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Pseudohomogeneous liquid-phase oxidation of cyclohexene with O_2 in the presence of heterogenised copper(II) chelates

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The liquid-phase oxidation of cyclohexene with dioxygen in the presence of mononuclear chelate *N,N'*-propylene-bis(2-methyl-1-benzoylglyoxal-1-phenylhydrazoneiminato)copper(II) (1), zeolite-anchored complexes 1, and a polynuclear derivative obtained by condensation of 1 with benzidine was studied.

The problem of the connection between homogeneous and heterogeneous catalyses is of growing importance. Chelate metal complexes of organic ligands are known to be efficient homogeneous catalysts for a lot of reactions. However, the application of the chelate metal complexes as homogeneous liquid-phase catalysts is limited by their low solubility in water and organic media.

On the other hand, zeolite-supported metal chelates known as ‘ship-in-the-bottle’ systems[1–6] are often inefficient due to the second sieve effect.

In order to improve the efficiency of zeolite-supported homogeneous catalysts, a new method for the supporting of metal complexes with organic ligands was developed.[7–10] The metal complexes are retained on zeolite by means of anchors, which are in turn ‘irreversibly’ trapped within the zeolitic supercages. The anchoring of metal chelates takes place by means of sterically hindered molecules within supercages fronting towards an external surface of the zeolitic crystallites.

Here we report on a study of the catalytic activity of chelate copper(II) complexes **1** and **2** (Figure 1) topologically anchored on CaA zeolite.

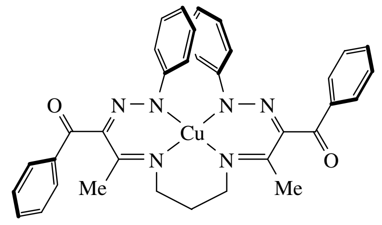
The samples containing zeolite-anchored complexes **1** and **2** (5.0×10^{-8} and 2.01×10^{-6} mol of copper atoms per gram of air-dried CaA zeolite, respectively) were prepared as described elsewhere.[9,10] Liquid-phase oxidation of cyclohexene (RH) was studied in a toluene solution (20 cm^3) in a static system in the presence of 0.1 mol dm^{-3} of cyclohexenyl hydroperoxide (ROOH). The reaction kinetics was monitored volumetrically by O_2 uptake in a glass shaking reactor at room temperature (22±1 °C). The reaction mixture was analysed by GC (Chrom-5, Separon column, 1.5 m×4 mm, 423 K). The amount of copper from chelate complexes **1** and **2** anchored on the CaA zeolite was determined iodometrically.

In order to compare the catalytic activities of the samples prepared, the oxidation of cyclohexene was studied as a test reaction. The mechanism of the liquid-phase oxidation of cyclohexene with O_2 in the presence of related chelate compounds of Cu^{II} was studied in detail elsewhere.[11–15]

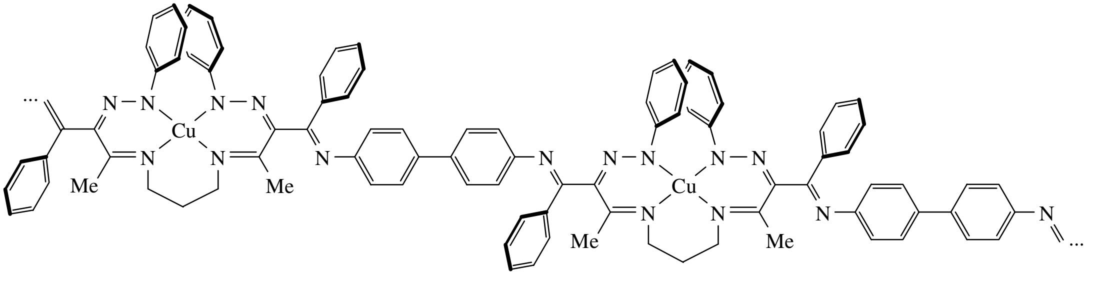
The liquid-phase oxidation of cyclohexene in the presence of zeolite-anchored chelate copper(II) complexes **1** and **2** was found to yield cyclohexen-2-one, cyclohexen-2-ol and 1,2-epoxycyclohexene in a 2:1:1 molar ratio. The uptake of O_2 begins after the addition of cyclohexenyl hydroperoxide to the solution. No consumption of oxygen occurs without ROOH.

