

Supporting Information for

**Probing the Low-Temperature Water-Gas Shift Activity of Alkali-promoted Platinum Catalysts Stabilized on Carbon Supports**

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### Oxygen Content of MWNT Support and Catalysts

The oxygen content of the annealed MWNT support after acid treatment (1000-2h-C<sub>N</sub>) and the Pt and Pt-O-Na catalysts prepared using this support was determined from XPS analysis and is given in Table S1.

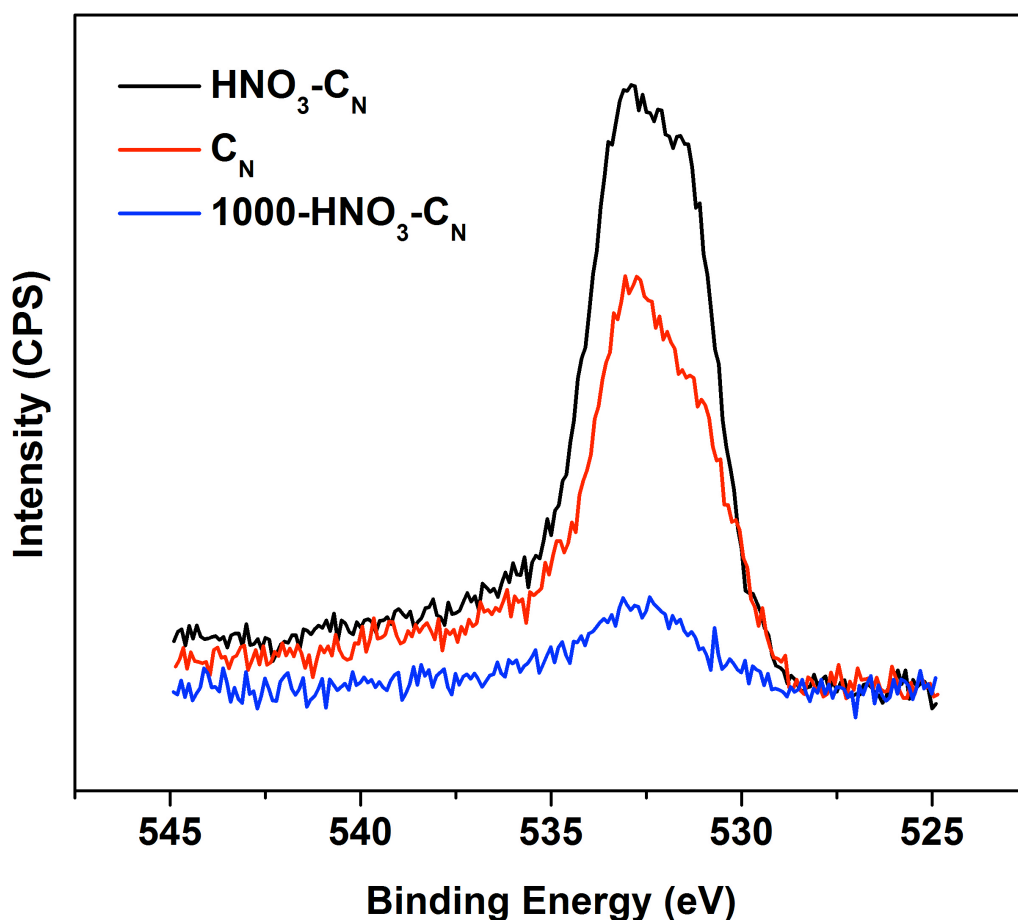
**Table S1. Surface oxygen concentration of annealed MWNT support and catalysts after calcination in He at 400 °C.**

Catalyst	Oxygen Content (at. %)
1000-2h-C <sub>N</sub> <sup>*</sup>	0.7
1 wt% Pt/1000-2h-C <sub>N</sub>	0.9
1 wt% Pt <sub>1</sub> Na <sub>6</sub> /1000-2h-C <sub>N</sub>	0.9

