

## Model Ag/HOPG and Ag/Alumina Catalysts: STM and XPS Study

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### Abstract

Combined XPS and *ex situ* STM study of the specially prepared model supported silver catalysts was performed. The drastic difference in the Ag particle shape, size distribution and spreading over the support surface were observed for alumina support as compared with pyrographite one. This effect emphasizes the important influence of the substrate nature on the morphology and surface mobility of the supported metal particles.

### INTRODUCTION

The fundamental study of the supported metal catalysts is quite important for understanding and improving their catalytic behavior. The morphology of the metal particles (their shape and size), the distribution over the support surface as well as the interaction with substrate affect dramatically the catalytic activity [1, 2]. The support itself – the nature, surface structure and composition – in many respects determines these characteristics of the catalysts particles. The combination of scanning tunneling microscopy and X-ray photoelectron spectroscopy is very promising tool to study the supported catalysts as it gives the complementary information both about the particle/support morphology (STM) and about the surface composition and electronic structure (XPS).

Still, very often it is rather difficult to apply these techniques to the direct study of the “real” *i. e.* industrial catalysts – either due to methodical restrictions or because the obtained data result in the overcomplicated or ambiguous interpretation. The usual oxide support samples are non-conductive (except for titania and MgO single crystals [3]) and therefore they could not be studied directly by STM technique. To avoid these problems the special model catalytic systems are usually prepared. Among these, Me/HOPG (*i. e.* metal particles deposit-

ed at Highly Oriented Pyrolytic Graphite) systems are the simplest and most widely used ones. Still, the results and conclusions obtained for HOPG systems can hardly be adapted to the oxide supports (to say, alumina or silica), because the nature and the strength of the metal to substrate adhesion forces are absolutely different in these cases.

Some authors have reported on the successful application of Atomic Force Microscopy for the investigation of the alumina supported catalysts [4], and another team has achieved the interesting STM results by the preparation of very thin – and therefore remaining conductive – alumina layer over the surface of NiAl single crystal [5, 6]. We have prepared another model support by the formation of the conductive alumina film over the metal substrate – Fe–Cr–Al alloy. Here we present the first results of the comparative XPS and *ex situ* STM study of two model supported silver catalysts – Ag/HOPG and Ag/Al<sub>2</sub>O<sub>3</sub> film.

### EXPERIMENTAL

The microscopy study has been carried out on air by means of STM/AFM multi-microscope SMM2000T equipped with Pt tips cut by scissors. The magnification has been varied from  $2 \cdot 10^4$  for the maximal scan range of

$6 \times 6 \mu\text{m}$  to  $10^7$  for the precise scans. For HOPG samples STM pictures were acquired with 0.2 V bias and 3 nA tunneling current, while for alumina ones the scanning parameters were varied up to 2.2 V and 10 nA, correspondingly. The practical vertical (1 nm) and lateral (3 nm) resolution was evaluated by using fresh cleaved HOPG sample. To prove the received STM pictures are representative the sets of several (from ten to twenty) points at every chosen magnification were explored for the each sample. The histograms were plotted after analyzing of more than hundred observed particles.

All stages of the sample preparation as well as XPS measurements were performed in the preparation chamber of VG ESCALAB HP electron spectrometer. XPS spectra were recorded using  $\text{AlK}_{\alpha}$  irradiation and calibrated against  $\text{Au } 4f_{7/2}$  (BE = 84.0 eV) and  $\text{Cu } 2p_{3/2}$  (BE = 932.7 eV) lines [7]. For the vapour deposition of metal particles on HOPG samples we have used the “silver droplet” source pre-made by melting of Ag wire wrapped around the tungsten wire spiral. The distance between the source and target was *ca.* 25 mm. To prepare Ag/alumina samples the similar construction was applied: the massive Ag (of 99.99 purity) slab was inserted inside the tungsten wire spiral. In this case the source was moved very close to the sample (1–2 mm), so the substrate temperature was monitored. The temperature of the support sample and Ag source were measured by K-type thermocouples attached to back side of the sample holder and very near to the piece of silver, correspondingly. Sample temperature had not exceeded 70 °C during deposition. The pieces of 0.6 mm thick foil of ALFA-IV alloy (Allegheny Ludlum Corp.) have been used to prepare alumina samples. The major composition of the alloy includes Fe (74 %), Cr (20 %) and Al (5 %).

