Oxidation of 2-Methoxyphenol by Synthetic Copper-ferrite

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Copper-ferrite (Cu-ferrite) prepared by the wet formation process was applied to oxidation of 2-methoxyphenol as a model reaction for the removal of pollutants from water. Cu-ferrite was easily recovered with little loss following repeated use of a magnet. The activity of Cu-ferrite was maintained during 3 batch reactions and Cu-ferrite was found to be suitable for the removal of pollutants. The reaction product of both the 2nd and 3rd batches was different from that of the 1st batch. X-Ray diffraction suggested that the structure of Cu-ferrite was changed by leakage of copper ion (Cu^{2+} ion) from the Cu-ferrite lattice after the 1st batch reaction. Such a structural change was considered to change the reactivity of Cu-ferrite. It is considered that an improvement in the formation process leads to Cu-ferrite being a more useful and effective catalyst for removing pollutants from water.

Key words Cu-ferrite; repeated use; 2-methoxyphenol oxidation; structural change;l pollutants removal

Spinel ferrites possess the general formula $M_xFe_{3-x}O_4$ (M being a bivalent metal ion), and are used as magnetic materials. Various processes of ferrite formation have been widely investigated to obtain a suitable ferrite with excellent magnetic properties. The wet ferrite formation process has also been applied to the treatment of waste water.[1] The sludge obtained needs to be used effectively. Many investigations have been carried out in an attempt to use this ferrite sludge as a magnetic materials.[1,2] However, no industrial application of ferrite sludge has been reported, yet. It is necessary to investigate the use of such spinel ferrites in other areas.

Aihara *et al.* reported that a copper–ascorbic acid–oxygen (Cu^{2+}–AA–O_2) system was effective for selective oxidation of 2-alkoxyphenols to oxido-labile catechols in water.[3—6] If copper-ferrite (Cu-ferrite)–AA–O_2 system is able to oxidize phenols, one class of pollutant, in water as Cu^{2+}–AA–O_2 system, the Cu-ferrite–AA–O_2 system may be useful as a heterogeneous catalyst for the removal of pollutants from water. As Cu^{2+}–AA–O_2 system is a homogeneous catalyst, its repeated use as a catalyst would be difficult. However, Cu-ferrite can be easily recovered because of its magnetc properties and used repeatedly.

In this paper, we want to report the properties and catalytic function of Cu-ferrite–AA–O_2 and its repeated use.

Experimental

Materials Iron(II) sulfate, copper(II) sulfate, and 2-methoxyphenol were obtained from Wako Pure Chemical Industries, Ltd., Osaka. Other chemicals were also purchased from commercial sources. All chemicals were used without further purification throughout this study.

Apparatus X-Ray diffraction profiles of ferrites were obtained using an RINT 1200 X-ray diffractometer (Rigaku). The HPLC system consisted of a Waters M45J pump and Lambda-Max Model 481 detector. Shimadzu UV-150-02 spectrophotometer was used for the colorimetric analysis.

Preparation of Spinel Ferrites Cu-ferrite was prepared by the method of Kitamura *et al.*[1] Briefly, 20 mmol iron(II) sulfate and 4 mmol copper(II) sulfate were dissolved in 200 ml water, and 2 mol/l sodium hydroxide solution was added in the required amount. Then, oxidation of the resulting suspension was carried out by bubbling air at constant rate of 240 ml/h for 3 h at 65 °C. The Cu-ferrite obtained was collected by filtration and dried. Control ferrite containing only iron without copper was also prepared by the same process.

Reaction of Ferrite with 2-Methoxyphenol 100 mg ferrite was added to 50 ml solution containing 0.05 mmol 2-methoxyphenol and 0.5 mmol AA. Reaction was carried out at 30 °C for 24 h with shaking (120 strokes/min). Control run was carried out using control ferrite.

Analytical Methods The amounts of reactant and products were measured by HPLC: column, Waters Nova-pack C18 (3.9×150 mm); eluent, acetonitrile–50 mmol/l ammonium phosphate buffer (pH 2.9) (1 : 4) containing 10 mmol/l sodium 1-hexanesulfonate; flow rate, 1.2 ml/min; detection; 210 nm.

Results and Discussion

No Cu^{2+} and iron (Fe^{3+}) ions were found in the filtrate after removing ferrite sludge. Therefore, Cu-ferrite has the formula of $Cu_{0.5}Fe_{2.5}O_4$. 10.2 mg (0.16 mmol) copper is contained in 100 mg Cu-ferrite. Some of the properties of Cu-ferrite were examined.

