



The role of palladium carbides in the catalytic hydrogenation of ethylene over supported palladium nanoparticles

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ABSTRACT

Palladium nanoparticles (NPs) find numerous applications as catalysts for hydrogenation of hydrocarbons. Under reaction conditions, formation of palladium hydrides and carbides may occur, which affects the catalytic properties of the catalyst. Unlike pure hydride phase, whose phase diagram is well-studied, conditions of formation of palladium carbides and mixed hydride/carbide structures in Pd NPs is poorly investigated. We present an *operando* study of a supported Pd/C catalyst during ethylene hydrogenation reaction in a variable C₂H₄/H₂ ratio. By simultaneous analysis of the extended X-ray absorption fine structure (EXAFS) and X-ray absorption near-edge structure (XANES) spectra, we demonstrated an irreversible behavior in the catalyst structure explained by carbide phase formation even in the instant excess of molecular hydrogen with respect to molecular ethylene in the gas feed. The relevant role of the carbide phase was demonstrated by correlations between the carbide phase amount and ethylene conversion. An interesting behavior of the atomic structure of the Pd NPs has been observed upon periodic variation of the amount of ethylene in the reaction mixture. The obtained results provide significant information about the structural evolution of Pd NPs during ethylene hydrogenation reaction and highlight the importance of *operando* XANES spectroscopy for characterization of the working catalysts.

1. Introduction

The catalytic properties of palladium, palladium nanoparticles (NPs) and palladium supported on various supports have been studied for a long time [1,2]. In particular, supported Pd NPs are widely applied in petrochemical industry for selective and non-selective hydrogenation of hydrocarbons [3]. In particular, selective semi-hydrogenation of acetylene impurities in the ethylene-rich mixtures avoiding full hydrogenation to ethane is fundamental for purifying the feed for ethylene polymerization reactions [4]. Catalyst exposure to hydrogen/hydrocarbon mixtures may lead to formation of palladium hydrides and carbides [34], which affect its catalytic activity [3,5]. In particular, palladium hydride phase is generally considered to be responsible for non-selective hydrogenation [5]. However, a number of studies reported both carbide formation during non-selective hydrogenation [6,7] and high selectivity to ethylene over β -hydride [8]. The lack of

the information on the conditions of palladium carbide formation and the discrepant reports on its role in the hydrogenation reactions, motivated us for an *operando* X-ray absorption spectroscopic study [9,10] of an industrial catalysts, exploiting as a model reaction the ethylene to ethane conversion. In this regard, of particular interest is the study of Zhao et al. [11] who performed a combined TEM, IR, XAFS *operando* investigation of the structural dynamics of a SiO₂-supported Pd catalyst during ethylene hydrogenation, highlighting that the reaction conditions drive pronounced composition and structural transformations in Pd NPs. They observed the presence of both palladium hydride and carbide phases changing the C₂H₄/H₂ ratio of the feed.

In the present work, the complementary analysis of the extended X-ray absorption fine structure (EXAFS) and X-ray absorption near-edge structure (XANES) spectra provided a new insight on the structural evolution of the Pd NPs under reaction conditions, which were correlated with their catalytic activity. Without excluding the fact that bulk

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dissolved hydrogen is important for hydrogenation, we unambiguously highlight the relevant role of carbide phase in catalysis, showing that, from the one hand, it appears as a consequence of the catalyst exposure to a reaction mixture, but from the other, its presence is required for the high ethylene conversion.

2. Materials and methods

5 wt.% Pd/C catalyst, supplied by Chimet S.p.A., was made by Pd NPs supported on a wood-based activated carbon (surface area = 980 m² g⁻¹; pore volume = 0.62 cm³ g⁻¹), following the deposition-precipitation method described elsewhere [12]. This method gave Pd NPs with the average size of about 2.6 nm. Detailed characterization of the sample has been performed in our previous studies [13–19]. Experimental Pd *K*-edge XAS data were collected at BM26A beamline [20] of ESRF synchrotron (Grenoble, France). The spectra were collected in transmission mode in the energy range from 24.15 till 25.15 eV ($k_{\text{max}} = 14.4 \text{ \AA}^{-1}$) with 1 eV step in the XANES region and 0.04 \AA^{-1} step in the EXAFS region.

