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## Study of Local Environment of Metal in M/CeO<sub>2</sub> (M = Pt) Automobile Catalysts by XAFS

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In continuation of our work on CeO<sub>2</sub> supported noble metal catalysts, we undertook study of Pt/CeO<sub>2</sub> catalysts by XAFS. EXAFS spectra at Pt L<sub>III</sub> edge in as prepared and preheated samples of 1%, 2% and 4% Pt/CeO<sub>2</sub> and their model compounds were recorded on BL01B1 in transmission and fluorescence mode using Si(111) as monochromator.

The Fourier transforms (FT) of Pt L<sub>III</sub>-edge EXAFS for Pt metal, Pt(II)acetylacetonate and PtO<sub>2</sub> are shown in Fig.1. The FT spectra of model compounds are in good agreement with those reported in literature. In Fig.2, the FT spectra of 1% Pt/CeO<sub>2</sub> as prepared and preheated at 800°C samples recorded in fluorescence mode are presented along with 4% Pt/CeO<sub>2</sub> (as prepared and pre-heated) samples recorded in transmission mode. 2% Pt/CeO<sub>2</sub> FT spectrum is similar to that of 4% sample. The FT spectra of catalysts show three peaks at 1.6Å, 2.6Å and 2.8Å respectively. The first peak is due to Pt-O correlation and the bond length of 2.04Å matches well with reported Pt-O bond distance in PtO. This indicates presence of Pt<sup>2+</sup> species in the catalyst. The second peak matches well with the first peak in Pt metal and therefore is ascribed to Pt-Pt correlation. This could be due to the presence of Pt metal particles in the sample. The third peak gives a bond length of 2.92Å which does not match with Pt-Pt bond length in either PtO or PtO<sub>2</sub>.

A detailed and more careful analysis is therefore necessary before coming to any final conclusions.

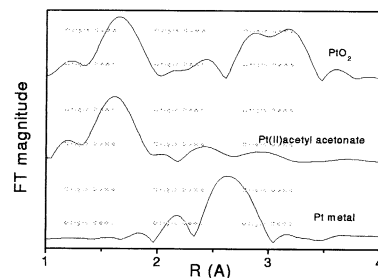


Fig.1 FT spectra of Pt metal, Pt acetylacetonate and PtO<sub>2</sub>

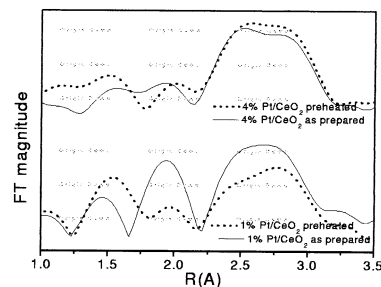


Fig.2 FT spectra of 4% and 1% Pt/CeO<sub>2</sub> Catalysts (solid line – as prepared, dotted line – preheated).

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## XAFS Analysis of Indium Supported by Zeolite Catalyst on De-NO<sub>x</sub> Reaction with Hydrocarbon in Diesel Engine Exhaust

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### 1. Introduction

From a point of view that protecting the global environment, the air pollution by nitrogen oxide (NO<sub>x</sub>) that is mainly emitted from transportation has been serious. Indium supported by zeolite catalyst on de-NO<sub>x</sub> reaction with hydrocarbon exhibited high activity in diesel engine exhaust. We have selected In/ZSM5 for de-NO<sub>x</sub> reaction with hydrocarbon for marine diesel engine exhaust, because the de-NO<sub>x</sub> performance of In/ZSM5 keeps high against sulfur oxide (SO<sub>x</sub>). However, it's not enough to elucidate the bonding structure of the catalyst, which should depend on the catalytic performance, and the reaction paths on the catalysts by means of conventional characterization methods. In this work, the structure of In/ZSM5 on de-NO<sub>x</sub> reaction with hydrocarbon in marine diesel engine exhaust was examined by In K-edge XAFS.

### 2. Experimental

In/ZSM5 were prepared by an ion-exchange method from indium nitrate (In(NO<sub>3</sub>)<sub>3</sub>) on honeycombs of Na/ZSM5. The loading of In was 1.0 wt%. The de-NO<sub>x</sub> reaction with propylene (C<sub>3</sub>H<sub>6</sub>) was carried out at 300~400°C in marine diesel engine exhaust. After In/ZSM5 of pre-test and after-test were crushed, they were made into the pellets for XAFS measurements. In K-edge XANES / EXAFS spectra were measured on the beam line BL01B1 at SPring-8. The spectra were collected in transmission mode at room temperature with a Si (311) single crystal monochromator. Two ion chambers filled with 100% of Ar and 50% of Ar + 50% Kr were used as detectors of I<sub>0</sub> and I, respectively.

### 3. Results and Discussion

Figure 1 shows the fourier transforms of the  $k^3 \chi(k)$  In K-edge EXAFS for In foil, In<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, In<sub>2</sub>O<sub>3</sub>, and In/ZSM5 reacted under several conditions. Hence it is clearly found in Fig. 1 that the intensity of the peak at 1.7 Å (In-O) of the In/ZSM5 reacted in the existence of 500ppm of SO<sub>x</sub> is greater than that of In/ZSM5 reacted in SO<sub>x</sub> free condition. It's revealed that the intensity of the In-O peak reacted at 400°C is smaller than that of reacted at 300°C, in which the catalyst is prone to lose the activity in comparison with at 400°C.

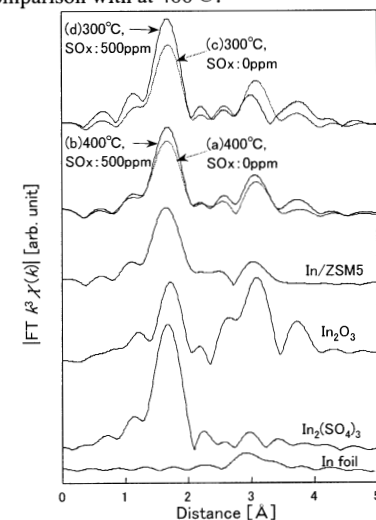


Figure 1 Fourier transforms of the  $k^3 \chi(k)$  In K-edge EXAFS for In foil, In<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, In<sub>2</sub>O<sub>3</sub>, and In/ZSM5 reacted under several conditions.