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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 the supported Pd/C catalyst during ethylene hydrogenation reaction in a variable C₂H₄/H₂ flux. 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 hydrogen. 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 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.

Keywords: Palladium hydrides, Palladium carbides, XANES, EXAFS, Ethylene hydrogenation

1. Introduction

Supported palladium nanoparticles (NPs) are widely applied in petrochemical industry for selective and non-selective hydrogenation of hydrocarbons [1]. In particular, ethylene polymerization requires selective semi-hydrogenation of acetylene in the ethylene-rich mixtures avoiding full hydrogenation to ethane [2]. Catalyst exposure to hydrogen/hydrocarbon mixtures may lead to formation of palladium hydrides and carbides, which affect its catalytic activity [3]. In particular, palladium hydride phase is generally considered to be responsible for non-selective hydrogenation [3]. However, a number of studies reported also carbide formation during non-selective hydrogenation [4, 5] and high selectivity over β -hydride [6].

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 of the real industrial catalysts, exploiting a model reaction of ethylene to ethane conversion. 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 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 was supplied by Chimet S.p.A. Detailed characterization of the sample have been performed in our previous studies[7-13]. Experimental Pd *K*-edge XAS data were collected at BM26A beamline of ESRF synchrotron (Grenoble, France). The spectra were collected in transmission mode in the energy range from 24.15 till 25.15 eV ($k_{\max} = 14.4 \text{ \AA}^{-1}$) with 1 eV step in the XANES region and 0.04 \AA^{-1} step in the EXAFS region.

The catalyst was loaded into an *in situ* cell with build-in heater [14] providing an absorption step of 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 a remotely controlled gas line 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 send to the sample. The hydrogen flow during the catalytic tests was kept at 15 mL/min and while the C₂H₄ and He flows were varied keeping the total flux at 50 mL/min. The output of the cell was monitored by online mass spectrometer (MS) manufactured by Pfeiffer.

The first-shell Fourier-analysis was performed in Demeter package [15] on k^2 -weighted EXAFS data in the k -range from 4 to 12 \AA^{-1} . XANES spectra were subjected to a principle component analysis (PCA) with subsequent vector rotation implemented in FitIt code [16].

3. Results and Discussion

The adopted experimental procedure and MS data are summarized in Figure 1. 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 [12, 13]. 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 conserve 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 mass spectra of ethylene and ethane shown in Figure S1, such ratio is proportional to the relative ratio between ethylene and ethane gas, and is varied from 0 for pure

ethylene to ~ 0.25 for pure ethylene and ethane, respectively. This way of normalization allows to exclude the possible instabilities and drifts in the MS signal [17].

The interesting fact is that for the low C_2H_4/H_2 ratios, lower conversion rates have been observed. Despite the fact that were lower than for the higher ones. Despite the fact that ethylene hydrogenation was reported to be zero or negative order reaction with respect to ethylene [18], the conversion grows with increasing C_2H_4 flow reaching its maximum at the end of each cycle. Another 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 [3]. This fact will be discussed in more detail in the following sections, after structural characterization of the sample by EXAFS and XANES will be given.

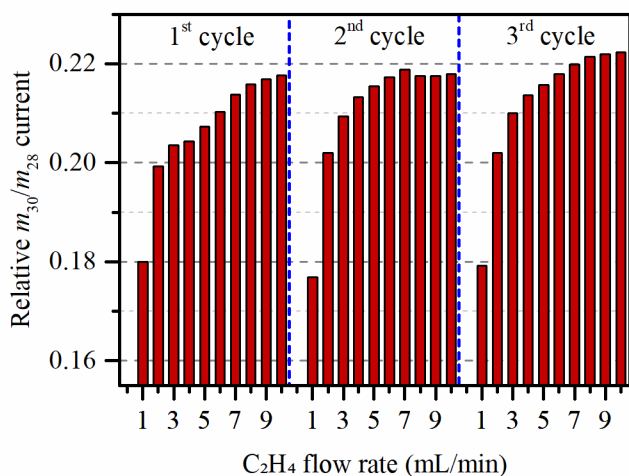


Figure 1. The relative fraction of the MS-detected signals for $m/Z = 30$ and $m/Z = 28$ as a function of ethylene flow during the three subsequent cycles with constant hydrogen flow of 15 mL/min and constant total flow of 50 mL/min (helium flow was varied to compensate for the changes of ethylene flow).

