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Functionalization of mesoporous MCM-41 with aminopropyl groups by co-condensation and grafting: a physico-chemical characterization

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Abstract

This work reports about the synthesis and characterization of NH₂-MCM-41, a well known hybrid material commonly used in biomedical and biotechnological applications, based on mesoporous silica and aminopropyl functionalities. Samples were prepared by post-synthesis grafting and by one-pot co-condensation methods, to achieve a relatively high organic loading (around 12% wt) and were characterized in terms of porosity, thermal stability and distribution of the aminopropyl moieties in the silica framework. The results suggest that grafting brings about an almost complete consumption of surface silanols, with structurally defined functional groups mainly located inside the material pores. On the contrary, co-condensation results in lower surface area and thermal stability, with ink-bottle-like pores. This suggests that the aminopropyl groups are not only linked to the pores inner surface but could be located in the pore walls or at their entrance.

Keywords: MCM-41, co-condensation, grafting, silylation, FTIR spectroscopy

Introduction

In recent years great efforts have been devoted to the synthesis and characterization of hybrid organic-inorganic compounds, the so called *Periodic Mesoporous Organosilicas* (PMO) [1,2]. These materials are the subject of many studies for their great versatility due to variety of organic groups which can be easily bridge-bonded within the framework of a silica mesostructure. In this way it is possible to tune physical and chemical properties and to obtain functionalized materials that can be used as precursors for the bonding of molecules with interesting application in many fields such as catalysis [3-6], sensing [7], life science [8-10], drug-delivery [11, 12], etc.

Two main methods for the synthesis of organic-inorganic materials have been proposed: post-synthesis modification (grafting) and one-pot synthesis (co-condensation) [13]. Grafting of organic functionalities on the silica surface is usually carried with the pre-constituted mesoporous material and the appropriate alkoxy silane, to covalently bond the functional group to the surface silanol groups. This modification is called *silylation* and should not affect the long range order related to mesostructuration. Major drawbacks of the method are low control of loading and distribution of functionalities, which are expected to be mainly located on inner surface of the pores, thus decreasing pore size as a consequence of steric hindrance.

As for the co-condensation method, it consists of the hydrolytic polycondensation of a silica precursor with the proper alkoxyorganosilane in presence of a structure directing agent (SDA also called template, generally long chain ammonium salts or non ionic co-polymers) and an acid or a base [14-21]. With this procedure one can directly introduce in a single step the organic functionality into the silica framework and should better control the loading and spatial distribution of the organic groups by choosing a desired silica/organosilane ratio. For these reasons, co-condensation has been proposed as the most advantageous and innovative method, the main drawback being the limited choice of organic functionalities available as commercial alkoxyorganosilane precursors.

In this work, we prepared and characterized 3-aminopropyl-modified MCM-41 (NH₂-MCM-41), a well known substrate largely employed as carbon-carbon coupling-agent in biomedical applications [12, 22-24]. The results obtained with the two different methods, co-condensation and grafting, are compared in samples prepared with a relatively high loading of organic (12 wt%), to check the limitations of the procedures. Notwithstanding the potentiality of the one-step approach to develop novel materials with intriguing properties, our results indicate that for this simple structure this method is not competitive with respect to the well established grafting procedure.

Experimental

Materials

n-Cetyltrimethylammonium bromide (CTAB), Silica, Sodium Hydroxide (NaOH), Tetraethoxysilane (TEOS), 3-Aminopropyl Triethoxysilane (APTS), Hydrochloric acid (37%), Methanol were purchased from Sigma-Aldrich and used without further purification.

Synthesis

Purely siliceous mesoporous MCM-41 was synthesized according to literature employing CTAB as SDA and fumed silica [25]. Before functionalization, the SDA was removed by calcination at 823 K, first under nitrogen and subsequently under oxygen flow.

NH₂-MCM-41 (post) was prepared following Ref. [26], by suspending 1 g of calcined MCM-41 in 30 ml of toluene. 0.6 ml of APTS were added drop wise and the mixture was allowed to reflux for 8 hours. The reaction solution was centrifuged and the deposited gel washed first with ethanol and then with deionized water. The obtained white solid was filtered, washed with methanol and dried in vacuo.

