

Low temperature CO oxidation on differently prepared TiO₂(110) supported Au catalysts

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Abstract. The preparation of Au/TiO₂(110) planar catalysts and the low temperature (LT) oxidation of CO (in H₂) were investigated by Scanning Tunnelling Microscopy (STM), Auger-electron Spectroscopy (AES) and Thermal Programmed Reaction (TPR). The distribution and the mean size of the Au particles were modified by different pretreatments of the support: (A) Ar⁺ bombardment; deposition to (B) 0.05 ML of K or (C) 0.5 ML of Mo. It was shown that the mean size of the Au particles formed at RT is 3–4 nm on the clean TiO₂(110) surface and this value decreased to 1.5–2 nm for all pretreated supports. These 2D catalysts were tested in the LT oxidation (PROX) of CO. The same reaction conditions were kept for all experiments: the reaction chamber was filled up to 0.5 hPa O₂, 0.5 hPa CO and 9 hPa H₂ and the temperature of the catalyst was increased from 310 K to 400 K, 450 K or 500 K for 60 minutes. The clean, Ar⁺ pretreated, K or Mo preexposed oxide surfaces exhibited no activity in the PROX reaction. By the deposition of Au of 1–3 monolayer on to these surfaces, however, an enhancement of CO₂ in the gas phase was clearly detected. The clean TiO₂(110) surface proved to be the best support for gold, any modification of the support resulted in a loss of the activity. For all cases dependently on the pretreatments, the mean size of the Au particles increased significantly up to 4–8 nm in the PROX at 500 K.

1. Introduction

The nanostructured gold exhibits an extremely large activity at LT in several reactions like CO oxidation, NO reduction, hydrocarbon reforming and photocatalytic azo-dye degradation [1–5]. Because of its technological importance, the preferential oxidation of CO at low temperature in H₂ ambient became recently one of the most studied catalytic reactions [6–16]. In search of the best catalyst, several different supports and supported metals were tested (see also the references therein): Au on TiO₂ [1, 2, 6, 8–11], Fe₂O₃ [1, 6, 15], Fe₂O₃-MgO [6], NO_x [6], CoO_x [4], ZrO₂ [10], Al₂O₃ [10,11], MgAl₂O₄ [11] and Pt on SnO₂ [7], Al₂O₃ [7], C-vulcan [7], CeO₂ [12], Pd on CeO₂ [12] moreover Au-Cu on TiO₂-nanotube [16]. By comparing the activity of these catalysts, it turned out that the reducible oxides (like TiO₂ and Fe₂O₃) are the most efficient supports, probably because of their oxygen adsorbing and storing ability [1, 6]. In the case of these oxides the effect of the particle size is much smaller than on more stable (inert) ones (like Al₂O₃ or SiO₂) on which the high activity can be achieved only at very fine Au dispersity [6]. The presence of H₂ in the gas phase decreased the differences of the PROX reaction rates for the different supports, probably by activating the O₂ adsorption from the gas phase [10]. The main route for the oxygen supply is presumably the molecular adsorption of oxygen on the defect sites of the oxide supports in the form of O₂⁻ species [7]. In order to

identify the active sites of these catalysts on atomic scale, numerous studies were performed on planar model catalysts (2DMC). Most of the studies were executed on Au/TiO₂(110) where the important features of the particle formation are well known [17-25]. The bonding of the gold atoms (low coverage limit) is highly preferred on the oxygen defect sites, moreover, the bonding on defect free regions can sensitively vary with the particle size as it was shown by theoretical calculations [26-28]. The formation of Au nanoparticles and the crucial coverage for the change of the 2D growth mode into a 3D mode also were accurately demonstrated [23]. The thermal induced agglomeration of the gold nanoparticles was partially explained by the Ostwald roughening, but it also can be caused by the diffusion of the particles smaller than 2-3 nm [21, 25]. From the catalytical point of view, these works contributed substantially to the prior catalyst preparation but it is obvious that the exposure of these catalysts at higher pressures can strongly alter the mean size and the distribution of the particles [29, 30]. The study of the adsorption of CO on different size Au nanoparticles supported on FeO(111) thin films revealed that low coordinated Au particles are mainly responsible for the increased bonding ability of CO and this feature can not be connected to any type of quantum size effect [31]. In contrast to this, TiO₂(110) supported Au catalyst exhibited sensitive size dependence and the particles consisting of two atomic layers proved to be the most effective for catalyzing the oxidation of CO [32, 33]. An exceptional catalytic activity of Au octamers (Au₈) bonded to the oxygen vacancy defects of MgO(001) were detected by using size selective deposition method [34].

