

**Electronic Supplementary Information (ESI) for**

**XPS and DRIFTS *operando* studies of an inverse CeO<sub>2</sub>/CuO WGS catalyst:  
deactivating role of interfacial carbonates on redox activity**

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## Experimental

An inverse CeO<sub>2</sub>/CuO catalyst with Ce:Cu atomic ratio of 4:6 was prepared by employing reverse microemulsions containing n-Heptane, Triton-X-100 and n-Hexanol as organic solvent, surfactant and cosurfactant, respectively, in amounts similar to those reported previously.<sup>1</sup> The required amount of Cu(NO<sub>3</sub>)<sub>2</sub> was dissolved in distilled water and added to the former mixture in order to form the reverse microemulsion. Simultaneously, another microemulsion of similar characteristics was prepared containing dissolved in its aqueous phase the required amount of tetramethyl ammonium hydroxide (TMAH). After 1 h stirring of the two microemulsions, the TMAH-containing one was added to the Cu-containing one and it was left for the period of 18–24 h in order to complete the precipitation reaction. Then, the resulting microemulsion was heated gently up to 333 K using a water bath. This microemulsion containing the precipitated copper was then mixed with another one of similar characteristics in which Ce had previously been precipitated following mixing of cerium nitrate- and TMAH-containing microemulsions. This final microemulsion containing both precipitated Cu and Ce components was kept under agitation for the period of 18–24 h. The resulting solid was then separated by centrifugation and decantation, rinsed with methanol and dried overnight at 373 K. Final calcination under air at 773 K was done during 2 h (after a heating ramp of 5 K min<sup>-1</sup>). Chemical analysis by X-ray fluorescence (see Table S1 below) confirmed quantitative precipitation of the two components.

XPS spectra in gas environment were obtained at ISISS station of the BESSY II synchrotron in Berlin. The sample was pressed into a pellet and mounted on a sapphire and tantalum holder which could be heated from the rear with an IR laser while the temperature control used a thermocouple in contact with the sample at a location close to the X-ray beam incidence point. During measurements the sample surface was swept with a gas mixture flowing at a ca. 15 sccm rate, with the experimental chamber being pumped at a rate such that the pressure on the sample was kept at 0.5 mbar. The gas flow, established with computer-driven mass flow controllers, contained when so desired 1 sccm of CO, 3 sccm of H<sub>2</sub>O (pumped from a vial at ambient temperature containing water previously degassed by freeze-pump-thaw cycles) and/or 3 sccm of O<sub>2</sub>, with He as balance. Previously to the measurements the sample was pretreated at 673 K under O<sub>2</sub>/He flow. Cu (2p), Ce (3d), O(1s) and C(1s) XPS spectra were recorded, after taking a survey spectrum with photon energy E<sub>ph</sub>=1200 eV, using photons with E<sub>ph</sub>=1100, 1050, 680 and 435 eV respectively, in order to record for all the spectra the main lines with an electron kinetic energy around 150 eV, which ensures a near-maximal surface sensitivity similar for all of them. The Cu L<sub>3</sub>VV Auger spectra were taken also with E<sub>ph</sub>=1100 eV excitation, although of course the surface sensitivity is smaller. Cu L edge XANES were obtained in the same experiments recording the total electron yield signal.

*Operando*-DRIFTS analysis was carried out using a Bruker Equinox 55 FTIR spectrometer fitted with an MCT detector. The DRIFTS cell (Harrick) was fitted with CaF<sub>2</sub> windows and a heating cartridge that allowed samples to be heated up to 773 K. Aliquots of *ca.* 70 mg were precalcined in situ at 773 K and then cooled to 298 K under diluted oxygen before introducing the reactant mixture; this consisted in either 3 % CO or 3 % CO + 3 % H<sub>2</sub>O diluted in He and was prepared by using mass flow controllers with *ca.* 70 cm<sup>3</sup> min<sup>-1</sup> total flow passing through the catalyst bed at atmospheric pressure. The spectra consisted in an average of 20 scans at 4 cm<sup>-1</sup> resolution. Bypass gases or those evolving from the DRIFTS cell were continuously analysed on line by

means of a quadrupole mass spectrometer Pfeiffer Omnistar.

