

Temperature-dependent Oxidation of Pt Nanoclusters on a Thin Film of Al₂O₃ on NiAl(100)

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Metal clusters on oxides have been widely explored in heterogeneous catalysis.¹⁻⁹ A focus of such exploration is the interaction of the dispersed metal with its support, because the reactivity and stability of an oxide-supported catalyst depends strongly on that interaction.¹⁻⁵ Such interfacial interaction was found to behave in a complicated manner, encompassing, for instance, electronic effects (arising from chemical interaction and charge transfer), structural effects (ascribed to structural stabilization), migration of support materials onto the metal, and diffusion and spillover through the metal-oxide interface.¹⁻⁵ A characterization of the interfacial interaction thus becomes non-trivial, but highly valuable for correlating the complicated interaction with the induced variation of catalytic properties.

In the present work we investigated temperature-dependent oxidation of Pt nanoclusters on a thin film of Al₂O₃ on NiAl(100), in the absence of a gaseous oxidizing agent. The Pt clusters (of mean diameter 2.2 nm and height 0.4 nm) grown from vapor deposition on the thin film of Al₂O₃ on NiAl(100) at 300 K became partially oxidized, as charge transfer from the Pt clusters to the oxide was indicated by a significant negative shift (0.4 - 0.5 eV) of binding energy (BE) of Al^{ox} 2p and O 1s states from Al₂O₃. The oxidation of the cluster proceeded to a further level when the sample was annealed above 450 K; the Pt 4f_{7/2} core-level moved positively from BE 72.0 eV with increasing annealing temperature and eventually attained 72.6 eV above 650 K, which indicates a state of Pt²⁺. Accompanying this further oxidation, signals of both Al^{ox} 2p and O 1s shifted back to greater BE. The valence spectra indicate that the Pt-Al₂O₃ interaction was sustained whereas a new Pt-O bond was formed. Formation of a Pt_xAl_yO_z complex is proposed to explain the observations. The new Pt-oxide binding was substantially stronger than the initial one, as was evident from the oxidized clusters being resistant to sintering induced in electrochemical processes. The oxidation was associated also with a migration of oxide materials onto the Pt clusters, as both Al₂O₃(100) and NiAl(001) facets roughened after the annealing, and a probe of methanol adsorption showed no bare Pt clusters exposed but alumina-like structures on the surface.

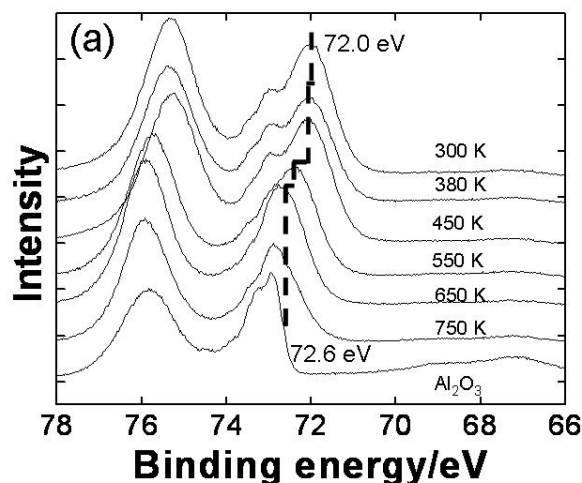


Fig. 1: Photoelectron spectra from 3.2 ML Pt deposited on thin-film Al₂O₃/NiAl(100) at 300 K and annealed to selected temperatures as indicated in the figure; the dashed line indicates the shift of Pt 4f_{7/2}.

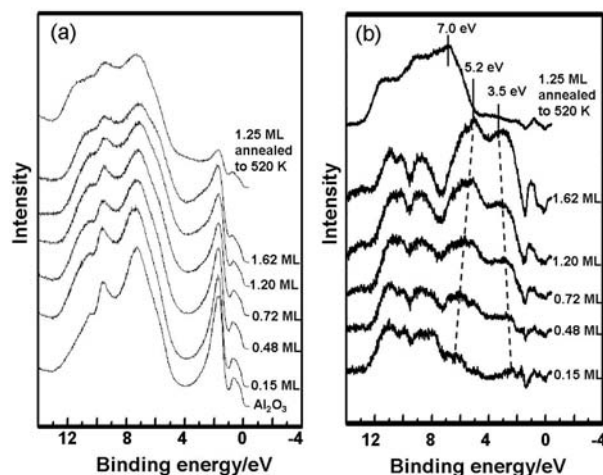


Fig. 2: Photoelectron spectra in the valence regime from varied coverages, as indicated, of Pt clusters formed on the thin-film Al₂O₃/NiAl(100) at 300 K. (a) shows the original spectra and (b) shows difference spectra obtained on subtracting the contributions of the Al₂O₃/NiAl(100) substrate. The dashed lines indicate the evolution of Pt 5d state-derived feature with the coverage.