The catalyst (30 mg) was loaded into an in situ cell with build-in heater [21] providing an absorption step of $\Delta\mu x = 0.35$. A fraction of the catalyst sieved to 100–150 μm was used to avoid overpressure, controlled by Bourdon tube pressure gauge. The cell was connected to the remotely controlled gas line permanently present on BM26A [22] and equipped with Bronkhorst mass flow controllers (MFCs). All MFCs were calibrated using Agilent flow meter. The total flux of the gas mixture through the sample was always kept at 50 mL/min. The sample was initially activated for 30 min at 125 °C in the flow of 10 mL/min H₂ and 40 mL/min He to reduce the oxidized palladium NPs to a pure metallic state. Then, the cell was cooled down to 80 °C and the catalytic mixture of H₂ and C₂H₄ was sent to the sample. The hydrogen flow during the catalytic tests was kept at 15 mL/min, while the C₂H₄ and He flows were varied keeping the total flux at 50 mL/min (see Section 3.1). At each C₂H₄/H₂ ratio, the sample was kept for ca. 15 min which was required to collect an EXAFS spectrum with few exceptions due to the technical problems during the experiment. At the end of each hydrogenation cycle the C₂H₄ flow was switched off and 15 and 35 mL/min of H₂ and He respectively were sent through the sample for 15–30 min. The described procedure was repeated three times. The output of the cell was monitored by online quadrupole mass spectrometer (MS) manufactured by Pfeiffer.

The first-shell Fourier-analysis of EXAFS spectra was performed in Demeter package [23] on k^2 -weighted EXAFS data in the k -range from 4 to 12 \AA^{-1} . The fitting was performed in the R -space from 1 to 3 \AA with four independent variable parameters for each spectrum: first shell interatomic Pd–Pd distance ($R_{\text{Pd-Pd}}$), coordination number (N), Debye-Waller parameter (σ^2), and inner potential correction (ΔE_0). The value of amplitude reduction factor was obtained by fitting the spectrum of Pd foil and kept fixed during the fit of the nanoparticles.

XANES part of the normalized spectra were subjected to a principle component analysis (PCA) with subsequent principle vector rotation implemented in FitFit code [24]. This method allows, first, to determine the number of independent components needed to correctly describe the whole experimental dataset and then transforms the abstract principle components into physically meaningful spectra that can be interpreted as spectra of the pure species in the sample.

3. Results and discussion

3.1. MS data

The adopted experimental procedure and analyzed MS data are summarized in Fig. 1, parts a and b, respectively. In the starting point, the activated sample was subjected to a flow of 15 and 35 mL/min of H₂ and He, respectively, at 80 °C. The partial hydrogen pressure in such mixture is 300 mbar, which corresponds to a β -phase region at 80 °C

according to the phase diagrams obtained before for this sample [18,19]. Starting with the pre-hydrogenated sample, the C₂H₄ flow was increased from 0 to 10 mL/min with a step of 1 mL/min, while the corresponding He flux was decreased from 35 to 25 mL/min with the same step to preserve the total flux of the gas mixture through the sample. This procedure was repeated three times. The ethylene conversion was estimated by monitoring the relative ratio of the MS signals with $m/Z = 30$ and 28. According to the preliminary calibration obtained by sending different ratios of ethylene and ethane without a catalyst, this ratio is varied from 0 to ~0.22 (see Section S1) for pure ethylene and ethane, respectively. This way of normalization allows to exclude the possible instabilities and drifts in the MS signal [25].

The interesting fact is that for low C₂H₄/H₂ ratios, lower conversion has been observed, and the conversion grew with the increasing C₂H₄/H₂ ratio. Considering the ethylene hydrogenation to be zero or negative order reaction with respect to ethylene [26], this observation suggests that catalytic activity may change due to the changes in the catalyst structure (See Sections 3.2 and 3.3). Another particular feature is that for the first cycle, conversion grows slower than for the subsequent ones. This means that, the pre-hydrogenated sample exhibits lower catalytic activity, which is quite unexpected since β -hydride phase of palladium is generally claimed to be the most active [5,17]. This fact will be discussed in more detail in the following sections, after the structural characterization of the sample by EXAFS and XANES will be given.

