Mendeleev Commun., 1998, 8(3), 100–101

Catalytic and structural properties of ultradispersed silver powder, prepared by a wire explosion technique

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Ultradispersed silver powder obtained by electric explosion revealed 100% selectivity in the catalytic epoxidation of ethylene with molecular oxygen.

Interest in the study of the catalytic properties of energy-saturated ultradispersed metals obtained by electric explosion of wires in gaseous media has increased in recent years.[1] They have been found to be more active and selective than ordinary metal powders in several catalytic reactions.[2] Unfortunately, the literature does not provide data on the structure of ultradispersed powders (UDP), which would make it possible to explain their unusual catalytic properties.

In this work, we have studied the structure of silver UDP exploded in an argon atmosphere, to explain its extremely high selectivity in ethylene epoxidation. For comparison, similar studies were carried out with ordinary catalysts (Ag powder, Ag/C) prepared by equilibrium procedures.

The catalytic activity was measured in a flow-circulation set-up described elsewhere.[3] In comparison with ordinary Ag powder, the activity of UDP decreases more rapidly with time, whereas the activity of the Ag/C catalyst remains almost unchanged (Figure 1). Under nearly steady state conditions, the activity of the samples follows the order: ordinary powder >> >> Ag/C > UDP. The selectivity changes in the opposite order, *i.e.* the ultradispersed powder shows the highest selectivity in epoxidation (90%), while the ordinary silver powder has the lowest selectivity (40%).

Preliminary treatment of UDP and Ag/C samples with oxygen at enhanced temperatures (230–260 °C) decreases their catalytic activity but sharply increases their selectivity (Figure 1). However, the selectivity of the ordinary powder remains practically unchanged. Almost 100% selectivity with respect to ethylene oxide is achieved in the case of the ultradispersed powder. This is surprising for the gas-phase production of ethylene oxide on solid catalysts, since such high selectivities have previously been observed only in homogeneous epoxidation of olefins by peroxide compounds.

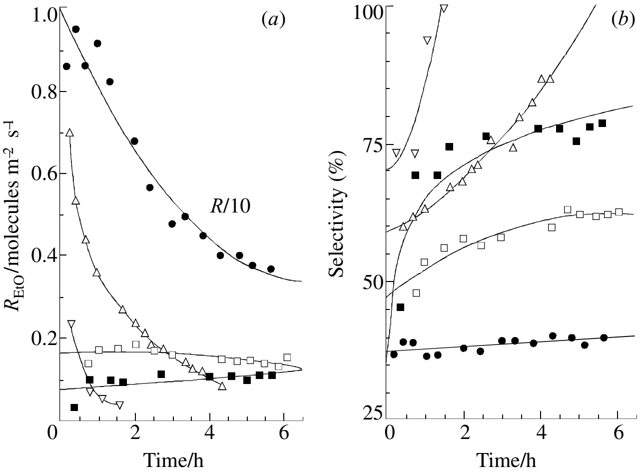

Figure 1 Time dependences of epoxidation rate (*a*) and selectivity with respect to ethylene oxide (*b*) at 230 °C on different samples: ●, ordinary Ag powder; △, Ag UDP; ▽, Ag UDP preoxidized at 260 °C for 2 h; □, Ag/C; ■, Ag/C preoxidised at 240 °C for 2 h. Feed gas: C_2H_4 (2%), O_2 (7%), He (91%).

According to HREM data (JEM-2010 microscope), a fresh sample of silver UDP consists of metallic globules 50–200 nm in size (mean size 100 nm) linked in chains. Silver particles contain a large number of extended defects of a polysynthetic twin type along the (111) planes of the face-centred silver lattice, which are repeated each 1–10 nm. The selected-area electron diffraction pattern of these particles contains reflexes of twins and elongated reflexes along (111), indicating the presence of both twins and many (over-equilibrium) stacking faults. In fact, a high-resolution picture (Figure 2) clearly displays planes with distance d_{111} = 2.35 Å, and a modulation frequency of their image intensity up to the lattice spacing. Evidently, the exit of frequently alternating defects on the surface leads to a strong roughening of the regular structure of the faces, *e.g.* many atomic-size steps form.

Treatment of silver UDP in oxidative or reaction mixtures results in the complete annealing of stacking faults, while twin defects are retained. In this respect, silver UDP behaves similarly to Ag/α-Al_2O_3 catalysts.[4] The significant difference between silver UDP and Ag/C catalysts and ordinary silver powder and Ag/α-Al_2O_3 is that when a silver surface is treated with O_2 or the reaction mixture, specific particles of ordered structure up to 10 nm in size appear on the surface (Figure 3). These particles are localised only at sites of exit of extended defects onto the surface (twinning boundaries), whereas they are not detected on regular areas. Direct resolution of the lattice gives interplanar distances of 3.3 and 2.7 Å, which are close to the parameters of the silver oxide (Ag_2O) cubic lattice.

