

The combined application of XPS and TPD to study of oxygen adsorption on graphite-supported silver clusters

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Abstract

Oxygen adsorption on supported silver depending on the cluster sizes is studied by XPS and TPD using a model carbon-supported silver catalyst. It has been shown that the electrophilic oxygen active in ethylene epoxidation is produced on the small silver clusters (≤ 100 Å) more effectively than on the bulk metal, most probably, due to formation of subsurface oxygen. The desorption of the electrophilic oxygen at 450 K proves the thermodynamic possibility of its participation into ethylene oxide formation. Enlargement of the silver particles decreases the amount of subsurface oxygen and results in the appearance of nucleophilic oxygen. These results are used for discussion of the possible explanation of the size effect in ethylene epoxidation over Ag/Al₂O₃ catalysts. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Motivation of this work arises from attempt to consider the “material gap” problem for silver catalysts for ethylene epoxidation. Indeed, the discrepancy in the nature of bulk and supported silver limits the use of numerous data about oxygen adsorption on bulk samples to explanation of catalytic behavior of the real supported catalysts. This can be one of the reasons why the idea about influence of the chemical state of adsorbed oxygen onto routes of ethylene oxidation has never been considered for analysis of the size effect in ethylene epoxi-

ation on Ag/Al₂O₃ catalysts which is observed at unusually large sizes of the Ag particles (300–500 Å [1]).

To tackle this problem, we have studied O₂ adsorption on supported silver clusters with various sizes. However, due to the intense O1s emission from the support, this investigation could not be carried out for Ag/Al₂O₃ using XPS. We therefore chose to study oxygen adsorption on silver particles deposited on a graphite substrate.

2. Experimental

All experiments were carried out using a VG ESCALAB HP photoelectron spectroscopy. X-ray tube with MgK α irradiation (1253.6 eV) and hemispherical energy analyzer were used to

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take X-ray photoelectron spectra (XPS) and VG Q7B mass-spectrometer — to measure temperature-programmed desorption (TPD) spectra. To use XPS and TPD simultaneously, we developed a special procedure to prepare the samples consisting in graphitization of Ta foil (thickness of 0.2 mm) by decomposition of ethylene at $T = 1300$ K and $P(\text{C}_2\text{H}_4) = 1000$ Pa followed by UHV deposition of silver, with both the procedures being made inside the electron spectrometer. Such construction of the sample makes it possible to heat the sample with the rate of around 5 K/s that is high enough to record TPD spectra.

Thickness of the carbon layer was controlled by ex situ measurement of XPS spectra and was carried out to full disappearance of all Ta lines from the spectra. Both survey spectra and narrow spectra of C1s region taken from the carbonized Ta foil and from bulk graphite sample are compared in Fig. 1. Observation of the shake-up satellite in the C1s spectra of the both

sample together with C1s binding energy (BE) value of 284.4 eV (see inset of Fig. 1) suggests graphitic origin of the carbon layer produced by ethylene decomposition on tantalum. This makes it possible to compare the results of this work with data of our previous investigation with bulk graphite [2].

3. Results and discussion

Fig. 2 shows O1s spectra and TPD spectra of O_2 recorded after O_2 adsorption (100 Pa for 10 min at 420 K) as a function of silver coverage expressed as R_{Ag} , the measured Ag3d to C1s intensity ratio. In full accordance with our previous data obtained using bulk graphite as support [2], a single O1s feature with a binding energy of 530.5 eV is observed for $R_{\text{Ag}} < 10$, whereas for larger coverage a second feature develops at a binding energy of 528.4 eV (Fig. 2a). These values testify the formation of two

