

Time-dependent carbide phase formation in palladium nanoparticles

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ABSTRACT

Palladium-based catalysts are widely applied for the selective hydrogenation of acetylene in acetylene/ethylene mixtures. Under reaction conditions, palladium hydride or carbide phases can be formed, which change the catalytic properties of material. In the current work, we focus on the process of carbide phase formation in supported palladium nanoparticles (NPs) exposed to acetylene and ethylene at 100 °C. The evolution of carbide phase was monitored *in situ* by X-ray absorption near edge structure (XANES) spectroscopy, extended X-ray absorption fine structure (EXAFS) spectroscopy and X-ray powder diffraction (XRPD). The degree of the lattice expansion determined by XRPD and EXAFS was extrapolated to obtain the saturated values, which were found to be similar for ethylene- and acetylene-exposed samples, while the rate of carbide formation was higher in the case of acetylene.

1. Introduction

The industrially relevant chemical reaction of selective hydrogenation of acetylene to ethylene in acetylene/ethylene mixtures over palladium catalyst, results in formation of various carbide and hydride phases at the surface and in the bulk of the catalyst (Borodziński and Bond, 2006; Bugaev et al., 2018a). There are numerous theoretical (Carstansen et al., 1978; Nishijima et al., 2005) and experimental (Bugaev et al., 2014; Nag, 2001) works on formation of palladium hydride phase. In contrast, palladium carbides are much less studied (Zhao et al., 2017). Unlike the hydride one, palladium carbide phase is known to be formed irreversibly (Bugaev et al., 2017a; Tew et al., 2012) or partially irreversibly (Bugaev et al., 2018a,b), which means that once formed in the catalyst, palladium carbide will be permanently present under reaction conditions.

Being associated with palladium lattice expansion, both phases have been extensively studied by X-ray powder diffraction (XRPD) and X-ray absorption spectroscopy (XAS). In the recent works, we showed

that the combination of these techniques can highlight the difference between surface and bulk regions of the nanoparticle (NP) (Bugaev et al., 2017b, 2018a). In addition, XAS spectroscopy was also shown to be directly sensitive not only to Pd-Pd bond distances, but also to the presence of hydrogen atoms in the interstitial states (Bugaev et al., 2013) and adsorbed hydrocarbon molecules at the surface of the NPs (Bugaev et al., 2018a).

In the present work, we investigate the progressive palladium carbide formation in supported palladium NPs by *in situ* Pd *K*-edge X-ray absorption near edge structure (XANES) (Guda et al., 2018) and extended X-ray absorption fine structure (EXAFS) spectroscopies, complemented by X-ray powder diffraction (XRPD). The process of carbide formation was initiated by exposure of the catalyst to acetylene and ethylene at 100 °C, and its evolution was monitored over more than three hours. The obtained results indicate that the rate of carbide formation is higher in acetylene than in ethylene, while the final structures obtained after 3 h of treatment were similar in both acetylene and ethylene cases.

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2. Materials and methods

2.1. Materials

The experiment was performed on Pd NPs (Chimet S.p.A.) with average size 2.6 ± 0.4 nm supported on carbon (5wt%). The sample has been already studied in our previous works (Bugaev et al., 2016, 2017b, 2018a).

2.2. Experimental procedure

XAS and XRPD data were collected at the BM31 beamline (van Beek et al., 2011) of ESRF (Grenoble, France). The measurements were performed in transmission geometry using 2 mm glass capillaries filled by sample powder and connected to a gas flow system. The gas blower located under the sample was used to control the temperature.

Prior to exposure to hydrocarbons, the samples were activated in 20 mL/min flow of 20% H₂/He at 125 °C for 30 min and then kept in He flow to ensure the initial metallic state of Pd. Then, the process of carbide formation was induced in two different atmospheres: in the flow of 5% acetylene in helium and in pure ethylene at 100 °C, the total flow being always 20 mL/min.

XRPD and XAS data were measured quasi-simultaneously, starting from XRPD (2 min) followed by XAS (8 min). The switch from XRPD to XAS geometry took less than 30 s. XRPD patterns were measured in Debye-Scherrer geometry using Dexcela CMOS 2D detector and photon wavelength of 0.51105 Å.

XAS spectra were collected in transmission mode at Pd K-edge (24.35 keV) from 24.2 to 25.6 keV in the continuous scanning mode. Pd foil was measured simultaneously using a third ionization chamber for energy calibration.

2.3. Data analysis

XRPD data were analyzed using Jana2006 code (Petříček et al., 2014), which allowed obtaining the changes of the cell parameter during carbide formation in comparison with metallic Pd NPs. The amorphous carbon support without Pd NPs was measured to subtract its contribution to diffuse scattering from XRPD patterns. All patterns were refined using two phases with different cell parameters (corresponding to metallic palladium and palladium carbide). Lorentz functions was used to fit the peak shape.