## RESULTS AND DISCUSSION

### *The study of Ag/HOPG system*

The STM investigation of the Ag/HOPG samples has proved that the particles morphology strictly depends on the properties of the support. We have found the “decoration” effect

when silver particles were preferentially located at the polyatomic steps or the damaged/distorted patches of graphite surface. Such particles had usually the hemispherical shape in contrast to their spheroid mates at flat surface. As silver particles demonstrate the preferential localization at specific patches, we assume that they have the high mobility over the graphite surface during the vapour deposition and, therefore, the temperature of the Ag source would be determinative for the particle size distribution.

Indeed, raising the Ag source temperature has noticeably changed the size distribution (Fig. 1, *a, b*). It became more even – due to decreasing of the smallest (<10 nm) particles amount and broader – as the very large (>120 nm) particles appeared. The probable explanations are:

– at higher temperature the hotter smallest particles can diffuse over the surface for the

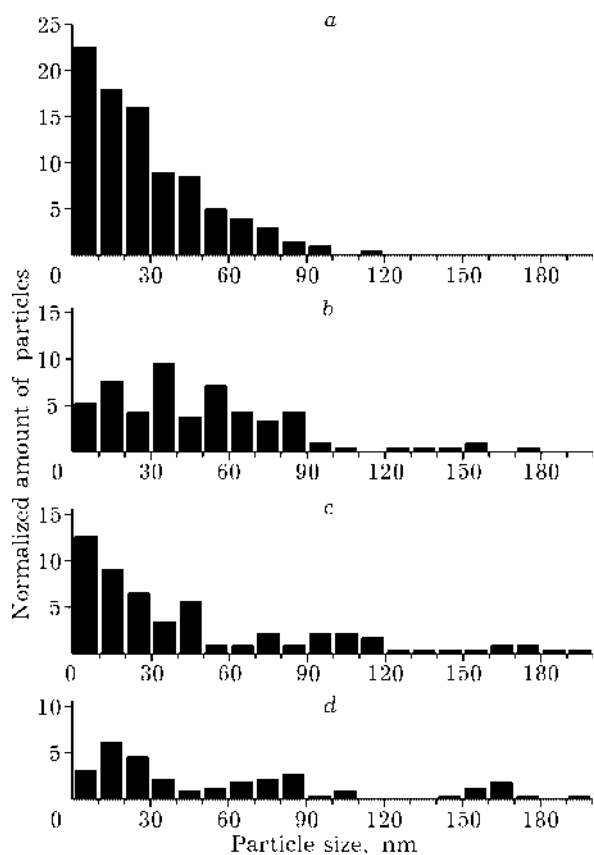


Fig. 1. Particles size distribution histograms: for fresh samples prepared at different Ag source temperature (*a, b*) and after samples heating at 570 K for 10 min (*c, d*). Samples prepared at 670–720 K (*a, c*) and 820–870 K (*b, d*).

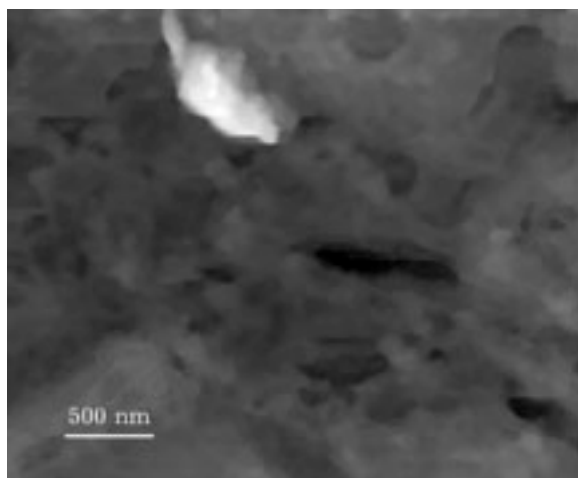


Fig. 2. STM picture of Ag/HOPG sample with very large silver particle ( $3.3 \mu\text{m} \times 2.7 \mu\text{m} \times 73 \text{ nm}$ ).

