Experimental report

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Proposal: **7-05-514**

Council: 10/2019

Title: Dynamics of Pt-H species on an industrial Pt/Al2O3 catalyst as a function of hydrogenation temperature

Research area: Chemistry

This proposal is a new proposal

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Samples: Pt-gamma alumina

Instrument	Requested days	Allocated days	From	To
IN1 LAG	4	3	02/02/2021	05/02/2021

Abstract:

The aim of this experiment is the characterization of the Pt-hydride (Pt-H) species formed on an industrial 5% wt loaded Pt/Al2O3 catalyst under different hydrogenation conditions. It is known from the literature and it was observed in our previous works that Pt-H species are sensible to the partial pressure of H2 and to the temperature of the environment. The dependence on the partial pressure will be the focus of our next experiment (DIR-177, planned for Nov 6-10 2019), while the present experiment would be intended to complement it by exploring also the effects of temperature. We consider fundamental to study both routes because, according to previous IR measurements, the evolution of the Pt-H species is different in the two cases. The results will have a relevance in determining the properties of Pt-based catalysts under hydrogenation conditions.

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).

Experimental report 7-05-514 and DIR-177

Dynamics of Pt-hydrides on an industrial Pt/Al2O3 catalyst as a function of hydrogenation

1.Introduction

In this experiment, we investigated the changes in the INS spectra of the Pt-H species in a Pt/Alumina (TO 309) sample as a function of the H_2 partial pressure. As predicted by the simulations performed by Mager-Maury et al [1], small Pt nanoparticles are expected to reconstruct when varying the H_2 pressure and the temperature (i.e. their H coverage). These results are summarised in the thermodynamic plot in Figure 1A. With this premise in mind, this experiment was aimed to expand our understanding on the H_2-driven reconstruction by measuring the INS spectra of the system at different H-coverage.

The very first measurement on this sample (Nov 2016, proposal number 7-05-466) was made in the temperature and pressure conditions indicated by label 1 in Figure1A, which correspond to very high H-coverage conditions [2]. A first trial of the current experiment (September 2020), during which we treated the sample offline at 450°C and run measurements at T~20 K after quenching, has not been successful. Modification of the bare sample background as well as uncontrolled possible formation of ice on the cell while quenching prevented any possibility of profiting of the difference method. This time instead, to reduce at minimum the manipulation of the sample stick, we made use of the brand-new heating insert of IN1, never used before. Despite the novelty, we succeeded performing the experiment keeping the sample always on the displex cryostat of LAGRANGE at a temperature of 450K, and then sending increasing pressures of H_2. In particular, for the first measurements of this series, we expected to measure very weak Pt-H intensities at the limit of sensitivity of LAGRANGE spectrometer, meaning that a good statistics (i.e. long scans) was fundamental. The evaluation of the amount of H_2 to be sent in order to do not overshoot the target Pt-H coverage posed a significant challenge for this experiment. The most realistic plan consisted in sending an increasing and low amount of H_2 on the sample, read the residual pressure after a 2h time of contact, and then measure. We also intended to study the effect of the increasing temperature on the H-coverage, i.e. following path 3 in Figure 1A, but because of the requirement of high counting statistic we faced with path 2 we could not make it within the available time.

2.Experimental

The activation procedure was performed at our home university and consisted in: 1) outgassing the sample at RT; 2) further outgassing at 300°C (~ 570 K); 3) cooling down to 120°C (~ 393 K) and reducting in H_2 (three repetitions); 4) heating up again at 300°C and final outgassing. The procedure was intended to remove all the physisorbed water on the sample and the most weakly bounded fraction of the hydroxyls groups at the alumina surface, as well as to reduce the nanoparticles to their metallic form. The sample activation temperature was chosen to be higher than the one employed during the experiments (450 K) in order to avoid any further removal of surface hydroxyl groups during the measurements, and thus to ensure a stable spectral features for the bare sample. This aspect demonstrated to be of fundamental importance, as neglecting it was one of the reasons of the failures of the first attempt to this experiment performed in September 2020.

