Supporting Information

Chemical and Electronic Changes of the CeO_2 Support During CO Oxidation on Au/CeO_2 Catalysts:

Time resolved Operando XAS at the Ce L_{III} Edge

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1. Comparison of changes in the CO_2 formation rate upon change in the reaction gas mixture from standard gas mixture to CO-rich gas mixture: comparison with earlier data

Here it is important to note that in our former experiments (Figure 12 in [1]) we used to initially pass the reaction gas via a bypass for 3.5 h before starting the measurements in the CO-rich reaction gas (5% CO, 1% O_2, 94% N_2), while leaving the catalyst in the standing standard reaction gas mixture (1% O_2, 1% CO and 98% N_2). This will result in an accumulation of CO_2 in the gas mixture in the reactor. When switching from bypass to reactor and starting the measurements, this results in a high initial CO_2 level, until the gas in the reactor is completely exchanged. In later experiments (during X-ray absorption measurements) this bypass phase was skipped. The gas flow was directly switched to the reactor and the measurements were started immediately after changing the reaction gas mixture. To test whether this has an influence on the reaction behavior we performed a test measurement with a commercial catalyst (1wt% Au in CeO_2, from Haruta Gold Inc., Tokyo, Japan, RR2Ce-1, with 114 m^2/g), following the same procedure as used previously (see Figure S1, Supporting Information). This showed a similar trend as reported in ref. [1], indicating that there is no principal difference in the reaction behavior of the two catalysts. The difference is mainly due to the build-up /accumulation of stable adsorbed species such as surface carbonates on the catalyst surface, by reaction with the reaction gas components and in particular with CO_2 formed while standing in the reactor during the bypass phase.

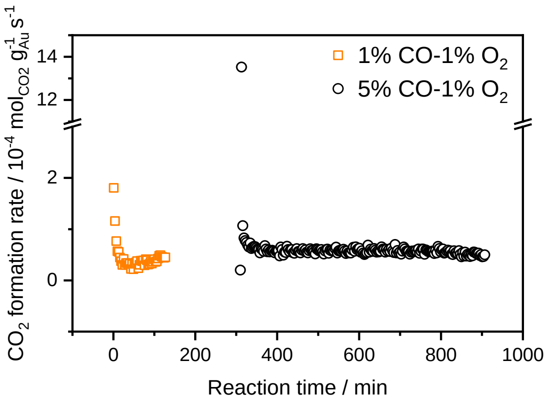

Fig. S1: CO_2 formation rate upon reaction gas exchange on an O400 pretreated (10% O_2, balance N_2) commercial 1 wt.% Au/CeO_2 catalyst (Haruta Gold Inc.): orange symbols: standard reaction gas mixture at 80°C: 1% CO, 1% O_2, balance N_2; black symbols: CO–rich gas mixture (5% CO, 1% O_2, balance N_2). The sample was kept in a standing standard reaction gas mixture for 2 h, simulating the bypass phase in the previous measurements.

2. Comparison of different CO400 pretreatments

The measurements performed after a CO400 pretreatment in 10% CO in N_2 in this work resulted in significantly different reaction behavior compared measurements after CO400 pretreatment in 2% CO in N_2, as used in ref. [1]). In order to verify that the differences in reaction behavior are indeed only caused by the different CO concentrations during pretreatment, we repeated a measurement of the CO_2 formation rate after CO400 pretreatment 2% CO in N_2 using a commercial Au/CeO_2 (1 wt.% Au) catalyst. The resulting time dependence of the CO_2 formation rate (see below) shows a trend comparable to the data published in [1].

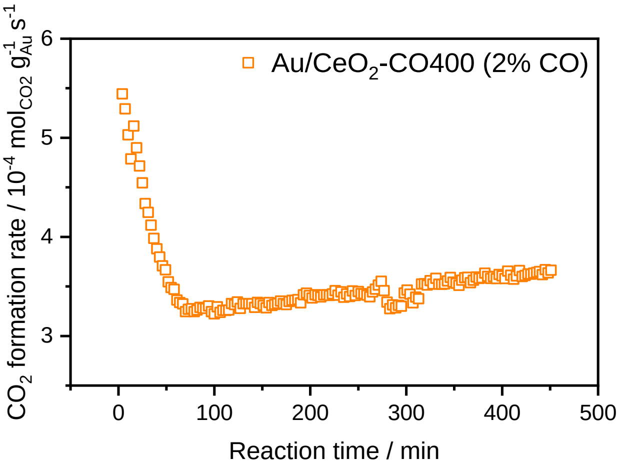

Fig. S2: CO_2 formation rate after a CO400 pretreatment in 2% CO (balance N_2) on a commercial 1wt.% Au/CeO_2 catalyst in a standard reaction gas mixture: 1% CO, 1% O_2, balance N_2 at 80°C.

