Structural analysis of dispersed Pt in TiO$_2$-SiO$_2$-supported Pt-MgO catalyst by XAFS.

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The Pt-MgO catalyst supported on TiO$_2$-SiO$_2$, which exhibits a high activity for the catalytic combustion of CO and VOC and simultaneously makes it possible to remarkably reduce quantity of use of expensive Pt, has been developed by Nippon Shokubai Co., Ltd. However, the chemical structure of supported Pt influencing on catalytic activity has scarcely been clarified. In this study, the effect of the support and the promoter such as MgO and CaO on the chemical structure of supported Pt was investigated using XAFS spectroscopy.

The 0.2 wt.% Pt supported catalysts were prepared by impregnating TiO$_2$-SiO$_2$ which was prepared by the coprecipitation method, with a homogenous solution containing Pt salt and Mg(or Ca) acetate, followed by drying, calcining at 450°C in a flowing air (1). The XANES spectra for the catalyst samples were measured using synchrotron radiation XAFS spectroscopy with Si(III) monochromater at Spring-8 (BL 19B2).

As shown in Fig. 1, the X-ray energy of the Pt L2-edge XANES spectra for Pt/TiO$_2$-SiO$_2$ catalyst and that doped with 1 wt.% MgO and 1 wt.% CaO is lower than that for PtO$_2$ and is similar to that for Pt-foil. This indicates that the Pt species dispersed on TiO$_2$-SiO$_2$ exist as metal. Moreover, CaO-doped catalyst exhibits the XANES spectra similar to undoped catalyst, whereas MgO-doped catalyst shows a weaker peak intensity of spectra and slightly different changes in spectra at higher energy region, compared to undoped catalyst. This suggests that by the addition of MgO, the atomic-scale structure around Pt species is slightly changed, which seems to lead to that the oxidation activity of CO is promoted by MgO but not by CaO.

Layered oxychalcogenides LaCuOCh ($Ln$ = lanthanide, Ch = chalcogen) are novel wide-gap p-type semiconductors. The origin of the p-type conduction is due to the (Cu$_2$-Ch)$_2$ layer because the valence band maximum is composed of well-hybridized bands of Cu 3d and Ch $p$ orbitals. Recently, we found that amorphous LaCuOCh (Ch = Se) films also exhibit p-type electrical conduction by post-irradiation of KrF excimer laser after the thin film deposition. In this study, to clarify the local structure of the amorphous LaCuOCh films, EXAFS measurements were performed and the local structure was compared with that of the crystal. First, we tried to measure absorption spectra of La K-edge, which can be measured only at Spring-8 because the beam power is much stronger than conventional XAFS equipment. The spectrum of La K-edge of the crystalline sample could measure, but that of the amorphous sample could not be exactly obtained since the signal of La ions, which will be slightly mixed in glass substrates, was superimposed in the obtained spectrum. Therefore, we chose the Cu K-edge spectra to compare the local structures between amorphous and crystalline phases. Left figure shows the RDF spectrum of Cu K-edge of the amorphous sample. The spectrum was fitted by using the result of the crystalline as a standard. The first neighboring S atoms are clearly observed. The coordination number was 4.1. In the right figure, we compared the RDF spectrum of the amorphous sample with that of the crystalline. It is revealed that the local structure, i.e. the distance and coordination number, of the amorphous sample is almost the same as that of the crystalline. The fact suggests that the electronic structures of both phases are similar and that the p-type conduction of the novel amorphous phase is originated from the hybridized band of Cu 3d and S 3p like crystalline LaCuOCh.

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Fig. 1 Pt L2-edge XANES spectra of Pt/TiO$_2$-SiO$_2$, (a), Pt-MgO/TiO$_2$-SiO$_2$, (b), Pt-CaO/TiO$_2$-SiO$_2$, (c), PtO$_2$, (d), Pt-foil, (e).

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