

XPS, TPD and TPR studies of Cs–O complexes on silver: their role in ethylene epoxidation

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Abstract

Various Cs oxides formed on the Ag(111) and Ag(110) single crystals depending on cesium coverage, oxygen pressure have been identified by XPS and TPD. The comparison of the determined characteristics with the data for the Ag/Al₂O₃ catalysts allows us to select those of the Cs–O structures which are common for both types of samples: cesium peroxide and cesium suboxide. Mechanisms of their influence onto routes of ethylene oxidation are discussed. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Cesium-promoted metallic silver as a catalyst for ethylene epoxidation is of great interest for the recent decades [1–3]. However, despite the application of surface sensitive techniques to clarify the role of cesium into the reaction, the researchers could not achieve unambiguous opinion on the chemical nature of Cs–O compounds involved in the catalytic reaction. Moreover, experimental data for this system are also rather contradictory. Two reasons seem to explain this situation. One of them is the well-known “material gap problem” which origi-

nates from the discrepancy in nature of bulk and dispersed silver, so that the results obtained in model experiments with Cs-doped Ag foil or single crystals (model UHV experiments) cannot be directly applied to real supported silver catalysts. The second one originates from the possible formation of various Cs–O structures with different influence on catalytic properties of the silver. Namely, the latter reason seems to explain the discrepancy in experimental data of similar model investigations applied to identical samples — Cs-promoted Ag(111) single crystals [1,2].

The purpose of this work is to measure XPS and TPD spectra for Cs–O structures formed on surfaces of Ag(111) and Ag(110) single crystals at different conditions and to compare the measured spectroscopic characteristics with the literature data for bulk and surface Cs–O compounds [4–7] with the aid of their identification.

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Subsequent comparison with Cs–O complexes found in Cs-promoted Ag catalysts supported on α -alumina should allow us to define those of them which play an active role in catalytic reaction of ethylene epoxidation.

2. Experimental

XPS, TPD and TPR experiments were carried out with a VG ESCALAB high pressure photoelectron spectrometer which has been described elsewhere [8]. The system is equipped with an X-ray source to produce $\text{MgK}\alpha$ (1253.6 eV) radiation for XPS measurements, a cathode gas discharge lamp to produce HeI (21.2 eV) and HeII (40.8 eV) radiation for UPS measurements and a VG Q7B quadrupole mass-spectrometer for TPD/TPR experiments. Ag(111) or Ag(110) single crystals with spot-welded Pt/Pt–Rh thermocouple were mounted on a specially designed holder permitting to regulate the sample temperature. Cleaning of the sample surface was performed by Ar^+ ion etching followed by annealing in oxygen atmosphere or in vacuum. Cesium deposition was performed with getter flash source at Ag surface temperature of 420 K. After deposition of Cs and treatment with gases in the preparation chamber, the sample was evacuated to UHV and transferred into the analyzer chamber for measurement of XPS and TPD/TPR spectra. Since we could not observe any ordered LEED patterns at the temperature used, so to estimate the Cs coverage we were compelled to measure the intensities of Auger CsMNN and AgMNN peaks for one of the Cs coverages ($I_{\text{Cs3d}}/I_{\text{Ag3d}} = 0.15$) and recalibrate their ratio to $\Theta(\text{Cs})$ using the literature data. Taking into account the data of Ref. [9] which have shown that $I_{\text{CsMNN}}/I_{\text{AgMNN}} = 0.16$ corresponds to the Cs concentration of 4.8×10^{18} atoms/ m^2 and densities of Ag atoms in surface layers for Ag(111) and Ag(110) single crystals ($\sim 14 \times 10^{18}$ atoms/ m^2 and $\sim 8.4 \times 10^{18}$ atoms/ m^2 , respectively), the following expres-

sions connecting the cesium coverage with the relative XPS intensity ratios can be produced:

$$\Theta(\text{Cs}) = 1.74 \times \frac{I(\text{Cs3d}_{5/2})}{I(\text{Ag3d}_{5/2})} \quad \text{for Ag(111),}$$

$$\Theta(\text{Cs}) = 2.85 \times \frac{I(\text{Cs3d}_{5/2})}{I(\text{Ag3d}_{5/2})} \quad \text{for Ag(110),}$$

