

Size Effect in Ethylene Oxidation over Silver Nanoparticles Supported on HOPG

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A preparation procedure for a model catalyst – stable silver nanoparticles with a narrow size distribution supported on highly oriented pyrolytic graphite (Ag/HOPG) – is presented. This procedure is carried out under ultra high vacuum conditions and consists of three stages: 1 – surface defect formation by soft Ar⁺-treatment; 2 – silver deposition; 3 – defect annealing by heating at $T = 300$ °C. The analysis of oxygen forms on a silver surface was carried out by *in-situ* X-ray photoelectron spectroscopy (XPS). The simultaneous presence of two oxygen species (electrophilic and nucleophilic) on the silver surface was found to be necessary for high activity of the model catalyst in ethylene epoxidation. An alternative explanation of the size effect in ethylene oxidation has been suggested: size dependence of the reaction rate may result from the existence of a ring-shaped zone at the edge of silver particles in which the surface concentration of nucleophilic oxygen is not uniform.

Keywords: Nanoparticles, Graphite, Scanning Tunneling Microscopy, X-ray Photoelectron Spectroscopy, Surface Oxygen Species, Ethylene Oxidation.

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1. INTRODUCTION

The industrial production of ethylene oxide by catalytic partial oxidation of ethylene over silver particles supported on α -Al₂O₃ is one of the most large-scale chemical processes whose annual output amounts to tens of millions tons [1]. This is a reason and motivating force for extensive and detailed studies of the reaction mechanism in an effort to increase reaction activity and selectivity and to decrease a catalyst cost. Nevertheless, there are some problems in understanding of this mechanism. Among them is an unusual size dependence of the catalyst activity [2], which decreases over particles smaller than 40nm. The established interpretation of this effect is the variation of the amount of intergrain boundaries that exist in silver particles [3]. However, a novel knowledge about the oxygen species active in this reaction [4] leads to a search for other possible interpretations. To resolve this discrepancy, oxygen species on a catalyst surface must be studied directly under reaction conditions (the pressure of the reaction mixture and the temperature of a catalyst). Such studies with real catalysts by surface sensitive methods are impossible because of the low surface concentration of the active component and masking it by signals from functional groups of the support (Al₂O₃). A possible solution of this problem may be the use of model catalysts deposited on oxygen-free supports. This paper is devoted to preparation and characterization of a model Ag / HOPG catalyst and its investigation under conditions of ethylene epoxidation.

2. EXPERIMENTAL

The preparation of Ag / HOPG samples and investigation of their thermal stability were carried out in a vacuum chambers of a SPECS spectrometer equipped with a source of monochromated X-ray radiation (AlK α , $h\nu = 1486.74$ eV) and a PHOIBOS-150-MCD-9 hemispherical analyzer. The sample preparation procedure included cleaning of the initial HOPG support (HOPG

SPI-3, Structure Probe Inc.) and annealing it in a high vacuum at 500 °C for 1 h. The purity of the surface was checked by recording a survey X-ray photoelectron spectrum and examining it for the presence of impurities. Defects on the HOPG surface were generated by soft Ar⁺ ion sputtering (argon pressure $P_{Ar} = 3.2 \times 10^{-6}$ mbar, accelerating voltage of 0.5 kV, treatment time of 2-3 s).

Silver was evaporated by electron-beam heating of the target (99.95 % Ag, Omicron EFM3 evaporation system) under constant conditions (accelerating voltage of 0.8 kV, emission current of 3.5 mA) and was then deposited on a support maintained at room temperature. The surface concentration of the metal on a support was controlled by varying the evaporation time. After Ag deposition, the samples were heated to 300 °C for stabilization of nanoparticles on surface defects to prevent their agglomeration. The necessity of the last stage was ascertained empirically and confirmed in our previous study [5].

Samples were examined at room temperature by scanning tunneling microscopy (STM) on a GPI_300.02 microscope, which provided atomically resolved images of the graphite surface. The STM images were obtained using a platinum tip. Scanning was performed in the tunneling current range from 0.5 to 1.0 nA and in the voltage range from –30 to –1500 mV. Image processing included average slope subtraction and drift elimination by means of the WS \times M software [6].