Any further manipulation was performed within a glove-box in order to avoid contaminations with atmospheric moisture and the re-oxidation of the sample. About 8,76 of samples were charged in the gas injection cell inside the glove-box. Prior to the experiment, the sample was outgassed at the instrument for about 2 days.

The sample was measured at 450K as such and in the presence of increasing H amounts corresponding to:

(a) 90 mbar of H_2 sent on the sample, corresponding to 235.72 µmol of adsorbed H
(b) Additional 500 mbar of H_2 sent on the sample, corresponding to 1316.71 µmol of adsorbed H

The corresponding H-coverage values are indicated with the blue and red star in Figure1a. respectively. Lower H_2 pressures were attempted, but the obtained spectra were undistinguishable from the bare catalyst ones.

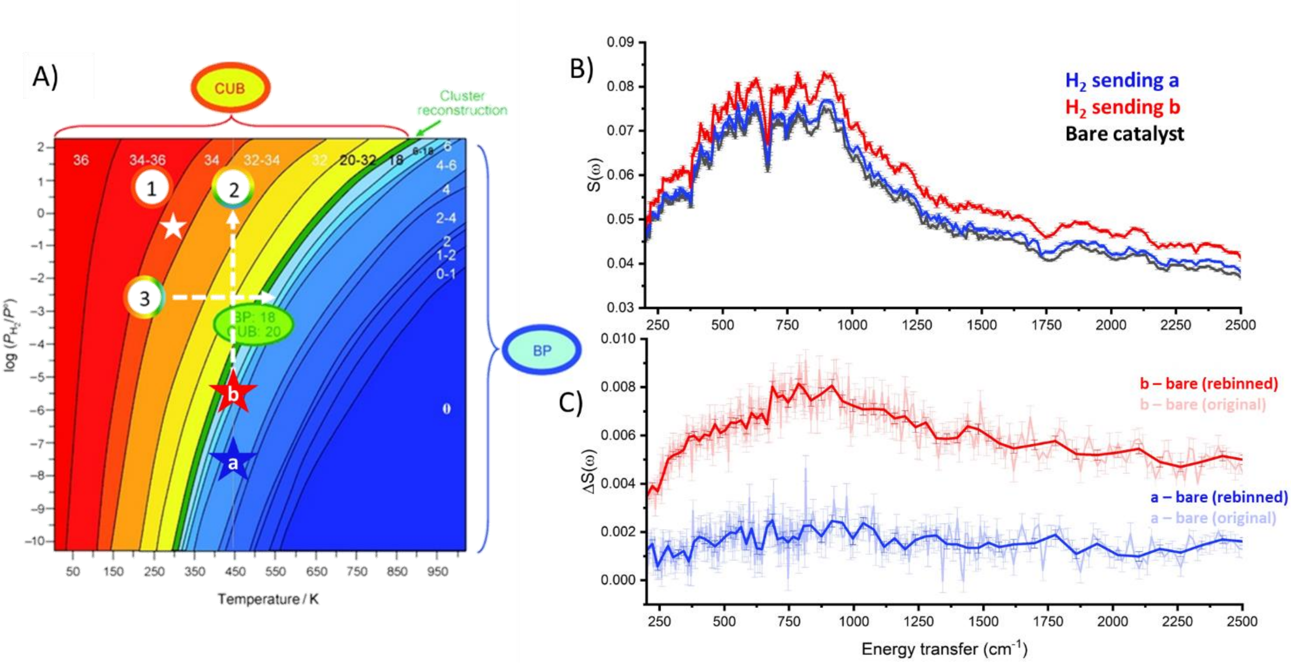

Figure 1. Part A) thermodynamic plot of Pt-H nanoparticle stability as a function of H_2 partial pressure and temperature (ref [1]): 1 corresponds to the data available prior to the present experiment; path 2 is the path followed during the present experiment performed by changing H_2 partial pressure, and path 3 corresponds to the experiment intended to follow the effect of the rising temperature, which we did not manage to perform due to time constrains. The blue and red stars correspond to the H_2 conditions of dosing (a) and (b) of this experiment, respectively. Part B) INS spectra measured on the sample as such and during H_2 dosing (a) and (b). The spectra were corrected by a Bose-Einstein factor to make them fully comparable with the former ones measured under cryogenic conditions. Part C) Difference spectra between the spectra measured in the presence of H_2 and the bare sample. A re-bin over 5 consecutive points was also performed to reduce the noise level of the signals.

3.Results and Discussion

The Pt/Alumina sample was measured as such and after adding two increasing amounts of H_2 at a temperature of 450 K, obtaining the spectra shown in Figure 1B. The spectrum of the bare catalyst was then subtracted to the others, in order to highlight the new spectral contributions attributed to the hydrogenous species formed under those conditions of H_2 partial pressure and temperature (Figure 1C). All the spectra profiles were corrected by a Bose-Einstein factor to make them comparable with the former spectra collected under cryogenic conditions.

The amount of H_2 employed evidently approaches the sensibility limit of the Lagrange instrument, in particular for sending (a). As a result, the difference spectra appear very noisy and weak in intensity. To reduce the noise level, during the data analysis a new re-binning over 5 consecutive points was performed. In this way it was possible to unambiguously point out the presence of new bands significantly more intense than the error bars at least for H_2 sending (b), allowing us to propose an assignment. For H_2 sending (a) instead, albeit a small rise in the signal intensity, the difference signal profile is not well defined enough for attempting an assignment.

