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An Oxidation System for Green Chemistry
– Synthesis of Bi-Metallic Schiff Base Complexes and Oxidation of Phenols in the Presence of the Complexes –

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Summary: Bimetallic copper complexes were synthesized from the schiff bases which were obtained by the reaction between bis(3-aminophenyl) sulphone and salicylaldehyde and the derivatives in order to clarify the active site of the immobilized polymer catalyst. The complex-H_2O_2 system showed effective oxiation of phenols. The active site was elucidated by UV spectrum.

Introduction

Selective oxidation or oxidation of organic substance is important in the organic synthetic chemistry. Nowadays mimicking enzymatic type activity in simple molecules and the usage of oxygen or hydrogen peroxide as an oxidant are of interest for a green chemistry under mild condition. Binuclear copper center as an active site in tyrosinase-monooxygenase binds dioxygen as a peroxide. A similar binding mode is found in hemocyanin.

Barton's Gif system shows monooxygenase activity.[1] The active point was found to be non-hemiron containing complex, In this case the complex was composed by tri-metal complex. An active site in these cases comes from polynuclear metallic complex which is combined with dioxygen or oxygen bridge. We have found that bimetallic copper and iron complexes immobilized on an organic-inorganic hybrid silica was effective for the oxidation of hydrocarbons.[2] From the standpoint of GreenChemistry the usage of the immobilized catalyst is preferred similar to the use of oxygen or hydrogen peroxide as an oxidant. However the reaction mechanism of the active point could not be made clear, because the metallic complex site was supported by the polymer compound. So, we try to synthesize monomer type-bimetallic complex in order to investigate the

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behavior of the active species. We obtained the bimetallic copper complex from the schiff base synthesized by the reaction between bis(3-aminophenyl)sulphone and salicylaldehyde. And, other derivatives of salicylaldehyde were used for the synthesis of other schiff bases; 3-*t*-butyl-2-hydroxybenzaldehyde, 3,5-dichloro-2-hydroxybenzaldehyde, 3-*t*-butyl-2-hydroxy-5-methoxybenzaldehyde, 3,5-di-*t*-butyl-2-hydroxybenzaldehyde.

Results and Discussion

Oxidation of cyclohexane in the presence of the immobilized bimetallic complex

Bimetallic complex was synthesized on the immobilized silica as shown in Fig 1.

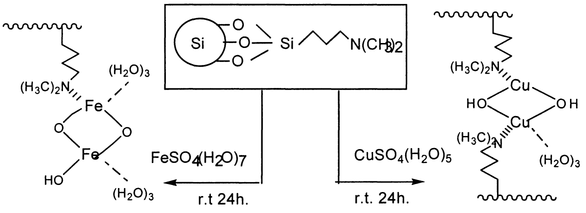


Fig 1. Synthesis of the bimetallic complexes.

Deioxygen oxidation of cyclohexane was carried out in the presence of the above mentioned metal complexes. The overall yields were low (0.06 – 4 %) and the predominant product was cyclohexanol. However, traces of cyclohexanone, in some cases as much as 1.0%, were observed.[2]

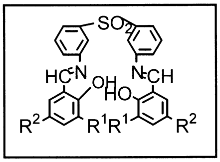
Oxidation with binuclear metal complexs

In the previous section we described the results of studies of the oxidation of cyclohexane with silica-bound iron and copper complexes catalysts, which appears to be a binuclear structure. It is therefore desirable to synthesize model compounds that are known to possess a binuclear or polynuclear structure and test their effectiveness as oxidants in green chemistry.

