

## Combining X-ray absorption and X-ray diffraction techniques for *in situ* studies of chemical transformations in heterogeneous catalysis: advantages and limitations

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### Supporting Information

The setup for the *in situ* experiments included a mass spectrometer for the analysis of the gases at the output of reaction chamber. Figure S1 shows the production of CO<sub>2</sub> as the CeO<sub>2</sub>/CuO catalyst is being reduced and oxidized. It is worth mentioning that the space constraints for the combined XRD/XAFS experiment forced to place the mass spectrometer quite far from the reaction chamber, so a delay is to be expected on the mass spectrometer signal when correlating it with XRD or XAFS data. At a temperature of 200 °C under CO flow, we can observe a peak for the production of CO<sub>2</sub>, which correlates with the phase transition from CuO to Cu. The CeO<sub>x</sub>/CuO catalyst is oxidizing the CO to CO<sub>2</sub> by providing O atoms from its structure. Once the reduction of the sample is complete, the production of CO<sub>2</sub> diminishes. At that point, while keeping the temperature at 200°C we switched the gas directly to a 20% O<sub>2</sub>/He flow in order to monitor the re-oxidation of the sample. We immediately observed another peak in the CO<sub>2</sub> production which has the following origin. As the sample is oxidized, the CO adsorbed on the sample is been cleaned away and also oxidized to CO<sub>2</sub>. This CO<sub>2</sub> production correlates with the phase transition of Cu→Cu<sub>2</sub>O observed on the diffraction analysis. At this temperature the conditions seem to be strong enough for eliminating all CO adsorbed but too mild to achieve the full oxidation of copper, so a steady state of the Cu<sup>+</sup> intermediate is obtained. Increasing the temperature up to 300 °C is needed to fully accomplish the oxidation to CuO and CeO<sub>2</sub> phases, as observed in Fig. 4, though this time no further chemical reaction is observed on the mass spectrometer.

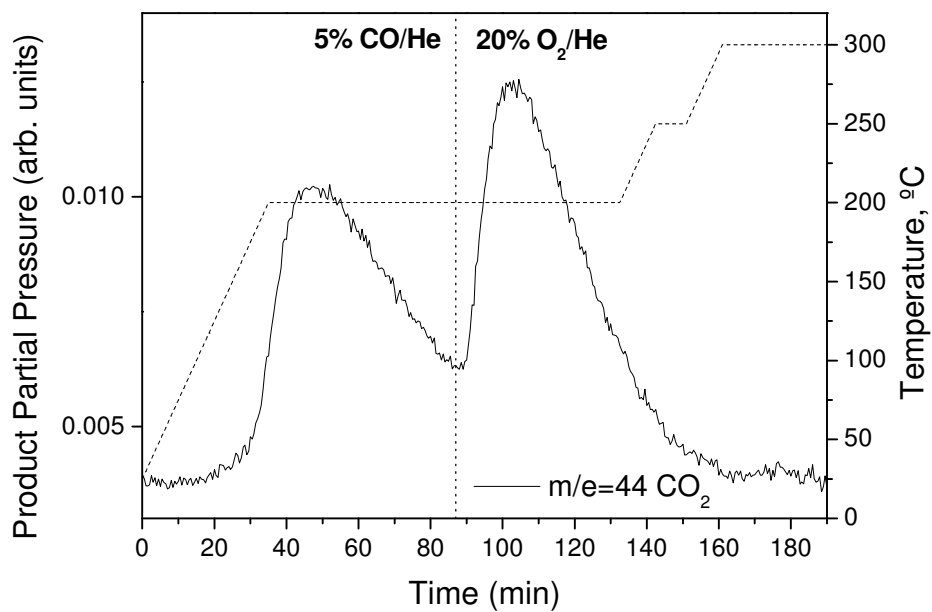


Figure S1. Product analysis during reduction and subsequent reoxidation.  $\text{CO}_2$  production during the in situ reduction and oxidation cycle along with the temperature program for the experiment is shown in figure.