

Evolution of Pd/CeO₂ surface morphology *in situ* monitored by FTIR spectroscopy

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Ceria supported nanoparticles (NPs) of noble metals are well-known catalysts for diverse hydrogenation and oxidation reactions [1, 2]. Their catalytic activity depends on the dispersion and shape of NPs, support, functionalization, etc. However, the use of high Z-support and small NPs limits their diagnostics especially in laboratory conditions [3]. In this study, we demonstrate a possibility of *in situ* monitoring the size and surface morphology of Pd/CeO₂ catalysts during the growth by using FTIR spectroscopy of adsorbed CO.

Ceria NPs used as support were synthesized according to the method described in [4] and impregnated by PdCl₂ [3]. Then, the material was put into the reaction chamber and heated in a flow of Ar up to 30, 150 or 300 °C (samples Pd-30, Pd-150, Pd-300) for 30 min. A mixture of H₂, CO and Ar (2.5, 1 and 46.5 mL/min) was passed through the sample for 1 hour to reduce Pd NPs.

XRPD didn't allow distinguishing Pd NPs for all samples (Fig.1a). This fact could be explained by the small size of synthesized Pd NPs which caused broadening of peaks. Tests of catalytic (procedure described in [3]) shown that CO conversion was 25-70% for all samples at 150 °C even without calcination (in case of Pd-150 and Pd-300) and decreased in row Pd-30>Pd-150>Pd-300.

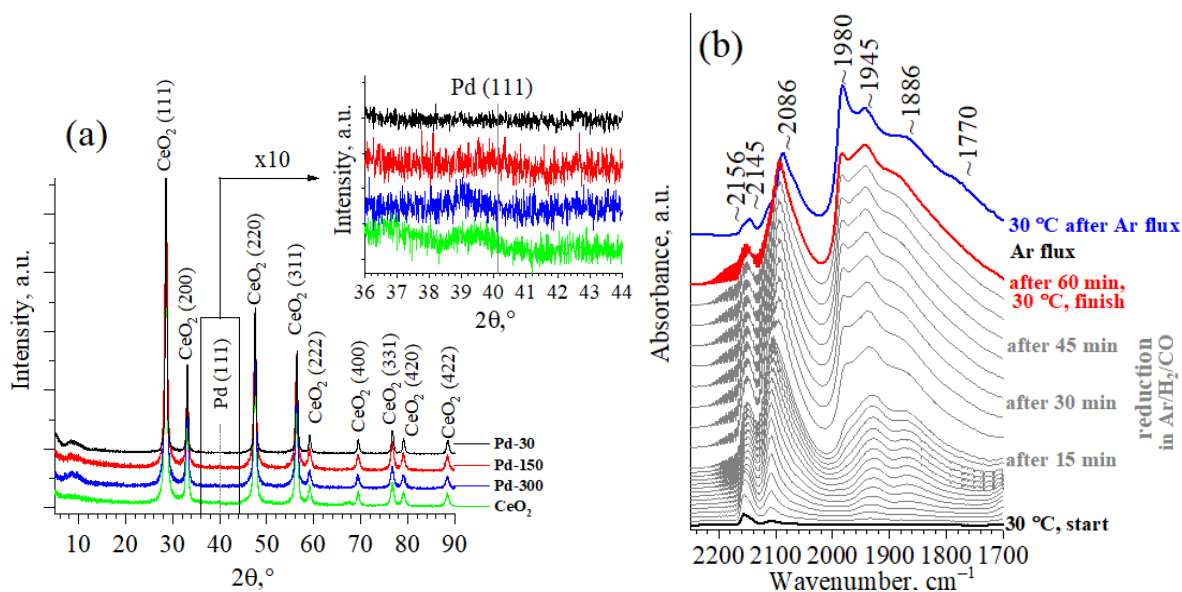


Figure 1. (a) XRPD patterns of all samples; (b) series of FTIR spectra during the synthesis of Pd-30.

The series of spectra collected *in situ* demonstrated that the reduction at high temperature (Pd-300 and Pd-150) was much faster than at low temperature (Pd-30). Also, it was observed that reduction was not complete for all samples: peaks of CO adsorbed on Pd²⁺ and Pd⁺ ions were observed (ca. 2160 and 2110 cm⁻¹). The last fact is explained by ceria support that prevented complete reduction. The process of reduction was observed in detail for the Pd-30 (Fig.1b) where the decrease of CO adsorbed on Pd ions was accompanied by the increase of peaks related to bridged carbonyls – evidence of appearing and growth of the extended surfaces. FTIR spectra allowed to determine the size of NPs which is proportional to the ratio of areas under peaks attributed to bridged (below 2000 cm⁻¹) and linear (2000-2100 cm⁻¹) carbonyls. Size decreased in row Pd-300>Pd-150>Pd-30. The dynamics of growth was clearly observed for Pd-30 and Pd-150 sample whereas for Pd-300 CO adsorbed only at 2- and 3-folded sites. Only carbonyls on Pd(111) faces were detected for Pd-150 and Pd-300 when both Pd(100) and Pd(111) facets were found for the Pd-30 sample.

While conventional techniques are limited by size of NPs (XRPD), poor contrast (TEM), require large scale facilities (XAS, SAXS), described *laboratory* technique allows determining the size and surface morphology *in situ*, at any desired moment of NPs growth.

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Keywords: palladium; ceria; nanoparticles; CO probing molecules; FTIR; adsorption;

The study was carried out with the financial support of the Russian Foundation for Basic Research (RFBR) in the framework of the scientific project №20-32-70227