

Zeolite-Based Nitrogen Monoxide Sensor

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When nitrogen monoxide (NO) coordinates to the metal center, the color of the complex changes. In order to materialize this unique phenomenon as a sensor, the metal complex has to be supported on porous solids. We are interested in the encapsulation of the metal complexes within zeolite cavity. For the first step, NO coordination to Co^{2+} in Y-type zeolite is characterized by UV-vis spectrometer near room temperature. The change in absorbance is observed at 300nm-450nm by the NO coordination, and that by coexisting water is at 500nm-700nm. These two regions are not overlapped each other, suggesting that the NO can be detected by the color change under water vapor existence. Once NO coordinates to cobalt, however, it is difficult to remove from the metal center. Suitable ligands should be selected toward the reusable NO sensors.

Key words: gas sensor, metal complex, zeolite, NOx, coordination

1. INTRODUCTION

Nitrogen oxides (NOx) are not only harmful to our health, but also origins of public pollution. The rapid, reliable and precise sensing will contribute to the reduction of NOx level in atmosphere.

M^{n+} -EDTA_{ac} (EDTA: Ethylenediamine-N, N, N', N'-tetraacetic) is known as a NO absorber¹⁾. When NO coordinates to M^{n+} , the UV-vis spectrum changes. The acetic part of EDTA (ligand) enhances the affinity with NO²⁾. In order to utilize this phenomenon as a gas sensor, their function should be materialized in a solid form.

Zeolites are aluminosilicate crystals constructed from TO_4 tetrahedra (T: Si, Al, etc.), and have uniform size of micropores or channels (Fig.1). Zeolite Y occludes "supercages" (cavity diameter: 13Å, entrance diameter: 7.4Å). The cavity and ion exchange sites are distributed

regularly, therefore, the aggregation of the metals and their complexes can be prevented.

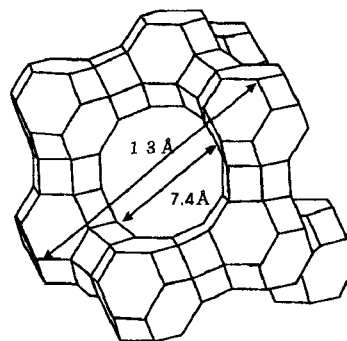


Fig.1 The structure of zeolite Y

In this work, cobalt is used as a sensing center and zeolite Y is as the host. The changes in optical property by the NO coordination are studied in UV-vis region.

2. EXPERIMENT

2.1 Sample preparation

Cobalt ion-exchanged samples were prepared by a conventional ion exchange method. First, Zeolite Y (Si/Al=2.8) was stirred in ammonium nitrate (NH_4NO_3 , Wako Pure Chemical Industries, Ltd.) solution, and next in Cobalt(II) acetate tetrahydrate ($(\text{CH}_3\text{COO})_2\text{Co}\cdot 4\text{H}_2\text{O}$, >99.0% Wako Pure Chemical Industries, Ltd.) solution under atmosphere for 24 hours at 90°C . Then the sample was recovered by filtration and dried at 85°C . After the ion exchange, the sample color turned from white to pink. The color was derived from the H_2O complex ($[\text{Co}(\text{H}_2\text{O})_6]^{2+}$). The degree of the ion exchange was determined by inductive coupled plasma mass spectroscopy (ICP-MS, HP-4500, Yokogawa Analytical Systems). After the ion exchange, the powder was soaked in the EDTA (>99.5% Dojindo) solution. The formation of metal complex was confirmed by Ar adsorption measurement and thermogravimetry-mass spectroscopy (TG-MS, TG8120 Thermo plus2, Rigaku). According to powder x-ray diffraction (XRD, M03XHF22, MAC Science) with Cu-K α radiation source, the crystal structure of zeolite was not changed during the sample preparation.

2.2 NO gas sensing experiment

The sample was placed in a handmade Teflon[®] holder. The holder was set in a quartz tube. NO gas diluted with helium (2000, 1000, 500, 250ppm) was introduced to the tube at a flow rate of 100ml/min (Fig.2).

