Journal of Catalysis 299 (2013) 53-66

Contents lists available at SciVerse ScienceDirect

# Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

# Active site and reaction mechanism for the epoxidation of propylene by oxygen over $CuO_x/SiO_2$ catalysts with and without Cs<sup>+</sup> modification

# Jieli He, Qingge Zhai, Qinghong Zhang, Weiping Deng, Ye Wang\*

State Key Laboratory of Physical Chemistry of Solid Surfaces, National Engineering Laboratory for Green Chemical Productions of Alcohols, Ethers and Esters, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China

# ARTICLE INFO

Article history: Received 15 September 2012 Revised 21 November 2012 Accepted 22 November 2012 Available online 11 January 2013

Keywords: Propylene Molecular oxygen Epoxidation Allylic oxidation Selectivity control Copper oxide catalyst Cesium Cu<sup>1</sup> active site

# 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<sub>2</sub>O [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

\* Corresponding author. Fax: +86 592 2183047.

# 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  $O_2$ .

© 2012 Elsevier Inc. All rights reserved.

JOURNAL OF CATALYSIS

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<sub>3</sub> clusters deposited on ultrathin Al<sub>2</sub>O<sub>3</sub> 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



E-mail address: wangye@xmu.edu.cn (Y. Wang).

<sup>0021-9517/\$ -</sup> see front matter @ 2012 Elsevier Inc. All rights reserved. http://dx.doi.org/10.1016/j.jcat.2012.11.032

 $C_{3}H_{6}$ , while Cu(111) favors the formation of propylene metallacycle, an intermediate for PO formation, owing to the lower basicity of adsorbed oxygen species on Cu(111) [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<sub>2</sub>O by  $O_2$ . Several studies have claimed the epoxidation of  $C_3H_6$  by  $O_2$ over metallic Cu (Cu<sup>0</sup>)-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<sub>2</sub> partial pressure led to a decrease in PO selectivity to <5% over these catalysts, possibly due to the transformation of Cu<sup>0</sup> to oxidized copper species (Cu<sup>I</sup> or Cu<sup>II</sup>) [29,30]. A recent study showed that the addition of a small amount of Cu to Ag/ BaCO<sub>3</sub> 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<sup>+</sup>, which started from Cu<sup>II</sup> 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<sup>0</sup>-based catalysts [29,30]. The superior performance of these supported CuO<sub>x</sub> catalysts was further demonstrated by other groups [35,36]. The modification of CuO<sub>x</sub> with VO<sub>x</sub> or RuO<sub>x</sub> could enhance its activity and selectivity for PO formation [37–40].

However, it is noteworthy that supported  $\text{CuO}_x$  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  $\text{CuO}_x$ -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<sup>+</sup>) 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<sup>1</sup> 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<sub>x</sub>/SiO<sub>2</sub> and the alkali-metal-ion-modified CuO<sub>x</sub>/SiO<sub>2</sub> 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<sub>3</sub>)<sub>2</sub> 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<sup>II</sup>, catalysts containing Cu<sup>0</sup> and Cu<sup>I</sup> as the starting copper species were also prepared, to gain insights into the changes of Cu<sup>0</sup> and Cu<sup>I</sup> under our reaction conditions and the possible active sites. The catalyst containing Cu<sup>0</sup> was produced by treating the catalyst prepared above in a H<sub>2</sub>–He gas flow  $[P(H_2) = 10.1 \text{ kPa}]$  at 773 K for 30 min, while that containing Cu<sup>I</sup> was obtained by treating this reduced catalyst in a N<sub>2</sub>O–He gas flow  $[P(N_2O) = 20.3 \text{ K}]$  at 573 K for 30 min. Generally, a lower temperature is employed in N<sub>2</sub>O oxidation for the generation of Cu<sup>I</sup> on the surfaces of Cu<sup>0</sup> particles while the bulk is kept as Cu<sup>0</sup> [45]. We found that a higher temperature (573 K) used for N<sub>2</sub>O oxidation could transform the whole Cu<sup>0</sup> particles in the reduced catalyst to Cu<sub>2</sub>O particles. We confirmed that no Cu<sup>II</sup> or CuO was generated during the oxidation of the reduced catalyst by N<sub>2</sub>O 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<sup>-1</sup>) and  $O_2$  (10 mL min<sup>-1</sup>) at 823 K for 0.5 h, followed by purging with He (60 mL min<sup>-1</sup>) 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<sub>3</sub>H<sub>6</sub> and O<sub>2</sub>. 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  $\times$  0.53 mm  $\times$  1.0  $\mu$ m) 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<sup>-1</sup>, 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 K $\alpha$  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<sub>2</sub> 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<sub>2</sub> 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.

H<sub>2</sub> temperature-programmed reduction (H<sub>2</sub> TPR) and NH<sub>3</sub> temperature-programmed desorption (NH<sub>3</sub> TPD) were carried out using a Micromeritics AutoChem II 2920 instrument. Typically, the sample (0.1 g) was pretreated in a quartz reactor with a gas flow containing O<sub>2</sub> and He at 823 K for 1 h, followed by purging with high-purity He. For H<sub>2</sub> TPR measurements, after the sample was cooled down to 303 K, a H<sub>2</sub>-Ar (5 vol.% H<sub>2</sub>) mixture was introduced into the reactor and the temperature was raised to 1173 K at a rate of 10 K min<sup>-1</sup>. The consumption of  $H_2$  was monitored by a thermal conductivity detector. For NH<sub>3</sub> TPD measurements, the adsorption of NH<sub>3</sub> was performed at 393 K in an NH<sub>3</sub>-He mixture (10 vol.% NH<sub>3</sub>) for 1 h, and the remaining or weakly adsorbed NH<sub>3</sub> was purged with high-purity He. TPD was performed in He flow by raising the temperature to 1000 K at a rate of 10 K min<sup>-1</sup>. The desorbed NH<sub>3</sub> was detected with a mass spectrometer (ThermoStar GSD 301 T2) by monitoring the signal with m/e = 16.

In situ FT-IR spectroscopy studies of CO adsorption were carried out with a Nicolet FTIR 380 or Nicolet 6700 instrument equipped with an MCT detector. Transmission FT-IR spectra were recorded with a resolution of 4 cm<sup>-1</sup>. The sample was pressed into a self-supporting wafer and was placed in an in situ IR cell, where it could be treated directly under different conditions.

# 3. Results

# 3.1. Catalytic behavior of Cs<sup>+</sup>-modified CuO<sub>x</sub>/SiO<sub>2</sub> catalysts

Table 1 shows the effect of the modification of the 5 wt%  $CuO_{y}$ SiO<sub>2</sub> catalyst by various alkali metal ions on the catalytic performance in epoxidation of C<sub>3</sub>H<sub>6</sub> by O<sub>2</sub>. The CuO<sub>x</sub>/SiO<sub>2</sub> without modification exhibited a high C<sub>3</sub>H<sub>6</sub> conversion (15%) but a low PO selectivity (1.8%). The main partial oxidation product was acrolein (selectivity 49%) over this catalyst. This is consistent with the consensus that the supported  $CuO_x$  catalyzes the allylic oxidation of  $C_3H_6$  [41–44]. The modification of  $CuO_x/SiO_2$  by an alkali metal ion decreased the conversion of C<sub>3</sub>H<sub>6</sub> and the selectivity to acrolein. At the same time, the selectivity to PO increased significantly, and the yield of PO also increased remarkably despite the decrease in C<sub>3</sub>H<sub>6</sub> conversion. With the alkali metal ion changed from Li<sup>+</sup> to Cs<sup>+</sup> in the modified catalysts, although there was no definite trend in the change of C<sub>3</sub>H<sub>6</sub> conversion, the selectivity to PO increased in the order  $\text{Li}^+ < \text{Na}^+ \approx \text{K}^+ < \text{Rb}^+ < \text{Cs}^+$ . The selectivity to PO over the  $Cs^+$ – $CuO_x/SiO_2$  catalyst reached 34% at a  $C_3H_6$  conversion of 7.5%. A PO yield of 2.6% was attained, which was  $\sim$ 10 times higher than that over the 5 wt% CuO<sub>x</sub>/SiO<sub>2</sub> catalyst. Although the selectivity to  $CO_x$  was increased by modification with alkali metal ions, the Cs<sup>+-</sup>  $-CuO_x/SiO_2$  catalyst exhibited the lowest selectivity to  $CO_x$  among all the alkali-metal-ion-modified catalysts displayed in Table 1. This catalyst exhibited a better PO formation activity than the K<sup>+</sup>-CuO<sub>x</sub>/SBA-15 catalyst reported in our previous studies, which provided PO selectivity of  $\sim 20\%$  at a C<sub>3</sub>H<sub>6</sub> conversion of  $\sim 5\%$  [32]. Table 2 shows the effect of the Cs/Cu molar ratio on catalytic performances of the Cs<sup>+</sup>-modified CuO<sub>x</sub>/SiO<sub>2</sub> catalysts in the epoxidation of C<sub>3</sub>H<sub>6</sub> by O<sub>2</sub> at 523 K. It should be mentioned that no conversion of C<sub>3</sub>H<sub>6</sub> has been observed over Cs<sup>+</sup>/SiO<sub>2</sub> without loading CuO<sub>x</sub>, confirming that CuO<sub>x</sub> accounts for the oxidation of C<sub>3</sub>H<sub>6</sub> by O<sub>2</sub>. Table 2 clarified that the addition of Cs<sup>+</sup> to the CuO<sub>x</sub>/SiO<sub>2</sub> catalyst, even with a low content (Cs/Cu = 0.1), caused a decrease in the conversion of C<sub>3</sub>H<sub>6</sub>. However, as the ratio of Cs/Cu rose from 0.1 to 0.4, the conversion of C<sub>3</sub>H<sub>6</sub> did not change significantly. At the same time, the selectivity to PO increased gradually from 15% to 34%. A further increase in the Cs/Cu ratio decreased both C<sub>3</sub>H<sub>6</sub> conversion and PO selectivity. Thus, the Cs<sup>+</sup>-5 wt% CuO<sub>x</sub>/SiO<sub>2</sub> catalyst with a Cs/Cu ratio of 0.4 afforded the highest PO yield. Accompanied by an increase in the selectivity to PO, the selectivity to acrolein declined.

