Kinetics and Catalysis, Vol. 45, No. 5, 2004, pp. 730–734. Translated from Kinetika i Kataliz, Vol. 45, No. 5, 2004, pp. 771–775.

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Application of Scanning Tunneling Microscopy and X-ray Photoelectron Spectroscopy in the Investigation of the Sintering of Ag/Al_2O_3 Model Supported Catalysts

A. V. Nartova and R. I. Kvon

Boreskov Institute of Catalysis, Siberian Division, Russian Academy of Sciences, Novosibirsk, 630090 Russia

Received July 4, 2003

Abstract—The results of a study of a specially prepared Ag/Al_2O_3 model system by scanning tunneling microscopy (STM) and X-ray photoelectron spectroscopy (XPS) are presented. The surface morphology of a model support (a thin alumina film on a conducting support) and a model supported catalyst (Ag/Al_2O_3) was characterized using STM. The first experimental results obtained in the STM and XPS study of the sintering of supported catalysts are reported, which demonstrate the capabilities of these techniques for studies of this kind.

INTRODUCTION

Thermal stability is one of the fundamental properties of supported metal catalysts [1–3]. The monitoring of morphological changes, that is, the detection of changes in parameters such as the particle size distribution of the supported metal over the surface and changes in the shape of particles before and after treatment, is a method for studying thermal stability.

The combined application of scanning tunneling microscopy (STM) and X-ray photoelectron spectroscopy (XPS) in the study of supported systems provides complementary data on both the morphology (STM) [4] and the chemical composition (XPS) [5] of metal particles and supports. However, physical techniques not always can be directly used for studying real systems, because of both methodological limitations and the complex and ambiguous nature of the data obtained experimentally. Therefore, special model systems which, on the one hand, meet the requirements imposed by the experimental techniques and, on the other hand, retain the main properties of real catalytic systems and obey the same laws, should be designed [6, 7].

One of the methodological requirements imposed by STM is the conductivity of a sample; therefore, oxide systems, which are of great interest in heterogeneous catalysis, cannot be studied directly (except for single crystals of titanium oxide and MgO [8]). However, it was found that a tunneling effect occurs in the case of a thin nonconducting film on a conducting substrate, and the morphology of these systems can be studied using STM. This fact was used for preparing model supports and supported systems based on aluminum oxide, which are suitable for STM studies [6, 9–12]. The results of an STM study of an ultrathin alumina film on the surface of an NiAl single crystal were published [9, 10]. Moreover, the $Pt/Al_2O_3/NiAl(110)$ and $Ag/Al_2O_3/NiAl(110)$ model systems were studied by STM [11, 12].

Here, we report the results of a combined STM–XPS study of a model system, which is an analog of a commercial Ag/Al_2O_3 catalyst, as well as the first results of an STM and XPS study of the effect of thermal treatment on the morphology of this system.

EXPERIMENTAL

The STM study was performed in air with the use of a CMM2000T microscope (ZAO KPD, Zelenograd, Russia) a maximum scanning range of 6×6 μm. The resolution of the instrument was 0.5 nm in which has vertical and 1 nm in the sample plane. Scissors-cut platinum/iridium tips were used in the experiments. The scanning parameters were varied over wide ranges: the tunneling voltage, from –4.5 to +4.5 V, and the tunneling current, from 3 to 10 nA. Because STM allows only local measurements, an array of points (from 20 to 30) over the surface were studied at each magnification for each sample in order to confirm the reliability and representativeness of the resulting STM images. The histograms of particle size distribution were constructed in each particular case based on an analysis of more than one hundred observed particles.

