

Oscillatory Behavior of NiAu Nanocatalyst in Wet Gas Environment

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Water vapor existed in many catalysis processes, such as hydrogenation of carbon oxide (CO and CO₂), oxydehydrogenation of alkane, and water gas shift (WGS) reaction. Both positive and negative effects of water vapor to catalytic reactions have been reported.[1-4] Insights into the role of water is important for unveiling reaction mechanisms, and thus critical in helping to optimize the catalyst or reaction recipes involving water. Despite the importance, the introduction of water vapor into the transmission electron microscope (TEM) was hindered due to the fear of contaminating the high-vacuum TEM columns as well as the lack of pressure and flow rate control. In this work, we will present the structure and composition oscillations of NiAu nanocatalyst under hybrid dry gas and water vapor gas environment, enabled by a flow and pressure-controlled vaporizer for in-situ/operando gas and heating TEM.

DENSSolutions' Climate G+ with vaporizer system, and a FEI Titan (TEM) operated at 300 kV were used in this work. The NiAu nanoparticles were firstly dispersed in ethanol and then transferred to the Climate Nano-Reactor by drop-casting.

As shown in Figure 1, three different architectures of a NiAu nanoparticle appear under three different gas conditions. In H₂ and He environment, a Ni core with ultra-thin Au shell architecture forms. Introducing 100% RH water vapor, i.e. H₂+H₂O+He, led to a loose NiO shell and Ni-Au side-by-side phase separation (different from core-shell phase separation). Under H₂O and He environment (with about 100% RH), the loose NiO shell became compact and stable.

Reducing water vapor amount to 25% RH and mixing with H₂ led to the structure and composition oscillations of NiAu nanoparticles, as shown in Figure 2. The NiO outline is marked with a blue dashed line, and the Au regions are marked with yellow dashed line. Here *t* represents the starting time of the data presented. In this condition, the Ni-Au phase separated structure change reversibly between with and without NiO loose layer. From *t*+0 s to *t*+55 s, the NiO shell grows as the oxidation process dominates. From *t*+55 s to *t*+66 s, the NiO shell disappears as an opposite reduction process occurs.

More details about gas composition, pressure, and nanoparticle size influence to the oscillatory behavior of NiAu nanoparticles, and related mechanisms will be discussed on site [5].

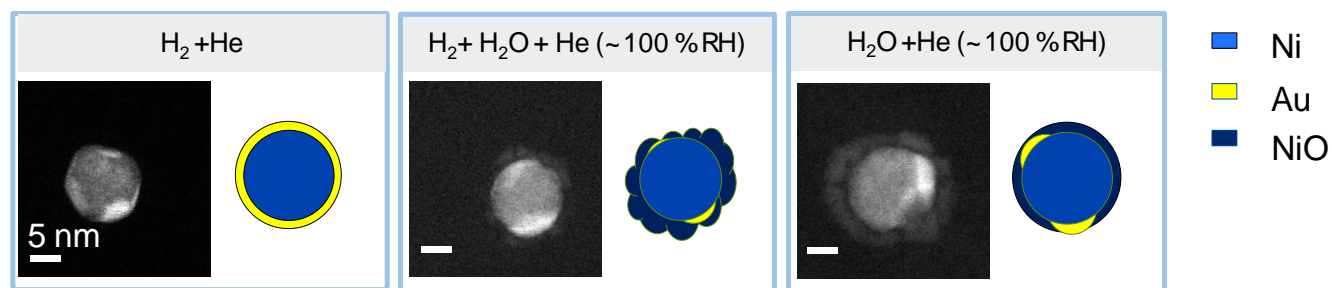


Figure 1. HAADF images and schematic views of the Ni@Au nanoparticles under different gas environments. All scale bars are 5 nm.

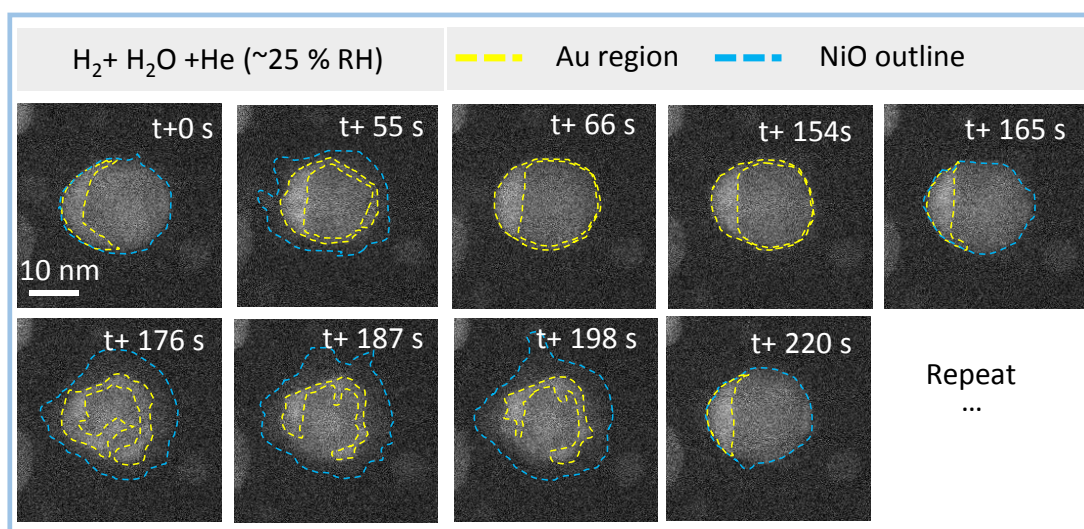


Figure 2. Reversible Ni-Au nanoparticle structure evolution under H_2 and lower water pressure (compared to Figure 1). All scale bars are 10 nm.

References:

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