# 3.2. Kinetic and reaction route studies for 5 wt% $CuO_x/SiO_2$ catalysts with and without $Cs^+$ modification

Fig. 1 shows the dependence of catalytic performance on reaction temperature under O<sub>2</sub>-rich conditions, that is,  $P(O_2)/P(C_3H_6) = 39/1$  $[P(O_2) = 98.8 \text{ kPa}, P(C_3H_6) = 2.53 \text{ kPa}]$ , for the 5 wt% CuO<sub>x</sub>/SiO<sub>2</sub> and the Cs<sup>+</sup>–5 wt% CuO<sub>x</sub>/SiO<sub>2</sub> (Cs/Cu = 0.4) catalysts. The conversion of C<sub>3</sub>H<sub>6</sub> over both catalysts increased almost exponentially with reaction temperature. The apparent activation energies of C<sub>3</sub>H<sub>6</sub> conversions calculated using the Arrhenius plots were 64 and 56 kJ mol<sup>-1</sup> over the  $CuO_x/SiO_2$  and the  $Cs^+$ - $CuO_x/SiO_2$  catalysts, respectively. Regarding the product selectivity, acrolein was the main product at low temperatures under  $O_2$ -rich conditions over the 5 wt% Cu $O_x/$ SiO<sub>2</sub> catalyst without Cs<sup>+</sup> modification (Fig. 1A). Besides acrolein and CO<sub>x</sub>, PO and allyl alcohol were also formed with lower selectivities. The increase in temperature decreased the selectivities to acrolein, PO, and allyl alcohol and increased that to CO<sub>x</sub>. After the modification by Cs<sup>+</sup>, PO was formed as a major product instead of acrolein (Fig. 1B). PO selectivity of 53% could be obtained at 473 K (C<sub>3</sub>H<sub>6</sub> conversion, 1.7%). Although the selectivity became significantly lower, acrolein was also formed after the modification by Cs<sup>+</sup>. However, no allyl alcohol was observed even at lower temperatures. The increase in temperature decreased the selectivity to PO, but a PO selectivity of  $\sim$ 23% could still be sustained at a C<sub>3</sub>H<sub>6</sub> conversion of 17% at 573 K, providing a PO yield of 3.9%.

We have also investigated the effect of temperature on catalytic behavior over the 5 wt%  $CuO_x/SiO_2$  and the Cs<sup>+</sup>–5 wt%  $CuO_x/SiO_2$  (Cs/Cu = 0.4) catalysts under conditions of  $P(O_2)/P(C_3H_6) = 1$  [ $P(O_2) = P(C_3H_6) = 50.7$  kPa]. Under such conditions, the conversion of C<sub>3</sub>H<sub>6</sub> over both catalysts was lower (Fig. 2). From the Arrhenius plots derived from the C<sub>3</sub>H<sub>6</sub> conversion rates versus reaction temperature, the apparent activation energies for the catalysts with and without Cs<sup>+</sup> modification were evaluated to be 63 and 62 kJ mol<sup>-1</sup>, similar to those under the O<sub>2</sub>-rich conditions. However, the selectivity patterns became somewhat different at

Table 1

Catalytic performance of 5 wt% CuO<sub>x</sub>/SiO<sub>2</sub> catalysts modified by different alkali metal ions.<sup>a</sup>

| Catalyst <sup>b</sup>                               | Conversion (%) | Selectivity (% | Selectivity (%) |                     |                 |      |  |  |
|---|----------------|----------------|-----------------|---------------------|-----------------|------|--|--|
|   |                | РО             | Acrolein        | Others <sup>c</sup> | CO <sub>x</sub> |      |  |  |
| CuO <sub>x</sub> /SiO <sub>2</sub>                  | 15             | 1.8            | 49              | 4.6                 | 42              | 0.27 |  |  |
| $Li^+-CuO_x/SiO_2$                                  | 5.8            | 12             | 3.8             | 0.3                 | 84              | 0.70 |  |  |
| Na <sup>+</sup> -CuO <sub>x</sub> /SiO <sub>2</sub> | 8.0            | 22             | 6.7             | 0.5                 | 70              | 1.8  |  |  |
| $K^+$ – $CuO_x/SiO_2$                               | 6.8            | 20             | 4.5             | 0.4                 | 75              | 1.4  |  |  |
| $Rb^+-CuO_x/SiO_2$                                  | 5.4            | 25             | 7.3             | 0.3                 | 68              | 1.4  |  |  |
| $Cs^+-CuO_x/SiO_2$                                  | 7.5            | 34             | 8.5             | 0.8                 | 57              | 2.6  |  |  |

<sup>a</sup> Reaction conditions: W = 0.2 g, T = 523 K, F = 60 mL min<sup>-1</sup>,  $P(C_3H_6) = 2.53$  kPa,  $P(O_2) = 98.8$  kPa.

<sup>b</sup> The molar ratio of alkali metal ion to Cu is 0.4.

<sup>c</sup> Other oxygenates include allyl alcohol, propanal, acetone, and acetaldehyde.

| Table 2  |
|--|
| Effect of the molar ratio of Cs/Cu on catalytic performance of Cs $^+$ -5 wt% CuO <sub>x</sub> /SiO <sub>2</sub> catalysts. <sup>a</sup> |

| Cs/Cu (Molar ratio) | Conversion (%) | Selectivity ( | PO yield (%) |                     |                 |      |
|---------------------|----------------|---------------|--------------|---------------------|-----------------|------|
|                     |                | РО            | Acrolein     | Others <sup>b</sup> | CO <sub>x</sub> |      |
| 0                   | 15             | 1.8           | 49           | 4.6                 | 42              | 0.27 |
| 0.1                 | 7.1            | 15            | 35           | 1.6                 | 48              | 1.1  |
| 0.2                 | 7.3            | 21            | 27           | 0.7                 | 51              | 1.5  |
| 0.4                 | 7.5            | 34            | 8.5          | 0.8                 | 57              | 2.6  |
| 0.6                 | 5.1            | 28            | 7.1          | 1.6                 | 64              | 1.4  |

<sup>a</sup> Reaction conditions: W = 0.2 g, T = 523 K, F = 60 mL min<sup>-1</sup>,  $P(C_3H_6) = 2.53$  kPa,  $P(O_2) = 98.8$  kPa.

<sup>b</sup> Other oxygenates include allyl alcohol, propanal, acetone, and acetaldehyde.



**Fig. 1.** Dependence of catalytic performance on reaction temperature: (A) 5 wt%  $CuO_x/SiO_2$ ; (B)  $Cs^+-5$  wt%  $CuO_x/SiO_2$  (Cs/Cu = 0.4). Reaction conditions: W = 0.20 g, F = 60 mL min<sup>-1</sup>,  $P(C_3H_6) = 2.53$  kPa,  $P(O_2) = 98.8$  kPa.

 $P(O_2)/P(C_3H_6) = 1$ . For the 5 wt% CuO<sub>x</sub>/SiO<sub>2</sub> catalyst, although acrolein was still a main product, allyl alcohol, and PO were also formed with considerable selectivity (>20% and >10%, respectively) at low temperatures (Fig. 2A). The increase in the temperature decreased the selectivity to allyl alcohol and PO and increased that to acrolein and CO<sub>x</sub>. On the other hand, over the Cs<sup>+</sup>-modified CuO<sub>x</sub>/SiO<sub>2</sub> catalyst at  $P(O_2)/P(C_3H_6) = 1$ , almost no allyl alcohol was observed (Fig. 2B). However, the selectivity to acrolein also became considerable (25–33%), although PO was still the main product.

To gain information about the reaction routes over the 5 wt%  $CuO_x/SiO_2$  and the  $Cs^+-5$  wt%  $CuO_x/SiO_2$  (Cs/Cu = 0.4) catalysts, we have investigated the dependence of catalytic performance on the pseudo contact time, which is expressed as the ratio of catalyst weight to total flow rate (W/F). Fig. 3 shows the results at 523 K under  $O_2$ -rich conditions [ $P(O_2)/P(C_3H_6) = 39/1$ ]. The conversion of  $C_3H_6$  increased almost proportionally to the contact time over both catalysts. We evaluated the rates of  $C_3H_6$  conversion,  $r(C_3H_6)$ , using the slopes of these straight lines;  $r(C_3H_6)$  were 2.9 and 1.6 mmol h<sup>-1</sup> g<sup>-1</sup> at 523 K over the catalysts with and without  $Cs^+$  modification, respectively. Thus, the modification by  $Cs^+$  decreased the  $C_3H_6$  conversion rate by a factor of 0.55. The main products were acrolein and  $CO_x$  over the 5 wt%  $CuO_x/SiO_2$ , and the increase in the contact time decreased the selectivity to acrolein and increased that to  $CO_x$ . PO was a main product over



**Fig. 2.** Dependence of catalytic performance on reaction temperature: (A) 5 wt% CuO<sub>x</sub>/SiO<sub>2</sub>; (B) Cs<sup>+</sup>-5 wt% CuO<sub>x</sub>/SiO<sub>2</sub> (Cs/Cu = 0.4). Reaction conditions: W = 0.20 g, F = 60 mL min<sup>-1</sup>,  $P(C_3H_6) = P(O_2) = 50.7$  kPa.

the Cs<sup>+</sup>–5 wt% CuO<sub>x</sub>/SiO<sub>2</sub> catalyst, and a PO selectivity of 63% was attained at a C<sub>3</sub>H<sub>6</sub> conversion of 1.1% at a shorter contact time (Fig. 3B). Acrolein could still be obtained with a selectivity of >10% at shorter contact times. The increase in the contact time decreased the selectivity to PO and acrolein and increased that to  $CO_x$ .

Fig. 4 shows the dependence of the catalytic performance of the 5 wt%  $CuO_x/SiO_2$  and the Cs<sup>+</sup>-5 wt%  $CuO_x/SiO_2$  (Cs/Cu = 0.4) catalysts on the contact time at 523 K at  $P(O_2)/P(C_3H_6) = 1/1$ . From the linear relationship between C<sub>3</sub>H<sub>6</sub> conversion and contact time, the rates of  $C_3H_6$  conversion were calculated to be 5.3 and 5.1 mmol  $g^{-1} \ h^{-1}$  for the 5 wt%  $CuO_x/SiO_2$  and the  $Cs^+\text{--}5$  wt%  $CuO_x/$ SiO<sub>2</sub>, respectively. Thus, although  $C_3H_6$  conversion was lower at  $P(O_2)/P(C_3H_6) = 1/1$ , the rates of  $C_3H_6$  conversion were higher. Moreover, the difference in the rates of C<sub>3</sub>H<sub>6</sub> conversion between catalysts with and without Cs modification was smaller. At shorter contact times. PO and allvl alcohol also formed with considerable selectivities, besides acrolein, over the 5 wt% CuO<sub>x</sub>/SiO<sub>2</sub> catalyst. The increase in the contact time decreased the selectivity to PO and increased that to allyl alcohol and acrolein slightly. The selectivity to CO<sub>x</sub> also increased with the contact time. On the other hand, over the Cs<sup>+</sup>-5 wt% CuO<sub>x</sub>/SiO<sub>2</sub> catalyst, almost no allyl alcohol was formed over the whole range of contact times. PO and acrolein were both formed, and the selectivity to PO was signifi-



**Fig. 3.** Dependence of catalytic performance on contact time: (A) 5 wt% CuO<sub>x</sub>/SiO<sub>2</sub>; (B) Cs<sup>+</sup>-5 wt% CuO<sub>x</sub>/SiO<sub>2</sub> (Cs/Cu = 0.4). Reaction conditions: W = 0.025 - 0.30 g, T = 523 K, F = 60 mL min<sup>-1</sup>,  $P(C_3H_6) = 2.53$  kPa,  $P(O_2) = 98.8$  kPa.



**Fig. 4.** Dependence of catalytic performance on contact time: (A) 5 wt% CuO<sub>x</sub>/SiO<sub>2</sub>; (B) Cs<sup>+</sup>-5 wt% CuO<sub>x</sub>/SiO<sub>2</sub> (Cs/Cu = 0.4). Reaction conditions: W = 0.025 - 0.30 g, T = 523 K, F = 60 mL min<sup>-1</sup>,  $P(C_3H_6) = P(O_2) = 50.7$  kPa.

cantly higher than that of acrolein. The increase in the contact time decreased the selectivity to PO and increased that to  $CO_x$ .

