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Catalysis Today 131 (2008) 496–504

CATALYSIS TODAY

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Copper-based efficient catalysts for propylene epoxidation by molecular oxygen

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Abstract

Among a series of SBA-15-supported transition metal oxides with and without modification, the CuO_x/SBA-15 after K^+ modification exhibited the best catalytic performance for the epoxidation of propylene by molecular oxygen. Potassium was the best modifier among various alkali and alkaline earth metal ions examined, and potassium acetate was a superior precursor of K^+ for propylene oxide formation. The highest propylene oxide selectivity was obtained over a catalyst with copper content of 1 wt.% and K/Cu molar ratio of 0.7. Kinetic studies reveal that the allylic oxidation mainly proceeds over the CuO_x/SBA-15 providing acrolein as the main partial oxidation product, and the K^+ modification switches the main reaction route from allylic oxidation to epoxidation. The characterizations suggest that copper species with content of ≤ 5 wt.% are located in the mesoporous channels of SBA-15 existing mainly as CuO_x clusters and Cu^{2+} ions, and there exists an interaction between K^+ and the copper species. This interaction is proposed to play pivotal roles in epoxidation of propylene. As compared with other reported Cu-based catalysts for propylene epoxidation, the present catalyst possesses several distinct features.

Keywords: Propylene epoxidation; Oxygen; Copper; SBA-15; Potassium modification

1. Introduction

Propylene oxide (PO) is an important synthetic intermediate. In the current chemical industry, PO is mainly produced by the chlorohydrin and the organic hydroperoxide processes, but both processes have caused the production of a large amount of waster water or organic by-products, which have brought about serious environmental problems, and thus are not atomically economic [1]. Therefore, it becomes urgent to establish a direct and green epoxidation route for PO production. Many studies have been contributed to the direct C_3H_6 epoxidation using a proper catalyst combined with an appropriate oxidant. The use of H_2O_2 [2–4], O_2–H_2 gas mixture [5–8], and N_2O [9–14] as the oxidant can provide excellent PO selectivities at reasonable C_3H_6 conversions if a proper catalyst is used, but these oxidants are still expensive. Oxygen or air is the most ideal oxidant for selective oxidation. The epoxidation of ethylene by O_2 has been commercialized for several decades using Ag-based catalysts, but the epoxidation of propylene by O_2 is not successful [15]. Ag- and Cu-based catalysts have mainly been reported so far for this reaction, but PO selectivity can hardly exceed 50% even at a lower propylene conversion [16–21]. The epoxidation of C_3H_6 by O_2 remains one of the most challenging targets in catalysis.

The existence of the allylic C–H bonds, which are much more active toward oxidation than the vinyl C–H bonds in C_2H_4, is believed to cause the lower selectivity in C_3H_6 epoxidation. It is known that the nucleophilic oxygen such as lattice oxygen species will attack preferentially the reactive allylic hydrogen atoms and cause the allylic oxidation, while the epoxidation needs the electrophilic oxygen. Therefore, our approach is to suppress the reactivity of lattice oxygen species, and to generate electrophilic oxygen species. Moreover, the site isolation may overcome the problem of consecutive oxidation of PO. Thus, the catalysts with highly dispersed active sites may be promising. Recently, we reported that a KCl-modified FeO_x/SBA-15 could work as a highly selective C_3H_6 epoxidation catalyst when N_2O was used as an oxidant [11]. It was elucidated that the highly dispersed Fe^{3+} (or Fe^{2+} generated in situ during the reaction) sites located in mesoporous channels

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doi:10.1016/j.cattod.2007.10.022

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

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

2. Experimental

2.1. Catalyst preparation

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

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

2.2. Characterization

The structures of catalysts were characterized by Powder X-ray diffraction (XRD), N_2-physisorption, transmission electron microscopy (TEM), and H_2-temperature programmed reduction (H_2-TPR). XRD measurements were performed with a Panalytical X'Pert Pro Super X-ray diffractometer with Cu-K_α radiation (40 kV, 30 mA). N_2-physisorption at 77 K was carried out with a Micromeritics TriStar 3000 surface area and porosimetry analyzer. The sample was pretreated at 573 K in vacuum for 3 h before N_2 adsorption measurements. TEM observations were carried out with a FEI Tecnai 30 electron microscope (Phillips FEI) operated at an acceleration voltage of 300 kV. The sample for TEM observations was suspended in ethanol and ultrasonically dispersed, and then drops of suspensions were applied on a copper grid coated with carbon. H_2-TPR and NH_3-TPD were performed using a Micromeritics AutoChem II 2920 instrument. Typically, the sample (100 or 200 mg) was first pretreated in a quartz reactor with a gas flow containing O_2 and N_2 at 823 K for 1 h followed by purging with high-purity N_2. For H_2-TPR, after the sample was cooled to 323 K, a H_2–Ar (5 vol.% H_2) gas flow was introduced into the reactor, and the temperature was raised to 1173 K at a rate of 10 K/min. The consumption of H_2 was monitored by a thermal conductivity detector. For NH_3-TPD, the adsorption of NH_3 was performed at 393 K in an NH_3–He (10 vol.% NH_3) mixture for 1 h, and the remaining or weakly adsorbed NH_3 was purged by high-purity He. TPD was performed in He flow by raising the temperature to 973 K at a rate of 10 K min^{-1}. The desorbed NH_3 was detected with a mass spectrometer (ThermoStar GSD 301 T2) by monitoring the signal of $m/e = 16$.

