ENHANCED BONDING OF GOLD NANOPARTICLES ON OXIDIZED TiO$_2$(110)

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Introduction

Finding of distinctive catalytic properties of dispersed gold nanoparticles on oxide supports [1] has stimulated extensive research activities [2, 3], and a general consensus now exists on several aspects of this system. The size of the gold particles significantly affects the catalytic activity, and the gold clusters must be smaller than 5 nm for high catalytic activity [2, 4]. The choice of the oxide support influences the catalytic activity, so there is a strong 'support effect' in addition to the 'size effect' [2]. However, the relation of the adhesion properties of nanosized gold to catalytic activity is still unresolved.

Here we present a study addressing the fundamental mechanisms of gold–oxide support adhesion by means of scanning tunneling microscopy (STM) and density functional theory (DFT) calculations. We compare the nucleation of Au clusters on one support material that had been prepared in different oxidation states. Rutile TiO$_2$(110) was chosen as the model support, because Au/TiO$_2$ is a good catalysts for CO oxidation at low temperatures [4, 5].

Experimental

The experiments were carried out in an ultrahigh vacuum (UHV) chamber with a base pressure of 3×10^{-11} Torr equipped with a homebuilt, temperature-variable STM [6]. The density of bridging oxygen (O$_{br}$) vacancies on freshly prepared TiO$_2$(110)–(1 × 1) samples was in the range of 5–8% ML, with 1 ML (monolayer) being the density of the (1 × 1) units, 5.2×10^{14}/cm^2. The DFT calculations were performed using the DACAPO package [7] with a plane-wave basis set (E$_{cut}$ = 25 Ry) and ultrasoft pseudopotentials. The TiO$_2$(110) surface was modelled using periodic slabs of three tri-layers, the first tri-layer being fully relaxed. A (4 × 2) surface unit cell and the theoretically derived lattice constants were used.

Results and discussions

The three TiO$_2$(110) supports chosen were (i) reduced having bridging oxygen vacancies (*r*-TiO$_2$(110)), (ii) hydrated having bridging hydroxyl groups (*h*-TiO$_2$(110)), and (iii) oxidized having oxygen ad-atoms (*o*-TiO$_2$(110)) [8]. After exposing these three different TiO$_2$ surfaces to Au (3% of a monolayer (ML)) at room temperature (RT), we observed quite different Au cluster morphologies. In case of the *r*-TiO$_2$(110) surface, numerous rather small Au clusters are distributed homogeneously on the terraces (Fig. 1a). In contrast, on *h*-TiO$_2$(110), we found fairly large Au clusters that decorate preferentially the step edges of the substrate, and no small Au clusters on the terraces are seen (Fig. 1b). However, on the *o*-TiO$_2$(110) surface we again found Au clusters to nucleate homogeneously on the terraces (Fig. 1c). Based on these results, we conclude that stronger Au–TiO$_2$ interactions exist on *r*- and *o*-TiO$_2$(110) than on *h*-TiO$_2$(110).

