Experimental report

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Proposal: **7-05-493** **Council:** 10/2018

Title: Hydrides formation and spillover effect investigation on Pd-based catalysts

Research area: Chemistry

This proposal is a new proposal

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Samples: activated carbon
gamma Al2O3
Pd / C
Pd/gamma Al2O3

Instrument	Requested days	Allocated days	From	To
IN1 LAG	6	3	19/06/2019	22/06/2019

Abstract:

The aim of the study is to exploit the potentialities of INS for investigating the interaction and reaction of H2 with highly dispersed Pd nanoparticles supported on Al2O3 and C supports, focusing on Pd-hydride formation and spillover effect. The unprecedented sensitivity of LAGRANGE spectrometer together with its optimal resolution will give access to spectroscopic details previously not observable, thus allowing us to shade new light on the properties of supported Pd catalysts under hydrogenation conditions. We have already succeeded in performing analogous measurements on supported Pt-based samples on the LAGRANGE instrument (proposal 7-05-466), which provided relevant results relative to the particles location, to the physisorbed and chemisorbed hydrogenous species and to the spillover effect. We are thus confident to gain analogous relevant results also for supported Pd-based catalysts.This proposal is part of the joint ILL-UniTo PhD project of Eleonora Vottero and of a collaboration with Chimet S.p.A. (an Italian company leader in the recovery and refining of precious metals for the industries).

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1. Aim of the experiment

The aim of the current experiment is the investigation of the interaction of H_2 with finely dispersed supported Pd nanoparticles catalysts of industrial interest.

Under reaction conditions, H_2 is homolitically split into Pd-hydride species, which successively can hydrogenate the substrate. Several types of Pd-hydrides may be formed, including bulk ones, differing in the local coordination and in the nature of the adsorption site. The Pd-H vibrational frequencies are sensitive indicators of the nature of the hydride, since they depend on the hydrogen coordination on the metal and on the coordination of the adsorption site. In this regard, INS spectroscopy is the technique of choice due to its specificity in detecting the vibrational modes involving H atoms.

The few INS works conducted on similar samples [1, 2] focus on high loaded samples (20% wt), but from our previous experience with INS spectroscopy employed in the study of a 5% wt Pt loading in the presence of H_2 (experiment 7-05-466) [3, 4], we know that, nowadays, it is possible to obtain high resolution results also for samples with a low metal loading. In the frame of our past study a very fine analysis of the spectra was possible, providing detailed data about the multi-fold Pt-H species formed and the physisorbed H_2 species. Thus, the aim of the current work is to study is to apply the same approach to two analogous catalysts with a 5% wt Pd loading.

2. Experimental

2.1. The samples

Two catalysts have been measured during the current experiment. Both samples have been provided by Chimet S.p.A. [5] and prepared following the deposition–precipitation method described in [6, 7]. In both cases, the Pd loading corresponded to the 5% wt and the nanoparticles underwent a pre-reduction step in HCOONa at 55 °C for 1 h, followed by water washing and drying at 120 °C overnight. The first sample, **Pd(R)/CwA**, is supported on an activated carbon obtained from a wood precursor by a physical activation route in steam. The second sample instead, **Pd(R)/Alu**, is supported on a high surface area γ-alumina.

