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Theoretical Explanation of Pt Trimers Observed by Z-Contrast STEM

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First-principles quantum-mechanical calculations on γ-alumina have revealed a fascinating "reactive sponge" phenomenon. γ-alumina can store and release water, but in a unique, "reactive" way. This "reactive sponge process" facilitates the creation of aluminum and oxygen vacancies in the alumina surface. Earlier atomic-resolution *Z*-contrast STEM images of ultradispersed Pt atoms on a γ-alumina support showed the individual atoms to form dimers and trimers with preferred spacings and orientations that are apparently dictated by the underlying support [Nellist and Pennycook, *Science* **274**, 413 (1996)]. In turn, the reactive sponge property of γ-alumina is the key to understanding the Pt clusters. Our calculations demonstrate that if three Pt atoms fill three vacancies created during the reactive sponge process, the resulting geometry precisely matches that of the Pt trimers observed in the *Z*-STEM images. Understanding the initial nucleation of small clusters on the complex gamma alumina surface is an essential first step in determining the origins of catalytic activity.

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DFT Calculations for γ-Alumina Bulk and (110) Surface

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Density functional theory calculations on γ-alumina bulk and the preferentially exposed (110) surface are reported. The calculations reveal that γ-alumina may contain hydrogen over a range of concentrations and that this hydrogen becomes mobile at elevated temperatures. Calculations of the energy barrier to hydrogen diffusion predict kinetics in excellent agreement with experiments. It is found that that when the (110°C) layer of γ-alumina is exposed, it undergoes a massive spontaneous reconstruction. The three-coordinated Al atoms initially in the surface layer drop into vacant octahedral interstices in the next lower layer. This result explains the perplexing experimental observation that no three-coordinated Al is observed on γ-alumina surfaces, despite the fact that its presence should be expected based on the bulk structure. Understanding the structure of the complex gamma alumina surface is an essential first step in determining the origins of catalytic activity.

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