NH₂-MCM-41 (co) was prepared according to the method described in [7]. 0.70 g of CTAB (0.002 mol) were dissolved in 336 ml of deionized water. Then 2.45 ml of a fresh NaOH solution

(2M) were added and the temperature was raised to 353 K. Afterwards 3.5 ml of TEOS (0.018 mol) and 0.43 ml of APTS (0.002 mol) were slowly and simultaneously added drop wise to the reaction solution and the mixture was allowed to stir for 2 h. The obtained white precipitate was filtered, washed with abundant deionized water and methanol and dried in vacuo at room temperature (RT). The removal of the organic template was achieved by reflux of the product for 24 h in a solution of HCl (37%) and methanol followed by extensive washing with deionized water and methanol. The obtained NH₂-MCM-41 (co) was filtered and dried in vacuo.

Characterization

Specific surface areas (SSA), pores volume and size were measured by N₂ adsorption–desorption isotherms at 77 K using Micromeritics ASAP 2020. The SSA was calculated by the Brunauer–Emmet–Teller (BET) method, the average pore size according to the Barrett–Joyner–Halenda (BJH) method, employing the the Kruk-Jaroniec-Sayari equations on the adsorption branch of the isotherms. Prior to analyses, samples were outgassed at RT overnight.

Powder X ray diffraction (XRD) patterns were collected on a Philips X'Pert Pro Bragg Brentano diffractometer using Cu K α radiation (1.54 Å), with a scan speed of 0.01°/min.

FTIR spectra were recorded using a Jasco FTIR-5300 spectrometer equipped with a DTGS detector, working with resolution of 4 cm⁻¹ over 32 scans. Samples were in the form of self-supporting pellets suitable for transmission IR experiments and were placed in a quartz cell equipped with KBr windows, designed for RT studies in vacuum and controlled atmosphere. Before FTIR analysis samples were outgassed at RT to remove physically adsorbed water and impurities.

Thermal gravimetric analysis (TGA) was carried out on a TAQ600 (TA Instruments) heating the samples in a nitrogen flow, after equilibration, from 303 K to 1273 K at a rate of 10 K/min. Once reached the final temperature an isotherm was run for 15 minutes in air.

Results and discussion

Fig. 1a reports a comparison between the low angle XRD patterns of NH₂-MCM-41 (post) sample and the parent MCM-41. Bare MCM-41 shows the typical (100) and (110) peaks due to an ordered hexagonal (P6mm) network of mesopores, with the weak (200) and (201) peaks indicating the long range order of the structure. The intensity of the latter peaks decreases after functionalization (dashed curve). This could be interpreted as a decrease in the scattering contrast between pores and walls, suggesting the inclusion of the functional groups inside the pores.

The XRD pattern of NH₂-MCM-41 (co), measured after SDA extraction, is reported in Fig. 1b. Even if the peaks position are similar to those described above, their broader character indicates a minor order in the mesoporous structure, as testified by transmission electron microscopy measurements (TEM, not reported). A shift in the (100) peak position with respect to MCM-41 and NH₂-MCM-41 (post) indicates a slightly higher d-spacing (Table 1).

The TGA profiles of the two NH₂-MCM-41 and of the parent MCM-41 samples are reported in Fig. 2. All samples show a first weight loss below 423 K, related to the desorption of water molecules strongly interacting with the surface. The amount of water desorbed in the three samples is quite similar (Table 2), suggesting that the functionalization did not drastically affect the hydrophilicity of the samples. For the parent MCM-41 sample the monotonous weight decrease up to 1273 K can be explained by a gradual dehydroxylation of surface Si-OH groups. Above 423 K the TGA profiles of the two functionalized samples are quite different: NH₂-MCM-41 (co) shows a main weight loss around 573 K, followed by a more gradual decrease, while for NH₂-MCM-41 (post) the main weight loss is observed at 843 K (data referring to the first derivative maximum, not shown). These results indicate a different stability of the organic moieties in the two samples, which could be due to a distinct location or binding to the silica surface. We can hypothesize that during the synthesis some of the organic linkers were incorporated within the silica walls, thus forming a less ordered and stable structure.

