Experimental report

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Title: Exploring the surface chemistry ofactivated carbons by INS and DFT calculations

Research area: Chemistry

This proposal is a resubmission of 7-04-159

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Samples: activated carbon
Pd/C

Instrument	Requested days	Allocated days	From	To
IN1 LAG	3	3	10/09/2018	13/09/2018

Abstract:

The aim of the study is to extend our knowledge on the surface properties of activated carbons used in industrial catalysis by exploiting the potential of INS. We already collected a series of INS spectra on TOSCA at ISIS on activated carbons of different origin and subjected to different post-activation treatments, and we conducted a detailed DFT study on several models allowing the assignment of all the features in the 700-1650 cm-1 region. Our calculation demonstrated that some of the features in the 700 - 200 cm-1 region are due to H vibration of functional groups including atoms other than C, but the experimental data were of poor quality in that region.

We recently had the possibility to re-measure one of the carbons on LAGRANGE at ILL. The quality of the spectrum is much better and in particular the signal to noise ratio is largely improved in the 700 - 300 cm-1 region. Hence, we plan to conduct systematic INS measurements on several activated carbons as a function of the post-activation treatments and on related catalysts, to be coupled with DFT calculation. This proposal is part of the joint ILL-UniTo PhD project of E. Vottero and of a collaboration with Chimet S.p.A.

Exploring the surface chemistry of activated carbons by INS and DFT calculations
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1. Aim of the experiment

This experiment aimed to increase our knowledge on the surface properties of a wide range of activated carbon samples and of related catalysts of industrial interest by exploiting the potentialities of INS spectroscopy. This experiment was conducted from the 9th to the 13th September 2018, putting together the days for the proposal INTER-427 and 7-04-162.
A previous experiment conducted on the Tosca instrument at ISIS (prior to the last past major instrument update) on some of the considered samples [1, 2] highlighted how INS spectra of different activated carbons exhibit significant differences, but the high noise level of the signal did not allow a detailed analysis of the spectra. Following, two similar samples were measured on the Lagrange instrument at ILL in the frame of a different experiment (exp 7-05-466**)**, allowing us to obtain the high resolution spectra of a physically activated carbon sample and of the correspondent Pt catalysts, and to analyze also relatively small changes caused by the introduction of the metal phase and to the hydrogen spillover effect. [3]
With the current experiment, we have collected the high resolution INS spectra of a large number activated carbons and related catalysts on the Lagrange instrument, aiming to analyze the spectral differences among samples obtained from different sources and activated following different methods, but also the changes caused by oxidative post treatments or by the procedure of deposition of the metal nanoparticles. For a better interpretation of the experimental spectra and the assignation of the observed peaks to precise surface species in the activated carbon samples, a large DFT simulation work has been conducted in parallel.

2. Experimental

2.1. The samples

All the samples measured during this experiment are provided by Chimet S.p.A [4]. During this experiment, four parent activated carbons were measured: one of wood origin chemically activated in H_3PO_4, one of wood origin physically activated by steam and two of peat origin physically activated by steam. In addition, two carbons post-activated with an oxidative step in concentrated HNO_3 at room temperature were also measured. All the activated carbon samples measured are summarized in **Table 2. 1**

Table 2. 1: *Summary of the activated carbons considered in this work and their descriptions*

Name	Description
Cchemi	AC of wood origin chemically activated with H_3PO_4
CchemiOx	Sample Cchemi after post-activation treatment in concentrated HNO_3 (67% w/w) at room temperature and successive washing in distilled water until reaching neutral pH
CwA	AC of wood origin physically activated with steam (measured in the exp 7-05-466)
CwAOx	Activated carbon of wood origin and physically activated (sample CwA) after post-activation treatment in concentrated HNO_3 (67% w/w) at room temperature and successive washing in distilled water until reaching neutral pH
CwB	AC of wood origin physically activated with steam
CpA	AC of peat origin physically activated with steam
CpB	AC of peat origin physically activated with steam

These activated carbons have been employed as supports for the preparation of supported Pd or Pt nanoparticles catalysts. All the catalysts were prepared in the Chimet S.p.A. laboratories employing the deposition-precipitation method described in [5] for the Pd based catalysts and in [6] for the Pt based catalysts. Some of the catalysts underwent a pre-reduction step of the metal phase, performed in the presence of sodium formate at 65°C for one hour. All the catalysts have a metal loading of 5 wt%. The characteristics of the Pd and Pt-based catalysts considered in this work are summarized in **Table 2. 2**.