longer time and distance until they meet another one(s) or any graphite surface defect;

- the larger Ag clusters can initially leave the source;
- the incident Ag flux upon the sample surface is more dense, and so silver particles impacted the surface closer to each other.

The role of the surface diffusion is illustrated by the results of the 10 min heating of Ag/HOPG samples at 570 K (see Fig. 1, c, d). One can see that again the fraction of smaller particles drops and very large Ag “pieces” are formed, but the size distribution remains asymmetric. Note that the sample prepared at higher temperature demonstrates the minimal changes of size distribution (see Fig. 1, b, d), probably because highly mobile silver particles have already occupied preferential positions at the support surface just during the deposition. As concerning with sample annealing effects (*i. e.* “thermal stability” of deposited silver particles), there were two main interdependent effects: the growth of very large objects at the flat areas of the surface and the migration of

smaller particles out of there. At higher magnifications we have succeeded to reveal that the observed formations consist of the several smaller particles. Figure 2 shows one of such agglomerates with the lateral size of 400 nm and the height of 40 nm (the latter is characteristics for the separate particles). We suppose that the stronger bonded to the surface particles (either fixed at point imperfections or just of larger size) are the centers of such agglomeration. One should note that we have failed to resolve the “fine structure” of medium (30–60 nm) objects. It obviously means the smallest particles are merged each other to form the united larger ones either by ripening mechanism or through sintering together. The shape of the larger particles is mainly hemispherical while the isolated ones remain quasi-spherical, so that one probably can use the height profiles of the observed particles to rule out whether they are agglomerated or not.

XPS data confirm the assumption made on the basis of STM pictures (see Table 1). Raising the deposition temperature leads to the higher Ag load at the surface (even for shorter deposition time) and just the slight decrease of Ag 3d XPS signal after annealing means no significant coarsening of the silver particles occurs for this sample. Vice versa, sintering of the smaller metal particles observed by STM for HOPG4 sample is proved by decreasing of Ag/C ratio due to silver self-screening effect.

Thus, it is Ag source temperature that contributes mainly to the resulted patterns of the size distribution and their changes after the samples annealing. Still, the further cross-linked experiments (with both HOPG sample and Ag source temperatures to be varied) are in need for better understanding these surface rearrangements.

TABLE 1

Silver deposition parameters and XPS data for Ag/HOPG samples

Sample ID	Deposition temperature, K	Deposition time, s	Ag/C before heating*	Ag/C after heating*
HOPG2	820–870	30	0.014	0.013
HOPG4	670–720	510	0.0098	0.0077

\*As estimated by XPS.

### The preparation of the model alumina support

Before the alumina film preparation all alloy samples were cleaned by argon etching to remove the organic contamination and oxidized layer of the surface. Then the samples were annealed in vacuum at 870–930 K for 10–15 min. XPS spectra show that this procedure causes the dramatic increase of Al 2s and O 1s intensity (Fig. 3, *a*, *b*) indicating the surface segregation of aluminum and bulk dissolved oxygen. Al 2s binding energy value of the main peak component (~120.1 eV) corresponds to oxide

