Supporting Information

High activity and negative apparent activation energy in the low temperature CO oxidation – Present on $Au/Mg(OH)_2$, absent on Au/TiO_2

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Estimate of the intrinsic activity of Au/TiO₂ at low temperatures (-50°C)

Based on previous experimental IR results from Green et al.¹ we estimated the intrinsic activity of a Au/TiO₂ catalyst for $CO_{2,ad}$ formation at -50°C in the initial period of the reaction, in the absence of blocking effects caused by $CO_{2,ad}$ species.

For this purpose we first determined the decrease in the CO_{ad} signal with time on stream at -153 °C, which is given by the initial slope in the temporal evolution of the CO_{ad} signal (see fig. 2A in ref. 1). Next we determined the absolute amount of stable adsorbed CO_{ad} that is present in the beginning of the reaction, before the introduction of O_2 . Considering the Au loading and the mean Au diameter,¹ and assuming surface saturation with CO_{ad} on the surface of the Au nanoparticles (NPs) at such low temperatures (about 0.75 monolayers), we calculated an absolute amount of about 7.5×10¹⁹ adsorbed CO molecules on the Au NPs (per gram catalyst). For the following estimate of the reaction rate, one has additionally to consider that under these conditions (-153°C) mainly CO adsorbed on TiO₂ is reacting with O₂ in the reaction gas to $CO_{2,ad}$, but not CO adsorbed on Au.¹ From fig. 2A in ref. 1 the amount of CO adsorbed on TiO₂ is roughly 25% of that on the surface of the Au NPs. Using this value we finally converted the decrease in the CO_{ad} signal with time into mass normalized reaction rates, which yields a value of 4×10^{-8} mol·g_{cat}⁻¹·s⁻¹ (5×10^{-7} mol·g_{Au}⁻¹·s⁻¹) at -153 °C).

From this reaction rate for the intrinsic CO oxidation on Au/TiO₂ (formation of CO_{2,ad} only) at -153 °C we finally calculated the reaction rate at -50 °C according to the Arrhenius equation based on the apparent activation energy determined by Green et al. (0.16 eV),¹ which yields values of 5×10^{-5} mol·g_{cat}⁻¹·s⁻¹ / 6×10^{-4} mol·g_{Au}⁻¹·s⁻¹.

References

1. I.X. Green, W. Tang, M. Neurock, and J.T. Yates, *Spectroscopic Observation of Dual Catalytic Sites During Oxidation of CO on a Au/TiO*₂ Catalyst Science **333** (2011) 736-739



Figure S1: CO oxidation rates on a mesoporous Au/Mg(OH)₂ catalyst as a function of time at different partial pressures of O₂ between 5 mbar and 15 mbar (0.5% - 1.5% O₂ at atmospheric pressure) at a) -20°C and b) +80°C.

Note that these measurements were also performed on catalyst batch #2 with slightly larger Au particles and, hence, lower activities.



Figure S2: Comparison of CO oxidation rates (initial and steady-state) on mesoporous $Au/Mg(OH)_2$ with different O_2 partial pressures between 5 mbar and 15 mbar (1% CO, 0.5-1.5% O_2 , balance N_2) at a) -20°C and b) +80°C.



Figure S3: Double-logarithmic plot of the reaction rates (in the initial-state as well as in the steady-state) for CO oxidation on a mesoporous $Au/Mg(OH)_2$ catalyst with varying O_2 partial pressure between 5 mbar and 15 mbar (1% CO, 0.5-1.5% O_2 , balance N_2) at -20°C and +80°C.



Figure S4: DRIFT spectra recorded during CO oxidation on the mesoporous Au/Mg(OH)₂ catalyst at different temperatures, ranging from -90°C to 120°C. The spectra were recorded after 10 min (upper panel) and 360 min (lower panel) reaction time, respectively. Note that the gas phase CO signal was already subtracted.



Figure S5: DRIFT spectra recorded during a) CO_2 adsorption and b) subsequent N_2 purging on Au/Mg(OH)₂ at -20°C. c) Comparison of IR band intensities as a function of time at -20°C between sample after CO_2 pre-adsorption and the same sample after re-calcination (units in Kubelka-Munk multiplied by a constant). The impact of $CO_{2,ad}$ on the activity of a Au/Mg(OH)₂ catalyst at -20°C was tested by exposing a freshly calcined catalyst (O275) at -20°C to a continuous flow of a CO₂ gas mixtures (0.5% CO_2/N_2) for 30 min. During the CO₂ adsorption measurement (Figure S5a), $CO_{2,ad}$ species are hardly visible, while the gradual build-up of surface carbonate species (band around 1700 cm⁻¹) is observed. During subsequent N₂ purging step at -20°C (see Figure S5b), the CO₂ signal decreased rapidly, while the intensity of the surface carbonate band and hence the coverage of these species hardly changes. Comparing the CO oxidation rates measured at -20°C directly after the CO₂ treatment /N₂ purging (see Figure S5c, left) with that obtained after recalcination of the same sample (see Figure S5c, right) reveals a much lower activity in the first case, indicating a significant deactivation induced by the CO₂ treatment. In contrast to the Au/TiO₂ catalyst, however, this is not caused by surface blocking by adsorbed CO₂ ('self poisoning'), but by the build-up of surface carbonate species during exposure to CO₂.