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Preferential CO oxidation in hydrogen (PROX) on ceria-supported catalysts, part II: Oxidation states and surface species on Pd/CeO_2 under reaction conditions, suggested reaction mechanism

O. Pozdnyakova [a], D. Teschner [a,b,*], A. Wootsch [a], J. Kröhnert [b], B. Steinhauer [b], H. Sauer [b], L. Toth [c], F.C. Jentoft [b], A. Knop-Gericke [b], Z. Paál [a], R. Schlögl [b]

[a] *Institute of Isotopes, CRC, HAS, POB 77, Budapest, H-1525, Hungary*
[b] *Department of Inorganic Chemistry, Fritz-Haber-Institut der Max-Plank-Gesellschaft, Faradayweg 4-6, D-14195 Berlin, Germany*
[c] *Research Institute for Technical Physics and Materials Science, HAS, Budapest, POB 49, H-1525, Hungary*

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Abstract

The aim of the PROX reaction is to reduce the CO content of hydrogen feed to proton-exchange membrane fuel cells (PEMFCs) by selective oxidation of CO in the presence of excess hydrogen. Both Pt and Pd on ceria are active in CO oxidation (without hydrogen), whereas Pd is poorly active in the presence of hydrogen. In this paper we explore the reasons for such behavior, using the same techniques for Pd/CeO_2 as used for Pt/CeO_2 in Part I: catalytic tests, in situ DRIFTS, high-pressure XPS, HRTEM, and TDS. We also examine the reaction mechanism of CO oxidation (without hydrogen), which does not occur via exactly the same mechanism on Pt and Pd/CeO_2 catalysts. In the presence of hydrogen (PROX) at low temperature ($T = 350$–380 K), the formation of Pd β-hydride was confirmed by high-pressure in situ XPS. Its formation greatly suppressed the possibility of CO oxidation, because oxygen both from gas-phase and support sites reacted rapidly with hydride H to form water, which readily desorbed from Pd. Nevertheless, CO adsorption was not hampered here. These entities transformed mainly to surface formate and formyl (–CHO) species instead of oxidation as observed by DRIFTS. The participation of a low-temperature water–gas shift type reaction proposed for the platinum system (see Part I) was hindered. Increasing temperature led to decomposition of the hydride phase and a parallel increase in the selectivity toward CO oxidation. This still remained lower on Pd/CeO_2 than on Pt/CeO_2, however.

Keywords: Hydrogen purification; Fuel cell; Preferential CO oxidation; PROX; Palladium; Palladium-hydride; Pd/CeO_2; Ceria; High pressure XPS; In situ DRIFT; TDS; HRTEM

1. Introduction

The importance of the PROX reaction has been described in detail in Part I [1]. Briefly, for the proper operation of proton-exchange membrane fuel cells (PEMFCs), as a rule the CO content of the hydrogen feed must be kept under 1–100 ppm [2]. The aim of the preferential oxidation (PROX) reaction is to selectively oxidize CO, reducing its concentration from 1–1.5% to <100 ppm without oxidation of the excess hydrogen present [1,3,4].

Catalyst formulations found to be active in the PROX reaction can be classified as gold-based catalysts [5–8], supported Pt [5,8–12], Rh [9], Ru [9,13], bimetallic Pt–Sn [11,14] and other systems not containing metallic phase, such as CuO/CeO_2 [5,15]. These systems as a rule are also active in low-temperature CO oxidation. Palladium-based catalysts represent a class of its own; whereas Pd on different supports, especially on those active in the transient oxygen storage (such as ceria) is remarkably active in CO oxidation [16–20], it shows very low selectivity toward CO oxidation in the presence of hydrogen [9,21–23].

This low activity/selectivity of Pd in the PROX reaction has not yet been elucidated in detail. One group [9,21] explained

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[*] Corresponding author. Fax: +49 30 8413 4676.
E-mail address: teschner@fhi-berlin.mpg.de (D. Teschner).

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this by the change in the oxidation state of Pd. The highly active reduced Pd form (active in low-temperature CO oxidation) could be oxidized to PdO_x, which is less active in CO oxidation (without hydrogen). This change occurred around 360 K on Pd/Al_2O_3 in the presence of oxygen [9]. The authors stated that this PdO_x was very active in hydrogen oxidation, whereas it showed low activity in CO oxidation and thus low selectivity in the PROX reaction. They also suggested that other metals, like Au or Pt, cannot be oxidized as easily as Pd, and the rate of CO oxidation on their metallic form was higher than that of H_2 oxidation. This tentative proposition was not supported by any experimental evidence, however.

In the present work we studied the PROX reaction on Pd/CeO_2 catalysts, active in CO oxidation in both the presence [19] and absence of oxygen (OSC) [24,25], using the same experimental methods as in Part I [1]: catalysis, high-pressure XPS, TDS, HRTEM, and in situ DRIFT spectroscopy. The aims of this paper are to clarify the reaction mechanism of both CO oxidation and the PROX reaction on a Pd catalyst, to study the role of the reducible ceria support, and to compare its behavior with that of Pt/CeO_2, which was found to be remarkably active in the PROX reaction [1,12].