3.2. First shell EXAFS analysis

Evolution of the Pd–Pd interatomic distances was monitored by *operando* EXAFS spectroscopy. The results of the first-shell Fourier-analysis are presented in Fig. 2. For the fresh pre-hydrogenated catalyst, the value of $R_{\text{Pd-Pd}} = 2.806 \pm 0.007 \text{ \AA}$ is consistent with the values obtained for the β -hydride phase of palladium [15,19,27]. With the increasing of the ethylene flow, the interatomic distances decrease, which can be explained by the fact, that ethylene hydrogenation reaction consumes hydrogen and decreases its partial pressure. At the end of the first cycle, $R_{\text{Pd-Pd}}$ is slightly higher ($2.750 \pm 0.006 \text{ \AA}$) than that of pure metallic NPs (2.74 \AA) indicating that the α -hydride phase should be present. During the second cycle, the obtained interatomic distances are virtually the same as during the first cycle, which indicates that the changes occurred in the structure of the NPs along the first cycle are reversible. However, during the third cycle, the interatomic distances are slightly lower than those observed during the first two cycles at the similar ethylene flows. Although small, this effect is reliable as it occurs systematically for all the eleven different ethylene flows measured in the cycle. In addition, the phase transition from β - to α - phase occurs at lower ethylene flows. A similar fact was observed by Pradier et al. for acetylene hydrogenation, when the β -hydride was formed at higher pressures than predicted from standard phase diagram [8]. These results indicate that the structural changes in the Pd NPs occurring during the hydrogenation reaction are to a large extent reversible. As we demonstrated in the previous works, the analysis based solely on the interatomic distances does not provide a complete information about the actual phase of palladium, especially under reaction conditions [15–17]. For unambiguous determination of possible hydride and carbide phases, the XANES spectra have been also considered.

3.3. PCA analysis of the XANES data

In presence of a large number of XANES spectra collected during time-resolved experiments, the use of statistically-based analytical methods allows a deeper and more solid understanding of the investigated process [28–31]. In the present case, XANES analysis has been performed within a PCA approach with subsequent rotation of the components implemented in FitFit code [24] to generate the corresponding XANES spectra of the pure phases (see Section S2 of the

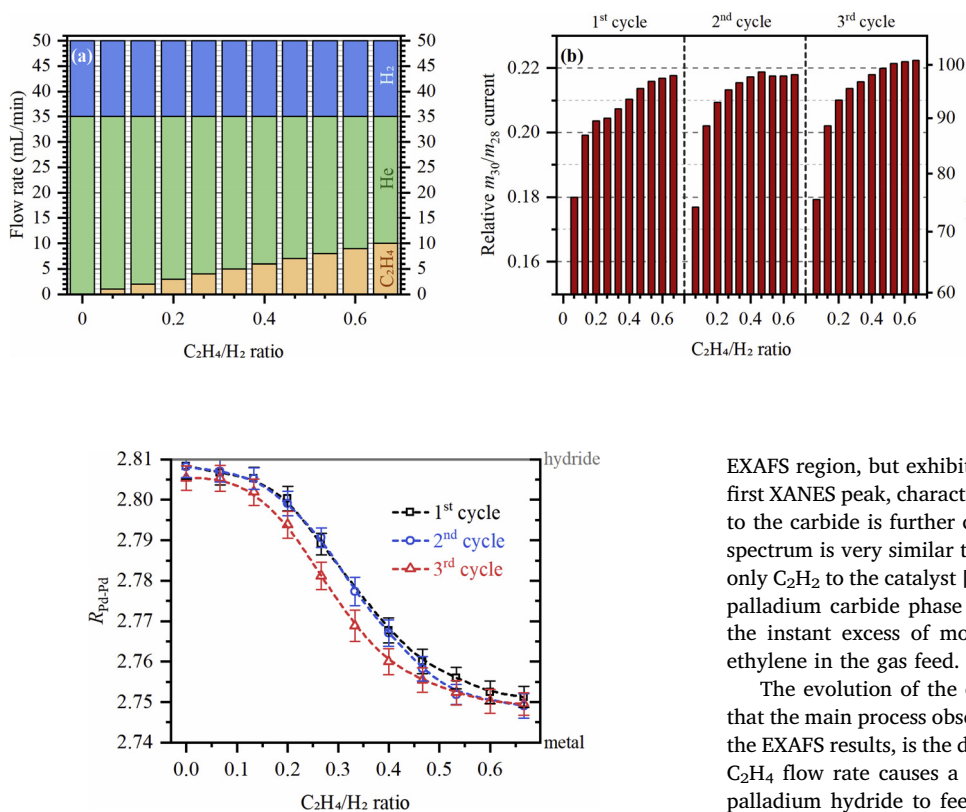


Fig. 1. (a) Variation of the flow of H₂ (blue), C₂H₄ (orange) and He (green) through the sample within one cycle. (b): The relative fraction of the MS-detected signals for $m/Z = 30$ and $m/Z = 28$ (left axis) as a function of C₂H₄/H₂ ratio during the three subsequent cycles. The corresponding values of conversion estimated based on the MS calibration (Fig. S2) are shown on the right axis. The last two bars in part (b) have values slightly higher than 100%: which is within the experimental error of the measurement, as discussed in Section S1 of the Supporting information (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

