A Microstructual Study of Architecturally-Controlled Pt-Ru Core/Shell and Alloy Nanoparticles

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Alloys are probably the most studied and the best understood multi-metallic systems. Bimetallic nanoparticles (NPs) with various particle architectures, in particular alloy and core/shell structures, have growing applications in catalysis. RuPt alloys NPs have already found applications as CO tolerant H_2 catalysts. However, their rather ill-defined surface atomic structures impede their characterization. The synthesis of well-characterized bimetallic NPs is the key for understanding their versatile electronic and catalytic properties. Core/shell structure, on the other hand, is promising in terms of its novel atomic makeup. This study describes the structural characterization and catalytic properties of the architecturally-controlled bimetallic nanoparticles (NPs) of platinum and ruthenium using TEM/STEM.

The Ru@Pt core/shell NPs of tunable core sizes and shell thicknesses, and the PtRu alloy NPs of various compositions were prepared via poly-ol reduction reactions by using sequential deposition techniques. The core/shell and alloy NPs were characterized by using a combination of TEM/STEM-EDS, XRD, XPS and FTIR-CO probe experiments [1, 2], and evaluated toward preferential oxidation of CO in H_2 feeds (PROX), a key reaction in purification of CO contaminated-H_2 fuels. Full structural analysis employing techniques such as Extended X-Ray Absorption Fine Structure (EXAFS) and atomic Pair Distribution Function (PDF) was also performed for the 4.1 nm Ru@Pt NPs comprising of 3.0 nm cores and 1-2 MLs thick shells and the 4.4 nm $Pt_{50}Ru_{50}$ alloy NPs [3].

A thorough TEM investigation, as shown in Fig. 1, revealed crystallographically poorly ordered Ru NPs (a), rather well-crystallized core shell NPs (b), and single-domain alloy nanocrystals (c), respectively. EDS line spectra helped to identify the architectural information of different bimetallic NPs of similar size and composition (Fig. 2). Although the representative HRTEM image (Fig. 1b) revealed little contrast on core/shell structure due to the < 0.5 nm thick shell, the EDS line scan spectrum clearly depicted a 4.1 nm Ru@Pt NP with 3.0 nm Ru core and 1-2 MLs thick Pt shells (Fig. 2a). HRTEM image of a 4.4 nm $Pt_{50}Ru_{50}$ alloy nanoparticle showed a single domain with lattice fringes (Fig. 1c). Using 1.5 nm electron probe, the relative atomic % of Pt and Ru were clearly revealed in EDS line profile. The well-characterized core/shell and alloy NPs were evaluated for preferential oxidation of CO in H_2 feeds (PROX). Catalytically, the core/shell NPs were superior to their alloy counterparts with similar particle sizes and identical compositions [1]. The Temperature Programmed Reaction (TPR) results for H_2 feeds contaminated with 1% CO suggest unique H_2 activation behavior for each established structure (Fig. 3). The core/shell structure has been shown to be much more active and selective toward CO oxidation than the alloy architecture. The far superior catalytic behavior of Ru@Pt NPs to PtRu alloy NPs of similar geometry and surface area have been attributed to the altered electronic structure of surface-Pt (Fig. 1).

