Novel dicopper(II) complex catalyst $Cu_2(II)(\mu\text{-}Cl)_2/SiO_2$: a study on synthesis of EC from CO_2 reaction with ethylene oxide

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Abstract

A novel process has been developed for synthesis of the silica supported dicopper(II) complex catalyst in which one Cu atom exchanging with two ion exchange sites on the surface of silica. The material was synthesized by reaction of NaOEt modifying the silica surface with dicopper(II) complex $[Cu_2(\mu\text{-}Cl)_2](ClO_4)_2 \cdot 8H_2O$ synthesized as pre-catalyst. The structure of the catalyst has been characterized comparatively with the dicopper(II) complex by element analysis, IR spectra and electronic spectra. The reaction of CO_2 with EO (ethylene oxide) has been investigated by temperature programmed desorption and in situ IR spectroscopy. TPD and IR results indicated that CO_2 and EO can be chemisorbed on the surface of the catalyst reversibly and desorbed at 393 and 378 K, respectively. TPSR-MS experiments have shown that EO desorbed dissociatively at high-temperature to form desorbed CO and CH_4 species. CO_2 and EO react on the surface in the temperature range of 353–397 K. In TPSR-IR investigation, EC (ethylene carbonate) produced was detected at 353 K, which is lower than the reported temperature of 393 K for homogeneous catalytic reaction. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Dicopper(II) complexes; Silica carrier; Supported catalyst; Carbon dioxide chemisorption; Ethylene oxide chemisorption; Synthesis of ethylene carbonate

1. Introduction

Synthesis of five-membered cyclic carbonates directly from CO_2 and oxirane is an important subject since the activation and utilization of CO_2 are critical for the substitution of toxic species such as phosgene and isocyanates [1] involved in this reaction. These carbonates can be used as aprotic polar solvent, source for polymer synthesis [2] and synthesis of lithium rich graphite intercalation compounds [3]. Many transition metal complexes are known to catalyze the oxirane-CO_2 reaction [4–6] in which metal ions ready to accept oxygen atoms are the active centers for the catalytic reaction. Meanwhile alkali metal halides [7] are also active catalysts because halide anions are the key element for activation of oxiranes. In our investigation, both virtues of these two types of catalysts are combined to design Cl^--bridged dicopper(II) complex and thus, grafted on the surface of silica. The chemisorption properties of both CO_2 and EO on the catalyst are investigated thoroughly and the reactivity of the reactants was studied by TPD, TPSR-MS and TPSR-IR techniques.

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2. Experimental

2.1. Material and equipment

Silica used as supporting material, was washed in 1N HNO_3, H_2O three times and dried at 473 K under vacuum (24 h). Other materials used were purchased from Peking Chemical Company and of analytical grade.

Metal contents were determined by EDTA titration. The infrared spectra were recorded with a Perkin-Elmer IR spectrophotometer, Model 983G, using KBr-disks. Electronic spectra (in methanol) were measured on a shimdze UV-240 spectrophotometer. Solution electrical conductivity measurements were made with a DDS-11A conductometer. TPD product were detected with a quadruple mass spectrometer, Model LZL-203.

2.2. Preparation of $[Cu_2(\mu\text{-}Cl)_2](ClO_4)_2 \cdot 8H_2O$

To a solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (1 mmol) in methanol (10 ml) was added solid state NaCl (1 mmol) and magnetically stirred for 2 h, then a yellow-green solution and the same colored crystal were obtained. The final product was separated, washed with absolute methanol and diethyl ether three times and dried in vacuum to give a satisfactory analysis data.

2.3. Preparation of silica supported catalyst $Cu_2(II)(\mu\text{-}Cl)_2/SiO_2$

To a solution of 44.8 ml ethanol containing 12.8 mmol NaOEt, 8 g SiO_2 carrier (350 $m^2\,g^{-1}$ BET area) was added. After reaction for 2 h at ca. 333 K protected by purging dinitrogen, 3.2 mmol $[Cu_2(\mu\text{-}Cl)_2](ClO_4)_2 \cdot 8H_2O$ was added. After stirring for 2 h, the white colored silica changed into green and the green colored solution changed into colorless. Then the catalyst synthesized was filtered, washed by EtOH for three times and dried in vacuum at 353 K.