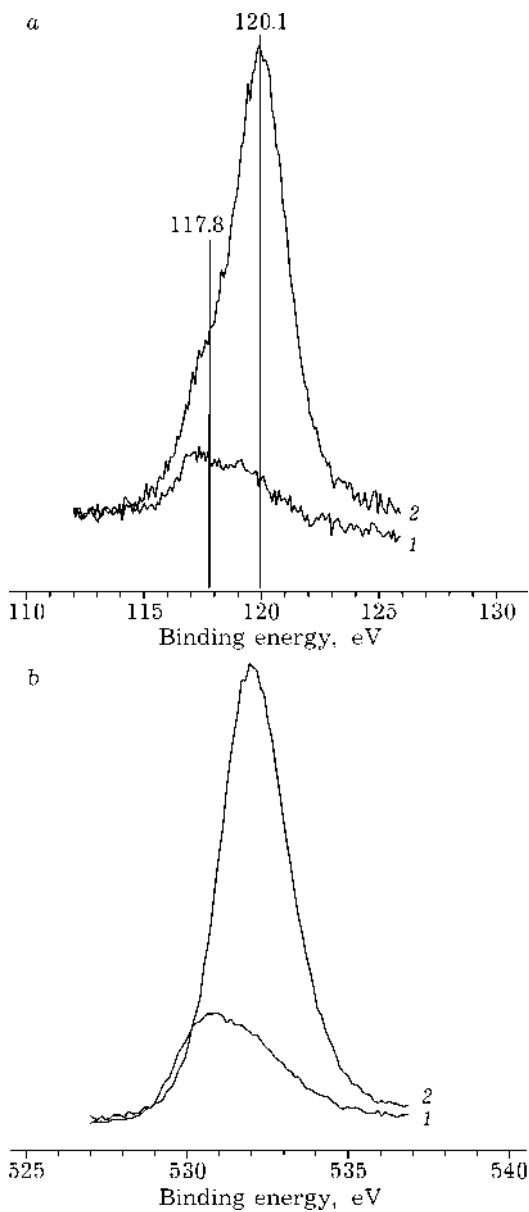


Fig. 3. Al 2s spectra (*a*) and O 1s spectra (*b*) before (curve 1) and after (curve 2) the alloy sample annealing.

state of aluminum [7]. Still, some Al remains in metallic state, but the variation of the electron take-off angle results in the noticeable drop of its intensity, so that one could resume this component to originate from unaltered alloy lattice beneath the prepared alumina film. Indeed, the analysis of Fe 2p and Cr 2p peak positions demonstrates that no oxidation of these elements occurs, and the peak intensities are attenuated due to screening effect of alumina overlayer. We have used the latter effect to estimate that the thickness of the produced Al<sub>2</sub>O<sub>3</sub> films does not exceed 4.5 nm [8].

STM investigation of the films shows that their surface consists of the irregular but rather plain formations of very large sizes (see Fig. 4) – for 6×6 μm scans the heights difference is hundreds nanometers. At higher magnifications the sample surface looks very flat (the height drop of 10–15 nm for 150×150 nm scans). No “particle-like” objects to misidentify them as silver particles are found.