Normalization of XAS spectra for XANES analysis, background subtractions and first-shell Fourier-analysis of EXAFS spectra, were performed using Athena and Artemis codes of Demeter package (Ravel and Newville, 2005) with parameters reported in the Supporting Information. XANES spectra were fitted by linear combination analysis (LCA) taking the spectrum of the initial metallic Pd NPs and an average of 10 spectra after continuous exposure to acetylene as two basis vectors for LCA.

3. Results and discussion

Upon exposure to acetylene or ethylene, immediate changes indicative to carbide formation were observed in the experimental data. In XANES spectra, a broadening of the first maximum towards higher energies is observed, which is characteristic for palladium carbide (Fig. 1a). The frequency of oscillations in EXAFS is increased, indicating the elongation of Pd—Pd distances (Fig. 1b). Finally, Pd reflections in XRPD patterns were shifted towards lower 2θ angles due to the lattice expansion (Fig. 1c). The calculated expansion of the lattice parameter and interatomic distances are shown in Fig. 2 (left ordinate axis). Considerable increase by around 1.4% and 0.4% was detected in acetylene

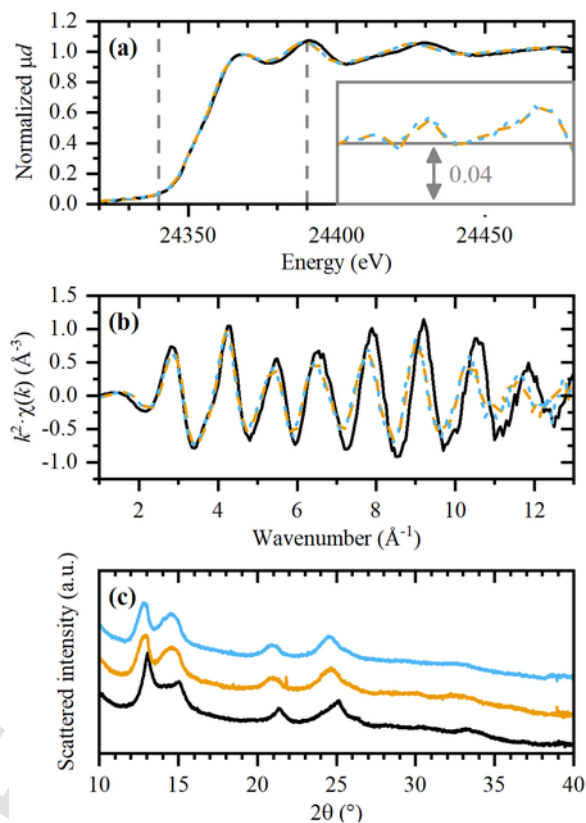


Fig. 1. XANES spectra (a), EXAFS oscillations (b) and XRPD patterns (c) of metallic Pd NPs in He (black), and after 3 h exposure to acetylene (orange) and ethylene (blue) at 100 °C. The inset in part (a) shows the spectra collected in acetylene (orange) and ethylene (blue) after subtraction of the spectrum of metallic Pd NPs in the energy range from 24,340 to 24,390 eV highlighted by dashed grey vertical lines on the main part of panel (a). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

(part a) and ethylene (part b), respectively, already in the first spectra in both series. In the case of acetylene, the lattice expansion occurs much faster than in ethylene. However, the saturated values after 3 h of exposure are similar in both cases. In addition, a similar behavior was obtained from LCA of XANES spectra (Fig. 2, right ordinate axis).

Slower rate of palladium carbide formation in ethylene can be explained by the fact that ethylene is more energetically stable molecule and, moreover, its decomposition to atomic carbon requires breaking of four C—H bonds versus two for acetylene. In acetylene, the limited time resolution of the data acquisition setup, did not allow us to observe the gradual transformation from metal NPs to their carbide. However, it is clear that in both cases the process occurs in two stages: fast carbide formation with lattice expansion by ca. 1.6%, and further much slower expansion. The saturation values of lattice expansion and elongation of Pd—Pd interatomic distances, were obtained by exponential fit of the values shown in Fig. 2. According to XRPD data, the saturated values of lattice expansion were 2.02 ± 0.02 and $1.98 \pm 0.02\%$ for acetylene and ethylene, respectively. The determined elongation of Pd—Pd interatomic distances from EXAFS was $1.82 \pm 0.02\%$ and $1.82 \pm 0.03\%$ for acetylene and ethylene, respectively. The relative expansion of Pd NPs is systematically lower in EXAFS, than in XRPD. Although the difference may originate from the absolute errors in determination of cell parameters and interatomic distances, this observation can be also explained by contribution of the surface of NPs to EXAFS, where the concentration of carbon atoms may not be as high as in the bulk, similar to what was observed for Pd hydride NPs (Bugaev et al., 2017b).