A rough quantification of the desorbed organic was calculated by assuming that the weight loss at high temperature (above 950 K) is due to surface dehydroxylation involving the Si-OH groups not involved in the linkage with the aminopropyl functionality (Table 2). The calculated values give a similar loading for the two samples, close to 12% wt. By assuming a density of surface OHs between 2 and 4 OH/nm², as estimated by different groups [27, 28], this would roughly correspond to an aminopropyl moiety for every 2-4 surface silanol groups. This quantification is probably an overestimate in sample NH₂-MCM-41 (co), where we cannot exclude the presence of impurities, formed during the synthesis or the template extraction (see later).

The low temperature nitrogen isotherms of the two functionalized NH₂-MCM-41 materials are reported in Fig. 3, together with that of the parent MCM-41 for comparison. All samples show the type IV isotherm typical of mesoporous materials: the slope at intermediate P/P⁰ (below 0.4) testifies of the capillary condensation of nitrogen inside the mesopores, while the type H1 hysteresis loop at high P/P⁰ (< 0.90) is related to interparticle macroporosity. Comparison of the three curves in Fig. 3 clearly shows that the SSA decreases passing from parent MCM-41, to NH₂-MCM-41 (post) to NH₂-MCM-41 (co) (see also Table 1). Also, in parent MCM-41 the first capillary condensation is steep and at the typical value of P/P⁰ = 0.35, while it moves downward and becomes broader after functionalization. On the contrary, the hysteresis loop at high P/P⁰ is not affected by grafting. This indicates that grafting procedure affected the pores size and available volume (Table 1), without modification of the porosity due to interparticle spaces, in agreement with the hypothesis that the aminopropyl groups are anchored within the inner surface of the pores.

As for NH₂-MCM-41 (co), the capillary condensation occurs in a broader range with respect to the other samples, indicating less homogeneously distributed pore sizes with a lower volume (Table 1). Moreover, this material shows a small hysteresis loop associated to this capillary condensation (closing at P/P⁰ = 0.42, in agreement with what expected for the tensile strength of the adsorptive gas N₂). This kind of hysteresis loop is compatible with ink-bottle-like pores, suggesting that some

of the pores have restricted access, probably because of the presence of functional groups at the entrance [29].

FTIR spectroscopy was employed to study the nature and structural integrity of the aminopropyl functionalities grafted on the silica surface. To this aim the two samples were measured in vacuo after different thermal treatments. The corresponding spectra are reported in Figs. 4 and 5, high and low frequency ranges in panels a) and b) for samples NH₂-MCM-41 (post) and NH₂-MCM-41 (co), respectively. Both samples show intense bands related to the organic functionality: i) the vibrational modes of the amino groups, asymmetric and symmetric N-H stretching modes (NH₂ ν_{as} and ν_s) at 3370/3375 and 3300/3310 cm⁻¹, and corresponding bending (δ NH₂) at 1594 cm⁻¹, ii) the stretching and bending modes of CH₂ groups, ν_{as} and ν_s at 2930 and 2870 cm⁻¹, δ CH₂ at 1470, 1448, 1410 and 1385 cm⁻¹. Several differences can be observed between the two samples, concerning i) the density of surface Si-OH groups; ii) the homogeneity of the functional groups and iii) the thermal stability of the functional groups.

As for the density of surface Si-OH groups, comparison between the high stretching region of the two samples (Figs. 4a and 5a) clearly shows that all the silanols of sample NH₂-MCM-41 (post) have been consumed by grafting, a fraction of which becomes available only after activation in vacuo at 823 K with consequent degradation/desorption of the organic. On the contrary, Si-OH groups (ν OH at 3744 cm⁻¹) are abundantly present in sample NH₂-MCM-41 (co), where they are involved in hydrogen bonding with water molecules before thermal treatments (strong absorption in the 3700 -2700 cm⁻¹ interval and δ OH of adsorbed water at 1620 cm⁻¹) [30]. In these conditions (after outgassing at RT), the latter sample also shows the presence of protonated NH₃⁺ groups (δ_{as} and δ_s at 1620 and 1514 cm⁻¹, respectively) probably formed as a consequence of proton transfer from strongly adsorbed water molecules [31]. We cannot exclude the formation of similar species in minor amount also on sample NH₂-MCM-41 (post).