The XPS measurements were performed using an ESCALAB HP electron spectrometer with the use of AlK_α radiation. The XPS spectra were calibrated with reference to Au $4f_{7/2}$ (E_b = 84.0 eV) and Cu $2p_{3/2}$ (E_b = 932.7 eV) lines [13]. Samples were prepared in the preparation chamber of the spectrometer. The source of silver for deposition onto the surface of samples with alumina films was a coiled tungsten wire with a silver slab (of 99.99 purity) inside. The tungsten wire and the sample were heated resistively. K-type thermocouples, which were used for measuring the temperatures of the silver source and the substrate, were tightly fixed to the

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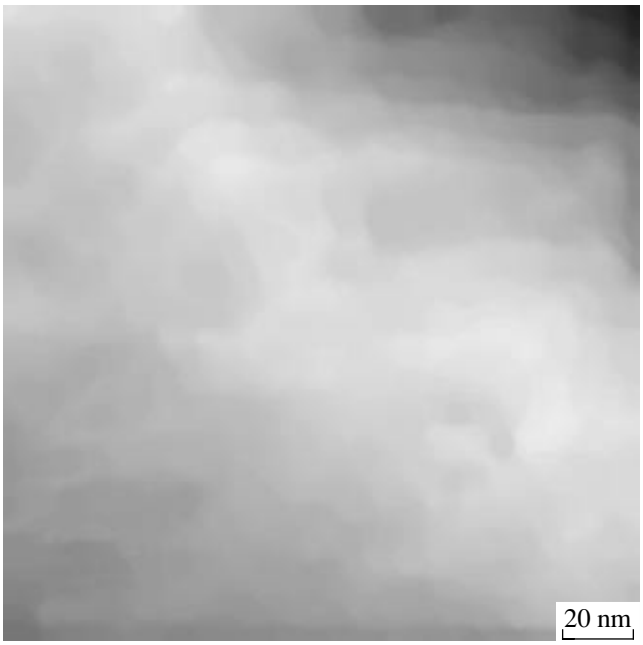

Fig. 1. STM image of the surface of an Al_2O_3 film (177 × 177 × 14 nm).

Fig. 2. STM image of the surface of sample 1 (Ag/Al_2O_3) (181 × 204 × 18 nm).

silver plate and the backside of the sample, respectively. To prepare the alumina samples, the foil of an ALFA-IV alloy (Allegheny Ludlum Corp.) was used; the main components of this alloy are Fe (74%), Cr (20%), and Al (5%). The Al2*s* (E_b = 118 eV) XPS line was used for analyzing the chemical state of aluminum, because the Cr 3*s* line (E_b = 75 eV) is close to the main Al 2*p* line (E_b = 73 eV); this results in overlapping of the lines and makes identification difficult [13]. The film thickness of Al_2O_3 was evaluated from attenuation in the intensity of the Fe 2*p* signal in the XPS spectra, which was due to screening by the film formed [14].

In accordance with the previously described procedure [15, 16], a series of samples of a model catalyst support as an alumina film on a conducting substrate was prepared. This model support was suitable for STM studies of supported catalytic systems. The method consisted of the vacuum heating of ALFA-IV foil. An analysis of XPS spectra demonstrated that the heating resulted in the formation of a continuous ultrathin film of Al_2O_3 on the foil surface. The estimated film thickness varied from 0.5 to 4.5 nm in various samples. The procedure used for the preparation of the support allowed us to change the thickness and ordering of Al_2O_3 films by varying sample heating temperature and time.

RESULTS AND DISCUSSION

An STM study of the surface morphology of this model support demonstrated that the surface was composed of disordered but sufficiently flat formations; it was free from particle-like objects, and its height changed smoothly [15]. At high magnifications, the surface appeared rather smooth (at scanning ranges of about 150 × 150–200 × 200 nm, the total height differences were generally no higher than 10–15 nm). Figure 1 shows the STM image of the surface of an alumina film.