2.4. TPSR-IR experiments

The catalyst was grinded into powder under 2 μm, and dispersed on KBr wafer, which were loaded into a controlled atmosphere of copper IR cell with KBr windows. The sample was pre-treated by heating to 373 K under vacuum (0.1 Pa). Spectra of samples with adsorbed CO_2 or EO were taken after exposure of samples to 0.5 mmol CO_2 or EO gas for 2 h and then cleared the excess gas under vacuum of 0.1 Pa. The same process was used in the TPSR-IR experiment, when CO_2 and EO were co-adsorbed on the surface of the catalyst. The IR spectra were monitored in the range of 273–433 K.

2.5. TPD and TPSR-MS experiments

In the TPD experiment, 500 mg catalyst was loaded in a quartz micro-reactor and the two sides were stuffed by asbestos fiber. Before the adsorption of CO_2 and EO, the catalyst was treated by heating to 373 K under vacuum (1×10^{-4} Pa) for 2 h. The adsorption was performed at 298 K by injection of 0.5 mmol of CO_2 or EO. After 2 h, excess amount of CO_2 or EO was removed by evacuation to 1×10^{-4} Pa. The catalyst was ramped as a linear heating rate of 8 K min^{-1}. The desorbed gases were analyzed by a quadruple mass spectrometer at $m/e = 44$ (for CO_2 and EO are the same), $m/e = 28$ and 16, respectively. TPSR-MS was performed in the same condition and the samples were treated with mixture of CO_2 and EO (0.5 mmol, respectively). The observed intensity for CO_2 and EO were analyzed with respect to elucidate the surface reaction definitely.

3. Results and discussion

3.1. Surface structure of $Cu_2(\mu\text{-}Cl)_2/SiO_2$

Titration analysis data indicated that the ratio of Cu:Cl is equal to 1:1 (Table 1) and the molar

Table 1
Physical and chemistry data for dicopper(II) complexes and the catalyst

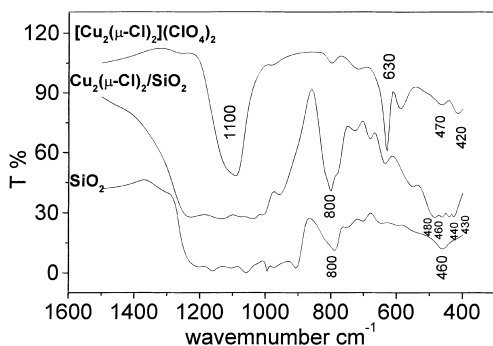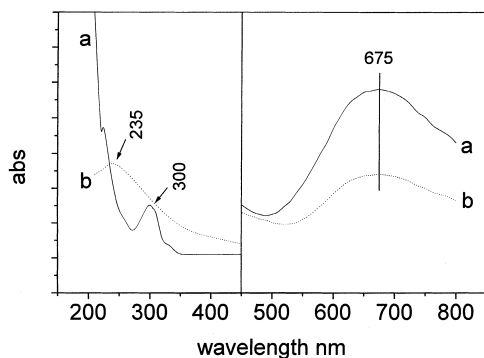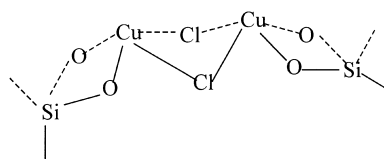| Sample	Cu%	Analysis Cl %	Cu:Cl	Color	Λ ($\Omega^{-1}\,cm^2\,mol^{-1}$) in MeOH
$[Cu_2(\mu\text{-}Cl)_2](ClO_4)_2 \cdot 8H_2O$	23.5	13.1	1:1	Green	182
$Cu_2(\mu\text{-}Cl)_2/SiO_2$ (0.4 mmol Cu_2/g SiO_2)	4.57	2.55	1:1	Green	195

Fig. 1. IR spectra of the catalyst.

Scheme 1. Proposed structure of the catalyst.

conductance value for the solution resulted when the catalyst was treated with four equivalent of $HClO_4$ fall in the range of 1:2 electrolyte.

In IR spectra of the catalyst (Fig. 1), a strong band at $800 \, cm^{-1}$ was found, which was assigned to the Cu–O–Si vibration, no bands at 1100 and $630 \, cm^{-1}$ expected for the ClO_4^- group was detected in the spectra of the catalyst indicating that the ion exchange process has taken placed. Bands at 420 and $470 \, cm^{-1}$ were ascribed to Cu–Cl–Cu structure of the dicopper(II) complex, however, they split to quadruple peaks in the spectra of the catalyst when coupling with the vibration of silica ($460 \, cm^{-1}$) in this region.