2.2. The INS measurements

The INS measurements were performed on the IN1 Lagrange spectrometer at ILL. The instrument can cover the 0-500 meV (0-4033 cm-1) energy transfer range with a resolution of $\Delta E/E$ of about 2%. The instrument is equipped with three different monochromators employed for recording the spectra in different energy transfer ranges: the Si(111) for the 7.5-20.0 meV range, Si(311) for the 16.0-30.7 meV range, and Cu(220) for the 26.0-525.0 meV range. All the three monochromators were employed for the Pd(R)/CwA sample, and the obtained spectra segments were merged in order to obtain a single spectrum following the procedure described in [4]. For the Pd(R)/Alu sample instead, the available time only allowed to measure the range of the Cu(200) monochromator. All the spectra were subtracted for the contribution of the empty cell. The INS spectra were recorded at 20 K in order to reduce thermal effects causing the thermal broadening of the spectral features. The raw data were opportunely reduced to the scattering function $S(\omega)$ and plotted versus energy transfer (in units of cm^{-1}). Prior to the measure, both samples were outgassed at 120°C in order to remove the physisorbed water (equilibrium pressure below 10^{-3} mbar), successively reduced in H_2 at the same temperature and then outgassed again (two H_2/outgassing cycles were performed). Any further manipulation was performed within a glovebox in order to avoid any contamination with air moisture. A weighted amount of each sample (2.4 g for Pd(R)/CwA and 6.2 g for Pd(R)/Alu) was inserted in a cylindrical Al-cell (4 cm high, 16 mm diameter) and sealed with In-wire.

For both samples three measurements were made: in the first one the sample was previously outgassed, while the others were made in the presence of H_2. The gas was dosed at room temperature employing a Hiden

Isochema gas volumetric device, which was used to reach H_2 equilibrium pressures of about 230 mbar for the second measure and 430-450 mbar for the third.

3. Results

The INS spectra collected on the Pd(R)/CwA sample as such and in the presence of H_2 are reported in Figure 3. 1A. The observed profile is the one typically observed in the case of activated carbon samples: the 150-700 cm^{-1} region contains the riding vibrational modes of the carbon support, enhanced by the presence of H bonded to it; the 700-1000 cm^{-1} region corresponds to the out-of-plane bending modes of the terminal C-H groups, while the 1000-1700 cm^{-1} corresponds to the in-plane bending modes of the C-H groups. Upon H_2 dosing, it is immediately possible to observe an increase in the general intensity of the spectrum, which is a consequence of the high scattering cross section of Hydrogen. More in details, it is also possible to observe the modification of some spectral features, which are more evident in the difference plot reported in Figure 3. 1B. Two main differences can be observed:

- The appearance of a new broad band centered at about 500 cm^{-1}. This band is well described in the literature, and assigned to the vibrational modes of the β-PdH phase [8].
- The increase of intensity of the three bands in the 700-1000 cm^{-1} region and of the broad band centered at 1100 cm^{-1}. These are the characteristic bands of the bending modes of terminal C-H groups, and their increasing clearly indicated the occurrence of H spillover onto the support.