Fig. 5 shows the effects of partial pressure of O<sub>2</sub>, that is,  $P(O_2)$ , on catalytic performances over 5 wt% CuO<sub>x</sub>/SiO<sub>2</sub> and Cs<sup>+</sup>–5 wt% CuO<sub>x</sub>/SiO<sub>2</sub> (Cs/Cu = 0.4) catalysts at a fixed partial pressure of C<sub>3</sub>H<sub>6</sub> [ $P(C_3H_6) = 50.7$  kPa]. Over both catalysts, the rate of C<sub>3</sub>H<sub>6</sub> conversion increased with increasing  $P(O_2)$ . From the plots of the logarithm of  $r(C_3H_6)$  against the logarithm of  $P(O_2)$ , we obtained



**Fig. 5.** Effect of partial pressure of O<sub>2</sub> on catalytic performance: (A) 5 wt% CuO<sub>x</sub>/SiO<sub>2</sub>; (B) Cs<sup>+</sup>-5 wt% CuO<sub>x</sub>/SiO<sub>2</sub> (Cs/Cu = 0.4). Reaction conditions: W = 0.20 g, T = 523 K, F = 60 mL min<sup>-1</sup>,  $P(C_3H_6) = 50.7$  kPa.

reaction orders of 0.51 and 0.54 with respect to  $O_2$  over the catalysts without and with  $Cs^+$  modification, respectively. For the catalyst without  $Cs^+$  modification, acrolein, PO, and allyl alcohol were all formed, as well as  $CO_x$  and small amounts of other products, including propionaldehyde and acetaldehyde. With increasing  $P(O_2)$ , the selectivity to PO and ally alcohol decreased and that to acrolein increased. The selectivity to  $CO_x$  changed only slightly at the same time. After modification with  $Cs^+$ , the selectivity to PO became higher, while that to acrolein became lower. Allyl alcohol was formed with a lower selectivity to allyl alcohol and increase in  $P(O_2)$  decreased the selectivity to allyl alcohol and increased that to acrolein. The selectivity to PO and  $CO_x$  did not change significantly with changing  $P(O_2)$ .

The effects of  $P(C_3H_6)$  on the rates of  $C_3H_6$  conversion and the product selectivity over the 5 wt%  $CuO_x/SiO_2$  and the  $Cs^+-5$  wt%  $CuO_x/SiO_2$  (Cs/Cu = 0.4) catalysts at a fixed  $P(O_2)$  (50.7 kPa) are displayed in Fig. 6. From the plots of the logarithm of  $r(C_3H_6)$  against the logarithm of  $P(C_3H_6)$ , we obtained reaction orders of 0.58 and 0.55 with respect to  $C_3H_6$  over the catalysts without and with  $Cs^+$  modification, respectively. Thus, we could express the rate equations for these two catalysts as follows:

for 5 wt% CuO<sub>x</sub>/SiO<sub>2</sub> : 
$$r(C_3H_6) = k_1 P(C_3H_6)^{0.58} P(O_2)^{0.51}$$
; (1)  
for Cs<sup>+</sup> - 5 wt% CuO<sub>x</sub>/SiO<sub>2</sub> :  $r(C_3H_6) = k_2 P(C_3H_6)^{0.55} P(O_2)^{0.54}$ , (2)

where  $k_1$  and  $k_2$  were the apparent rate constants for the two catalysts. At a fixed  $P(O_2)$ , an increase in  $P(C_3H_6)$  increased the selectivity to PO and acrolein and decreased that to  $CO_x$  over the 5 wt%  $CuO_x/SiO_2$  catalyst. The selectivity to allyl alcohol did not vary significantly at the same time. Over the  $Cs^+-5$  wt%  $CuO_x/SiO_2$  catalyst, the increase in  $P(C_3H_6)$  also increased the selectivity to PO and acrolein and decreased that to  $CO_x$ , but almost no allyl alcohol was formed in the whole range of  $P(C_3H_6)$  in this case.

To further clarify the reaction routes, we have performed the conversion of PO over the  $5 \text{ wt\% CuO}_x/\text{SiO}_2$  and the  $\text{Cs}^+-5 \text{ wt\%}$   $\text{CuO}_x/\text{SiO}_2$  (Cs/Cu = 0.4) catalysts. Table 3 shows that PO could be



**Fig. 6.** Effect of partial pressure of  $C_3H_6$  on catalytic performance: (A) 5 wt% CuO<sub>x</sub>/SiO<sub>2</sub>; (B) Cs<sup>+</sup>-5 wt% CuO<sub>x</sub>/SiO<sub>2</sub> (Cs/Cu = 0.4). Reaction conditions: W = 0.2 g, T = 523 K, F = 60 mL min<sup>-1</sup>,  $P(O_2) = 50.7$  kPa.

converted considerably over the 5 wt% CuO<sub>x</sub>/SiO<sub>2</sub> catalyst. An increase in  $P(O_2)$  at 523 K or an increase in temperature at  $P(O_2)$  of 84 kPa increased the conversion of PO significantly over this catalyst. Propanal was formed as a main product, together with allyl alcohol and acrolein, in the absence of O<sub>2</sub>. The former two products should be formed by the isomerization of PO [46], while acrolein may be formed by the oxidation of allyl alcohol by lattice oxygen on the catalyst surface. In the presence of O<sub>2</sub>, allyl alcohol and acrolein became two predominant products over the 5 wt% CuO<sub>x</sub>/SiO<sub>2</sub> catalyst. An increase in temperature decreased the selectivity to allyl alcohol and increased that to acrolein, confirming that acrolein was formed by the oxidation of allyl alcohol. On the other hand, over the Cs<sup>+</sup>-5 wt% CuO<sub>x</sub>/SiO<sub>2</sub> (Cs/Cu = 0.4) catalyst, the conversion of PO became significantly lower. This clearly indicates that the modification by Cs<sup>+</sup> inhibits the conversion of PO. Although allyl

#### Table 3

Conversion of PO over 5 wt% CuO<sub>x</sub>/SiO<sub>2</sub> and Cs<sup>+</sup>-5 wt% CuO<sub>x</sub>/SiO<sub>2</sub> (Cs/Cu = 0.4) catalysts.<sup>a</sup>

alcohol and acrolein were still two main products, the selectivity to  $CO_x$  increased in most cases over the  $Cs^+-5$  wt%  $CuO_x/SiO_2$  (Cs/ Cu = 0.4) catalyst.

# 3.3. Characterizations of fresh CuO<sub>x</sub>/SiO<sub>2</sub> and alkali-metal-ionmodified CuO<sub>x</sub>/SiO<sub>2</sub> catalysts

The XRD patterns for the 5 wt% CuO<sub>x</sub>/SiO<sub>2</sub> samples modified by different alkali metal ions are displayed in Fig. 7A. A broad peak at  $2\theta$  of  $22^{\circ}$ – $23^{\circ}$ , assignable to the amorphous silica, was observed for all the samples. The 5 wt% CuO<sub>x</sub>/SiO<sub>2</sub> exhibited two distinct diffraction peaks at  $2\theta$  of  $35.4^{\circ}$  and  $38.6^{\circ}$ , and these peaks could be ascribed to the  $(\overline{1}11)$  and (111) reflections of monoclinic CuO. Although these diffraction peaks still remained after modification with alkali metal ions, the peaks became significantly weakened and broadened, suggesting that the crystallite size of CuO became smaller, possibly due to strong interactions between CuO and the alkali metal ions. We have estimated the sizes of CuO crystallites in these samples using the Scherrer equation, and the results are summarized in Table 4. The size of CuO crystallites decreased dramatically from 29 to 7.8 nm after modification by Cs<sup>+</sup>. These observations indicate an enhancement in the dispersion of the CuO phase after modification with alkali metal ions, although the BET surface areas for the modified samples become lower (Table 4).

The XRD patterns for the Cs<sup>+</sup>–5 wt% CuO<sub>x</sub>/SiO<sub>2</sub> catalysts with different Cs/Cu ratios (Fig. 7B) showed that the diffraction peaks ascribed to CuO crystallites became weakened and broadened with an increase in the ratio of Cs/Cu. At a Cs/Cu ratio to 0.6, the diffraction peaks of CuO crystallites almost disappeared, and only a broad peak at  $2\theta$  of ~23°, belonging to amorphous SiO<sub>2</sub>, was observed. The crystallite sizes of CuO calculated by the Scherrer equation are also listed in Table 4. The increase in the ratio of Cs/Cu decreased the size of CuO crystallites.

Fig. 8 displays the typical TEM micrographs for the 5 wt% CuO<sub>x</sub>/ SiO<sub>2</sub> catalysts modified by different alkali metal ions. CuO nanoparticles were found to be dispersed homogeneously on SiO<sub>2</sub> over each catalyst. The mean sizes of CuO nanoparticles in these samples have been evaluated by counting 100–200 particles and are listed in Table 4. The mean size of CuO particles was 18 nm over the 5 wt% CuO<sub>x</sub>/SiO<sub>2</sub> catalyst, and modification with an alkali metal ion significantly decreased the CuO particle size. With the alkali metal ion changed from Li<sup>+</sup> to Cs<sup>+</sup>, the mean size of the CuO nanoparticles decreased in the order Li<sup>+</sup> > Na<sup>+</sup> > K<sup>+</sup> > Rb<sup>+</sup> > Cs<sup>+</sup>. For the Cs<sup>+</sup>-5 wt% CuO<sub>x</sub>/SiO<sub>2</sub> (Cs/Cu = 0.4) catalyst, the mean CuO particle size was 5.8 nm. This tendency is in agreement with that observed

| Catalyst                           | $P(O_2)$ (kPa) | <i>T</i> (K) | Conv. (%) | Selectivity (%) <sup>b</sup> |               |          |                 |
|------------------------------------|----------------|--------------|-----------|------------------------------|---------------|----------|-----------------|
|                                    |                |              |           | Propanal                     | Allyl alcohol | Acrolein | CO <sub>x</sub> |
| CuO <sub>x</sub> /SiO <sub>2</sub> | 0              | 523          | 9.7       | 67                           | 19            | 12       | 0               |
|                                    | 8.4            | 523          | 24        | 0.5                          | 15            | 59       | 14              |
|                                    | 34             | 523          | 31        | 0.7                          | 10            | 70       | 16              |
|                                    | 84             | 523          | 48        | 0                            | 11            | 75       | 10              |
|                                    | 84             | 473          | 12        | 1.6                          | 42            | 47       | 0               |
|                                    | 84             | 498          | 25        | 0.4                          | 30            | 57       | 5.5             |
|                                    | 84             | 548          | 80        | 0                            | 4.5           | 73       | 20              |
| $Cs^+-CuO_x/SiO_2$                 | 0              | 523          | 0.8       | 10                           | 54            | 25       | 0               |
|                                    | 8.4            | 523          | 2.9       | 0                            | 11            | 31       | 50              |
|                                    | 34             | 523          | 3.3       | 0                            | 9.0           | 30       | 57              |
|                                    | 84             | 523          | 3.7       | 0                            | 11            | 29       | 58              |
|                                    | 84             | 473          | 0.9       | 0                            | 69            | 25       | 0               |
|                                    | 84             | 498          | 2.0       | 0                            | 27            | 30       | 40              |
|                                    | 84             | 548          | 6.1       | 0                            | 9             | 25       | 65              |

<sup>a</sup> Reaction conditions: W = 0.05 g, F = 60 mL min<sup>-1</sup>, P(PO) = 0.084 kPa, P(Ar) = 8.4 kPa. He was used as a balance gas.

