

Atomic-Resolution Characterization of Surface Structures and Metal-Support Interfaces on Nanostructured Pt/CeO₂ Catalysts Performing CO Oxidation

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In reactions involving gas-solid interactions on nanostructured supports, the distinction between catalytically significant atomic structures and unreactive spectators is obscured by the variety of surface states that exist under reaction conditions. Studies of catalysts with well-defined support morphologies could assist in limiting the scope of structural configurations under consideration. Cerium dioxide (CeO₂), a technologically important redox catalyst owing to its aliovalent behavior, can be synthesized into nanocrystalline cubes and rods; cubes surface-terminate with {100} planes, while rods surface-terminate with {110} and {100} planes [1]. Density functional theory (DFT) calculations indicate that CeO₂ {100} surfaces are less stable than {110} surfaces, which suggests that cubes should be more reactive than rods [2]. However, for the CO oxidation reaction, rods are reported to be more active than cubes [1, 3]. No atomic-resolution, *in situ* information exists for the surface structures or metal-support interfaces that occur on CeO₂ rod/cube-supported catalysts, so we may only speculate upon the origin of the rods' superior activity. This study employs *ex situ* and *in situ* environmental transmission electron microscopy (ETEM) to probe the atomic processes that give CeO₂ rod-supported catalysts enhanced catalytic activity.

Nanocrystalline CeO₂ cubes and rods were synthesized via the hydrothermal method described by Mai *et al.* [1]. Both samples were impregnated with an aqueous solution of PtCl₄ to obtain 1.0 wt% loadings of platinum (Pt) metal. After impregnation, the samples were calcined in air at 490 °C for 3.5 hours, and then reduced at 450 °C for 4 hours in a stream of 5% H₂/Ar flowing at 40 standard cubic centimeters per minute (SCCM). Images of the fresh catalyst powders were obtained with a FEI CM200 TEM operating at 200kV and a FEI Titan aberration-corrected TEM operating at 300kV. The CO oxidation performance of each catalyst was tested. Each catalyst was loaded into an ISRI RIG-150 microreactor, through which 2 SCCM O₂ and 40 SCCM 10% CO/He reactant gasses were flowed while the reactor bed was heated from 25 – 350 °C. Product gasses were analyzed with a Varian 3900 gas chromatograph.

The resultant light-off curves for the two catalysts are shown in Figure 1, and prove that the rod sample exhibits higher activity than the cube sample. A typical cube catalyst particle is shown in Figure 2. The inset confirms that the cubes surface-terminate with the high-energy [100] plane. In Figure 3, 1 – 2 nm Pt nanoparticles are seen to be well-dispersed over the support surfaces. Many rods in our sample display similar crystallographic character as those prepared by other researchers [1, 3], although other rods, such as the one shown in Figure 4, expose [111] planes over a considerable portion of their surface. DFT calculations predict the [111] plane to be the lowest energy CeO₂ surface [2]. The fact that rods exhibit higher activity than cubes – despite the cubes exposing almost only the theoretically more reactive surface – demonstrates that the catalytic activity is not simply dependent on the support surface energy.

The enhanced activity of the rods may be attributed to a higher density of short-range order surface defects. Careful examination of the rods and cubes below reveals a disparity between the rod surfaces, which are predominated by edge and step defects, and the cube surfaces, which appear more uniformly smooth. An alternative hypothesis is that the catalytic activity is governed by metal-support interactions, likely through

a Mars Van Krevelen mechanism. Nevertheless, the present results indicate that elucidating the relationship between surface structure and catalyst activity will necessitate *in situ* observations. No previous research has provided atomic-resolution information of these systems under reaction conditions. To this end, *in situ* ETEM experiments will be performed to determine the form and composition of surface structures and metal-support interfaces under reaction conditions; results will be presented [4].

References:

[1] Mai, H. *et al.*, Journal of Physical Chemistry B **109**, (2005), p. 24380 – 24385.

[2] Jiang, Y. *et al.*, Journal of Chemical Physics **123** (2005), p. 064701-1 – 9.

[3] Wu, Z. *et al.*, Journal of Catalysis **285** (2012), p. 61 – 73.