The analysis of the νCH region shows that the bands are narrow and well resolved in $\text{NH}_2\text{-MCM-41}$ (post) sample, indicating a homogeneous distribution of the alkyl chains. On the contrary, those of $\text{NH}_2\text{-MCM-41}$ (co) show additional components at 2974 and 2850 cm^{-1} , probably due to methoxy or Si-CH_3 groups formed during the synthesis, the template extraction, or the thermal activation. It is noticeable that both samples show degradation products as a consequence of the thermal activation (mentioned νCH_3 and corresponding δ of Si-CH_3 at 1410 cm^{-1} , νNH at 3430 cm^{-1} [31, 32]), but these products appear at lower temperature on $\text{NH}_2\text{-MCM-41}$ (co) sample, in agreement with TGA.

Conclusions

Aminopropyl functionalized MCM-41 hybrid materials ($\text{NH}_2\text{-MCM-41}$) were prepared by grafting and co-condensation and also characterized about their physico – chemical properties. In both cases a high loading of organic functionalities (around 12%) resulted in mesoporous materials.

The results show that the surface population of the two functionalized samples is quite different, regarding the density of Si-OH groups and the distribution of the aminopropyl moieties. As for $\text{NH}_2\text{-MCM-41}$ (post) sample, an almost total consumption of surface silanols results in structurally defined and well dispersed functional groups, which are mainly located inside the pores as testified by the changes in the low angle XRD pattern and in the porosity. This sample is also characterized by appropriate thermal stability.

$\text{NH}_2\text{-MCM-41}$ (co) sample on the contrary, is characterized by lower surface area, lower thermal stability and ink-bottle-like pores. These results suggest that in this case the aminopropyl functionalities are not homogeneously distributed at the inner surface of the pores, but could be also located in the pores walls and at their entrance, explaining the low thermal stability and ink-bottle-like pores shape. Moreover, vibrational spectroscopy shows the presence of unreacted surface Si-OH groups and of organic impurities (methoxy or Si-CH_3 groups), which could be formed during

the synthesis (incomplete hydrolyzation of TEOS and APTS) or during the template extraction with the methanol/HCl mixture.

This study shows that for NH₂-MCM-41 samples the classical grafting method is competitive with respect to the one-pot one, notwithstanding the great potential of the latter methodology in the search of materials with new properties. We cannot exclude that these results are related to the relatively high loading of aminoproyl groups. Moreover, the combined use of different characterization techniques allowed to disclose the complexity of an apparently simple hybrid material, widely employed as drug delivery system or as carrier for biotechnology applications. We hope that this study will be useful for researchers working in these fields.

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Figure captions

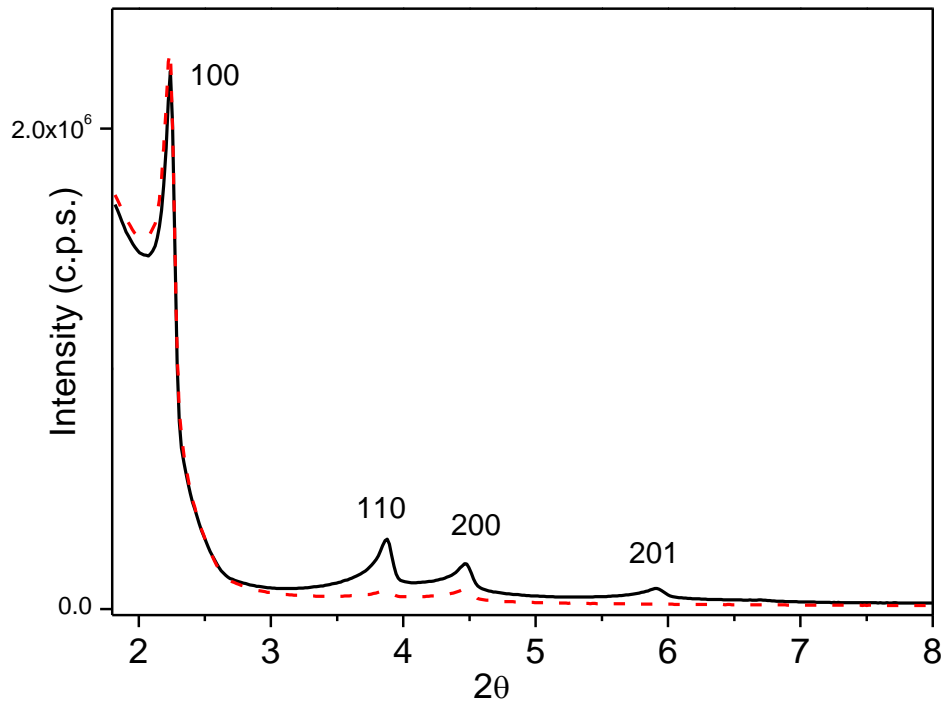
Figure 1. Powder XRD patterns of a) MCM-41 and NH₂-MCM-41 (post), full and dashed lines, respectively; b) NH₂-MCM-41 (co) after template extraction.