Since the radius of the cesium atom is twice higher than the radius of the silver one, the closely packed hexagonal layer of cesium (1 ML) on Ag(111) surface is $\Theta(\text{Cs}) = 0.25$, which corresponds to $I(\text{Cs3d}_{5/2})/I(\text{Ag3d}_{5/2}) = 0.14$. Unfortunately, the same estimation using other literature data leads to the value of the intensity ratio which is almost four times less than 0.14. Because of this discrepancy, in this paper the cesium coverage is expressed in $I(\text{Cs3d}_{5/2})/I(\text{Ag3d}_{5/2})$, but not in Θ . However, the $\text{Cs3d}_{5/2}/\text{Ag3d}_{5/2}$ intensity ratio value of 0.14 can be considered as 1 ML.

3. Results and discussion

Cesium deposition in vacuum on a single crystal surface initially results in formation of a Cs overlayer characterized by $\text{Cs3d}_{5/2}$ signal at 725.5 eV (Fig. 1). Even the smallest dose of O_2 during subsequent adsorption shifts $\text{Cs3d}_{5/2}$ spectrum by 1.3 eV to lower binding energies (BE). Such a shift has been observed in previous papers [4–7] when metallic cesium is oxidized to Cs^+ ion. Note: the same binding energy value of 724.2 eV was measured for individual compounds with ionically bonded cesium — CsOH , CsNO_3 [10]. The achieved $\text{BE}(\text{Cs3d}_{5/2})$ value of 724.2 eV does not depend upon oxygen pressure (Fig. 1b), cesium coverage, silver surface structure, etc. This fact testifies the constancy of the chemical state of cesium for this system and the conditions used.

The more complicated picture of lines is observed in O1s spectra indicating the formation of different oxygen-containing species at

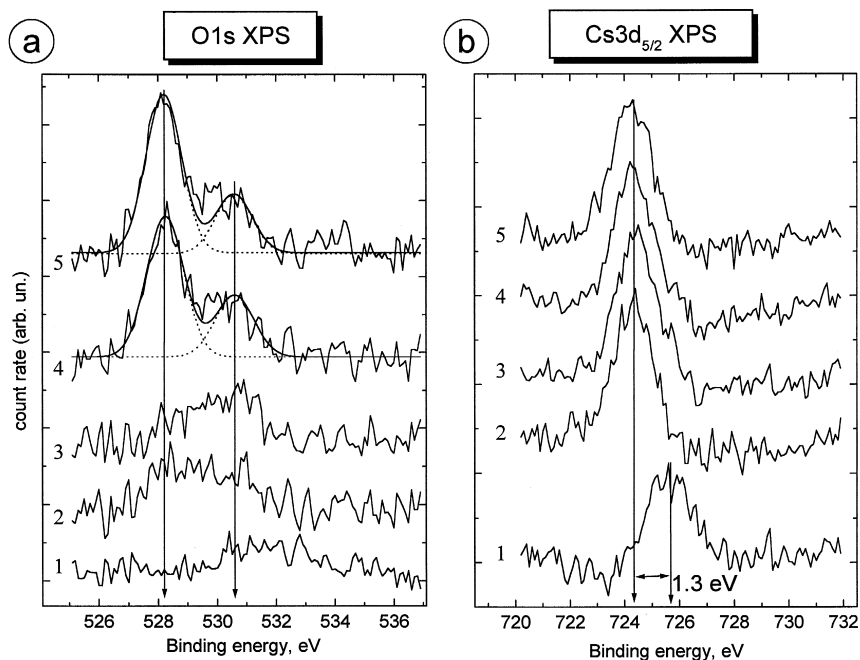


Fig. 1. O1s (a) and Cs3d_{5/2} (b) spectra recorded after UHV deposition of cesium (1) on Ag(111) followed by O₂ adsorption for 5 min at 420 K and various pressure (2–5): 2 — 10⁻³ Pa, 3 — 10⁻² Pa, 4 — 1 Pa, 5 — 10 Pa.

the surfaces (Figs. 1a and 2). Additional analysis of the O1s spectra depending on O₂ pressure, Cs coverage and Ag surface structure followed by a comparison of XPS and TPD characteristics with the literature data were necessary to assign the observed XPS lines to particular Cs–O or Ag–O structures.