[1] S. Alayoglu et al., Nat. Mater. 7 {2008} 333.
[2] S. Alayoglu et al., ACS Nano, submitted.
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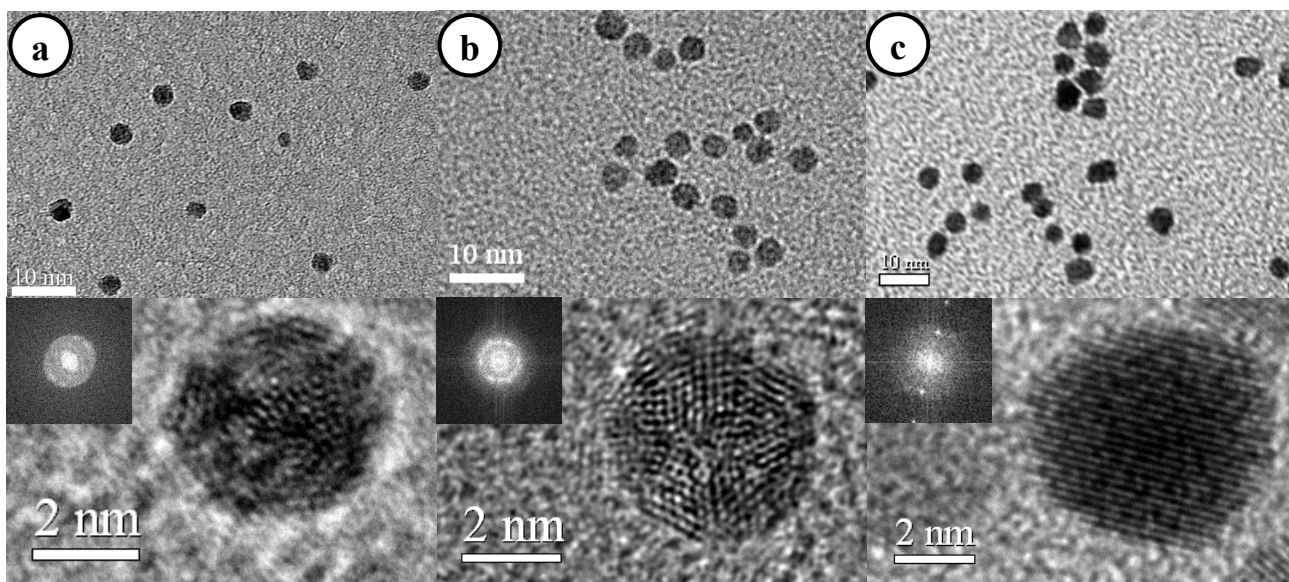
Fig. 1. TEM images showing general morphology and ultra-high resolution image of a 3.0 nm Ru NP (a), a 4.1 nm Ru@Pt NP with 3.0 nm Ru core and 1-2 MLs thick Pt shells (b), and a 4.4 nm $Pt_{50}Ru_{50}$ alloy NP (c). Insets are FFT of HRTEM images.
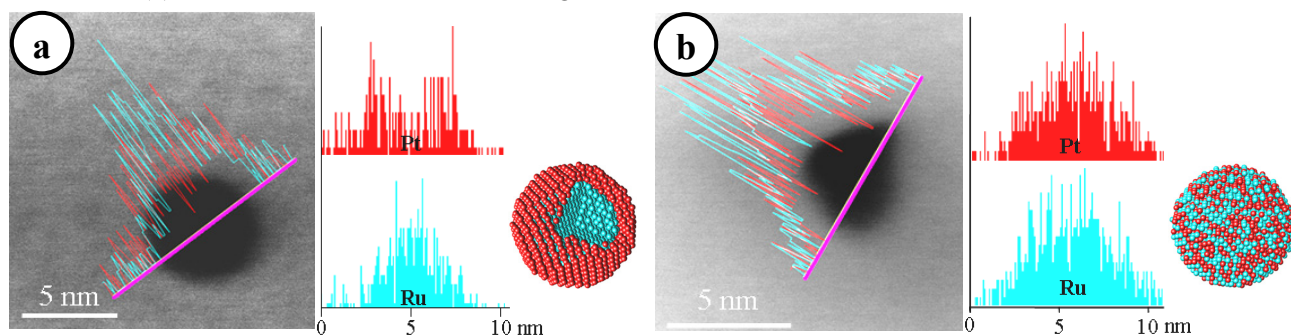

Fig. 2. Representative EDS line spectra of a 4.1 nm Ru@Pt NP with 3.0 nm Ru core and 1-2 MLs thick Pt shell (a), and a 4.4 nm $Pt_{50}Ru_{50}$ alloy NP (b). EXAFS and TEM derived cluster models (ca. 2500 atoms core/shell and ca. 3000 atoms alloy, respectively) are given next to each spectrum.
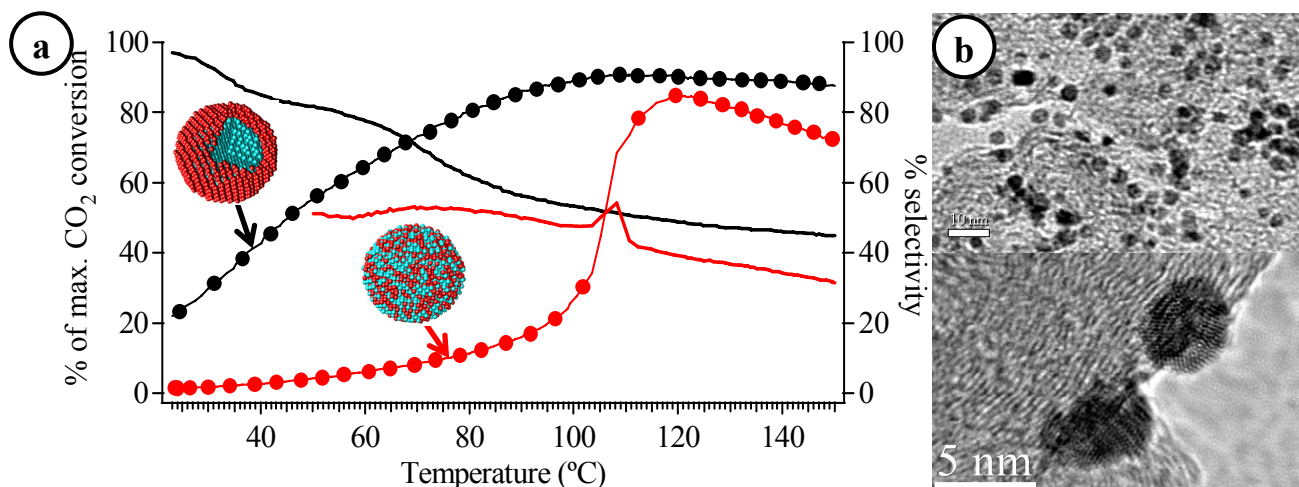

Fig. 3. TPR plots for the PROX reaction showing CO_2 formation (connected circles) and CO selectivity (continuous lines) at 1% CO level for the as-synthesized core/shell NP catalyst and the alloy NP catalyst (a). TEM images of the supported core/shell NPs catalyst (b).