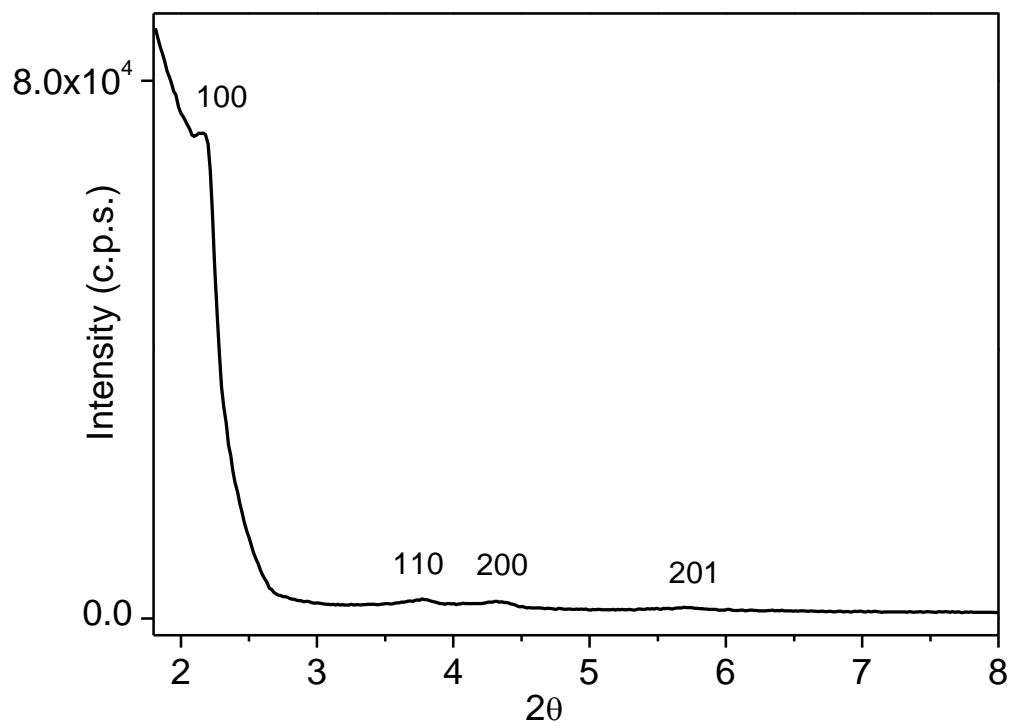
Figure 2. TGA profiles of a) MCM-41, b) NH₂-MCM-41 (co) and c) NH₂-MCM-41 (post).

Figure 3. Nitrogen isotherm adsorption (∇) and desorption (□) on a) MCM-41, b) NH₂-MCM-41 (post) and c) NH₂-MCM-41 (co).