After the STM and XPS characterization of the surfaces of the support samples, a series of samples of the Ag/Al_2O_3 model system was prepared [15, 16]. Silver was supported by vapor deposition in a vacuum. The use of deposition under various conditions (various silver source temperatures and deposition times) allowed us to prepare samples with different silver contents and particle size distributions. According to the XPS data, silver is in a metal state. An analysis of the survey STM scans demonstrated that particles were rather uniformly distributed over the surface. Figure 2 shows the STM image of small silver particles (to 5 nm in diameter) distributed over the surface of sample 1. Based on an analysis of the STM data, we plotted the histograms of particle size distribution (Figs. 3a, 3b) (samples 1 and 2 differed in silver source deposition temperatures, which were 750 or 800 K, respectively). The histograms indicate that the particle-size distribution was sufficiently narrow, and the maximum particle diameter was no greater than 15 nm. All of the observed particles were quasi-spherical in shape [15].

Sample 1 was heated in a vacuum at 570 K for 10 min. An analysis of the XPS spectra demonstrated that the chemical state of silver remained unchanged

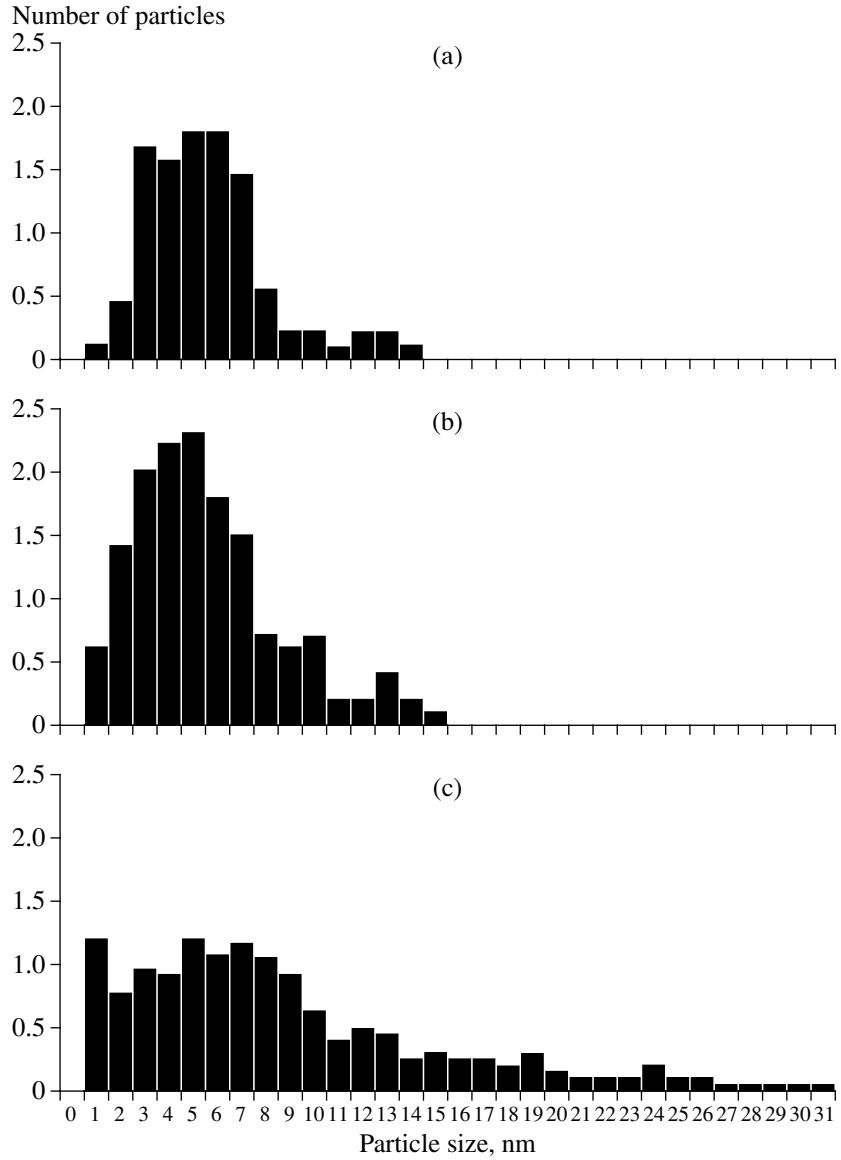

Fig. 3. Histograms of particle size distribution (the number of particles was normalized to the number of test points): (a) sample 2, (b) sample 1 (before heating), and (c) sample 1 (after heating).