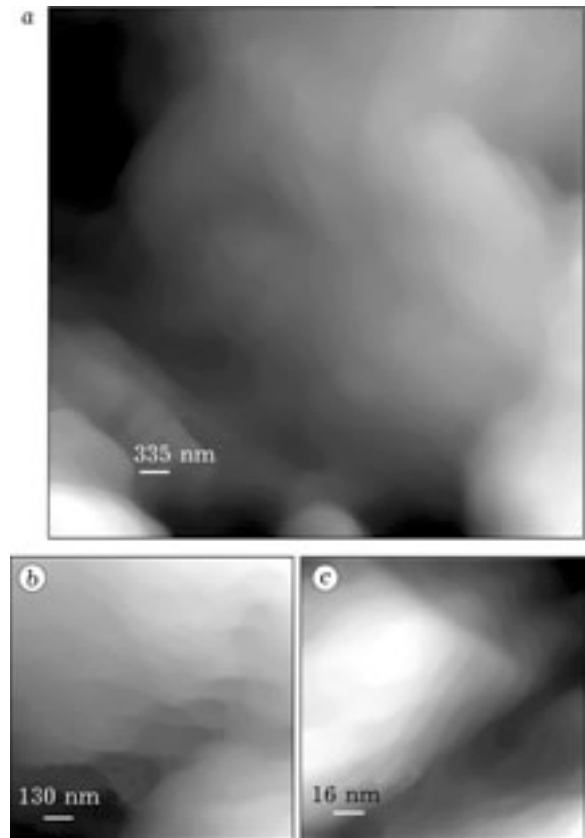


Fig. 4. STM pictures of clean surface of alumina film ( $U = 200$  mV,  $I = 3$  nA) at various magnifications: *a* – survey scan 5.9 μm × 5.9 μm × 600 nm; *b* – 1.2 μm × 1.2 μm × 250 nm; *c* – 150 nm × 150 nm × 16 nm.

TABLE 2

The parameters of alumina film and Ag/alumina samples preparation

Sample ID	Film preparation		$d^*$ , Å	Ag deposition		Ag/Al*
	$T$ , K	$\tau$ , s		$T$ , K	$\tau$ , s	
FCA1	870	600	45	700	960	0.028
FCA2	870	490	31	800	300	1.56
FCA3	930	600	5	750	300	0.188
				850	300	14.5

\* As estimated by XPS.

*The study of model Ag/Al<sub>2</sub>O<sub>3</sub> system*

After the detailed STM and XPS characterization of the produced alumina films the vapour deposition of silver has been performed. The Ag source temperature was varied from 650 K to 850 K and the duration of evaporation ranged from 5 to 16 min (see Table 2). However, XPS estimation of silver coverage revealed that below 750 K the procedure time became too long (several hours for one monolayer of silver). Here we present the results for the samples prepared at  $T \geq 750$  K.

The survey STM scans of the Ag/alumina samples show that silver particles are evenly

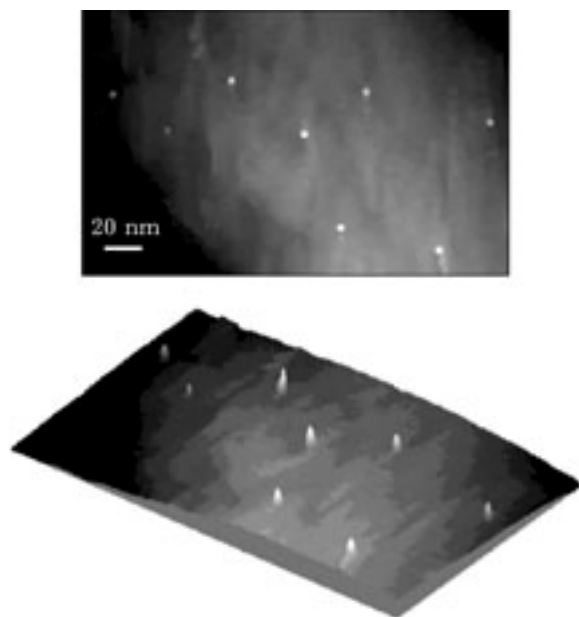


Fig. 5. STM scan (upper panel) and corresponding 3D-picture (lower panel) of isolated Ag particles at alumina surface (220 nm  $\times$  136 nm  $\times$  40 nm);  $U = -2000$  mV,  $I = 5$  nA.

distributed over the surface (see Fig. 5). The size distribution is very narrow and the maximal size of the particles does not exceed 15 nm. Now STM data explain the substantially higher Ag/Al atomic ratio as compared with Ag/C values for HOPG samples – the smaller silver particles do not exhibit XPS screening effect at all. The analysis of histograms (see Fig. 6) reveals that the effect of the silver source temperature is much slighter (but still observable) most likely due to the lack of the particles mobility over alumina surface. Probably the size of evaporated Ag clusters is mainly responsible for the observed difference in size distribution. The shape of all observed silver particles is quasi-spherical; the picture of such particle and the typical height profile are shown in Fig. 7.

