Core-Shell particle restructuring during CO oxidation cycles: A DRIFTS investigation

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We show how oxidizing and reducing conditions restructure the surface of 5 nm Ru@Pt core/shell nanoparticle catalysts (Ru core, Pt shell). A combination of TEM line scans, *in situ* DRIFTS studies and catalytic evaluations show that the Ru atoms in the Ru core are brought to the surface to form a RuO/Pt alloy surface structure under oxidizing conditions and return to their sub-surface sites under reducing environments to re-generate an essentially pure Pt surface. Evaluation of the supported Ru@Pt catalysts for CO oxidation shows reactivity identical to that of the alloyed PtRu alloy, which is consistent with the *in situ* DRIFTS studies that show the same surface structure for both particles. Under reducing conditions, the DRIFTS studies show markedly different surface structures for the Ru@Pt vs. PtRu alloy particles. Evaluation of the preferential oxidation of CO in hydrogen feeds (PROX) reaction (*i.e.* CO oxidation under reducing conditions) shows significantly better activity for the core-shell catalysts relative to the alloy catalysts and are also in agreement with the DRIFTS experiments. Post catalysis TEM-EDS studies show that the core-shell structure is retained for the Ru@Pt NPs. The data show that the alloy NPs are essentially invariant in their surface and core structures under oxidizing and reducing conditions whereas the Ru@Pt core-shell particles undergo facile and reversible surface-to-subsurface migrations.