Catalytic properties of model catalysts were studied at the Innovative Station for In Situ Spectroscopy (ISSS beamline, BESSY II synchrotron radiation source, Berlin). The exciting radiation energy was set so that the initial kinetic energy of photoelectrons was the same (220 eV) for all lines examined. Ethylene oxide as a component of the product mixture was determined on a proton-transfer-reaction mass spectrometer (ionicon Analytik, Austria) in which H⁺ from the H₃O⁺ ion (produced in a special hydronium ion source) is transferred to the ethylene oxide molecule (C₂H₄O) and the resulting C₂H₅O⁺ ion is detected at $m/z = 45$.

3. MORPHOLOGY AND THERMAL STABILITY OF MODEL CATALYST

Fig. 1 shows STM images and corresponding particle size distributions for two samples prepared under identical conditions, but with silver deposited onto the support for different time intervals. The relative content of the supported metal was determined as a ratio of areas of the silver and carbon core electron peaks (S_{Ag3d} / S_{C1s}) and was designated as Ag / C. As seen from Fig. 1, an increase in the amount of evaporated metal leads to the growth of the mean diameter (d_{mean}) of silver nanoparticles from 8 to 40 nm. The surface of the sample with Ag / C = 0.4 (Fig. 1a) is uniformly covered with separate silver particles, and the number of particles that are in contact with one another is small. The Ag nanoparticles are characterized by a rather narrow size distribution with $d_{mean} = 8$ nm (Fig. 1c). The surface of the second sample, with Ag / C = 4.0 (Fig. 1b), is almost entirely covered with metal particles being in close contact and showing distinct interparticle

boundaries. As expected, the particle size distribution in this case is much wider and d_{mean} is about 40 nm (Fig. 1d).

The procedure that was used to prepare the Ag / HOPG model catalysts makes it possible to obtain materials with the preset size of the metal nanoparticles in the range 1–40 nm with a sufficiently narrow particle size distribution. Moreover, the obtained catalysts are stable under typical reaction temperatures (up to 250 °C), which was proved in a special experiment applied to check the upper temperature limit of the HOPG stability against oxidation.

Fig. 2 shows SEM images from the Ag / HOPG catalyst recorded after catalytic experiments at different temperatures.

These SEM images indicate that silver particles can promote the oxidation of the HOPG surface at temperatures higher than 250 °C, but at typical temperatures of ethylene epoxidation (180–230 °C) the Ag / HOPG sample remains stable against combustion of the HOPG.

