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Ambient pressure X-ray photoelectron spectroscopy during electrochemical promotion of ethylene oxidation over a bimetallic Pt–Ag/YSZ catalyst

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ABSTRACT

The electrochemical promotion of the $C_2H_4 + O_2$ reaction over a bimetallic Pt/Ag catalyst (Pt:Ag ratio ≈ 1.5) interfaced to yttrium stabilized zirconia (YSZ) has been studied at 0.25 mbar and $T = 650$ K using X-ray photoelectron spectroscopy as *in situ* method. Applying a positive potential of 2 V causes a relative rate increase in the CO_2 production up to 120%; the electrocatalytic promotion effect is non-Faradaic ($\Lambda \approx 2$). An electrochemical promotion is found to occur only at high enough $p(C_2H_4)$ when a carbonaceous CH_x layers builds up inhibiting O_2 adsorption. The CH_x film is estimated to be about 5–6 layers thick. Only at low $p(C_2H_4)$, the application of an electric potential causes a decrease in the carbon signal associated with a growth of the O1s signal at 529.3 eV. The latter species can be assigned to an electrochemically generated oxygen spillover species at Ag sites.

1. Introduction

An electrochemical promotion of heterogeneously catalyzed reactions (EPOC) can be achieved with porous thin film electrodes interfaced to a solid electrolyte [1–5]. Upon application of an electric potential to the electrodes, a reaction which is catalyzed by the metal may be strongly enhanced. Pioneered by Vayenas et al., the EPOC effect has been demonstrated for about 100 reaction systems comprising a vast range of different reactions, catalytic metals, and different solid electrolytes such as the O^{2-} conducting yttrium stabilized zirconia (YSZ) and the Na^+ conducting β''-Al_2O_3 [2–5]. Typically, the electrochemically induced rate increase is non-Faradaic with respect to the ionic current. The interface Pt/YSZ has also received considerable interest in connection with the performance of solid oxide fuel cells [6].

Mechanistically, the electrochemical promotion effect could be traced back to the spillover of the transported ionic species from the three-phase-boundary (tpb) metal/solid electrolyte/gas phase where it is discharged onto the surface of the metal electrode [4,5,7,8]. Despite a large body of empirical data, fundamental questions still remain unresolved [5,9]. One open question is that after the identity of the oxygen spillover species in the system Pt/YSZ. A special spillover species $O^{\delta-}$ ($\delta \approx 2$) with properties different from regular chemisorbed oxygen on Pt has been postulated by Vayenas et al. [3,4,10]. While low pressure (10^{-6}–10^{-10} mbar) experiments with Pt/YSZ model catalysts unambiguously demonstrated that the spillover species is identical with regular chemisorbed oxygen [7], it remains open whether or not such a special spillover species develops at higher pressure. A second issue discussed controversially in the literature is the origin of the non-Faradaic behavior in EPOC experiments. A "sacrificial promoter mechanism" based on the existence of a special spillover oxygen species was postulated by Vayenas et al. [3,4] Alternatively, an ignition mechanism has been proposed by Toghan et al. [9,11,12]. The ignition mechanism does not require a special oxygen spillover species and instead assigns the spillover species the role of triggering the reactive removal of an inhibitory adlayer. A third possibility has been introduced earlier by Sobyanin et al. who suggested that an electrochemically initiated chain mechanism might be responsible for the non-Faradaic rate increase [13–15].

Most of the difficulties in coming to a clear mechanistic picture of the EPOC effect can be traced back to the well-known pressure and material gap in heterogeneous catalysis. Nearly, all of the EPOC studies have been conducted in the mbar to atmospheric pressure range with structurally and chemically badly defined catalysts. A small number of surface science type studies have been conducted but what is completely missing are high-pressure studies characterizing the state of the catalyst with *in situ* techniques [5,16,17]. For this reason, we use here a differentially pumped X-ray photoelectron spectrometer with which *in situ* XPS experiments are feasible up to ≈1 mbar. The reaction system we investigate is catalytic

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ethylene oxidation with O_2 on a bimetallic Pt–Ag/YSZ catalyst. In preceding studies, we investigated the $C_2H_4 + O_2$ reaction on Pt/YSZ in an UHV environment using photoelectron emission microscope (PEEM) as main method [11,12]. This reaction system played a kind of paradigmatic role in the EPOC studies because it exhibited the strongest non-Faradaic effect of all reaction systems investigated so far [18,19]. Ag is used as catalyst for the epoxidation of ethylene. For both separate systems, Pt/YSZ and Ag/YSZ, the electrochemically induced oxygen spillover has been characterized by XPS under low pressure conditions [7,8,20].

The electrocatalytic behavior of bimetallic electrodes was shown recently to exhibit quite favorable properties with respect to hydrazine oxidation where a non-Faradaic pathway indicating EPOC behavior was found [21]. The question we address here is whether the presence of two metals leads to new unexpected results with respect to spillover and electrochemical promotion or whether the two metals just act independent of each other, so that, the resulting behavior is just a superposition of the known behavior of each of the two metals. As will be shown, the two metals largely retain their individual properties in this electrochemical experiment.

