

The Role of γ -Al₂O₃ Single Crystal Support to Pt Nanoparticles Construction

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Here we report the preparation of a model Pt/ γ -Al₂O₃ catalyst and its characterization by a cross-sectional high-resolution electron microscopy (XHREM) method. Pt/ γ -Al₂O₃ is the most important technologically-relevant heterogeneous catalyst in the fuel cell, oil refining and chemical industries. The nanoparticle/support interactions, particularly the role of their interface, play a key role in the 3-dimensional (3D) particle shape, surface morphology and sintering behaviors of catalyst nanoparticles (NPs) which determine the heterogeneous catalysts' chemical properties. Experimental measurements [1] and theoretical simulations [2] were initiated to quantitatively study the interfacial atomic and electronic structure and adhesion energy between the NPs and their support. Previous investigators have used single crystal oxide supports to resolve the nanoparticle/support structure and shape relations that can be directly compared to the theoretical simulations [2]. However, commercial γ -Al₂O₃ is polycrystalline and irregular in shape; hence, our aim is to create a single crystal γ -Al₂O₃ thin film in order to build up a model system to solve the structural and electronic relations between the Pt and γ -Al₂O₃ support, and compare our experimental results with theoretical predictions.

The γ -Al₂O₃(111) thin film was prepared via oxidization of β -NiAl(110) at T=850°C and dry air for 1 hour, while the primary orientation relation (O.R.) was determined to be NiAl(011)[110]|| γ -Al₂O₃(111)[211] and NiAl(011)[100]|| γ -Al₂O₃(111)[110] which is the classical Nishiyama-Wasserman O.R., Figure.1. Pt NPs were deposited onto γ -Al₂O₃(111) surface by electron-beam evaporation under ultrahigh vacuum. High-angle annular dark-field (HAADF) imaging and HREM imaging (Figure. 2a and b) shows a significant fraction of the Pt NPs covering the support with intimate contact to the γ -Al₂O₃ support. The shape of the Pt NPs is a truncated octahedron which correlates with a dewetting shape, Figure 2c. The dominant surface facets are the {111} and {100} low- index planes which are the favorable facets for catalytic reactions [3]. The O.R. of the Pt NPs was found to be Pt(111)[211]|| γ -Al₂O₃(111)[211] and Pt(100)[011]|| γ -Al₂O₃(111)[211], Figure.2b and c, where the interface planes Pt(110)|| γ -Al₂O₃(110) followed the classical lattice matching epitaxy. Considering that the γ -Al₂O₃ support has a strong impact on the structural shape and electron density of the catalytic NPs, as an extension of the Wulff construction for 3D facets, Kaishew theorem, was used to analyze the support effects on the Pt particle shape. Electron energy-loss spectrum (EELS) will be applied to study the electronic structure of Pt NPs and clarify the preferred Pt anchoring sites on the γ -Al₂O₃.

References

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- [3] Erik Schmidt, et al. *Journal of the American Chemical Society* 131, 12358-67 (2009).
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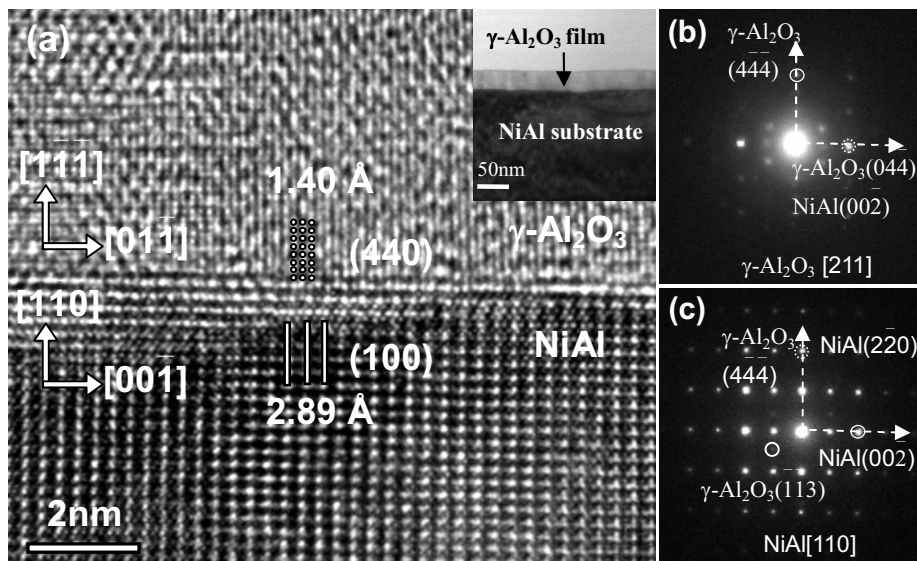


Figure.1 (a) Cross-sectional HREM image of 850 °C 1 hour oxidized NiAl/ γ -Al₂O₃ interface, (b). NB-EDP from upper γ -Al₂O₃ film, (c). SAD from NiAl/ γ -Al₂O₃ interface.

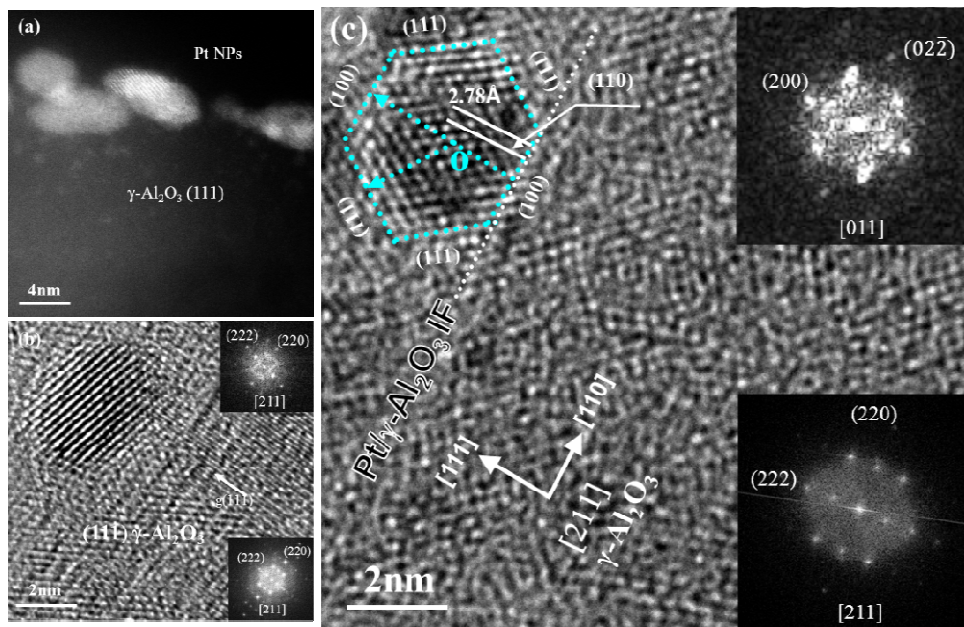


Figure.2. HAADF image (a) and HREM image (b) shows the Pt NPs directly seated on the γ -Al₂O₃(111), ES Pt NP Pt (c) with interface planes: Pt(220) || γ -Al₂O₃ (440).