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Preparation of a zeolite X-encapsulated copper(II) chloride complex and its catalysis for liquid-phase oxygenation of enamines in the presence of molecular oxygen

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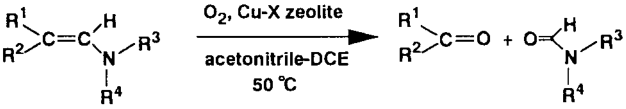
Copper(II) chloride complexes were readily prepared within pores of zeolite X with the modified zeolite found to act as a heterogeneous catalyst for the oxygenation of a variety of enamines in the presence of molecular oxygen without leaching of the active copper species.

Highly selective transformation of organic compounds catalysed by solid materials can contribute to the strong demand of environmental concerns in chemical processes because of the following advantages: (i) simple work-up procedures, (ii) reusable catalysts, and (iii) high thermal stabilities.[1–3] Use of metal catalysts in a liquid phase, however, sometimes leads to leaching of the active species from the solid surface into solution[4] which causes a serious loss of activity and contamination of the products. Here, we describe the synthesis of a Cu(II) chloride complex catalyst within the pores of zeolite X for the selective oxygenation of enamines in the presence of molecular oxygen (Scheme 1). This catalyst can be reused without leaching of the Cu species and retains its high catalytic activity and selectivity for the above oxygenation.



Scheme 1

Copper ion-exchanged X zeolite (Cu–X) was prepared by a treatment of Na–X zeolite, $Na_{86}(Al_{86}Si_{106}O_{384})\cdot 264H_2O$ (Si/Al = 1.23, Wako Co. Ltd.), with a 0.01 M aqueous solution of $Cu(NO_3)_2\cdot 3H_2O$. The powder was washed with deionized water, followed by drying and calcination at 300 °C to give a sky-blue Cu–X sample. The Cu content in this sample was 12.0 wt%, which corresponds to 83% ion exchange degree of Na^+. Retention of the crystal structure of the X zeolite was confirmed by XRD. *In situ* EPR, UV–VIS and Cu K-edge XANES spectra for the Cu–X sample indicated dispersed divalent Cu^{2+} with a centrosymmetric coordination environment, *i.e.* octahedral. Curve-fitting analysis of the Fourier-transformed copper EXAFS showed that the Cu^{2+} cations displayed Jahn–Teller distorted CuO_6 octahedra[5] with four short Cu–O distances (1.91 Å) and two long Cu–O distances (2.28 Å). The Cu–O distance of 1.91 Å is slightly shorter than the value of 1.97 Å found in Cu–Y zeolites.[6] A lack of a peak at *ca.* 3 Å in the Fourier transform of the Cu K-edge EXAFS indicated selective formation of monomeric Cu^{2+} species. A coordination sphere of the CuO_6 octahedra within the zeolite pores is proposed as shown in Fig. 1(a) where the Cu^{2+} ion is reasonably located in a vicinity of the exchangeable site II, just outside the sodalite cage in a large pore with 7.4 Å diameter.[7]

Cu–X (0.50 g) was further treated with 1,2-dichloroethane (DCE, 10 mL) at 50 °C for 1 h, followed by drying to afford an emerald greenish powder, Cu(Cl)–X. The presence of Cu–Cl bonds was confirmed by XPS measurements and elemental analysis; the atomic ratio of Cu to Cl was 1 : 1.8. EXAFS analysis of Cu(Cl)–X also revealed a Jahn–Teller distorted Cu^{2+} octahedron with four Cu–O bonds (1.92 Å) and two Cu–Cl bonds (2.29 Å). The Cu–Cl distance of 2.29 Å is consistent with a Cu–Cl bond length of 2.30 Å in $CuCl_2$ and a proposed structure of the monomeric Cu^{2+} chloride complex is shown in Fig. 1(b). To our knowledge, this is the *first* example of the synthesis of a copper(II) chloride species within a pore of zeolite X. It has been stated that Cu chloride complexes can not be formed within the pores of zeolite X by a simple exchange reaction of Na–X with $CuCl_2$ solution because of destruction of the faujasite structure of zeolite X.[8] In zeolite Y, adoption of burdensome methods such as chemical vapor deposition[6] or a solid-state ion-exchange[8] can afford monovalent copper chloride species. The chlorine in Cu(Cl)–X originates from a DCE molecule during the treatment of Cu–X with DCE. The fact is supported by the formation of dibenzyl ether upon treatment of Cu–X with benzyl chloride in place of DCE.[9]

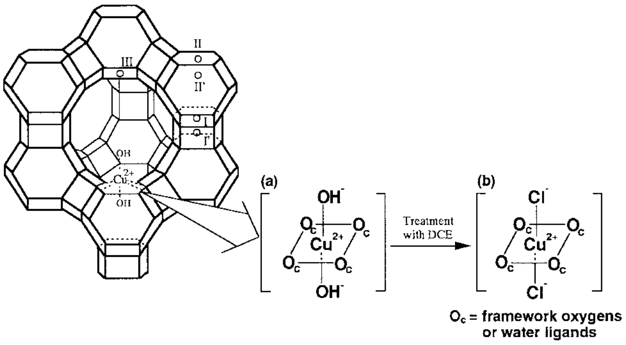


Fig. 1 Proposed schematic structure of Cu^{2+} octahedral species within the framework structure of zeolite X. (a) CuO_6 octahedral species, (b) CuO_4Cl_2 octahedral species. The octahedral CuO_4X_2 species is coordinated to oxygens of zeolite framework and H_2O ligands. The positions of exchangeable cations are indicated by Roman letters.