Table 2. 2*: Summary of the carbon-supported Pd and Pt catalysts considered in this work. The support, the metal and the reduction state of the metal phase are reported.*

Sample Name	Support	Metal	Pre-reduced
CwA/Pd(NR)	CwA	Pd	no
CwA/Pd(R)	CwA	Pd	yes
CwB/Pt(R)	CwB	Pt	yes
CpA/Pt(R)	CpA	Pt	yes
CpB/Pt(R)	CpB	Pt	yes

2.2. Collection of the INS spectra

The INS measurements were performed on the IN1 Lagrange spectrometer at ILL. 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, and the obtained spectra segments were merged in order to obtain a single spectrum following the procedure described in [7]. 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(**Q**,ω) and plotted versus energy transfer (in units of cm^{-1}). Prior to the measure, all the activated carbon samples were outgassed at 120°C in order to remove the physisorbed water (equilibrium pressure below 10^{-3} mbar), and any further manipulation was performed within a glovebox in order to avoid any contamination with air moisture. A weighted amount of each sample (in the order of about 2-3 g) was inserted in a cylindrical Al-cell (4 cm high, 16 mm diameter) sealed with In-wire, and then measured.

3. Experimental results

Some of the considered samples were already previously measured at a lower resolution on the Tosca instrument at Isis (prior to the last major instrument update) [1, 2]. The spectral features are in general agreement with the previously collected one, but with a much greater intensity that allows us to perform a more detailed analysis (as shown in **Figure 3. 1**).

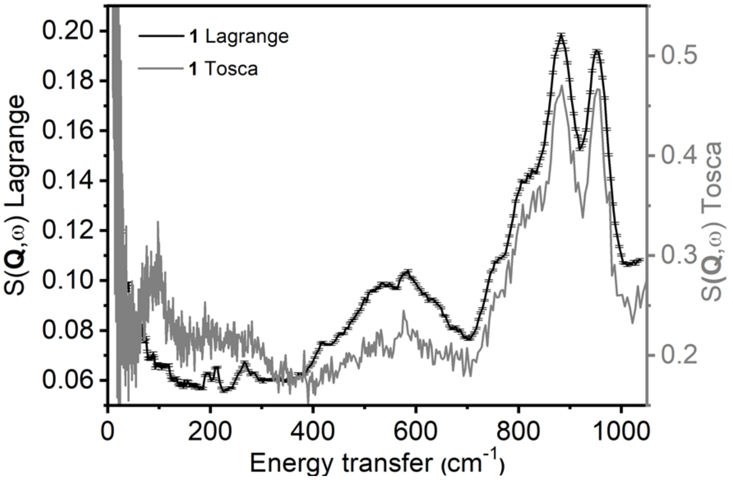

Figure 3. 1: *comparison between the INS spectrum of sample **1** collected on Lagrange and on Tosca (in the latter case, the error bar is omitted for clarity).*

Previous studies form our group pointed out how the most detailed information about the nature of the C-H terminations in a sample can be obtained from the 700-1020 cm^{-1} region of the spectrum [1, 2, 8] Therefore, for the interpretation and comparison of the measured spectra it was decided to focus on this spectral region. For a better comparison among the spectra of the catalysts and of their starting supports, all the catalysts spectra were normalized to the baseline of the parent carbon. The obtained spectra are reported in **Figure 3. 2**.

As already previously pointed out [9], the deposition of the metal nanoparticles on the support tends to decrease the intensity of all the peaks, with the strongest decreasing observed for the central band. The entity of this decrease varies greatly from sample to sample, but it is evident also in the new catalysts spectra collected during this experiment (**Figure 3. 2a**, **b**, **c** and **d**). In the case of the oxidative post activation treatment in HNO$_3$ instead, for both samples the procedure seems to introduce modifications that deeply alter the general features of the INS spectrum (**Figure 3. 2e** and **f**).