2. Experimental

2.1. Samples and electrochemical set-up

For the preparation of the sample, we used a square-shaped (1 1 1) oriented YSZ single crystals (13 mol% yttrium, MaTeck GmbH, Germany) with a thickness of 1.5 mm and of the dimensions $16 \times 16\ \mathrm{mm}^2$. Only one side was polished with a surface roughness <0.5 nm. The counter (CE) and the reference electrodes (RE) were prepared with Pt paste on the unpolished side of the YSZ substrates followed by calcination at 1120 K in air for several hours (≈9 h) in order to remove the organic compounds. The working electrode (WE) was prepared on the polished side of single crystal YSZ (1 1 1) in two stages. Firstly, Pt and Ag were codeposited by sputtering onto YSZ substrates in an inert atmosphere ($p(Ar) = 2 \times 10^{-2}$ mbar) at 300 K. The sputter deposition was followed by annealing in air at 1120 K for 3 h. In order to obtain a metal film with high enough electric conductivity, in a second step, a thin coating of Pt paste (A1118 Demetron) was deposited with a brush followed by annealing in air at 1120 K for 3 h. As shown by XPS, the Ag segregates to the surface of the Pt film forming a Pt/Ag alloy (see below). The morphology of the Pt/Ag WE after sintering in air for 3 h at 1123 K was investigated by scanning electron microscopy (SEM, JEOL JSM-6700F) and by surface profilometer (Veeco Dektak 6 M stylus). A porous network film with a thickness on the order of a few μm was obtained (see Fig. S1 in Supporting information). X-ray diffraction (XRD) of the Pt–Ag film turned out to be identical to the pure Pt film [22].

For the electrochemical measurements, a standard three-electrode setup was used as displayed in Fig. 1 with a potentiostat controlling the potential of the working electrode (WE) with respect to a reference electrode. Under high-pressure conditions (0.1–1 mbar), there is practically no difference between the potentials of the CE and the RE versus the WE; at low pressure, and in particular under UHV conditions, the difference can reach up to several Volt. Since no gas reference electrode was used, the potential of the reference electrode is not fixed but may shift due to zirconia reduction at the interface YSZ/Pt of the reference electrode. As discussed in detail in Ref. [23], the measured potentials depend also on the cell geometry, that is, upon dimensions and layout of the electrodes because these geometric factors will control the current distribution. In our case, we do not explicitly calculate the error, which is potentially introduced by the geometry because the main uncertainty in the measured potentials is caused by not working with a reference electrode with fixed potential.

2.2. XPS and data analysis

The XPS experiments were performed using the monochromatized radiation of the ISSIS beamline at the synchrotron facility BESSY II of the HZB in Berlin. A specially designed differentially pumped XPS system was used [24]. Details of the reaction cell and the differentially electrostatic lens system are described elsewhere [25]. X-rays were admitted to the experimental cell through a 50-nm-thick Si_3N_4 window. The photoelectrons, emitted under normal emission, entered a differentially pumped electrostatic lens system and were focused on the entrance slit of a standard electron energy analyzer, where high-vacuum conditions were maintained by an additional pumping stage. This setup allowed a variation of the total pressure in the reaction cell between 10^{-7} and 0.5 mbar.

As indicated in Fig. 1a, the working electrode is at ground potential, and all binding energies are therefore referenced to the Fermi level of the working electrode. The excitation (photon energy) for Pt4f, C1s, Ag3d, and O1s core level spectra was 220, 435, 518, and 680 eV, respectively, resulting in the same high-surface sensitivity with an inelastic mean free path (IMFP) of the photoelectrons of about 0.86 nm in carbon and 0.4 nm in platinum [26]. The Pt4f, Ag3d, C1s, and O1s envelopes were fitted using Casa XPS software after subtraction of a Shirley background [27,28]. The fitting of the spectra was done with Gaussian–Lorentzian functions fixing the peak position within ±0.1 eV.

The spectra have been normalized to the impinging photon flux that has been determined by a cleaned Au foil and corrected for the fraction of higher order of the monochromator and the electron current in the storage ring. Quantitative XPS data analysis was performed assuming homogeneous model distribution of the elements using theoretical cross sections according to the following equation [29]:

$$I_A^* = I_A/(\sigma \cdot r \cdot n_\gamma) \tag{1}$$

where I_A is the measured intensity and I_A^* the normalized intensity of species A; σ is the theoretical cross section, r is the ring current in mA, and n_γ is the number of photons per mA ring current (photon flux). Correcting for the different photoionization cross sections, one calculates a Pt:Ag ratio of 1.5 assuming a homogeneous mixture of the two components in the alloy.

The abundance C_X was obtained as:

$$C_X = \frac{I_X^*}{\sum_{\text{all } Y} I_Y^*} \cdot 100 \tag{2}$$

The abundance calculated in this way is a rough approximation because one assumes a homogeneous mixing of the elements (Pt, Ag, C, O, and Si) in the probed surface region (≈10 layers), which typically is not the case. The thickness of the carbon overlayer was determined by applying the exponential attenuation by overlayer model according to the following equation [30]:

$$I_C^*/I_S^* = (1 - e^{(-t/\lambda C)})/e^{-t/\lambda S} \tag{3}$$

where t is the overlayer thickness, I_C^* is the normalized intensity of the carbon overlayer, and I_S^* is the normalized intensity of the Pt substrate. The inelastic mean free path (IMFP) for C1s and Pt4f at 150 eV kinetic energy is denoted as λ_C and λ_S, respectively. For expressing the thickness in number of monolayers, the interplanar spacing of graphite of 0.34 nm was taken [31].