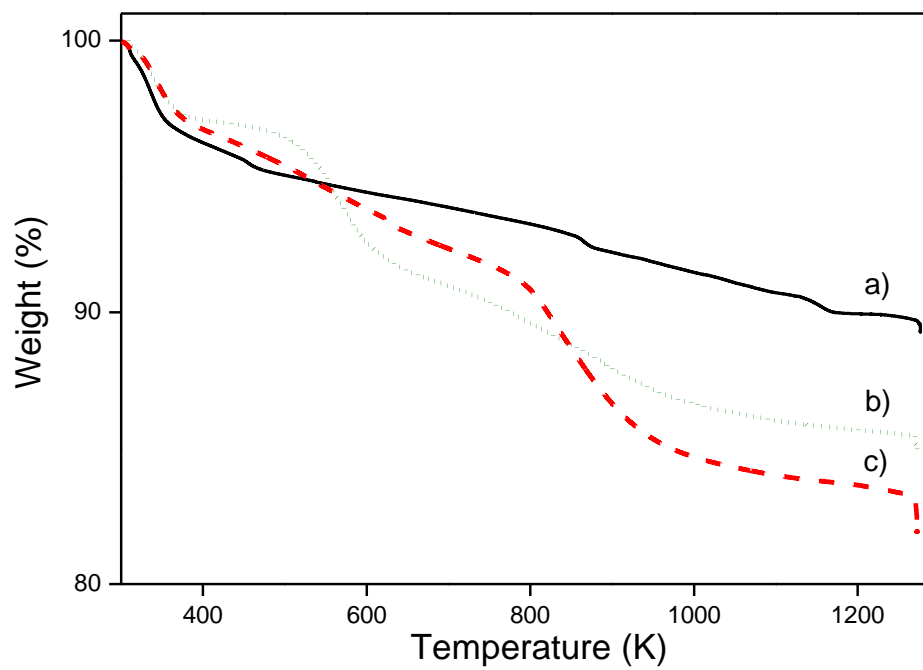
Figure 4. FTIR spectra of sample NH₂-MCM-41 (post) outgassed at increasing temperature: a) high frequency and b) low frequency ranges. Spectra were vertically shifted for easier comparison.

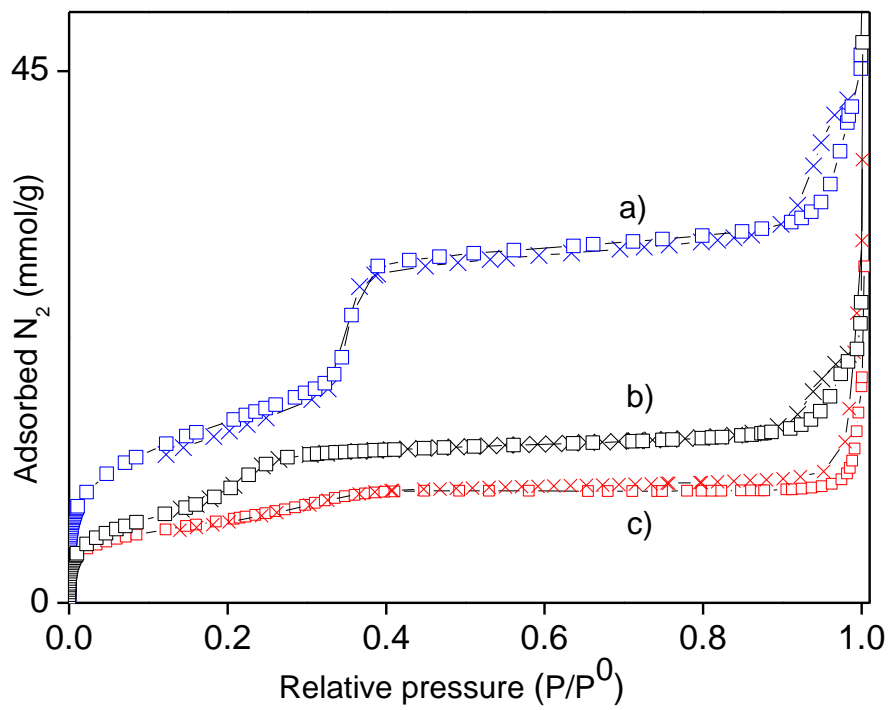
Figure 5. FTIR spectra of sample NH₂-MCM-41 (co) outgassed at increasing temperature: a) high frequency and b) low frequency ranges. Spectra were vertically shifted for easier comparison.