Properties of Cu-ferrite As a model reaction for the removal of pollutants from water, the oxidation of 2-methoxyphenol was used. Phenols are one class of pollutant and 2-methoxyphenol was used as model phenol. Another reason for using 2-methoxyphenol is as follows: 2-methoxyphenol is used in the reaction of Cu^{2+}–AA–O_2 system, and it is very useful to use the same substrate for comparing reactivity between homogeneous and heterogeneous systems.

Oxidation of 2-methoxyphenol by Cu-ferrite was examined. A total of 41.12% (S.D.=2.70) of the 2-methoxyphenol was consumed in 24 h. The product was almost entirely catechol. This result is similar to that obtained in the Cu^{2+}–AA–O_2 system.[3] No 2-methoxyphenol was consumed by the control. As described in the experimental section, ferrite containing no copper was used in the control run.

The magnetic properties were also investigated. Both Cu-ferrite and control are ferromagnetic materials and showed residual magnetization (data not shown). Cu-ferrite was easily recovered using a magnet because of its ferromagnetism. This property is an advantage in that Cu-ferrite can be easily recovered and used repeatedly.

Repeated Use of Cu-ferrite The repeated use of Cu-ferrite in the oxidation of 2-methoxyphenol was examined. As described above, Cu-ferrite was easily recovered with little loss using a magnet. Figures 1a, b, and c showed the consumption of 2-methoxyphenol, formation of catechol, and leakage of copper ion (Cu^{2+} ion) from Cu-ferrite in each

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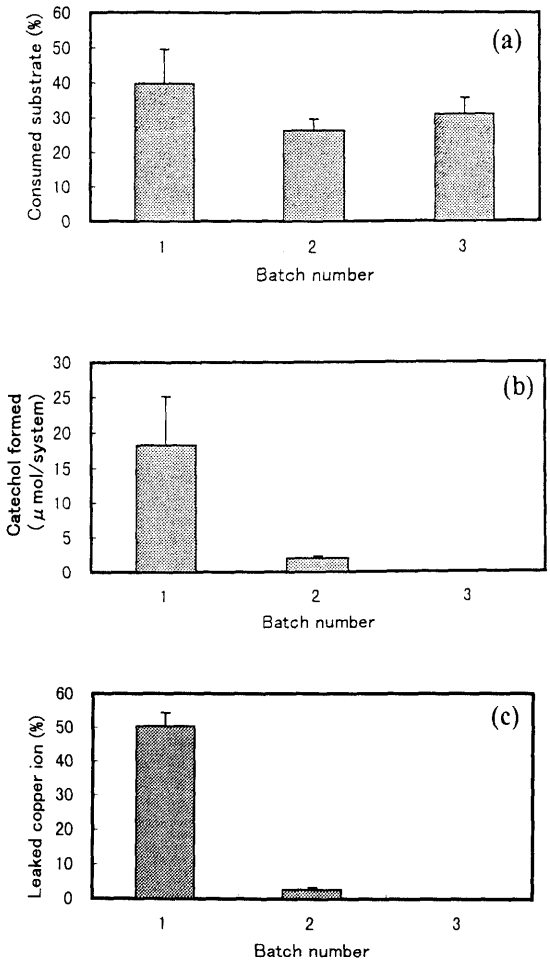

Fig. 1. Repeated Use of Cu-ferrite for the Oxidation of 2-Methoxyphenol

The amounts of substrate (a), catechol formed (b), and leaked copper ion (c) are shown in each batch. Values are the means±S.D. of three experiments.

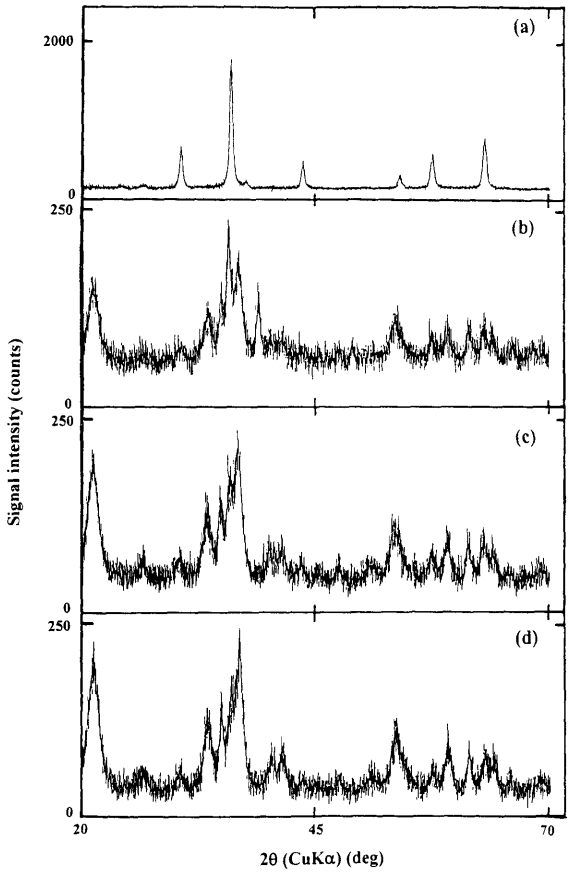

Fig. 2. X-Ray Diffraction Profiles of Control (a), Cu-ferrite before the 1st Batch (b), after the 1st Batch (c) and after the 3rd Batch (d)