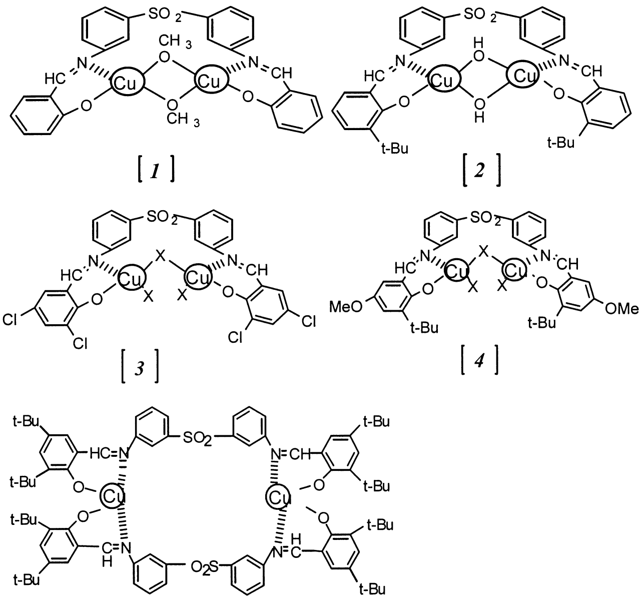
We synthesized various schiff bases as shown in Table 1.

Table 1 Various schiff bases synthesized in this experiment.

	(1)	(2)	(3)	(4)	(5)
R^1	H	t-Bu	Cl	t-Bu	t-Bu
R^2	H	H	Cl	OMe	t-Bu



Copper complexes were obtained from the schiff bases by the reaction with $Cu(OAc)_2$ in methanol. They are shown in Fig 2.

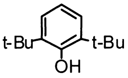
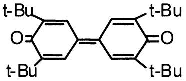
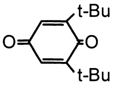
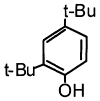
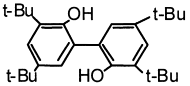
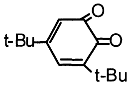
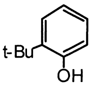
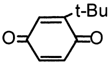
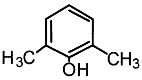
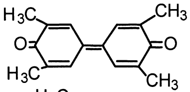
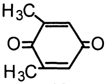
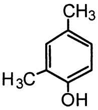
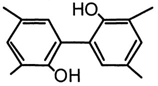
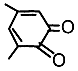
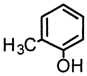
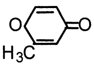
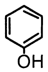
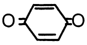
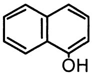
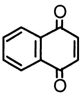


[*1*] [*2*] [*3*] [*4*] [5]

Fig 2. Copper complexes obtained from $Cu(OAc)_2$.

Their structure were estimated from IR/UV spectrum, elemental analysis, FAB-Mass and X-ray structural analysis. The complexes containing X in the structure shown above need to be investigated further.

Table 2 Results of oxidation of various phenols

Substrate	Products	Yield %	
		cat. [*1*]	cat. [*2*]
		42 (43)	12
		25 (3)	40
		26 (47)	31
		16 trace	13
		no reaction	9
		22 (39)	22
		0	23 (6)
		18 (16)	32
		trace	trace
		no reaction	10
		no reaction	8
		no reactiom	13

reaction condition: substrate 1.0 mmol, H_2O_2 1.5 mmol, [*1*] and [*2*]=[Cu] 0.01 mol, solvent THF (CH_2Cl_2), temp. -50°C, time 24 hr

Oxidation of phenols by binuclear metal complexes

These metal complexes are inactive but show activity by the combination of hydrogen peroxide. The oxidations of 2,4-di-tert-butylphenol and 2,6-di-tert-butylphenol using the copper complexes described above were carried out (refer to Table 2). In methylene chloride, the product are mainly coupling products besides quinines. In tetrahydrofuran, the products are not only coupling products but also quinines. The reactivity of [*3*] is low in methylene chloride because of its low solubility. This oxidation shows effect on the conformation of the metal complex rather than the substituents in this results. However, this relation between reactivity and the complex are now under investigation.

Consideration of complex-hydrogen peroxide system

The UV-VIS spectra of the reaction of [*1*] and hydrogen peroxide in tetrahydrofuran (-50°C) was shown in Fig 3. The peak of 581 nm peak grow and 398 nm shoulder peak appears. These peaks show the appearance of the $\mu-\eta^2:\eta^2$peroxide intermediate. The ligand was essentially unchanged by the reaction of hydrogen peroxide. This was shown by UV-VIS spectrum. When the time-course of UV-VIS spectrum of the reaction of [*4*] and hydrogen peroxide was investigated, the spectral changes, divided into Stage 1 and 2, are shown in Fig 4. Stage 1 shows 297 nm and 444nm peaks starts to decay after the addition of hydrogen peroxide.

