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Active site and reaction mechanism for the epoxidation of propylene by oxygen over CuO_x/SiO_2 catalysts with and without Cs^+ modification

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ABSTRACT

Among alkali metal ions, Cs^+ was found to be the most efficient promoter of the CuO_x/SiO_2 catalyst for the epoxidation of propylene to propylene oxide (PO) by O_2. Stronger interactions between Cs^+ and CuO_x nanoparticles were proposed to favor the selective formation of PO. Kinetic studies indicated that PO was formed as a primary product in parallel with acrolein over the CuO_x/SiO_2 catalyst, but PO readily underwent isomerization to allyl alcohol, followed by oxidation to acrolein, without Cs^+ modification. The modification by Cs^+ inhibited the isomerization of PO because of the weakened acidity, contributing to the increase in PO selectivity. The inhibition of the reactivity of the lattice oxygen in the presence of Cs^+ also promoted PO selectivity by suppressing the allylic oxidation route. In situ X-ray diffraction, CO-adsorbed Fourier-transform infrared, and pulse-reaction studies suggest that Cu^I sites generated during the reaction account for the epoxidation of propylene by O_2.

1. Introduction

Propylene oxide (PO) is an important bulk chemical for the production of polyether polyols and propylene glycol. Currently, PO is produced by the chlorohydrin and organic hydroperoxide processes in industry, but these processes produce large amounts of by-products together with PO and are not green chemical processes. Many studies have been devoted to the catalytic epoxidation of propylene using a proper oxidant [1–6]. PO can be formed with good selectivities using H_2O_2 as an oxidant in the liquid phase [7], and the production of PO using H_2O_2 catalyzed by TS-1 has been commercialized by Dow–BASF [8]. H_2–O_2 gas mixture [6,9–11] and N_2O [12–18] are also effective for the epoxidation of propylene in the presence of a proper catalyst. However, only limited success has been achieved for the epoxidation of propylene by O_2, which is the most desirable route and has been viewed as the "Holy Grail" for PO production [2].

On the other hand, the Ag-catalyzed epoxidation of ethylene by O_2 has been commercialized for several decades [1–3]. Many studies have attempted to apply Ag-based catalysts to the epoxidation of C_3H_6 by O_2, but the selectivity of PO was very low under the reaction conditions where reasonably high C_3H_6 conversions could be obtained [3,19,20]. It is believed that the main difficulty arises from the higher reactivity of the allylic C–H bonds in C_3H_6. The allylic oxidation would proceed more readily than the epoxidation in the case of C_3H_6 oxidation by O_2 over most heterogeneous catalysts including Ag, leading to lower selectivity to PO [6]. Previous studies suggested that larger Ag particles favored selectivity to PO [3,19,20]. However, a recent communication claimed that Ag nanoparticles ~3.5 nm in size aggregated from Ag_3 clusters deposited on ultrathin Al_2O_3 could afford high PO selectivities at lower C_3H_6 conversions [21].

Besides the Ag-based catalysts, Au- and Cu-based catalysts have also been exploited for the epoxidation of C_3H_6 by O_2 [6]. Recently, a few research groups found that the supported Au nanoclusters could catalyze the epoxidation of C_3H_6 by O_2 in the presence of H_2O [6,22–24]. For example, the Au/TS-1 with a mean size of Au nanoclusters of 1.8 nm exhibited a PO selectivity of 52% at C_3H_6 conversion of 0.88% at 473 K [24]. It is proposed that smaller Au nanoclusters could activate O_2 and H_2O to form hydroperoxy species (*OOH), which may account for the epoxidation of C_3H_6 [22–24].

Surface chemistry studies over Ag and Cu single-crystal surfaces have demonstrated that the Cu surface preadsorbed with oxygen species is more selective than the Ag surface for the epoxidation of alkenes with allylic C–H bonds [25,26]. It is found that only isolated oxygen adatoms over Cu surfaces can lead to epoxidation while islands of "oxidic" oxygen cannot [25,26]. A theoretical study also reveals that Ag(111) favors allylic hydrogen stripping from

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C_3H_6, while Cu(1 1 1) favors the formation of propylene metallacycle, an intermediate for PO formation, owing to the lower basicity of adsorbed oxygen species on Cu(1 1 1) [27]. However, Monnier and Hartley [28] once pointed out that Cu might be difficult to use as a true epoxidation catalyst under reaction conditions because metallic Cu may be readily oxidized into CuO or Cu_2O by O_2. Several studies have claimed the epoxidation of C_3H_6 by O_2 over metallic Cu (Cu^0)-based catalysts [29,30]. High PO selectivities (40–50%) can be obtained only at very low C_3H_6 conversions (<0.3%), and the increase in C_3H_6 conversion to >1% with increasing reaction temperature or O_2 partial pressure led to a decrease in PO selectivity to <5% over these catalysts, possibly due to the transformation of Cu^0 to oxidized copper species (Cu^I or Cu^{II}) [29,30]. A recent study showed that the addition of a small amount of Cu to Ag/$BaCO_3$ to form Cu–Ag bimetallic catalysts significantly promoted the epoxidation of C_3H_6 by O_2 [31].

On the other hand, recently, a few copper oxide (CuO_x)-based catalysts have been reported to show interesting catalytic behavior for the epoxidation of C_3H_6 by O_2. We found that CuO_x/SBA-15 and CuO_x/SiO_2 modified with K^+, which started from Cu^{II} and did not undergo any reductive pretreatments, could catalyze the epoxidation of C_3H_6 by O_2 [32–34]. The epoxidation occurred efficiently even under O_2-rich conditions over our catalysts, and the PO formation rate was one order of magnitude higher than those obtained over the previously reported Cu^0-based catalysts [29,30]. The superior performance of these supported CuO_x catalysts was further demonstrated by other groups [35,36]. The modification of CuO_x with VO_x or RuO_x could enhance its activity and selectivity for PO formation [37–40].

