Experimental report

14/02/2017

Proposal:	**7-05-466**	**Council:**	4/2016
Title:	Study of the Pt-hydride formation and spillover effect on Pt/Al2O3 and Pt/C catalysts		
Research area:	Other...		

This proposal is a new proposal

Main proposer:	**Andrea PIOVANO**
Experimental team:	Andrea LAZZARINI Andrea PIOVANO Michele CAROSSO ELENA GROPPO Carlo LAMBERTI Maela MANZOLI Eleonora VOTTERO Sara MORANDI
Local contacts:	Monica JIMENEZ RUIZ Andrea PIOVANO

Samples:	Pt/C Pt/Al2O3

Instrument	Requested days	Allocated days	From	To
IN1 LAG	8	8	08/11/2016	16/11/2016

Abstract:

Pt-based catalysts are widely employed for hydrogenation reactions of industrial interest. In hydrogenation conditions H2 is activated by Pt nanoparticles and homolitically split to give Pt-hydrides and atomic hydrogen that then spills on the support. Several types of Pt-hydrides may be formed and the Pt-H frequencies are sensitive indicators of their nature. We would investigate the interaction/reaction of H2 with highly dispersed Pt nanoparticles supported on Al2O3 and C supports with Inelastic Neutron Scattering. It will allow to monitor the vibrations of H-containing species and so to follow simultaneously the changes occurring on the metal and on the support in the presence of H2. The collected data will be compared with those already obtained by in situ FT-IR spectroscopy. The unprecedented sensitivity of LAGRANGE spectrometer together with its optimal resolution will give access to spectroscopic details previously not accessible and it will help shading more light on the PtH phases formed, on their stability and on the support sites where hydrogen spills in different conditions, i.e. metal dispersion, support type, hydrogen content and activation temperature.

INS spectra of hydrogen adsorbed on Pt/C and Pt/Al_2O_3 catalysts: a brief report

1. Aim of the experiments

The set of experiments described in the present report is devoted to fully characterize the hydrides species formed upon adsorption of H_2 on two different supported platinum nanoparticles catalysts (5% Pt/C and 5% Pt/Al_2O_3). Indeed, these species are those directly involved in catalytic hydrogenation reactions of industrial interest in which these systems are massively employed, and a complete characterization of hydrides species is of primary importance in understanding the efficiency of these systems. Moreover, we will search for spectral evidences of eventual spillover effect (that is, transfer of atomic hydrogen from the precious metal surface to the support surface).

INS (Inelastic Neutron Scattering) technique was chosen because the scattering cross section of neutrons with H is one order of magnitude greater with respect to that of any other element, which makes INS an election technique in investigating hydrogenous species. Moreover, no selection rules are involved in this spectroscopy (differently form Infrared spectroscopy, which relies on the dipole moment, and from Raman spectroscopy which depends on polarizability). This allows observing, in principle, all the vibration modes of hydrogenous species. Finally, INS technique allows detecting the vibrations of hydrogenous species in the whole spectral range (4000-10 cm^{-1}), which is impossible with FT-IR spectroscopy when dealing with highly absorbing samples (such as Pt/C or Pt/Al_2O_3).

2. Experimental

2.1 Samples description and activation procedures

Two Pt containing samples and the respective bare supports were investigated. All the samples were provided by Chimet S.p.A.

- 5% Pt/C (TO-296): this is a pre-reduced sample with a nominal platinum dispersion of 80% (as determined by CO chemisorption measurement);
- 5% Pt/Al_2O_3 (TO-309): this is a not pre-reduced sample, with a nominal platinum dispersion of 80%;
- CW bare support (TO-178): activated in steam at high temperature;
- Al_2O_3 bare support.

In the following, we samples will be indicated with a nomenclature that indicates the presence of Pt and its nominal dispersion, the nature of the support (C and Alu, respectively), and the activation temperature. Hence, Pt80C120 refers to the 5% Pt/C catalyst activated at 120°C, while Alu120 refers to the bare alumina support activated at 120 °C.

2.2 Collection of the INS data

The INS measurements were performed at the ILL (Institute Laue-Langevin) facility, at the IN-1 Lagrange spectrometer.

After the activation, the sample was inserted in a 60.04719 mL (as determined by He volumetric calibration) cell with the help of a He-filled glove-box. The cell (a small cylinder, 4 cm high, 16 mm of diameter) is realized in Al, which is almost completely transparent to neutrons, and is sealed with an indium wire by screwing the closure part on top of the small cylinder. The sealed Al cell was connected to a can and inserted into an He-cooled cryostat (20 K). The He contained in the cell was degassed and the sample allowed to cool down to 20 K.

