Application Note

Atmosphere™

Novel Catalyst Structure Dynamics Captured at the Atomic Scale Using the Protochips Atmosphere Gas E-cell System

Introduction

Over the past several years, attention has increasingly focused on engineering catalysts at the nanometer scale to simultaneously increase catalytic activity and reduce the amount of expensive precious metals. Catalytic activity is directly proportional to the active material's surface area, and small nanoparticles and nanoclusters are attractive for catalysis applications because they provide a high surface area per unit volume by reducing the amount of material required to maintain high catalytic activity. However, significant hurdles remain before widespread adoption of nanoparticle catalysts occurs. Catalysts typically operate at high temperatures, and small nanoparticles can behave differently than bulk materials, sintering and losing surface area at relatively low temperatures. For this reason, nanoparticle thermal stability remains a key focus of catalyst research groups around the world.

In 2012, a group at the University of Pennsylvania developed a new nanoparticle catalyst system with exceptional activity for methane combustion. The catalyst consists of modular palladium–ceria core–shell subunits on silicon-functionalized alumina, as illustrated in Figure 1. The thermally stable ceria shell structure protects small palladium nanoparticles from sintering at elevated temperatures while maintaining access to the active palladium surface. The authors show the core-shell structure was successfully synthesized via transmission electron microscopy (TEM), but a thorough analysis of the catalyst behavior over a wide temperature range was required to understand catalyst behavior under reaction conditions.

Until recently, researchers were unable to carry out *in situ* gas reactions inside the TEM. The TEM alone only provides a means to analyze a sample in high vacuum at room temperature, which does not well represent real-world catalyst reaction conditions. Reactions normally occur at or near atmospheric pressure, and several hundred degrees Celsius. With the introduction of the Protochips Atmosphere 200 E-cell system, researchers can now expose catalyst samples to gases and temperatures that closely match actual reaction conditions — up to 1 atm of pressure and 1000 °C. Atmosphere features a patented silicon carbide based heating membrane with best in class temperature uniformity and accuracy, and ultra stable heating for atomic resolution imaging at high temperature. It provides a means to safely visualize atomic scale processes in real time, so experiments yield more meaningful and relevant information with minimal additional effort.

To better understand their catalyst behavior under reaction conditions, the University of Pennsylvania researchers collaborated with the University of Michigan, who used advanced electron microscopy techniques, including the Atmosphere 200 system, to image and analyze samples in controlled gas and temperature environments at atomic resolution. Their *in situ* analysis demonstrated that the modular palladium–ceria core–shell subunits undergo structural evolution over a wide temperature range, producing two distinct forms: a mixture of palladium, cerium, silicon and oxygen with very high dispersion, and a coarse mixture of ceria and palladium particles.

Experiment

Both *ex situ* and *in situ* experiments were carried out on an aberration-corrected JEOL JEM-2100F 200 kV STEM in the University of Michigan's EMAL facility. *In situ* gas cell experiments were done using the Protochips Atmosphere 200 system, which consists of a MEMS-based closed cell holder, fully automated gas manifold and the Atmosphere Clarity workflow-based software. The closed cell uses two E-chips (MEMS devices) — a heating E-chip with a thin SiC heating membrane and a window E-chip with a SiN membrane. When stacked in the TEM holder and sealed with o-rings, a thin gas layer is formed between the E-chips that is isolated from the high vacuum of the TEM column. The heater temperature is actively controlled with the Atmosphere Clarity software, which automatically maintains the temperature setpoint in different gas environments and pressures (up to 1 atm), The samples, Pd-CeO_2 catalyst on a silicon-functionalized alumina support, were deposited directly on the heating E-chip device from a methanol suspension. During the experiment the sample was imaged under 150 Torr of pure oxygen to simulate air calcination at temperatures between 500 and 800 °C.

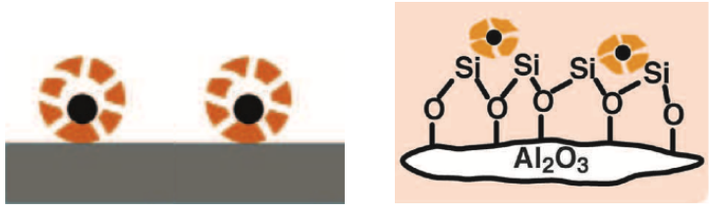

Figure 1: Left — Pd-CeO_2. The core shown in black represents Pd, and the porous shell in orange represents CeO_2. The gray support is Al_2O_3. The right image shows the silicon functionalized support.

