

Development of Cu/Ni Binary Catalyst for Hydrothermal Oxidation of Refractory Compounds

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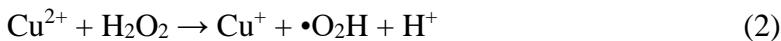
ABSTRACT

We have reported that Cu-based materials show a remarkable catalytic effect for the treatment of refractory organic compounds such as chlorophenol and trichloroethylene by catalytic hydrothermal oxidation, because of enhanced generation of hydroxyl radicals through Fenton-like reaction catalyzed by Cu(I) ion under hydrothermal condition. Here, we report that Cu/Ni binary catalyst exhibits a higher activity than Cu for the hydrothermal oxidation of 3,4-dichlorophenol. It is indicated by EXAFS data that the atomic interaction between Cu and zero-valent Ni may accelerate Fenton-like reaction, resulting in enhanced degradation and mineralization of 3,4-dichlorophenol.

INTRODUCTION

A large quantity of persistent and hazardous compounds including dioxins, PCBs, 1,4-dioxane, etc. have been discharged from various industrial factories and plants. Environmental pollution and adverse effects on ecosystem caused by such compounds have been serious global issues. Therefore, the demand for developing safe and cost-effective treatment method has been increasing in recent years.

We have reported that the oxidative decomposition of refractory organic pollutants such as chlorobenzene, 4-chlorophenol and trichloroethylene by hydrothermal oxidation method can be dramatically enhanced by using copper-based materials as a catalyst under reaction condition around 130–200°C and 1–30 MPa. This enhancement was found to result from Fenton-like reaction (Equations 1 & 2) accelerated under hydrothermal conditions, which effectively produced a great deal of •OH radicals having a strong oxidation power [1-3].



This makes it possible to treat refractory organic pollutants by catalytic hydrothermal oxidation method under much gentler reaction conditions compared with conventional techniques which have usually employed the reaction condition above critical temperature and pressure of water ($T_c = 374^\circ\text{C}$, $P_c = 22.1 \text{ MPa}$). In this study, we have attempted to develop a catalyst having higher performance than Cu by combination of Cu and another 3d transition element, Ni. It was demonstrated that zeolite-supported Cu/Ni binary catalyst showed an excellent catalytic effect for hydrothermal oxidation of

3,4-dichlorophenol which was employed as a model compound of refractory organic pollutants.

EXPERIMENTAL METHODS

Zeolite powder (0.5–1.2 mm in diameter, X type) used for catalyst support were obtained from Tosho Corp. (Japan). 35% H₂O₂ was obtained from Mitsubishi Gas Chemical Company Inc. (Japan). Other reagents are of special grade purchased from Kishida Chemical Corp. Ltd. (Japan) and used without further purification. All solutions were prepared using deionized distilled water.

Zeolite-supported Ni/Cu binary catalyst was prepared in the following manner. 10 g of zeolite powder was dispersed in the mixed solution containing 0.02 M CuCl and 0.02 M NiCl₂ (50 ml) and stirred for 24 hours. Then, it was dried under reduced pressure and sintered at 500°C for 1.5 hour in air. Zeolite-supported Cu or Ni catalysts were also prepared in a similar manner.

The treatment of 3,4-dichlororphenol by catalytic hydrothermal oxidation was performed using a flow-type packed-bed reactor system [2]. The reactor was made of a titanium tube (6 mm o.d., 4 mm i.d., 19 cm length) connected with two in-line filters (SS-4FWS-05, Swagelok Co.) at both ends and a 0.5 g of catalyst powder was filled within it. The sample solution containing 1 mM 3,4-dichlorophenol and 12 mM H₂O₂ was continuously fed into the reactor by a HPLC pump (PU-2080, Jasco Co.) with a flow rate controlled at 4 cm³/min, so that average residence time of reaction mixture within the reactor was about 0.5 min. The reaction temperature was kept at 200°C by immersion of the reactor in a thermostated salt bath. Pressure was controlled at 10 MPa by a back pressure valve. To minimize the effect of adsorption of 3,4-dichlorophenol inside of the reactor system, the sample solution was let flow for more than 1 hour before the start of the reaction. After treatment, the concentrations of residual 3,4-dichlorophenol and TOC (total organic carbon) were determined using an HPLC and a TOC meter, respectively, and the degradation efficiency of 3,4-dichlorophenol and removal efficiency of TOC were calculated.