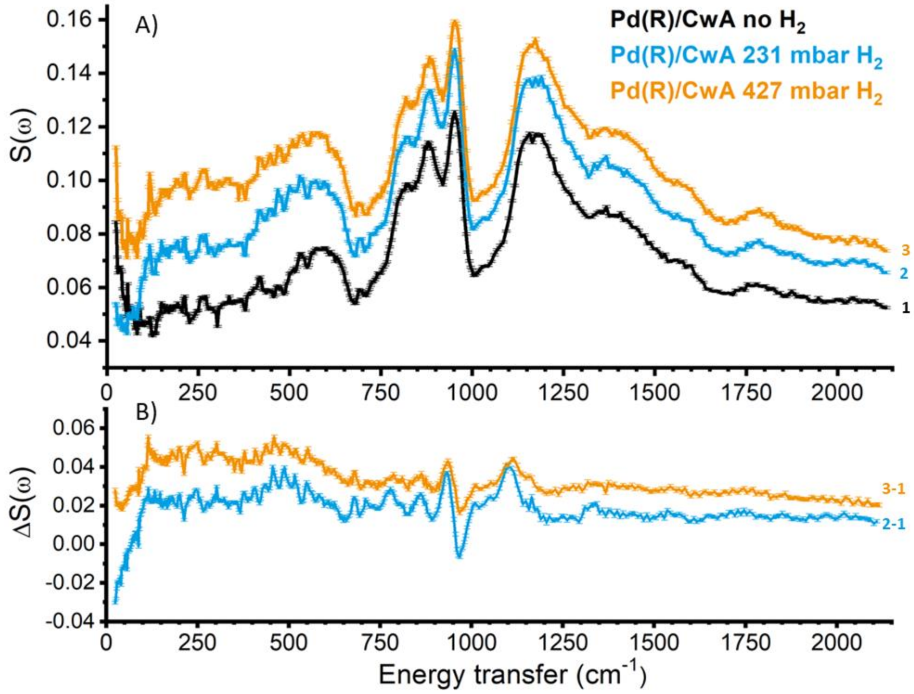

Figure 3. 1: Part A) INS spectra of the Pd(R)/CwA sample in vacuum (black spectrum), and in the presence of an H_2 equilibrium pressure of 231 mbar (blue spectrum) and 427 mbar (orange spectrum). Part B) Difference spectra collected in the presence of H_2 and the spectrum collected in vacuum, underlying the characteristic bands of the PdH species and the H spillover phenomenon.

Analogously, Figure 3. 2 reports the spectra measured on the Pd(R)/Alu. The spectrum of the catalyst under vacuum is dominated by a very broad band centered at about 900 cm^{-1}, which is assigned to deformation modes of hydroxyl groups at the alumina surface. Upon H_2 dosing we can again observe a generalised increasing in the spectral intensity, and also the emergence of a new and intense band centered at 470 cm^{-1} (more evident in the difference spectra reported in Figure 3. 2B). This new bands is analogous to the β-PdH signal observed for the previous sample, but much more intense and resolved due to the highest absolute amount of Pd present within the sample holder (both samples have a Pd loading of 5%, but the alumina supported sample is much more dense than the carbon supported one).

The better resolution of this features also allows to individuate a weaker and very broad band centered at about 950 cm^{-1}, which can be attributed to vibrations of the multi-fold surface Pd-H species. [8]

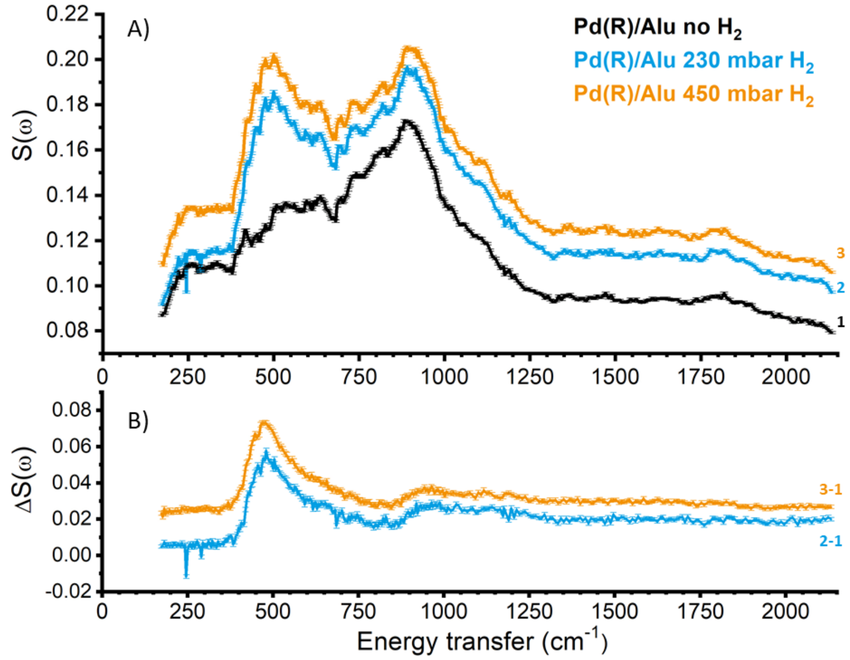

Figure 3. 2: Part A) INS spectra of the Pd(R)/Alu sample in vacuum (black spectrum), and in the presence of an H_2 equilibrium pressure of 230 mbar (blue spectrum) and 450 mbar (orange spectrum). Part B) Difference spectra collected in the presence of H_2 and the spectrum collected in vacuum, underlying the characteristic bands of the PdH species.

A more detailed analysis of these spectra, including a parallel DFT simulation work on model system, is planned for the near future.

References

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