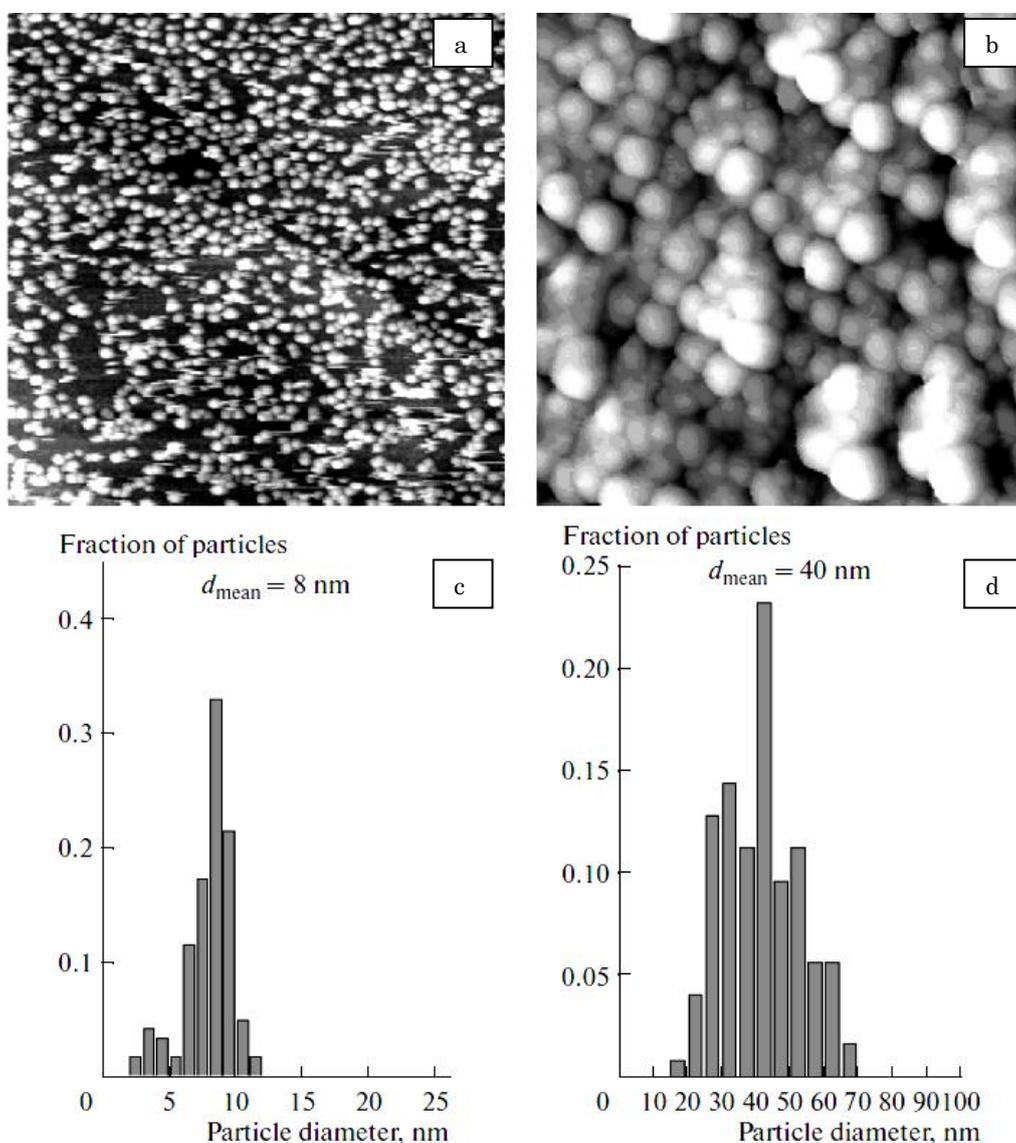


Fig. 1 – STM images (500 × 500 nm) and particle size distribution for Ag / HOPG with Ag / C = (a, c) 0.4 and (b, d) 4.0. Imaging conditions: a) $I = 1.0$ nA, $V = -30$ mV; b) $I = 0.5$ nA, $V = -500$ mV