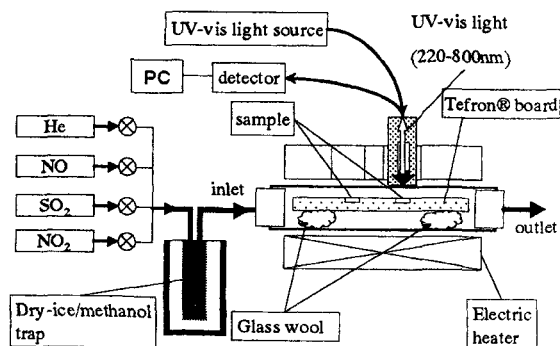


Fig.2 Experimental apparatus

The UV-vis spectrum of the diffusion reflectance was monitored *in situ* (MCPD2000, Otsuka Electronics Co. Ltd.) since quartz and zeolite is transparent in UV-vis region. Powdered Al_2O_3 was used as the reference.

Before the contact with NO, the samples were dried at 200°C for 2 hours. After the pre-treatment, the color of sample turned to violet. During the measurement, a trace of water was removed with a dry-ice/methanol trap.

3. RESULTS and DISCUSSION

3.1 Sample preparation

The degree of the ion exchange was 115%. Mostly stoichiometric exchange was attained.

The result of TG-MS (Fig.3) and Ar adsorption (Fig.4) implied that only small amount of Co-EDTA was formed inside the zeolite Y. When Co ion-exchanged Y was soaked in EDTA solution, cobalt seemed to be extracted.

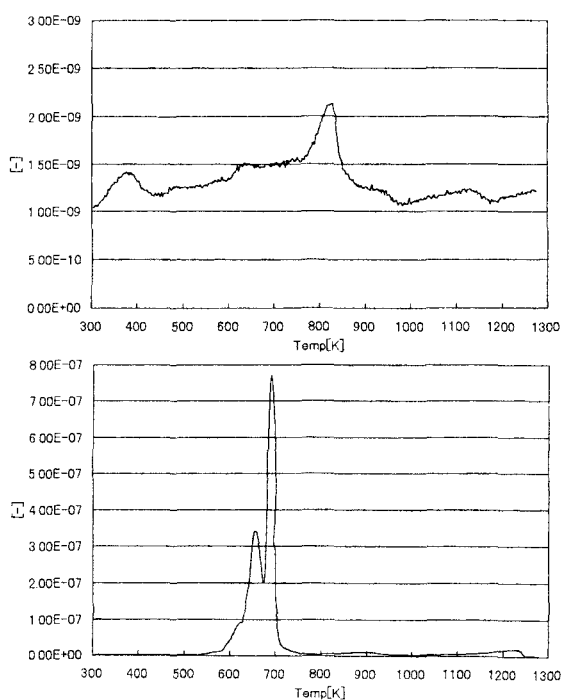


Fig.3 The result of TG-MS (mass number: 44)

Upper: Co^{2+} -EDTA inside zeolite Y

Lower: Co^{2+} -EDTA

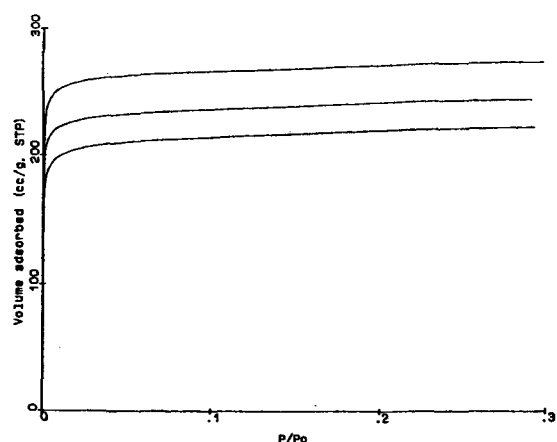


Fig.4 Ar adsorption isotherm

Accordingly, the following characterization was performed as for $\text{Co}^{2+}\text{-Y}$ and $\text{Co}^{2+}\text{-EDTA}$.

3.2 NO gas sensing experiment

NO gas sensing experiments of $\text{Co}^{2+}\text{-Y}$ with dry-ice/methanol trap indicated that the change in the region of 300nm-450nm was due to the coordination NO to cobalt. It took 3 minutes for saturation (Fig.5).

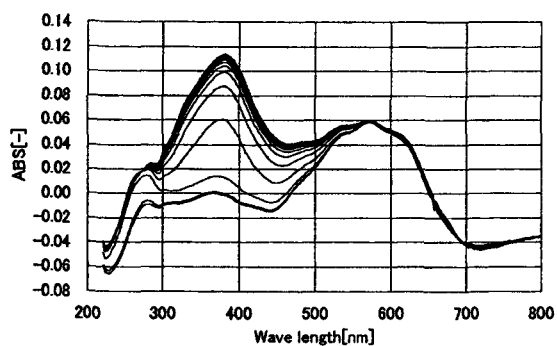


Fig.5 UV-vis spectrum of $\text{Co}^{2+}\text{-Y}$ [with H_2O trap]

Each spectrum is obtained every 20sec(NO: 2000ppm)

The degree of the UV-vis absorbance shift was increased with NO concentration (Fig.6). In this $\text{Co}^{2+}\text{-Y}$ sample, NO could not be removed after the coordination³⁾.

