.g. over SBA-15-supported CuO_x , MnO_x , Ag and CrO_x catalysts, but PO selectivity was very low in general. Over all the catalysts examined here, PO selectivity was less than 5% without K^+ modification under the reaction conditions used in Fig. 1. It is of interest that, after the modification with K^+ with a K/M ratio of 1.0, PO selectivity increases significantly on several occasions although C_3H_6 conversion decreases at the same time. The highest PO selectivity (~18%) was obtained over the K^+ - $CuO_x/SBA-15$ catalyst, and moreover, this catalyst exhibited a better C_3H_6 conversion (5.9%) than all other investigated K^+ -

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