

Study of Local Atomic Environment of Metal Ions in Combustion Synthesized M/CeO₂-TiO₂ (M = Pd, Pt) Catalysts by X-ray Absorption Fine Structure (XAFS)

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In recent years much attention has been focused on CeO₂ supported noble metal catalysts for their applications in the automotive exhausts, oxygen storage capacity and stabilization of dispersed metals. Recently it has been found that the oxygen storage capacity of these ceria supported catalysts can be greatly enhanced by substitution of Ti ions to form Ce_{1-x}Ti_xO₂ solid solutions [1].

We have synthesized M/CeO₂-TiO₂ type catalysts with M = Pd and Pt using novel solution combustion technique. The particular samples of interest were 2% Pd/Ce_{0.75}Ti_{0.25}O₂ as prepared and heat treated at 650°C and 2% Pt/Ce_{0.75}Ti_{0.25}O₂. The aim of this study was to investigate the local environment of the metal ions in this ceria-titania matrix and correlate it to the observed catalytic properties. The EXAFS spectra were recorded at the Pd K and Pt L_{III} edge in these catalysts and model compounds on BL7C and at PF using Si(311) monochromator.

The XANES spectra at Pd K and Pt L_{III} edges clearly indicate that both Pd and Pt are ionically dispersed in the ceria-titania matrix. In fact the XANES spectra of Pd K edge in Pd/CeO₂-TiO₂ is similar to that in PdO. The presence of white line in Pt L₃ XANES in Pt/CeO₂-TiO₂ also points to the presence of ionic Pt in the catalyst samples.

The fourier transforms (FT) of the Pd K-edge EXAFS for 2% as prepared and heat treated samples are shown in Figure 1. The FT spectra of both these samples show three peaks at 1.6 Å, 2.6 Å and 3.1 Å. The first peak at 1.6 Å corresponds to Pd-O correlation indicating thereby that the first nearest neighbours of Pd are oxygen atoms. The second and third peaks are likely due to Pd-Pd interactions but the possibility of the Pd-Ce correlation cannot be ruled out. In fact, in a similar study on Pd/CeO₂ catalysts we have shown Pd-O-Ce linkages which are responsible for enhanced catalytic activity [2].

In figure 2, the FT spectra of 2% Pt/Ce_{0.75}Ti_{0.25}O₂ as prepared sample is presented. The spectrum shows a strong peak at about 1.4 Å most likely corresponding to Pt-O correlation. In addition there is a broad peak comprising of at least two correlations in the region 2.2 to 3.2 Å. The deconvolution of this broad peak gives two correlations at 2.8 Å and 3.0 Å respectively. The first correlation matches well with Pt-Pt interaction in Pt metal and hence could be ascribed to such a interaction even in the catalyst. The second correlation at 3.0 Å does not match with any correlation either in PtO or PtO₂. This

could be possibly due to Pt-Ce interaction that results due to substitution of Pt ions in the ceria-titania matrix. Such a interaction has been observed by us in EXAFS study of Pt L₃ edge in Pt/CeO₂ catalysts [3]. However a more careful analysis of EXAFS data is required before arriving at any conclusion.

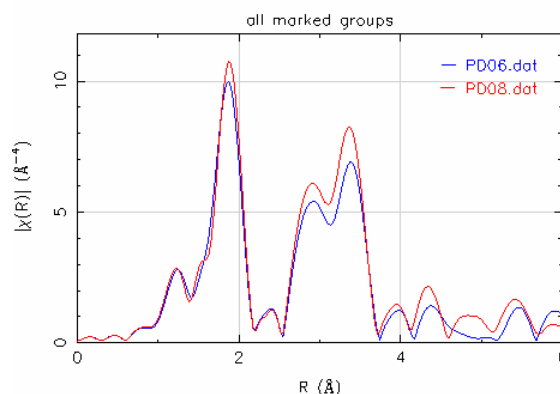


Figure 1 Fourier Transform (FT) spectra at Pd K-edge EXAFS in Pd/CeO₂-TiO₂ catalysts

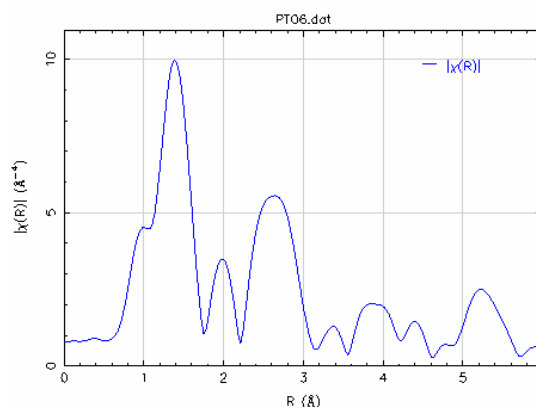


Figure 2 Fourier Transform (FT) spectra at Pt L₃-edge EXAFS in Pt/CeO₂-TiO₂ catalysts

References

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