A three-dimensional silver oxide phase can hardly form from the metal due to the thermodynamics at these O_2 pressures and temperatures. Therefore, it is unlikely that these unusual

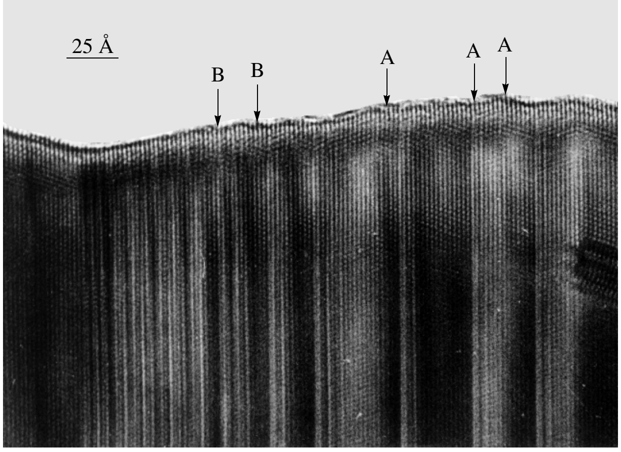

Figure 2 High-resolution electron microscopic image of twins and stacking faults at (111) planes in a silver UDP crystal. Angles and roughnesses on the surface show the exits of extended defects: twinning boundaries (A) and stacking faults (B).

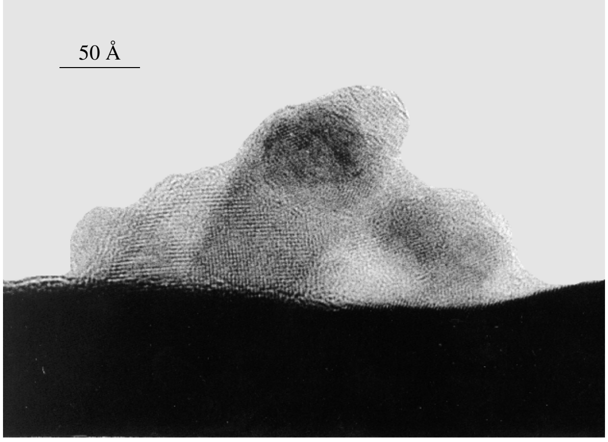

Figure 3 High-resolution electron microscopic image of an oxide-like particle located on the surface of a silver crystal.

particles are Ag_2O ionic crystals. As follows from *ex situ* HREM, they disappear on sample storage in air and reappear after treatment of the sample with oxidative or reaction mixtures at $T = 230$–260 °C. Finally, the XPS study did not reveal photoelectron lines of the surface Ag_2O oxide at a depth up to 10 nm on etching with He^+ ions. Both in the starting UDP samples and in those treated with oxidative or reaction mixtures, only the lines of metallic Ag and of the so-called 'covalent' (electrophilic) oxygen[5] were observed. It should be noted that analogous oxide-like structures formed, though in much smaller amounts, on the Ag/C catalyst. However, such structures have not been observed on the ordinary silver powder and on Ag/ -Al_2O_3.

As we found previously, the epoxidation rate is proportional to the concentration of -complexes of C_2H_4 with Ag^+ cations,[6] or, which is the same, to the concentration of chemisorbed (nucleophilic) O^{2-} oxygen ions. Moreover, electrophilic oxygen atoms localised on defect surface areas show epoxidating ability,[5–7] rather than nucleophilic oxygen atoms, which are reactive only in deep oxidation reactions. Since chemisorbed oxygen (O^{2-}) is slightly submerged under the surface,[7] the chemisorption of O_2 molecules increases the micro-strains of the silver lattice due to an increase in the Ag–Ag interatomic distances in the oxide layer. Obviously, these micro-strains will relax much more easily in the case of more defective crystals. Considering that treatment with O_2 or the reaction mixture leads to the complete annealing of the over-equilibrium stacking faults, the relaxation process should be accompanied by the transfer of many silver and oxygen atoms. It may be assumed that during rearrangement and rationalisation of the Ag surface layers, oxygen chemisorbed on the defects is accumulated in the vicinity of the more stable extended defects (exits of twin boundaries on the surface) thus eventually producing small oxide-like particles and causing the complete disappearance of the oxide layer. It therefore becomes clear why the formation of oxide-like structures is accompanied by a monotonous decrease in the reaction rate along with an increase in the selectivity towards ethylene oxide (Figure 1).

Most probably, epoxidation acts occur in the vicinity of the boundary between the metal and oxide-like particles, where Ag^+ cations and electrophilic oxygen atoms are localised. They are necessary for the activation of C_2H_4 and epoxidation acts, respectively. In our opinion, the absence of substantial coverage by nucleophilic oxygen causes high selectivities. The reaction energy in the case of ordinary Ag powder is clearly insufficient to produce oxide-like structures. Therefore, reaction evidently occurs on randomly appearing centres, whose immediate vicinity contains nucleophilic and electrophilic oxygen atoms. As a consequence, the activity of the ordinary Ag powder is much higher than that of UDP, while, on the contrary, the selectivity is much lower.

This study was financially supported by the Russian Foundation for Basic Research (grant no. 97-03-32544a).

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Received: Moscow, 3rd March 1998
Cambridge, 25th March 1998; Com. 8/02179A