

## Materials and Methods

### Experimental Procedure for Illumination Experiments and Oil Bath Controls

In each trial a stir bar is placed inside a 40 mL borosilicate glass vial. These vials are purchased from Kimble-Chase and have a screw-on polypropylene cap with a built-in PTFE coated silicone septum (Part No. 60942A-40). The vial without the cap is tared on a scale and 10.0 g of Ni nanopowder is weighed out. Then the vial is purged with the 4:1 H<sub>2</sub>:CO<sub>2</sub> gas mixture using a 50 mL syringe and two 18 G needles. The full volume of the vial is pushed through a 3" needle that blows through the particles while the other ½" needle provides pressure relief. This is repeated three times and then both needles are removed. The septa on top of the vial is then covered with fresh 5 minute epoxy mixture. This is carefully applied to cover the entire septa. After 5 min, a balloon of H<sub>2</sub> gas is attached to the ½" needle and pushed through the epoxy and septa. If it is an illumination trial, the vial is fixed in place with a clamp on the stir plate set at 1000 rpm and the lamp is placed at a set distance away calibrated to provide a set illumination to the vial. If it is a dark trial then the vial is covered in foil to block light and clamped in place in a stirred oil bath, also stirring at 1000 rpm. At the end of the trial the light is turned off or the vial is removed from the bath. At the same time the balloon and needle are both removed from the vial.

### Experimental Procedure for Gas Chromatography Measurements

Analysis was performed using a Agilent Technologies 7890B Gas Chromatograph (GC) System, outfitted with both a Flame Ionization Detector (FID), and a Thermal Compositions Detector (TCD). The column used is a CARBONPLOT-1010. Nitrogen is the carrier gas along with Hydrogen and Air tanks for the FID flame. For each run, a 200 µL sample is injected into the inlet, which is held at 200 °C. Gas is flowed through column at a rate of 8 mL/min for 5 min while the column is ramped up from 40 °C to 300 °C over the course of 30 seconds. Then for the next 4.5 min it is held there while gas flows through the column and out to the detectors. The FID is held at 350 °C and has 40 mL/min Hydrogen gas, 400 mL/min air gas and 10 mL/min Nitrogen gas makeup flowing through it. The TCD is held at 300 °C while 15 mL/min reference flow and 12 mL/min combined from the analyte stream of Nitrogen flow through. Each run goes for 5 min but can be stopped early.

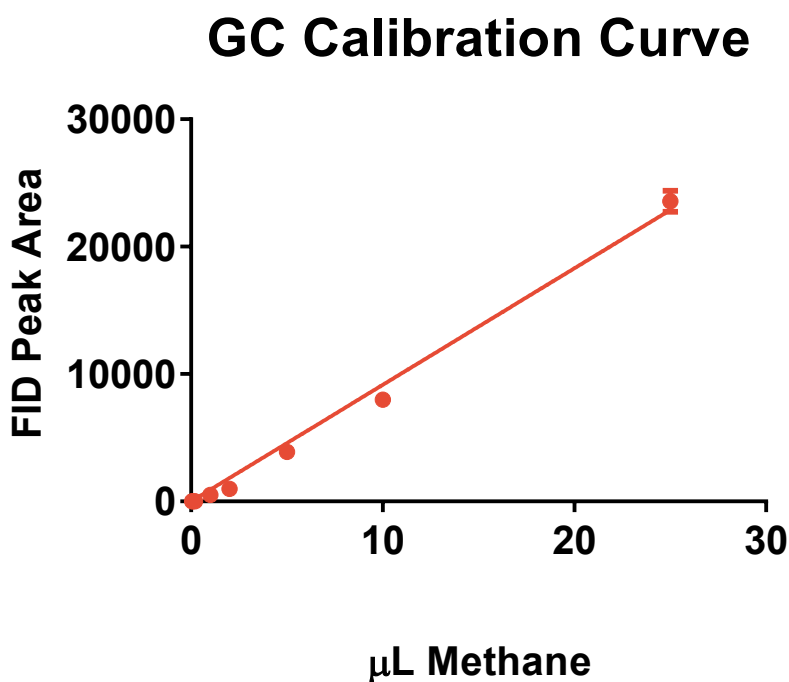
The methane peak was determined to be at 1.62 min via injection of a pure Methane standard from Cal Gas Direct. This peak was integrated automatically by the Agilent ChemStation software. The area of these peaks was used with the standard curve to identify the µL of Methane injected in each run. This value and the total volume of the injection sample was used to calculate the percentage methane in each run and subsequently either the methane in the injection volume or the methane in the reaction vessel, as shown in the equations below.

$$\text{Volume of Methane in Vial} = (\% \text{Methane from Calibration Curve in S1}) * (\text{Reaction Vial Volume})$$

$$\text{Volume of Methane in Sample} = (\% \text{Methane from Calibration Curve in S1}) * (\text{Injection Volume})$$

Standards at different amounts were each injected into the system in triplicate to generate the calibration curve in Fig S1. A linear regression was performed on the data, constraining the line to begin at the origin. The R squared value was 0.9908. Values were collected for both 50 and 100 µL as well as 0.10 and 0.05 µL, but at these values the relationship was no longer linear, likely due to detector saturation and low signal-to-noise ratio, respectively.