The consumption of O_2 by solutions of cyclohexene in the presence of **1** and **2** is shown in Figure 2. The observed initial rate of the cyclohexene oxidation, $r_{i(o)}$, (i = 1 and 2 for samples **1** and **2**, respectively) was found to be independent of the O_2 partial pressure in the range of 10–60 kPa. Meanwhile, $r_{i(o)}$ was found to depend on concentrations of RH and ROOH:

$$r_{i(o)} = k_i[\mathrm{RH}][\mathrm{ROOH}] \qquad (1)$$



Mononuclear chelate **1**



Polynuclear chelate **2**

Figure 1 Mononuclear (**1**) and polynuclear (**2**) chelate copper(II) complexes.

where [RH] and [ROOH] are the current concentrations of cyclohexene and cyclohexenyl hydroperoxide, respectively; k_i is the observed rate constant in the presence of **1** (k_1) or **2** (k_2).

The same results were obtained elsewere[11–15] for this reaction in the presence of related chelate Cu$^{\rm II}$ complexes under homogeneous conditions. A similarity of the reaction kinetics in the presence of the related Cu$^{\rm II}$ chelates and compounds **1** and **2** suggests a single mechanism of the cyclohexene oxidation with molecular O_2 discussed earlier.[11–15]

The observed rate constants k_1 and k_2 depend on the masses of samples **1** and **2**, respectively. Figure 3 shows the plot of k_i as a function of the masses of samples **1** and **2**. The plot of k_i *vs.* the masses of samples indicates a linear dependence of the reaction rate on the amount of chelate metal complexes **1** and **2** supported on CaA zeolite.

In order to monitor changes in catalytic activity after chelate copper(II) complexes **1** and **2** being anchored on the CaA zeolite, the same reaction was studied in the absence of the zeolite. The O_2 consumption by a solution of cyclohexene in toluene in the presence of **1** is also plotted in Figure 2.

Chelate compound **1** is very soluble and exhibits high catalytic activity. Polynuclear compound **2** is insoluble in the reaction mixture and could operate as a heterogeneous catalyst. However, the consumption of O_2 in the presence of **2** is extremely low (Figure 2) due to the negligible surface area of the solid.

It is difficult to compare the catalytic activities of copper complexes **1** and **2** under homogeneous and heterogeneous conditions. In order to compare the catalytic activities of chelate **1** and zeolite-anchored samples containing **1** and **2**, the observed conventional rate constants, k_c, were calculated as follows:

$$k_c = k_i/[\mathrm{Cu}], \tag{2}$$

where $[\mathrm{Cu}] = n/v$. Here, n is the number of moles of copper atoms in the solid and v is the volume of the liquid phase. For the reaction in the presence of homogeneous catalyst **1**, the [Cu] value is the real molar concentration of **1**. For the heterogeneous reactions, the [Cu] values formally represent the imaginary molar concentrations of copper atoms in the liquid-phase heterogeneous systems containing samples **1** or **2**. The k_c values calculated for the reaction in the presence of zeolite-anchored complexes **1** and **2** (Table 1) are comparable to k_c obtained for cyclohexene oxidation in the presence of homogeneous catalyst **1**. It means that there is no difference between the kinetic behaviours of the copper chelates under both homogeneous and heterogeneous conditions. In other words, heterogenised copper complexes **1** and **2** operate as pseudohomogeneous catalysts.