Given the stronger interactions with the *r*- and the *o*-TiO$_2$(110) surfaces, we explored the effect of heating on the Au cluster morphologies on these two TiO$_2$ supports. On *r*-TiO$_2$(110) we observed the formation of large Au$_n$ clusters with STM heights up to 10 Å after heating to 68 °C, while no such large clusters were identified on *o*-TiO$_2$(110) after identical thermal treatment. Based on a comparison of the Au height histograms, we propose that many stable
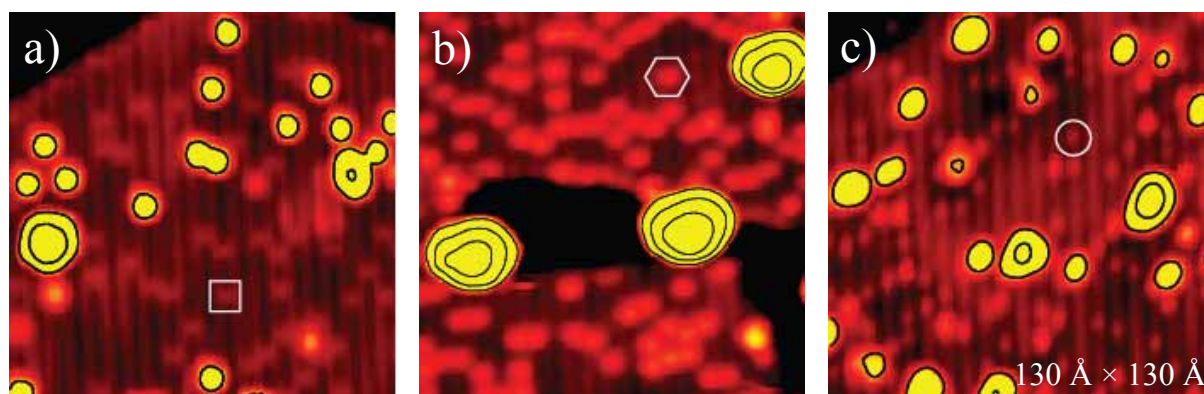
Figure 1. STM images of *r*-TiO$_2$(110) (a), *h*-TiO$_2$(110) (b) and *o*-TiO$_2$(110) (c) surfaces after 3% ML Au exposure at RT (1 ML is defined as 1.387×10^{15} atoms per cm^2 corresponding to Au(111)). Symbols indicate O$_{br}$ vacancies (□), H ad-atoms on O$_{br}$ sites (□) and O$_{ot}$ atoms in the Ti troughs (○).

Au$_n$ cluster configurations exist on *o*-TiO$_2$(110), while there are only few stable Au$_n$ cluster configurations on *r*-TiO$_2$(110) [9]. The Au–TiO$_2$ interaction is strongest on *o*-TiO$_2$(110).
To rationalize the STM results, we conducted DFT calculations addressing (i) the diffusion of Au monomers (Au$_1$) and (ii) the adhesion potential energies of selected Au$_n$ clusters on the three different TiO$_2$(110) surfaces of interest [9]. These calculations strongly corroborate the STM results, as we found that trapping of Au$_1$ is possible at RT on *r*- and *o*-TiO$_2$(110), but not on *h*-TiO$_2$(110). Furthermore, we revealed extraordinarily strong bonding of Au$_n$ clusters on the oxidized support, while we found that O$_{br}$ vacancies allow solely for the stabilization of Au$_1$ and Au$_3$ clusters. Finally, we analyzed the different Au–TiO$_2$ bonding mechanisms on the various model supports, and identified partially ionic bonding on *o*-TiO$_2$(110), i.e. the occurrence of cationic gold at the Au–*o*-TiO$_2$(110) interface [9].

Conclusions
A much stronger gold–oxide support adhesion exists on O-rich gold–support interfaces than on O-poor oxide support surfaces. This result suggests that in catalytic applications cationic gold at the Au–support interface might be a general feature.

References
[1] Haruta, M, Yamada, N., Kobayashi, T., Ijima, S., J. Catal. 115 (1989) 301-309.
[2] Meyer, R., Lemire, C., Shaikhutdinov, Sh.K., Freund, H.-J., Gold Bulletin 37 (2004) 72-124.
[3] Hashmi, A.S.K., Hutchings, G.J., Angew. Chem. Int. Ed. 45 (2006) 7896-7936.
[4] Valden, M., Lai, X., Luo, K., Guo, Q., Goodman, D.W., Science 281 (1998) 1647-1650.
[5] Kim, T.S., Stiehl, J.S., Reeves, C.T., Meyer, R.J., Mullins, C.B., J. Am. Chem. Soc. 125 (2003) 2018-2019.
[6] Lauritsen, J.V., Besenbacher, F., Adv. Catal. 50 (2006) 97-147.
[7] Bahn, S. R., Jacobsen, K. W., Comput. Sci. Eng. 4 (2002) 56; http://www.fysik.dtu.dk/campos.
[8] Wendt, S., Schaub, R., Matthiesen, J., Vestergaard, E.K., Wahlström, E., Rasmussen, M.D., Thostrup, P., Molina, L.M., Lægsgaard, E., Stensgaard, I., Hammer, B., Besenbacher, F., Surf. Sci. 598 (2005) 226-245.
[9] Matthey, D., Wang, J. G., Wendt, S., Matthiesen, J., Schaub, R., Lægsgaard, E., Hammer, B., Besenbacher, F., accepted for publication, see http://www.sciencemag.org/ (2007).