Thus, the appearance of the O1s signal at 528.2 eV during the first dose of O₂ (Fig. 1a, curve 2) accompanied by its subsequent disappearance at increasing the O₂ exposure (Fig. 1a, curve 3) allows us to assign this line to cesium oxide. Indeed, both the O1s binding energy value and the fact of easy transformation of Cs₂O to higher cesium oxides under the influence of O₂ had been reported earlier for supported and bulk cesium oxide [4–6]. In spite of coincidence of the binding energy value with that reported for oxygen-exposed non-cesiated silver [11], this signal cannot be assigned to silver surface oxide, since low sticking probability of O₂ to closely packed Ag(111) plane (10⁻⁶) [11] makes it impossible to get a measurable

amount of adsorbed oxygen at these pressures. It is well known that O₂ pressure higher than 10⁻¹ Pa is necessary to see XPS signal of adsorbed oxygen. Most probably, namely, surface Ag₂O is responsible for the repeat appearance of the O1s signal with the same BE value after O₂ dose but at high pressures (Fig. 1a, curves 4,5). The BE value of another signal observed in O1s spectra of Fig. 1a (530.6 eV) is characteristic of cesium peroxide which is known to be the following step of cesium oxide.

The assignment of the two latter lines is in agreement with the data of Fig. 2a which shows the O1s spectra recorded after O₂ adsorption on Cs-promoted Ag(111) depending on cesium coverage. The increase in cesium coverage decreases the intensity of the O1s line at 528.2 eV, while the opposite tendency is observed for the O1s signal at 530.6 eV, so that the ratio of its intensity to the Cs3d_{5/2} one remains constant. The calculation of the Cs/O atomic ratio using relative intensities for the corresponding XPS signals results in a value close to 1, which is in

