Synthesis and Characterization of Cu-Pt Bimetallic Nanoparticles

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Abstracted: Pt-based alloys have recently triggered a lot of attentions due to their important potential industrial applications. They provide great opportunities for the development of low-cost and high-performance fuel-cell catalysts. Many studies have already pointed out the excellent physico-chemical properties of Pt-based alloys, intimately related to their internal structure. Great efforts have been spent to characterize shape, homogeneity, dispersion, alloying extent and kinetic growth of Pt-based nano-particles. Here, we present Cu-Pt bimetallic nano-particles synthesized by the thermal decomposition method under oleylamine and OE coordination. HRTEM images show that Cu-Pt nanostructures having size of about 1.2 nm includes about 35 atoms capped by the surfactant with OA. Accurate structural information of this system has been obtained by XRD and XAFS. A charge transfer mechanism has been observed and Pt occupied Cu sites in these Cu-Pt nanoparticles.

Introduction

An increasing attention has been devoted to Pt-based alloys due to their important potential industrial applications¹,², which provide a great opportunity for the development of low-cost and high-performance industrial fuel-cell catalysts³,⁴. A variety of Pt-Me (Me: Metal) alloy nano-particles (NPs) such as Pt-Cu, Pt-Fe, Pt-Co, Pt-Mn have been synthesized with a precise control of size, shape and chemical composition⁵-⁷. These Pt-based alloys exhibit perfect properties hardly achievable by Pt metal Pt⁸-¹¹, especially in catalytic reactors¹²,¹³,¹⁴.

Excellent physico-chemical properties of Pt-Me alloy nano-particles depend on several factors, such as the extent of the alloying or the atomic distribution and the surface segregation of the particles¹⁵; the particle homogeneity and structure and shape of particles¹⁶; the ensemble effect, ligand and geometrical effects in Pt-Me alloys¹⁷. Therefore, in order to get the ultimate goal, i.e., the control of material properties, a lot of efforts have been devoted to characterize shape, homogeneity, dispersion, alloying extent, and kinetic growth of alloy nano-particles. Although it is well known that the structure of a material strongly influences its properties, it remains a challenge to understand both structure and dynamics of alloy nano-materials. It is then mandatory identify and set up accurate methods to characterize the internal structure of a bimetallic nano-particle¹⁸ at the atomic level.
In this work, we focus on the structure of Cu-Pt nano-clusters with size of ~1 nm by using advanced X-ray absorption spectroscopy (XAS), combined with transmission electron microscopy (TEM) and X-ray diffraction (XRD). Since the catalytic activity of the bimetallic cluster is strongly affected by the structure, but also by the atomic distribution, we will try to provide precise details of the atomic distribution of Cu-Pt bimetallic clusters.

Experimental

Cu-Pt nano-crystals were synthesized in agreement with a previous reported [19] with some modifications. In brief, a ratio of molar Pt(acac)$_2$ and Cu(acac)$_2$, 210 mg of the 1,2-hexadecanediol, 0.6 ml of oleic acid and 0.4 ml of oleylamine were mixed together with 5 ml of 1-octadecene in a 100 ml three-neck round-bottom flask. The flask was purged with Ar, heated to 120 °C for 20 min and then heated to 225 °C at a rate of 20 °C/min. After 30 min, the black-colored solution was cooled to room temperature. The resultant products were isolated by centrifugation, washed with ethanol for several times and resolved in the hexane for the other measurements.

Fig.1 TEM images of Cu$_2$Pt$_1$ (a) and Cu$_1$Pt$_2$ (b) nano-particles; (c) EDS of Cu-Pt nano-particles.

The Cu-Pt alloy nano-crystals with different molar ratios have been characterized by XRD, TEM and XAS, i.e., both X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine-structure (EXAFS). XRD measurements were performed using a PANalytical X’pert pro diffractometer using a graphite monochromatized Cu-Kα radiation source. Samples were also characterized with a JEOL JEM2100 transmission electron microscope operating at 200 keV. The samples for TEM were prepared by placing one drop of the hexane solution onto a carbon-coated Ni grid and allowing it to dry in air. XAS spectra at the Pt L$_{3}$- and Cu K-edge were collected in the transmission mode at the beamline U7C of the National Synchrotron Radiation Laboratory (NSRL, Hefei). The storage ring was working at the energy of 800 MeV with an average electron current of 150 mA. Hard X-rays were monochromatized with a Si(111) double-crystals monochromator. The incident and output beam intensities were recorded using ionization chambers filled by a 25% argon.
doped nitrogen mixture and argon gas, respectively. XAS data were analyzed by UWXAFS3.034 and USTCXAFS3.035 software packages.

