Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.
This journal is © the Owner Societies 2021

Supporting Information

Deactivation-Free Ethanol Steam Reforming at Nickel-Tipped Carbon Filaments

Yutichai Mueanngern[1], Cheng-Han Li[2], Meiling Spelic[1], Joshua Graham[1], Nathan Pimental[1], Yehia Khalifa[1], Joerg R. Jinschek[2], and L. Robert Baker[1]*

[1] Department of Chemistry and Biochemistry, The Ohio State University, Columbus Ohio 43210, United States.

[2] Department of Materials Science and Engineering, The Ohio State University, Columbus Ohio 43210, United States.

Table of Contents

1. Carbon Removal from CeO_2 Nanocubes by Catalyst Pre-Treatment

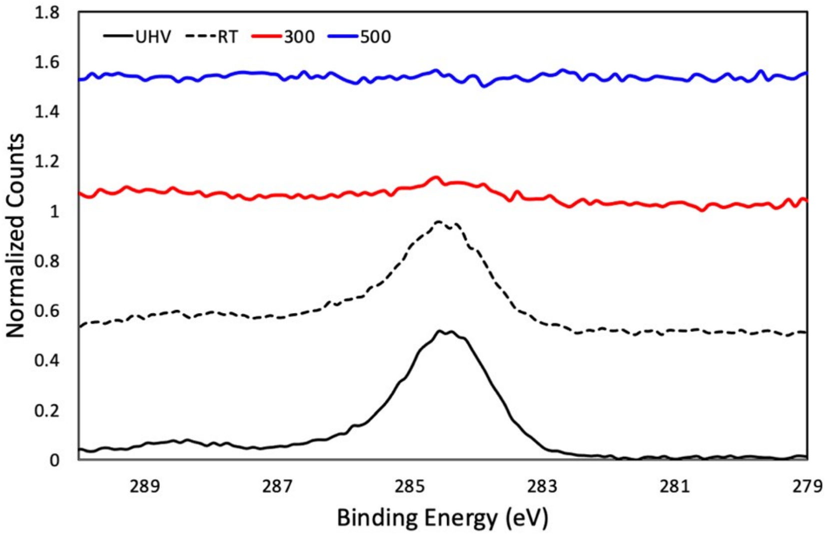

Figure S1 C 1s NAP-XPS spectra of a Ni/CeO_2 catalyst collected under 0.75 Torr O_2 as a function of increasing temperature. The broad feature centered at 284.5 eV represents aliphatic carbon, and the shoulder at higher binding energy represents carbon-oxygenates. Both features disappears completely by 500 ˚C indicating that complete removal of organic capping ligands is achieved during the calcination conditions employed for catalyst pre-treatment.