**Fig. S1** Calibration Curve and equation for methane using our standard method on the Gas Chromatography. Method described in detail above.



$$\mu\text{L Methane in Injected Sample} = 915 \times \text{Peak Area of GC Trace}$$

#### Measuring Experimental Sensitivity of Method to Carbon Monoxide

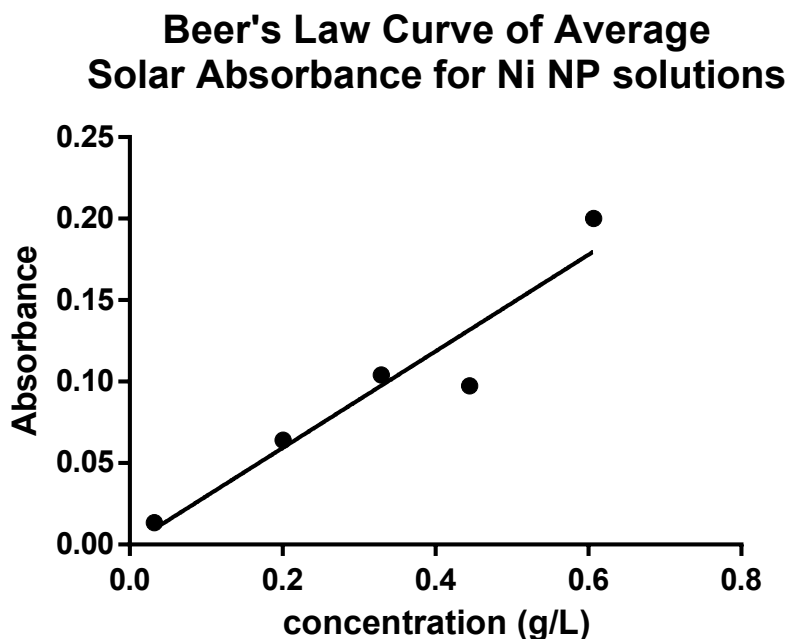
Using the experimental technique described above, we injected different volumes of a 1% carbon monoxide (CO) standard (balance Nitrogen) purchased from Cal Gas Direct. The size of the standards were titrated down, until the peak at 1.45 minutes was no longer detected by the system. The smallest injection to have a detected peak was 100 μL, so the detection limit was set to be 1 μL for CO. This corresponds to a 0.25% detection limit with a 200 μL injection.

#### Measurement of “Active” Catalyst and Subsequent Calculation of Adjusted Catalyst Efficiency

A challenge in our system was estimating the “active” catalyst. Rather than using a traditionally supported catalyst, the experiments summarized here use exclusively ball-milled Ni NPs. They are dispersed in the gas mixture and isolated solely by agitation. The system, at lower temperatures, is only active when the particles are dispersed. We therefore wanted to do a mathematical estimation of “active” Ni catalyst at any given point. In the figure S2, we describe how we used measured the absorbance for different concentrations of Ni NPs in water to create a Beer’s Law equation. With this equation we estimated the active catalyst in the reaction chamber to be 0.13 g/L. Assuming our catalyst when dispersed follows the same absorbance, then we calculated that for a 40 mL reaction chamber filled with 10 g, we have 5.3 mg of active catalyst at any time during the reaction. To estimate an active

catalyst amount to provide comparison to other similar systems, we therefore used the adjustment ratio of 2000:1 for active catalyst efficiency.

**Fig. S2** Beer's Law Plot for Ni NP solutions in water. The absorption of light in the solar spectrum for these water Ni solutions was compared to the absorption of light for the reaction chamber to estimate the active proportion of catalyst as described above. The Beer's Law equation is below the graph, the R squared value is 0.91. The estimated concentration inside the vial is 0.13 g/L, factoring in the 2.7x increase in path length from the cuvette to the reaction vial.



$$\text{Absorbance} = 0.2964 \times 1\text{cm} \times \text{Concentration (g/L)}$$

#### Collection of BET Adsorption Isotherms to Determine Available Catalytic Surface Before and After Experimenting

Brauner-Emmet-Teller (BET) analysis and experiments were performed using a Micrometrics 3-Flex system. Samples were weighed out on a high precision ( $\Delta 0.1$  mg) scale and placed in the analysis chamber. The system was cooled using liquid nitrogen to  $-196$  °C and pumped down to 7 mmHg, the gas used for analysis was  $\text{N}_2$ , and the each sample was taken through one full cycle of adsorption and desorption as show in the first figure of S3. A sample of particles fresh from an unopened bag of Ni nanodust were analyzed, a sample from a bag that that had been left exposed to atmosphere, and from a set of particles that had been used to successfully produce methane in an experiment.

**Fig. S3** Summary of BET Adsorption Data for Ni NPs comparing particles after a photo-thermal catalysis procedure, prior to any light of gas exposure, and prior to light exposure, but exposed to ambient atmosphere. Particles exposed to the atmosphere have slightly higher surface area implying that the surface may be slightly altered by exposure to the atmosphere. Used particles then seem to decrease in surface area, indicating that some of the catalyst surface may be altered or poisoned.

