

## Ultraviolet-assisted synthesis and structural characterization of the Pd nanoparticles on the CeO<sub>2</sub> substrate

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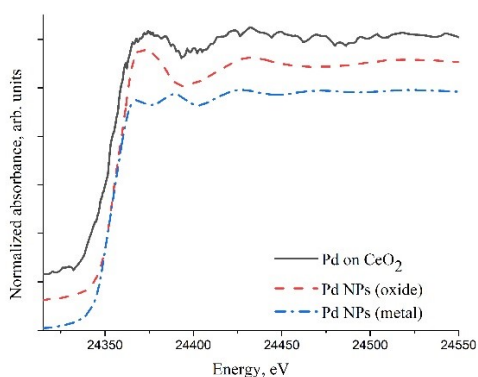
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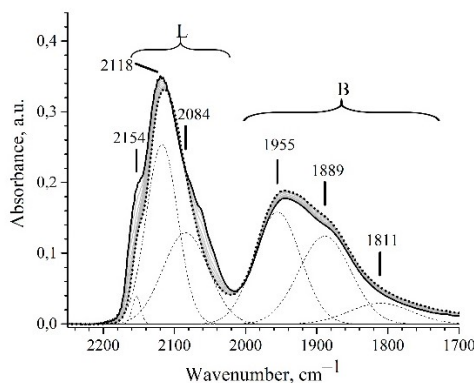
Noble metal nanoparticles, due to their relatively high stability and wide scope of application, attract a lot of researchers' attention. The catalyst effectiveness directly depends on the dispersion rate and the presence of active catalytic sites, since the higher the dispersion, the greater the surface area available for catalytic reactions. The substrate material also plays a large role in the efficiency of the final product. One of the new and effective methods for the synthesis of the noble metals ultrafine nanoparticles is *UV irradiation of their precursor salts*. The main advantages of this method are relative simplicity, high recovery rate and environmental friendliness. The nanoparticles synthesized in this way are less susceptible to agglomeration, which eliminates the need for introducing various surfactants and toxic solvents into the system, in contrast to standard methods. Due to the relatively high value of the electrode potential of the Pd<sup>2+</sup>/Pd<sup>0</sup> pair, as well as low photostability, complex palladium salts are quite easily restored, and the selection of the optimal salt and radiation power allows the process to be rapidly carried out.

In this work, palladium nanoparticles were synthesized in an aqueous solution by *UV irradiation* using complex palladium oxalate as a precursor. The synthesis consists of *UV irradiation* of an aqueous dispersion of CeO<sub>2</sub> containing the [Pd(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>]<sup>2-</sup> complex as one of the most photoactive *non-toxic* precursors. Cerium dioxide was synthesized by a simple one-step method and was selected due to its high thermal stability and relative chemical inertness, as well as its large oxygen storage capacity due to the formation of the Ce<sup>4+</sup>/Ce<sup>3+</sup> redox pair, which allows CeO<sub>2</sub> to efficiently release catalytically active oxygen species. Samples were studied by various laboratory methods, such as TEM, XRF, XRPD, XAFS spectroscopy, and diffuse reflection IR spectroscopy of CO probing molecules.

TEM images did not allow to distinguish Pd nanoparticles from the substrate material but showed the absence of the UV radiation influence on the sizes of CeO<sub>2</sub> nanoparticles. XRF data showed the presence of cerium and palladium atoms in the material. X-ray diffraction patterns indicate the presence of both a cerium dioxide phase and a phase of metallic palladium, while the analysis of XAFS spectra beyond the K edge of palladium also showed the presence of a PdO phase in the system (Fig. 1). The approximate size of palladium nanoparticles was estimated from the infrared spectra after CO adsorption (Fig. 2) and it was less than 2 nm, which is significantly smaller than the average size of Pd nanoparticles obtained by a similar method without a CeO<sub>2</sub> substrate (1.5–9.5 nm) [1].



**Figure 1.** X-ray absorption spectra beyond the K edge of Pd on CeO<sub>2</sub> in comparison with the spectra of palladium and palladium oxide nanoparticles



**Figure 2.** The IR spectra of the Pd on CeO<sub>2</sub>, measured during the desorption of CO at -140 °C, previously reduced at 200 °C in a 5% H<sub>2</sub>/Ar mixture

[1] Navaladian, S., Viswanathan, B., Varadarajan, T. K., & Viswanath, R. P. (2008). *Nanoscale research letters* 4(2), 181.

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