The electronic spectra of the dicopper(II) complex and the catalyst are given as Fig. 2. A weak and broad band at ca. 675 nm was discovered for the both samples. The profiles of the two envelopes are very similar indicating that the copper(II) ions are sited in the same co-ordination environment. In high-energy, band

at 300 nm was attributed to LMCT of O→Cu for curve a. Meanwhile band at 235 nm of curve b could be assigned to the Si–O→Cu transfer.

Based on the discussion above, the complex catalyst was proposed to have bis-μ-Cl^--bridged dicopper(II) structure with Cu(II) anchoring on silica in bidentate fashion. The formation of the catalyst could be interpreted as Scheme 1.

3.2. Chemisorption state of CO_2

Fig. 3 shows the IR spectra of CO_2 adsorbed on the catalyst. In curve c band at $680 \, cm^{-1}$ was attributed to CO_2, which shifted to $660 \, cm^{-1}$ in adsorption state spectra (curve b) suggesting that CO_2 was chemisorbed on the catalyst. In curve b, bands at 1120 and $960 \, cm^{-1}$ were ascribed to bridged adsorption state of CO_2 [8–10]. Band at $800 \, cm^{-1}$ (in curve a) splits to double peaks of 805 and $795 \, cm^{-1}$ (in curve b) indicating that the Si–O–Cu group participates the chemisorption process.

Fig. 4 shows the trace of CO_2 and CO desorbed from the catalyst following the CO_2 adsorption. For $m/e = 44$, two peaks were discovered at 393 and

Fig. 2. Electronic spectra of the dicopper(II) complex and the catalyst. (a) $[Cu_2(\mu\text{-}Cl)_2](ClO_4)_2$; (b) $Cu_2(\mu\text{-}Cl)_2/SiO_2$.
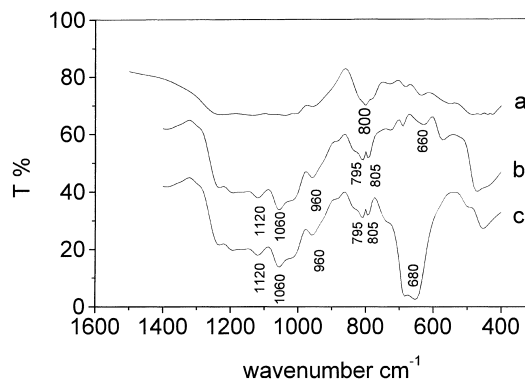
Fig. 3. IR spectra of CO_2 absorbed on the catalyst. (a) Catalyst; (b) catalyst + CO_2 (ads.); (c) catalyst + CO_2 (gas).

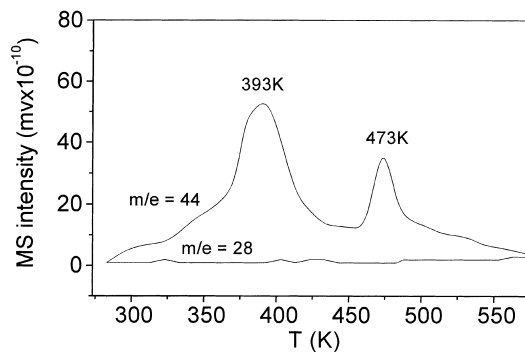Fig. 4. TPD-MS profile after CO_2 absorbed on the catalyst at $m/e = 44$ and 28.

Fig. 6. IR spectra of of EO absorbed on the catalyst. (a) Catalyst + EO (ads.); (b) catalyst + EO (gas).

473 K, respectively. The former is more intense than the later one, and there is no coverage between the two peaks suggesting that there exist two types of CO_2 chemisorption state on the surface of the catalyst. When monitored at $m/e = 28$, no CO were detected, presented that when CO_2 desorbed from the surface, CO_2 did not undergoes decomposing process.

Based on the discussion above, at low-temperature a reversible adsorption state was proposed (Fig. 5). The high-temperature TPD-MS band revealed could be attributed to the formation of a more stable bridged adsorption state.