By comparing the former INS spectra collected during the experiment 7-05-466 under high H-coverage conditions (Figure 2A) and the new spectrum measured after H_2 sending (b) during this experiment (Figure 2B), it is possible to observe to observe that they exhibit very different spectral profiles. These changes were attributed to changes in the hydrogenated nanoparticles morphology and/or the typology of Pt-H species formed (top, 2-fold bridged or 3-fold hollow) [1].

The low H-coverage INS spectrum collected during the present experiment (point (b) in Figure 1A) corresponds to a stoichiometry Pt:H or about 1:1. The new signals arising after the contact with H_2 consist in a quite broad signal which we separated into two contributions, the first one being centred at about 800 cm^{-1} and the second one consisting in a shoulder centred at about 500 cm^{-1}. As shown in Figure 2B, the former one was attributed to the formation of new hydroxyl groups at the surface of the alumina support. The spectrum employed for the comparison (aquamarine spectrum in Figure 2B) was obtained by subtracting the bare spectrum measured during this experiment (on a sample activated at 573 K) to the one collected in November 2016 (activated at 393 K). The difference between the two spectra corresponds to the fraction of hydroxyl groups at the surface of the alumina support which was removed in the temperature range between the two activation temperatures. Thus, the arise of this band in the INS spectrum of the catalyst measured under low H-coverage conditions is attributed to some H-spillover onto a strongly dehydroxylated alumina support. This was an unexpected, but very interesting finding of this experiment.

In order to propose an attribution also for the lower energy transfer shoulder, it was necessary to employ a parallel DFT simulation work on model systems. In this regard, the signal shows a very good agreement with the simulated spectrum of Pt-H species on the surface of relatively low H-coverage models in sensible interaction with the support (Figure 2B). On the contrary, the high H-coverage system is well described in terms of highly symmetric cuboctahedric models solvated by a large number of H atoms and in weak interaction with the support (Figure 2A). Put together, these data strongly support the dynamic reconstruction of the Pt-H system as a function of the H_2 partial pressure and of the temperature calculated in the thermodynamic simulations proposed in ref [1], and also already observed by our groups by coupling different techniques [2].