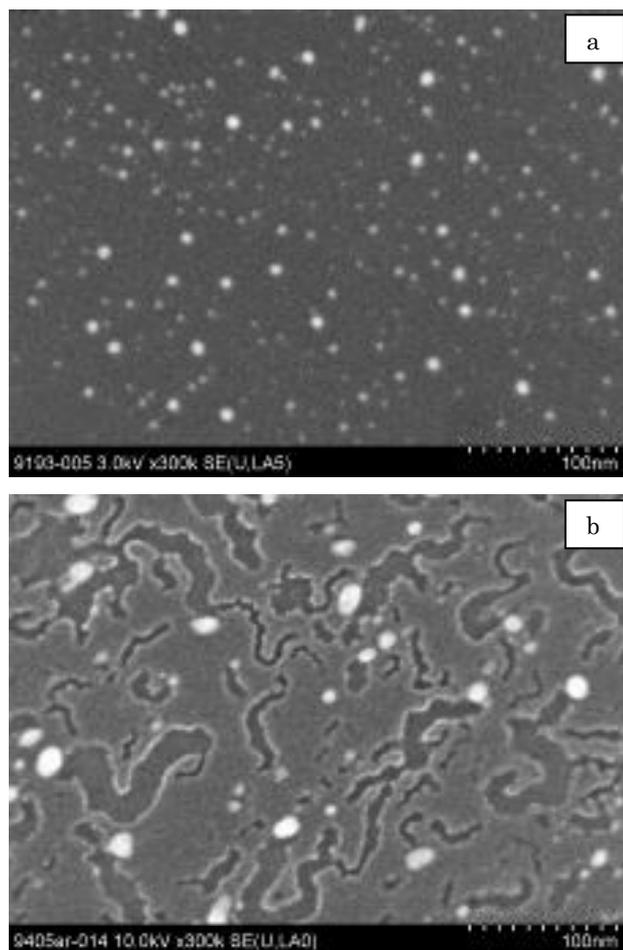


Fig. 2 SEM images (400 × 250 nm) of the Ag / HOPG catalyst after ethylene oxidation at 230 °C (a) and 250 °C (b), $P = 0.25$ mbar

Burning of graphite in the contact points with silver particles is accompanied by the migration of the metallic particles over the HOPG surface.

4. CATALYTIC PROPERTIES AND OXYGEN SPIECES

The Ag / HOPG samples were tested in ethylene oxidation by in situ XPS under the following conditions: ethylene:oxygen = 2 : 1, $P = 0.5$ mbar, $T = 150\text{--}210$ °C. The XPS spectra were recorded simultaneously with the ethylene oxide content in the reaction products detected by mass spectrometry [7]. The O1s spectra and the corresponding ethylene oxide mass spectra recorded for these samples between 150 and 210 °C are presented in Fig. 3. The O1s spectra of both samples show several photoelectron lines (Figs. 3a, 3b). According to the literature, the high energy region of the spectrum is the locus of the signals from oxygen d groups located on the graphite surface: the signals at BE = 531.6–532.2 eV are due to the groups with a C=O bond (carbonyl, carboxyl, and ester groups), and the signals at BE > 533 eV are due to the groups with a C–O bond (hydroxyl, carboxyl, and ether groups). The signals from the oxygen species adsorbed on the silver surface occur at lower energies (< 531 eV).

Under the reaction conditions, the silver particles

with a mean diameter of about 8 nm mainly accommodate oxygen species characterized by the O1s signal with BE = 530.8 ± 0.2 eV, which markedly increases with temperature (Fig. 3a). The absence of the $m/z = 45$ line due to ethylene oxide indicates that the sample with small Ag particles is inactive in epoxidation (Fig. 3c). The O1s spectrum of the sample with larger silver particles ($d_{\text{mean}} = 40$ nm, Ag / C = 4) recorded in the reaction medium at 150 °C shows two peaks due to oxygen species on the silver surface. These are the strong peak at 530.8 ± 0.2 eV and the weak peak at 529.2 ± 0.2 eV. Raising the temperature of the sample in the reaction medium to 210 °C considerably strengthens the peak at the lower binding energy. This indicates an increase in the concentration of oxygen adsorbed on silver.

Heating the sample in the reaction medium results in the formation of ethylene oxide (Fig. 3d). The sharp mass-spectrometric peak at the 30th minute is likely a consequence of the intense evolution of ethylene oxide from adsorbed complexes that are stable on the silver surface below 165 °C. After that, ethylene oxide formation comes to a steady-state level.

5. SIZE EFFECT

The obtained data make it possible to correlate the observed changes in the nature of the adsorbed oxygen species to the Ag particle size. The main oxygen species formed on small silver particles ($d_{\text{mean}} = 8$ nm) are characterized by BE = 530.8 ± 0.2 eV. According to the literature, these species can be identified both as electrophilic oxygen atoms adsorbed on the silver surface and as oxygen dissolved in the subsurface layers of the metal. The formation of surface carbonates, whose O1s binding energy has a similar value (~ 530.5 eV), can be excluded from consideration because their decomposition temperature is below 150 °C. The oxygen species formed under the reaction conditions on larger silver particles exhibit an additional component at BE = 529.2 ± 0.2 eV, which can be identified as nucleophilic oxygen. The simultaneous presence of adsorbed oxygen species with BE = 529.2 and 530.8 eV on the silver surface is the key factor in ethylene oxide formation on the Ag / HOPG model catalysts. Accordingly, the activity of the sample with larger Ag particles is due to the higher concentration of nucleophilic oxygen on its surface, implying an increase in the adsorbed ethylene coverage of the silver surface [2].