2.3. Catalytic reaction

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

3. Results and discussion

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

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

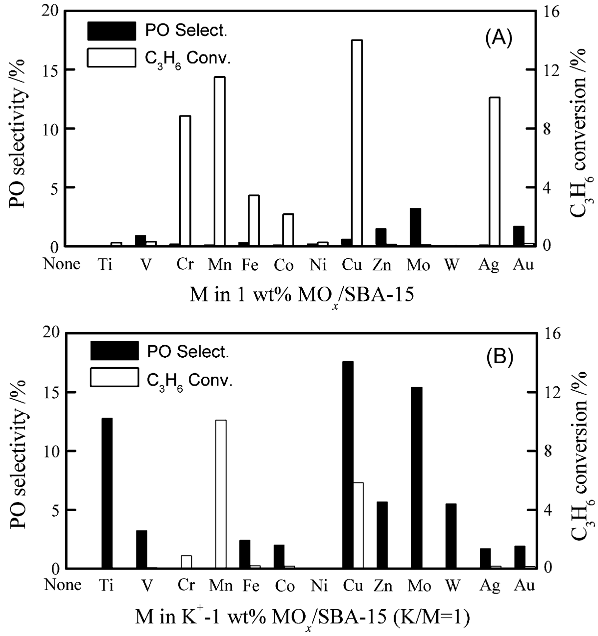


Fig. 1. Catalytic performances of SBA-15-supported transition metal oxides in the absence (A) and the presence (B) of K^+ modification for the epoxidation of C_3H_6 by O_2. Reaction conditions: catalyst weight, 0.20 g; temperature, 573 K; partial pressures of C_3H_6 and O_2, 2.5 and 98.8 kPa, respectively; total flow rate, 60 mL min^{-1}.

modified catalysts except for the Mn-based one, which did not provide PO.

As shown in Fig. 1, the Ag/SBA-15 catalysts with and without K^+ modification did not show good PO formation ability, and the K^+-FeO_x/SBA-15 catalyst was rather poor when O_2 was used as the oxidant. Although better PO selectivities were also observed over the K^+-MoO_x/SBA-15 and K^+-TiO_x/SBA-15, these two catalysts showed remarkably lower C_3H_6 conversions (<0.1%). Therefore, the Cu-based catalyst after modification was very unique for the epoxidation of C_3H_6 by O_2.

3.2. Optimization of modified CuO_x/SBA-15 catalyst

Since other alkali or alkaline earth metal ions such as Na^+, Cs^+ and Ba^{2+} have also been reported to be good catalyst modifiers in the epoxidation of propylene [7,9,10,16–21], we have investigated the modifying effect of various alkali and alkali earth metal ions (metal acetate as the precursor) for the CuO_x/SBA-15 (the ratio of modifier to Cu, 0.70). As shown in Fig. 2, the modification with an alkaline earth metal ion including magnesium, calcium or barium did not show significantly positive effect in enhancing the formation of PO (PO selectivity <2%). On the other hand, with a change of modifier in a sequence from Li^+ to Cs^+, PO selectivity increased significantly from Li^+ to K^+ and then kept almost unchanged, but C_3H_6 conversion decreased monotonically at the same time. By considering both PO selectivity and C_3H_6 conversion, K^+ was the best modifier for PO formation.

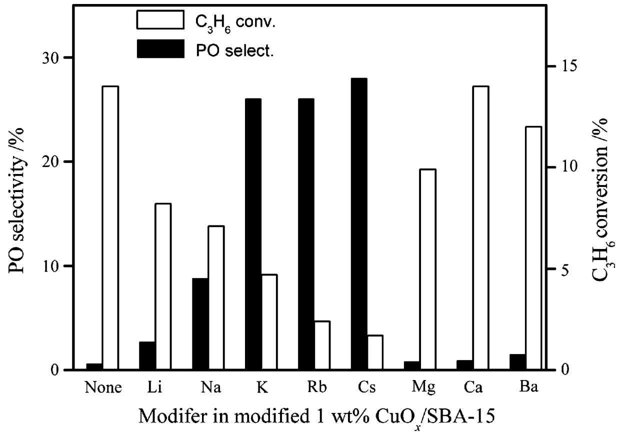


Fig. 2. Effect of various alkali metal or alkaline earth metal modifiers on catalytic performances for the epoxidation of C_3H_6 by O_2. Reaction conditions: catalyst weight, 0.20 g; temperature, 573 K; partial pressures of C_3H_6 and O_2, 2.5 and 98.8 kPa, respectively; total flow rate, 60 mL min^{-1}.

The precursor of potassium salt was found to be also vital in determining the PO formation activity. As shown in Table 1, the modification of the CuO_x/SBA-15 with each potassium salt investigated in our work could all enhance PO formation, but the use of KAc as the precursor provided the highest PO selectivity despite the lower C_3H_6 conversion. We further compared the PO selectivities for the catalysts using different potassium salts as the modifier precursors at different C_3H_6 conversions. From the selectivity–conversion plot shown in Fig. 3, where C_3H_6 conversions are adjusted by changing reaction temperature, it is clear that the catalyst with KAc as the modifier precursor exhibits higher PO selectivities than those with other potassium salts as the modifier precursors even at the same level of C_3H_6 conversions.

We have further investigated the catalytic performances of the K^+ (KAc)-CuO_x/SBA-15 catalysts with different copper and potassium contents. Table 2 shows the catalytic results over the catalysts with different copper content but with a fixed K/Si ratio (0.0075) or a fixed K/Cu ratio (1.0). In either case, C_3H_6 conversion increased with copper content up to 3 wt.% and then decreased sharply with a further increase in Cu content. PO selectivity did not show a definite tendency with changing the copper content, but the catalyst with a copper content of 1 wt.%

Table 1
Catalytic performances of K^+-CuO_x/SBA-15 catalysts prepared with different potassium salt precursors[a]

Catalyst[b]	C_3H_6 conv. (%)	Selectivity (%)				
		PO	Acrolein	Others[c]	CO	CO_2
CuO_x/SBA-15	14.1	0.6	17	1.3	20	62
(KAc)-CuO_x/SBA-15	4.7	26	4.0	0.7	10	60
(KCl)-CuO_x/SBA-15	6.4	13	4.5	0.3	16	67
(KNO_3)-CuO_x/SBA-15	8.0	8.4	5.3	0.4	16	70
(K_2CO_3)-CuO_x/SBA-15	5.9	11	4.3	0.5	15	69
(KOH)-CuO_x/SBA-15	6.1	18	4.6	0.6	14	63
(KBH_4)-CuO_x/SBA-15	7.5	9.3	3.6	0.3	15	72

[a] Reaction conditions: catalyst weight, 0.20 g; temperature, 573 K; partial pressures of C_3H_6 and O_2, 2.5 and 98.8 kPa, respectively; total flow rate, 60 mL min^{-1}.