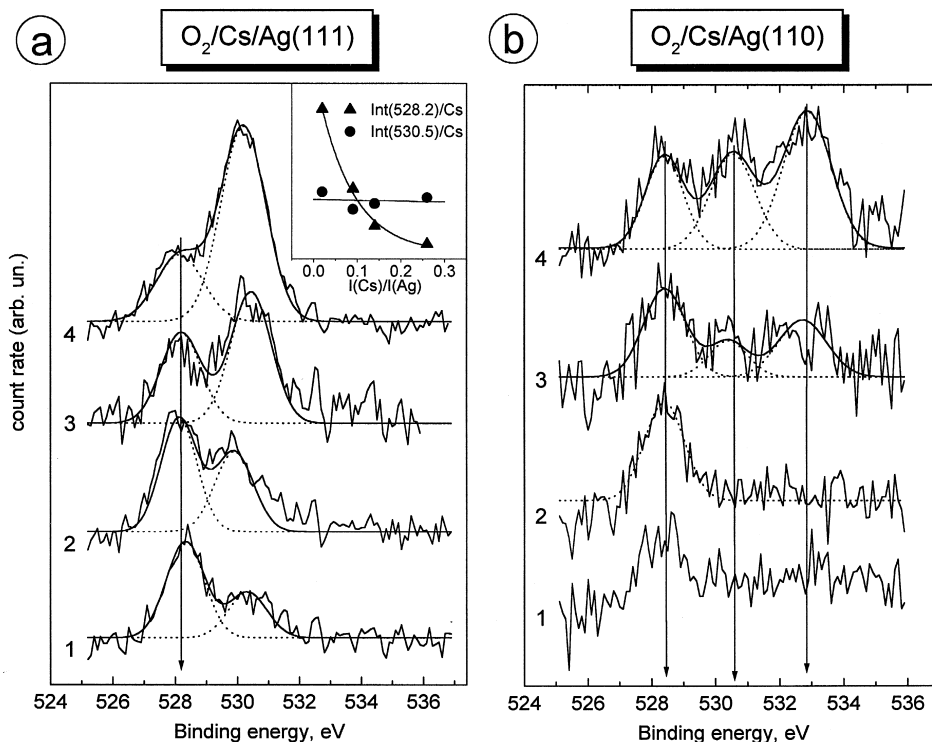


Fig. 2. O1s spectra recorded after O₂ adsorption for 5 min at 10 Pa and 420 K on Cs-covered surfaces of Ag(111) (a) and Ag(110) (b) with various Cs coverage (1–4): 1a — $I(\text{Cs}3d_{5/2})/I(\text{Ag}3d_{5/2}) = 0.02$, 1b — 0.03, 2a — 0.09, 2b — 0.10, 3a — 0.14, 3b — 0.20, 4a — 0.26, 4b — 0.32.

good agreement with the stoichiometry of cesium peroxide — Cs₂O₂. The decrease in intensity of the O1s signal at 528.2 eV with cesium coverage is consistent with the numerous occu-

pations of silver surface by Cs-containing structures that confirm the assignment of this signal to oxygen adsorbed on non-cesiated silver surface. The fact that this O1s feature is observed

Table 1
Spectroscopic characteristics and the conditions of the formation for various oxygen-containing species formed on Cs-modified silver surfaces

	Adsorbed oxygen		Cs oxides			
	ionic O ²⁻	covalent O ^{δ-}	suboxides Cs _{2+x} O	oxide Cs ₂ O	peroxide Cs ₂ O ₂	superoxide Cs ₂ O ₄
$E_b(\text{O}1s)$	528.2	530.5	530.6	< 528.0	530.2	532.9
$E_b(\text{Cs}3d)$	—	—	724.9	724.2	724.2	724.2
$T_{\text{des}}/T_{\text{decom}}$	580	780	780–820	720–760	550–580	520–550
<i>The conditions of appearance</i>						
Ag(111)	O ₂ /Ag $P \geq 10$ Pa $T \geq 420$ K	Et + O ₂ /Ag $P \geq 1000$ Pa $T \geq 420$ K	Cs + O ₂ /Ag $P \geq 10^{-2}$ Pa $T \geq 420$ K	O ₂ /Cs/Ag $P \leq 10^{-3}$ Pa $T \geq 420$ K	O ₂ /Cs/Ag $P \geq 10^{-3}$ Pa $T \geq 420$ K	—
Ag(110)	O ₂ /Ag $P \geq 10^{-3}$ Pa $T \geq 300$ K	Et + O ₂ /Ag $P \geq 100$ Pa $T \geq 420$ K	No data	O ₂ /Cs/Ag $T \geq 420$ K $\theta_{\text{Cs}} < 1$ ML	O ₂ /Cs/Ag $T \geq 420$ K $\theta_{\text{Cs}} > 1$ ML	O ₂ /Cs/Ag $T \geq 420$ K $\theta_{\text{Cs}} > 1$ ML
Ag/Al ₂ O ₃	Yes	Yes	Yes	No	Yes	No

even for Cs coverage exceeding 1 ML ($I(\text{Cs-}3d_{5/2})/I(\text{Ag}3d_{5/2}) = 0.14$) can be explained by the formation of three-dimensional islands of Cs peroxide. It is evident that much higher $\theta(\text{Cs})$ is necessary to cover all patches of unpromoted Ag(111) surface.

In addition to these species, O1s signal with binding energy of 532.9 eV appears when the

Ag(110) surface is covered by Cs in the amount above monolayer (Fig. 2b). The BE value of 532.9 eV allows us to attribute it to cesium superoxide Cs_2O_4 [6,7]. One more Cs–O structure is produced, if instead of the Cs deposition in UHV cesium deposition in 10^{-2} Pa O_2 followed by annealing the sample at 670 K is used for modification of the Ag(111) surface. As