<sup>b</sup> Other products include acetaldehyde and acetone.

the acidity.



**Fig. 7.** XRD patterns: (A) 5 wt%  $CuO_x/SiO_2$  modified with different alkali metal ions (the molar ratio of alkali metal ion to Cu is 0.4); (B) Cs<sup>+</sup>–5 wt%  $CuO_x/SiO_2$  with different Cs/Cu molar ratios.

| Table 4       |   |                                      |        |
|---------------|---|--------------------------------------|--------|
| Some physical | properties of alkali-metal-ion-modified | CuO <sub>x</sub> /SiO <sub>2</sub> s | amples |

| Sample <sup>a</sup>                                 | Ratio of<br>alkali metal<br>ion to Cu | BET surface<br>area<br>(m <sup>2</sup> g <sup>-1</sup> ) | Crystallite<br>size of<br>CuO (nm) <sup>b</sup> | Mean size<br>of CuO<br>(nm) <sup>c</sup> |
|---|---------------------------------------|--|---|--|
| CuO <sub>x</sub> /SiO <sub>2</sub>                  | -                                     | 693  | 29  | 18                                       |
| Li <sup>+</sup> -CuO <sub>x</sub> /SiO <sub>2</sub> | 0.4                                   | 323  | 15  | 8.9                                      |
| $Na^+$ – $CuO_x/SiO_2$                              | 0.4                                   | 191  | 12  | 7.6                                      |
| K <sup>+</sup> -CuO <sub>x</sub> /SiO <sub>2</sub>  | 0.4                                   | 198  | 8.9   | 6.9                                      |
| Rb <sup>+</sup> -CuO <sub>x</sub> /SiO <sub>2</sub> | 0.4                                   | 230  | 8.5   | 6.3                                      |
| $Cs^+$ - $CuO_x/SiO_2$                              | 0.4                                   | 390  | 7.8   | 5.8                                      |
| $Cs^+-CuO_x/SiO_2$                                  | 0.1                                   | 401  | 24  | -  |
| $Cs^+-CuO_x/SiO_2$                                  | 0.2                                   | 329  | 20  | -  |
| $Cs^+-CuO_x/SiO_2$                                  | 0.6                                   | 214  | -   | -  |

<sup>a</sup> CuO loading in each sample is 5.0 wt%.

<sup>b</sup> Evaluated from XRD patterns using the Scherrer equation.

<sup>c</sup> Evaluated from TEM images.

from the XRD measurements, indicating the strongest interactions between CuO nanoparticles and Cs<sup>+</sup>.

The H<sub>2</sub>-TPR profiles for the 5 wt% CuO<sub>x</sub>/SiO<sub>2</sub> catalysts in the absence and in the presence of alkali-metal-ion modifiers are shown in Fig. 9. The main reduction peak for the 5 wt% CuO<sub>x</sub>/SiO<sub>2</sub> catalyst was observed at 573 K, and this peak was attributable to the reduction of CuO to Cu<sup>0</sup>. The modification by an alkali metal ion shifted this reduction peak to a higher temperature (Fig. 9A), and the peak temperature increased in the order Li<sup>+</sup> (595 K) < Na<sup>+</sup> (597 K)  $\approx$  K<sup>+</sup> (597 K)  $\approx$  Co<sup>+</sup> (602 K). The H<sub>2</sub> TPR profiles for the Cs<sup>+</sup>-5 wt% CuO<sub>x</sub>/SiO<sub>2</sub> catalysts with different ratios of Cs/Cu (Fig. 9B) showed that the content of Cs<sup>+</sup> did not significantly affect the peak temperature for the reduction of CuO. These observations further confirm the interaction between alkali metal ions and CuO, which retards the reduction of CuO.

Fig. 10 shows the NH<sub>3</sub> TPD profiles for 5 wt% CuO<sub>x</sub>/SiO<sub>2</sub> catalysts modified by different alkali metal ions. For pure silica, no desorption of NH<sub>3</sub> molecules was observed (Fig. 10A), suggesting that

there are no acid sites on SiO<sub>2</sub> prepared in our work. After the loading of CuO<sub>x</sub>, a broad NH<sub>3</sub> desorption peak appeared at  $\sim$ 520 K, indicating the generation of acid sites. Obviously, this desorption peak arises from the NH<sub>3</sub> molecules coordinated to surface Cu species. According to the electronic acid-base theory proposed by Lewis [47], a metal ion, which can accept an electron pair from another molecular entity, is defined as a Lewis acid. In our system, we speculate that Cu<sup>II</sup> on CuO nanoparticles may function as a Lewis acid. Such a Lewis acid may form an adduct with PO by sharing the electron pair furnished by the oxygen in the epoxy cycle, causing the isomerization of PO by breaking the C-O bond and opening the cycle [46]. After modification by an alkali metal ion, the peak of NH<sub>3</sub> desorption shifted to a lower temperature, and the peak temperature decreased in the order Li<sup>+</sup> ( $\sim$ 510 K) > Na<sup>+</sup> ( $\sim$ 508 K) > K<sup>+</sup>  $(\sim 505 \text{ K}) > \text{Rb}^+$  ( $\sim 500 \text{ K}$ ) > Cs<sup>+</sup> ( $\sim 497 \text{ K}$ ). For the Cs<sup>+</sup>-5 wt% CuO<sub>x</sub>/ SiO<sub>2</sub> series of catalysts with different Cs/Cu ratios, the peak temperature decreased as the Cs/Cu ratio increased from 0.1 to 0.4 (Fig. 10B). These observations suggest that the Lewis acidity ascribed to CuO nanoparticles is decreased after modification by an

# 3.4. Characterizations of $CuO_x/SiO_2$ and $Cs^*$ -modified $CuO_x/SiO_2$ catalysts under working conditions

alkali metal ion, and Cs<sup>+</sup> is the most efficient modifier to eliminate

To gain information on the crystalline phase in the working catalyst, we performed in situ XRD measurements for the 5 wt%  $CuO_x/$  $SiO_2$  and the Cs<sup>+</sup>-5 wt% CuO<sub>x</sub>/SiO<sub>2</sub> (Cs/Cu = 0.4) catalysts under reaction conditions. Fig. 11 shows the evolution of XRD patterns with reaction time for both catalysts in a gas flow containing  $C_3H_6$  and  $O_2$  [*P*( $C_3H_6$ ) = 50.7 kPa, *P*( $O_2$ ) = 50.7 kPa] after the pretreatment with  $O_2$ -containing He [ $P(O_2)$  = 8.4 kPa] at 823 K, which is similar to that used for catalytic reactions. The temperature was cooled down to 523 K after the pretreatment, and time zero denoted the point just before the introduction of the reactant gas. Two diffraction peaks at  $2\theta$  of  $35.5^{\circ}$  and  $38.6^{\circ}$  belonging to CuO were observed for both catalysts. After the introduction of the reactant gas of  $C_3H_6$  and  $O_2$  at 523 K, new diffraction peaks at  $2\theta$  of  $36.4^{\circ}$  and  $42.3^{\circ}$ , assignable to the (111) and (200) reflections of cubic Cu<sub>2</sub>O, appeared for the 5 wt% CuO<sub>x</sub>/SiO<sub>2</sub> catalyst after 10 min of reaction (Fig. 11A). These two diffraction peaks could be observed during the reaction at 523 K for 240 min. For the Cs<sup>+</sup>–5 wt% CuO<sub>x</sub>/SiO<sub>2</sub> catalyst, the diffraction peak at  $2\theta$  of 36.4° belonging to Cu<sub>2</sub>O could also be observed clearly after the introduction of the reactant gas, although the weak peak of (200) reflection of Cu<sub>2</sub>O at  $2\theta$  of 42.3° was hard to discern. These observations demonstrate that part of the CuO has been transformed into Cu<sub>2</sub>O in both catalysts during the reaction in the in situ XRD cell. It should be noted that the intensities of diffraction peaks of CuO for these two catalysts did not change significantly with the formation of Cu<sub>2</sub>O during the reaction. We speculate that this may be because the sensitivity of CuO is lower than that of Cu<sub>2</sub>O in XRD and only a small fraction of CuO has been transformed into Cu<sub>2</sub>O under our reaction conditions. Moreover, the in situ reaction might change the smoothness or roughness of the surface of the sample pellet pressed in the sample holder, increasing the difficulty in directly comparing the absolute intensities of XRD peaks.

We also investigated the evolution of XRD patterns for the catalysts containing Cu<sup>0</sup> and Cu<sup>1</sup> as the starting copper species, which were prepared by treating the calcined catalyst by H<sub>2</sub> reduction or by H<sub>2</sub> reduction followed by N<sub>2</sub>O oxidation, respectively (see Section 2.1). For the Cs<sup>+</sup>-5 wt% CuO<sub>x</sub>/SiO<sub>2</sub> catalyst treated by H<sub>2</sub> reduction, two diffraction peaks at 2 $\theta$  of 43.0° and 50.2° were observed (Fig. 12A, 0 min), which could be attributed to the (111) and (200) reflections of cubic Cu<sup>0</sup>. After the introduction of C<sub>3</sub>H<sub>6</sub> and O<sub>2</sub> at 523 K, these two peaks disappeared rapidly, and another



Fig. 8. TEM micrographs: (A) 5 wt% CuO<sub>x</sub>/SiO<sub>2</sub>, (B) Li<sup>+</sup>-5 wt% CuO<sub>x</sub>/SiO<sub>2</sub> (Li/Cu = 0.4), (C) Na<sup>+</sup>-5 wt% CuO<sub>x</sub>/SiO<sub>2</sub> (Na/Cu = 0.4), (D) K<sup>+</sup>-5 wt% CuO<sub>x</sub>/SiO<sub>2</sub> (K/Cu = 0.4), (E) Rb<sup>+</sup>-5 wt% CuO<sub>x</sub>/SiO<sub>2</sub> (Rb/Cu = 0.4), (F) Cs<sup>+</sup>-5 wt% CuO<sub>x</sub>/SiO<sub>2</sub> (Cs/Cu = 0.4).

two diffraction peaks at  $2\theta$  of  $36.4^{\circ}$  and  $42.3^{\circ}$  ascribed to  $Cu_2O$  were observed. These two peaks became weaker after 60 min of reaction, and at the same time, a shoulder peak at  $35.4^{\circ}$ , which could be ascribed to CuO, appeared. This shoulder peak of CuO became stronger with further prolongation of the reaction time. These observations clarify that  $Cu^0$  is unstable under the present reaction conditions and can be readily transformed into  $Cu_2O$ , part of which is further transformed into CuO after a longer reaction time.

