



In situ preparation and investigation of Pd/CeO₂ catalysts for the low-temperature oxidation of CO

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ABSTRACT

The formation of Pd_{0.05}Ce_{0.95}O₂ catalysts for the low-temperature oxidation of CO by the thermal decomposition of Ce(NO₃)₃ and Pd(NO₃)₂ with oxygen was studied by X-ray photoelectron spectroscopy (XPS) and X-ray absorption spectroscopy (XAS) directly in the preparation chamber of a spectrometer. Palladium is represented by two species on the surface of the catalysts: solid solutions of Pd_xCe_{1-x}O_{2-δ} and palladium clusters. Pd clusters can be formed in an oxidized or reduced state depending on the reaction conditions. Treatment of the catalysts with hydrogen leads to a sharp increase in CO conversion because of the reduction of parts of the palladium accompanying the formation of the metallic clusters. The testing of “real” and model catalysts was conducted in a light-off mode. The correlation between the activity of the Pd/CeO₂ catalysts and the states of the palladium was proposed.

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1. Introduction

The Pd/CeO₂ catalytic system has been extensively investigated because it is an irreplaceable component of catalysts for the low-temperature oxidation of CO (LTO CO) [1–5], the water gas shift reaction (WGS) and selective methanation [6,7], CH_x oxidation [8,9] and other reactions. Despite a number of publications devoted to the investigation of the nature of these catalysts, ambiguous and contradictory data concerning the electronic and geometric structure of Pd/CeO₂ active centers persist. The electronic state of palladium in Pd/CeO₂ catalysts differs from that of Pd/Al₂O₃ catalysts. Palladium in Pd/Al₂O₃ catalysts exists in the form of metallic and PdO nanoparticles [10,11] that have typical binding energies (BE) of the Pd3d_{5/2} core level equal to 335.2 and 337.0 eV, respectively [10–15], while the position of the Pd3d_{5/2} level for Pd/CeO₂ catalysts is approximately 337.7–338.3 eV [4,16–21]. The elevated value of the BE for Pd3d_{5/2} is approximately 337.7–338.3 eV because of the formation of palladium dioxide (PdO₂) [16,18], fine particles of palladium oxide (PdO) [20,22] and a solid solution of Pd_xCe_{1-x}O₂ [4,5,16,21]. Previously, we showed that the main

palladium state of the Pd/CeO₂ catalysts was characterized by a BE for Pd3d_{5/2} of 338.0 eV, which corresponded to the substitutional solid solution of Pd_xCe_{1-x}O₂ at the surface and subsurface layers of the CeO₂ lattice [5,23]. The formation of these structures in the Pd/CeO₂ catalysts was confirmed by quantum-chemical calculations [24–26]. In addition, the formation of Pd–O–Ce superstructures on the (110) surface of CeO₂ has been reported by Colussi et al. [27]. However, the determination of the valence state of the Pd atoms in solid solutions of Pd_xCe_{1-x}O₂ remains controversial. Therefore, there is a great interest in the formation and investigation of Pd_xCe_{1-x}O₂ structures that play a key role in LTO CO.

Here, we present the synthesis of Pd_xCe_{1-x}O₂ surface structures during the formation of the catalyst directly in the preparation chamber of a photoelectron spectrometer under UHV conditions. The synthesis of ceria by the thermal decomposition of Ce(NO₃)₃ has been demonstrated [28,29], and we used this synthesis with nanoscale CeO₂ supports under clean conditions in the spectrometer preparation chamber. The derived model catalyst was compared to the real reference Pd/CeO₂ catalysts that had been prepared by incipient wetness impregnation (IWI) method [7,30].

To determine the valence state of the elements during the synthesis, X-ray photoelectron spectroscopy (XPS) and X-ray absorption spectroscopy (XAS) were used. Because XPS and XAS have different surface sensitivity, these methods were selected to detect the bulk and surface localization of the Pd structures

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