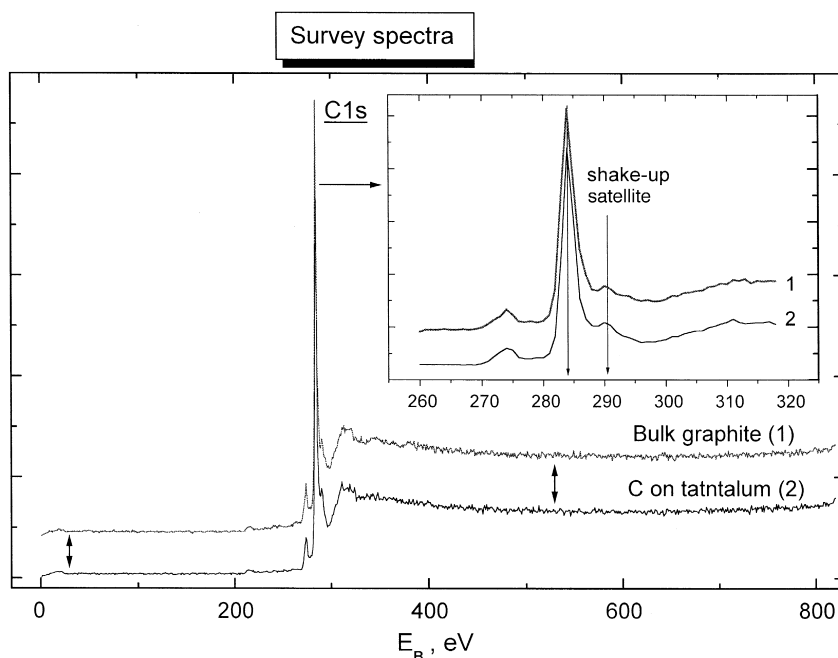


Fig. 1. Survey and C1s spectra recorded for bulk graphite and carbon layer on tantalum produced by ethylene decomposition for 30 min at $T = 1300$ K and $P(\text{C}_2\text{H}_4) = 1000$ Pa.

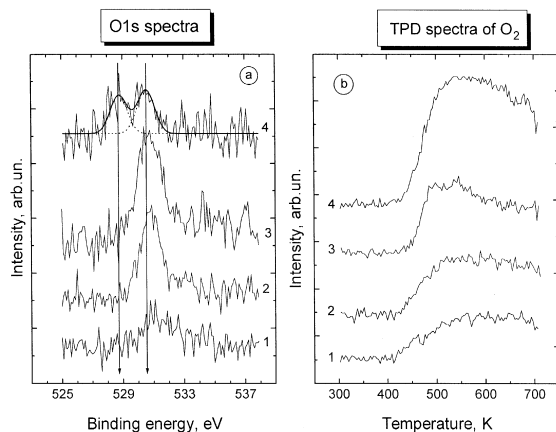


Fig. 2. O1s spectra (a) and TPD spectra of O₂ (b) recorded after oxygen adsorption (100 Pa, 10 min, 420 K) on silver deposited on a graphite, for increasing silver coverage (1–4): 1 – $R = I_{\text{Ag}}/I_{\text{C}} = 0.4$, 2 – $R = 1.5$, 3 – $R = 2.4$, 4 – $R = 13.1$.

atomically adsorbed oxygen species with different ionicities for the O–Ag bond: the component with lower BE is assigned to a nucleophilic oxygen species (O²⁻), and the second feature to an electrophilic one (O^{δ-}) [3]. These results indicate that the relative populations of the nucleophilic and electrophilic oxygen are strongly dependent on silver coverage. Since Ag atoms on graphite is well-known to agglomerate to three-dimensional particles even at room temperatures [4], it would be more correctly to say about silver particle size, but not about the coverage. To recalibrate XPS intensity ratio to the mean particle size we (i) have used the data of combined STM/XPS measurements obtained for the same system [4] and (ii) have made the ex situ STM measurements of Ag particle size for two coverages: $R_{\text{Ag}} \sim 3$ and 10. It has appeared that the mean particle sizes estimated by both approaches are in good agreement with each other: for example, the $R_{\text{Ag}} \sim 3$ and 10 correspond to $d_{\text{Ag}} \sim 50$ and 100 Å, respectively.

Growth of the background intensity of TPD spectra with temperature (Fig. 2b), together with constant increase in total TPD intensity with silver coverage, seem to indicate that the TPD spectra of O₂ reflect the desorption of dissolved oxygen. This suggestion is confirmed by the

data of Fig. 3, which shows the variation of both concentration of the adsorbed oxygen and amount of the desorbing oxygen with silver coverage. One can see that these dependencies exhibit different behaviors: increase in amount of evolving oxygen does not correlate with O1s/Ag3d_{5/2} intensity ratio which decreases with silver coverage. These data testify that the desorption of dissolved oxygen masks TPD spectrum of the adsorbed species and, hence, original TPD spectra of O₂ can not be used for identification of desorption characteristics of O_{ads}. To avoid this difficulty we have developed the special procedure of preparing the desorption spectra from XPS data described by us earlier [5]. In short, it consists of (1) registration of the change in O1s signal measured at binding energy value with maximum intensity, as the sample temperature increases; (2) subsequent smoothing and differentiating the experimental curve. In general, such procedure means the transformation of the curve of O1s intensity variation to the differential curve of the rate of this variation and, in fact, represents the rate of disappearing of the adsorbed oxygen. Correctness of this procedure has been tested by the desorption of the nucleophilic oxygen from Ag(111) surface [5].