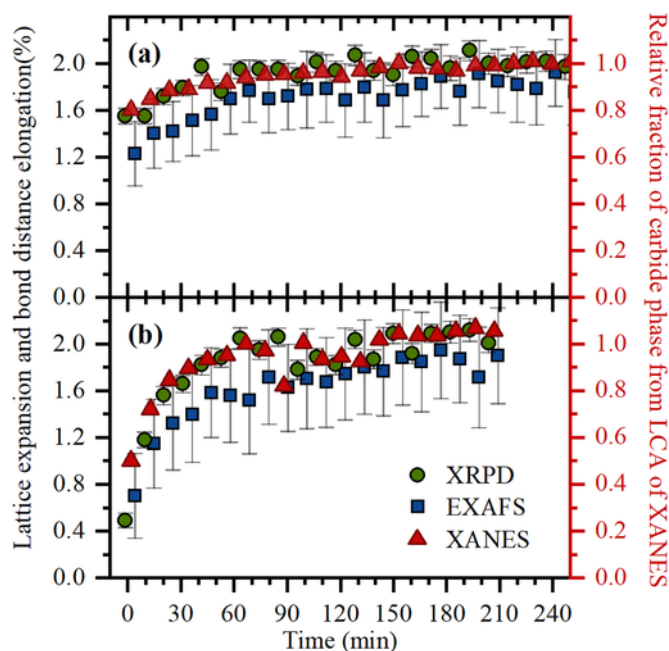


Fig. 2. Evolution of the cell parameter calculated from XRPD refinement (green circles, left ordinate axis), first shell Pd—Pd interatomic distances from EXAFS (blue squares, left ordinate axis) and relative fraction of carbide component from LCA of XANES during exposure of Pd NPs to acetylene (a) and ethylene (b) at 100 °C. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

4. Conclusion

We have investigated the time evolution of palladium carbide formation supported Pd NPs exposed to acetylene and ethylene at 100 °C. Combination of XRPD, EXAFS, and XANES allowed us to characterize the process of carbide formation by the increase of the cell parameter, elongation of the first shell interatomic distances, and formation of Pd—C bonds, respectively. The following properties of the carbide formation process were highlighted:

- In both acetylene and ethylene, the process of carbide formation occurs in two stages. Initially, rapid changes are observed immediately after exposure to hydrocarbons. Then, gradual and slow lattice expansion was observed over few hours.
- The rate of carbide formation is higher in acetylene than in ethylene.
- The resulting structures of palladium carbides after 3 h of exposure to acetylene and ethylene are identical.