\* Determined using ex-situ XPS

## Ex-situ XPS

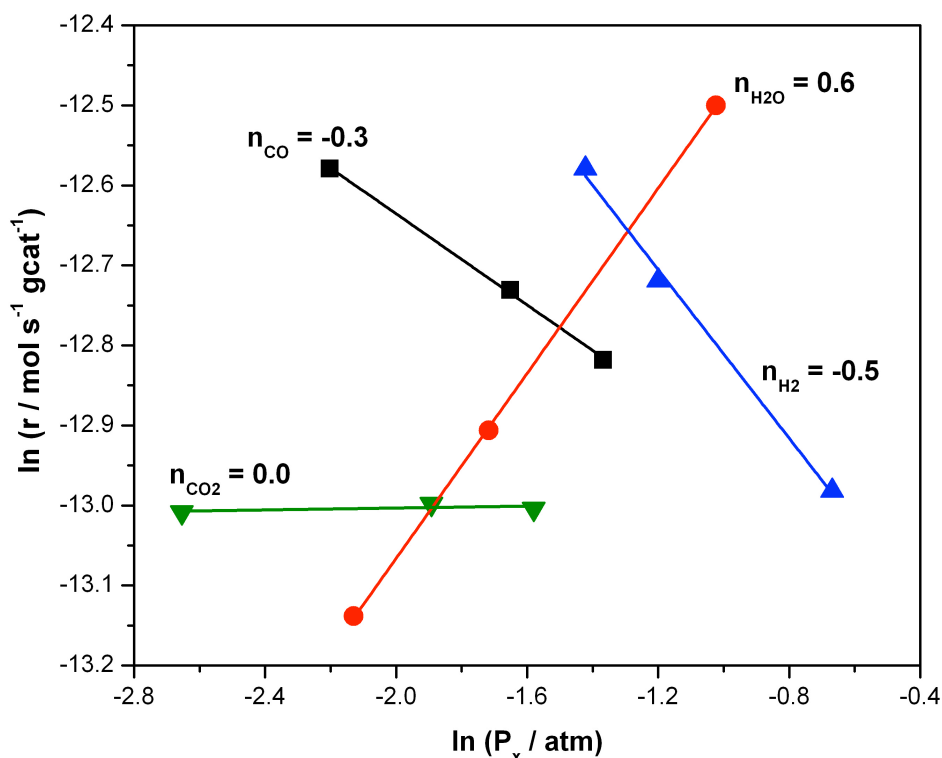
X-ray photoelectron spectroscopy (XPS) studies were performed at the Center for Nanoscale Systems at Harvard University using a Thermo Scientific K-Alpha system equipped with an Al source and a 180° double focusing hemispherical analyzer and 128-channel detector. Survey scans were collected using a step size of 1 eV and a pass energy of 100 eV. High resolution scans were collected using a step size of 0.05 eV and a pass energy of 40 eV. XP spectra were analyzed using the CasaXPS software suite. All scans were calibrated in energy to the C 1s carbon peak at 284.5 eV. The results are shown in Figure S1, and show the relative surface oxygen concentration on as-received, HNO<sub>3</sub>-treated, and annealed (1000 °C) multi-walled carbon nanotubes.



**Figure S1.** Ex-situ XPS showing surface oxygen of as received MWNT (C<sub>N</sub>), nitric acid treated MWNT (HNO<sub>3</sub>-C<sub>N</sub>), and annealed MWNT (1000-HNO<sub>3</sub>-C<sub>N</sub>; 1000-2h-C<sub>N</sub>).