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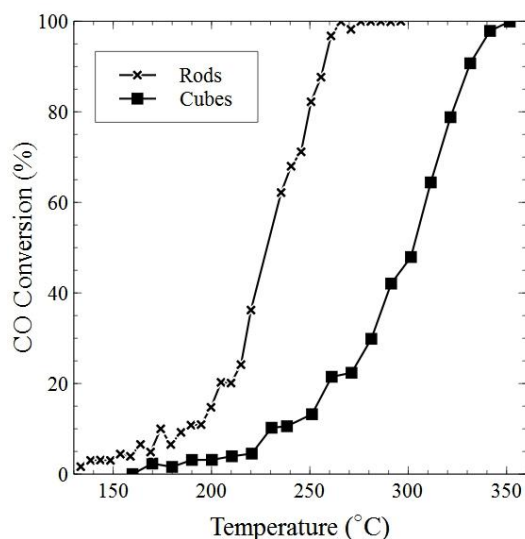


Figure 1. Light-off curves demonstrate that rods are more reactive for CO oxidation than cubes.

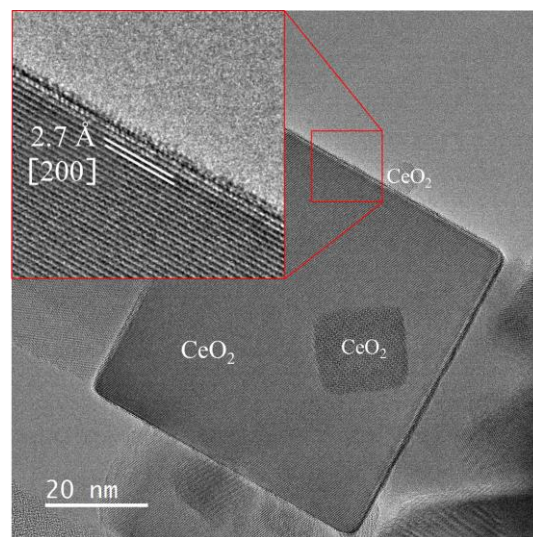


Figure 2. TEM image of fresh cube catalyst shows fairly smooth [100] terminating surfaces.

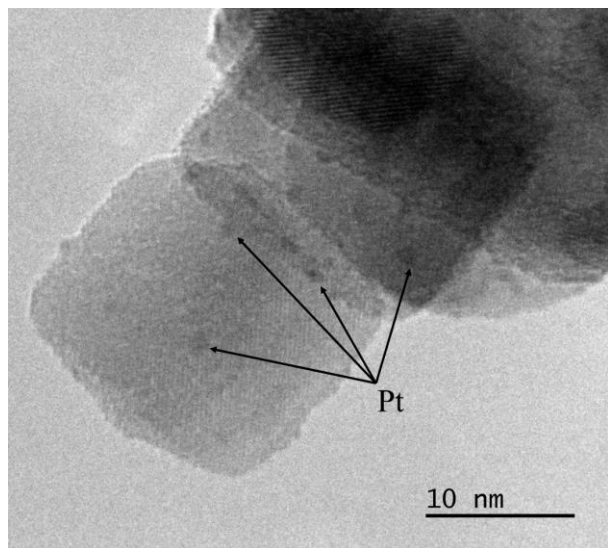


Figure 3. TEM image of fresh cube catalyst shows well-dispersed platinum nanoparticles.

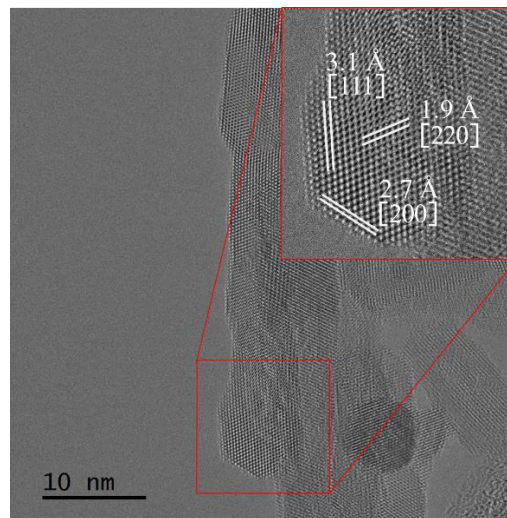


Figure 4. TEM image of a CeO₂ rod shows a high density of short-range order edge and step defects along a low-energy [111] surface.