For the Cs<sup>+</sup>–5 wt% CuO<sub>x</sub>/SiO<sub>2</sub> (Cs/Cu = 0.4) catalyst treated by H<sub>2</sub> reduction followed by N<sub>2</sub>O oxidation, only the diffraction peaks at  $2\theta$  of 36.4° and 42.3° attributed to Cu<sub>2</sub>O were observed (Fig. 12B,

0 min). This confirms that Cu<sub>2</sub>O can be formed as the sole copper phase by this pretreatment procedure. After the introduction of C<sub>3</sub>H<sub>6</sub> and O<sub>2</sub> at 523 K, the two diffraction peaks of Cu<sub>2</sub>O did not change significantly in the initial 30 min, but their intensities decreased gradually with further prolonging the reaction time. Simultaneously, the diffraction peak at 2 $\theta$  of 35.4° belonging to CuO appeared after 60 min and its intensity increased gradually with reaction time.

The results described demonstrate that the catalyst containing exclusively CuO,  $Cu_2O$ , or  $Cu^0$  as the starting copper phase will be transformed into a mixture of CuO and  $Cu_2O$  under our reaction conditions. However, the fraction of  $Cu_2O$  in the mixture depends



**Fig. 9.** H<sub>2</sub> TPR profiles: (A) 5 wt%  $CuO_x/SiO_2$  modified with different alkali metal ions (the molar ratio of alkali metal ion to Cu is 0.4); (B) Cs<sup>+</sup>-5 wt% CuO<sub>x</sub>/SiO<sub>2</sub> with different Cs/Cu molar ratios.



**Fig. 10.** NH<sub>3</sub> TPD profiles: (A) 5 wt% CuO<sub>x</sub>/SiO<sub>2</sub> modified with different alkali metal ions (the molar ratio of alkali metal ion to Cu is 0.4); (B) Cs<sup>\*</sup>-5 wt% CuO<sub>x</sub>/SiO<sub>2</sub> with different Cs/Cu molar ratios.

on the starting copper phase. The comparison of the intensities of diffraction peaks ascribed to  $Cu_2O (2\theta = 36.4^{\circ})$  and  $CuO (2\theta = 35.4^{\circ})$  after a longer time (300 min) of reaction suggests that the catalyst starting from the CuO phase (Fig. 11B) possesses a lower fraction of Cu<sub>2</sub>O than the catalyst starting from the Cu<sup>0</sup> and Cu<sub>2</sub>O phases (Fig. 12). The fractions of Cu<sub>2</sub>O in the latter two catalysts, that is,



**Fig. 11.** In situ XRD patterns for the catalyst, which has been pretreated with O<sub>2</sub>-containing He [ $P(O_2) = 8.4 \text{ kPa}$ ] at 823 K, under reaction conditions for different times: (A) 5 wt% CuO<sub>x</sub>/SiO<sub>2</sub>; (B) Cs<sup>+</sup>-5 wt% CuO<sub>x</sub>/SiO<sub>2</sub> (Cs/Cu = 0.4). Reaction conditions: *T* = 523 K,  $P(C_3H_6) = P(O_2) = 50.7 \text{ kPa}$ , *F* = 60 mL min<sup>-1</sup>.



**Fig. 12.** In situ XRD patterns for the Cs<sup>+</sup>–5 wt% CuO<sub>x</sub>/SiO<sub>2</sub> (Cs/Cu = 0.4) catalyst under reaction conditions for different times. Reaction conditions: T = 523 K,  $P(C_3H_6) = P(O_2) = 50.7$  kPa, F = 60 mL min<sup>-1</sup>. The catalyst has been pretreated with different procedures: (A) pretreated with H<sub>2</sub>-containing He [ $P(H_2) = 10.1$  kPa] at 773 K; (B) pretreated with H<sub>2</sub>-containing He [ $P(H_2) = 10.1$  kPa] at 773 K; followed by N<sub>2</sub>O [ $P(N_2O = 20.3$  kPa] oxidation at 573 K.

the catalysts starting from  $Cu^0$  and  $Cu_2O$ , after 300 min of reaction were quite similar to each other.

We further performed FT-IR studies using CO as a probing molecule for the 5 wt%  $CuO_x/SiO_2$  and the Cs<sup>+</sup>-5 wt%  $CuO_x/SiO_2$  (Cs/ Cu = 0.4) catalysts after different pretreatments and subsequent reactions. It is known that CO can be adsorbed strongly onto Cu<sup>1</sup> sites, whereas the adsorption of CO onto Cu<sup>II</sup> or Cu<sup>0</sup> sites is weak at room temperature [48,49]. Thus, the CO-adsorbed FT-IR studies can provide insights into the chemical states of copper on catalyst surfaces during the reaction. For the 5 wt% CuO<sub>x</sub>/SiO<sub>2</sub> catalyst after the pretreatment with  $O_2[P(O_2) = 8.4 \text{ kPa}]$  at 823 K, a weak IR band at 2129 cm<sup>-1</sup> was observed (Fig. 13A, curve a), while almost no IR band could be observed for the Cs<sup>+</sup>-5 wt% CuO<sub>x</sub>/SiO<sub>2</sub> catalyst after the same oxidative pretreatment (Fig. 13B, curve a). These observations are in agreement with the consensus that the adsorption of CO on  $Cu^{II}$  is very weak. CO adsorbed onto the 5 wt%  $CuO_x/SiO_2$ and the  $Cs^+$ -5 wt% CuO<sub>x</sub>/SiO<sub>2</sub> catalysts after H<sub>2</sub> reduction showed IR bands at 2120 and 2101 cm<sup>-1</sup>, respectively (curve b of Fig. 13A and B), and both peaks could be ascribed to CO adsorbed onto metallic Cu<sup>0</sup> [49]. The pretreatments of the 5 wt% CuO<sub>x</sub>/SiO<sub>2</sub> and the  $Cs^+$ -5 wt%  $CuO_x/SiO_2$  catalysts with H<sub>2</sub> followed by N<sub>2</sub>O oxidation provided strong IR bands at 2129 and 2123 cm<sup>-1</sup>, respectively (curve c of Fig. 13A and B). These bands were attributable to CO strongly adsorbed on Cu<sup>1</sup> sites [48–51]. After the reaction in a  $C_3H_6$  and  $O_2$  mixture [ $P(C_3H_6) = 50.7$  kPa,  $P(O_2) = 50.7$  kPa] at 523 K, intense IR bands of CO adsorption at  $2129 \text{ cm}^{-1}$  (for 5 wt%  $CuO_x/SiO_2$ ) and 2123 cm<sup>-1</sup> (Cs<sup>+</sup>-5 wt% CuO<sub>x</sub>/SiO<sub>2</sub>) were observed for the catalysts with all three different pretreatments (curves d, e and f of Fig. 13A and B). These observations suggest the presence of Cu<sup>1</sup> sites on catalyst surfaces after the reactions, irrespective of the pretreatment procedures. However, the intensity of the IR band of CO adsorption after the reaction over the 5 wt% CuO<sub>x</sub>/SiO<sub>2</sub> and the Cs<sup>+</sup>–5 wt% CuO<sub>x</sub>/SiO<sub>2</sub> catalysts was dependent on the pretreatment procedure, and pretreatment with O<sub>2</sub> led to a relatively lower intensity of IR band at 2129 or 2123 cm<sup>-1</sup>.

The results obtained from in situ XRD and CO-adsorbed FT-IR studies are in harmony with each other and have provided useful information on the chemical state of copper species during the reaction. In short, it becomes clear that  $Cu^{I}$  is generated during the reactions over both the 5 wt%  $CuO_{x}/SiO_{2}$  and the  $Cs^{+}-5$  wt%  $CuO_{x}/SiO_{2}$  catalysts, which have been pretreated with O<sub>2</sub>-containing He gas (similarly to the pretreatment used for catalytic reactions) and contain  $Cu^{II}$  as the starting copper species. We have further demonstrated that  $Cu^{0}$  species over the 5 wt%  $CuO_{x}/SiO_{2}$  and the  $Cs^{+}-5$  wt%  $CuO_{x}/SiO_{2}$  catalysts pretreated with H<sub>2</sub> would be transformed rapidly into  $Cu^{I}$  and then into a mixture of  $Cu^{II}$  as the sole starting copper species would also undergo changes during the reaction, and part of  $Cu^{I}$  would be transformed into  $Cu^{II}$ .

## 3.5. Pulse-reaction studies and catalyst stability

The lattice oxygen has been proposed to account for the allylic oxidation of propylene to acrolein over metal oxide catalysts including  $CuO_x$ -based catalysts [42,44,52]. To uncover the role of the lattice oxygen in the conversion of  $C_3H_6$  in our case, we have performed reactions of  $C_3H_6$  pulses with the 5 wt%  $CuO_x/SiO_2$  and



**Fig. 13.** FT-IR spectra of adsorbed CO over (A) 5 wt% CuO<sub>x</sub>/SiO<sub>2</sub> and (B) Cs<sup>+</sup>-5 wt% CuO<sub>x</sub>/SiO<sub>2</sub> (Cs/Cu = 0.4) after different pretreatments and subsequent catalytic reactions. (a) Pretreatment with O<sub>2</sub>-contaning He [ $P(O_2) = 8.4$  kPa] at 823 K; (b) pretreatment with H<sub>2</sub>-contaning He [ $P(H_2) = 16.9$  kPa] at 773 K; (c) pretreatment with H<sub>2</sub>-contaning He [ $P(H_2) = 16.9$  kPa] at 773 K; (c) pretreatment with N<sub>2</sub>O [ $P(N_2O) = 16.9$  kPa] at 573 K; (d) reaction for 1 h after (a); (e) reaction for 1 h after (b); (f) reaction for 1 h after (c). Reaction conditions: T = 523 K,  $P(C_3H_6) = -P(O_2) = 50.7$  kPa, F = 60 mL min<sup>-1</sup>.

the  $Cs^+-5$  wt%  $CuO_x/SiO_2$  (Cs/Cu = 0.4) samples pretreated with O<sub>2</sub>-containing He at 823 K, followed by purging with He at the same temperature and cooling down to 523 K in He. Table 5 shows that the reaction of the  $C_3H_6$  pulse with the 5 wt%  $CuO_x/SiO_2$  at 523 K produces acrolein as the predominant product (selectivity  $\ge$  95%), together with a small amount of CO<sub>x</sub>. The amount of  $C_3H_6$  converted or the conversion of  $C_3H_6$  decreased with an increasing number of successively introduced C<sub>3</sub>H<sub>6</sub> pulses, and almost no products could be detected after the reactions with  $\sim$ 62 C<sub>3</sub>H<sub>6</sub> pulses. By assuming that the lattice oxygen species associated with  $Cu^{II}$  were consumed by  $C_3H_6$  to form acrolein, CO and  $CO_2$ , we estimated that the reduction degree of  $Cu^{II}$  to  $Cu^{I}$  was ~4.0% for the 5 wt%  $CuO_x/SiO_2$ . Similarly, the reaction of  $C_3H_6$  pulses with the  $Cs^+-5$  wt%  $CuO_x/SiO_2$  also provided acrolein as the main product (selectivity  $\ge$  75%), together with CO<sub>x</sub>. However, the reactivity of the lattice oxygen in the Cs<sup>+</sup>-modified sample decreased drastically, becoming ~one order of magnitude lower than that in the sample without Cs<sup>+</sup> modification (Table 5). The estimated reduction degree decreased to  $\sim 0.34\%$  for the sample modified with Cs<sup>+</sup>. These results clearly demonstrate that the lattice oxygen species is responsible for the allylic oxidation of C<sub>3</sub>H<sub>6</sub> to acrolein over our catalysts, and the presence of Cs<sup>+</sup> modifier remarkably suppresses the reactivity of the lattice oxygen. It is worth mentioning that no PO could be detected in these experiments, suggesting that the lattice oxygen does not participate in the epoxidation route.