3.3. Chemisorption state of EO

IR spectra of EO adsorbed on the catalyst were presented in Fig. 6. In curve b, the feature band of EO at $860 \, cm^{-1}$ shifted to $890 \, cm^{-1}$ suggesting that EO undergoes chemisorption process (at high-energy, bands of 3020 and $1642 \, cm^{-1}$ shifted to 2980 and $1640 \, cm^{-1}$, respectively, not given). Bands at $1260 \, cm^{-1}$ denoting the inner-cyclic C–O band

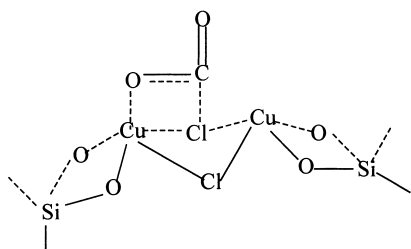disappeared in absorption state spectra Fig. 6(a), indicating that EO undergoes cyclic opening process on the surface. A new band at $1100 \, cm^{-1}$ (curve a) was found, which could be attributed to C–O vibration. Also in curve a, the characteristics of Cu–Cl–Cu vibration ($400–800 \, cm^{-1}$) changed significantly when compared with the IR spectra of the catalyst, suggesting that the Cu_2 unit participate the chemisorption process.

In the activation of EO, both reversible adsorption process of EO on metal catalyst [11,12] and ring opening reaction of EO on oxygen covered metal catalyst [13,14] have been reported. In our work, the TPD-MS profiles of desorption products are shown in Fig. 7. In the spectra of $m/e = 44$, two peaks were observed at around 378 and 468 K. When monitored at $m/e = 28$ and 16, respectively, the TPD profiles reveals that at high-temperature CO and CH_4 were produced. This
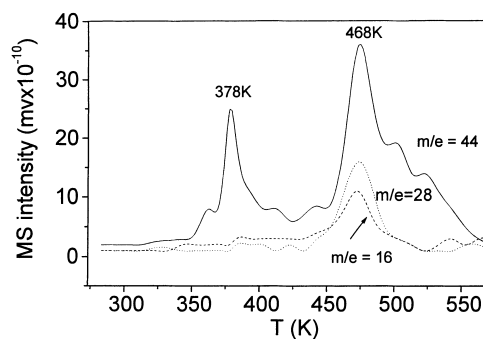

Fig. 5. Absorption model of CO_2 on the catalyst.

Fig. 7. TPD-MS profiles after EO absorbed on the catalyst at $m/e = 44$, 28 (CO) and 16 (CH_4).
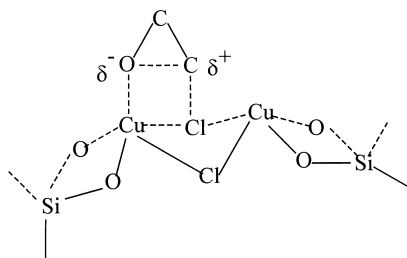
Fig. 8. Absorption model of EO on the catalyst.

phenomenon suggested that there exist two different chemisorption states of EO on the surface of the catalyst. In the low-temperature EO molecules desorbed from the surface reversibly. At high-temperature EO undergoes decomposing process.

Since halide anions atom is the best candidate to attack EO [15] and copper(II) ions is ready to co-ordinated with O^- thus, formed. The reversible adsorption state was proposed as Fig. 8. The high-energy peak of $m/e = 44$ TPD-MS curve is tentatively assign to the deep bonding species of EO with the surface complex (may form bridging structure).
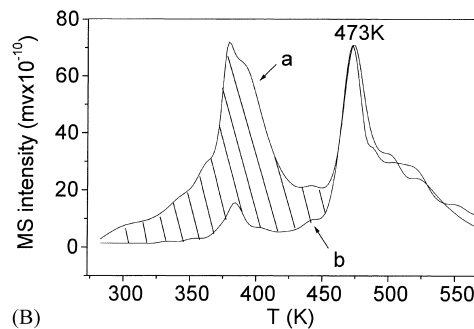
3.4. TPSR-MS results

Although the quadruple mass spectrometer used in this study could not detect products more then $m/e = 60$, and the product formed could not be monitored directly, however, the surface reaction profile monitored at $m/e = 44$ present the interaction behavior of CO_2 and EO (they both have the same m/e value). Fig. 9A shows the TPSR profile monitored at $m/e = 44$ in the temperature range of 273–573 K. Two single peaks at 393 and 573 K were observed (curve d). Since intensity of the low-temperature peak is lower than that of either CO_2 (curve b) or EO (curve c) and much lower than the plus of these two peaks (curve a), the chemisorbed molecules of the two reactants must react each other.