[b] Copper content, 1.0 wt.%; K/Cu = 0.70.

[c] Other products include allyl alcohol, acetone and acetaldehyde.

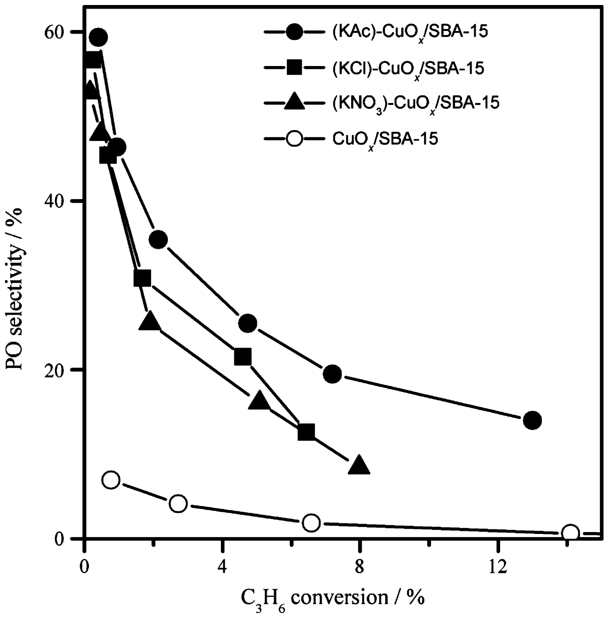


Fig. 3. PO selectivity as a function of C_3H_6 conversion over 1 wt.% CuO$_x$/SBA-15 and K$^+$-1 wt.% CuO$_x$/SBA-15 (K/Cu = 0.7) catalysts prepared with various potassium salts as the precursors. Reaction conditions: catalyst weight, 0.20 g; temperature, 498–623 K; partial pressures of C_3H_6 and O_2, 2.5 and 98.8 kPa, respectively; total flow rate, 60 mL min^{-1}.

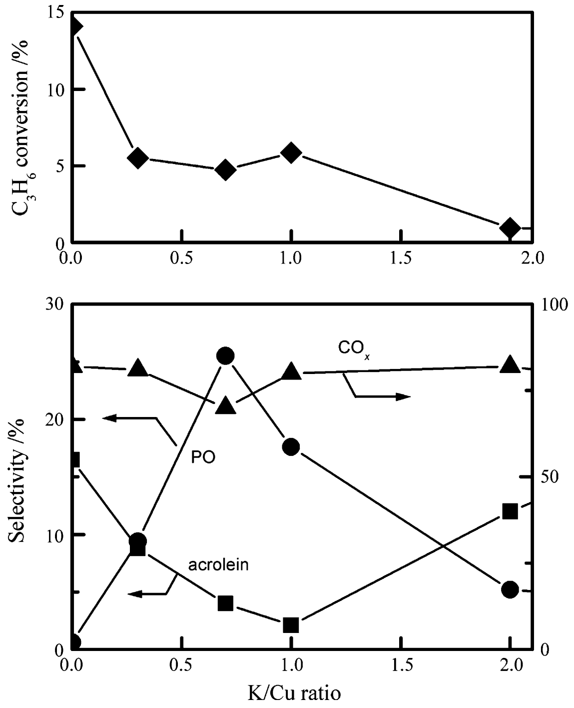


Fig. 4. Effect of K/Cu ratio on catalytic performances for the epoxidation of C_3H_6 by O_2 over K$^+$-1 wt.% CuO$_x$/SBA-15 catalysts. Reaction conditions: catalyst weight, 0.20 g; temperature, 573 K; partial pressures of C_3H_6 and O_2, 2.5 and 98.8 kPa, respectively; total flow rate, 60 mL min^{-1}.

exhibited the highest PO selectivity and a reasonably higher C_3H_6 conversion.

The effect of K/Cu ratio on catalytic performances for the catalysts with a copper content of 1 wt.% is shown in Fig. 4. The catalyst without K$^+$ exhibited higher C_3H_6 conversion but almost no PO formation. Acrolein was the main partial oxidation product. C_3H_6 conversion was decreased by the presence of even a small amount of K$^+$ (K/Cu = 0.3) but kept almost unchanged with increasing K/Cu ratio from 0.3 to 1.0. PO selectivity increased with increasing K/Cu ratio and reached a maximum at a K/Cu ratio of 0.7. A further rise in K/Cu ratio decreased PO selectivity. Therefore, the catalyst with a K/Cu ratio of 0.7 exhibited the best catalytic performance for PO formation. It is noteworthy that the modification with K$^+$ at an appropriate K/Cu ratio can shift the formation of acrolein to PO.

3.3. Kinetic studies of C_3H_6 epoxidation over CuO$_x$/SBA-15 with and without K$^+$ modification

To gain further information about the role of K$^+$ modification in affecting the reaction route, we have compared the kinetic features of C_3H_6 oxidation over the 1 wt.% CuO$_x$/SBA-15 and the K$^+$-1 wt.% CuO$_x$/SBA-15 (K/Cu = 0.7) catalysts.