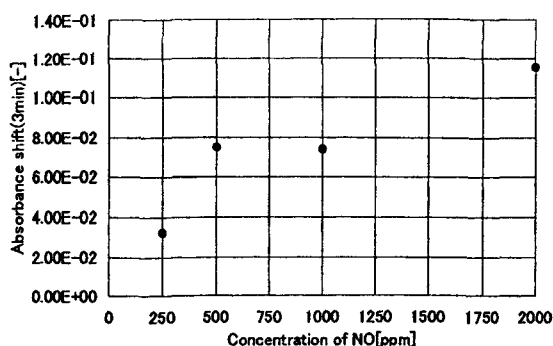


Fig.6 The shift of absorbance for 3min(not saturated)

NO: 250,500,1000,2000ppm [carrier gas: He]

Without dry-ice/methanol trap, the contribution of coexisting water was tested. At the NO gas sensing experiments, the changes in UV-vis spectrum were observed at 300nm-450nm and 500nm-650nm (Fig.7).

It took 55 minutes for saturation.

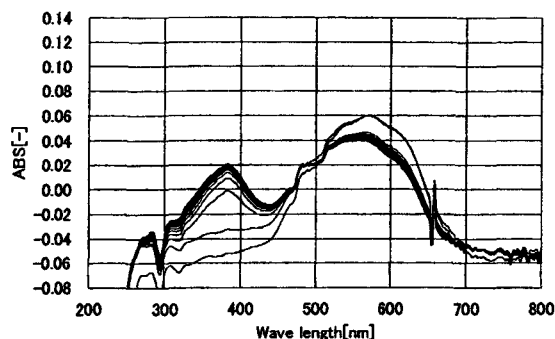


Fig.7 UV-vis spectrum of $\text{Co}^{2+}\text{-Y}$ [without H_2O trap]

Each spectrum is obtained every 300sec

When only helium gas was introduced without dry ice/methanol trap, the UV-vis spectrum changes only in the region of 500nm-650nm. The changes were identified due to H_2O coordination.

When NO sensing experiment was performed as for Co^{2+} -EDTA, the changes at 500nm and 650nm were not observed (Fig.8). This result indicated that the ligand inhibited H_2O coordination to cobalt. However, it took 70 minutes for saturation.

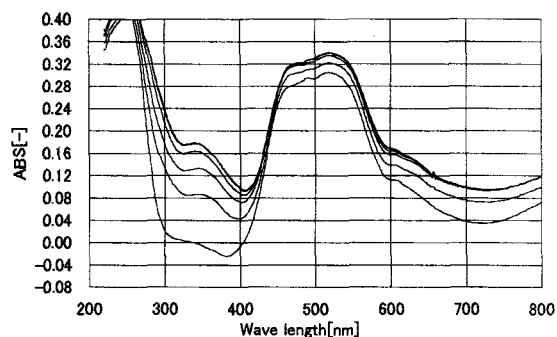


Fig.8 UV-vis spectrum of Co^{2+} -EDTA[without trap]

Each spectrum is obtained every 1200sec

In addition, NO coordinating to cobalt can be removed by heating at 200°C under helium gas flow. This result implies the possibility of reusable sensing.

When NO sensing experiments were performed as for Co^{2+} -EDTA encapsulated within zeolite Y, only changes at 300nm-400nm were observed. The changes were, however, much weaker since the amount of Co^{2+} -EDTA inside zeolite Y was very small.

The establishment of proper EDTA introduction will be needed.

4. CONCLUSION

NO coordination to cobalt-exchanged zeolite Y with and without EDTA was characterized. The coordination of NO and H_2O to cobalt was competitive.

When a trace of H_2O were removed from the sensing system, this NO sensor responded within a few minutes. When there exists H_2O in the measuring system, however, it took longer to change ligand from H_2O to NO.

The change in the region of 300nm-450nm was due to NO coordination to cobalt and that of 500nm-700nm

was due to H_2O coordination.

H_2O must be removed for rapid response. The establishment of dehydration method and the selection of relevant ligands that can control the strength of NO coordination (for reusable sensing) and inhibit H_2O coordination (for rapid response) will be needed.

4.ACKNOWLEDGMENT

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