2. Experimental

2.1. Catalysts

Two catalysts with nominally 1 and 5% metal loadings were prepared on the same ceria support used in Part I [1] (Rhodia Catalysts & Electronics, France; BET $= 96\ m^2\,g^{-1}$ [26]), by wet impregnation with an aqueous solution of $Pd(NH_3)_4(NO_3)_2$ [12,27]. The impregnated samples were dried at 393 K overnight and calcined for 4 h at 773 K in flowing air (30 mL/min), then reduced at 672 K for 4 h in flowing H_2 (30 mL/min). Dispersion was determined by low-temperature (223 K) H_2 adsorption after reduction [28,29]. The received values were $D = 68\%$ for 1% Pd/CeO_2 and 23% for 5% Pd/CeO_2.

2.2. Catalysis

Catalytic tests were carried out in the same atmospheric continuous-flow reactor system as in the studies reported in Part I [1], using stainless steal tubing and connections and analytical-grade gases controlled by mass-flow controllers. Products were analyzed by a gas chromatograph (TCD) equipped with a polar column (Poropak Q) separating CO_2 and H_2O from the other outlet gases, and by a hydrogen-compensated flue-gas analyzer (type MRU DELTA 65-3) for CO and O_2 quantification. Methane formation did not occur on Pd catalysts; CO_2 and H_2O were detected only as products, similar to Pt [1]. The total gas inlet was 100 N mL/min, containing 1% CO, 0.4–1% O_2 (oxygen excess, λ, 0.8–2) and the rest H_2.

The catalysts were activated in situ in flowing air (30 mL/min) at 573 K before catalytic tests. A charge of 95 mg 1% Pd/CeO_2 and 83 mg 5% Pd/CeO_2 was used in the catalytic reactor and reactivated between different measurement series by the aforementioned procedure [12]. CO and O_2 conversion, as well as selectivity, were calculated as described previously [1,12].

2.3. Temperature-programmed desorption

Different gas mixtures were adsorbed at room temperature on the 5% Pd/CeO_2: $CO + O_2$ (10^{-2} mbar $O_2 + 2 \times 10^{-2}$ mbar CO for 20 min) and $H_2 + CO + O_2$ (4.7×10^{-1} mbar $H_2 + 2 \times 10^{-2}$ mbar CO $+ 10^{-2}$ mbar O_2 for 20 min). After adsorption, the sample was evacuated and transferred to the UHV part of the setup to follow the desorption pattern (heating rate, 1 K/s). For more details, see Part I.

2.4. In situ diffuse reflectance infrared spectroscopy

DRIFTS experiments were carried out under the same conditions as in Part I [1], with the same Bruker spectrometer. Inlet gases were analytical grade and were controlled by mass-flow controllers. The total gas flow was 50 N mL/min, containing 1% CO in N_2 (referred to as *CO alone*), 1% CO and 1% O_2 in N_2 (*CO + O_2*), or 1% CO and 1% O_2 in H_2 (*PROX*).

All measurements were carried out on a ca. 100-mg fresh sample previously pretreated in situ in flowing air (30 mL/min) at 573 K. The catalyst was purged in N_2 while being cooled to the desired reaction temperature of 383 or 523 K. A spectrum of the activated sample before adsorption was collected in N_2 at the reaction temperature, then the reaction mixture—premixed in a bypass—was introduced to the catalyst in a single step. Spectra were collected as a function of time on stream for 90 min in all cases. Only spectra under steady-state conditions are shown here.

The gas composition was analyzed only in the case of the PROX reaction by a mass spectrometer. Selectivity and activity values were calculated using the same formula as presented earlier [1].

2.5. High-pressure X-ray photoelectron spectroscopy

The in situ XPS experiments were performed at beamline U49/2-PGM2 at BESSY in Berlin. Ce 3d, O 1s, Pd 3d, and C 1s spectra were recorded with photon energies of $h\nu = 1035$, 920, 725, and 670 eV. The binding energies (BEs) were calibrated using internal references, such as the Ce 3d V (882.4 eV) and U''' (916.7 eV) hybridization states or the Ce 4f state in the band gap. Decomposition of the Pd 3d, O 1s, and C 1s regions was performed using Gauss–Lorentz curves, except for the metallic Pd 3d component at 335 eV, which was fitted using a Gauss–Lorentz profile with an exponential tail. The 5% Pd/CeO_2 pellet (~100 mg) was activated in situ in oxygen (0.5 mbar, 573 K). The PROX mixture contained 0.45 mbar H_2, 0.031 mbar CO, and 0.015 mbar O_2. Gas-phase analysis was carried out using a quadrupole Balzers mass spectrometer. For more details, see Part I.

2.6. High-resolution transmission electron microscopy

HRTEM investigations were performed with a Philips CM200 FEG electron microscope operated at 200 keV. The microscope