Table 3 shows the effect of reaction temperature on catalytic behaviors over these two catalysts. For the catalyst without K$^+$,

Table 2
Catalytic performances of K$^+$(KAc)-CuO$_x$/SBA-15 catalysts with different copper contents[a]

Catalyst	C_3H_6 conv. (%)	Selectivity (%)				
		PO	Acrolein	Others[b]	CO	CO_2
K$^+$/SBA-15 (K/Si = 0.0075)	<0.1	–	–	–	–	–
K$^+$-0.5 wt.% CuO$_x$/SBA-15 (K/Si = 0.0075)	1.3	12	7.2	0.7	15	66
K$^+$-1 wt.% CuO$_x$/SBA-15 (K/Si = 0.0075)	5.9	18	2.1	0.3	11	69
K$^+$-3 wt.% CuO$_x$/SBA-15 (K/Si = 0.0075)	14	7.3	2.9	0.2	11	78
K$^+$-5 wt.% CuO$_x$/SBA-15 (K/Si = 0.0075)	4.0	16	3.9	0.3	14	66
K$^+$-10 wt.% CuO$_x$/SBA-15 (K/Si = 0.0075)	1.3	11	6.2	0.9	9.3	73
K$^+$-0.5 wt.% CuO$_x$/SBA-15 (K/Cu = 1.0)	3.5	15	3.4	0.4	13	68
K$^+$-1 wt.% CuO$_x$/SBA-15 (K/Cu = 1.0, K/Si = 0.0075)	5.9	18	2.1	0.3	11	69
K$^+$-3 wt.% CuO$_x$/SBA-15 (K/Cu = 1.0)	6.6	13	2.4	0.1	12	72
K$^+$-5 wt.% CuO$_x$/SBA-15 (K/Cu = 1.0)	0.18	1.8	18	6.8	16	58
K$^+$-10 wt.% CuO$_x$/SBA-15 (K/Cu = 1.0)	0	–	–	–	–	–

[a] Reaction conditions: catalyst weight, 0.20 g; temperature, 573 K; partial pressures of C_3H_6 and O_2, 2.5 and 98.8 kPa, respectively; total flow rate, 60 mL min^{-1}.

[b] Other products include allyl alcohol, acetone and acetaldehyde.

Table 3
Effect of reaction temperature on catalytic behaviors over the 1 wt.% CuO_x/SBA-15 and the K^+-1 wt.% CuO_x/SBA-15 catalysts[a]

Catalyst[b]	T (K)	C_3H_6 conv. (%)	Selectivity (%)				
			PO	Acrolein	Others[c]	CO	CO_2
CuO_x/SBA-15	498	0.8	6.9	41	16	11	25
	523	2.7	4.1	25	6.0	14	51
	548	6.6	1.8	21	2.9	18	56
	573	14	0.6	17	1.3	20	62
	623	33	0.1	12	0.8	26	61
K^+-CuO_x/SBA-15	498	0.4	59	8.7	3.5	4.2	24
	523	1.0	46	6.4	1.9	5.5	40
	548	2.1	35	4.9	1.1	9.1	49
	573	4.7	26	4.0	0.7	10	60
	598	7.2	20	3.4	0.5	13	63
	623	13	14	2.9	0.3	16	67

[a] Reaction conditions: catalyst weight, 0.20 g; partial pressures of C_3H_6 and O_2, 2.5 and 98.8 kPa, respectively; total flow rate, 60 mL min^{-1}.
[b] Copper content, 1.0 wt.%; K/Cu = 0.70.
[c] Other products include allyl alcohol, acetone and acetaldehyde.

acrolein was the main partial oxidation product, and PO was formed with a selectivity of larger than 5% (6.9%) only at a low temperature where C_3H_6 conversion was low (0.8%). PO became the main partial oxidation product over the K^+-modified catalyst in the whole temperature range investigated. PO selectivity of ~60% was obtained at a low C_3H_6 conversion (0.4%), and it could still be maintained at 46% as C_3H_6 conversion was increased to 1.0%. It is worthy mentioning that PO selectivities of 40–50% can only be obtained at C_3H_6 conversions of less than 0.3% over the Cu-based catalysts such as NaCl-modified $VCe_{1-x}Cu_xO_y$ [17], NaCl-modified Cu/SiO_2 [18] and Cu/SiO_2 prepared by a microemulsion technique [19] reported to date. Thus our present K^+-CuO_x/SBA-15 catalyst is very unique for the epoxidation of C_3H_6 with O_2.

From the temperature-dependence of C_3H_6 conversions, we have calculated the apparent activation energies for the 1 wt.% CuO_x/SBA-15 and the K^+-1 wt.% CuO_x/SBA-15 (K/Cu = 0.7) catalysts, and Fig. 5 shows the Arrhenius plots. These give apparent activation energy values of 92 and 72 kJ mol^{-1} for the two catalysts, respectively.

To further clarify the reaction routes over the catalysts with and without K^+ modification, we have investigated the effect of the pseudo-contact time, expressed as W/F, on the conversion of C_3H_6 to various products at 573 K, where W and F denote the catalyst weight and the total flow rate, respectively. Fig. 6 shows that the selectivity to acrolein increases and that to CO_x decreases as the contact time decreases over the 1 wt.% CuO_x/SBA-15 catalyst. PO can only be formed with a very low selectivity even at the very initial reaction stage over this catalyst. On the other hand, over the K^+-modified CuO_x/SBA-15 catalyst, PO selectivity increased significantly with decreasing the contact time, and thus PO was the major primary product although the formation of acrolein was also observed at very short contact times. Fig. 6 shows that the selectivities to PO and acrolein approach 80 and 20% as the contact time approaches zero over the K^+-1 wt.% CuO_x/SBA-15 catalyst. The reaction pathways over the two catalysts are summarized in Scheme 1. It becomes quite clear that the major reaction route is switched from allylic oxidation to epoxidation after the K^+ modification.