The experimental curve of O1s intensity variation with temperature recorded after O₂ ad-

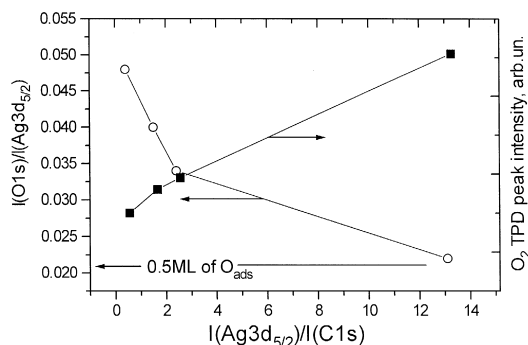


Fig. 3. Variation of O1s/Ag3d_{5/2} intensity ratio and amount of the desorbing oxygen with silver coverage measured after oxygen adsorption (100 Pa, 10 min, 420 K) on silver deposited on a graphite.

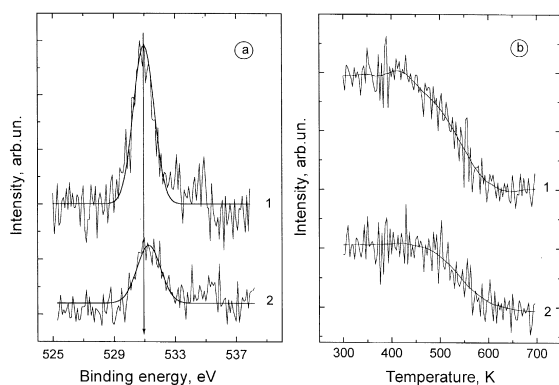


Fig. 4. O1s spectra (a) and curves of temperature-induced variation of O1s intensity with BE = 530.8 eV (b) measured before (1) and after (2) titration by H_2 (10^{-2} Pa for 10 min, at 420 K) of oxygen-exposed (100 Pa for 10 min, at 420 K) silver deposited on a graphite for $R(=I_{Ag}/I_C) = 2.4$.

sorption on Ag/C for $R_{Ag} = 2.4$ ($d_{Ag} \sim 30\text{--}50$ Å) along with the corresponding O1s spectrum is presented in Fig. 4 (curve 1). Narrower range of temperatures, where complete disappearing of O1s signal at 530.8 eV occurs, than that characteristic of the O_2 evolving into the gas phase (Fig. 4b) confirm our suggestion that TPD spectra of O_2 reflects desorption of the dissolved oxygen. It should be however noted that the amount of adsorbed oxygen calculated from O1s spectrum of the Fig. 4a is more than two times higher than maximum coverage (0.5 ml) for oxygen chemisorbed on bulk silver [3]. The same conclusion about greater concentration of oxygen adsorbed on small Ag particles in comparison with the bulk silver follows also from the quantitative data of the Fig. 3. Increase in Ag particle size decreases constantly the concentration of adsorbed oxygen, so that for large particles it reaches the level characteristic of bulk silver (Fig. 3). One of the possible explanations of this fact is the formation of subsurface oxygen, which is located in the subsurface silver layers contributing to XPS signal ($< 20\text{--}30$ Å). Note, the same conclusion has been made by van Santen et al. [6] at studying the oxygen adsorption on silver powder. To

check this suggestion we have studied the reactivity of adsorbed layer towards hydrogen.

The same Fig. 4 shows the O1s spectrum and curve of O1s intensity variation recorded after treatment of the oxygen-exposed Ag/C surface by H_2 (10^{-2} Pa for 10 min) at 420 K (Fig. 4, curves 2). One can see that the titration of the original surface by hydrogen transforms both O1s spectrum (decrease in intensity and small shift to higher BE) and O1s intensity variation curve. Increase in titration time and hydrogen pressure up to 1 Pa does not change the spectra determining relative inactivity of the rest part of oxygen. These data indicate inhomogeneity in oxygen adlayer produced by oxygen adsorption on small silver particles.

To compare the spectra of the Fig. 4 in more detail we have smoothed O1s spectra and differentiated the curves of O1s intensity variation with temperature. The corresponding spectra, as well as the difference ones, are shown in Fig. 5. In fact, the difference spectra characterize the oxygen species removed by hydrogen, i.e., surface-located oxygen active in reaction with H_2 . One can see that despite similarity of the characteristics of the removed and remained oxygen species, the titration of oxygen layers by H_2 allows us not only to confirm subsurface loca-

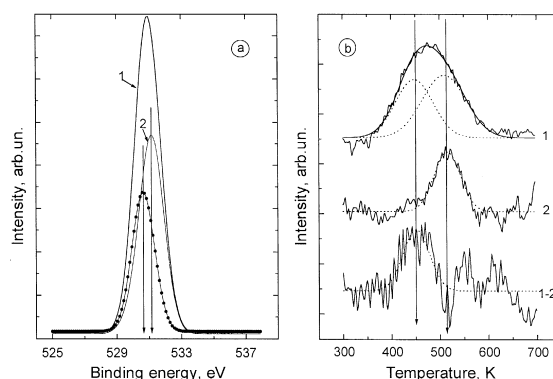


Fig. 5. Smoothed O1s spectra (a) and differentiated temperature curves of O1s intensity variation (b) measured before (1) and after (2) titration by H_2 (10^{-2} Pa for 10 min, at 420 K) of oxygen-exposed (100 Pa for 10 min, at 420 K) silver deposited on a graphite for $R(=I_{Ag}/I_C) = 2.4$. The corresponding difference spectra (1–2) are also shown.

tion of “inactive” oxygen, but also to separate the individual BE(O1s) values and desorption temperatures for the electrophilic oxygen adsorbed at the silver surface and subsurface oxygen.

