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XANES AND EXAFS ANALYSIS OF COPPER ION-EXCHANGED ZSM-5 ZEOLITE CATALYST USED FOR NITROGEN MONOXIDE DECOMPOSITION

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XANES and EXAFS analysis of Cu ion-exchanged ZSM-5 zeolite, a highly active catalyst for NO decomposition, is performed. The copper species in the zeolite are Cu(II) ions in the zeolite cages. The contribution of Cu–Cu local structure is suggested for high loading samples. The Cu atoms in the zeolite are more ionic than CuO. The analysis of the catalyst deactivated by SOx treatment suggests the presence of Cu atoms surrounded by SO_4 ions which blocks the adsorption of NO molecules.

1. Introduction

Catalytic decomposition of nitrogen monoxide is considered to be an ideal method for the removal of nitrogen oxides (NOx) from exhaust gas streams. Recently, it was reported that the decomposition proceeds on various Cu ion-exchanged zeolites. Among them Cu/ZSM-5 zeolite is especially active for the reaction [1,2]. It is invaluable for developing new types of highly active catalysts to clarify the structure of the active site on Cu/ZSM-5 catalysts. However, the entity of active species in this catalyst is still obscure.

Among various techniques to investigate unknown species, the X-ray absorption spectroscopy (XAS; XANES and EXAFS) is well suited for this catalyst since it can persue changes of electronic structure and local structure of specific atoms. In this paper, characterization of copper species in Cu/ZSM-5 zeolite catalyst was performed by means of XAS. The catalyst deactivated by SOx treatment was also investigated, since the catalyst is known to be sensitive to SOx.

2. Experimental

The parent Na/ZSM-5 zeolite with a SiO_2/Al_2O_3 molar ratio of 70 was prepared in an autoclave with a usual hydrothermal synthesis from silica sol, $Al(NO_3)_3$, and NaOH by using tetrapropylammonium bromide as a template, followed by calcination at 793 K in air. The zeolite was then ion-exchanged three times at room temperature in an aqueous copper(II) acetate solution, washed with distilled water and dried at 383 K in an oven for a night. Cu loading of the catalyst was found to be 3.6% by titration after extracting all the copper ions in it with concentrated nitric acid. 0.86% Cu/SiO_2 (Fuji-Davison Cariact-10) was also prepared as a reference sample with the same method.

The fresh catalyst was then pretreated in flowing helium (or air) at 773 K for 1 h before reaction. The reaction was carried out by using a fixed-bed flow reactor. The reactant gas contained 2% NO and helium balance, its flow rate was 30 cm^3/min and the catalyst weight was 1 g. SOx treatment of Cu/ZSM-5 was made by passing SO_2 (124 ppm)–O_2 (4%)–H_2O (17%) mixed gas through the catalyst at 773 K for 48 h.

Transmission X-ray absorption measurements were performed on beam line 7C at the Photon Factory in National Laboratory for High Energy Physics. Powdery samples were pressed into wafers with the aid of methyl cellulose as a binder. The samples were mounted on a holder in a vessel, which was then cooled to around 10 K with a closed cycle cryocooler. All XAS data were collected at the Cu K absorption edge at the temperature. CuO, Cu_2O, $Cu(OAc)_2 \cdot H_2O$, $Cu(OH)_2$, and anhydrous $CuSO_4$ were selected as reference samples.

The XANES spectra were normalized in such a way that absorption intensities in the EXAFS range are constant after subtraction of background absorption. EXAFS analysis was performed by the method reported previously [3]. The EXAFS Fourier transforms in this paper are presented with the Cu–O phase shift correction.

Characterization of the samples by other methods such as XRD, XPS, and gas chemisorption measurements were also tried.

3. Results and discussion

First, the activity of Cu/ZSM-5 and Cu/SiO_2 catalysts was measured. As was reported, Cu/ZSM-5 showed high activity for NO decomposition. The conversion of NO to N_2 was 56% at 673 K and 82% at 773 K. Although the conversion fell down to 58% in the presence of 5% oxygen, no catalyst deactivation occurred. On the other hand, Cu/SiO_2 did not show catalytic activity, the conversion being 0.2% at the same temperature. When Cu/ZSM-5 was treated by SO_2–O_2–H_2O mixed gas, the activity fell down drastically to less than 1%. However, the original catalytic activity was restored after carrying out the reaction at 973 K for 1 h.