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Discussion

The researchers first subjected the samples to *ex situ* calcination at 500 and 800 °C to study their thermal stability. At 500 °C, the ceria and palladium particles remain stable, with little change in the physical structure. When temperatures reached 800 °C, a distinct change in the structure occurred — smaller atomic-scale clusters appear, which coexist with larger palladium and ceria nanoparticles.

To better understand this phenomenon, *in situ* experiments using Atmosphere followed the calcination process step by step. In 150 Torr of oxygen the temperature was increased to 500 °C, and up to this temperature the sample remained stable. Beyond 500 °C, the researchers observed changes in the structure, where nanoparticles began to disassociate, the smallest first, followed by larger particles, into highly dispersed atomic-scale species (figure 2). As the temperature increased to 650 °C, a second structural change occurred. Ceria particles surrounded by atomic-scale species of ceria began to coalesce and form larger faceted nanoparticles (figure 3).

With these results, the researchers could better understand the process and behavior of the catalyst. At 500 °C ceria begins to disassociate and very small, atomic-scale species form. These small species are not found in samples without the silicon functionalized surface, and the authors suggest that silicon plays a role in stabilizing the small clusters of ceria either physically or chemically. As the temperature increases, the small species are no longer stable, and coalesce into larger nanoparticles, but only if an existing particle is in close proximity. Otherwise they will nucleate into very small clusters. Both *ex situ* and *in situ* experiments confirmed the formation of the two distinct structures, the larger nanoparticles and highly dispersed atomic-scale clusters. The authors surmise the highly dispersed structures, stabilized by silicon, is the source of the exceptional catalyst activity.