Evolution of the Pd-Pd interatomic distances was monitored by *operando* EXAFS spectroscopy. The results of the first-shell Fourier-analysis are presented in Figure 2. For the fresh pre-hydrogenated catalyst, the value of $R_{Pd-Pd} = 2.806 \pm 0.007 \text{ \AA}$ is consistent with the values obtained for the β -hydride phase of palladium [9, 13, 19]. 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. In the end of the first cycle, $R_{Pd-Pd} = 2.750 \pm 0.006 \text{ \AA}$ is slightly higher than that of pure metallic NPs indicating that the α -hydride phase should be present. During the second cycle, the obtained interatomic distances are exactly the same as during the first cycle, which indicates that the changes occurred in the structure of the NPs are fully reversible. During the

third cycle, the interatomic distances are systematically lower than those observed during the first two cycles at the similar ethylene flows. 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, that predicted from standard phase diagram [6]. These results indicate that the structural changes in the Pd NPs occurring during the hydrogenation reaction are to a large extent reversible. However, in the previous works, we have already demonstrated that the analysis based on the interatomic distances only does not give a complete picture about the actual phase of palladium, especially in a reaction mixtures [9-11]. Therefore, for unambiguous determination of possible hydride and carbide phases, the XANES spectra have been considered.

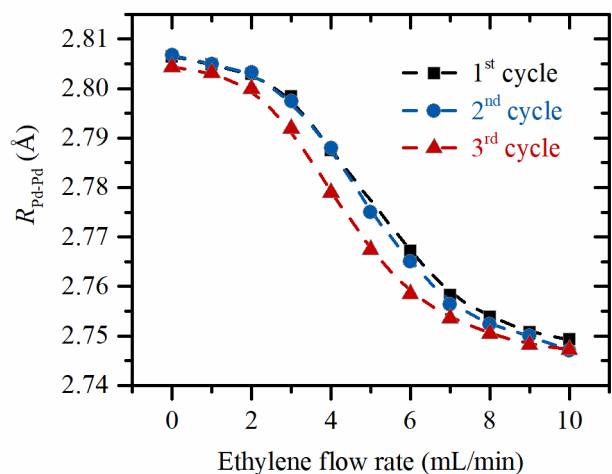


Figure 2. The first-shell Pd-Pd interatomic distances as a function of ethylene flow for the first (black squares), second (blue circles) and third (red triangles) cycles.

XANES analysis has been performed within a PCA approach with subsequent rotation of the components (See Section S2 of the Supporting Information). At the first step, we determined that in the whole series of spectra there are three independent components (Figure S3). In the following step these three PCA components were rotated in order to obtain the spectra of different 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. The other two obtained components and their evolution during the ethylene hydrogenation reaction at different ethylene flows are shown in Figure 3 (parts (a) and (b), respectively). The second component has a similar shape in the region of the first XANES peak at 24.36 keV, characteristic for palladium hydride, but the more distance peaks are shifted 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 is similar to the second one in the EXAFS region, but demonstrates strong changes in shape

and position of the first XANES peak, characteristic for palladium carbide. This means, that palladium carbide phase is formed under reaction conditions even in the instant excess of hydrogen.

The evolution of the obtained components (Figure 3b) demonstrated that the main process observed during the first cycle is the phase transition between β to α -hydride phases, in agreement with the conclusions made based on the EXAFS analysis. However, a small fraction of palladium carbide is readily formed at higher C_2H_4/H_2 ratios. Due to the low amount of this carbide and the interatomic distances similar to that of α -palladium hydride, the two phases cannot be resolved by standard EXAFS analysis [20]. Only the fact, that carbide was formed not in a single spectrum, but was present in a considerable fraction of the spectra in a series (vide infra), makes it statically relevant and allows its detection by PCA analysis. In the second cycle, the relative changes of the three components are similar to the first cycle, with the only difference that in high ethylene flow more carbide phases with respect to α -hydride is formed. In the last cycle, the carbide is remained stable even in pure hydrogen flow, and continues to grow to its maximal value in the end of the cycle.