3.4. Structural properties of CuO_x/SBA-15 with and without K^+ modification

N_2-sorption measurements showed that SBA-15 prepared in this study possessed a BET surface area of 761 m^2 g^{-1}, pore volume of 0.93 cm^3 g^{-1}, and pore diameter of 5.8 nm. As seen in Table 4, the surface areas and pore volumes decreased gradually after the introduction of copper and potassium species. The typical TEM images shown in Fig. 7 for the 1 wt.% CuO_x/SBA-15 and the K^+-1 wt.% CuO_x/SBA-15 (K/Cu = 0.7) indicated that the ordered mesoporous structure was sustained after the introduction of copper and potassium species into

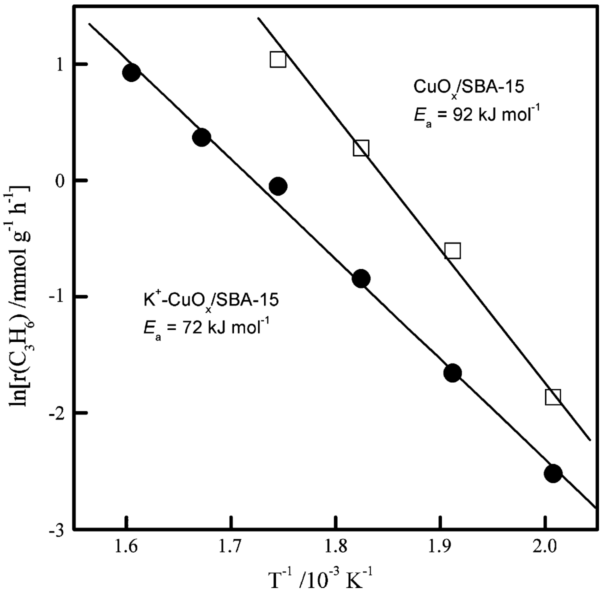


Fig. 5. Arrhenius plots for the oxidation of C_3H_6 over 1 wt.% CuO_x/SBA-15 and K^+-1 wt.% CuO_x/SBA-15 (K/Cu = 0.7) catalysts. See Table 3 for reaction conditions.

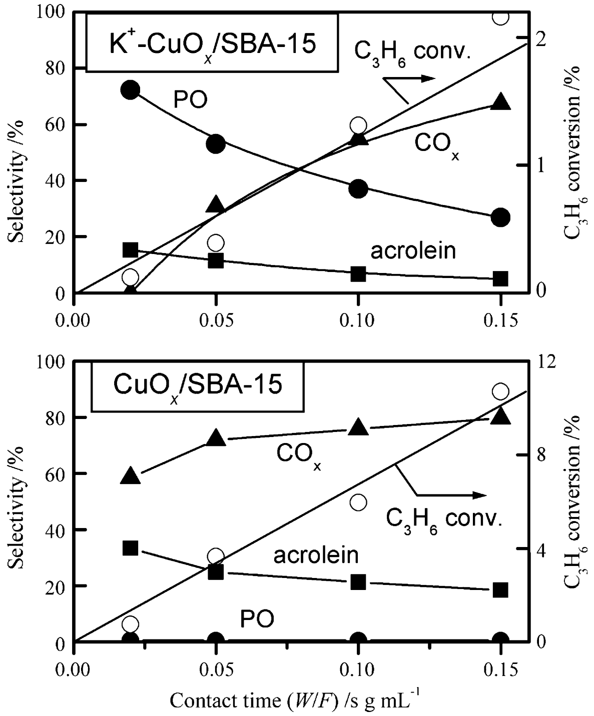
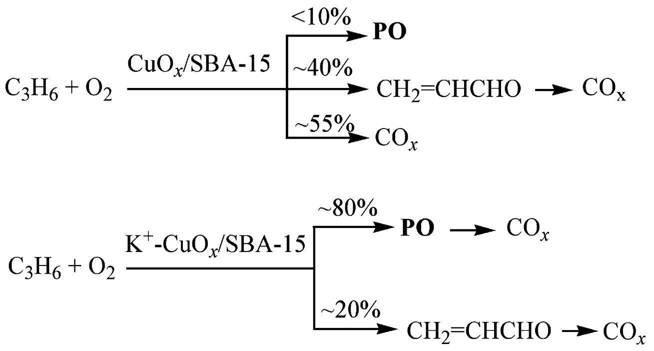


Fig. 6. Effect of contact time (expressed as *W*/*F*) on catalytic behaviors for the epoxidation of C_3H_6 over 1 wt.% CuO_x/SBA-15 and K^+-1 wt.% CuO_x/SBA-15 (K/Cu = 0.7) catalysts. Reaction conditions: temperature, 573 K; partial pressures of C_3H_6 and O_2, 2.5 and 98.8 kPa, respectively.



Scheme 1. Reaction pathways for the oxidation of C_3H_6 by O_2 over 1 wt.% CuO_x/SBA-15 and K^+-1 wt.% CuO_x/SBA-15 (K/Cu = 0.7) catalysts.

Table 4
Porous properties derived form N_2-sorption for CuO_x/SBA-15 and K^+-CuO_x/SBA-15 samples

Sample	S_{BET} ($m^2 g^{-1}$)	Pore volume ($cm^3 g^{-1}$)	Pore diameter (nm)
SBA-15	761	0.93	5.8
0.5 wt.% CuO_x/SBA-15	647	0.86	5.6
1 wt.% CuO_x/SBA-15	622	0.72	5.6
3 wt.% CuO_x/SBA-15	603	0.71	5.6
K^+-1 wt.% CuO_x/SBA-15 (K/Cu = 0.3)	464	0.70	5.9
K^+-1 wt.% CuO_x/SBA-15 (K/Cu = 0.7)	436	0.69	5.6
K^+-1 wt.% CuO_x/SBA-15 (K/Cu = 1)	361	0.66	6.2