RESULTS AND DISCUSSION

Figures 1(a) & (b) show the degradation efficiency of 3,4-dichlorophenol and removal efficiency of TOC after treatment of 3,4-dichlorophenol by catalytic hydrothermal oxidation with H₂O₂ at 200°C and 10 MPa using zeolite-supported Cu, Ni, and Cu/Ni binary catalysts, respectively. It is evident in view of these results that Cu/Ni binary catalyst has the highest catalytic activity among them. The degradation efficiency of 3,4-dichlorophenol reached almost 100% for Cu/Ni, while it was about 94–95% for Cu. For Ni, the degradation efficiency of 3,4-dichlorophenol was about 93% at the beginning of treatment, however it rapidly decreased to about 50% being at roughly the same level as that for non-catalytic treatment. More remarkable difference between catalysts could be seen for the removal efficiency of TOC. For Cu/Ni, the removal efficiency of TOC was about 57% at the beginning of treatment and it was increased gradually up to about 80% with elongation of treatment. For Cu, about 55% of TOC could be removed and it was almost independent of treatment time. Ni was found to show little effect on the TOC removal.

As Cu/Ni binary catalyst exhibited much higher catalytic effect than Cu did and Ni has little effect for hydrothermal oxidation 3,4-dichlorophenol, it will be indicated that

the interaction between Cu and Ni played a crucial role on the catalysis mechanism of Cu/Ni binary catalyst. To examine the local atomic structures of Cu and Ni atoms incorporated in the catalyst, the measurement of extended X-ray absorption fine

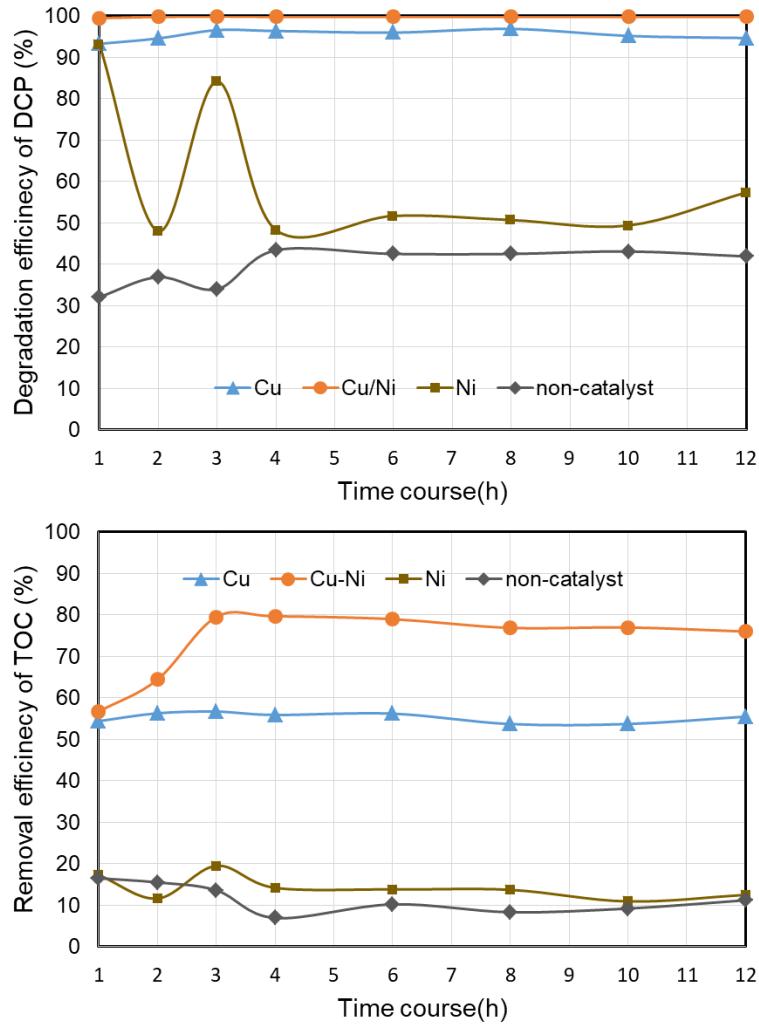


Figure 1. The degradation efficiency of 3,4-dichlorophenol (upper panel) and removal efficiency of TOC (lower panel) after treatment by catalytic hydrothermal oxidation at 200°C and 10 MPa with zeolite-supported Cu, Ni, or Cu/Ni binary catalyst as a function of time course of treatment.

