

## Insights into the Structure-Reactivity of Supported Au Nanocatalyst during Butadiene Selective Hydrogenation by Atomic Scale *In Situ* Environmental TEM

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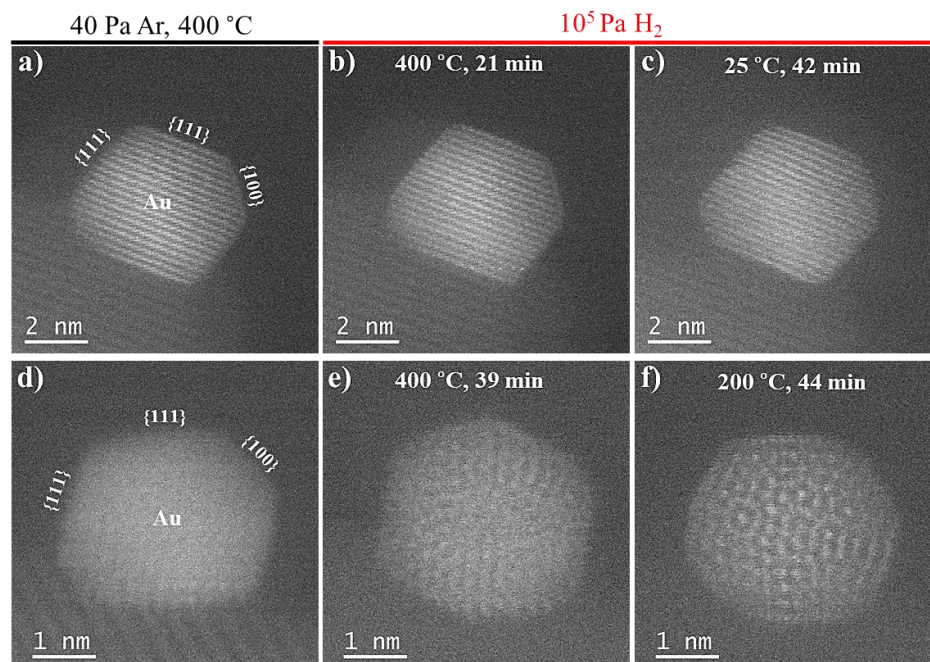
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Although bulk gold is chemically inert, gold catalysts containing small gold nanoparticles (NPs < 10 nm) are known to be reactive in various oxidation and hydrogenation reactions [1]. In particular, oxide-supported Au has been identified since 1973 as an active catalyst in alkene hydrogenation and selective hydrogenation of diolefins like 1,3 butadiene [2] [3]. In this reaction, it was generally admitted that the rate determining step is the dissociative adsorption of H<sub>2</sub> molecules on the catalyst surface. Several experimental and theoretical studies have hinted that the activity of Au catalysts is generally attributed to the dissociation of H<sub>2</sub> molecules on the low coordinated neutral Au atoms (corner and edge positions) with little or no change of particle structure and morphology during reaction [4]. This paradigmatic picture of Au catalysts is still under debate due to the lack of direct observation of gold nanoparticles in the reaction environment. In this contribution, we present a new atomic scale insight into the structural dynamics of a small (~5 nm) and ultrasmall (~3 nm) Au NPs under H<sub>2</sub> at atmospheric pressure and in hydrogenation of butadiene (C<sub>4</sub>H<sub>6</sub>) using environmental TEM (ETEM).

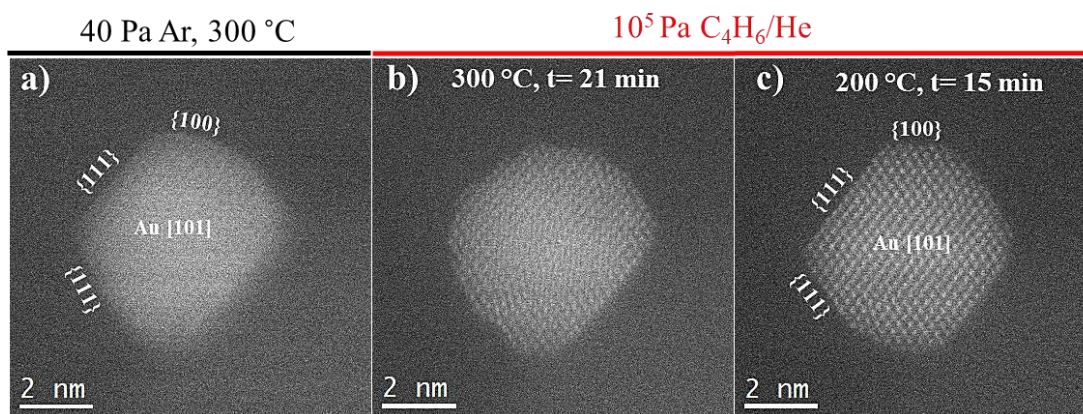
The studied Au NPs were synthesized by deposition-precipitation with urea on anatase TiO<sub>2</sub> support [5]. ETEM experiments were performed on a double aberration-corrected JEOL ARM 200 F microscope using a Protochips Atmosphere<sup>TM</sup> TEM environmental high-pressure gas cell. The structural evolution of small (~ 5 nm) and ultrasmall (~3 nm) Au NPs was studied during the exposure to static (i) H<sub>2</sub> pure gas (ii) C<sub>4</sub>H<sub>6</sub>/He gas mixtures and (iii) H<sub>2</sub>/C<sub>4</sub>H<sub>6</sub>/He gas mixtures at atmospheric pressure and temperatures up to 400 °C. Figure 1 and Figure 2 show *in situ* HAADF-STEM imaging of the atomic structure and morphology of FCC Au NPs under 10<sup>5</sup> Pa of H<sub>2</sub> and C<sub>4</sub>H<sub>6</sub>/He respectively. Under 10<sup>5</sup> Pa of H<sub>2</sub>, size-dependent reactivity of Au NPs is revealed. While small Au NPs (~5 nm) remain rigid and maintain their initial FCC structure during cooling from 400 to 25°C, ultrasmall Au NPs (~3 nm) exhibit structural fluctuations from FCC to non FCC structures (icosahedral symmetries, disordered multi-domain structures) at temperature as high as 400 °C. In contrast, *in situ* HAADF-STEM observations of small Au NPs (~5 nm) under 10<sup>5</sup> Pa of C<sub>4</sub>H<sub>6</sub> shows instantaneous changes in the shape of Au NPs at 300 °C, while maintaining its initial FCC structures. These observations will be discussed in conjunction with the catalytic performances results of these Au NPs in the selective hydrogenation of butadiene reaction during laboratory catalytic test.

## References:

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**Figure 1.** *In situ* STEM observation of the structure of a small Au NP of 4.5 nm (high row) and an ultrasmall Au NP of 3.5 nm (low row) in Au/TiO<sub>2</sub> catalyst. (a,d) under 40 Pa of Ar at 400 °C, (b,e) under 10<sup>5</sup> Pa of H<sub>2</sub> at 400 °C, (c,f) after to 25 °C.



**Figure 2.** *In situ* STEM observation of the structure of a small Au NP of 5 nm in Au/TiO<sub>2</sub> catalyst. (a) under 40 Pa of Ar at 300 °C, (b,c) under 10<sup>5</sup> Pa of C<sub>4</sub>H<sub>6</sub> at 300 °C and 200 °C.