The pulse-reaction technique may also provide information on the catalytic behavior of the catalyst instantly after pretreatment, which may contain a peculiar active species unstable under reaction conditions [53]. To gain information on the catalytic behavior of the Cs<sup>+</sup>–5 wt% CuO<sub>x</sub>/SiO<sub>2</sub> (Cs/Cu = 0.4) catalyst containing Cu<sup>0</sup>, Cu<sup>I</sup>, or Cu<sup>II</sup> as the starting copper species, we have performed reactions of  $(C_3H_6 + O_2)$  pulses over this catalyst after different pretreatments. The results are displayed in Fig. 14. For the catalyst pretreated with O<sub>2</sub>-containing He gas flow, which contains Cu<sup>II</sup> as the starting copper species, the reaction of the first  $(C_3H_6 + O_2)$ pulse only gave a C<sub>3</sub>H<sub>6</sub> conversion of 0.1% and a PO selectivity of 7%. This suggests that Cu<sup>II</sup> is less active and less selective for the epoxidation of C<sub>3</sub>H<sub>6</sub>. Fig. 14 shows that the increase in pulse numbers significantly increases both the conversion of C<sub>3</sub>H<sub>6</sub> and the selectivity to PO. After  $\sim$ 250 successive (C<sub>3</sub>H<sub>6</sub> + O<sub>2</sub>) pulses, C<sub>3</sub>H<sub>6</sub> conversion and PO selectivity rose to ~0.40% and ~40%, respectively, and they did not undergo significant changes with further increases in pulse numbers. This observation implies the generation of active sites during the successive  $(C_3H_6 + O_2)$  pulse reactions. From the in situ characterization results described previously, it is easy to deduce a conclusion that the Cu<sup>1</sup> sites generated gradually on the catalyst surface during the successive  $(C_3H_6 + O_2)$  pulse reactions are responsible for the epoxidation of  $C_3H_6$  by  $O_2$ .

On the other hand, when the  $Cs^+-5$  wt%  $CuO_x/SiO_2$  catalyst had been pretreated with H<sub>2</sub> to give Cu<sup>0</sup> or with H<sub>2</sub> followed by N<sub>2</sub>O to provide  $Cu^{I}$  as the starting copper species,  $C_{3}H_{6}$  conversion was higher (1.25% and 0.97%) during the reaction of the first  $(C_3H_6 + O_2)$  pulse (Fig. 14A). This indicates that  $Cu^0$  and  $Cu^1$  are both active for the oxidation of C<sub>3</sub>H<sub>6</sub> by O<sub>2</sub>. However, the selectivities to PO were low (7.6% and 12%) in the reactions of the first  $(C_3H_6 + O_2)$  pulse in these cases (Fig. 14B). The selectivity to PO increased with an increase in the successive pulse number. At the same time, the conversion of C<sub>3</sub>H<sub>6</sub> decreased gradually. The steady-state PO formation activities achieved after ~600 successive  $(C_3H_6 + O_2)$  pulses were similar for these two pretreatment procedures. In steady states, PO selectivities in these two cases ( $\sim 20\%$ ) were lower than that in the case of pretreatment with  $O_2$  (~40%), while C<sub>3</sub>H<sub>6</sub> conversions were slightly higher. This suggests that a lower concentration of Cu<sup>I</sup> on catalyst surfaces favors the PO selectivity. This will be discussed later.

| Sample  | Pulse number | $C_3H_6$ converted (µmol) | C <sub>3</sub> H <sub>6</sub> conv. (%) | Selectivity (%) |          |                 |
|---|--------------|---------------------------|---|-----------------|----------|-----------------|
|   |              |                           |   | РО              | Acrolein | CO <sub>x</sub> |
| CuO <sub>x</sub> /SiO <sub>2</sub>                  | 1            | 0.16                      | 0.62                                    | 0               | 97       | 2.9             |
|   | 2            | 0.056                     | 0.22                                    | 0               | 96       | 3.8             |
|   | 3            | 0.040                     | 0.16                                    | 0               | 95       | 4.6             |
|   | 4            | 0.033                     | 0.13                                    | 0               | 97       | 3.2             |
|   | 5            | 0.028                     | 0.11                                    | 0               | 97       | 3.0             |
|   | 6            | 0.027                     | 0.10                                    | 0               | 97       | 3.3             |
| Cs <sup>+</sup> –CuO <sub>x</sub> /SiO <sub>2</sub> | 1            | 0.016                     | 0.061                                   | 0               | 88       | 12              |
|   | 2            | 0.011                     | 0.043                                   | 0               | 86       | 14              |
|   | 3            | 0.0064                    | 0.025                                   | 0               | 80       | 20              |
|   | 4            | 0.0056                    | 0.021                                   | 0               | 75       | 25              |
|   | 5            | 0.0038                    | 0.015                                   | 0               | 79       | 21              |
|   | 6            | 0.0032                    | 0.012                                   | 0               | 83       | 17              |

Table 5Reaction of  $C_3H_6$  pulses with 5 wt%  $CuO_x/SiO_2$  and  $Cs^+-5$  wt%  $CuO_x/SiO_2$  (Cs/Cu = 0.4).<sup>a</sup>

Preaction conditions: W = 0.15 g, T = 523 K, amount of C<sub>3</sub>H<sub>6</sub> pulse = 0.63 mL (STP) (~28 µmol), F(He carrier) = 80 mL min<sup>-1</sup>.



**Fig. 14.** Dependence of catalytic performance on the number of successive  $(C_3H_6 + O_2)$  pulses over the  $Cs^+-5$  wt%  $CuO_x-SiO_2$  (Cs/Cu = 0.4) catalyst after different pretreatments. (A)  $C_3H_6$  conversion; (B) PO selectivity. (a) Pretreatment with  $O_2$ -containing He  $[P(O_2) = 8.4 \text{ kPa}]$  at 823 K; (b) pretreatment with  $H_2$ -containing He  $[P(H_2) = 16.9 \text{ kPa}]$  at 773 K; (c) pretreatment with  $H_2$ -containing He  $[P(H_2) = 16.9 \text{ kPa}]$  at 773 K; (c) pretreatment with  $H_2$ -containing He  $[P(H_2) = 16.9 \text{ kPa}]$  at 773 K, followed by oxidation with  $N_2O$   $[P(N_2O) = 16.9 \text{ kPa}]$  at 573 K. Reaction conditions: W = 0.10 g, T = 523 K,  $P(C_3H_6) = P(O_2) = 50.7$  kPa, pulse volume = 0.63 mL (STP), F(He carrier) = 80 mL min<sup>-1</sup>.

We have further performed flow-mode reactions for a longer time for the Cs<sup>+</sup>-5 wt% CuO<sub>x</sub>/SiO<sub>2</sub> catalysts starting from both Cu<sup>II</sup> and Cu<sup>I</sup>. The results are shown in Fig. 15. The reaction conditions used here are the same as those employed for the pulse reactions in Fig. 14, except for the reaction mode. Fig. 15A shows that, for the catalyst after O<sub>2</sub> treatment, which contains Cu<sup>II</sup> as the starting copper species, C<sub>3</sub>H<sub>6</sub> conversion slightly decreases, while PO selectivity slightly increases when the time on stream is prolonged to 4 h. After the treatment of the used catalyst with an O<sub>2</sub>-He flow, the catalytic performance could be recovered. From Fig. 15B, we clarified that, for the catalyst treated by H<sub>2</sub> reduction followed by N<sub>2</sub>O oxidation, which contained Cu<sup>I</sup> as the starting copper species, neither C<sub>3</sub>H<sub>6</sub> conversion nor PO selectivity changed significantly with time on stream.

# 4. Discussion

# 4.1. Reaction pathways over $CuO_x/SiO_2$ and $Cs^+-CuO_x/SiO_2$ catalysts

The analyses of the changes of product selectivities with varying kinetic parameters, particularly the contact time (expressed as *W*/*F*), may provide useful information on the reaction pathways. The primary products could be deduced from the product selectivities at very short contact times, that is, the initial reaction stage. Over the 5 wt% CuO<sub>x</sub>/SiO<sub>2</sub> catalyst, acrolein was a main product (selectivity ~50%) at shorter contact times (Figs. 3A and 4A). The formation of PO could also be observed at shorter contact times, and the selectivity to PO approached ~20% as the contact time decreased the selectivity to PO and increased that to CO<sub>x</sub>. The selectivity to acrolein decreased slightly with increasing the con-



**Fig. 15.** Changes of catalytic performance of the Cs<sup>+</sup>–5 wt% CuO<sub>4</sub>/SiO<sub>2</sub> (Cs/Cu = 0.4) catalyst after different pretreatments with time on stream: (A) after O<sub>2</sub> pretreatment in O<sub>2</sub>–He [P(O<sub>2</sub>) = 8.4 kPa] at 823 K; (B) after H<sub>2</sub> pretreatment in H<sub>2</sub>–He [P(H<sub>2</sub>) = 16.9 kPa] at 773 K followed by oxidation with N<sub>2</sub>O in N<sub>2</sub>O–He [P(N<sub>2</sub>. O) = 16.9 kPa] at 573 K. Reaction conditions: W = 0.20 g, T = 523 K, F = 60 mL min<sup>-1</sup>, P(C<sub>3</sub>H<sub>6</sub>) = P(O<sub>2</sub>) = 50.7 kPa.

tact time under O<sub>2</sub>-rich conditions (Fig. 3A), but it rather increased slightly with the contact time under the condition  $P(O_2)/$  $P(C_3H_6) = 1$  (Fig. 4A). Allyl alcohol was also formed in significant amounts at  $P(O_2)/P(C_3H_6) = 1$ , and the selectivity to allyl alcohol increased slightly with the contact time (Fig. 4A). These results allow us to speculate that the primary products over the 5 wt%  $CuO_x/SiO_2$ catalyst are acrolein and PO as well as  $CO_x$  (Fig. 16A). Allyl alcohol must be an isomerization product (a secondary product) from PO, and the consecutive oxidation of allyl alcohol further provides acrolein. CO<sub>x</sub> may further be formed via the consecutive oxidation of PO and acrolein. In other words, there are two parallel routes for the partial oxidation of  $C_3H_6$  over the 5 wt%  $CuO_x/SiO_2$  catalyst. One is the allylic oxidation route to form acrolein, and the other is the epoxidation route to form PO. PO could be converted further to acrolein via allyl alcohol. Actually, the facile transformation of PO to allvl alcohol and acrolein over the 5 wt% CuO<sub>v</sub>/SiO<sub>2</sub> catalyst has been confirmed by experimental results using PO as a reactant (Table 3). Allyl alcohol could be obtained with higher selectivity at lower temperatures in the conversion of both PO and C<sub>3</sub>H<sub>6</sub> (Table 3 and Fig. 2A) over the 5 wt% CuO<sub>x</sub>/SiO<sub>2</sub> catalyst. At lower temperatures or shorter contact times, the sum of the selectivities to PO and allyl alcohol can reach 30-40% (Figs. 2A and 4A), indicating that the epoxidation route over the 5 wt%  $CuO_x/SiO_2$  catalyst is not a minor route, as expected. The lower selectivity to PO over this catalyst should be due to the higher reactivity of PO over this catalyst (Table 3). This is a significant result because supported  $CuO_x$ catalysts are well known for the allylic oxidation of C<sub>3</sub>H<sub>6</sub> to acrolein [41–44] but not for the epoxidation reaction. Vaughan et al. once reported that Cu/SiO<sub>2</sub> could catalyze the epoxidation of  $C_3H_6$  by  $O_2$  with a selectivity of ~53% at a low  $C_3H_6$  conversion ( $\sim$ 0.25%), but they emphasized that the active phase was Cu<sup>0</sup> [30]. Here, we have clearly demonstrated that  $CuO_x/SiO_2$  catalyzes the epoxidation of  $C_3H_6$  to PO as well as the allylic oxidation to acrolein, and part of the acrolein in the final products stems from the epoxidation route via PO and allyl alcohol.

