Supporting Information

Deactivation of Au/CeO$_2$ catalysts in the CO oxidation reaction: Influence of pretreatment and reaction conditions

Ayman Abd El-Moemen[1,+], Ali M. Abdel-Mageed[1,#], Joachim Bansmann[1],
Magdalena Parlinska-Wojtan[2], R. Jürgen Behm[1], Gabriela Kučerová[1*]

[1] *Institute of Surface Chemistry and Catalysis, Ulm University, D-89069 Ulm, Germany*
[2] *Institute of Nuclear Physics Polish Academy of Sciences, PL-31342 Krakow, Poland*

---

[*] Author, to whom correspondence should be addressed: gabriela.kucerova@uni-ulm.de
[+] *Present address: Chemistry Department, Faculty of Science, Suez Canal University, Ismailia, Egypt*
[#] *Permanent address: Department of Chemistry, Faculty of Science, Cairo University, Giza 12613, Egypt*

Table S1: Reaction rates during CO oxidation at 80°C in 1% CO, 1% O_2, rest N_2 gas mixture on differently pretreated Au/CeO_2 catalyst including reproduction.

Catalyst pretreatment	Experiment No.	Initial rate / $mol \cdot g_{Au}^{-1} \cdot s^{-1}$	Rate after 1000 min / $mol \cdot g_{Au}^{-1} \cdot s^{-1}$	Decrease in reaction rate after 1000 min / %
O400	1	3.6×10^{-3}	2.4×10^{-3}	34
	2	3.5×10^{-3}	2.4×10^{-3}	32
N400	1	3.5×10^{-3}	2.1×10^{-3}	40
	2	3.6×10^{-3}	2.3×10^{-3}	36
CO400	1	3.1×10^{-3}	1.7×10^{-3}	46
	2	3.3×10^{-3}	1.9×10^{-3}	43
H400	1	1.9×10^{-3}	$1. 6 \times 10^{-3}$	21
	2	2.0×10^{-3}	$1. 5 \times 10^{-3}$	25

XPS on ceria support

The Ce(3d) spectra (Fig. S1) obtained from the various catalysts show rather complicated features, which result from the presence of three (two) different final states of the Ce^{4+} (Ce^{3+}) species. For the assignment of the different peaks and their respective BEs we used the same model and notation as described previously (for details, see [1,2]). The components related to the Ce^{3+} state (color-coded by red and pink) are denoted by (v_0, u_0) and (v',u'), the others are assigned by (v,u), (v'',u''), and (v''', u''') and represent photoelectrons from Ce^{4+} states. Since the Ce^{3+} species have been considered as (more) active species in the CO oxidation reaction on a Pt/CeO_2 catalyst [3], we evaluated the fraction of Ce^{3+} surface species (see Table 2). It turned out, however, that this fraction is essentially constant for all measurements (0.19±0.02). Hence, it is independent of the pretreatment (O400, N400, CO400, and H400) and does not change measurably after the respective CO oxidation reactions. (Note that the error margin mainly results from differences in the background subtraction, rather than from the fitting procedure itself.) The relative amounts of Ce^{3+} species obtained from the present XPS analysis are somewhat lower / agree well with those recorded earlier on Au/CeO_2 catalysts after comparable reductive / oxidative treatment [1,2].

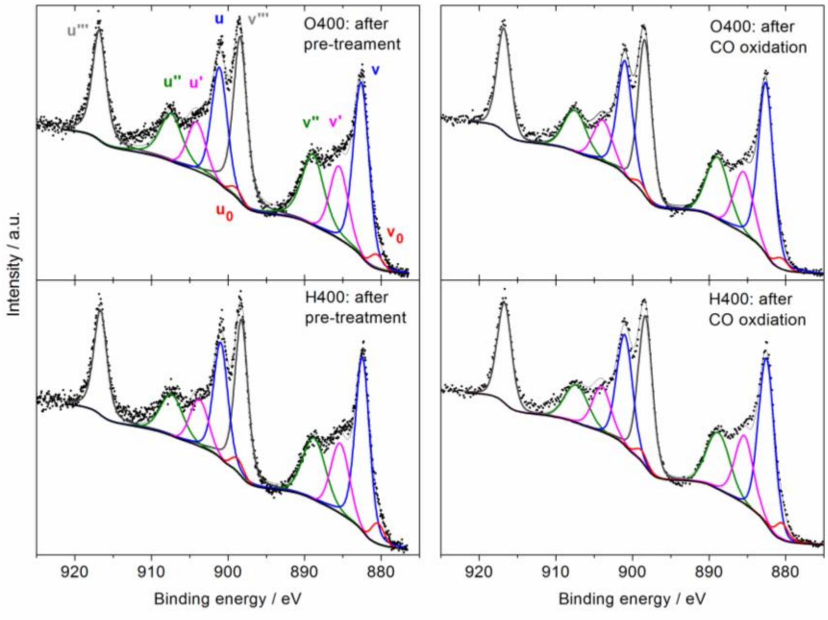

Figure S1. XP spectra of the Ce(3d) region of a 4.5wt.% Au/CeO_2 catalyst recorded *ex situ* after O400 (top) and H400 pretreatment (bottom). Left panels: before, right panels after CO oxidation reaction (1000 min , 1% CO, 1% O_2, rest N_2 at 80°C).