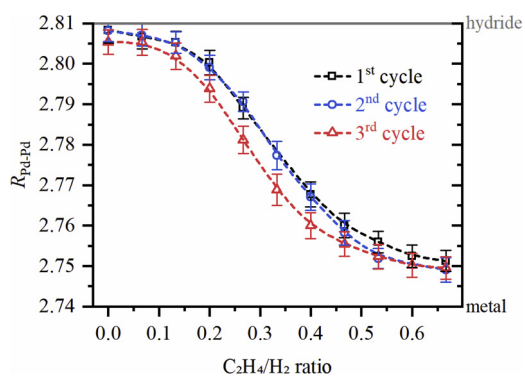


Fig. 2. The first-shell Pd-Pd interatomic distances as a function of C₂H₄/H₂ ratio for the first (black squares), second (blue circles) and third (red triangles) cycles. The reference values for Pd hydride NPs in pure hydrogen and metal Pd NPs in pure helium are 2.81 and 2.74 Å, respectively (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

Supporting information). At the first step, we determined that in the whole series of spectra there are three independent components (Fig. S3). In the following step these three PCA components were rotated in order to obtain the spectra of different pure Pd-phases in the sample. To decrease the number of free variables in determination of the rotation matrix, the first component was fixed to the first spectrum in the series, which corresponds to pure β -hydride phase of Pd NPs [35]. The other two obtained components and their evolution during the ethylene hydrogenation reaction at different ethylene flows are shown in Fig. 3, parts (a) and (b), respectively. The spectrum of the second component is characterized by the shift of the maxima towards the higher energies, indicating the decrease of the Pd-Pd interatomic distances. Therefore, this component was assigned to the α -phase of palladium hydride. The third component cannot be distinguished from the hydride one in the

EXAFS region, but exhibits strong changes in shape and position of the first XANES peak, characteristic for palladium carbide [36]. Assignment to the carbide is further confirmed by the fact that this PCA extracted spectrum is very similar to the experimental spectrum collected dosing only C₂H₂ to the catalyst [15]. The data reported in Fig. 3b indicate that palladium carbide phase is formed under reaction conditions even in the instant excess of molecular hydrogen with respect to molecular ethylene in the gas feed.

The evolution of the obtained components (Fig. 3b) demonstrated that the main process observed during the first cycle, in agreement with the EXAFS results, is the decomposition of β -hydride: the increase of the C₂H₄ flow rate causes a depletion of atomic hydrogen from the bulk palladium hydride to feed the conversion of C₂H₄ to C₂H₆ (Fig. 1b), displacing the $\alpha \rightleftharpoons \beta$ equilibrium to the left. However, at the end of the first cycle (Fig. 3b), a small fraction of palladium carbide is readily formed at high C₂H₄/H₂ ratios. Due to the low amount of this carbide and the interatomic distances similar to that of palladium hydride [34], the two phases cannot be resolved by standard EXAFS analysis [32]. The fact that carbide was presented not in a single spectrum but in a considerable fraction of the spectra makes it statistically relevant and allows its detection by PCA analysis. However, its lower amount with respect to other two components resulted in a more noisy behavior at the edge (Fig. 3a). In the second cycle, the relative changes of the three components are similar to that in the first cycle, with the only difference that at high ethylene flow, the fraction of the formed carbide phases is slightly larger, while the hydride component decreases to 0. In the last cycle, the carbide remained stable even in pure hydrogen at the beginning of the cycle. Concentration of this phase continues growing to its maximal value in the end of the cycle.