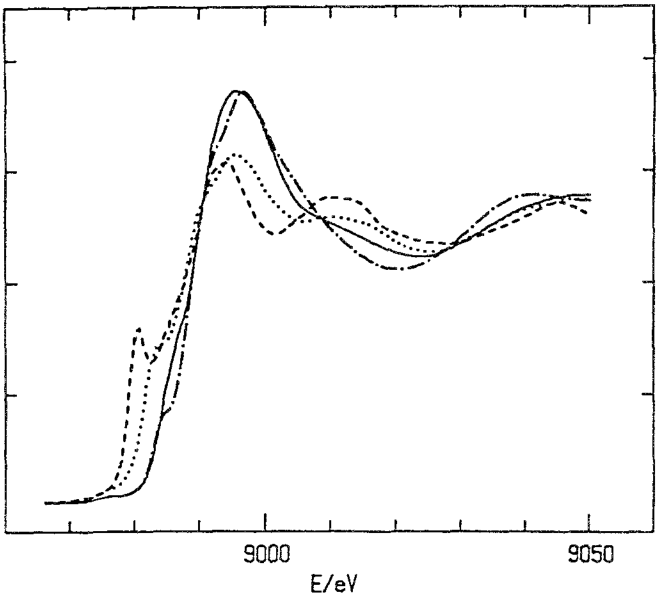

Fig. 1. XANES spectra of Cu/ZSM-5 and reference samples. ——— Cu/ZSM-5, ······ CuO, - - - - - - Cu_2O, ·—·—· $Cu(OAc)_2 \cdot H_2O$.

The XANES spectra of Cu/ZSM-5, CuO, Cu_2O, $Cu(OAc)_2 \cdot H_2O$ are compared in fig. 1. The spectrum of Cu/ZSM-5 is quite different from other reference samples, indicating that the copper species of Cu/ZSM-5 is neither

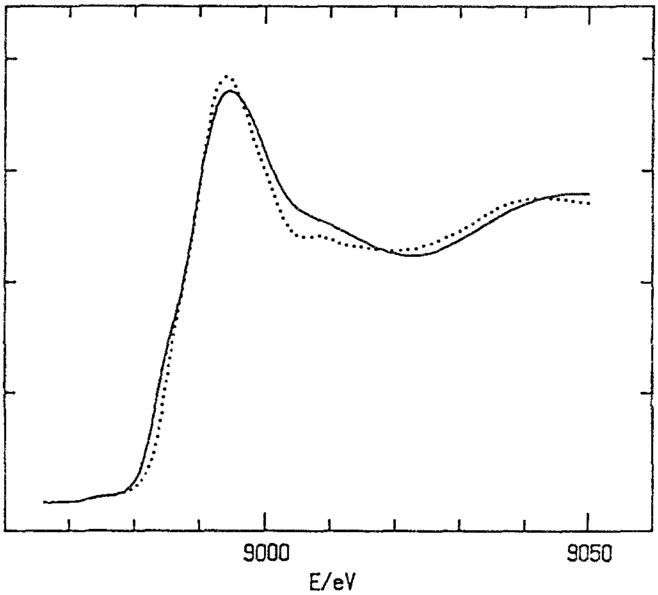

Fig. 2. XANES spectra of Cu/ZSM-5 and $Cu(OH)_2$. ——— Cu/ZSM-5, ······ $Cu(OH)_2$.