Besides the efforts for finding the optimal nanomorphology of the PROX catalysts, it is obviously an important task to study the appropriate conditions for the stabilization of the nanoparticles and the prevention of the sintering of those [34]. In this work we apply predeposited (potassium and molybdenum) to modify the interface between the TiO₂(110) support and the deposited gold. The main aim of this work is not only to follow the morphology changes of the supported Au particles in the PROX reaction but also to check the catalytic performance of these planar catalysts.

2. Experimental

The experiments were carried out in an UHV chamber equipped with a RT-STM, a CMA for AES and a QMS for gas analysis. A TiO₂(110) single crystal of 5 x 5 x 1 mm³ was stuck to a Ta-filament with an oxide adhesive (ceramobond-571, AREMCO Products) and mounted on a transferable sample holder. It was heated by flowing current through the Ta-filament. The temperature was measured by a thermocouple (K-type) stuck onto the side of the sample.

The cleanliness of the probe surface and the metal adlayers were checked by AES. Mo and Au were deposited by a commercial MVD source equipped by Mo rod and Au powder of high purity (99.95 %) filled in a C-crucible. Potassium was deposited by a SAES alkali source. The coverage of K and Mo is expressed in equivalent monolayer (eqML) which corresponds to approximately 1.5×10^{15} atom cm⁻² and calibrated by the relative AES intensity (I_{K252} / I_{Ti385} and I_{Mo185} / I_{Ti385}) measured after the deposition at room temperature [25, 36]. The actual coverage of Au was calculated by the determination of the volume of the particles [25]. Electrochemically edged W-tips were used for STM imaging (+1.5 V and 0.2 nA, typically) and they were sharpened "in situ". The reaction chamber of 3.2 dm³ was connected to the main UHV chamber by quartz capillary. While the reaction chamber was filled up with CO of 5×10^{-1} hPa, O₂ of 5×10^{-1} hPa and H₂ of 9 hPa, the pressure of 2×10^{-7} hPa was measured in the main chamber evacuated by an iongetter pump. The gas content of the reaction chamber decreased gradually because approximately 5-6 % of the filled gas flew through the capillary an hour. The next procedure was executed in all PROX experiments in this work: (i) the transfer of the prepared sample into the reaction chamber; (ii) admission of the gases described above; (iii) switching the MS on and waiting for stabilization of the intensities; (iv) start a reaction cycle consisting of 60 minutes at 310 K, annealing ($\beta = 2 \text{ K s}^{-1}$) to the reaction temperature ($T_{Re} = 400\text{K}, 450 \text{ K}$ or 500 K), keeping the temperature for 60 minutes at T_{Re} , cooling back to room temperature and keeping at RT for 60 minutes. The content of CO₂ accumulated in the closed reaction chamber was calibrated by admission of an appropriate amount of CO₂ into the reaction chamber in a separate experiment. The surface concentration of the gold atoms was estimated on the basis of the assumption

of coin shape Au nanoparticles. Regarding to the amount of the active sites in the present work, it was assumed that all of the surface gold atoms participate in the reaction. All of the kinetics data are calculated for the particle distribution measured at the beginning of the reaction.

3. Results and discussion

3.1. Au supported on clean and Ar⁺ bombarded TiO₂(110) surface. The TiO₂(110) samples used in this work exhibited large atomic terraces (in order of 100 nm) separated by steps of [001]. The terraces exhibited additional 1D strands running in the direction of [001] and 0D dots distributed randomly on the surface. The interstrands regions (96-98 % of the total area of the probe) can be identified as bulk terminated 1x1 ordered surface where the light rows separated by 0.65 nm correspond to the 5-fold Ti⁴⁺ sites. More details about the structure of the clean TiO₂(110) support and also about the thermal behaviour of the deposited Au on clean and Ar⁺ treated surfaces can be found in a previous paper [25, 36]. The main conclusion of these works was that the generation of oxygen defect sites both by Ar⁺