batch, respectively. As shown in Fig.1a, the activity of Cu-ferrite was stable for the 3 batch reactions. In each reaction, 50 μmol 2-methoxyphenol was used as substrate. From Fig. 1a, if 2-methoxyphenol was completely converted to catechol, the amount of catechol formed was 19.9, 13.2, and 15.5 μmol for the 1st, 2nd, and 3rd batch, respectively. As shown in Fig. 1b, more than 90% of the 2-methoxyphenol was converted to catechol in the 1st batch, but hardly any 2-methoxyphenol was converted to catechol in the 2nd and 3rd batches. To clarify the reason for this phenomenon, the leakage of Cu^{2+} ion from the Cu-ferrite lattice was examined by colorimetry,[7] and the results are shown in Fig. 1c. When Cu-ferrite was incubated in the solution containing no substrate with shaking, no leakage of Cu^{2+} was observed. As 100 mg Cu-ferrite contains 10.2 mg (0.16 mmol) Cu, about 50% (80 μmol) of Cu^{2+} ion leaked from the Cu-ferrite lattice in the 1st batch. In the 2nd and 3rd batches, very little Cu^{2+} ion leaked from the Cu-ferrite lattice. As in Fig. 1a, amount of 2-methoxyphenol consumed was almost constant in the 3 batches. Therefore, oxidation of substrate was not considered to be catalyzed by leaked Cu^{2+} ion alone. Cu-ferrite also has a catalytic function. The leakage of Cu^{2+} ion in the 1st batch caused a structural change in Cu-ferrite, and resulted in the change in reactivity of Cu-ferrite in the 2nd and 3rd batches. The reaction product has not yet been identified in the 2nd and 3rd batches, and further study is needed to identify this.

When using catechol as a substrate at the same concentration (50 μmol/system) instead of 2-methoxyphenol, no catechol was consumed in the 1st batch. In the 3rd batch, however, catechol was consumed at a rate about 3.3 μmol/h. In the case of forming catechol in the 2nd and 3rd batches, this rate is fast enough to consume any catechol formed in the 2nd and 3rd batches during the reaction time. However, as there is a possibility that catechol was formed by only leaked Cu^{2+} ion, further study is needed to clarify the reaction mechanism. Our object, removing phenol derivatives from water, was accomplished by repeated use of Cu-ferrite.

X-Ray Diffraction of Cu-ferrite Figures 2a, b, c, and d show the X-ray diffraction profile of control, Cu-ferrite before the 1st batch, after the 1st batch, and after the 3rd batch, respectively. As in Fig. 2a, the crystal structure of the control (Fe_3O_4) was not affected by the wet formation process. The amorphous region in the sample was also found to be a little greater by the wet process than by sintering.

As in Figs. 2b, c and d, Cu-ferrite had a large amorphous region in its structure. As the peak of 2θ at 38 deg. disappeared in Figs. 2c and d, the structure of Cu-ferrite after the 1st and 3rd batches was clearly different form that before the 1st batch. The structure of Cu-ferrite after the 1st and 3rd batches was the same. These results support the hypothesis described above that Cu^{2+} ion leaked from the Cu-ferrite lattice in the 1st batch reaction because of the large amorphous region in its structure, and that such leakage of Cu^{2+} ion in the 1st batch caused a structural change in Cu-ferrite.

In conclusion, Cu-ferrite was easily prepared by the wet process, and was found to act as a catalyst in the oxidation of

2-methoxyphenol. This catalytic activity was equal to that of a homogeneous system of Cu^{2+}–AA–O_2. Cu-ferrite could be also used repeatedly, but the reaction product differed between the 1st and 2nd batch because of leakage of Cu^{2+} ion. As 2-ethoxyphenol is also oxidized by the Cu-ferrite–AA–O_2 system, this can be applied to oxidation of 2-alkoxyphenols.

Europium(Eu)-or ruthenium(Ru)-ferrite also catalyzes the oxidation of 2-methoxyphenol, but the yield is lower than that of Cu-ferrite. It is also considered that spinel-ferrite containing Cu and other metals has the ability to oxidize phenols except 2-alkoxyphenols.

By improving the reaction conditions in the wet formation process, leakage of Cu^{2+} ion can be suppressed, and Cu-ferrite is considered to be a more effective and stable catalyst, and can be used to remove pollutants from water.

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