3. Influence of water traces in reaction gas mixtures

In order to exclude possible effects caused by traces of water in the reaction gas, we performed a set of two measurements on a commercial 1 wt.% Au/CeO_2 catalyst which resemble those shown in Figures 4 – 6 in the main text. One measurement was performed without a water filter (black triangles), one with a water filter (red triangles), see Figure S3. Although the switching between the different reaction gas mixtures occurred at slightly different times, there is no difference in the CO_2 formation rates measured with or without water filter. The water filter (Agilent, CP17971) was applied to realize dry reaction conditions (<0.2 ppm of H_2O).

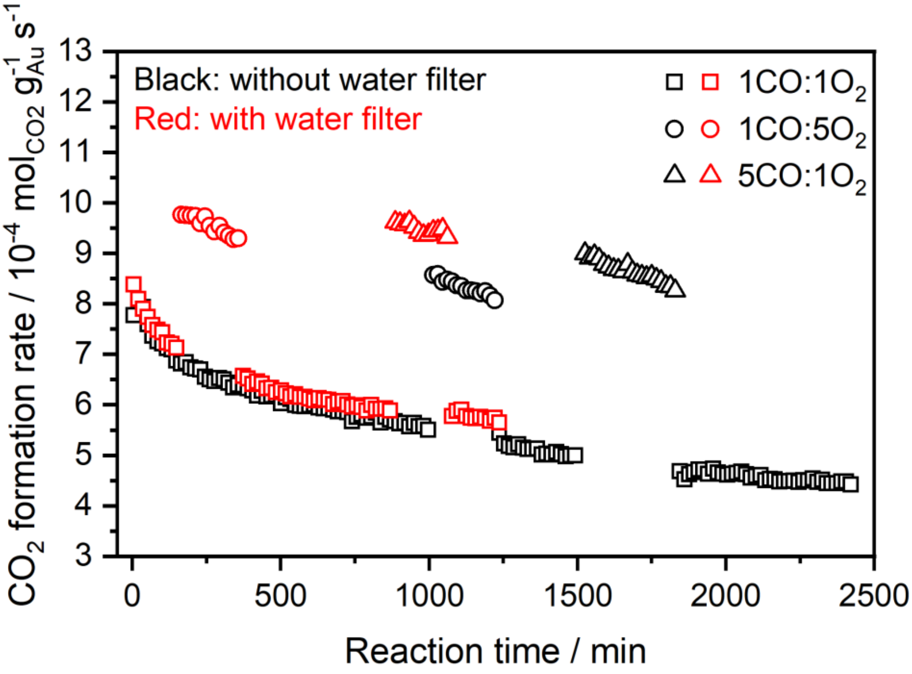

Fig. S3: CO_2 formation rate on a commercial 1 wt.% Au/CeO_2 catalyst in different reaction gas atmospheres after a O400 pretreatment in 10% O_2 (balance N_2): black open symbols: without additional water filter, red open dots: with water filter. Sequence of gas mixtures at 80°C: 1: standard reaction gas mixture (1% O_2, 1% CO, 98% N_2), squares; 2: O_2-rich gas mixture (1% CO, 5% O_2, 94% N_2), circles; 3: again standard reaction gas mixture; 4: CO-rich gas mixture (5% CO, 1% O_2, 94% N_2), triangles, 5: again standard reaction gas mixture.

4. Comparison of O400 pretreatments on different Au/CeO_2 catalysts

A similar sequence of different reaction gas mixtures was measured on a commercial Au/CeO_2 catalyst (Haruta Inc. 1 wt.% Au loading) after O400 pretreatment. The much lower Au loadings resulted of course in lower CO_2 formation rates compared to the 4.5 wt.% Au catalysts used in this study, but the general trends shown in Figure S4 fully agree with the data presented in Figure 4. Due to the limited time for measurements at the XAFS beamline at Elettra, the intervals are shorter and only one XAS measurement was recorded per reaction gas mixture to obtain the Ce^{3+} ratio (results, see Table S1).