2. C 1s and O 1s NAP-XPS Spectra of the Ni@CFIL Active Phase

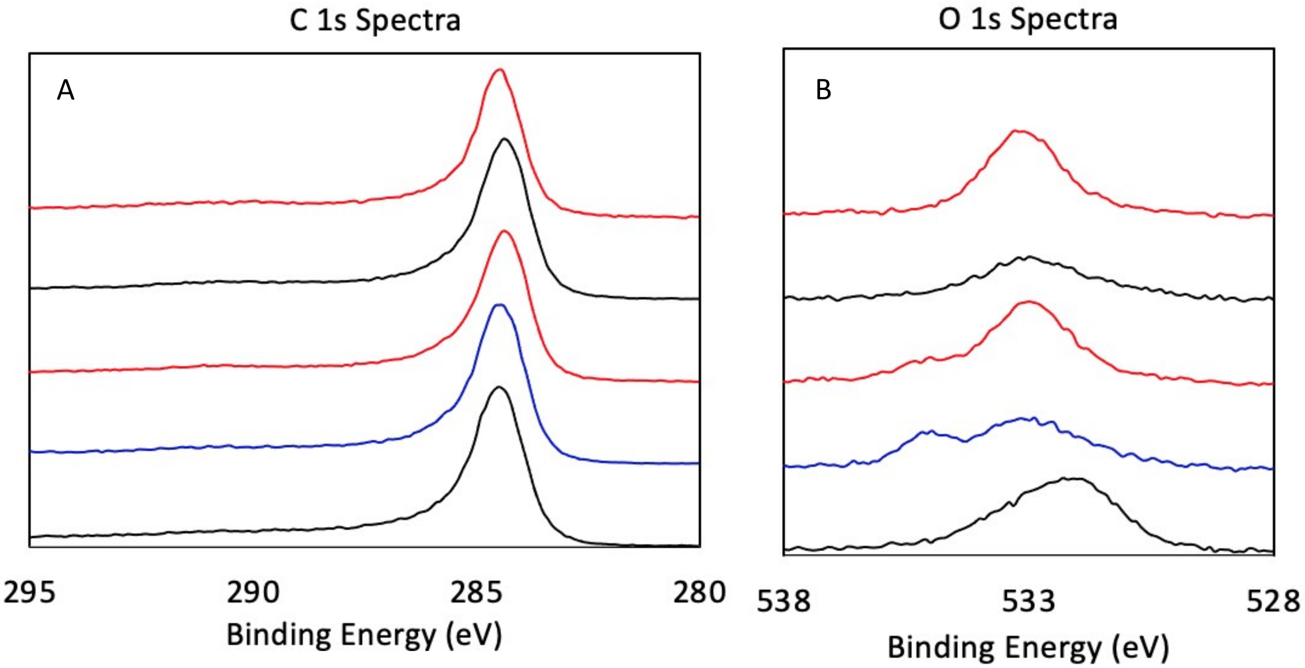

Figure S2. In situ NAP-XPS measurements of the C 1s spectrum **(A)** and the O 1s spectrum **(B)** on Ni/CeO_2. Spectra are obtained in 0.75 Torr of a 1:3 ethanol:water mixture at 280 °C (blue spectra) and 360 °C (red spectra) following the ex situ formation of the Ni@CFIL active phase. For reference spectra of the Ni@CFIL active phase under UHV at room temperature is shown in black. These spectra correspond with the Ni 2p and Ce 3d spectra reported in Figure 3 of the main manuscript.

3. Pre-Reaction XPS Spectra of Ni/CeO$_2$ Catalyst

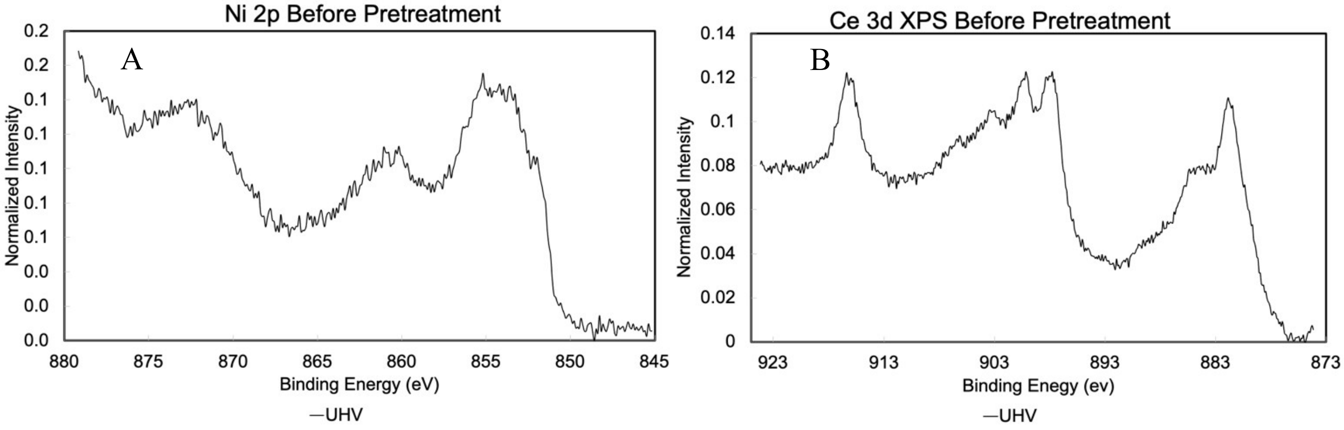

Figure S3. Ni 2p (A) and Ce 3d (B) XPS spectrum of as prepared Ni/CeO$_2$ catalyst prior to reaction.