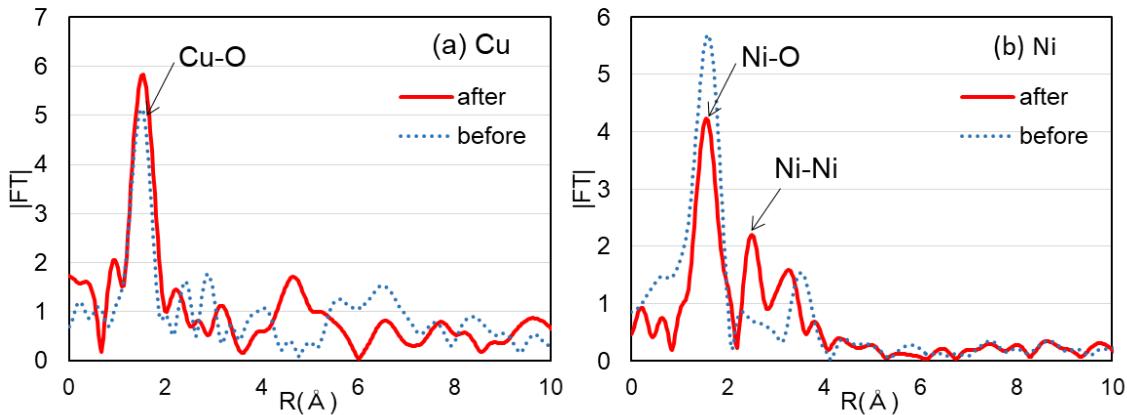


Figure 2. Fourier transforms of Cu (a) and Ni (b) K-edge EXAFS spectra for Zeolite-supported Cu/Ni binary catalyst before and after use for the experiment of catalytic hydrothermal oxidation.

structure (EXAFS) spectra has been carried out at Aichi Synchrotron Radiation Center. Figure 2 shows the Fourier transforms of Cu and Ni K-edge EXAFS spectra for Cu/Ni binary catalyst before and after use for experiments of catalytic hydrothermal oxidation. For the local atomic structure of Cu in Figure 2(a), a sharp peak appeared at 1.5Å, which could be attributed to Cu-O bond distance of cupric oxide (CuO) [4,5]. As only a little change was seen in the local shell structure of Cu after use for hydrothermal oxidation experiments, it is indicated that Cu was mainly in the form of divalent cation, Cu(II), during catalysis. On the other hand, a distinctive change was observed for the local shell structure of Ni. A sharp peak corresponding to Ni-O bonds of nickel oxide (NiO) appeared at 1.6Å, while the intensity of this peak was decreased and a new peak corresponding to Ni-Ni bonds of metallic nickel appeared at 2.5Å after use of hydrothermal oxidation experiments. This indicates that a part of Ni cations in Cu/Ni binary catalyst was reduced to zero-valent Ni during catalysis.

It has been known that a rate-determining step of Fenton-like reaction is the reduction of Cu(II) to Cu(I) described by Eq. (2) [6-9]. Based on the results of EXAFS spectra, it is assumed that the interaction between Cu and zero-valent Ni may promote this rate-determining step to proceed, leading to the overall acceleration of Fenton-like reaction and degradation of 3,4-dichlorophenol. Such consideration is not inconsistent with the observation that the removal efficiency of TOC was increased gradually with elongation of treatment time and reached equilibrium at 80% after 3 hours, because there are only Ni(II) in the pristine catalyst and it will take some time to be reduced to zero-valent Ni.

CONCLUSION

It has been demonstrated that zeolite-supported Cu/Ni binary catalyst shows a better performance than Cu for catalytic hydrothermal oxidation of 3,4-dichlorophenol. The degradation efficiency of 3,4-dichlorophenol reached almost 100% and the removal efficiency of TOC was as high as 80% after treatment at 200°C and 10 MPa. According to the analysis by EXAFS measurements, zero-valent Ni was generated in the catalyst during treatment. It is indicated that this may interact with Cu, accelerating overall Fenton-like reaction and degradation of 3,4-dichlorophenol.

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REFERENCES

- [1] N. Kometani, Y. Sumiyoshi, *Chem. Lett.*, Vol.42, 2013, pp.804–806.
- [2] A. Shimokawa, H. Honda, K. Nakao, N. Kometani, *J. Chem. Eng. Jpn.*, Vol. 46, 2013, pp. 821–826.
- [3] N. Kometani, R. Takami, K. Nakao, *Japanese J. Multiphase Flow*, Vol.29, 2015, pp.302-308.
- [4] P. Khemthong, P. Photai and N. Grisdanurak, *Int. J. Hydrogen Energy*, Vol.38, 2013, pp.15992–16001.
- [5] Y. Tanizawa, T. Shido, W. J. Chun, K. Asakura, M. Nomura, Y. Iwasawa, *J. Phys. Chem. B*, Vol.107, 2003, pp.12917–12929.
- [6] J. I. Nieto-Jiarez, K. Pierzchla, A. Sienkiewicz, T. Kohn, *Environ. Sci. Technol.*, Vol.44, 2010, pp.3351–3356.
- [7] J. W. Moffett, R. G. Zika, *Environ. Sci. Technol.*, Vo.22, 1987, pp.804-810.
- [8] A. C. K. Yip, F. L. Y. Lam, X. Hu, *Chem. Comm.*, 2005, pp.3218–3220.
- [9] F. L. Y. Lam, A. C. K. Yip, X. Hu, *Ind. Eng. Chem. Res.*, Vol.46, 2007, pp.3328-3333.