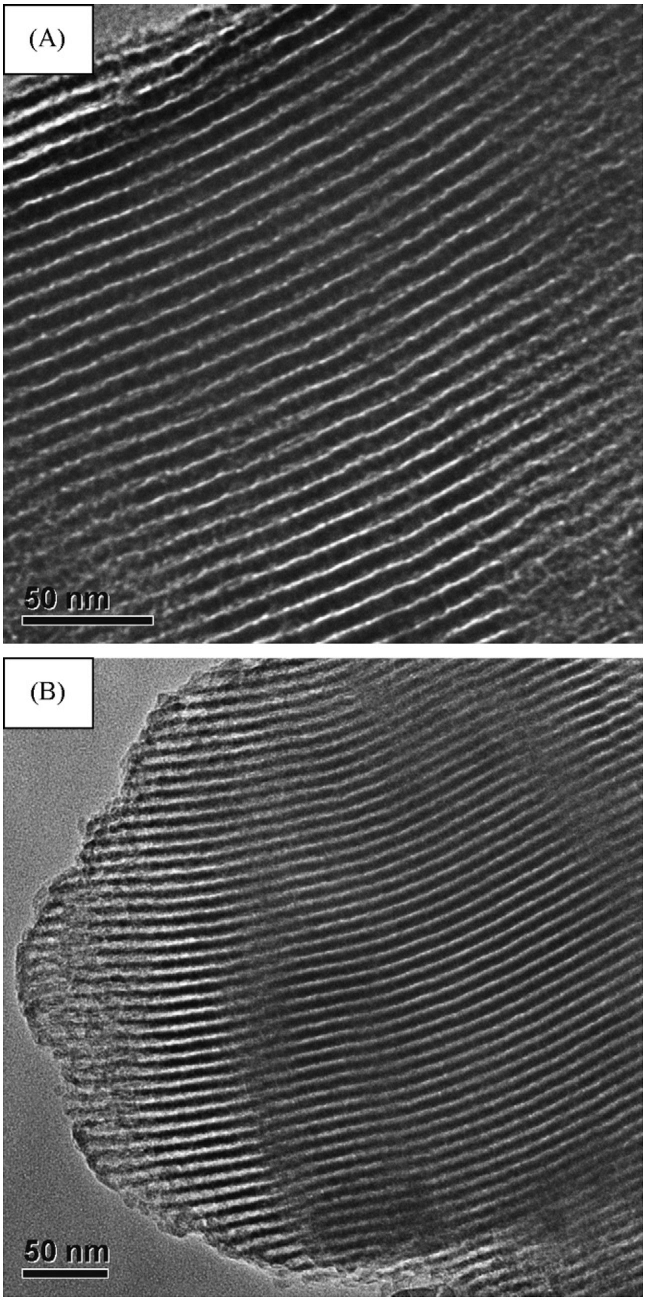


Fig. 7. TEM images of 1 wt.% CuO_x/SBA-15 (A) and K^+-1 wt.% CuO_x/SBA-15 (K/Cu = 0.7) (B).

SBA-15. This was also confirmed by XRD measurements. No copper- or potassium-related crystalline phases were observed as copper content was lower than 5 wt.%. All these observations suggest that copper and potassium species are probably located and highly dispersed inside the mesoporous channels of SBA-15.

Fig. 8 shows the H_2-TPR profiles for the CuO_x/SBA-15 with and without K^+ modification. Two reduction peaks at 503–513 K and 753–851 K were observed for the CuO_x/SBA-15 samples with copper contents of 0.5–3 wt.% (Fig. 8A), whereas only a single reduction peak at 569 K was observed for CuO crystallites. We tentatively assigned the two reduction peaks at 503–513 K and 753–851 K to the reductions of the $Cu^{II}O_x$

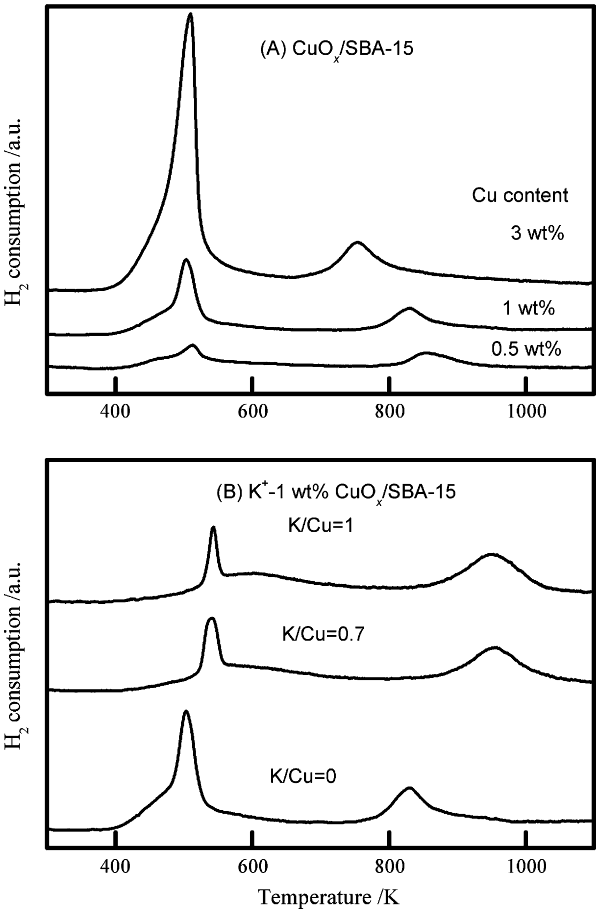


Fig. 8. H$_2$-TPR profiles for (A) CuO$_x$/SBA-15 samples with different copper contents and (B) K$^+$-1 wt.% CuO$_x$/SBA-15 samples with different K/Cu ratios.

clusters and the Cu^{2+} ions with strong interactions with the SBA-15, respectively. The modification with K$^+$ shifted these two peaks significantly to higher temperatures (Fig. 8B). This observation suggests that there exist interactions between K$^+$ and the copper species, i.e., CuO$_x$ clusters or Cu^{2+} ions, and the reactivity of lattice oxygen associated with CuO$_x$ clusters or Cu^{2+} ions is suppressed due to such interactions. It is quite interesting to note that, although the use of other potassium salts as the precursors of K$^+$ instead of KAc can also cause the shift of the reduction peaks, the reduction peaks are much broader in the case of using other potassium salts (Fig. 9). We speculate that the interaction between K$^+$ and the copper species in the case of using KAc precursor is more effective in forming homogeneously dispersed domains containing both K$^+$ and nearby Cu^{II} species. This may be responsible for the better PO selectivity obtained over the K$^+$-CuO$_x$/SBA-15 catalyst using KAc as the precursor (Table 1).