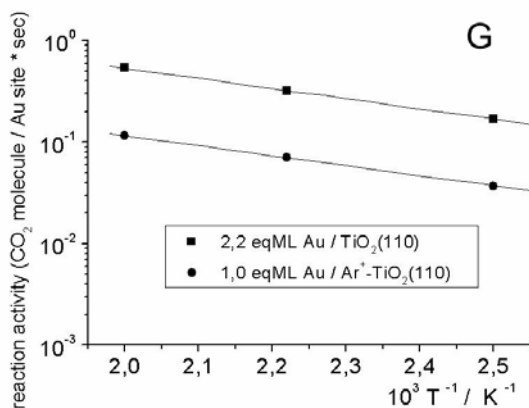
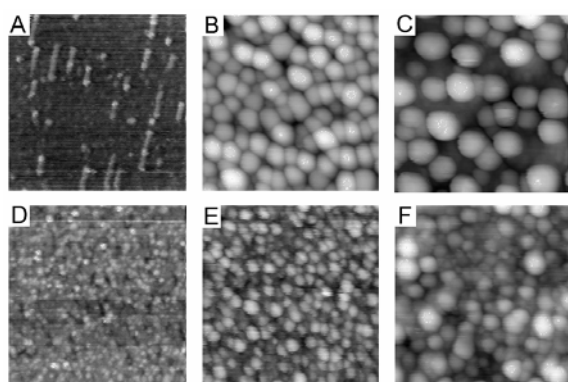


Figure 1: STM images of 50 x 50 nm² of (A) clean TiO₂(110) support, (B) after deposition of 2.2 eqML of Au, (C) following the PROX reaction at 500 K, (D) Ar⁺ treated clean TiO₂(110) surface, (E) after depositiopn 1,0 eqML of Au, (F) following the same PROX reaction (see also in the text). (G) Reaction activity in function of T⁻¹ for the two different catalysts.

can be compared for the two catalysts (Fig. 1G). It can be seen clearly that the Ar⁺ pretreatment significantly decreased the activity of the gold particles. It is worth mentioning that in spite of the different amount of Au deposited to the surfaces, the concentration of the surface gold atoms (because of the different particle size) was nearly the same in the two cases. By taking into account the different particle diameters and distributions, the concentration of the Au atoms at the perimeter (outline) of the nanoparticles is at least 2-3 times less for the untreated TiO₂(110) surface. It means an even larger difference in the activity if one assumes that only the perimeter atoms participate in the PROX

treatment or by chemical reaction (formation of surface K_xO_y) results in an increased wetting ability of gold.

A characteristic STM image (50 x 50 nm²) taken up on the clean TiO₂(110) surface decorated with outrising strings in the direction of [001] is shown in Fig. 1A. The Ar⁺ treatment (0,5 keV, 1x10⁻⁵ A cm⁻²) of this surface results in the TiO_x nanodots of 1-2 nm (Fig. 1D). The morphology of the model catalyst after the deposition of 2.2 eqML or 1.0 eqML of Au on to the clean and the ion treated surfaces can be seen in Fig. 1B, E, respectively. On the clean surface the average size of the particles is 4-5 nm while in the case of the Ar⁺ treated surface this value is significantly smaller, about 2 nm. This behaviour can be interpreted by the stronger bonding of the Au atoms to the oxygen defect sites resulting in the enhancement of the formation of Au seeds. A significant change of this morphology can be seen on the catalysts after three cycles (at 500 K, 450 K and 400 K) of the PROX reactions (see above): in the case of the clean support the particle diameter increased from 4-5 nm up to 7-8 nm while in the case of the treated support the 1-2 nm particles sintered in ones of 2-5 nm with a rather wide size distribution (Fig. 1 C, F). By plotting the reaction activities (number of CO₂ molecules formed on one Au atom a second) in the function of 10³ T⁻¹, the activities can be

reaction. At the same time the slope of the two curves in Fig 2 G are similar which means an approximately same activation energy of $18 \pm 2 \text{ kJ mol}^{-1}$ which is a very similar value that was found in the case of the polycrystalline Au/TiO₂ catalysts [6, 7].