Fi

4. Quantification of Nanoscale and Mesoscale Interface Density

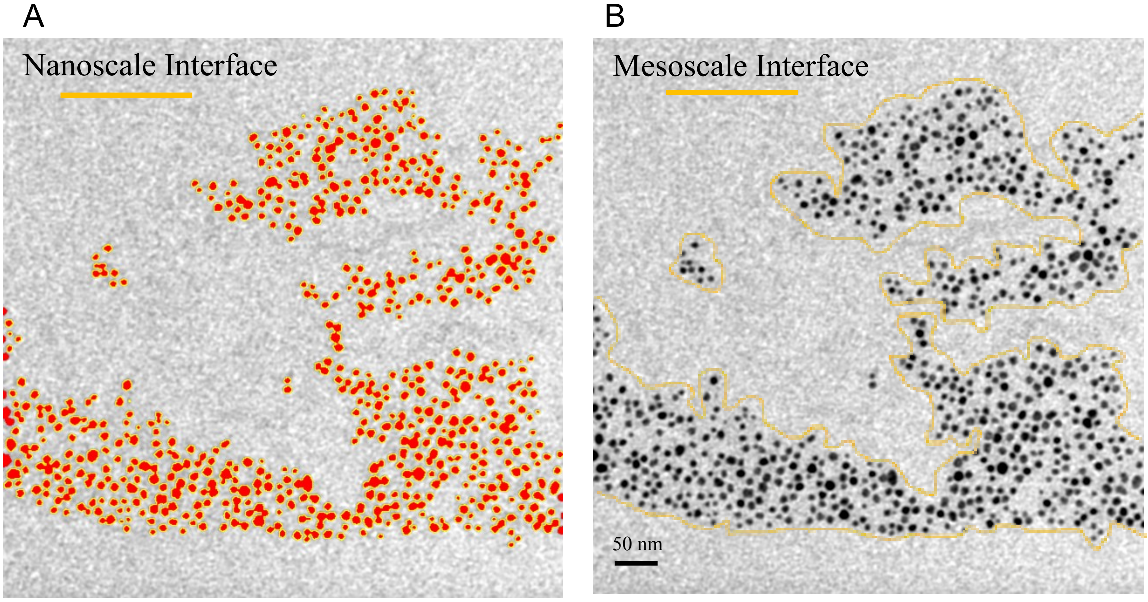

Fig S4 Image analysis for quantification of nanoscale interface **(A)** and the mesoscale interface **(B)**. Nanoscale interface is defined as the total boundary length in nm around individual nanoparticles per nm^2 of the total catalyst. Mesoscale interfaces is defined as the boundary length in nm around the perimeter of closely packed domains of CeO_2 nanocubes per per nm^2 of the total catalyst. Similar image analysis was performed on numerous images of CeO_2 nanocubes deposited at various total coverages, resulting in the quantification with error bars of nano and mesoscale interface density shown in Figure 5 of the main manuscript.

5. Thermal Stability of CeO_2 Nanocubes

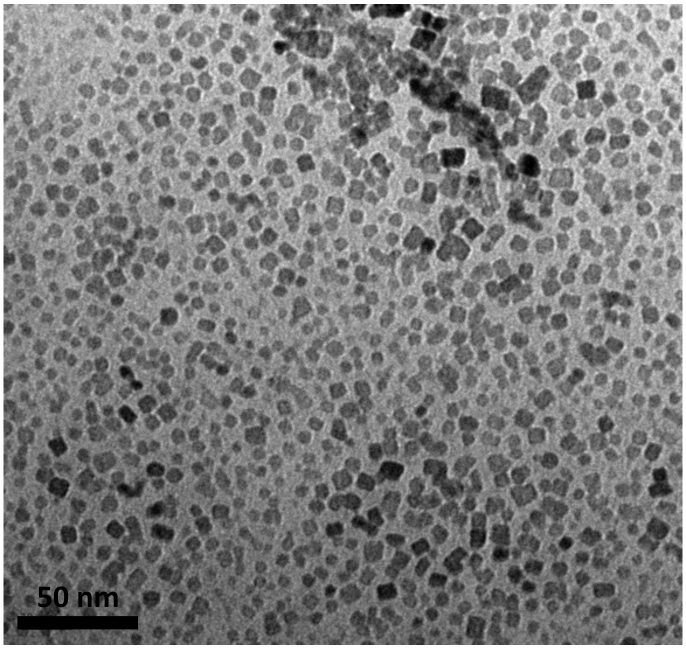

Fig S5. TEM images of CeO_2 nanocubes supported on Si_3N_4 membranes following calcination at 500 °C in O_2 and subsequent reduction at 250 °C in H_2. These images can be compared with the image of as-deposited nanucubes in Figure 6A of the main manuscript confirming that the morphology of CeO_2 nanocubes is unchanged before and after pre-treatment and that the degree of nanoparticle sintering is very low.