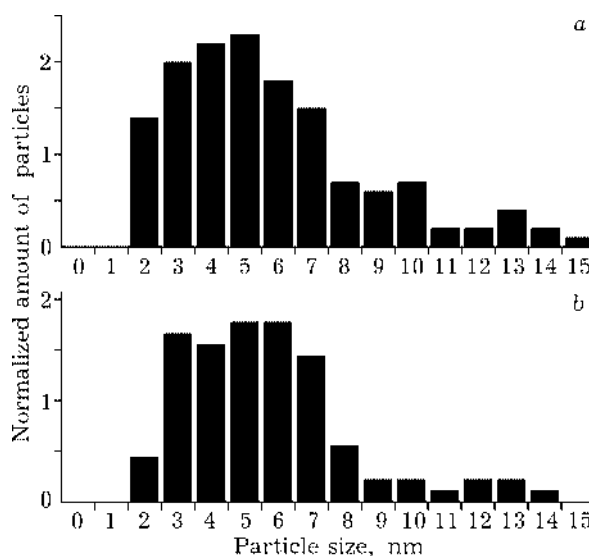


Fig. 6. Particles size distribution histograms: for Ag/alumina samples prepared at different Ag source temperature: *a* – 800 K; *b* – 750 K.

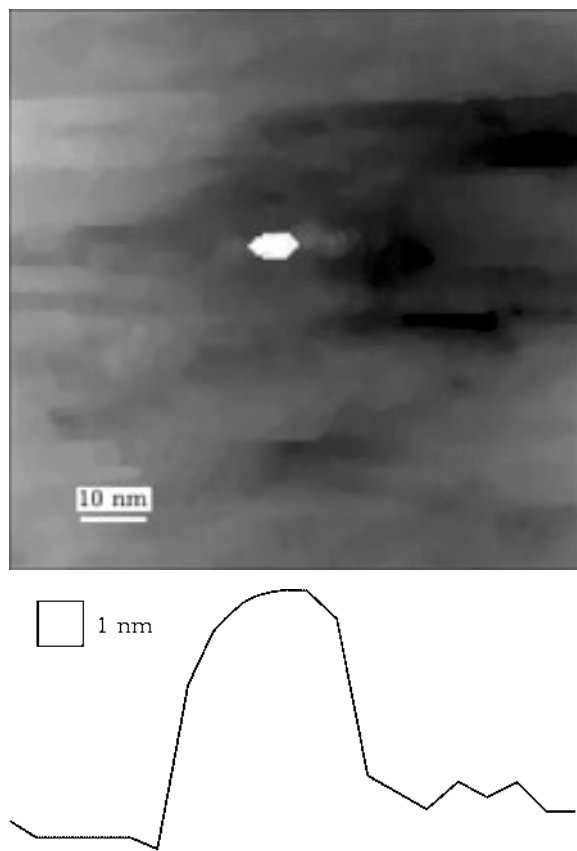


Fig. 7. Upper panel: STM image of single silver particle at the  $\text{Al}_2\text{O}_3$ -film sample ( $92 \text{ nm} \times 91 \text{ nm} \times 20 \text{ nm}$ ),  $U = 200 \text{ mV}$ ,  $I = 7 \text{ nA}$ . Lower panel: height profile of this particle (in vertical direction).

## CONCLUSION

Two model supported catalysts – Ag/HOPG and Ag/alumina – were prepared and studied by STM and XPS methods. The vacuum annealing of the HOPG supported samples at 570 K revealed silver particles to migrate over graphite surface and agglomerate to the larger formations. These observations indicated the very high mobility of silver particles at the inert support that results in the rather broad size distribution for the vapour

deposited metal particles. On the contrary, we have found the very narrow size distribution for alumina supported catalysts indicating the total immobilization of deposited Ag particles, obviously due to much stronger metal – support bonding. Thus it proved again the nature of the support to be very important for the thermal stability of supported metal catalysts both during their preparation and (especially) under the reaction conditions. Our preliminary research of the specially constructed model alumina supported catalysts have shown such systems to be very useful for the further investigations on the morphology and the stability of the oxide supported metal catalysts.

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