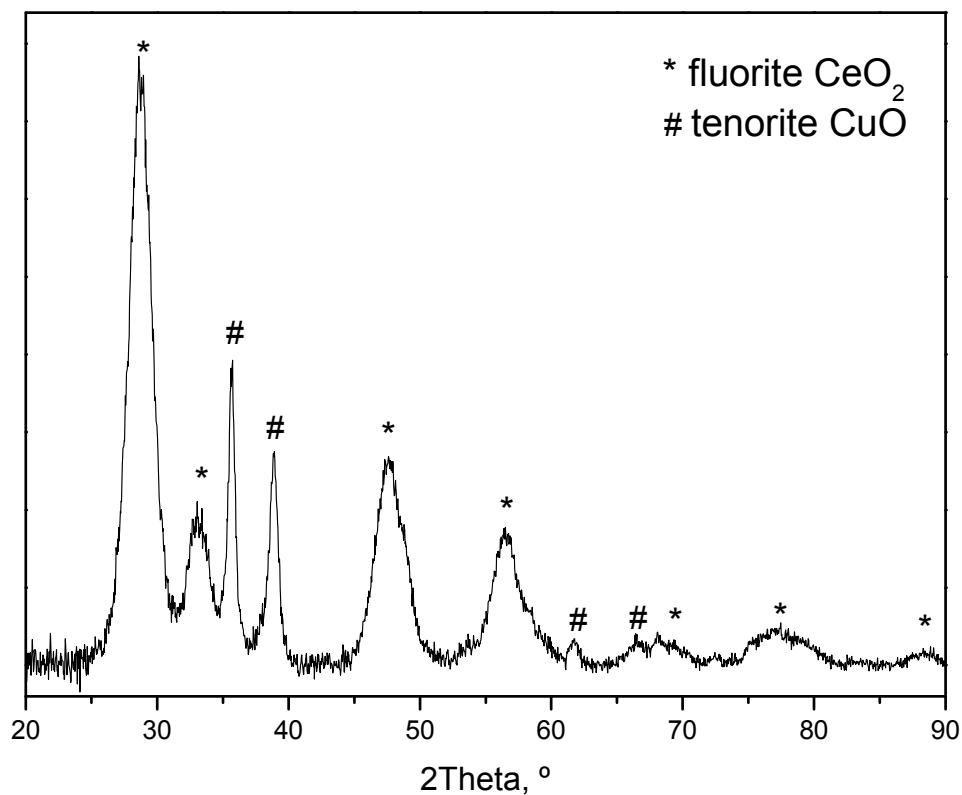
XRD pattern of the catalyst (see Fig. S1) was recorded on a Seifert XRD 3000P diffractometer using nickel-filtered CuK $\alpha$  radiation operating at 40 kV and 40 mA using a 0.02° step size and 2 s counting time per point. Analysis of the diffraction peaks was done with the computer program X'Pert HighScore Plus version 2.2.1.

$S_{\text{BET}}$  specific surface area of the catalyst was determined from N<sub>2</sub> adsorption isotherms of the specimen preoutgassed during 12 h at 413 K which were recorded with automatic equipment Micromeritics 2100.