3.2. Au supported on TiO₂(110) surface deposited by K and Mo. In this section the effect of two differently predeposited additives will be studied. Both K and Mo have a larger affinity to the surface oxygen than the Ti atoms have, therefore, they are able to reduce the TiO₂(110) surface. Additionally, the potassium oxides are more stable (have a larger band gap), and the formation of Mo oxides is rather sensitive for the local oxidation state of the TiO₂ substrate sublayers [36-38]. The STM images of $50 \times 50 \text{ nm}^2$ in Fig 2A, D depict the surface after the deposition of 0.15 eqML of K and 0.5 eqML of Mo, respectively. In both cases the surface exhibits the presence of nanodots of 1 nm. The deposition of Au on these surfaces results in formation of Au nanoparticles of 2-3 layers high with diameter of 2.5 nm. In this case the Au nanoclusters are obviously smaller than at the Au/TiO₂(110) system and similar to the case of Au/TiO₂(110)-Ar⁺ treated system. The STM pictures taken up after the PROX reaction performed at 500 K exhibited an explicit increase of the mean size of the particles (Fig. 2 B, E) which is larger on the K deposited surface. For the latter catalyst the reaction rate at 500 K is similar to the value measured on the clean oxide, at the same time the activation energy is much higher, $68 \pm 5 \text{ kJ mol}^{-1}$. In the case of the Mo precovered surface it was impossible to measure any activity. These results indicate that the PROX reaction depends sensitively on the Au/TiO₂ interface and rather insensitive for the size of the Au particles. The electron donation from the oxygen deficient sites to the Au nanoparticles has probably a poisoning effect on the reaction rate which can not be compensated by the stronger bonding of CO on the Au atoms of lower coordination.

4. Summary

The stability of the Au nanoparticles were studied on different 2D Au/TiO₂(110) catalyst used in the LT oxidation of CO. It was shown that the predeposition of the oxide surface with submonolayers of K or Mo results in a significant decrease in the mean size of the Au particles (from 3-4 nm to 1-2 nm). The PROX reaction runned at 500 K, however, causes a significant increase of this parameter up to 4-8 nm, depending on the pretreatment. All the modifications of the support described in this work caused an explicit poisoning of the PROX reaction. In the case of the K predeposition, the activation energy decreased significantly. Regarding to the TiO₂(110) surface predosed to Mo, the reaction rate decreased under the detection limit.

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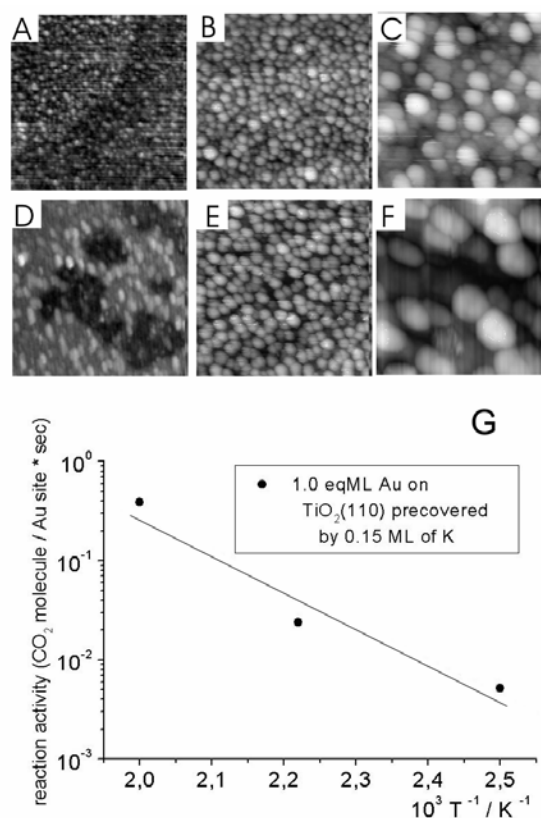


Figure 1: STM images of $50 \times 50 \text{ nm}^2$ of (A) TiO₂ (110) exposed to 0.50 eqML of Mo, (B) after deposition of 1.0 eqML of Au, (C) following the PROX reaction at 500 K, (D) TiO₂(110) exposed to 0.50 eqML of Mo, (E) after deposition 1,2 eqML of Au, (F) following the same PROX reaction (see also in the text). (G) Reaction activity in function of T^{-1} for the Au/K/ TiO₂(110) catalyst (see the text).

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