The reaction pathways over the  $Cs^+$ -5 wt%  $CuO_x/SiO_2$  catalyst are summarized in Fig. 16B. PO was formed as a main product (selectivity 50-65%) at short contact times (Figs. 3B and 4B). Acrolein was also formed with relatively lower selectivities (20-30%) in the initial stage over this catalyst. The increase in the contact time decreased the selectivities to PO and acrolein (particularly the former) and increased that to CO<sub>x</sub>. No significant formation of allyl alcohol could be observed over this catalyst even at lower temperatures and  $P(O_2)/P(C_3H_6) = 1$  (Fig. 2B). The selectivity to other oxygenates such as propanal and acetone also became lower over the Cs<sup>+</sup>-modified catalyst (Tables 1 and 2). This suggests that the modification by Cs<sup>+</sup> inhibits the isomerization of PO to allyl alcohol and other oxygenates. The experiments using PO as a reactant confirmed the significantly lower activity of the Cs<sup>+</sup>–5 wt% CuO<sub>2</sub>/SiO<sub>2</sub> catalyst in the conversion of PO (Table 3). Our results further suggest that, as compared to the catalyst without Cs<sup>+</sup> modification, the Cs<sup>+</sup>-5 wt% CuO<sub>x</sub>/SiO<sub>2</sub> catalyst possesses a higher initial selectivity for the epoxidation route (Fig. 16).

# 4.2. Role of Cs<sup>+</sup>

Our catalytic studies have demonstrated that the main partial oxidation product over 5 wt%  $CuO_x/SiO_2$  is acrolein, and the modification of 5 wt%  $CuO_x/SiO_2$  by an alkali metal ion significantly enhances the selectivity to PO. Among the alkali metal ions,  $Cs^+$  is the most efficient promoter for enhancing the selectivity to PO (Table 1). Kinetic analyses reveal that both acrolein and PO are formed as primary products via the allylic oxidation and epoxidation routes over 5 wt%  $CuO_x/SiO_2$ , but PO would be further isomerized to allyl alcohol and subsequently oxidized to acrolein over this catalyst. The presence of  $Cs^+$  inhibits the consecutive conversion of PO. This



**Fig. 16.** Reaction routes for the oxidation of C<sub>3</sub>H<sub>6</sub> by O<sub>2</sub>: (A) 5 wt% CuO<sub>x</sub>/SiO<sub>2</sub> and (B) Cs<sup>+</sup>-5 wt% CuO<sub>x</sub>/SiO<sub>2</sub> (Cs/Cu = 0.4). The number in parentheses below a primary product is the estimated fraction of this product in all the primary products.

should be one of the main reasons for the increase in the selectivity to PO after modification by  $Cs^+$ . We have further clarified that the presence of  $Cs^+$  also increases the selectivity to PO and decreases that to acrolein in the initial reaction stage, although both are primary products irrespective of the presence of  $Cs^+$  (Fig. 16).

Characterizations of catalysts using XRD and TEM techniques suggest that there exist strong interactions between  $CuO_x$  species and Cs<sup>+</sup> or other alkali metal ions. The presence of an alkali metal ion significantly decreased the size of CuO<sub>x</sub> nanoparticles. Such interactions between CuO<sub>x</sub> and Cs<sup>+</sup> were stronger than those between  $CuO_x$  and other alkali metal ions because the size of  $CuO_x$ was the smallest over the  $Cs^+$ - $CuO_x/SiO_2$  catalyst (Table 4). We further clarified that the strong interactions between CuO<sub>x</sub> and alkali metal ions affected the acidity and the redox properties of the modified catalysts. NH<sub>3</sub> TPD studies suggested that CuO<sub>x</sub> particles possessed acidity, and modification by an alkali metal ion decreased the acidity of CuO<sub>x</sub> particles. Cs<sup>+</sup> was the most effective modifier to weaken the acidity of  $CuO_x$ , since the peak temperature for NH<sub>3</sub> desorption was lowest over the Cs<sup>+</sup>-CuO<sub>x</sub>/SiO<sub>2</sub> catalyst (Fig. 10A). H<sub>2</sub> TPR results indicated that the reducibility of Cu<sup>II</sup> in the catalyst was lowered due to the presence of an alkali metal ion. The peak temperature observed from H<sub>2</sub> TPR was the highest over the Cs<sup>+</sup>-modified catalyst.

We propose that the decrease in acidity due to the presence of Cs<sup>+</sup> or another alkali metal ion mainly contributes to the inhibition of the consecutive conversion of PO. It is known that Lewis acids can catalyze the isomerization of PO to allyl alcohol, which can be readily oxidized to acrole in the presence of  $O_2$  [46]. On the other hand, the decrease in the reducibility of CuO<sub>x</sub> after modification by Cs<sup>+</sup> or another alkali metal ion indicates a decrease in the reactivity of the lattice oxygen in the CuO<sub>x</sub> species. The lower reactivity of the lattice oxygen in the Cs<sup>+</sup>-modified catalyst has also been confirmed by the pulse-reaction studies (Table 5). Our pulse-reaction studies further clarify that the lattice oxygen is responsible for the allylic oxidation of  $C_3H_6$  to acrolein. This is in agreement with the consensus that the lattice oxygen is a nucleophilic oxygen species, which preferentially attacks the allylic H atoms in C<sub>3</sub>H<sub>6</sub> molecule and results in allylic oxidation. Thus, the decrease in the reactivity of lattice oxygen can contribute to the decrease in the selectivity of acrolein in the primary products after the modification by Cs<sup>+</sup>.

# 4.3. Active sites and possible reaction mechanism

As described above, it is clear that the lattice oxygen species in the present CuO<sub>x</sub>-based catalysts is responsible for the allylic oxidation of  $C_3H_6$  to acrolein. It is generally accepted that epoxidation requires an electrophilic oxygen species, which is typically a kind of adsorbed oxygen species such as  $O_2^-, O_2^{2-}, O^-$ , or \*OOH formed by the activation of  $O_2$  or another oxidant on the active site [1,3–6]. Here, we will first discuss the active site for the activation of  $O_2$  over our catalysts.

For the 5 wt% CuO<sub>x</sub>/SiO<sub>2</sub> and the Cs<sup>+</sup>–5 wt% CuO<sub>x</sub>/SiO<sub>2</sub> catalysts pretreated by O<sub>2</sub>-containing He, which contain Cu<sup>II</sup> as the starting copper species, our in situ XRD and CO-adsorbed FT-IR studies have clarified that Cu<sup>I</sup> is generated during the reaction. Moreover, it has been demonstrated that the Cu<sup>0</sup> species over the same catalysts pretreated by H<sub>2</sub> reduction is rapidly transformed into Cu<sup>I</sup> and then into a mixture of Cu<sup>I</sup> and Cu<sup>II</sup> under reaction conditions. The instability of Cu<sup>0</sup> species under reaction conditions can exclude the possibility of Cu<sup>0</sup> as the active site for the present catalytic system. On the other hand, it is also difficult to assume that Cu<sup>II</sup> can work for the activation of O<sub>2</sub>. Actually, our pulse-reaction studies showed that the reaction of the first (C<sub>3</sub>H<sub>6</sub> + O<sub>2</sub>) pulse over the Cu<sup>II</sup>-containing Cs<sup>+</sup>–5 wt% CuO<sub>x</sub>/SiO<sub>2</sub> catalyst provided very low C<sub>3</sub>H<sub>6</sub> conversion and low PO selectivity, and the increase in the number of



**Fig. 17.** Proposed reaction mechanism for the formations of primary products over the  $CuO_x/SiO_2$  catalysts with and without  $Cs^+$  modification.  $Cu^1$  generated over the  $CuO_x/SiO_2$  catalyst with and without  $Cs^+$  modification during the reaction accounts for the formation of propylene oxide, while the lattice oxygen is responsible for acrolein formation.

successive  $(C_3H_6 + O_2)$  pulses significantly increases the conversion and PO selectivity (Fig. 14). This confirms that  $Cu^{II}$  is not active for the epoxidation of  $C_3H_6$  by  $O_2$ . Combining these results and analyses, we conclude that  $Cu^I$  works as the active site for the epoxidation of  $C_3H_6$  by  $O_2$  over our present  $CuO_x$ -based catalysts.

The catalysts, starting from both Cu<sup>1</sup> and Cu<sup>0</sup>, would be transformed into those containing a mixture of Cu<sup>1</sup> and Cu<sup>II</sup> under our reaction conditions (Figs. 12 and 13). In these cases, the ratios of Cu<sup>1</sup> to Cu<sup>II</sup> were higher than that over the catalyst starting from Cu<sup>II</sup> (Section 3.4). Our ( $C_3H_6 + O_2$ ) pulse-reaction and flow-reaction studies both revealed that the PO selectivity was lower over the catalyst starting from Cu<sup>1</sup> or Cu<sup>0</sup>, although the C<sub>3</sub>H<sub>6</sub> conversion was higher (Figs. 14 and 15). These observations allow us to assume that a lower concentration of Cu<sup>1</sup> on the catalyst surface favors PO selectivity. Generally, for a selective oxidation reaction, the spatial isolation of active oxygen species is a key, as proposed by Grasselli [54]. Similarly, we speculate that a larger concentration of adjacent oxygen species formed over the catalyst with a higher concentration of Cu<sup>1</sup> is unfavorable to the selective formation of PO.