Furthermore, comparative analysis of O1s line shapes in the region of BE = 532–536 eV prompts to assume the noticeable influence of the silver/support interface around the particle perimeter onto the nature of oxygen species on the silver surface. Actually, this assumption permits the existence of some ring-shaped zone at the particle boundaries (and a few nanometers wide) where nucleophilic oxygen is absent or exists in insufficient concentrations. Such an effect can not be explained only in terms of a silver structure. Most likely, it can be explained by the influence of specific chemical properties of the silver / support interface. A crucial role in these properties may belong to hydroxyl and hydroxyl-groups adsorbed around particles boundaries.

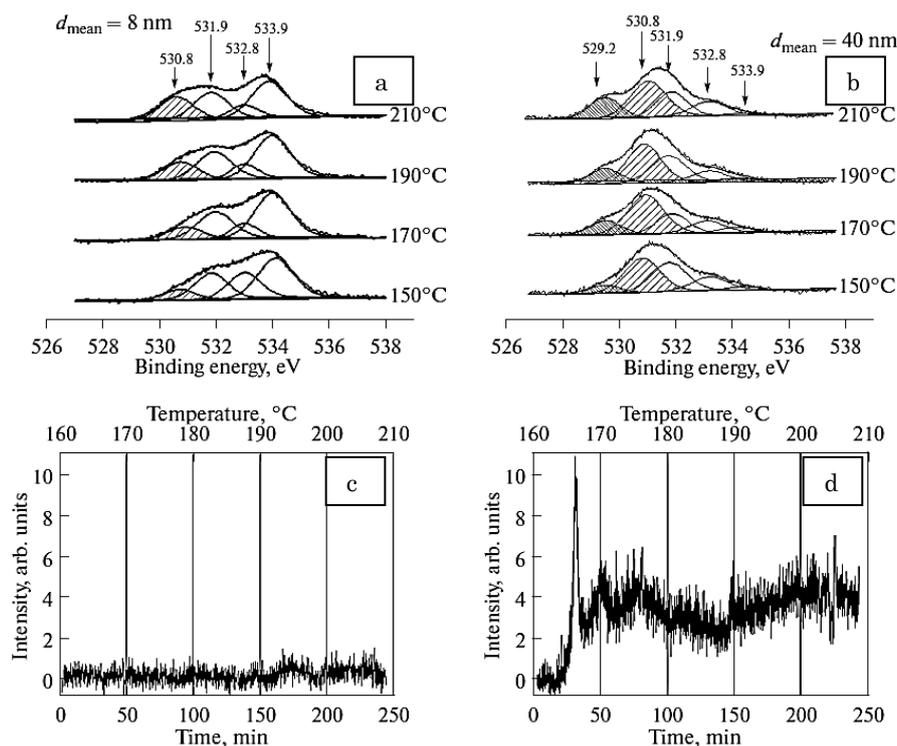


Fig. 3 – O1s photoelectron spectra of Ag/HOPG samples with Ag / C = 0.4 (a) and 4.0 (b) and a yield of ethylene oxide (c, d) formed on these samples as a function of temperature and reaction time. Experimental conditions: $C_2H_4 : O_2 = 2 : 1$, $P = 0.5$ mbar. The mean Ag particle size is indicated on panels (a) and (b). The signals from the oxygen species adsorbed on silver are hatched

Thus, thermal evaporation of silver on a defect-containing HOPG surface provides a means to obtain model catalysts with a narrow and variable particle size distribution in the nanometer range. The resulting catalysts are sintering-resistant at temperatures up to 250 °C. In this study, Ag / HOPG catalysts with different Ag particle sizes have been tested in ethylene epoxidation using in situ XPS. The most abundant oxygen species formed on silver particles ~ 8 nm in diameter in the C_2H_4 / O_2 reaction mixture is electrophilic

oxygen. On larger silver particles 30-50 nm in diameter, the formation of nucleophilic oxygen species also takes place. The presence of both adsorbed oxygen species makes the sample with larger silver particles be active in ethylene oxide formation.

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