after heating the sample (Fig. 4a). A decrease in the Ag 3*d* line intensity after heating can be explained by the self-screening of silver as the particle size increased. An analysis of the decomposition of the XPS spectrum of the Al 2*s* line before and after heating demonstrated that no changes in the ratio between oxidized and metal aluminum species resulted from heating (Fig. 4b). An increase in the intensity of the Al 2*s* line after heating can be explained by the partial removal of substrate screening by supported silver as a result of particle agglomeration.

Based on an analysis of the STM images, we plotted a histogram of particle size distribution (Fig. 3c). A comparison between the histograms representing before and after heating demonstrated that temperature treatment resulted in an increase in the number of particles of sizes smaller than 2 nm. It is likely that the fraction of these particles increased because of the intense agglomeration of silver clusters of sizes smaller than 1 nm, which cannot be resolved with this instrument. Small particles readily agglomerated even at 570 K; the particle size increased, and the particles become apparent in STM images. In other respects, the character of the distribution remained unchanged in principle as a result of heating; the distribution was only expanded to the region of coarser particles. As before, the distribution maximum occurred at 5 nm. Figure 5 demonstrates the STM image of "coarse" silver particles (greater than 10 nm in diameter) on the surface of sample 1 after heating. The agglomerates of coarser particles were not detected on the surface. Thus, even at 570 K morphological changes occurred, which

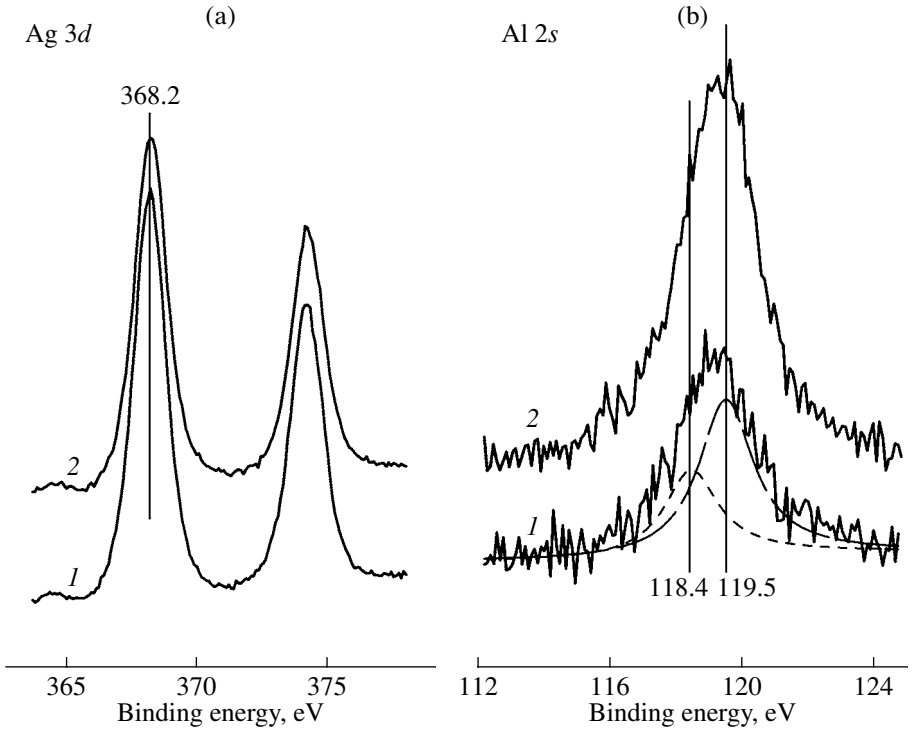

Fig. 4. XPS spectra of sample 1 (*1*) before and (*2*) after heating: (a) Ag 3*d* line and (b) Al 2*s* line.