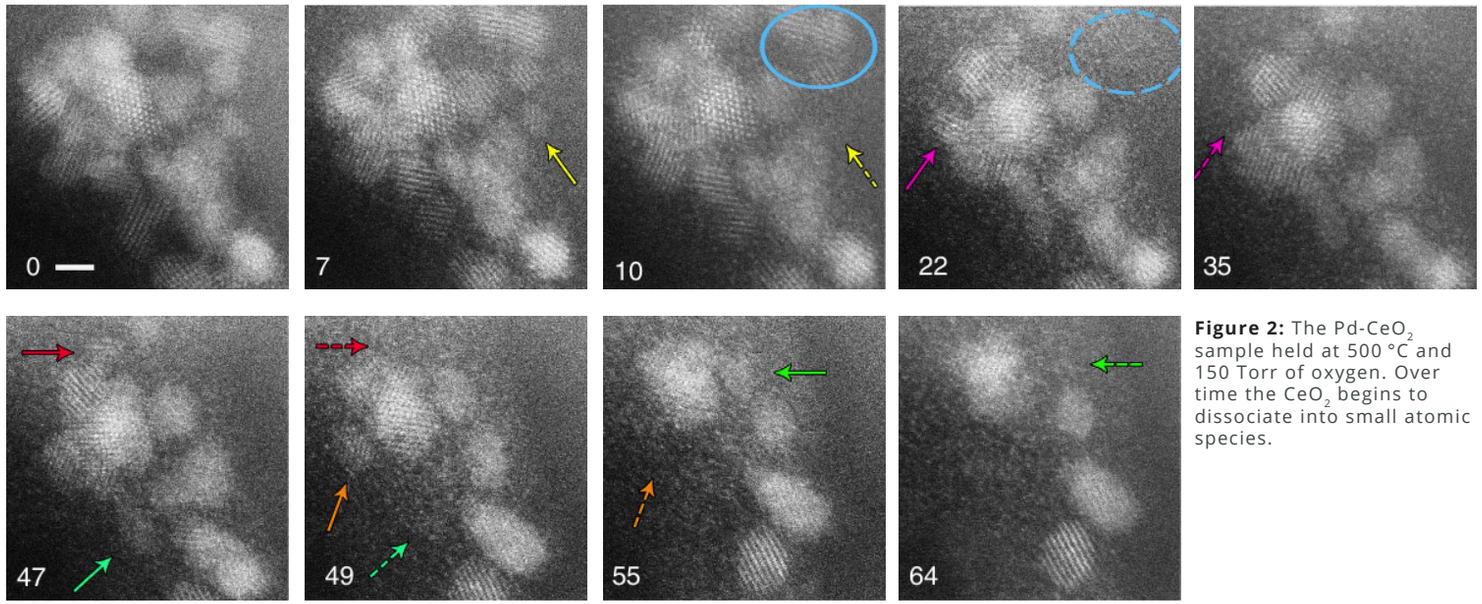

Figure 2: The Pd-CeO_2 sample held at 500 °C and 150 Torr of oxygen. Over time the CeO_2 begins to dissociate into small atomic species.

Shuyi Zhang, lead author on the study, states that "Without *in situ* observation, the dynamic structural evolution is unlikely envisioned by any *ex situ* method, and more importantly, this finding may open new perspectives about the origin of the activity of this catalyst."

Applications

Catalyst materials used in a myriad of industry sectors are critical components in creating consumer and industrial products and materials. Nanoparticle catalysts show exceptional promise in these applications and processes if critical hurdles are overcome. TEM analysis of nanoparticle catalysts show extraordinary

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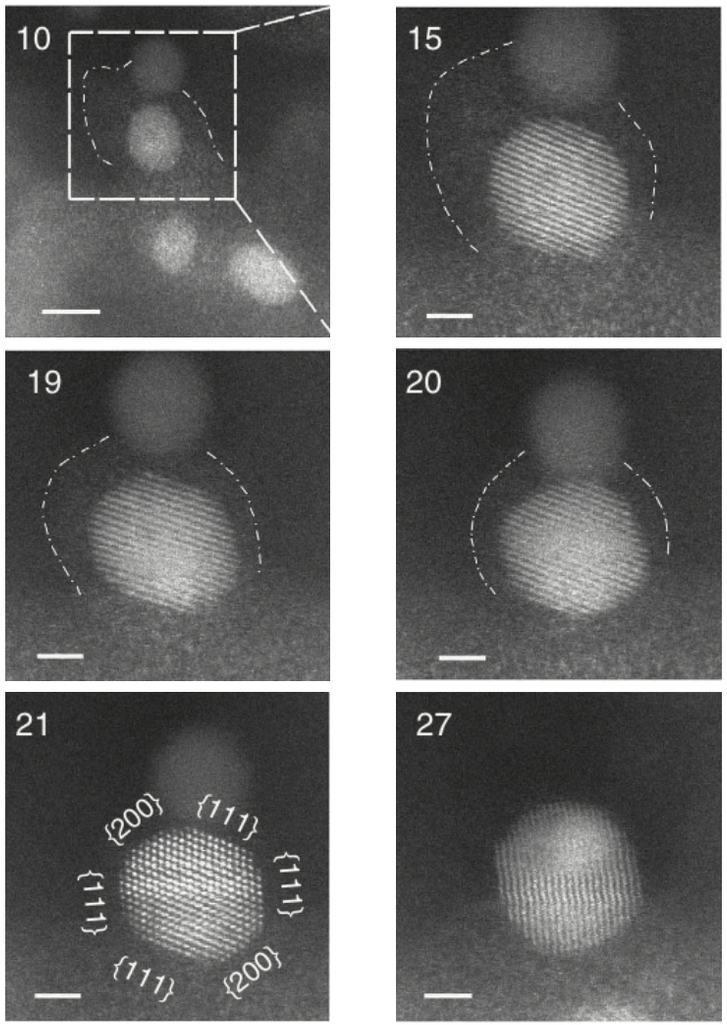

results in spite of the high vacuum conditions found in the column of the TEM. Atmosphere builds on those results by providing the means to apply accurate temperatures over a wide pressure range, without degrading the performance of the most powerful TEMs on the market today. A holder based system, Atmosphere is compatible with most modern TEMs, and can be safely added to new and existing instruments with no modifications. Contact us to discuss the full range of capabilities of the Atmosphere E-cell System for your applications. We can be reached at (919) 341-2612 or contact@protochips.com.

Figure 3: At temperatures reaching 800 °C, small species of CeO_2 begin to coalese on larger, neighboring nanoparticles. As the particle increases in size, it begins to facet, to reduce surface energy.

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