

Anchoring Pt Single Atoms on CeO_x Nanoclusters for CO Oxidation

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Downsizing noble metal particles to clusters or single atoms is highly desirable for maximizing the effective use of expensive and rare noble metals for catalytic transformations of chemicals [1]. Recent advances in synthesizing single-atom catalysts (SACs) demonstrated that SACs can be highly active and selective for a variety of catalytic reactions [2]. Unless they are strongly anchored by defect sites supported metal atoms are, however, thermodynamically unstable, especially at elevated temperatures [2]. Therefore, for practical applications of SACs it is imperative to develop feasible strategies to stabilize atomically dispersed metal atoms. Surface steps have recently been reported to trap Pt atoms and can become stable on certain metal oxides such as CeO₂ [3]. In this work, we demonstrate a novel strategy of using CeO_x clusters as nanoglues to anchor Pt single atoms onto high surface area, inexpensive, and abundant SiO₂ supports (Fig. 1a). Furthermore, the highly reducible CeO_x clusters are expected to act as an oxygen gateway to store/release oxygen during selected catalytic reactions. We use CO oxidation as a probe reaction to test the performance of Pt₁/CeO_x clusters which are dispersed onto SiO₂ nanoparticles.

The preparation of CeO_x-SiO₂ nanocomposites was accomplished by adsorbing Ce salt precursors onto SiO₂ powders via a wet chemistry method. The Ce-containing precipitates were washed with deionized water, dried and calcined in air to form CeO_x clusters on the SiO₂ nanoparticles. A strong adsorption method was used to disperse Pt salt precursors onto the surfaces of the as-prepared CeO_x-SiO₂ nanocomposite powders. The Pt/CeO_x-SiO₂ precipitates were then filtered, washed and dried at 60°C for 5 h. The Pt₁/CeO_x-SiO₂ powders, with a nominal loading of 0.5wt.% of Pt, were calcined and/or reduced to form the final Pt₁ SACs. Aberration-corrected HAADF-STEM was used to examine the fresh and used CeO_x-SiO₂ nanocomposite supported Pt₁ SACs.

Figure 1b shows a representative HAADF-STEM image of the as-synthesized Pt₁/CeO_x-SiO₂ SACs. The bright patches (indicated by the yellow arrows) represent uniformly dispersed CeO_x clusters with an average size of ~ 2 nm. The crystalline nature and the dispersion of the CeO_x clusters are clearly shown in Figure 1c. Some small CeO_x clusters are almost atomically dispersed and do not possess a crystalline phase. Although it is difficult to distinguish single Pt atoms from those of the highly dispersed Ce atoms/clusters we have not detected, in the as-prepared and used SACs, any Pt particles/clusters which are distinguishable from the CeO_x clusters. Figure 1d shows the catalytic testing data clearly demonstrating the high activity and stability of the Pt₁/CeO_x-SiO₂ SACs for the CO oxidation reaction. Other catalytic reactions on, and the structural stability of, such hierarchically nanostructured SACs will be discussed [4].

References:

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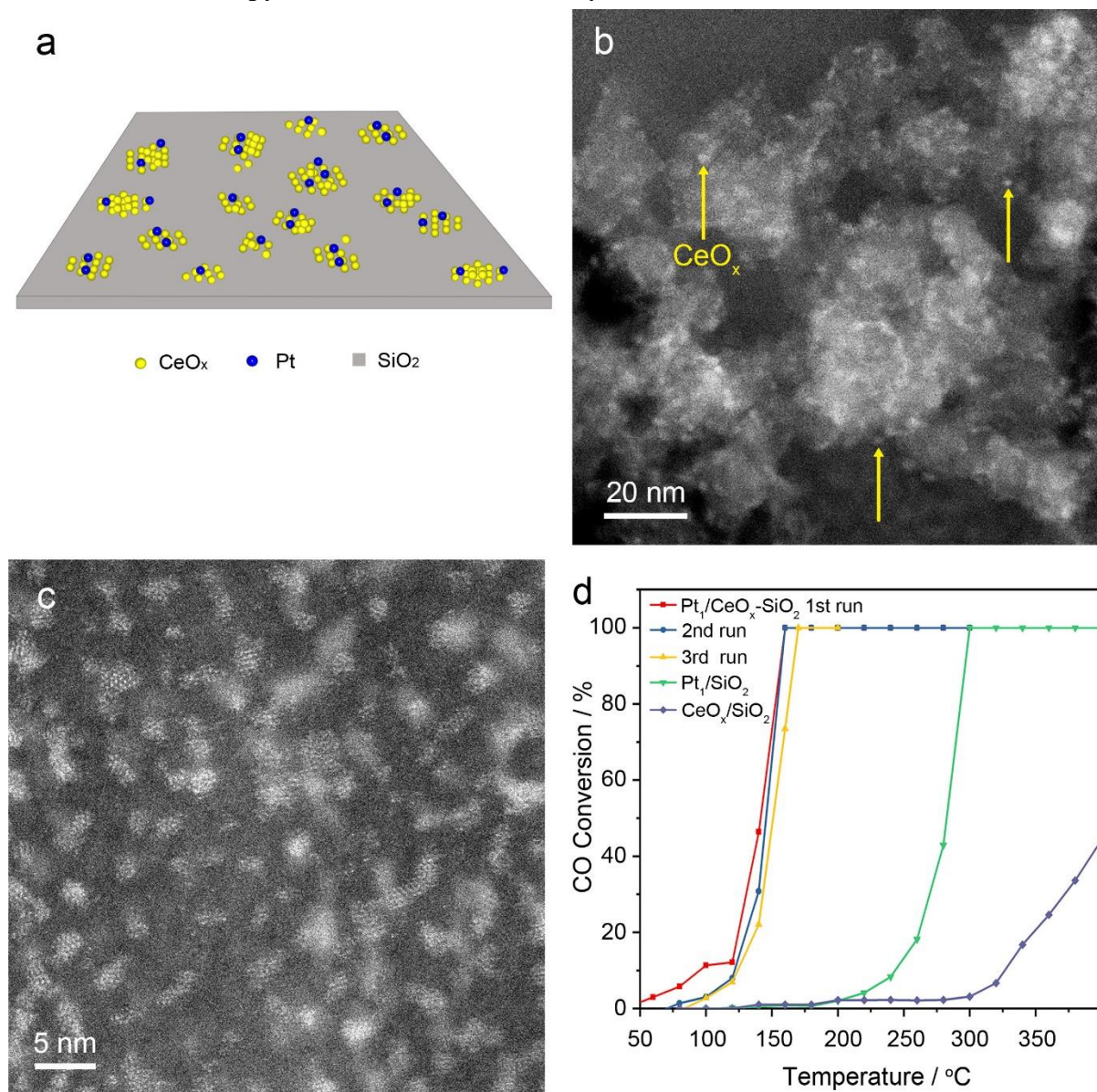


Figure 1. Schematic diagram illustrates the design of the CeO_x-SiO₂ supported Pt₁ SACs (a); HAADF images of a typical Pt₁/CeO_x-SiO₂ SAC show spatial distribution (b) and atomic structure (c) of CeO_x clusters; and catalytic testing data for CO oxidation (d). Reaction conditions: [O₂] = 4% and [CO] = 1% balanced with He at a gas hourly space velocity of 20,000 ml g_{cat}⁻¹ hour⁻¹, temperature ramping at 2°C/min, and ambient pressure.