

EXAFS Measurements Characterized Local Structure of Copper Complex Catalysts Encapsulated in Y-Zeolite Catalysts

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Introduction

The synthesis of phenol through a direct oxidation of benzene in an aqueous solution of acetic acid was studied by using copper supported catalysts. It was recognized that the high yield of phenol was obtained as a main product in this reaction. Though the reusability of used catalysts is quite low due to the elution of copper species into the reaction solution. Then, we prepared copper complex catalysts encapsulated in Y-zeolite. The effect of the steric hindrance between several ligands and pore size was investigated on the elution of vanadium species.

In this study, EXAFS measurements characterized local structure of these catalysts.

Experimental

Catalyst preparation

Copper complex catalysts encapsulated in Y-zeolite were prepared by following method. Copper was supported on Y-zeolite by ion exchange method, and the product named Cu-Y. Cu-Y was mixed with solution of ligand such as picolinic acid, quinaldic acid, and pyrazine carboxylic acid, and Cu complex catalysts encapsulated in Y-zeolite were got. Encapsulated catalyst used picolinic acid was named CuPA-Y, quinaldic acid was named CuQA-Y, pyrazine carboxylic acid was named CuPCA-Y.

EXAFS measurements

EXAFS region of the X-ray absorption coefficient was analyzed to have information about the local environment of copper ions, in term of interatomic distances and coordination numbers. X-ray absorption spectroscopy was performed for the Cu K-edge. As a standard reference, X-ray absorption spectra in transmission mode were recorded for CuO crystalline powder. EXAFS data processing was carried out by REX2000.

Result and discussion

EXAFS measurements of Cu K-edge of Cu complex encapsulated catalysts were carried out in order to obtain the information of the local structures. Table1 shows the results of curve fitting of Cu K-edge EXAFS data. The interatomic distances of the neighboring oxygen in the every catalyst are the almost same, ca. 1.94-1.95 Å. It is indicated that the four neighboring oxygen in CuQA-Y catalyst is two. Hence the structure of Cu species in the CuQA-Y catalyst seems to be different from other catalysts. We previously reported that the activity of CuQA-Y for the benzene oxidation to phenol was higher than the other two catalysts. It is speculated that these

difference of coordination structures affects the catalytic activity. The models of these Cu complexes are described in Fig.1. The size of ligands of CuQA-Y is larger than the others. Therefore, the coordination structure of only CuQA-Y may be different from the CuPA-Y and CuPCA-Y due to the steric hindrance between ligands and pore size of Y-zeolite.

Table1 Results of the Curve Fitting of Cu-Kedge EXFAS Data for Cu Catalyst

Catalysts	Shell	R(Å)	N	dE	DW
CuPA-Y	Cu-O	1.94	3.2	-2.76	0.048
CuQA-Y	Cu-O	1.95	2.4	-4.56	0.068
CuPCA-Y	Cu-O	1.95	3.7	-0.953	0.061

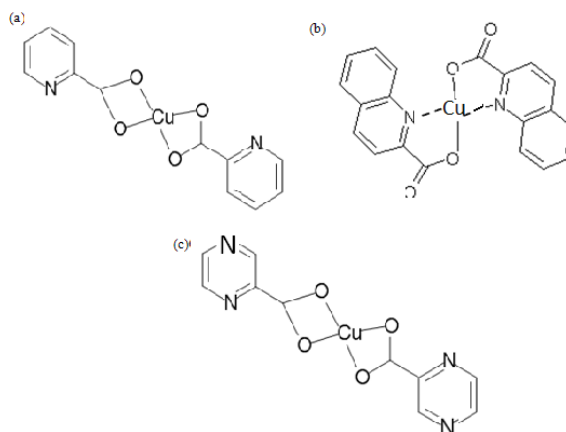


Fig. 1 Models of Cu complex (a)CuPA-Y (b)CuQA-Y (c)CuPCA-Y

Conclusion

The interatomic distances between Cu atom and neighboring oxygen was 1.94-1.95 Å. Cu atoms were coordinated by four neighboring oxygen in CuPA-Y and CuPCA-Y, though the coordination number of neighboring oxygen in CuQA-Y was two due to the steric hindrance between ligands and pore size of Y-zeolite.