We have already reported that copper chloride compounds are effective homogeneous catalysts for the oxidative cleavage of carbon double bonds of enamines in the presence of molecular oxygen.[10] To explore the potential catalytic abilities of the Cu(II) chloride complexes within the zeolite X,[11] oxygenation of enamines using Cu–X was performed.† Typical results for the oxygenation of enamines with Cu–X in acetonitrile–DCE are summarized in Table 1.‡ The carbon double bonds of many enamines were smoothly cleaved to give the corresponding amides and ketones (entries 1, 2 and 4–8). For a bulky enamine such as 1-(4-morpholino)-2,2-diphenylethene, the oxygenation rate with Cu–X was slower than that of a homogeneous $CuCl_2$ catalyst (entry 9 *vs.* 10). This different activity between the heterogeneous Cu–X and the homogeneous $CuCl_2$ catalyst might be ascribed to a shape-selective effect of Cu^{2+} species within the three-dimensional zeolite pores. The Cu–X catalyst was also active for the oxygenation of 2,3-dimethylindole (entry 11).§

The Cu–X catalyst could be easily separated from the reaction mixture and reused without an appreciable loss of its

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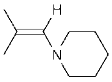
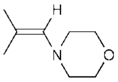
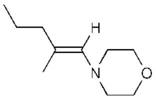
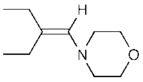
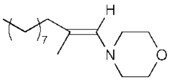
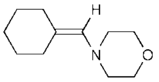
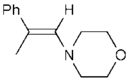
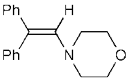
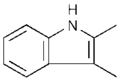
Table 1 The oxidative cleavage of enamines catalysed by Cu–X zeolite in the presence of molecular oxygen[a]

Entry	Substrate	t/h	Conv. (%)	Yield of products (%)[b]	
				Amide	Ketone
1		5	100	97	*c*
2		5	100	93 (fresh)	*c*
		5	98	90 (reuse-1)	*c*
		5	99	90 (reuse-2)	*c*
		5	98	90 (reuse-3)	*c*
3[d]		1	100	80	*c*
4		6	100	83	80
5		5	100	90	82
6		5	100	96	97
7		5	100	76	73
8		5	100	70	84
9		24	91	61	66
10[d]		1	100	95	87
11		3	100	84[e]	

[a] Substrate (2 mmol); Cu–X (0.10 g, 0.19 mmol-Cu); solvent (8 mL; acetonitrile–DCE, 7 : 1); temperature = 50 °C; O_2 atmosphere. [b] Yields based on enamine. [c] Acetone formed, however, the yields were not determined. [d] Homogeneous oxidation using $CuCl_2$ (0.19 mmol). [e] *N*-(2-Acetylphenyl)acetamide isolated by column chromatography on silica gel.

activity for the oxygenation; the first, second and third runs of the reused catalyst for 1-(4-morpholino)-2-methylpropene gave *N*-formylmorpholine in > 90% yield. The loss of Cu content in the spent Cu–X catalyst after several reuse experiments was < 1%; the Cu content in the catalyst did not change even after the third reuse. ICP analysis of copper in the liquid phase after oxygenation showed that leached copper from the catalyst was < 1% in the spent Cu–X catalyst.¶ The fact that the active copper complex does not leach from the zeolite X during the oxygenation and recycling procedures, indicates a reusable heterogeneous catalyst for the liquid-phase oxidation.

We presume that the oxygenation catalysed by the Cu(Cl)–X catalyst might involve one-electron transfer from the enamine to molecular oxygen in a ternary Cu^{2+} complex bonded to enamine and O_2, followed by the formation of Cu^{2+} and a dioxetane intermediate.[10] Strong binding of the Cu chloride complexes on the zeolite is due to the location of the divalent Cu ions within large supercages, bound to oxygens of the zeolite framework [Fig. 1(b)].[12] During the oxygenation, facile coordination of enamine and O_2 to the active Cu center can occur since some ligands such as H_2O on the Cu active species are labile.

In conclusion, monomeric copper(II) chloride species within the pore of zeolite X can be synthesized by a novel and convenient method, and are found to be effective catalysts for the cleavage of enamine double bonds in the presence of molecular oxygen. This zeolite X-encapsulated copper chloride complex is a unique instance of a heterogeneous and reusable catalyst which does not undergo leaching of the active species.

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Notes and references

† The order of the catalytic activity of various copper catalysts for the oxygenation of 1-(4-morpholino)-2-methylpropene is: Cu–X(93) > Cu–Y(82) > Cu-mordenite(76) > Cu/Al_2O_3(72) > Cu/SiO_2 (38), where values in parentheses are yields of *N*-formylmorpholine.

‡ We confirmed that the catalysis of Cu–X in the mixed solvent corresponded to that of Cu(Cl)–X. Cu(Cl)–X itself effectively oxygenated the enamine in acetonitrile alone (yield: 70%). Solvents having high dielectronic constants such as acetonitrile, DMF and ethanol were effective co-solvents for DCE, as similarly observed in the homogeneous catalyst system using $CuCl_2$.[10]

§ Interestingly, this heterogeneous catalyst showed higher activity than $CuCl_2$ for 2,3-dimethylindole,[13] however, the oxidation of 3-methylindole resulted in a low yield (34% after 24 h).

¶ When the filtrate at 50% enamine conversion was allowed to react further at 50 °C under an oxygen atmosphere, oxygenation did not occur.

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