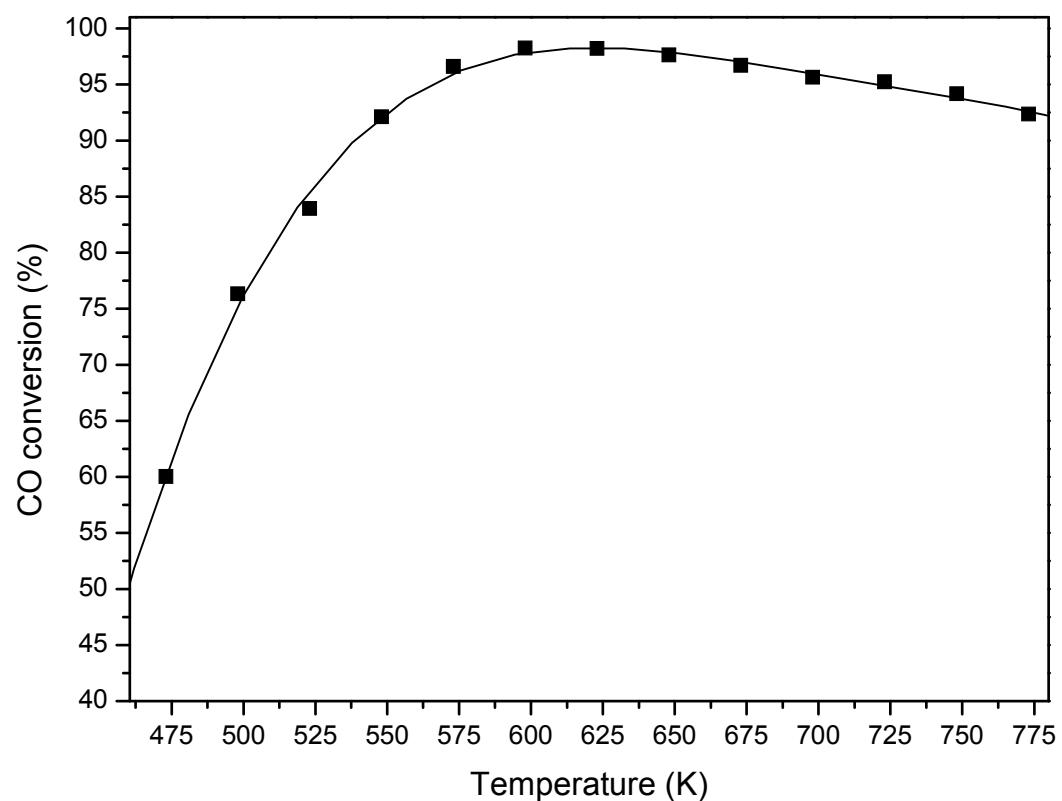
Water-gas shift (WGS) reaction activity test shown in this part was carried out using a fixed-bed reactor system from PID Eng&Tech (model Microactivity Reference) at atmospheric pressure. 1 g of a calcined catalyst (diluted with 4 g of CSi) was positioned inside the 9 mm ID Hastelloy C reactor. Prior to reaction, the catalyst was calcined in situ in a 20% O<sub>2</sub>/He gas mixture at 773 K for 1 h. Reactant gas mixture consisted of 5 % CO and 15 % H<sub>2</sub>O diluted in He. Distilled water was dosed by means of a Gilson 307 HPLC pump and evaporated in a heat box, operating at 453 K, which is integrated in the reactor system. The total reactant flow was 250 cm<sup>3</sup> min<sup>-1</sup> (STP), which corresponds to GHSV of ca. 15.000 h<sup>-1</sup>. The analysis of the outlet flow was made under apparent steady state conditions (temperature stabilized over, at least, 45 minutes) every 50 K from 473 K to 773 K. Reaction products and remaining reactants were efficiently separated by means of capillary columns, and qualitatively and quantitatively analyzed with a Shimazdu gas chromatograph equipped with a TCD detector. The transfer line between the reactor system and gas chromatograph was heated to 363 K using a heating tape in order to prevent water vapour condensation and to ensure acquisition of reliable data.

**Table S1.** Main physicochemical parameters of the initial calcined CeO<sub>2</sub>/CuO catalyst extracted from characterization results.

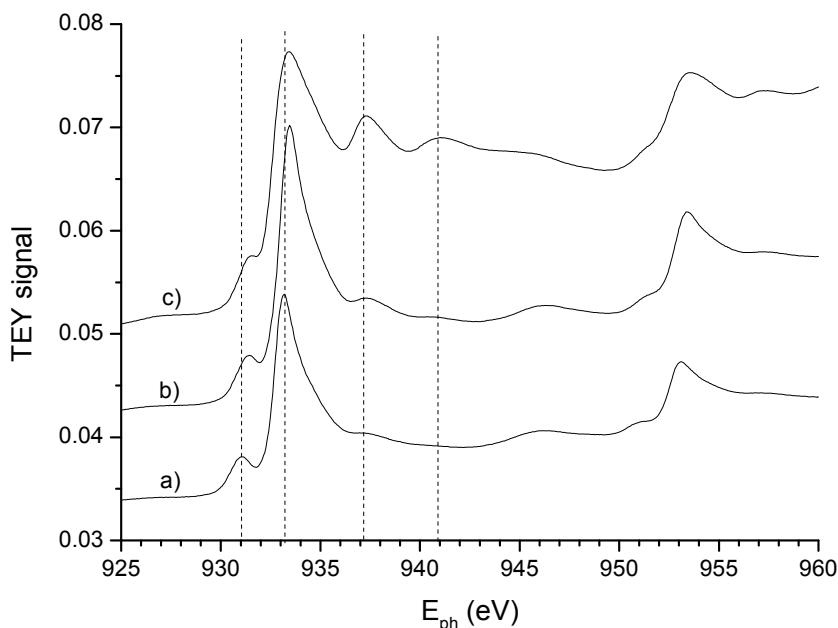
XRF Cu/Ce atomic ratio (nominal value)	S <sub>BET</sub>	XRD CuO cristal size	XRD CeO <sub>2</sub> crystal size	XRD CuO lattice parameters	XRD CeO <sub>2</sub> lattice parameter
1.465 (1.5)	98 m <sup>2</sup> g <sup>-1</sup>	13.4 nm	4.2 nm	a = 4.751 Å; b = 3.427 Å; c = 5.096 Å	a = 5.417 Å



