

# Carbon Overcoating of Supported Metal Catalysts for Improved Hydrothermal Stability

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## Introduction

The transformation of biomass-derived oxygenated feedstocks to fuels and chemicals is carried out in the aqueous phase due to their solubility and reactivity in water, often at temperatures of 473 K or higher [1]. Conventional oxide supports designed for gas-phase reactions are not suitable for aqueous-phase reactions at these elevated temperatures. Previously, we reported a simple and inexpensive approach for modifying the surfaces of oxides, such as silica and alumina, with thin carbon layers causing them to become hydrothermally stable in liquid water at 473 K [2]. Our approach is based on the use of sugars that are pyrolyzed on the oxide support leading to monolayer coverage that protects the oxides from hydrolytic attack. Herein we describe an unexpected benefit of carbon coating on the stability of metal nanoparticles, such as Pd, deposited on carbon-coated silica support. This approach was tested with Cu/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts used for aqueous-phase hydrogenation of biomass-derived furfural to value-added furfuryl alcohol. The carbon overcoats are synthesized at mild temperatures and result in an open structure as revealed by <sup>13</sup>C NMR, which helps explain why the overcoats do not interfere with catalytic reactivity.

## Materials and Methods

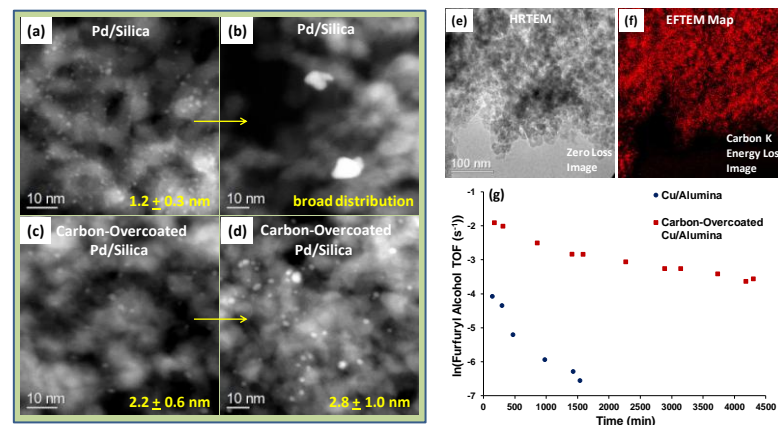
To overcoat oxide-supported metal catalysts, an aqueous solution of sucrose (<sup>13</sup>C glucose for NMR) was mixed with the catalyst at room temperature until the water evaporated. The dried product was partially pyrolyzed under flowing N<sub>2</sub> gas (90 SCCM) at 673 K (5 K min<sup>-1</sup> ramp) for 2 hr. Hydrothermal aging test was conducted in pure water, without any reactants, in an autoclave at 473 K and 15.6 bar for 12 hr. The carbon coating approach for a catalytic reaction was conducted in furfural hydrogenation in water (403 K and 22 bar H<sub>2</sub>).

## Results and Discussion

Figure 1 shows that Pd/SiO<sub>2</sub> contains highly dispersed Pd nanoparticles (a), but after aging in liquid water we found Pd has sintered to form larger particles with a broad particle size distribution, and this Pd sintering is accompanied by the grain growth and coarsening of silica particles (b). In contrast, for carbon-overcoated Pd/SiO<sub>2</sub> (c), after hydrothermal aging there is no change in the structural integrity of the silica support (d). We see some growth in Pd particle size, but the extent is significantly less than seen on Pd on uncoated silica. Since a near monolayer of carbon is deposited on the catalyst, it is not readily

evident in HRTEM image (e) but the presence of carbon is confirmed via EFTEM elemental map (f) suggesting that the carbon is uniformly distributed throughout the Pd/SiO<sub>2</sub> catalyst.

Figure 1 also shows the furfuryl alcohol production rate (TOF) with time for the uncoated and carbon-overcoated Cu/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts (g). Deactivation of Cu/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> rapidly occurred over 30 hr time-on-stream. In contrast, carbon-overcoated Cu/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> showed lower activity loss during the first 25 hr after which the catalyst stabilized and remained active for over 75 hr time-on-stream. The first-order deactivation rate constant for Cu/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> is 0.102 hr<sup>-1</sup> while the deactivation rate constant for carbon-overcoated Cu/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> is 0.024 hr<sup>-1</sup>, which represents a 4-fold improvement over the uncoated catalyst.



**Figure 1.** HAADF-STEM images of (a) Pd/SiO<sub>2</sub> and (c) carbon-overcoated Pd/SiO<sub>2</sub>, and after hydrothermal aging in liquid water (b) Pd/SiO<sub>2</sub> and (d) carbon-overcoated Pd/SiO<sub>2</sub>. (e) Bright-field and (f) energy filtered images of carbon-overcoated Pd/SiO<sub>2</sub>. (g) Furfural hydrogenation in water using uncoated and carbon-overcoated Cu/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

## Significance

The carbon overcoating approach is a facile, inexpensive route for modifying the performance of a supported catalyst, and may also provide benefits in suppressing access of biogenic impurities which can irreversibly poison catalysts during bio-renewable conversions.

## Acknowledgements

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## References

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