Results and discussion
1. XRD and TEM characterizations

TEM images (Fig.1a and 1b) show highly homogenous Cu-Pt nano-clusters. The magnified TEM images show nano-clusters with size of ~1.2 nm, which contains approximately 40 atoms. The Cu/Pt ratio of these structures can be obtained with the Energy Dispersive Spectrometry (EDS) (Fig1.c). It points out that the ratio of Cu2Pt1 and Cu1Pt2 samples are consistent with that of Cu(acac)2 and Pt(acac)2 raw materials. The XRD patterns of the Cu-Pt bimetallic nano-clusters with different molar ratios are shown in Fig.2 and rules out the presence of Cu, Pt metal and their oxides in the prepared samples. Due to the small size of the nano-cluster, XRD patterns of CuPt samples present only the peak of (111). We may recognize that these clusters have very similar XRD patterns with only a small shift of the (111) peak (Fig.2a). On the basis of the Scherrer formula, the sizes of both Cu2Pt1 and Cu1Pt2 were evaluated to be about 1.2 nm from the half width of the diffraction peaks, in good agreement with TEM data.

Fig.2 XRD patterns (a) and Cu K-edge XANES spectra (b) of Cu-Pt bimetallic nano-clusters with different molar ratios; Cu K-edge EXAFS of Cu2Pt1 and Cu1Pt2 bimetallic nano-clusters (c) and their FTs (d).
2. XANES spectroscopy at Cu K-edge and Pt L3-edge

Fig. 2b shows Cu K-edge XANES spectra of Cu-Pt clusters with different molar ratios. The main peak at 8995 eV, which corresponds to the transition from 1s to 4p, reflects the character of the 4p unoccupied states\(^8\). The increasing intensity of the main feature means that the number of unoccupied states of the Cu 4p electrons in the Cu\(_2\)Pt\(_1\) cluster increases compared to the Cu\(_1\)Pt\(_2\) cluster, with a decreasing Cu composition. The threshold peak which occurs at 8980 eV is due to the hybridization between p- and d-states and probes the 3d character of the unoccupied states. The increasing intensity of this feature probes also the enhancement of the p-d hybridization at Cu sites upon alloying. Fig. 3a shows Pt L3-edge XANES spectra of Cu-Pt nanoclusters. The Pt L3-edge XANES is a dipole allowed transition from 2p\(_{3/2}\) to 5d\(_{3/2}\) and 5d\(_{5/2}\) states. However, it only involves unoccupied states of 5d\(_{5/2}\) due to the lack of 5d\(_{3/2}\) holes in Cu-Pt nanoparticles. Indeed, it is very clear that the intensity of the white line (WL) decreases, increasing the Cu concentration. The behavior can be explained because in these nanostructures 5d\(_{5/2}\) Pt unoccupied states were partially occupied by electrons transferred from the Cu site. From the theoretical point of view, the loss of Cu electrons induces an increase of the Cu chemical value. The hypothesis is confirmed by the shift of the Cu edge towards high energy (Fig. 2b). Therefore, an effective charge transfer is detected in Cu-Pt nanoparticles, similar to what has been observed in Cu-Pt and Cu-Pd alloys by Lee and Cho with XANES experiments\(^{20}\). Increasing the Cu/noble metal molar ratio they also observed a clear reduction of the Pt L3-edge WL intensity.

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**Fig. 3** (a) Pt L3-edge XANES spectra of Cu-Pt clusters with different molar ratios; (b) Pt L3-edge EXAFS oscillation functions and (c) the corresponding FTs of Pt foil, Cu\(_2\)Pt\(_1\) and Cu\(_1\)Pt\(_2\) bimetallic nano-clusters.
3. EXAFS spectroscopy for Cu K- and Pt L3-edge.

Fig. 2d and 3c show the $k^3$-weighted Fourier transforms (FT) of the EXAFS of the two Cu-Pt samples at the Cu K-edge and at the Pt L3-edge, respectively. Figures clearly show that the FTs of the Cu K-edge EXAFS of the CuPt NPs have a double peak in the region 1.7-3.3 Å (Fig. 2d) with a lower-R (1.8-2.0 Å) and a higher-R (2.6-2.9 Å) contribution. Both can be associated to first shell (the nearest) metal-metal bonds. The splitting of the first shell peak is due to the interference between the EXAFS oscillations of Cu-Cu and Cu-Pt bonds, whose phase shift and amplitude are different. However, as the Cu concentration increases, the intensity of the peak at lower R decreases. Moreover, the EXAFS oscillations at the Pt L3-edge (Fig. 3b) of as-prepared samples show significant differences in contrast to those of Pt foil, not only in the phase but also in the intensity. From the EXAFS analysis, we may also conclude that due to the formation of Cu-Pt bond the bond distances in our samples decrease, as clearly shown from the FTs in Fig. 3c. The FTs of the Cu-Pt NPs also show that the Pt-Cu distance is ~2.7 Å, which is just the length of the Cu-Cu bond in agreement with the claiming that in these nano-particles Pt occupies Cu sites.

Conclusions

In summary, synthesized Cu-Pt alloy nano-particles with different molar ratios were homogenous systems with an average size of ~1 nm as characterized by XRD, TEM, EDS and XAS. Moreover, from EXAFS results Pt atoms occupy Cu sites and Pt-Cu bonds are formed. An evident charge transfer from Cu to Pt is also detected by XANES in Cu-Pt nano-clusters. All together, the structural and electronic characterizations provide useful information to understand the properties of such small nano-clusters.

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