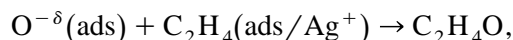
Thus, the study of oxygen adsorption on graphite-deposited silver particles depending upon their mean size leads us to identification of a number of oxygen species, the XPS and TPD characteristics of which are summarized in Table 1.

The fact that the temperature of the electrophilic oxygen desorption is lower than that of the nucleophilic one (580 K) is intuitively pleasing since this makes it thermodynamically possible to produce ethylene oxide using this oxygen with lower heat of adsorption [6]. Indeed, the more strongly bounded nucleophilic oxygen leads to total oxidation of ethylene only [3,5]. The use of the desorption temperature of 450 K for rough estimation of the heat of adsorption for the electrophilic oxygen leads to 25–27 kcal/mol (for $\Theta = 0.5$) that is in good agreement with upper limit for that of epoxidizing oxygen proposed in Refs. [6,7].

Other interesting result of this work is the experimental evidence for coexistence of subsurface oxygen and adsorbed oxygen active in ethylene epoxidation or the electrophilic O_{ads} . In addition to the already mentioned paper of van Santen et al. [6], who firstly have concluded that under influence of subsurface oxygen, the chemisorbed oxygen changes its chemical nature to become active in ethylene oxide production, the paper of Bulushev and Bal'zhinimaev

[8] should be also cited. The author suggests participation of subsurface oxygen into formation of active sites for ethylene epoxidation to explain isotopic experiments carried out on the alumina-supported silver catalysts. Our data seem to confirm both of the observations. Indeed, the more effective formation of the electrophilic oxygen on the small supported silver particles in comparison with bulk metals (it appears as a result of O_2 adsorption, while $C_2H_4 + O_2$ reaction mixture treatment has been necessary in the case of the foil or single crystals [3,5]) occurs in the presence of the subsurface oxygen. Enlargement of silver particles causes both decrease in the amount of subsurface oxygen and replacement of electrophilic oxygen by the nucleophilic one. Moreover, if silver particle sizes become higher than 500 Å, only nucleophilic oxygen and oxygen dissolved in the bulk silver particles are identified by XPS and TPD. This is quite consistent with the data for bulk silver samples.

The data of this work allow us to suggest the explanation of the size effect in ethylene epoxidation observed at unusually large sizes of alumina-supported silver particles [1]. Taking into account the following scheme of ethylene epoxidation stage:



where Ag^+ is the center of ethylene molecule adsorption created by nucleophilic oxygen, O^{2-} , and the disappearance of the latter at decreasing the Ag particle sizes (Fig. 1), one can conclude that less effective adsorption of ethylene in the case of small silver particles will decrease the rate of ethylene epoxidation.

Table 1
XPS and TPD characteristics of various oxygen species adsorbed on Ag/C

Type of oxygen	BE (eV)	T_{des} (K)	d_{Ag} (Å)	Reactivity towards H_2
$O_{\text{nucleophilic}}$	528.5	~ 580	> 100	+
$O_{\text{electrophilic}}$	530.5	~ 450	≤ 100	+
O_{ss}	531.2	~ 520	≤ 100	– (?)
O_{bulk}	–	> 600	> 100	– (?)

4. Summary

O_2 adsorption on graphite-supported silver causes the formation of the same species of atomically chemisorbed oxygen (nucleophilic

and electrophilic) as those which have been identified earlier for the bulk silver samples. This is of importance in the context of the suggestion that these oxygen species are necessary for ethylene epoxidation. It has been shown that their relative populations are dependent on silver cluster size, the nucleophilic oxygen only being appeared for particle sizes greater than 300 Å. This result indicates that decrease in the rate of ethylene epoxidation on Ag/Al₂O₃ catalysts for silver particle sizes < 300–500 Å can be associated with the disappearance of the nucleophilic oxygen which creates the sites for ethylene adsorption. The electrophilic oxygen active in ethylene epoxidation is produced on the supported silver more effectively than on the bulk metal, most probably, due to formation of subsurface oxygen. The desorption of the electrophilic oxygen at 450 K proves the thermodynamic possibility of its participation into ethylene oxide formation.

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