The time for a single measurement depends on several factors (number of integrations and spectral range), but on average a measure with a good statistic in the whole 4000 – 0 cm^{-1} range required approximately 8-9 hours. The whole energy range that we can cover with IN-1 Lagrange spectrometer is 7.5-525 meV, which is collected by merging the ranges acquired with three different monochromators: Si(111) and Si(311) cover low energy region (respectively 7.5-20 meV and 16-30.75 meV) and Cu(220) covers the region 26-525 meV. (check the energy of the incident neutron beam and the order of the monochromators)

3. Normalization, subtraction and processing of the INS data

3.1 INS spectra of the bare Cw support in the absence and in the presence of H_2

Figure 1 shows the INS spectra of the bare Cw support, as such and in the presence of two different H_2 pressures. The spectrum of bare Cw presents a lot of well-defined peaks, which are due to vibrations involving the terminating hydrogen atoms at the edge of the sp^2 graphitic domains. The assignment of the principal peaks due to C-H species has been provided in Lazzarini et al. Table 1 summarizes the main peak position (labelled in the graph by a number) and the relative assignment.

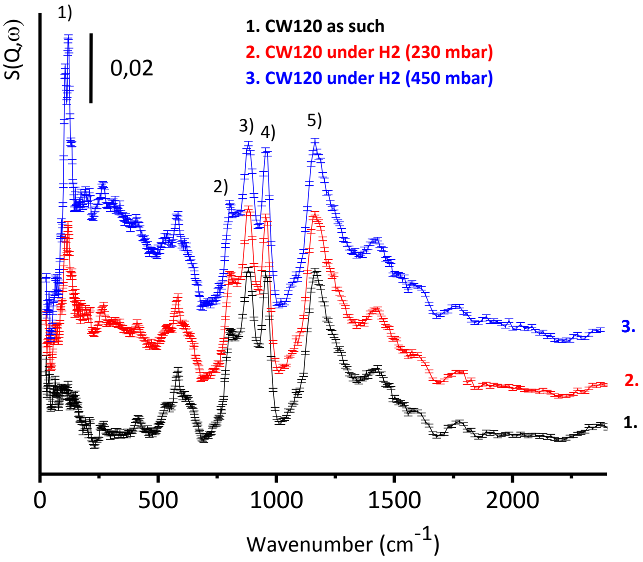

Figure 1. INS spectra of CW120 as such and in the presence of two different equilibrium pressures of hydrogen.

Table 1. Attribution of the main peaks observed in the INS spectra of CW120 and Pt80CW120.

Position (cm^{-1})	Attribution
1) 120 cm^{-1}	H_2 rotor
2) 803 cm^{-1}	C-H out-of-plane of due and trio
3) 880 cm^{-1}	C-H out-of-plane of solo at extended borders
4) 957 cm^{-1}	C-H out-of-plane of due and trio at irregular borders
5) 1163 cm^{-1}	C-H in-plane bending

The whole spectral intensity is enhanced in the presence of hydrogen. This is due to the presence of physisorbed hydrogen on the carbon surface, which is favoured by the high porosity. In order to determine the spectral manifestation of physisorbed H_2, the spectrum of CW120 was subtracted from those of the same sample in the presence of hydrogen. The difference spectra are characterized by two broad bands (similar to oscillations) centred around 260 and 1400 cm^{-1}, and by a sharp peak around 120 cm^{-1}, which is attributed to the rotation of molecular hydrogen.

3.2 INS spectra of Pt80CW120 in the absence and in the presence of H_2

Figure 2 shows the INS spectra of the Pt80CW120 catalyst as such and in the presence of two different pressures of hydrogen. The INS spectrum of Pt80CW120 is very similar to that of the bare CW support, although the scattering intensity is slightly lower in the whole spectral range. This can be easily explained by considering that 5% of the sample is constituted by Pd and not by carbon. Indeed, when multiplying the spectrum of Pt80CW120 for a factor of 1.05, it overlaps that of CW120 in almost all the spectral region, except for the three bands characteristic of the C-H species at the edge of the graphitic sp^2 domains (negative bands in the difference spectrum not reported). These differences can be accounted for by considering that *the Pt nanoparticles are mainly located at the edges of the graphitic sp^2 domains and contribute to the diminishing of the hydrogen terminating species*.

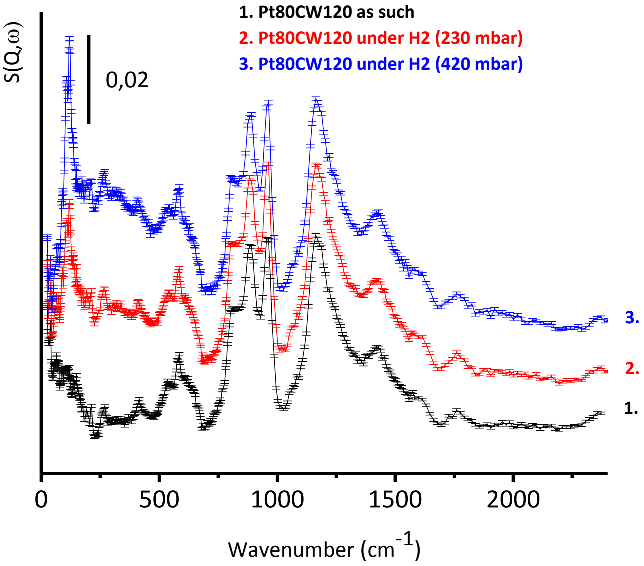

Figure 2. INS spectra of Pt80CW120 as such and in the presence of two different equilibrium pressures of hydrogen.