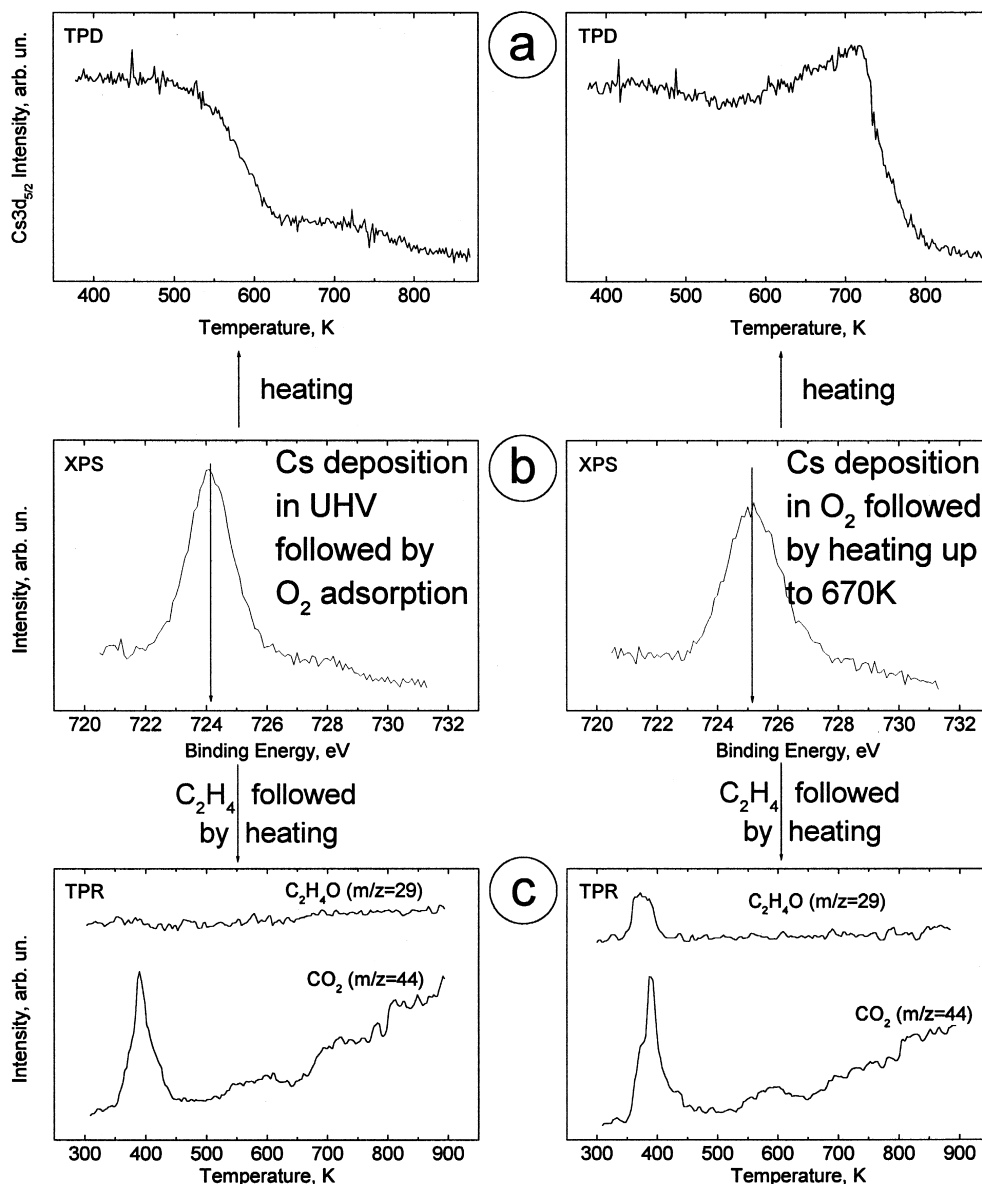


Fig. 3. TPD spectra of Cs (a), Cs_{3d_{5/2}} spectra (b) and TPR spectra of C₂H₄O and CO₂ (c) for cesium peroxide (left column) and for cesium suboxide (right column). The conditions of their formation are cited in the text.

opposed to the Cs oxides, this structure is characterized by higher Cs3d_{5/2} binding energy (~ 725 eV) and higher desorption (decomposition) temperature (780–820 K) than those of any of the oxides. According to the data of Ebbinghaus and Simon [5], this Cs–O structure can be attributed to cesium suboxide, Cs_{2+x}O.

