

Atomic structure of Pt-CoO_x cluster catalysts for preferential oxidation of CO in H₂

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The oxide support has been found to have a remarkable promotion effect on catalytic activity. Oxide supported metal nanoparticle catalysts are broadly applied to industrial catalytic reactions. The oxide support, particularly a reducible oxide, has been found to have a remarkable promotion effect on catalytic activity. Unveiling the structure of metal-oxide interface under reaction conditions is of great importance for establishing the structure-activity relations.

Here, we prepared subnano Pt-CoO_x clusters supported on SiO₂ by selective deposition of CoO_x on immobilized ionic PtCl_x^{δ-} species using atomic layer deposition (ALD) followed by oxidation/-reduction pretreatments at 250 °C. The Pt-CoO_x catalyst exhibited extremely high catalytic activity, selectivity and stability in a broad temperature range in the preferential oxidation of CO (PROX) reaction. *In-situ* X-ray absorption fine structure (XAFS) technique was employed to unveil the structures of Pt and Co species under different treatment conditions.

The X-ray absorption near-edge structure (XANES) curves at the Pt L₃-edge show that the Pt atoms in as-prepared PtCl_x^{δ-}/SiO₂ remained in the ~4+ oxidation state, and the Pt in the as-prepared 1cCo-PtCl_x^{δ-}/SiO₂ is slightly reduced. After undergoing oxidation/reduction pretreatment at 250 °C, the Pt valence states are considerably reduced. Under the PROX stream, the 1cCo-Pt/SiO₂ exhibits higher average oxidization state of Pt. Least-squares EXAFS curve-fittings show the average coordination numbers of Pt-O, Pt-Cl, Pt-Pt to be 1.0, 1.0, and 4.5, respectively, with a significantly elongated metallic Pt-Pt bonds of 2.86 Å. The Co K-edge XAFS analysis show that the Co atoms in 1cCo-Pt/SiO₂ under PROX condition are mainly in the form of an oxidized state, without the formation of visible Co-Co or Co-Pt coordination.

Combing the STEM measurements, our in-situ XAFS measurements showed electrostatic interaction induced SMSI and strong Pt-CoO_x interaction both play important roles in inhibiting severe Pt aggregations to form subnano Pt-CoO_x clusters. This work provides a new avenue to optimize metal-oxide interface for enhanced activity in catalytic reactions.