Supporting information

Highly Oxidized Gold Nanoparticles: in Situ Synthesis, Electronic Properties, and Reaction Probability Toward CO Oxidation

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The reaction probability estimation

The reaction probability (RP) characterizes the number of successful reaction acts ($CO+O=CO_2$) versus the total amount of CO molecules impinged on the surface. Thus, the RP=1 would mean that each CO molecule impinged on the surface was oxidized to CO_2. The reaction probability is an effective integral characteristic and includes factors like sticking probability of the CO molecules to the surface, the diffusion from support to active sites and the elementary acts of interaction.

The reaction probability of oxidized gold nanoparticles toward CO was calculated as the slope of the dependence of the number of oxidized gold atoms on the number of CO impingements on the surface.

- *The estimation of the number of oxidized gold atoms*

The number of oxidized gold atoms was estimated from the intensity of Ta 2p and Au 4f peaks in XPS spectra. The long-time RF-sputtering of gold nanoparticles on the Ta surface was performed to obtain a thick gold film. The thickness of this film was calculated based on the known dependence of the XPS line intensity of the support on the thickness of the covering layer[1]

$$I=I_0 exp(-d/\lambda sin\alpha)$$

where I is the XPS signal of the tantalum foil covered with a gold film of thickness d recorded at electron takeoff angle α, I_0 is the signal of the clean support, and λ is the mean free pass of the photoelectrons.

In our experiments $\alpha=20^o$ and λ was taken as 20 Å[1].

On the basis of the obtained d value (~22 Å), the thickness of the covering layer for all other samples was estimated proportionally to the I(Au 4f)/I(Ta 2p) ratio in the samples in an assumption that the nanoparticles form a thin oxidized film.

The resulted thickness of the oxidized films was obtained as ~1.3 Å for small nanoparticles and ~5.2 Å for larger ones. Based on the crystallographic data, we could estimate the number of gold atoms in 1 cm^2 of our layer. The unit cell volume of Au_2O_3 oxide is 517.9 $Å^3$ with 16 Au atoms in the unit cell[2]. Thus, the 1 cm^2 of the oxidized gold layer with a thickness 1.3 Å (5.2 Å) contains $2.5x10^{13}$ (10^{14}) unit cells and, consequently, $4x10^{14}$ ($1.6x10^{15}$) gold atoms.
The depletion of the number of oxidized gold species with increasing of CO exposure was monitored by the decrease of the Au^{3+} peak intensity in Au 4f spectrum.

- *The estimation of the number of CO impingements on the surface*

The number of CO impingements on the surface was estimated from the kinetic theory of gases[3].
The number of CO impingements on the surface per 1 second is proportional to the gas pressure and inversely proportional to the temperature:

$$Z = S \times P/(2\pi mkT)^{1/2}$$

where S is the area, P is the gas pressure in Pa, k is the Boltzmann constant in J/K, m is the molecular weight of CO in kg and T is the gas temperature in K.

REFERENCES

(1) Briggs, D.; Seah, M. P. (Eds.) *Practical Surface Analysis by Auger and X-ray Photoelectron Spectroscopy*; John Wiley & Sons, New York, NY, 1983

(2) Jones, P. G.; Rumpel, H.; Schwarzmann, E.; Sheldrick, G. M. Gold (III) Oxide. *Acta Crystallogr. Sect. B* **1979**, *35*, 1435

(3) E.A. Moelwyn-Hughes, Physical Chemistry, 2nd ed., Pergamon, Oxford, 1961