Formation of the carbide phase under reaction conditions explains the two following phenomena reported in the previous sections. First, carbide phase acts as the reason for the non-reversibility of the $R_{\text{Pd-Pd}}$ values during the third cycle (Fig. 2). While in the beginning of the first two cycles carbide phase is absent, the hydrogen atoms are allowed to penetrate inside Pd NPs. In accordance with the recent works of our

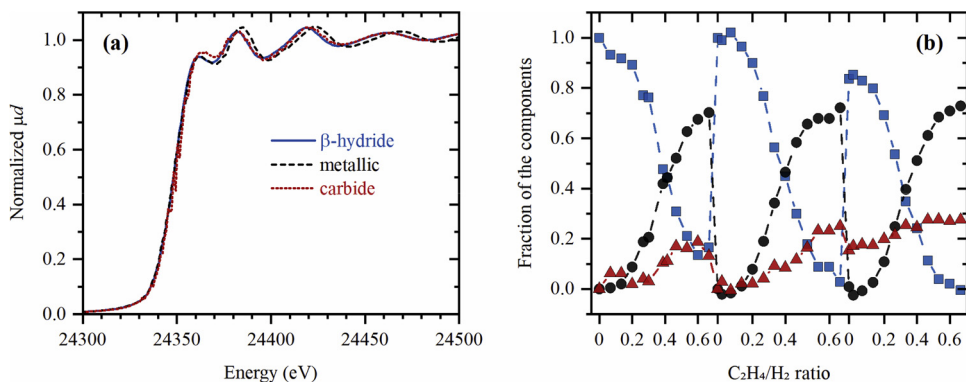


Fig. 3. Pure components, part (a), derived from PCA analysis with matrix rotation assigned to β -hydride (solid blue line), metallic (dashed black line), and carbide (dotted red line) phases of palladium and their relative fractions, part (b), during the three subsequent ethylene hydrogenation reaction cycles at increasing of C₂H₄/H₂ ratio (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

group [16,17], the fact of complete removal of carbide component, which is generally reported to form irreversibly, indicate that only surface carbide, or surface adsorbed hydrocarbon molecules are present during the first cycle, which can be removed by hydrogenation in H₂ flow. The irreversible fraction of carbide observed at the end of the second cycle is associated with bulk carbide formation. In the presence of bulk carbides, less hydrogen is able to be absorbed by the NPs, resulting in the lower R_{Pd-Pd} values. Second, the amount of carbide phase determined by XANES in Fig. 3b correlates with the ethylene conversion estimated from Fig. 1b. As we have already mentioned, this observation is not trivial, because hydride phase was reported to be more active and responsible for full hydrogenation of hydrocarbons [5]. However, for catalytic hydrogenation ethylene molecules should be adsorbed from the gas phase and form intermediates with palladium. Such intermediates form PdC bonds, which affects the shape of XANES spectra [16,17]. According to the obtained results, formation of PdC bonds is suppressed for the pre-hydrogenated sample, resulting in a lower catalytic activity. The lower activity of the pre-hydrogenated catalyst in comparison with the catalyst after continuous exposure to the reaction mixture was recently observed by Jung et al. [33] but left without explanation as no carbide phase was detected by EXAFS analysis. With the support from XANES data, we are now able to conclude that the carbide is an important component of the working catalyst, which, from the one hand, is inevitably formed under reaction conditions, and from the other hand, is necessary for the catalytic reaction. The higher activity of the partially carbided sample also explained why the β -hydride decomposition occurs at lower ethylene flows in the last cycle, which is another independent proof (in addition to MS data) of the higher ethylene and hydrogen conversion. Indeed, higher the conversion higher is the consumption of hydrogen and lower is the hydrogen partial pressure which causes the shift of the phase transition with respect to the first and second cycles.

4. Conclusions

We have performed an *operando* characterization of the palladium nanoparticles in an industrial Pd/C catalyst during ethylene hydrogenation reaction by X-ray absorption spectroscopy. Advanced analysis of XANES spectra allowed us to demonstrate that irreversible formation of palladium carbide phase occurs even in the instant excess of molecular hydrogen with respect to molecular ethylene in the gas feed. Despite the fact that palladium hydride phase is considered to be responsible for the hydrogenation, we have shown that the pre-hydrogenated sample has lower catalytic activity than the sample after exposure to a catalytic mixture, indicating that the co-presence of a carbide phase improves the catalyst activity. The conversion of ethylene to ethane correlates with the amount of carbide phase, which was shown to play a crucial role in the ethylene hydrogenation process. The obtained results provide new insight on the evolution of the atomic and electronic structure of Pd NPs under reaction conditions and highlight the importance of XANES spectroscopy for *operando* characterization of the working catalysts.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.cattod.2019.02.068>.

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