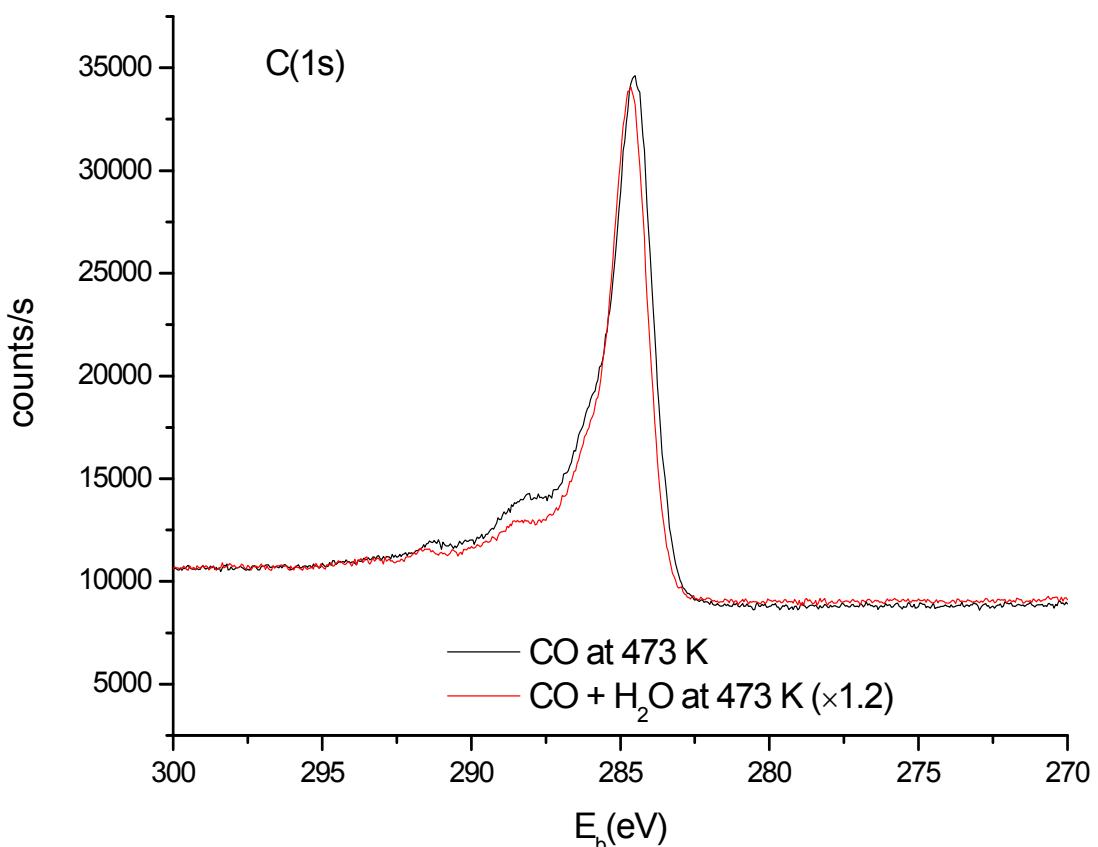
**Figure S1.** X-ray diffraction pattern of the initial calcined CeO<sub>2</sub>/CuO catalysts. Attribution of the observed peaks is indicated.