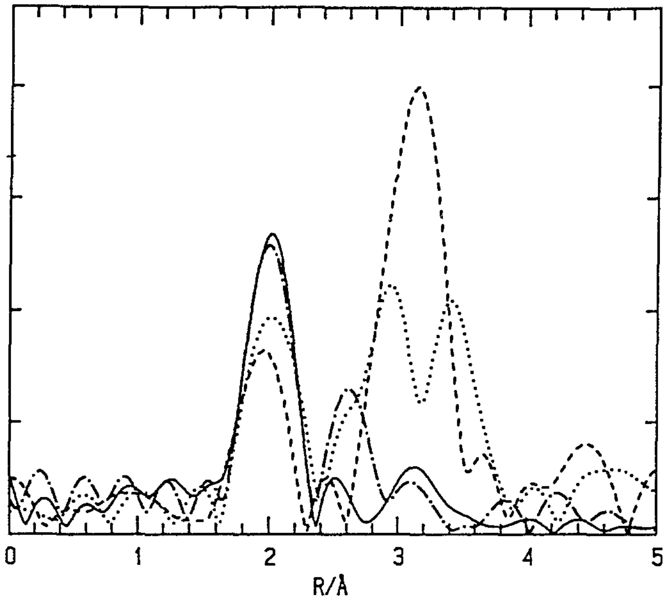

Fig. 3. EXAFS Fourier transforms of Cu/ZSM-5 and reference samples. ——— Cu/ZSM-5, ······ CuO, - - - - - - Cu_2O, ·—·—· $Cu(OAc)_2 \cdot H_2O$.

CuO, Cu_2O nor $Cu(OAc)_2 \cdot H_2O$ from which the catalyst was prepared. Figure 2 also shows the spectra of Cu/ZSM-5 and $Cu(OH)_2$. These two spectra are similar to each other. However there is small difference in the edge position between the two samples.

A small pre-edge peak in the spectrum of Cu/ZSM-5, which is due to 1s–3d transition, shows that Cu is divalent [4]. The edge position of Cu/ZSM-5, which is almost the same as $Cu(OAc)_2 \cdot H_2O$, is higher in energy than CuO and slightly lower than $Cu(OH)_2$, indicating that the Cu atoms in Cu/ZSM-5 are more ionic than CuO.

The Fourier transforms of EXAFS oscillations of Cu/ZSM-5 and other reference samples are presented in fig. 3 and fig. 4. In the spectrum of CuO, three prominent peaks appear at 2.01, 2.94, and 3.41. These are assigned to Cu–O, Cu–Cu, and Cu–Cu. Several peaks due to Cu–O and Cu–Cu bonds also appear in the spectra of Cu_2O, $Cu(OAc)_2 \cdot H_2O$ and $Cu(OH)_2$. However, Cu/ZSM-5 shows only one distinct and another low peak at 2.02 and 3.13, indicating again that the copper species in Cu/ZSM-5 is not in the form of CuO, Cu_2O, $Cu(OAc)_2 \cdot H_2O$ or $Cu(OH)_2$. The first peak, which lies at the same position as CuO and CuY zeolite [5], is considered to reflect the Cu–O bond. The larger peak area than CuO indicates either larger oxygen coordination number or smaller fluctuation of the oxygen atom around copper than CuO.

The assignment of the second small peak is not clear. However, it might reflect the Cu–Cu or Cu–Si bonds. As the peak could not be observed for 1.4% Cu/ZSM-5, the former case is more probable.

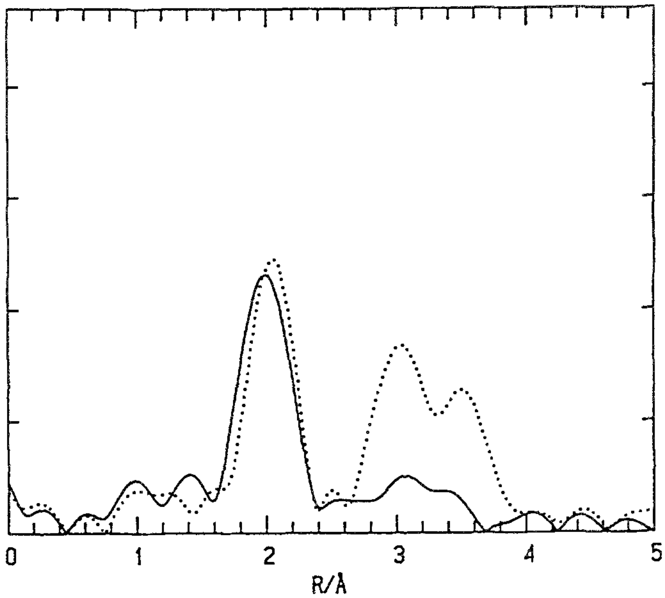

Fig. 4. EXAFS Fourier transforms of Cu/ZSM-5 and $Cu(OH)_2$. ——— Cu/ZSM-5, ······ $Cu(OH)_2$.