Quantitative analysis is presented in Fig. 9B. In the low-temperature (283–463 K) about 68% of adsorbed reactants have reacted each other. The formation of EC was identified by GC method. Significantly, for the high-temperature peak (473 K) the pseudo-plused intensity (curve a) is almost equal to the real profile (curve b), indicating that at high-energy the desorbed
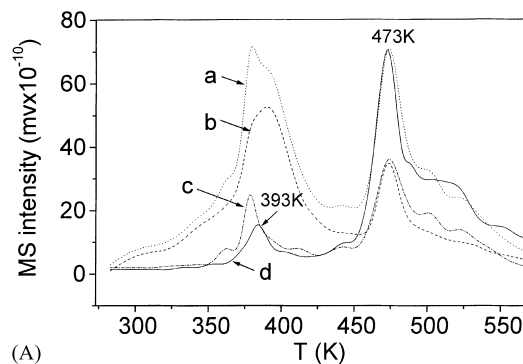
Fig. 9. (A) TPSR-MS profile of the catalyst adsorbed by CO_2 and EO. (a) Expected profile when CO_2 and EO do not react each other; (b) TPD profile of CO_2; (c) TPD profile of EO; (d) TPSR-MS result monitored at $m/e = 44$; (B) quantitative analysis of the TPSR-MS result (marked area denotes the amount of reacted reactants). (a) Expected profile when CO_2 and EO do not react each other; (b) TPSR-MS result monitored at $m/e = 44$.

species are not ready to react each other. This result is consistent with the decomposed desorption process discussed in Section 3.3.
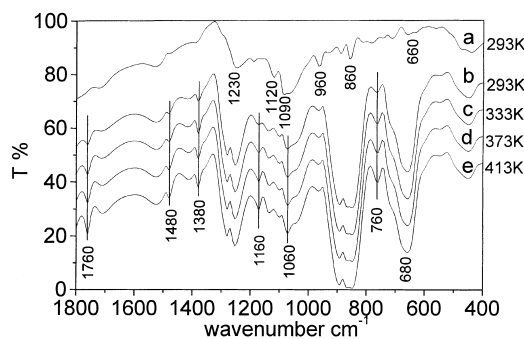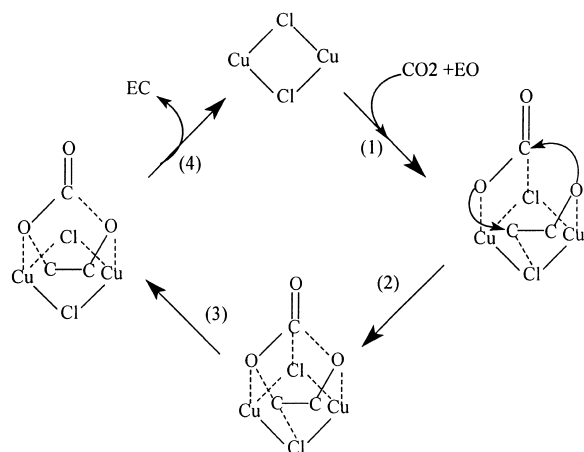

Fig. 10. (a) TPSR-IR spectra of CO_2 and EO co-adsorbed on the catalyst; (b–e) TPSR-IR spectra in the of range 293–413 K.

Scheme 2. Proposed mechanism of the catalytic reaction.

3.5. TPSR-IR experiments

The reactivity of CO_2 with EO was investigated by in situ IR technique. Fig. 10a shows the IR spectra of CO_2 and EO co-adsorbed on the surface of the catalyst. Bands at 1120, 960 and 660 cm^{-1} represent the adsorption state of CO_2, while bands at 1090 and 860 cm^{-1} were assigned to EO adsorbed on the surface. This result indicated that CO_2 and EO undergo competitive adsorption process. Fig. 10b–e represents the reaction process upon heating the catalyst in the range of 293–413 K. With the increase of the temperature, new bands at 1760, 1480, 1380, 1160, 1060 and 760 cm^{-1} revealed. All these bands are characteristic of ethylene carbonate.

3.6. Discussion of the reaction mechanism

Based on the discussion above, a typical mechanism for the catalytic reaction is indicated in Scheme 2.

When the reactants were mixed and purged on the surface of the catalyst, the essential steps involve:

1. two kinds of molecules may chemisorbed on the same Cu_2 unit, since it is bridged by bis-chloro ligands;
2. in the temperature from 373 to 393 K, both CO_2 and EO were activated on the surface, thus, forming the transition state;
3. essentially, halides anions showed considerable nucleophilicity and leaving ability in synthesis of EC [7]. It is reasonable that the C–Cl bonds breaks off prior that of the Cu–O band;
4. after the ring forming process, the carbonate molecules leave the Cu_2 unit and leave the initial catalyst ready to achieve another catalytic cycle.

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