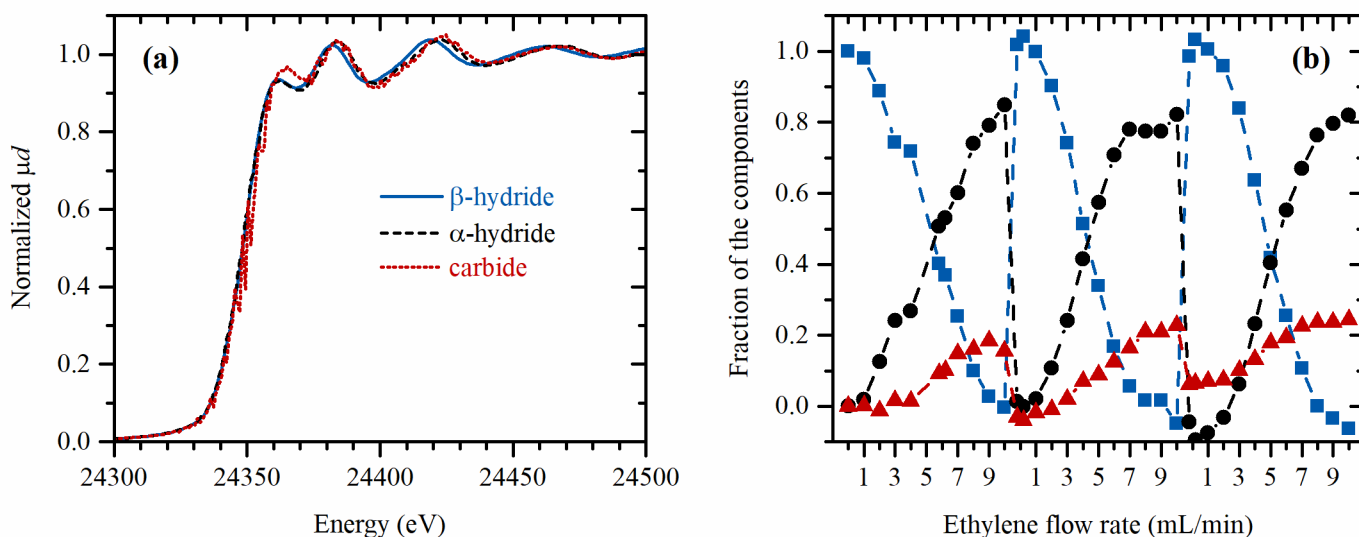


Figure 3. (The pure components (a) derived from PCA analysis with matrix rotation assigned to β -hydride (solid blue line), α -hydride (dashed black line), and carbide (dotted red line) phases of palladium and their relative fractions (b) during the ethylene hydrogenation reaction.

Formation of the carbide phase under reaction conditions explains the two following phenomena reported in the two previous sections. First, carbide phase acts as the reason for the non-reversibility of the R_{Pd-Pd} values during the third cycle. While in the beginning of the first two cycles carbide phase is absent, the hydrogen atoms are allowed to freely enter the inside the Pd NPs. In accordance with our recent work [10], 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 in 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 Figure 3b correlates with the ethylene conversion estimated from Figure 1. 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 [3]. However, for catalytic hydrogenation ethylene should be adsorbed and form intermediates with palladium. Formation of such intermediates assumes formation of Pd-C bonds, which affects the shape of XANES spectra [10]. According to the obtained results, formation of Pd-C 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. [21] but left without explanation as now 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 carbidized sample also explained why the β-hydride decomposition occurs at lower ethylene flows in the last cycle.

4. Conclusions

We have performed an *operando* characterization of the palladium nanoparticles 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 hydrogen. Despite of the fact that hydride phase is considered to be responsible for the hydrogenation, we have shown the pre-hydrogenated sample demonstrate lower catalytic activity than the sample after exposure to a catalytic mixture. The relative conversion rate of ethylene to ethane was correlated 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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