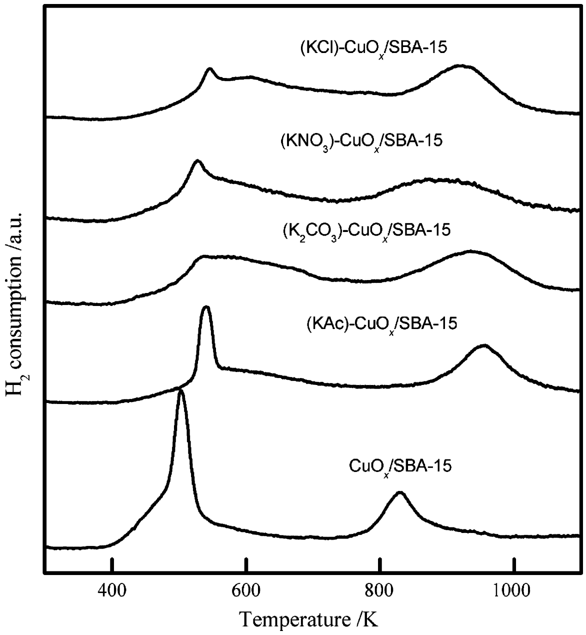


Fig. 9. H$_2$-TPR profiles for 1 wt.% CuO$_x$/SBA-15 and K$^+$-1 wt.% CuO$_x$/SBA-15 (K/Cu = 0.7) samples with different potassium salts as the precursors.

Diffuse reflectance UV–vis spectroscopic studies also suggested the strong interaction between K$^+$ and the copper species. As shown in Fig. 10, the 1 wt.% CuO$_x$/SBA-15 showed one strong absorption band at 235 nm, assignable to the charge-transfer transition of the ligand O^{2-} to metal center Cu^{2+} [24]. A very weak and broad band at ~800 nm was also observed for this sample (Fig. 10B), and this band can be ascribed to the d–d transition of CuO$_x$ clusters [24]. The center of the band shifted to a shorter-wavelength position and the band became relatively sharper after the modification with K$^+$ (Fig. 10B), indicating that the CuO$_x$ clusters became smaller due to the strong interaction between K$^+$ and CuO$_x$ clusters.

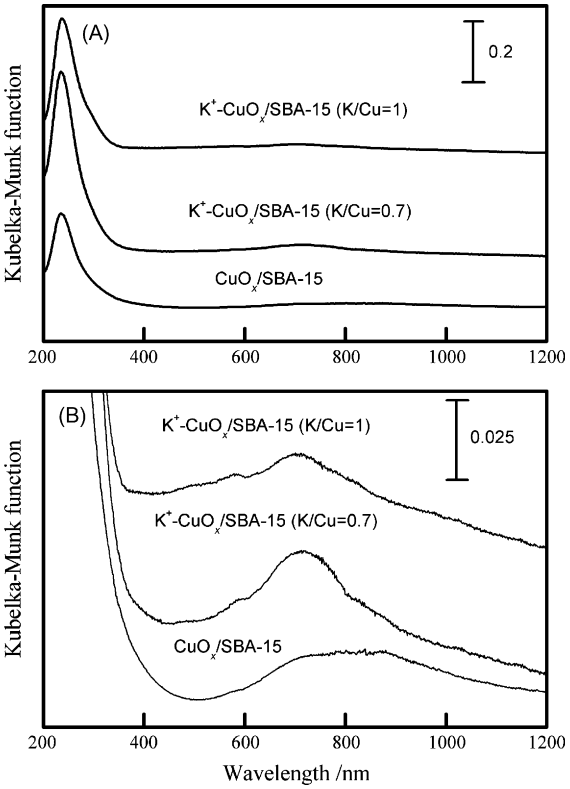


Fig. 10. Diffuse reflectance UV–vis spectra for 1 wt.% CuO$_x$/SBA-15 and K$^+$-1 wt.% CuO$_x$/SBA-15 samples with different K/Cu ratios.

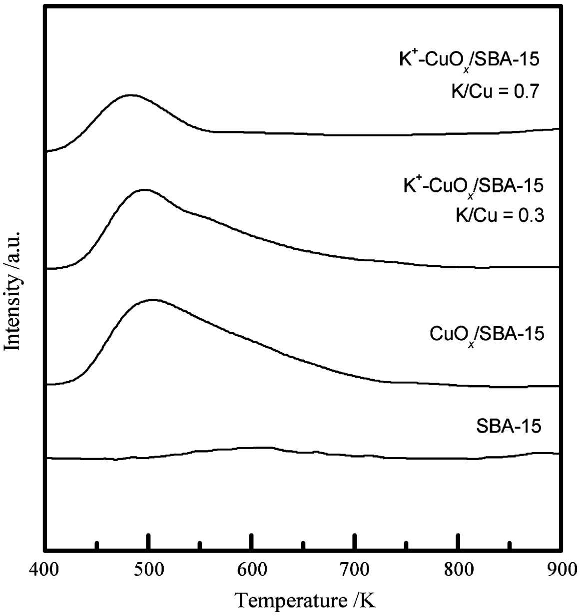


Fig. 11. NH_3-TPD profiles for SBA-15, 1 wt.% CuO_x/SBA-15 and K^+-1 wt.% CuO_x/SBA-15 samples with different K/Cu ratios.

The influence of the presence of K^+ on the acidity of the 1 wt.% CuO_x/SBA-15 was investigated by NH_3-TPD measurements. As shown in Fig. 11, almost no desorption of NH_3 was observed over SBA-15. A broad NH_3 desorption with peak position at ~505 K appeared over the 1 wt.% CuO_x/SBA-15, and this desorption could be ascribed to that from Lewis acid sites. The Lewis acid sites arose likely from the CuO_x clusters or Cu^{2+} sites introduced into SBA-15. After the modification with K^+, the intensity of the peak decreased, and the peak position shifted to 495 and 480 K for the samples with K/Cu ratios of 0.3 and 0.7, respectively. These observations clearly suggest that the interaction of CuO_x clusters or Cu^{2+} sites with K^+ decreased both the strength and the amount of acid sites. This may also contribute to the increase in PO selectivity because PO would undergo isomerization and further oxidation to CO_x under acidic circumstance [25].

