In-situ Characterization of Structural Evolution of Metal/Carbon Nanostructures in Mesoporous Silica

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In this project, we attempted to apply in-situ X-ray absorption spectroscopy (XAS) to study the structural evolution of metal nanostructures in the mesoporous silica-based metal/polypyrrole/silica composite materials. We have demonstrated the correlation between the polypyrrole (ppy) and the oxidant, $FeCl_3$ [1]. Furthermore, we have applied the same chemistry to prepare the nanocomposite materials of bimetallic PtRu nanoparticles, ppy and mesoporous silica. The PtRu catalyst system is considered a potential CO-resistant anode catalyst for direct methanol fuel cell.

The first part of this project was to study the confined pyrolysis of polypyrrole polymerized with $FeCl_3$ as the oxidant in mesoporous SBA-15 silica. Such pyrolysis has been shown to result in ordered mesoporous carbon with graphitic nature [1]. Figure 1 shows the Fourier transforms of Fe K-edge k^3-weighted EXAFS data. It shows that when the sample was heated up to 500 °C, Part of the iron atoms still coordinated to nitrogen atoms originally belonging to the pyrrole moieties of ppy. After pyrolysis up to 750 °C, all the iron atoms were reduced and formed large particles. Since the pore diameter of SBA-15 host silica is around 6 nm, which is smaller than the estimated particle size of iron, the result suggests that the iron may diffuse to the external surface of SBA-15. The in-situ XAS results are consistent with other characterizations of TEM and PXRD, and they provide valuable information for better control of the confined pyrolysis for the preparation of mesoporous carbon materials.

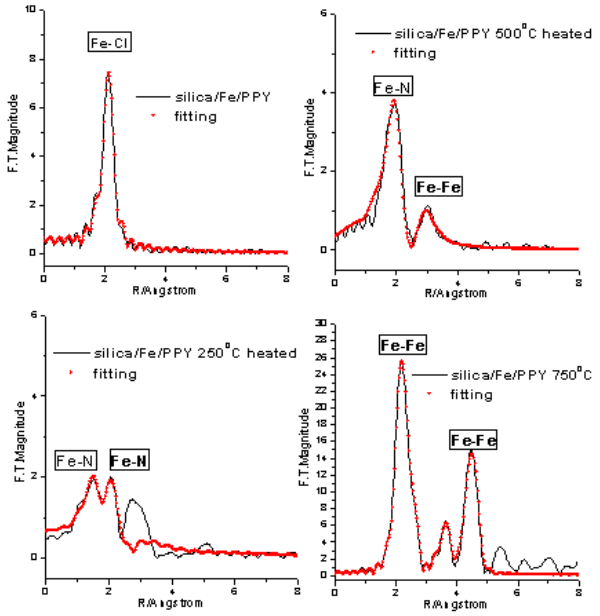

Figure 1. Fourier transforms of Fe K-edge k^3-weighted EXAFS data of Fe/ppy/SBA-15 sample during pyrolysis.

The second part of this project was to study structure of the bimetallic PtRu/ppy/SBA-15 composite catalysts. XAS studies showed that, depending on the way of metal incorporation, PtRu bimetallic catalysts with different morphology can be prepared. For example, when both the metal precursors for Pt and Ru are incorporated and reduced simultaneously, the resulting sample gives EXAFS data as shown in Figure 2. The results suggest a core-shell morphology of the PtRu nanoparticles. Based on our preliminary structural studies, further design and XAS studies are in progress.

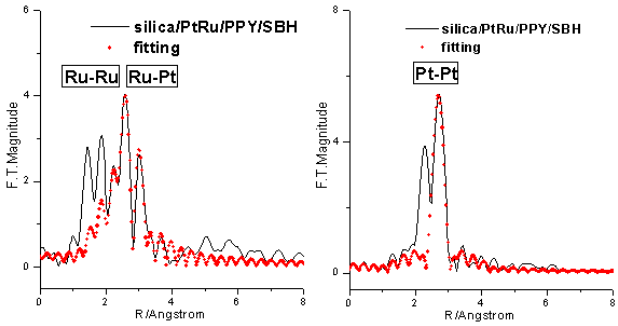

Figure 2. Fourier transforms of Ru K-edge (left) and Pt L_{III}-edge k^3-weighted EXAFS data of PtRu/ppy/SBA-15 sample after reduction by $NaBH_4$.

Reference:
1. Yang, C. M.; Weidenthaler, C.; Spliethoff, B.; Mayanna, M.; Schüth F. *Chem. Mater.* **2005**, *17*, 355.