The kinetic data (Table 1) provide information on the nature of the catalytic activity of mononuclear and polynuclear chelates **1** and **2**, respectively, anchored on CaA zeolite. The coincidence of k_c for both homogeneous and heterogenised chelates is valid if only the catalytic activity of mononuclear chelate **1** does not change after both the anchoring and the condensation of **1** with benzidine to yield zeolite-supported polynuclear complex **2**. The result obtained is unambiguous evidence for 'conservation'

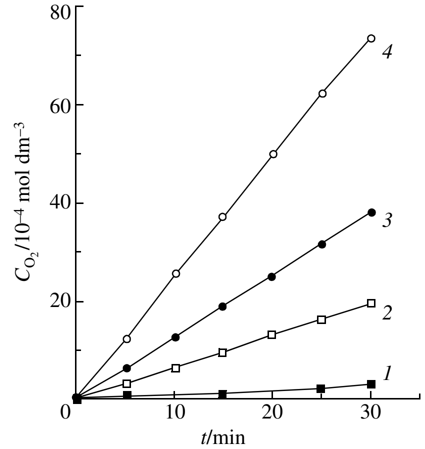


Figure 2 Consumptions of O_2 by solutions (20 cm^3) of cyclohexene in toluene (1:1) in the presence of **1** (*3*), **2** (*1*) and zeolite-anchored **1** (*2*) and **2** (*4*). Concentration of ROOH is 0.1 M, concentration of **1** is 4.5×10^{-6} M, the masses of the CaA samples with zeolite-anchored **1** and **2** are 1.0 and 0.1 g, respectively.

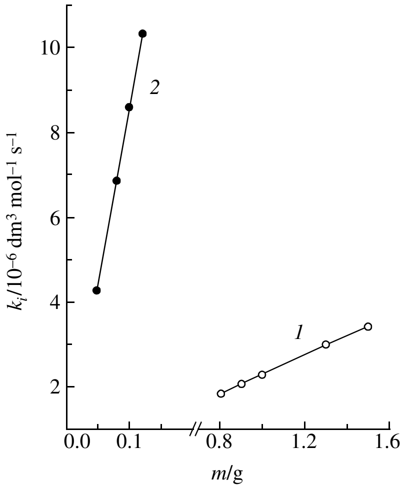


Figure 3 Plots of k_1 and k_2 *vs.* masses of the samples containing **1** (*1*) and **2** (*2*) for the liquid-phase oxidation of cyclohexene in toluene (1:1) by O_2. T = 294 K, P = 1×10^5 Pa.

Table 1 Conventional rate constants (k_c) for the liquid-phase oxidation of cyclohexene with dioxygen in toluene (1:1) in the presence of the samples containing **1** and **2** (294 K, total pressure is 1.03×10^5 Pa).

Catalyst	Sample mass, m/g	[Cu]/ 10^{-5} mol dm^{-3}	r_0/ 10^{-6} mol dm^{-3} s^{-1}	k_c/dm^6 mol^{-2} s^{-1}
1	—	0.45	2.1	1.03
Zeolite-ahchored **1**	1.0	0.25[a]	1.1	0.916
Zeolite-anchored **2**	0.1	10.1[a]	4.1	0.854

[a] Calculated according to equation (2).

of the catalytic activity of mononuclear chelate **1** by modification of the ligand with benzidine.

It is of interest to compare the catalytic behaviour of zeolite-anchored catalysts **1** and **2** with that of the corresponding zeolite-encapsulated (‘ship-in-the-bottle’) chelates in the same reaction. However, it is impossible to synthesise these compounds in the zeolite cavities as the dimensions of chelates **1** and **2** are greater than the effective diameter of the zeolitic supercages.

Though a surface density of the copper(II) atoms of zeolite-anchored mononuclear chelate **1** is limited, this work provides a way to increase many times the efficiency of the heterogenised catalyst by anchoring polynuclear metal chelates, as was shown here for complex **2**. The liquid-phase cyclohexene oxidation with O_2 catalysed by zeolite-anchored copper(II) complexes **1** and **2** was well described in terms of the pseudohomogeneous kinetics. It gives a solution for the problem of the connection between homogeneous and heterogeneous catalyses.

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