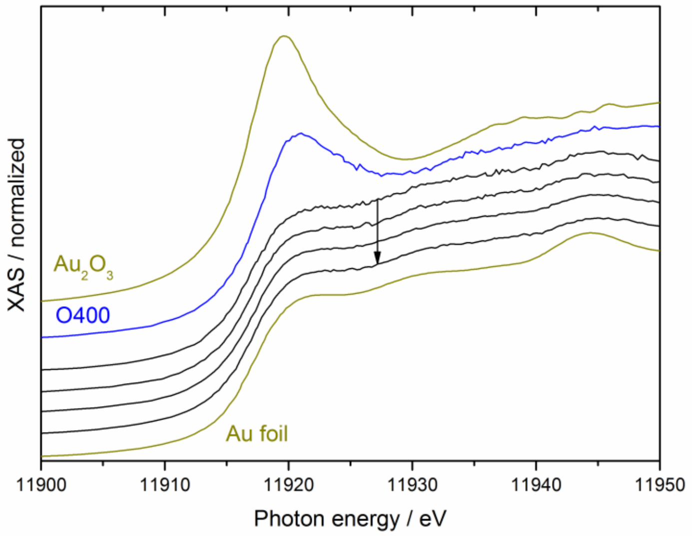

Figure S2. XANES spectra of a 4.5wt.% Au/CeO_2 catalyst directly after O400 pretreatment (10% O_2/N_2, 30 min at 400°C; red line) at 80°C in N_2 (blue line: O400) and during the CO oxidation reaction at 80°C (1% CO, 1% O_2, 98% N_2) at different reaction times (11, 75, 150, and 280 min, black lines, following the arrow). The spectra of the references, Au_2O_3 (dark yellow line, top) and Au foil (dark yellow line, bottom), are presented for comparison.

Details regarding XANES analysis of Au L_{III}-edge

A consistent fit of the XANES spectra, however, is difficult to perform since two counteracting effects contribute to the XANES spectrum. For metallic Au, the Au L_{III}-edge results mainly from an excitation from the Au($2p_{3/2}$) state into empty 6s continuum states above the Fermi level. The transition into Au(5d) states is strongly suppressed since the Au(5d) states are almost fully occupied. With increasing positive charge on the Au NPs, the excitation of electrons into the 6s continuum states shifts the inflection point to higher photon energies, as expected from the behavior of other materials. On the other hand, the presence of unoccupied Au(5d) states, which increases with the positive charge on the Au atoms, gives rise to a strong peak (white line) due to possible excitations from Au($2p_{3/2}$) states into these partially empty Au(5d) states. Since the latter absorption peak appears at slightly lower photon energies than the 2p → 6s excitation, both effects tend to cancel each other. Therefore, the inflection point of the measured Au L_{III} spectrum does not shift with increasing oxidation state, only the shape of the spectrum changes somewhat. Finally, the shape of the XANES spectrum also depends on the size of the Au NPs (for details, see [4]).

References:

1. R. Leppelt, B. Schumacher, V. Plzak, M. Kinne, and R.J. Behm, *Kinetics and Mechanism of the Low-temperature Water-Gas Shift Reaction on Au/CeO*$_2$ *Catalysts in an Idealized Reaction Atmosphere* J. Catal. **244** (2006) 137-152

2. A. Karpenko, Y. Denkwitz, V. Plzak, J. Cai, R. Leppelt, B. Schumacher, and R.J. Behm, *Low-temperature water-gas shift reaction on Au/CeO*$_2$ *catalysts - The influence of catalyst pretreatment on the activity and deactivation in idealized reformate* Catal. Lett. **116** (2007) 105-115

3. R. Kopelent, J.A. van Bokhoven, J. Szlachetko, J. Edebeli, C. Paun, M. Nachtegaal, and O.V. Safonova, *Catalytically Active and Spectator Ce*$^{3+}$ *in Ceria-Supported Metal Catalysts* Angew. Chem. Int. Ed. **54** (2015) 8728-8731

4. A. Pantelouris, G. Kueper, J. Hormes, C. Feldmann, and M. Jansen, Anionic gold in Cs_3AuO and Rb_3AuO established by X-ray absorption spectroscopy J. Am. Chem. Soc. **117** (1995) 11749-11753