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References

- Borodziński, A., Bond, G.C., 2006. Selective hydrogenation of ethyne in ethene-rich streams on palladium catalysts. Part 1. Effect of changes to the catalyst during reaction. *Cat. Rev. Sci. Eng.* 48, 91–144. <https://doi.org/10.1080/01614940500364909>.
- Bugaev, A.L., Guda, A.A., Lazzarini, A., Lomachenko, K.A., Groppo, E., Pellegrini, R., Piovano, A., Emerich, H., Soldatov, A.V., Bugaev, L.A., Dmitriev, V.P., van Bokhoven, J.A., Lamberti, C., 2017. In situ formation of hydrides and carbides in palladium catalyst: when XANES is better than EXAFS and XRD. *Catal. Today* 283, 119–126. <https://doi.org/10.1016/j.cattod.2016.02.065>.
- Bugaev, A.L., Guda, A.A., Lomachenko, K.A., Lazzarini, A., Srabionyan, V.V., Vitillo, J.G., Piovano, A., Groppo, E., Bugaev, L.A., Soldatov, A.V., Dmitriev, V.P., Pellegrini, R., van Bokhoven, J.A., Lamberti, C., 2016. Hydride phase formation in carbon supported palladium hydride nanoparticles by in situ EXAFS and XRD. *J. Phys. Conf. Ser.* 712, <https://doi.org/10.1088/1742-6596/712/1/012032> (Art. n. 012032).
- Bugaev, A.L., Guda, A.A., Lomachenko, K.A., Shapovalov, V.V., Lazzarini, A., Vitillo, J.G., Bugaev, L.A., Groppo, E., Pellegrini, R., Soldatov, A.V., van Bokhoven, J.A., Lamberti, C., 2017. Core-shell structure of palladium hydride nanoparticles revealed by combined X-ray absorption spectroscopy and X-ray diffraction. *J. Phys. Chem. C* 121, 18202–18213. <https://doi.org/10.1021/acs.jpcc.7b04152>.
- Bugaev, A.L., Guda, A.A., Lomachenko, K.A., Srabionyan, V.V., Bugaev, L.A., Soldatov, A.V., Lamberti, C., Dmitriev, V.P., van Bokhoven, J.A., 2014. Temperature- and pressure-dependent hydrogen concentration in supported PdH_x nanoparticles by Pd K-edge X-ray absorption spectroscopy. *J. Phys. Chem. C* 118, 10416–10423. <https://doi.org/10.1021/jp500734p>.
- Bugaev, A.L., Srabionyan, V.V., Soldatov, A.V., Bugaev, L.A., van Bokhoven, J.A., 2013. The role of hydrogen in formation of Pd XANES in Pd-nanoparticles. *J. Phys. Conf. Ser.* 430 <https://doi.org/10.1088/1742-6596/430/1/012028> (Art. n. 012028).
- Bugaev, A.L., Usoltsev, O.A., Guda, A.A., Lomachenko, K.A., Pankin, I.A., Rusalev, Y.V., Emerich, H., Groppo, E., Pellegrini, R., Soldatov, A.V., van Bokhoven, J.A., Lamberti, C., 2018. Palladium carbide and hydride formation in the bulk and at the surface of palladium nanoparticles. *J. Phys. Chem. C* 122, 12029–12037. <https://doi.org/10.1021/acs.jpcc.7b11473>.
- Bugaev, A.L., Usoltsev, O.A., Lazzarini, A., Lomachenko, K.A., Guda, A.A., Pellegrini, R., Carosso, M., Vitillo, J.G., Groppo, E., van Bokhoven, J.A., Soldatov, A.V., Lamberti, C., 2018. Time-resolved operando studies of carbon supported Pd nanoparticles under hydrogenation reactions by X-ray diffraction and absorption. *Faraday Discuss.* 208, 187–205. <https://doi.org/10.1039/c7fd00211d>.
- Carstanjen, H.D., Dünstl, J., Löbl, G., Sizmman, R., 1978. Lattice location and determination of thermal amplitudes of deuterium in α -PdD_{0.007} by channeling. *Phys. Status Solidi A* 45, 529–536. <https://doi.org/10.1002/pssa.2210450221>.
- Guda, A.A., Guda, S.A., Lomachenko, K.A., Soldatov, M.A., Pankin, I.A., Soldatov, A.V., Braglia, L., Bugaev, A.L., Martini, A., Signorile, M., Groppo, E., Piovano, A., Borfecchia, E., Lamberti, C., 2018. Quantitative structural determination of active sites from in situ and operando XANES spectra: from standard ab initio simulations to chemometric and machine learning approaches. *Catal. Today* <https://doi.org/10.1016/j.cattod.2018.10.071>.
- Nag, N.K., 2001. A study on the formation of palladium hydride in a carbon-supported palladium catalyst. *J. Phys. Chem. B* 105, 5945–5949. <https://doi.org/10.1021/jp004535q>.
- Nishijima, M., Okuyama, H., Takagi, N., Aruga, T., Brenig, W., 2005. Quantum delocalization of hydrogen on metal surfaces. *Surf. Sci. Rep.* 57, 113–156. <https://doi.org/10.1016/j.surfrep.2005.03.001>.
- Petríček, V., Dušek, M., Palatinus, L., 2014. Crystallographic computing system JANA2006: general features. *Z. Krist. Cryst. Mater.* 229, 345–352. <https://doi.org/10.1515/zkri-2014-1737>.
- Ravel, B., Newville, M., 2005. Athena, artemis, hephaestus: data analysis for x-ray absorption spectroscopy using ifeffit. *J. Synchrotron Radiat.* 12, 537–541. <https://doi.org/10.1107/S0909049505012719>.
- Tew, M.W., Nachtegaal, M., Janousch, M., Huthwelker, T., van Bokhoven, J.A., 2012. The irreversible formation of palladium carbide during hydrogenation of 1-pentyne over silica-supported palladium nanoparticles: in situ Pd K and L₃ edge XAS. *Phys. Chem. Chem. Phys.* 14, 5761–5768. <https://doi.org/10.1039/c2cp24068h>.
- van Beek, W., Safonova, O.V., Wiker, G., Emerich, H., 2011. SNBL, a dedicated beamline for combined in situ X-ray diffraction, X-ray absorption and Raman scattering experiments. *Phase Transit.* 84, 726–732. <https://doi.org/10.1080/01411594.2010.549944>.
- Zhao, S., Li, Y., Liu, D., Liu, J., Liu, Y.-M., Zakharov, D.N., Wu, Q., Orlov, A., Gewirth, A.A., Stach, E.A., Nuzzo, R.G., Frenkel, A.I., 2017. Multimodal study of the speciations and activities of supported Pd catalysts during the hydrogenation of ethylene. *J. Phys. Chem. C* 121, 18962–18972. <https://doi.org/10.1021/acs.jpcc.7b06270>.