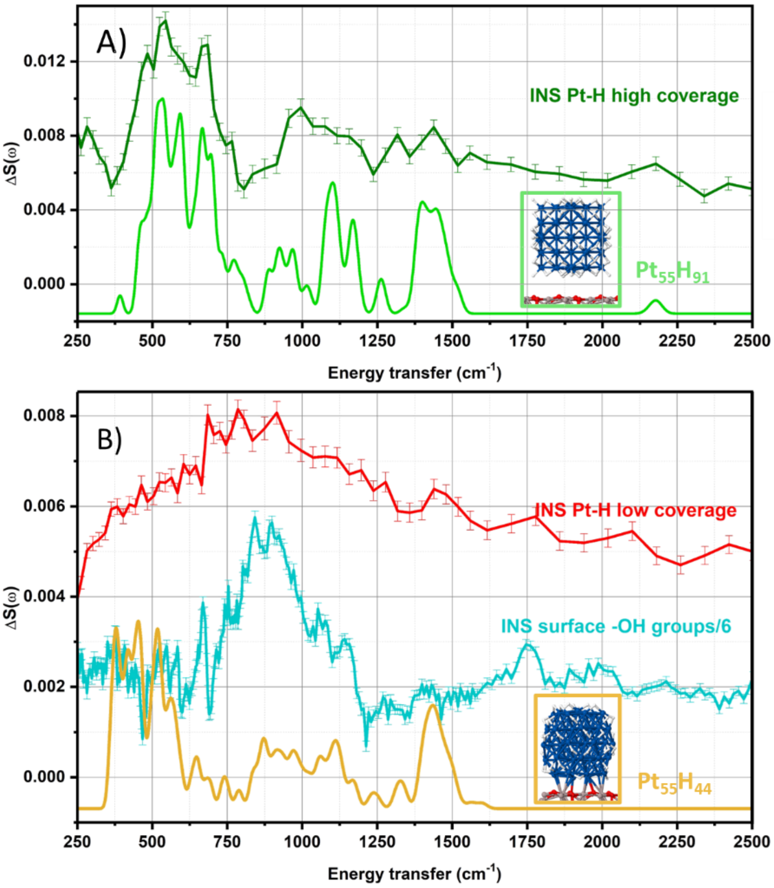

Figure 2. A) INS fingerprint of the hydrogenous species formed under high H-coverage conditions (experiment 7-05-466, dark green line) compared with the simulated spectrum of the high H-coverage model $Pt_{55}H_9$ (light green). B) INS fingerprint of the hydrogenous species formed with a 1:1 Pt:1 stoichiometry (current experiment, in red) compared with the profile of hydroxyl groups at the support surface (aquamarine line) and the simulated spectrum of the medium-low H-coverage model $Pt_{55}H_{44}$.

Conclusions

To be able to follow the modifications underwent by a catalyst in the presence of H_2 is of fundamental importance in the field of hydrogenation catalysis. Among the available techniques, INS is sensible to all the vibrational modes of H-containing species, providing a complete fingerprint of all the Pt-H species formed in the sample and making it possible to compare their modifications upon changes in the reaction conditions (such as the H_2 partial pressure or the temperature). In this respect, with this experiment we managed to exploit the sensibility of the Lagrange instrument to measure very weak signals of the Pt-H species formed in the presence of low amounts of H_2. These results, paired with the ones of experiment 7-05-466 (obtained under high H-coverage conditions) and with DFT simulations, allowed to point out a morphological reconstruction of the Pt nanoparticles when increasing their H-coverage, in very good agreement with the calculations proposed in reference [1] and with our previous experiments [2]. The presence of H spillover onto the support, rarely seen on alumina supports, is also an interesting results of this experiment. Overall, the observation of this kind of dynamics of the catalyst is fundamental for understanding its behaviour under reaction conditions.

References

[1] C. Mager-Maury et al, ChemCatChem 2011, 3, 200-207; [2] M. Carosso, et al, ACS Catal. 2019, 9, 7124-7136