However, it is noteworthy that supported CuO_x is also known as a representative catalyst for the allylic oxidation of C_3H_6 to acrolein by O_2 [41–44]. It is generally believed that the allylic oxidation competes with the epoxidation. There is little knowledge of selectivity control in the oxidation of C_3H_6 by O_2. Therefore, it is of great significance to gain insights into the factors controlling the reaction route for the formation of acrolein or PO over the CuO_x-based catalysts.

The present work is a continuation of our previous studies on C_3H_6 oxidation by O_2 over CuO_x-based catalysts. In our previous studies [32–34], we did not pay much attention to reaction networks over supported CuO_x catalysts. The first aim of the present paper is to clarify the reaction routes for the oxidation of C_3H_6 over CuO_x/SiO_2 catalysts in the absence and in the presence of an alkali metal ion modifier (particularly Cs^+) through kinetic studies. The roles of the alkali metal ion in affecting the reaction route will be discussed. Furthermore, although we have proposed that Cu^I is the active site for the epoxidation of C_3H_6 by O_2 [34], further evidence is required. This paper will report our recent studies on the chemical states of copper under working conditions through in situ X-ray diffraction (XRD) and CO-adsorbed Fourier-transform infrared (FT-IR) studies. The roles of oxygen species in the formation of acrolein or PO will also be discussed through pulse-reaction studies.

2. Experimental

2.1. Catalyst preparation

The CuO_x/SiO_2 and the alkali-metal-ion-modified CuO_x/SiO_2 catalysts were prepared by a sol–gel method. Briefly, an aqueous solution of alkali metal ion precursor (typically alkali metal carbonate) was first added slowly into a mixed aqueous solution of $Cu(NO_3)_2$ and ethylene glycol (20 mL), to obtain a homogeneous solution with a total volume of 60 mL. Subsequently, tetraethyl orthosilicate (TEOS, 10 g) was added dropwise into the mixed solution, and then, the mixture was kept at 343 K under vigorous stirring. A blue gel was finally obtained. After aging at room temperature for 24 h and further at 373 K for 48 h, the gel was calcined at 823 K in air for 6 h to obtain the catalyst.

In this paper, besides the catalyst starting from Cu^{II}, catalysts containing Cu^0 and Cu^I as the starting copper species were also prepared, to gain insights into the changes of Cu^0 and Cu^I under our reaction conditions and the possible active sites. The catalyst containing Cu^0 was produced by treating the catalyst prepared above in a H_2–He gas flow [$P(H_2) = 10.1$ kPa] at 773 K for 30 min, while that containing Cu^I was obtained by treating this reduced catalyst in a N_2O–He gas flow [$P(N_2O) = 20.3$ K] at 573 K for 30 min. Generally, a lower temperature is employed in N_2O oxidation for the generation of Cu^I on the surfaces of Cu^0 particles while the bulk is kept as Cu^0 [45]. We found that a higher temperature (573 K) used for N_2O oxidation could transform the whole Cu^0 particles in the reduced catalyst to Cu_2O particles. We confirmed that no Cu^{II} or CuO was generated during the oxidation of the reduced catalyst by N_2O under our conditions.

2.2. Catalytic reaction

Catalytic reactions were carried out on a fixed-bed reactor operated under atmospheric pressure. The catalyst was pretreated in the quartz reactor with a gas flow containing He (40 mL min^{-1}) and O_2 (10 mL min^{-1}) at 823 K for 0.5 h, followed by purging with He (60 mL min^{-1}) at the same temperature for another 0.5 h. After the catalyst was cooled down to the reaction temperature (473–573 K), the reactant gas mixture of C_3H_6 and O_2 was introduced into the reactor to start the reaction. In some cases, He was also used as a balance gas in the reactant mixture to regulate the partial pressures of C_3H_6 and O_2. The products were analyzed by two online gas chromatographs equipped with three columns. The separation of PO, acrolein, allyl alcohol, propanal, acetone, and acetaldehyde was performed by a capillary column (FFAP, 50 m × 0.53 mm × 1.0 μm) equipped with a flame ionization detector. The separation and detection of other components, such as O_2, C_3H_6, CO, and CO_2, were performed by Porapak Q and Molecular Sieve 5A columns and thermal conductivity detectors. All the lines and valves between the exit of the reactor and the gas chromatographs were heated to 393 K to prevent condensation of organic products.

Pulse reactions were performed to gain information about the reactivity of the lattice oxygen and the initial catalytic behavior of the catalysts pretreated under different conditions. For the pulse reaction, He, typically with a flow rate of 80 mL min^{-1}, was used as the carrier gas, and the pulse volume was typically fixed at 0.63 mL (STP). Other pretreatment and reaction conditions were the same as those used for the flow reaction.

2.3. Catalyst characterization

XRD measurements were carried out on a Panalytical X'pert Pro Super X-ray diffractometer with Cu Kα radiation (40 kV and 30 mA). For in situ XRD measurements, the sample was loaded into an XRK-900 cell, which was directly attached to the X-ray diffractometer. N_2 sorption at 77 K was performed 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. The surface area was calculated using the BET method. Transmission electron microscopy (TEM) was performed on a Philips Analytical FEI Tecnai 30 electron microscope operated at an acceleration voltage of 300 kV or on a JEM-2100 electron microscope operated at an acceleration voltage of 200 kV. Samples for TEM observation were suspended in ethanol and dispersed ultrasonically. Drops of suspensions were applied on a copper grid coated with carbon.