Based on the results and discussion described above, we propose a reaction mechanism in Fig. 17 for the formation of acrolein and PO, two main primary products, over the  $CuO_x/SiO_2$  catalysts with and without Cs<sup>+</sup> modification. The lattice oxygen is responsible for the allylic oxidation of C<sub>3</sub>H<sub>6</sub>, producing acrolein, and the reduced Cu<sup>I</sup> sites can be reoxidized to Cu<sup>II</sup> by O<sub>2</sub>. Although several early studies claimed that the lattice oxygen associated with Cu<sup>I</sup> in Cu<sub>2</sub>O was more selective for the formation of acrolein [42,44], our pulse-reaction results suggested that the lattice oxygen in CuO nanoparticles exhibited high selectivity for the conversion of  $C_{3}H_{6}$  to acrolein (Table 5). Besides the allylic oxidation route, we have clearly demonstrated that there exists an epoxidation route over the CuO<sub>x</sub>/SiO<sub>2</sub> catalysts with and without Cs<sup>+</sup> modification. The Cu<sup>I</sup>, with a lower concentration generated during the reaction, functions as the active site for the epoxidation of C<sub>3</sub>H<sub>6</sub> to PO. It is likely that the Cu<sup>1</sup> site activates molecular oxygen to form an active oxygen species ( $Cu^m - O^*$ ), accounting for the epoxidation of  $C_3H_6$ to PO by O<sub>2</sub>. PO would undergo isomerization to allyl alcohol and further oxidation to acrolein over the catalyst without Cs<sup>+</sup> modification. The modification by Cs<sup>+</sup> cannot only inhibit the consecutive conversion of PO but also decrease the reactivity of the lattice oxygen, contributing to high PO selectivity. Future studies using isotopic oxygen (<sup>18</sup>O<sub>2</sub>) are needed to provide further evidence for the roles of lattice oxygen and adsorbed oxygen species derived from O<sub>2</sub> in the formation of acrolein and PO.

# 5. Conclusions

The modification of the 5 wt%  $CuO_x/SiO_2$  catalyst, which mainly catalyzed the formation of acrolein, by an alkali metal ion in-

creased the selectivity and yield to PO in the oxidation of  $C_3H_6$  by  $O_2$ , although the conversion of  $C_3H_6$  decreased to some extent. The  $Cs^+$ -5 wt% CuO<sub>x</sub>/SiO<sub>2</sub> catalyst exhibited the highest PO selectivity and PO yield among a series of alkali-metal-ion-modified  $CuO_x/$ SiO<sub>2</sub> catalysts. Our characterizations showed that the modification by an alkali metal ion decreased the size of  $CuO_x$  nanoparticles, suggesting the existence of strong interactions between CuO<sub>x</sub> and alkali metal ions. Such interactions were strongest between CuO<sub>x</sub> and Cs<sup>+</sup>. The presence of Cs<sup>+</sup> or another alkali metal ion decreased the acidity arising from CuO<sub>x</sub> species and suppressed the reducibility of the catalyst. The kinetic studies clarified that acrolein and PO were formed in parallel as primary products via allylic oxidation and epoxidation routes over the catalysts with and without Cs<sup>+</sup> modification. PO underwent isomerization into allyl alcohol and further oxidation into acrolein over the 5 wt% CuO<sub>x</sub>/SiO<sub>2</sub> catalyst without Cs<sup>+</sup> modification. The modification by Cs<sup>+</sup> inhibited the consecutive conversion of PO by decreasing the acidity. We confirmed via pulse-reaction studies that the lattice oxygen species was responsible for the allylic oxidation of C<sub>3</sub>H<sub>6</sub> to acrolein. The lower reactivity of the lattice oxygen of the Cs<sup>+</sup>-modified catalyst further contributed to the increase in PO selectivity. Through in situ XRD, CO-adsorbed FT-IR, and pulse-reaction studies, we further clarified that Cu<sup>I</sup> generated during the reaction worked for the epoxidation of  $C_3H_6$  by  $O_2$ . It was proposed that  $Cu^1$  activated  $O_2$ , forming the active oxygen species for the conversion of  $C_3H_6$  to PO. However, too high a concentration of Cu<sup>I</sup> sites is unfavorable to the PO selectivity.

# Acknowledgments

This work was supported by the National Basic Program of China (No. 2010CB732303), the Natural Science Foundation of China (Nos. 21173174, 21033006, 21161130522, and 20923004), the Program for Changjiang Scholars and Innovative Research Team in University (No. IRT1036), and a Key Scientific Project of Fujian Province (2009HZ0002-1).

## References

- [1] J.R. Monnier, Appl. Catal. A 221 (2001) 73-91.
- M. McCoy, Chem. Eng. News 79 (43) (2001) 19–20.
  T.A. Nijhuis, M. Makkee, J.A. Moulijn, B.M. Weckhuysen, Ind. Eng. Chem. Res. 45
- (2006) 3447–3459.
- [4] Y. Wang, W. Zhu, Q. Zhang, Chin. J. Catal. 29 (2008) 857-865.
- [5] Q. Zhang, W. Deng, Y. Wang, Chem. Commun. 47 (2011) 9275-9292.
- [6] J. Huang, M. Haruta, Res. Chem. Intermed. 38 (2012) 1–24.
- [7] M.G. Clerici, G. Bellussi, U. Romano, J. Catal. 129 (1991) 159-167.
- [8] A. Tullo, Chem. Eng. News 82 (36) (2004) 15.
- [9] T. Hayashi, K. Tanaka, M. Haruta, J. Catal. 178 (1998) 566-575.
- [10] A.K. Sinha, S. Seelan, S. Tsubota, M. Haruta, Angew. Chem. Int. Ed. 43 (2004) 1546-1548.
- [11] B. Chowdhury, J.J. Bravo-Sárez, M. Daté, S. Tsubota, M. Haruta, Angew. Chem. Int. Ed. 45 (2006) 412–415.

- [12] V. Duma, D. Hönicke, J. Catal. 191 (2000) 93-104.
- [13] E. Ananieva, A. Reitzmann, Chem. Eng. Sci. 59 (2004) 5509-5517.
- [14] X. Wang, Q. Zhang, Q. Guo, Y. Lou, L. Yang, Y. Wang, Chem. Commun. (2004) 1396–1397.
- [15] X. Wang, Q. Zhang, S. Yang, Y. Wang, J. Phys. Chem. B 109 (2005) 23500-23508.
- [16] Q. Zhang, Q. Guo, X. Wang, T. Shishido, Y. Wang, J. Catal. 239 (2006) 105–113.
  [17] B. Moens, H.D. Winne, S. Corthals, H. Poelman, R. De Gryse, V. Meynen, P. Cool,
- B.F. Sels, P.A. Jacobs, J. Catal. 247 (2007) 86–100.
  - [18] S. Yang, W. Zhu, Q. Zhang, Y. Wang, J. Catal. 254 (2008) 251-262.
  - [19] J. Lu, J.J. Bravo-Suárez, A. Takahashi, M. Haruta, S.T. Oyama, J. Catal. 232 (2005) 85–95
  - [20] J. Lu, J.J. Bravo-Suárez, M. Haruta, S.T. Oyama, Appl. Catal. A 302 (2006) 283– 295.
  - [21] Y. Lei, F. Mehmood, S. Lee, J. Greeley, B. Lee, S. Seifert, R.E. Winsns, J.W. Elam, R.J. Meyer, P.C. Redfern, D. Teschner, R. Schlögl, M.J. Pellin, L.A. Curtiss, S. Vajda, Science 328 (2010) 224–228.
  - [22] M. Ojeda, E. Iglesia, Chem. Commun. (2009) 352-354.
  - [23] S. Lee, L.M. Molina, M.J. López, J.A. Alonso, B. Hammer, B. Lee, S. Seifert, R.E. Winans, J.W. Elam, M.J. Pellin, S. Vajda, Angew. Chem. Int. Ed. 48 (2009) 1467– 1471.
  - [24] J. Huang, T. Akita, J. Fays, T. Fujitani, T. Takei, M. Haruta, Angew. Chem. Int. Ed. 48 (2009) 7862–7866.
  - [25] R.M. Lambert, F.J. Williams, R.L. Cropley, A. Palermo, J. Mol. Catal. A 228 (2005) 27–33.
  - [26] R.L. Cropley, F.J. Williams, A.J. Urquhart, O.P.H. Vaughan, M.S. Tikhov, R.M. Lambert, J. Am. Chem. Soc. 127 (2005) 6069–6076.
  - [27] D. Torres, N. Lopez, F. Illas, R.M. Lambert, Angew. Chem. Int. Ed. 46 (2007) 2055–2058.
  - [28] J.R. Monnier, G.W. Hartley, J. Catal. 203 (2001) 253-256.
  - [29] J. Lu, M. Luo, H. Lei, X. Bao, C. Li, J. Catal. 211 (2002) 552-555.
  - [30] O.P.H. Vaughan, G. Kyriakou, N. Macleod, M. Tikhov, R.M. Lambert, J. Catal. 236 (2005) 401-404.
  - [31] X. Zhang, Q. Zhang, Y. Guo, W. Zhan, Y. Guo, Y. Wang, G. Lu, J. Mol. Catal. A 357 (2012) 106-111.
  - [32] H. Chu, L. Yang, Q. Zhang, Y. Wang, J. Catal. 241 (2006) 225-228.
  - [33] Y. Wang, H. Chu, W. Zhu, Q. Zhang, Catal. Today 131 (2008) 496-504.
  - [34] W. Zhu, Q. Zhang, Y. Wang, J. Phys. Chem. C 112 (2008) 7731-7734.
  - [35] W. Su, S. Wang, P. Ying, Z. Feng, C. Li, J. Catal. 268 (2009) 165-174.
  - [36] I. Onal, D. Düzenli, A. Seubsai, M. Kahn, E. Seker, S. Senkan, Top. Catal. 53 (2010) 92–99.
  - [37] L. Yang, J. He, Q. Zhang, Y. Wang, J. Catal. 276 (2010) 76-84.
  - [38] S. Seubsai, M. Kahn, S. Senkan, ChemCatChem 3 (2011) 174-179.
  - [39] A. Seubsai, S. Senkan, ChemCatChem 3 (2011) 1751-1754.
  - [40] W. Long, Q. Zhai, J. He, Q. Zhang, W. Deng, Y. Wang, ChemPlusChem 77 (2012) 27–30.
  - [41] H.H. Voge, C.R. Adams, Adv. Catal. 17 (1967) 151-221.
  - [42] B.J. Wood, H. Wise, R.S. Yolles, J. Catal. 15 (1969) 355-362.
  - [43] T. Inui, T. Ueda, M. Suehiro, J. Catal. 65 (1980) 166–173.
  - [44] J.B. Reitz, E.D. Solomon, J. Am. Chem. Soc. 120 (1998) 11467-11478.
  - [45] S. Sato, R. Takahashi, T. Sodesawa, K. Yuma, Y. Obata, J. Catal. 196 (2000) 195– 199
  - [46] J.M. Coxon, R.G.A.R. Maclagan, A. Rauk, A.J. Thrope, D. Whalen, J. Am. Chem. Soc. 119 (1997) 4712–4718.
  - [47] G.N. Lewis, Valency and Structure of Atoms and Molecules, Wiley, New York, 1923.
  - [48] K. Hadjiivanov, H. Knözinger, Phys. Chem. Chem. Phys. 3 (2001) 1132-1137.
  - [49] K.I. Hadjiivanov, G.N. Vayssilov, Adv. Catal. 47 (2002) 307-511.
  - [50] D. Scarano, S. Bordiga, C. Lamberti, G. Spoto, G. Ricchiardi, A. Zecchina, A.C. Otero, Surf. Sci. 411 (1998) 272-285.
  - [51] A. Frache, M. Cadoni, C. Bisio, L. Marchese, Langmuir 18 (2002) 6875–6880.
  - [52] J. Haber, W. Turek, J. Catal. 190 (2000) 320-326.
  - [53] Y. Li, D. An, Q. Zhang, Y. Wang, J. Phys. Chem. 112 (2008) 13700-13708.
  - [54] R.K. Grasselli, Top. Catal. 21 (2002) 79–88.