## Reaction Order Measurements

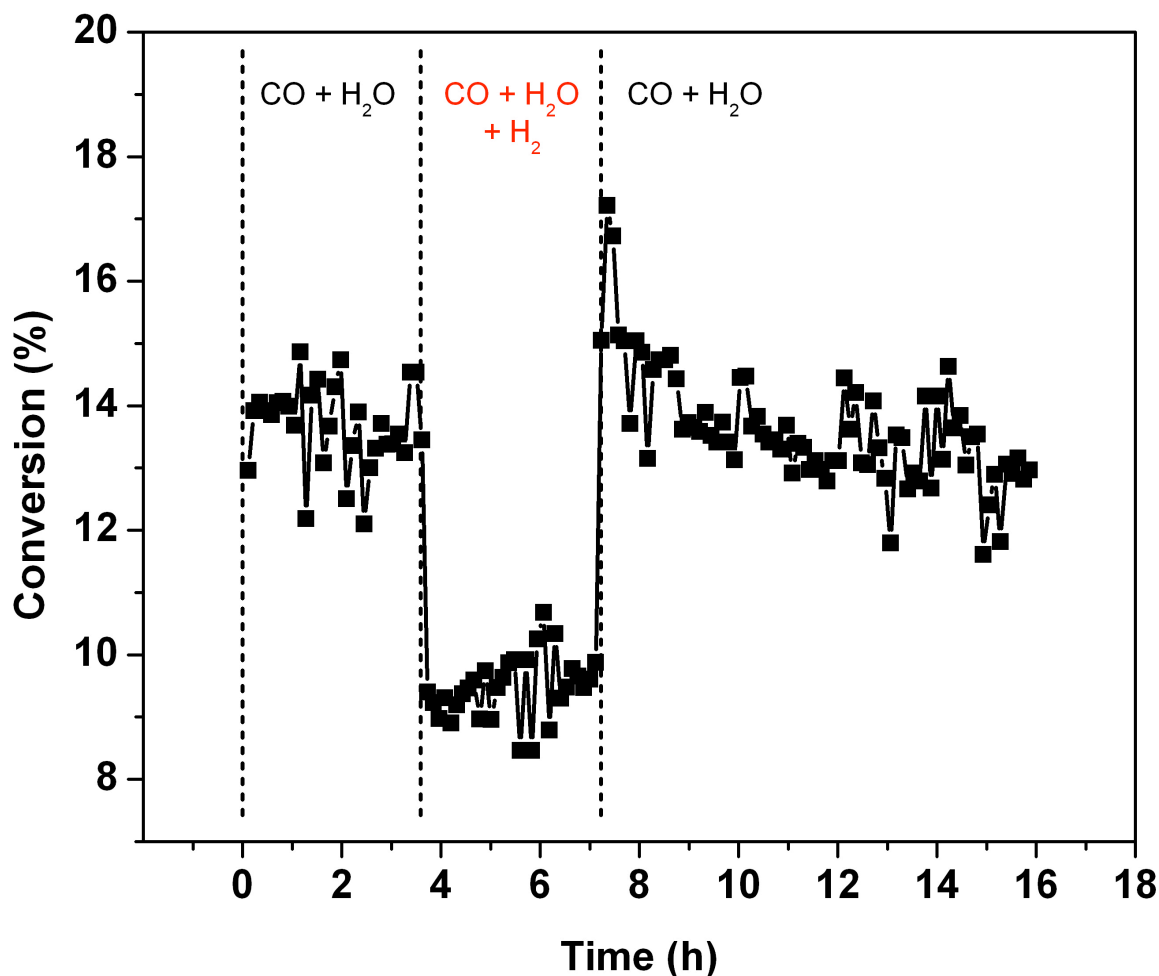
To determine the apparent reaction orders, 0.3 g catalyst was diluted with calcined quartz sand and loaded in a quartz tube between two plugs of quartz wool. The catalyst sample was heated *in-situ* in He to 400 °C prior to use. The sample was then subjected to the standard full gas conditions (11%CO–25% H<sub>2</sub>–25% H<sub>2</sub>O–7%CO<sub>2</sub>–32%He) from 200 °C to 350 °C in 25 °C increments, holding at each temperature for 1.5 h. Following this, the sample was cooled to 300 °C and held for ~48 h (i.e. until no deactivation beyond the initial fast decline in activity was observed). The sample was then cooled to 250 °C and the reaction orders were determined by varying CO from 1 – 25%, H<sub>2</sub>O from 1 – 36%, H<sub>2</sub> from 1 – 51%, and CO<sub>2</sub> from 1 – 21%. The conversion was kept below 15%. No methanation was observed during these experiments.



**Figure S2.** Apparent reaction orders for carbon monoxide, water, carbon dioxide, and hydrogen as measured using the 1 wt% Pt<sub>1</sub>Na<sub>6</sub>/1000-2h-C<sub>N</sub> catalyst at 250 °C.

### H<sub>2</sub> Addition to Product-Free WGS Reaction Gas Mixture

The effect of hydrogen on the WGS rate was studied by the addition of 9% H<sub>2</sub> to the product-free reaction gas mixture at 250 °C. The 1 wt% Pt<sub>1</sub>Na<sub>6</sub>/1000-2h-C<sub>N</sub> catalyst was first exposed to the product-free gas composition at 250 °C for ~2 h. The gas composition was then adjusted to include H<sub>2</sub> (2%CO – 9% H<sub>2</sub> – 10% H<sub>2</sub>O – 81% He), while maintaining the total gas flow rate and temperature constant. After ~ 2h, the product-free gas composition was restored. Reversibility of the rate inhibition due to hydrogen addition in the gas phase is clearly shown in Figure S3.



**Figure S3.** The response of the WGS rate on 1 wt% Pt<sub>1</sub>Na<sub>6</sub>/1000-2h-C<sub>N</sub> at 250 °C to the addition of hydrogen to product-free reaction conditions. Product-free condition: 70 mL/min (2% CO – 10% H<sub>2</sub>O – 88% He); H<sub>2</sub>-co-fed condition: 70 mL/min (2% CO – 9% H<sub>2</sub> – 10% H<sub>2</sub>O – 81% He).