3.5. Features of the present Cu-based catalyst

Previous studies have shown that Cu-based catalysts possess interesting catalytic behaviors in the epoxidation of C_3H_6 by O_2 [17–19]. Metallic copper (Cu^0) is proposed as the active phase in these studies, and the pre-reduction using H_2 has been carried out before reaction. However, high PO selectivities (40–50%) can only be obtained at very low C_3H_6 conversions (<0.3%), and the increase in C_3H_6 conversion to ~1% by increasing reaction temperature or O_2 partial pressure would lead to the decrease in PO selectivity to <5%. The transformation of Cu^0 to oxidized copper species (Cu^I or Cu^{II}) seems to be the main reason [18,19]. Monnier and Hartley [26] also indicated that Cu^0 may not be capable of functioning as an epoxidation catalyst because it would be rapidly transformed to an oxidized state.

In our studies presented here and reported previously [22], we found a unique catalyst showing distinct features from other reported Cu-based catalysts for C_3H_6 epoxidation by O_2. As shown in Table 3, although PO selectivity also decreases with increasing reaction temperature over the K^+-CuO_x/SBA-15 catalyst, but such decreases are not so steep as observed over other Cu-based catalysts reported to date [19]. Therefore, a high PO selectivity (46%) can still be maintained at a relatively higher C_3H_6 conversion (1%). Moreover, as shown in Table 5, in a large range of O_2 partial pressure including both O_2-rich and C_3H_6-rich conditions, PO selectivity did not undergo remarkable decreases with increasing O_2 pressure. We can obtain a PO formation rate of 2.2 mmol g^{-1} h^{-1} and a turnover frequency (TOF) for PO formation (based on the number of copper in the catalyst) of 18 h^{-1}. These values are 1–2 orders higher than those reported over other Cu-based catalysts [17–19]. These results also allow us to consider that it is not the metallic copper (Cu^0) but the copper in an oxidized state (Cu^I or Cu^{II}) that is responsible for the epoxidation of C_3H_6 by O_2.

Our characterizations (H_2-TPR and UV–vis) suggest that there exists a direct interaction between K^+ and copper species, both of which are probably located next to each other in the mesoporous channels. This interaction is proposed to play

Table 5
Effect of O_2 partial pressure on catalytic behaviors of the K^+-1 wt.% CuO_x/SBA-15 (K/Cu = 0.7) catalyst[a]

P (C_3H_6) (kPa)	*P* (O_2) (kPa)	C_3H_6 conv. (%)	Selectivity (%)				*r*(PO) (mmol g^{-1} h^{-1})	TOF[c] (h^{-1})
			PO	Acrolein	Others[b]	CO_x		
2.5	16.9	4.7	18	4.0	1.0	77	0.17	1.4
	33.8	6.9	17	3.3	0.6	79	0.24	1.9
	50.7	8.5	16	3.1	0.5	80	0.28	2.3
	67.6	10	16	3.1	0.4	81	0.31	2.6
	98.8	13	14	2.9	0.3	83	0.35	2.9
50.7	16.9	1.8	20	12	3.0	65	1.4	11
	25.3	1.8	23	11	2.7	64	1.6	13
	33.8	2.4	22	10	2.0	66	2.1	17
	42.2	2.2	24	11	2.0	63	2.2	18
	50.7	2.1	24	10	1.8	64	2.0	16

[a] Reaction conditions: catalyst weight, 0.20 g; temperature, 623 K; total flow rate, 60 mL min^{-1}.
[b] Other products include allyl alcohol, acetone and acetaldehyde.
[c] TOF was evaluated from the moles of PO formed per mole of Cu in the catalyst per hour.

pivotal roles in obtaining high PO formation activity. The interaction could suppress the reactivity of lattice oxygen species associated with the copper species as suggested by H_2-TPR. Since lattice oxygen species are generally regarded as nucleophilic oxygen species, the allylic oxidation, which causes the formation of acrolein, could thus be inhibited by the presence of K^+. The strength and amount of Lewis acid sites were also significantly decreased by the presence of K^+, favoring the PO selectivity. Therefore, the highly dispersed copper sites including isolated copper ions and small CuO_x clusters modified by the nearby K^+ ions are proposed to account for the epoxidation of C_3H_6 by O_2. We speculate that K^+ may further stabilize the electrophilic oxygen species (e.g., superoxide O_2^- or peroxide O_2^{2-} species) generated via the activation of oxygen on the nearby copper sites. In a Ag-catalyzed C_3H_6 epoxidation system, it has been proposed that the adsorbed alkali superoxides or peroxides may act as epoxidation agents [27]. Further elucidations of active oxygen species generated on our catalyst are underway in our laboratory.

4. Conclusions

We found that the K^+-modified CuO_x/SBA-15 catalyst exhibited outstanding catalytic performances in the epoxidation of propylene by oxygen. Copper was unique for this reaction among many transition metal elements investigated, and K^+ was found to be the best modifier for propylene oxide formation among various alkali and alkaline earth metal ions. The presence of K^+ could switch the main reaction route from allylic oxidation to epoxidation. Potassium acetate was the best precursor of K^+, and the interaction between K^+ and copper species played pivotal roles in obtaining higher PO selectivities. Propylene oxide selectivities of $\sim$50–60% can be obtained at propylene conversions of $\sim$0.4–1% over the present catalyst. The highest rate and turnover frequency for propylene oxide formation were $2.2\ \text{mmol g}^{-1}\ \text{h}^{-1}$ and $18\ \text{h}^{-1}$, respectively, which were 1–2 orders higher than those reported over other Cu-based catalysts.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (Nos. 20625310 and 20433030), the National Basic Research Program of China (Nos. 2003CB615803 and 2005CB221408), the Key Scientific Project of Fujian Province (No. 2005HZ01-3), the Programs for New Century Excellent Talents in University of China (No. NCET-04-0602) and in Fujian Province (grant to Q.Z.), and the Scientific Research Foundation for the Returned Overseas Chinese Scholars, State Education Ministry (grant to Q.Z.).

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