Both XPS and TPD characteristics, as well as the conditions of formation, for all Cs–O structures identified in this study are summarized in Table 1. The comparison of these characteristics with the data for the supported Ag/Al₂O₃ catalysts published by us earlier [3] indicates that only two of them, cesium suboxide and peroxide, are common for the considered model samples and supported silver catalysts promoted with Cs (Table 1). To check their role into ethylene epoxidation, we have developed the procedures of the individual preparation of these structures. Cesium peroxide has been prepared by the UHV deposition of Cs on Ag(111) at 420 K followed by oxygen adsorption (10 Pa for 10 min) at 420 K, and Cs deposition on Ag(111) in 10⁻² Pa followed by heating up to 670 K in UHV has been used for Cs suboxide formation. The latter procedure (heating in vacuum) was necessary to remove Cs peroxide (*T*_{des} ~ 600 K) coproduced with suboxide at the cesium deposition in atmosphere of O₂. Indeed, subsequent heating of the Ag(111) surface modified by Cs peroxide or Cs suboxide results in the desorption of cesium in different temperature ranges characteristic of these particular structures (Fig. 3a). Catalytic testing of these Cs-promoted Ag(111) surfaces (Fig. 3b) consisted of oxygen adsorption at *T* = 420 K and *P* = 10 Pa, subsequent ethylene adsorption at *T* = 300 K and *P* = 1 Pa followed by heating the samples in vacuum with simultaneous measurement of TPR spectra of ethylene oxide (*m/z* = 29), CO₂ (*m/z* = 44), CO (*m/z* = 28), etc. The corresponding spectra of CO₂ and ethylene oxide are shown in Fig. 3c. One can see that the Ag(111) surface modified by the Cs suboxide provides the appearance of C₂H₄O among the reaction product, while only the product of total oxida-

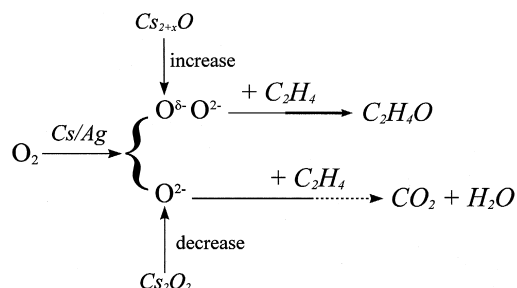


Fig. 4. The scheme illustrating the mechanisms of influence of Cs suboxide and Cs peroxide upon silver-catalyzed ethylene epoxidation.

tion, CO₂, is observed in the other case, the amount of CO₂ formed being decreased with an increase in the concentration of Cs peroxide.

Taking into account the mechanisms of ethylene epoxidation proposed by us earlier [12,13], the data of this work allow us to suggest the scheme of promotion of silver catalysts by cesium presented in Fig. 4. Cesium peroxide suppresses the formation of the “ionic” oxygen species which are active in the total oxidation of ethylene, whereas cesium suboxide seems to promote the formation of the “covalent” oxygen which is active in ethylene epoxidation. In the former case, the increase in selectivity to C₂H₄O will be provided by the decrease in the rate of total ethylene oxidation (or CO₂ production), and in the latter case, by the increase in the rate of ethylene epoxidation.

4. Summary

Detailed analysis of the Cs3d_{5/2} and O1s spectra, as well as TPD spectra of O₂, depending on oxygen pressure, cesium coverage, and silver surface structure allowed us to show the existence of few Cs oxides with various stoichiometry: from suboxide, Cs_{2+x}, to superoxide, Cs₂O₄. The spectroscopic characteristics of two of them (suboxide and peroxide) are also observed for Cs-promoted Ag/Al₂O₃ catalysts suggesting their existence in real catalytic con-

ditions. Their roles in silver-catalyzed ethylene epoxidation are different: peroxide seems to suppress the total oxidation, while promotion of ethylene epoxidation can be suggested for the suboxide.

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