## Deconvolution of AP-XPS spectra

The fitting results for the Pt 4f deconvolution are shown in Figure S4 and highlight the observed changes in the Pt-OH contribution (highlighted red). These relative contributions are shown in Figure 7 in the main text.

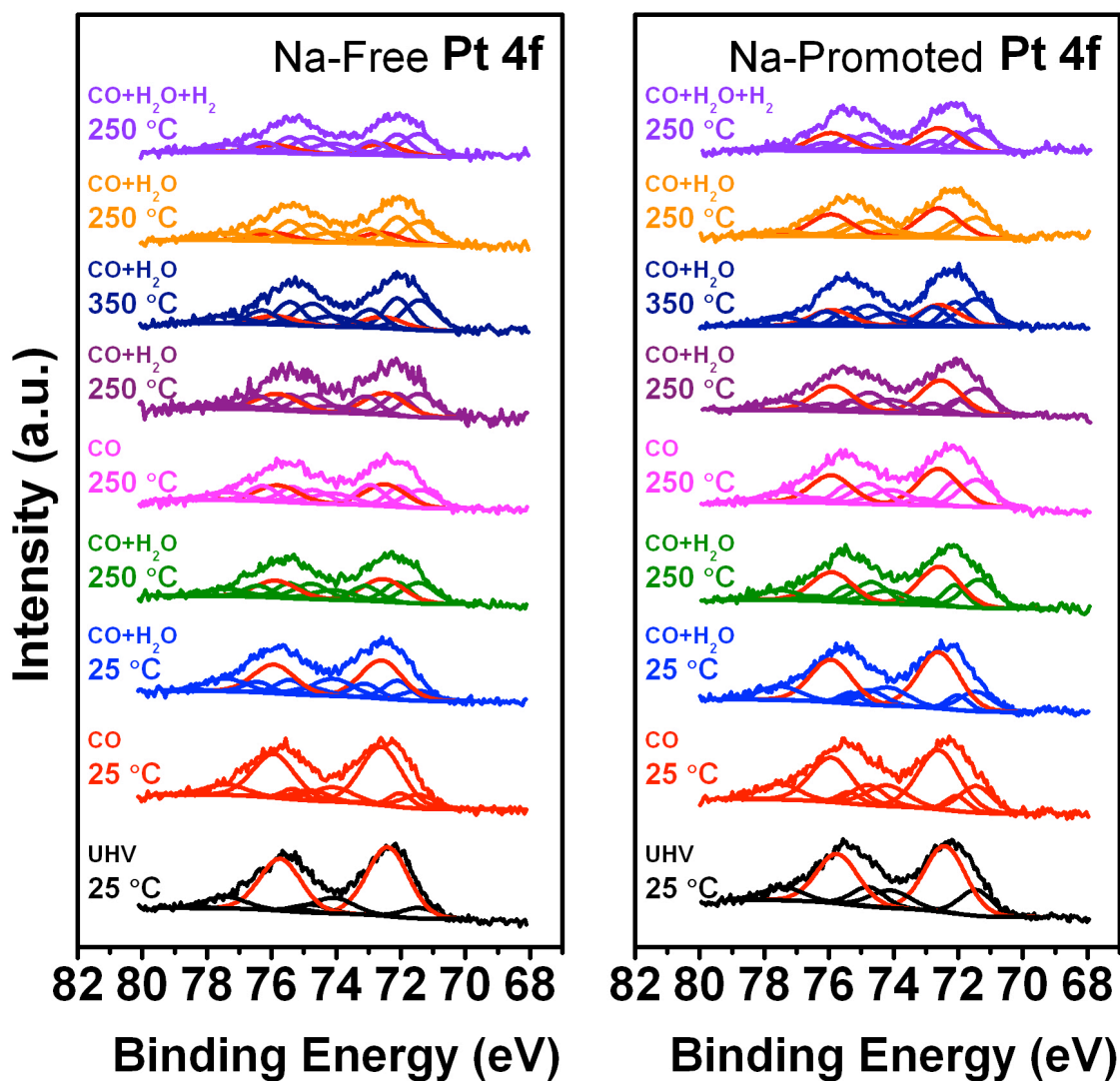


Figure S4. Deconvolution of Pt 4f spectra. Pt-OH highlighted in red.