



XAFS study of the defective boron nitride with atomically dispersed Pt atoms

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1. Background and research purpose

Atomically dispersed metal catalyst has emerged as a promising approach to maximize the metal utilization, especially for the earth-scarce metals such as Pt. To ensure a robust binding site, a strong metal-support interaction is necessary; a promising route is defects, for which it has been observed that metal cations tend to migrate and be reduced at vacancies to form a stronger interaction than defect-free supports^{1,2}. In this study, we demonstrate how the defect engineering in hexagonal boron nitride (BN) can be used to spontaneously reduce the ionic platinum (Pt⁴⁺) and silver (Ag⁺) into isolated Pt atoms and AgPt subnanocluster at the defective region, which contributes to efficient and stable catalytic behavior. As a complementary part of the study, we must understand the bonding environment of the Pt atoms which are responsible to the catalytic reactivity.

2. Experimental method

Platinum and silver cations were reduced by the defective BN (90BN) in aqueous solution at the room temperature. Then, the powder was washed with distilled water three times by centrifugation, followed by drying process at 60°C. The samples analyzed by XAFS at the Aichi Synchrotron facility at the BL5S1 line. The resulting patterns were analyzed using Athena software.

3. Results and discussion

To verify the atomically dispersed Pt atoms, extended X-ray absorption fine structure (EXAFS) spectra at the Pt L₃-edge was obtained for 90BN-Pt and 90BN-Ag₁Pt₁, as well as Pt foil and PtO₂ as the references. As seen in the Fourier transformed spectra (Figure 1a), there is one prominent peak at ~1.63 Å in 90BN-Pt and 90BN-Ag₁Pt₁ which is shorter length than Pt-Pt bonding (~2.55 Å) in Pt foil. Thus, the lack of Pt-Pt bond confirms the atomically dispersed Pt in 90BN-Pt and 90BN-Ag₁Pt₁ that no Pt particles or clusters are presented. Compared to PtO₂ reference spectra, the first peak of 90BN-Pt or 90BN-Ag₁Pt₁ (Figure 1a) is believed to be the contribution from the Pt-O bonding. Figure 1b is the normalized X-ray absorption near-edge structure (XANES) spectra of the samples 90BN-Pt and 90BN-Ag₁Pt₁ with the reference spectra of Pt and PtO₂. The white-line intensities of 90BN-Pt and 90BN-Ag₁Pt₁ are between those of Pt-foil and PtO₂, which indicates the positive charges on Pt in 90BN-Pt and 90BN-Ag₁Pt₁ due to the Pt-O bonds. These results confirm that the oxygen functional groups work as the nucleation site to form metal-O bonds, so that the charge transfer is allowed between metal and defective BN and ensure a strong metal-support interaction³.

4. References

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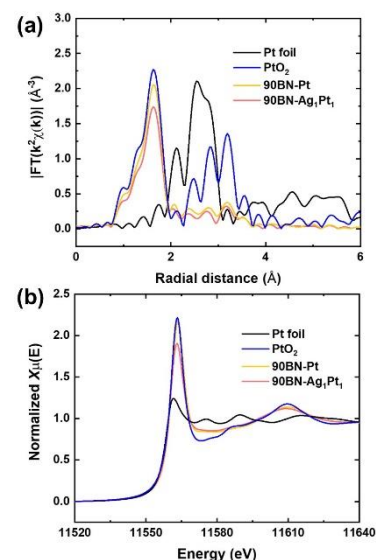


Figure 1 (a) The Fourier transformed R-space plot of EXAFS spectra and (b) Pt L₃-edge XANES spectra of 90BN-Pt, 90BN-Ag₁Pt₁, Pt foil and PtO₂.