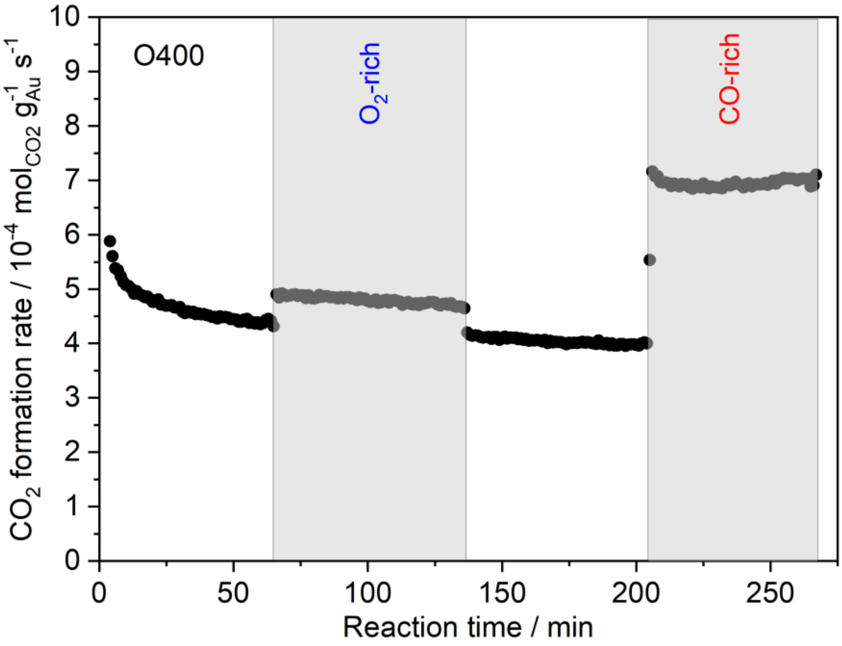

Fig. S4: CO_2 formation rate after an O400 pretreatment in 10% O_2 (balance N_2) on a commercial 1wt.% Au/CeO_2 catalyst in different reaction gas atmospheres at 80°C.

5. Comparison of CO400 pretreatments on different Au/CeO₂ catalysts

A similar sequence as shown in Figure S4, was also measured on the 1 wt.% Au/CeO_2 catalyst after CO400 pretreatment. This is depicted in Figure S5. Again, the general trends shown in Figure S5 fully agree with the data presented in Figure 6. XANES results on the relative Ce^{3+} content in the different phases presented in Table S1.

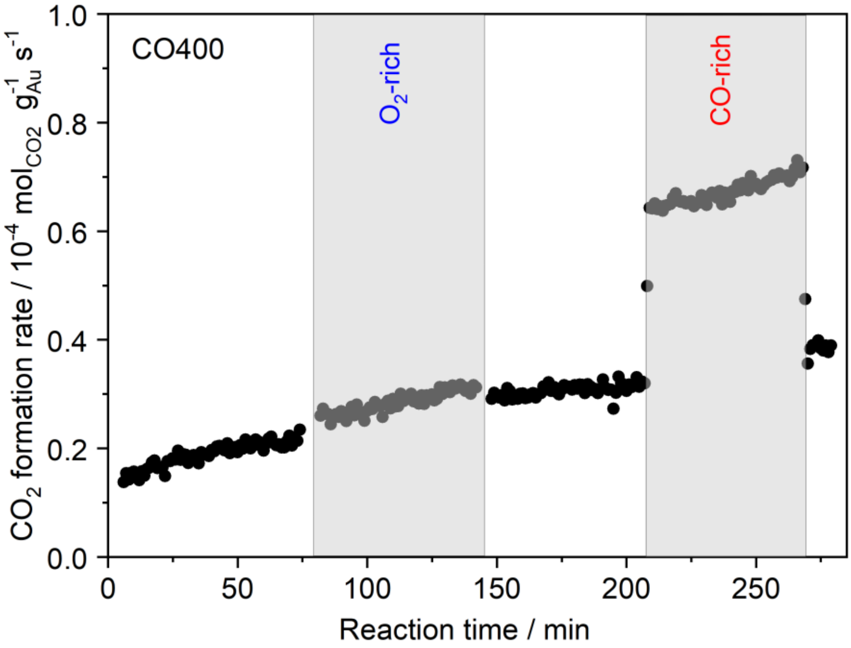

Fig. S5: CO_2 formation rate after a CO400 pretreatment in 10% CO (balance N_2) on a commercial 1 wt.% Au/CeO_2 catalyst in different reaction gas atmospheres at 80°C.

Table S1: Relative content of Ce^{3+} species on a commercial 1 wt.% Au/CeO_2 catalyst after oxidative (O400) and reductive (CO400) pretreatment and during subsequent reaction in different reaction gas mixtures at 80°C.

reaction gas mixture	O400	CO400
in N_2 after pretreatment / %	0	5.6
standard / %	0	0
O_2-rich / %	0	0
standard / %	0	0
CO-rich / %	0	0

Similar to the catalyst with 4.5 wt.% Au loading, the relative content of Ce^{3+} species is significantly higher after the reductive CO400 pretreatment than after the oxidative O400 pretreatment. During exposure to the reaction gas mixtures, the content of Ce^{3+} species is below the detection limit, even during reaction in the CO-rich gas mixture. This indicates facile re-oxidation of O vacancies.

Reference s

1. Abd El-Moemen, A.;Abdel-Mageed, A.M.;Bansmann, J.;Parlinska-Wojtan, M.;Behm, R.J.; Kucèrová, G., Deactivation of Au/CeO_2 catalysts in the CO oxidation reaction: Influence of pretreatment and reaction conditions. *J. Catal.* **2016**, *341*, 160-179.