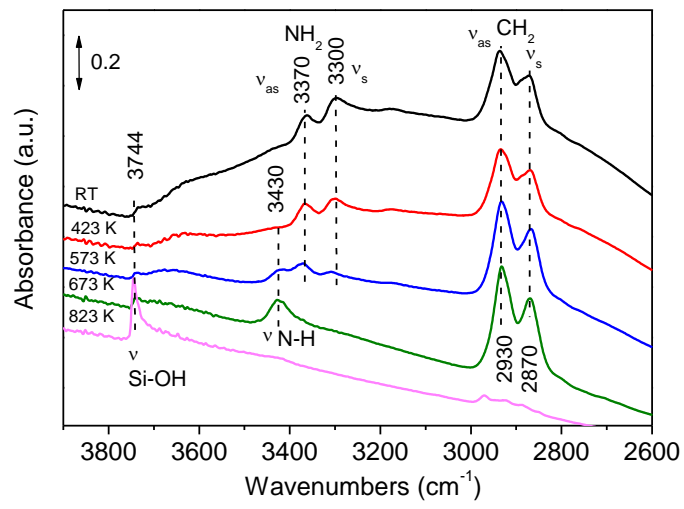


P. Iliade et al. Figure 2

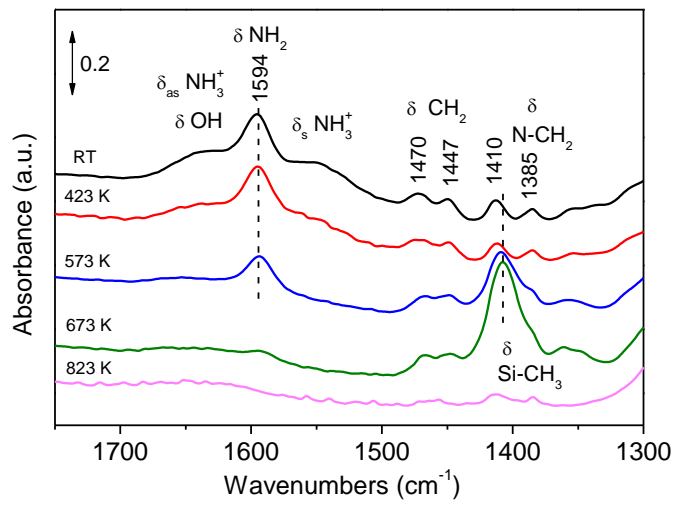




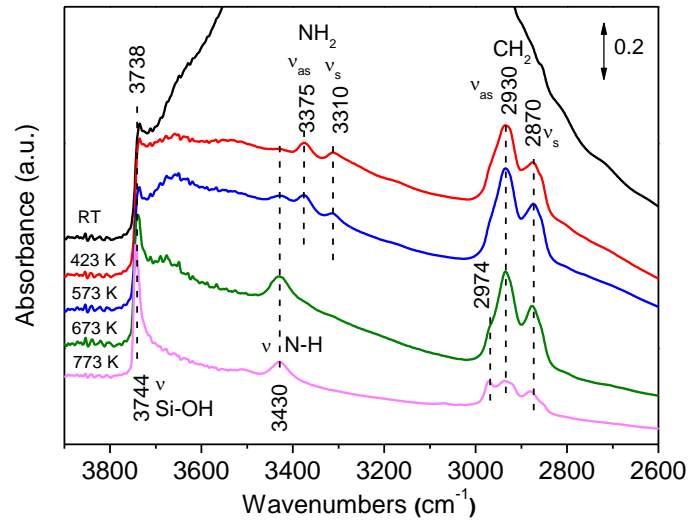
P. Iliade et al. Figure 4a



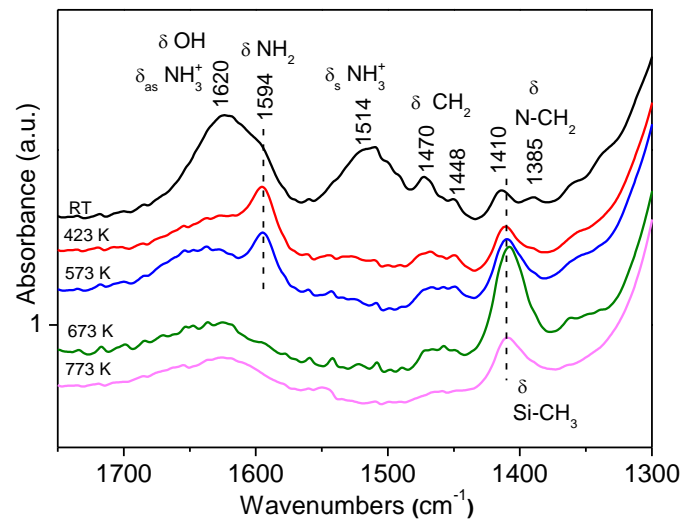
P. Iliade et al. Figure 4b



P. Iliade et al. Figure 5a



P. Iliade et al. Figure 5b



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