X-ray diffraction measurement of Cu/ZSM-5 showed only diffraction peaks of ZSM-5 zeolite framework and no peaks due to various copper species were detected. Moreover, the ratio of chemisorbed NO molecules per Cu atoms at

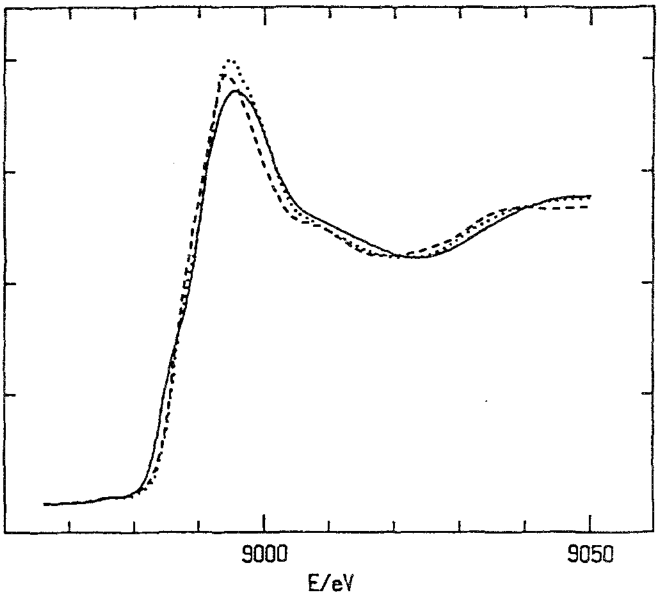

Fig. 5. Change of XANES spectra by SOx treatment. ——— Cu/ZSM-5 (before treatment), ······ Cu/ZSM-5 (SOx-treated), - - - - - - $CuSO_4$.

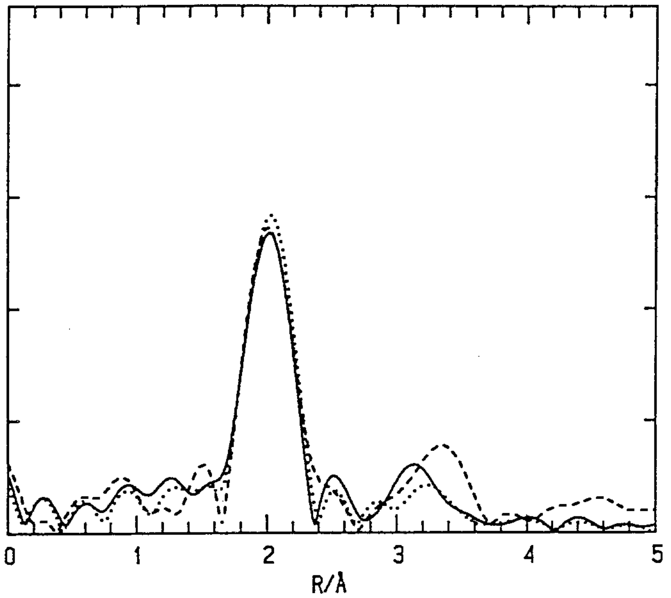

Fig. 6. Change of EXAFS Fourier transforms by SOx treatment. —— Cu/ZSM-5 (before treatment), ······ Cu/ZSM-5 (SOx-treated), - - - - - - $CuSO_4$.

room temperature, which was measured with a conventional constant-volume adsorption system, was about 2. These results indicate that Cu is almost atomically dispersed in the zeolite cages and that no large clusters of $Cu(OH)_2$ are formed. At present we think that the copper species in Cu/ZSM-5 are Cu(II) ions contained in the zeolite cages and that contribution of Cu–Cu local structure is suggested in the case of Cu/ZSM-5 with high loading.

No clear XANES and EXAFS spectrum change was observed among fresh(dried), pretreated (at 773 K), and used Cu/ZSM-5 zeolites. It is concluded that the copper species does not change during these treatments.

The change of XANES spectrum of Cu/ZSM-5 by SOx treatment is shown in fig. 5 along with the spectrum of $CuSO_4$. The position of the absorption edge of Cu/ZSM-5 deactivated by SOx is higher in energy than Cu/ZSM-5 before SOx treatment and the absorption onset is the same as $CuSO_4$. This difference in the edge position indicates that the Cu atoms in deactivated Cu/ZSM-5 have more ionic nature like $CuSO_4$ than Cu/ZSM-5 before treatment.

