XANES Investigation of the Valance States of Co in the CoTMPP Structure

Sun-Tang Chang (張孫堂)[1], Chen-Hao Wang (王丞浩)[2], Jeffrey Chi-Sheng Wu (吳紀聖)[1], Li-Chyong Chen (林麗瓊)[2], and Kuei-Hsien Chen (陳貴賢)[2,3]

[1]Department of Chemical Engineering, National Taiwan University, Taipei, Taiwan
[2]Center for Condensed Matter Science, National Taiwan University, Taipei, Taiwan
[3]Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei, Taiwan

X-ray absorption near-edge structures (XANES) spectroscopy was used to investigate the valence states of Co in the 5, 10, 15, 20 – Tetrakis (4 - methoxyphenyl) - 21H, 23H - porphine cobalt (II) (CoTMPP) structure (Fig. 1). From XANES measurements, we hope to understand the changes of CoTMPP structure by pyrolysis.

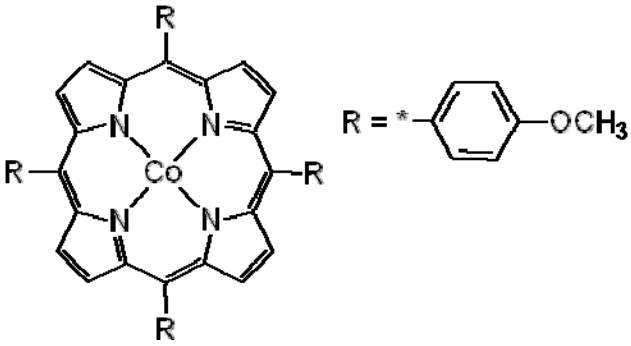

Fig. 1: The structure of CoTMPP.

From the Co K-eged curve of the CoTMPP, the unpyrolysis CoTMPP has a small peak at 7714 eV shown in Fig. 2, indicating that the pure CoTMPP structure is symmetric [1]. After the pyrolysis, the CoTMPP/C, becomes asymmetric which the porphine structure isdecomposed. The E_0 of each material can be calculated from Fig. 2 by the simulation calculated from Fig. 2 by the simulation as shown in Table 1. We try to use E_0 to check the valence states of Co; however, it seems each material has the same E_0, due to the energy are close on 7720.1 eV. From XANES spectra, the valence state of the Co of CoTMPP is not changed by the pyrolysis, though the porphine structure is decomposed. We need more analysis to further check this part.

From XANES spectrum of pyrolyzed CoTMPP/C, it has two peaks between 7720 eV and 7740 eV. CoO is the α-Co with HCP structure (lattice parameter: 2.507 Å), which it only shows one peak be between 7720 eV and 7740 eV. The pyrolyzed CoTMPP/C shows two peaks, which is the β-Co with FCC structure (lattice parameter: 3.54 Å) rather than a HCP structure [2].

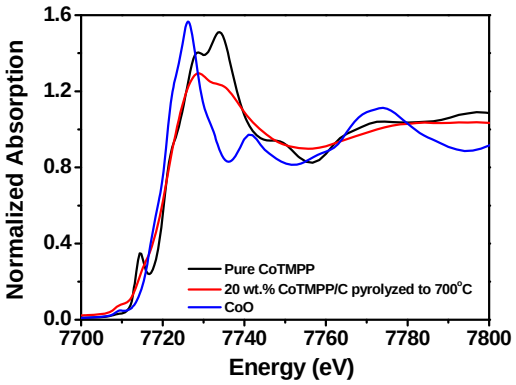

Fig. 2: XANES Co K-edge spectra for unpyrolysis CoTMPP (Black line), 20 wt.% CoTMPP/C pyrolyzed to 700 ℃(Red line) and CoO as our reference data (Blue line).

Sample	E_0 (eV)	Valence of Cobalt
Pure CoTMPP	7720.1	+2
20 wt.% CoTMPP/C 700℃	7720.2	+2
CoO	7720.8	+2

Table 1: The valence of Co of pure CoTMPP, 20 wt.% CoTMPP/C 700 ℃, and CoO.

References

[1] The Electrochemical Society Interface.Winter (2008).
[2] J. Phys. D: Appl. Phys. **42**, 185007 (2009).