6. Coverage-Dependent Deactivation Profiles of Ni/CeO_2 Catalysts

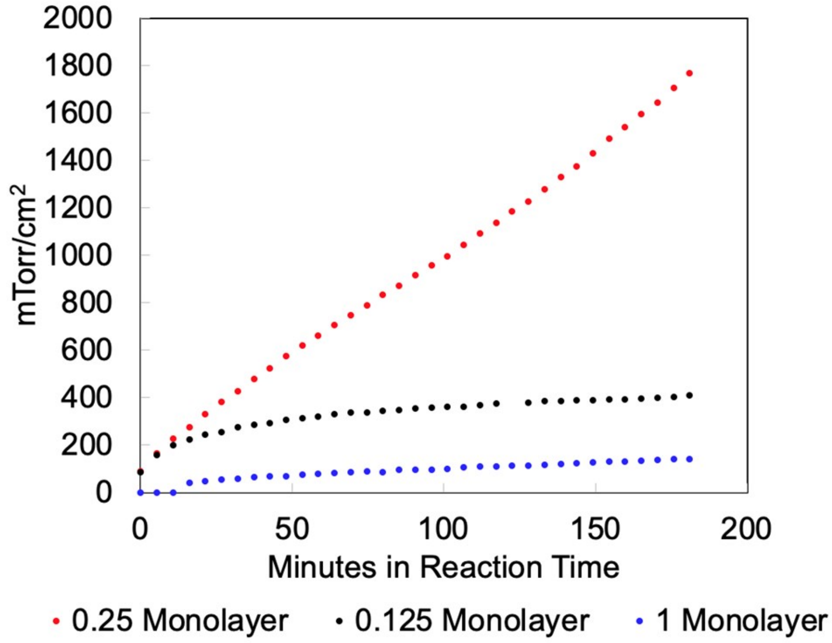

Figure S6. Deactivation profiles of H_2 production on Ni/CeO_2 catalysts as a function of CeO_2 nanocube coverage, corresponding to Figure 5D in the main manuscript. Results show that the mesoscale morphology resulting from a 0.25 monolayer coverage of CeO_2 nanocubes on Ni results not only in the highest activity, but also significantly increased resistance to deactivation.

7. Calculation of Turnover Frequency

H_2 production rates normalized to the geometric surface area of the planar catalysts are reported in Figure 5D of the main manuscript. Below we convert these rates to an approximate turnover frequency (TOF) for each catalyst. First, we calculate the number of H_2 molecules produced by

$$N_{H_2} = \frac{P \cdot V \cdot N_A}{R \cdot T}$$

where P is the H_2 pressure measured by gas chromatography, V is reactor volume (0.5 L), N_A is Avagadro's number, R is the ideal gas constant (62.36 L Torr K^{-1} mol^{-1}), and T is temperature of the gas phase (298 K).

To convert the H_2 production rate to a TOF, it is necessary to estimate the number of active sites. Unfortunately, it is not possible to directly measure the Ni dispersion in these planar catalysts. Consequently, we assume a Ni site density of 1.86×10^{15} cm^{-2} based on a clean Ni (111) surface prior to deposition of CeO_2 nanocubes. In reality, this represents an upper estimate of the active site density because only a small fraction of the total Ni surface area in the as-prepared catalyst is actually incorporated into the Ni@CFIL active phase (see Figures 2 and 3 of the main manuscript). Although this value underestimates the actual TOF, this provides a useful approximation for comparing the activity of the Ni@CFIL active phase to previously reported catalysts.

Assuming an ideal reaction stoichiometry of $CH_3CH_2OH + 3\ H_2O \rightarrow 6\ H_2 + 2\ CO_2$, the rate of H_2 production is converted to a TOF in units of ethanol molecules $site^{-1}$ s^{-1} by

$$TOF = \frac{N_{H_2}}{6 \cdot 1.86 \times 10^{15} \cdot A \cdot t}$$

where A is the geometric surface area in cm^2, and t is the total reaction time in s. Table S1 below provides the calculated TOF for Ni/CeO_2 catalysts as a function of CeO_2 nanocube coverage as well as for the pure Ni catalyst.

Table S1 H_2 production rate and TOF for Ni/CeO_2 catalysts as a function of CeO_2 nanocube coverage compared to pure Ni.