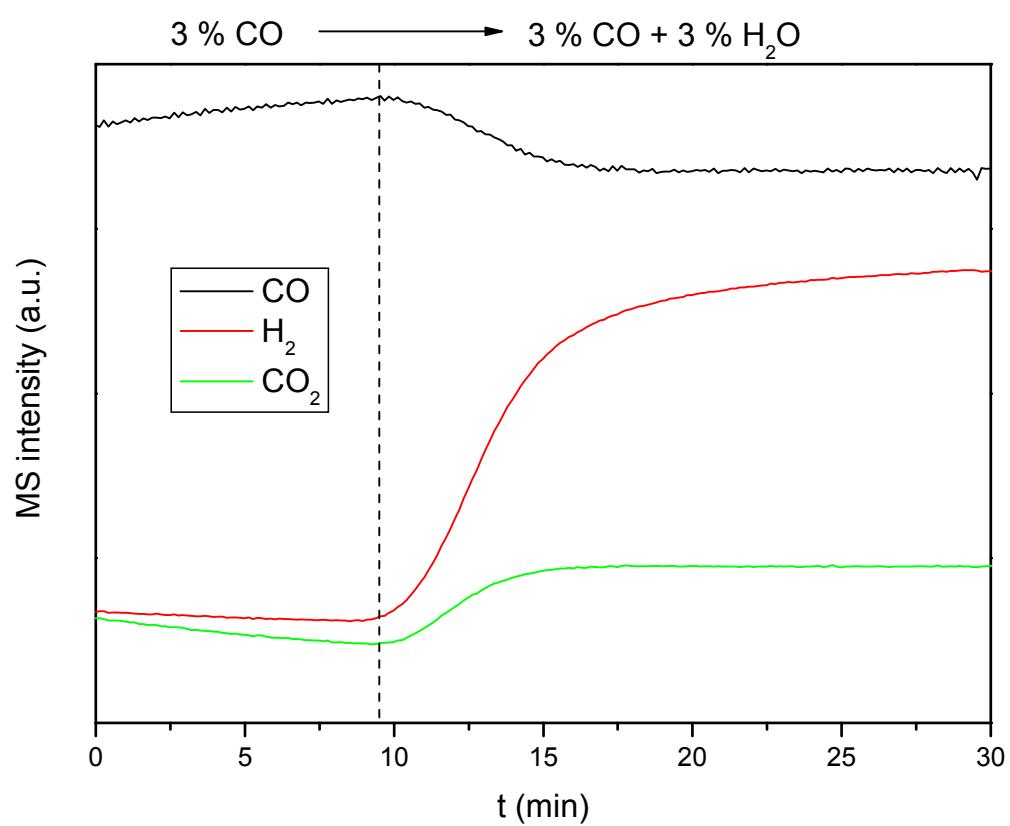
**Figure S2.** WGS activity of the  $\text{CeO}_2/\text{CuO}$  catalyst in the tubular reactor under 5 % CO and 15 %  $\text{H}_2\text{O}$ .



**Figure S3.** Cu L<sub>3,2</sub> XANES spectra of the catalyst upon contact with CO at 473 K (a), addition of H<sub>2</sub>O (b) and subsequent heating at 523 K (c). The peak at  $E_{\text{ph}} \approx 931$  eV is due to Cu<sup>2+</sup> and that at  $E_{\text{ph}} \approx 933$  eV to Cu<sup>+</sup> or Cu<sup>0</sup>, while the features at  $E_{\text{ph}} \approx 937$  and 941 eV reflect the formation of a Cu<sup>0</sup> phase (see text).



**Figure S4.** XPS spectra in the C 1s BE zone of the CeO<sub>2</sub>/CuO sample under indicated reactant mixtures at 473 K. A decrease in the 292–287 eV region, in which carbonates contribution is expected, is detected. Note that a multiplying factor of 1.2 is applied to the spectrum under CO + H<sub>2</sub>O mixture in order to correct for photoelectron screening by H<sub>2</sub>O.



**Figure S5.** Evolution of gases, according to MS monitoring, during *operando* DRIFTS experiments under indicated reactant mixtures at 473 K.

## References

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- <sup>1</sup> D. Gamarra, G. Munuera, A.B. Hungría, M. Fernández-García, J.C. Conesa, P.A. Midgley, X.Q. Wang, J.C. Hanson, J.A. Rodríguez and A. Martínez-Arias, *J. Phys. Chem. C*, 2007, **111**, 11026.