Fig. 5. STM image of the surface of sample 1 (Ag/Al_2O_3) after heating ($190 \times 234 \times 177$ nm).

can be interpreted as an early stage of the agglomeration of supported silver particles. In this case, it is most likely that smaller particles (up to 4–5 nm), which are most mobile, made the greatest contribution.

Thus, in this work, the Ag/Al_2O_3 model system was prepared and characterized by STM and XPS techniques. A comparison between STM and XPS data obtained in a sample before and after heating in a vacuum suggests that morphological changes occurred even at 570 K. These changes are indicative of the occurrence of an early stage of the agglomeration of silver particles. In this case, smaller particles (upto 4–5 nm), which are most mobile, made the greatest contribution. The experimental studies of the Ag/Al_2O_3 model system demonstrate the potential of the combined use of STM and XPS techniques for investigations into the thermal stability of supported catalytic systems.

ACKNOWLEDGMENTS

We are grateful to B.A. Loginov for fruitful discussions of the results obtained by STM. This study was supported by CRDF (BRHE grant no. REC-008) and the Russian Foundation for Basic Research (grant no. 03-03-32297).

REFERENCES

1. Boreskov, G.K., *Geterogennyi kataliz* (Heterogeneous Catalysis), Moscow: Nauka, 1988, p. 304.

2. *Chemisorption and Reactivity on Supported and Thin Films*, Lambert, R.M. and Pacchioni, G., Eds., Kluwer Academic, 1997, p. 526.
3. Satterfield C.N., *Heterogeneous Catalysis in Practice* New York: McGraw-Hill, 1980.
4. Magonov, S.N. and Whangbo-Weinheim Myung-Hwan, *Surface Analysis with STM and AFM: Experimental and Theoretical Aspects of Image Analysis,* New York: VCH, 1996, p. 323.
5. Minachev, Kh.M. and Khodakov, Yu.S., Abstracts of Papers, *XII Mendeleevskii s"ezd po obshchei i prikladnoi khimii* (XII Mendeleev Congress on the General and Applied Chemistry), Moscow: Nauka, 1981, p. 213.
6. Rainer, D.R. and Goodman, D.W., *J. Mol. Catal., A: Chem.*, 1998, vol. 131, p. 259.
7. Shaikhutdinov, Sh.K. and Kochubei, D.I., *Usp. Khim.*, 1993, vol. 62, no. 5, p. 443.
8. Henry, C.R., *Surf. Sci. Rep.*, 1998, vol. 31, p. 235.
9. Jaeger, R.M., Kuhelenbeck, H., and Freund, H.-J., *Surf. Sci.*, 1991, vol. 259, p. 235.
10. Libuda, J., Winkelmann, F., Baumer, M., Freund, H.-J., Bertrams, Th., Neddermeyer, H., and Muller, K., *Surf. Sci.*, 1994, vol. 318, p. 61.
11. Bertrams, Th., Winkelmann, F., Uttich, Th., and Freund, H.-J., and Neddermeyer, H., *Surf. Sci.*, 1995, vols. 331–333, p. 1515.
12. Freund, H.-J., Dillmann, B., Ehrlich, D., Habel, M., and Jaeger, R.M., *J. Mol. Catal.*, 1993, vol. 82, p. 143.
13. Moulder, J.F., Stckle, W.F., Sobol, P.E., and Bomben, K.D., *Handbook of X-ray Photoelectron Spectroscopy*, Eden Prairie: Perkin-Elmer, 1992, p. 261.
14. *Practical Surface Analysis by Auger and X-ray Photoelectron Spectroscopy*, Briggs, D. and Seah, M.P., Eds., New York: Wiley, 1983, p. 600.
15. Nartova, A.V. and Kvon, R.I., *Russian-Dutch Workshop "Catalysis for Sustainable Development,"* Novosibirsk, 2002, p. 444.
16. Nartova, A.V. and Kvon, R.I., *Chemistry for Sustainable Development*, 2003, vol. 11, p. 209.