Catalyst	H_2 Rate (mTorr cm^{-2} min^{-1})	TOF (s^{-1})
Ni/CeO_2 (0.13 monolayer)	1.1	0.027
Ni/CeO_2 (0.25 monolayer)	8.7	0.21
Ni/CeO_2 (1.0 monolayer)	0.71	0.017
Pure Ni	0.43	0.010

8. Carbon Selectivity of Ni/CeO$_2$ Catalysts

Selectivity for the C products is defined as

$$S_j = \frac{P_j \cdot n_j}{\sum_j P_j \cdot n_j} \times 100$$

where P_j is the pressure of the jth C-containing product, and n_j is the number of C atoms in respective product. At the relatively low temperatures employed in this study, H_2 production results primarily from the dehydrogenation of ethanol to produce acetaldehyde followed by the decomposition of acetaldehyde to produce CO and methane. CeO_2 is known to promote the water gas shift reaction as well as methane reforming leading to CO_2. However, consistent with the absence of CeO_2 from the Ni@CFIL active phase (see Figures 2 and 3), we observe only trace amounts of CO_2. Rather, primary C products observed here are CO, ethylene, acetaldehyde, and methane, and selectivity on the Ni/CeO$_2$ as a function of CeO$_2$ nanocube coverage is provided in Figure S6.

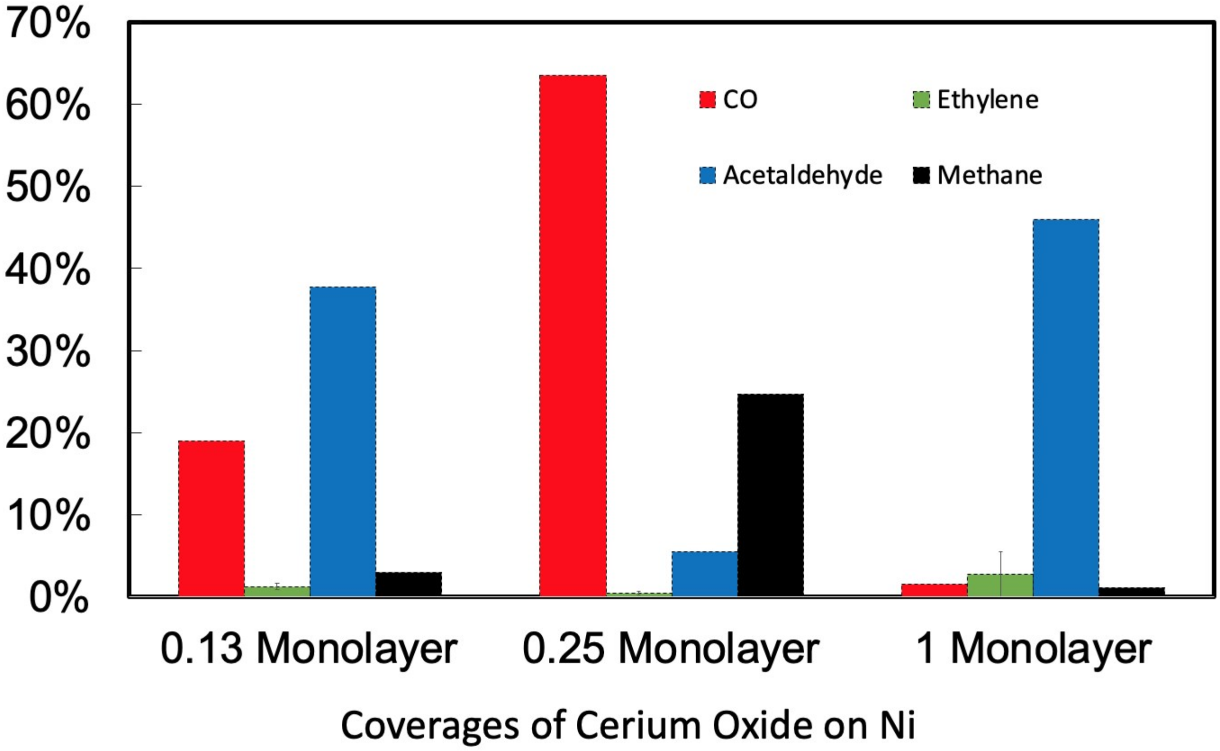

Figure S7 Selectivity of Ni/CeO$_2$ catalysts for C products as a function of CeO$_2$ nanocube coverage.