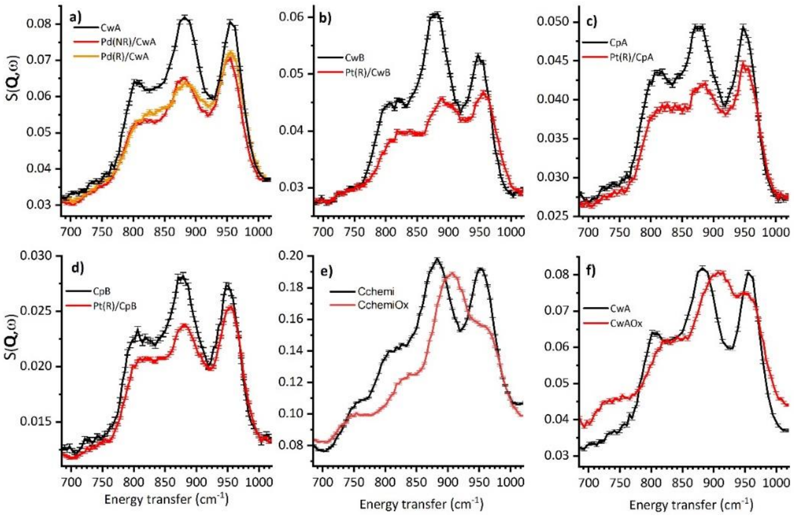

Figure 3. 2*: INS spectra collected during this experiment Sample CwA was measured in a previous experiment [9], but was included to show the comparison the correspondent catalysts and oxidized sample Part a) samples CwA, Pd/CwA(NR) and Pd/CwA(R). Part b) samples CwB and Pt/CwB(R). Part c) samples CpA and Pt/CpA(R). Part d) samples CpB and Pt/CpB(R). Part e) samples Cchemi and ChemiOx. Part f) samples CwA and CwAOx**.*

4. Preliminary comparison with DFT simulations

A large DFT simulation work was performed in order to better assign the observed features to precise C-H geometries in the activated carbons and catalysts samples. The simulations were performed on polycyclic aromatic hydrocarbon models at the 6-31G**/B3LYP level of theory using the CRYSTAL17 software for the geometry optimizations and the frequency calculations, and aCLIMAX [10] for the simulation of the INS spectra.

To summarize the result of the DFT simulation work:

- The simple polycyclic aromatic models employed for the simulations (16 models) are able to provide similar spectral features to the experimental ones. In particular, hexagonal models show a very good correspondence with the three main peaks in the spectra of all the non-oxidized samples (Cchemi, CwA, CwB, CpA, CpB and related catalysts), as shown in **Figure 4. 1a**.
- It is possible to decompose the total simulated spectra into the contribution of single C-H terminations, highlighting that different geometries of the C-H terminations lead to very different contributions to the total spectra (**Figure 4. 1b)**. Thus we can assign the changes observed in the experimental spectra to changes in the relative amounts of specific C-H terminations.
- Models only containing regular C-H terminations are not sufficient to fully describe the experimental spectra of the parent activated carbon supports and their catalysts, and they are not able at all to describe the samples oxidized in HNO_3. Further simulations demonstrated that the missing contributions in the simulated INS spectra are related to the presence of defects, disorder and functional groups in the real system. By simulating also the contributions arising from these features, we pointed out that physical defects contributions are essential to fully describe the spectra of non-oxidized samples. For the description of the latter instead, we can observe that main peak of the spectra of both CchemiOx and CwAOx can be assigned to C-H terminations perturbed by an adjacent carboxylic acid group, as shown in **Figure 4. 1c**.

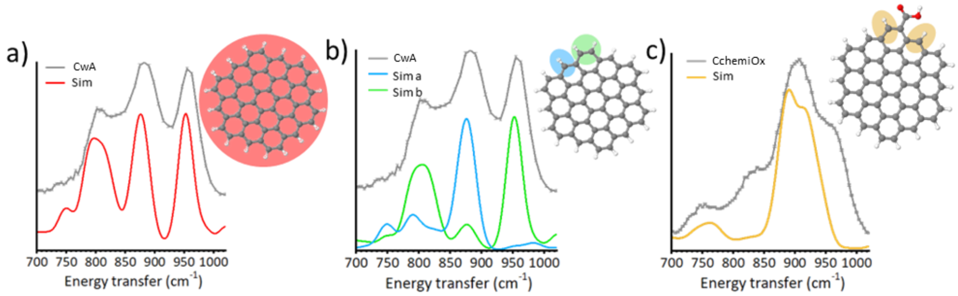

***Figure 4. 1**: preliminary comparison between experimental and simulated spectra. Part a) Comparison between the experimental spectrum of sample CwA and the hexagonal model $C_{54}H_{18}$. Part b) Comparison between the experimental spectrum of sample CwA and the contributions to the total spectrum of different typologies of C-H terminations. Part c) Comparison between the experimental spectrum of sample CchemiOx and the simulated spectra of C-H terminations perturbed by an adjacent carboxylic acid group.*

The redaction of a paper focusing on this work is currently in progress.

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