After 40 min the peak at 398 nm starts to decay as shown in stage 2 in Fig 4.

There is the growth of the peak at 380-390 nm and afterwards starts decay. This peak is characteristic absorption of $\mu-\eta^2:\eta^2-$peroxo species, and was observed in oxytyrosinase and oxyhemocyanin.

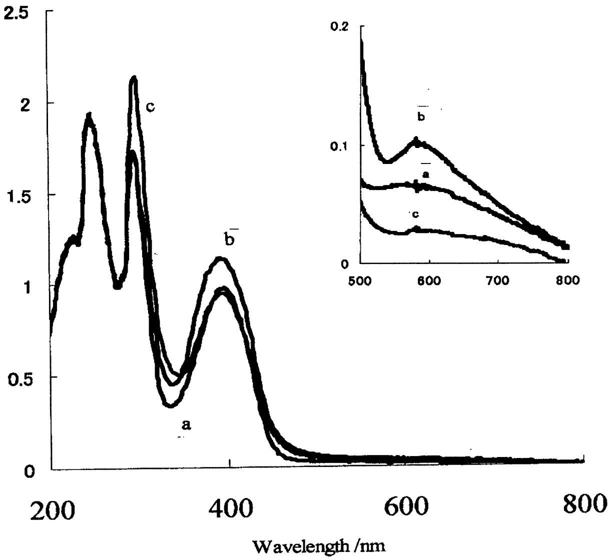


Fig 3. The spectral change of [*1*] after the addition of hydrogen peroxide.

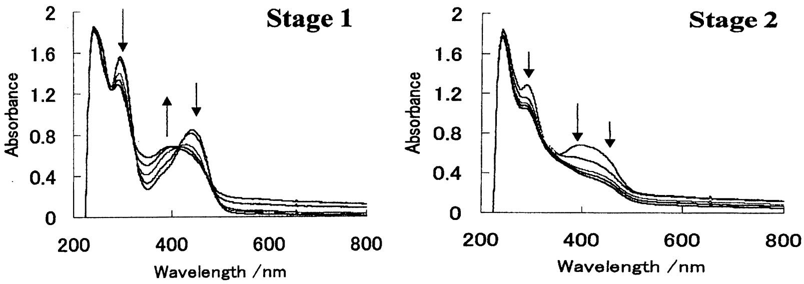


Fig 4.The spectral change of [*4*] on the addition of hydrogen peroxide. Stage 1 ; growth of the peak at 398 nm. Stage 2; the peak decay after 70 min accompanied by the growth of the peak at 398 nm.

Experimental

Materials and measurements

Triethylamine, tetrahydrofuran and diethyl ether were freshly distilled prior to use.
All other starting materials and solvent were purchased commercial and used as received. UV-VIS spectra were recorded with Shimadzu Multi Spec-1500.
The other instruments are described in the published reports. [3]

Synthesis of schiff bases and metal complexes

The other additional part of experiment and synthesis and oxidation reaction part will be published in Inorg.Chim.Acta. in press. [4]

Acknowledgement

The authors would like to thank all co-workers in our group whose names are cited in the references.

[1] D.H.R.Barton, .Dollar, *Acc.Chem.Res*.**1992**,*25*,504.and the references cited therein.
[2] Y.Kurusu, D.C.Neckers, *J.Org.Chem.* **1991**, *56*, 1981.
[3] A.M.Guidote,Jr., KAndo, Y.Kurusu. H.Nagao, Y.Masuyama, *Inorg.Chim.Acta.***2001**, *314*, 27
[4] A.M.Guidote,Jr. K.Ando, K.Terada, Y.Kurusu, H.Nagao, Y.Masuyama, *Inorg.Chim.Acta.* submitted for the publication.