Figure 6 indicates the EXAFS Fourier transforms of the same samples as fig. 5. No distinct variation by SOx treatment was observed in the first large peak. However difference in the second small peak is detected between original Cu/ZSM-5 and SOx-treated Cu/ZSM-5 although the spectrum of the latter is not the same as $CuSO_4$. In both XANES and EXAFS the spectrum of regenerated Cu/ZSM-5 is exactly the same as that of Cu/ZSM-5 before SOx-treatment.

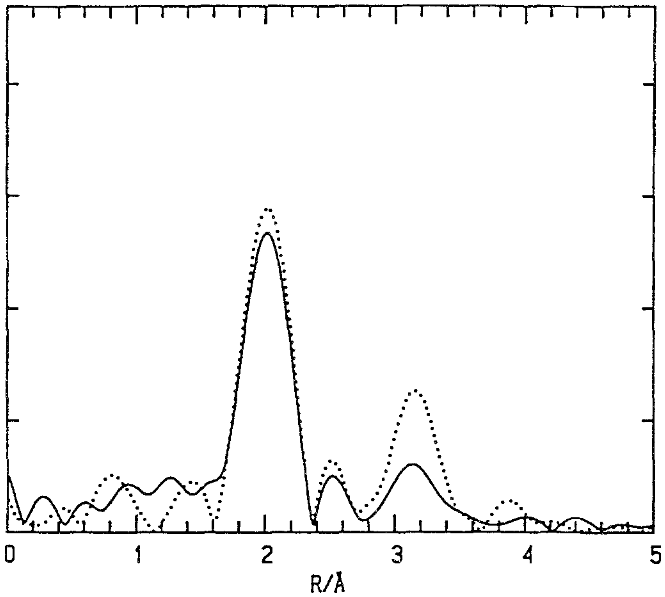

Fig. 7. EXAFS Fourier transforms of Cu/ZSM-5 and Cu/SiO_2. ——— Cu/ZSM-5, ······ Cu/SiO_2.

XPS measurement indicated clearly the presence of sulfur in the SOx-treated Cu/ZSM-5. Also, sulfuric acid was flowing out during catalyst regeneration. At present the structure of SOx-treated Cu/ZSM-5 is not clear. However, possibility of total rearrangement of the local structure around Cu atoms such as the formation of $CuSO_4$ species cannot be excluded because the first large Cu-O peak is not sensitive to the change of the local structure. From the consideration of both XANES and EXAFS results, the copper atoms in Cu/ZSM-5 deactivated by Sox may be surrounded by SO_4 ions, which blocks the adsorption of NO molecules, although large $CuSO_4$ clusters may not be formed. This must be closely related to the drastic decrease of catalytic activity by SOx treatment.

With respect to the XANES spectra of Cu/ZSM-5 and Cu/SiO_2, a great coincidence was observed. Therefore, the copper species in the two samples is suggested to have the same electronic structure. Figure 7 shows the EXAFS Fourier transforms of Cu/ZSM-5 and Cu/SiO_2 after pretreatment. Although no distinct change was detected in the first large Cu–O peak between the two catalysts, there is clear difference in the second peak. In the case of Cu/SiO_2, this peak is fairly large. This fact suggests the difference in the total structure around the Cu atoms between these two supported copper species, although XANES spectra indicates the same electronic structure. In the case of Cu/SiO_2, clusters of certain copper species may be formed since there are no micropores in SiO_2. Further study is needed to get full information on the supported copper species.

In conclusion, the copper species in Cu ion-exchanged ZSM-5 zeolites are Cu(II) ions contained in the zeolite cages and not in the form of CuO, Cu_2O, Cu metal, $Cu(OAc)_2 \cdot H_2O$ or $Cu(OH)_2$ clusters. The Cu atoms are more ionic than CuO. Contribution of local structure of Cu–Cu bond is suggested for Cu/ZSM-5 with high Cu loading. SOx treatment causes the change of electronic and local structure of the Cu species. Cu atoms surrounded by SO_4 ions are suggested as the most possible case. EXAFS spectra show the difference in the local structure between Cu/ZSM-5 and Cu/SiO_2, though the interpretation is not clear. Further characterization under the real reaction conditions will be necessary for full understanding of active site of the catalyst.

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