

NbP catalyst for furfural production: FT IR studies of surface properties.

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Abstract

The surface acidic properties of Niobium phosphate solid acidic catalyst (NbP) have been analyzed by FT IR spectroscopy before and after reactivity tests concerning the hydrolysis and dehydration to furfural of xylose, as model molecule, or of real corn stover hydrolysates. Nitriles adsorption over the fresh NbP catalyst evidences P-OH and Nb-OH groups acting as Brønsted acidic sites, whereas Nb⁵⁺ ions behave as Lewis exposed sites, showing medium strength acidity. The characterization of the used catalysts surface points out that, in spite of the strongly adsorbed surface species arising from the reactivity tests, both Lewis and Brønsted sites are still exposed, although slightly weaker in acidic strength and more heterogeneous than over the fresh catalyst. This effect can indeed explain the remarkably high reusability of this material, in terms of conversion and furfural yield. *In situ* IR studies of xylose conversion suggest that activation of xylose thorough coordination at Lewis sites is likely to occur in the reaction temperature range.

Keywords: Niobium Phosphate, acid catalysts, xylose catalytic conversion, furfural, FT IR spectroscopy

1. Introduction

Materials based on Niobium phosphate have proven to be interesting catalysts in several fields of applications due to their tunable acidic properties which arise from exposed Brønsted and Lewis sites. Nb oxide can be effectively supported over several oxidic materials, such as alumina, titania, silica, thus modulating their acidity and leading to catalysts very active in dehydration reactions (for instance, dehydration of methanol to diethylether, dehydration of butanol, dehydration of glycerol to acrolein [1,2,3]). Combination of Niobium oxide and phosphoric acid, i.e. niobium phosphate and phosphoric acid-treated niobic acid are also potentially useful in any application requiring heterogeneous acid catalysts. In particular, Niobium phosphate solid acidic catalyst (NbP) was evaluated to have a high acid strength of ($H_o \leq -8.2$) corresponding to the acid strength of 90% H₂SO₄. In water, or in a very highly protic medium, very few solid acids can maintain the desirable characteristics of activity and stability without deactivation of their acid sites

[4,5,6]. NbP has attracted great interest as catalyst, due to its strong acid properties which can be preserved in polar liquids and, unlike niobic acid ($\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$) it retains its properties at higher temperatures [7]. Amorphous NbP does not crystallize prior to 800°C and exhibits high catalytic activity even after heat treatment at temperatures as high as 500°C [8]. [Niobium Compounds: Preparation, Characterization, and Application in Heterogeneous Catalysis, Izabela Nowak and Maria Ziolek, Chem. Rev., 1999, 99 \(12\), pp 3603–3624](#)

Our group first evaluated the aqueous dehydration of C6 sugars to 5-hydroxymethyl-2-furaldehyde (HMF) over NbP obtaining 100% selectivity at low fructose conversions ($X=30\%$) [9]. ~~Deep spectroscopic characterizations found the presence of both terminal POH and NbOH groups, the former leading to a slightly stronger Brønsted acidity than NbOH sites. Lewis acidity is also present in this catalyst and it is assigned to coordinatively unsaturated Nb^{+5} sites [10].~~

Recently, the same catalyst has been used for the first time directly in the presence of biomass hydrolysates (corn stover's hemicellulosic sugars) with appealing results in terms of high furfural yield and mild reaction conditions, thus ultimately allowing a mineral acid-free conversion of this raw biomass hemicelluloses fraction [11].

Furfural represents the most promising derivative among the products derived from C5 sugars, since it is a key platform molecule for the synthesis of a broad range of important chemicals (furan, furfuryl alcohol, 2-methyl-tetrahydrofuran, 2-methylfuran, furoic acid, etc.) with a broad range of industrial applications, such as biofuels, plastics, and fine-chemicals production [J.P. Lange, E. van der Heide, J. van Buijtenen, R. Price, ChemSusChem. 5, (2012) 150 -166; K. Yan, G. Wu, T. Lafleur, C. Jarvis, Renew. Sust. Energ. Rev. 38 (2014) 663-676; C.M. Cai, T. Zhang, R. Kumar, C.E. Wyman, J. Chem. Technol. Biotechnol. 89 (2014) 2-10]. Up to now furfural is commercially produced in either batch or continuous processes using mineral strong acids as catalysts. This fact leads to serious drawbacks related to equipment corrosion, difficult catalyst recycling and consequent extra separation costs as well as environmental and health risks [S. Dutta, S. De, B. Saha, M.I. Alam, Catal. Sci. Technol., 2 (2012), 2025–2036]. Hence, numerous efforts have been made on the furfural manufacturing-process involving the use of heterogeneous catalysts instead of homogeneous ones. Few studies have been reported combining raw biomass with heterogeneous catalysts in aqueous medium and the ascertained yield is generally low, whilst a lot of investigation has been devoted to the use of heterogeneous catalysts on xylose aqueous (I. Agirrezabal-Telleria, I. Gandarias, P.L. Arias, Catalysis Today, 234 (2014) 42-58) and non-aqueous solutions [Dutta...]. For this reason the autohydrolysis of the hemicellulose fraction of corn stover followed by the successive conversion to furfural in presence of NbP catalyst represents a promising approach, addressing the process' major drawbacks with a catalyst that displays good resistance to deactivation, which allowed NbP recycling up to three consecutive runs [11].

Indeed, characterization of the nature of surface acidic sites is of the utmost interest in order to optimize reaction parameters and to understand reaction and deactivation mechanisms. In a previous work, deep spectroscopic characterizations of NbP catalyst found the presence of both terminal POH and NbOH groups, the former leading to a slightly stronger Brønsted acidity than NbOH sites. Lewis acidity is also present in

this catalyst and it is assigned to coordinatively unsaturated Nb⁺⁵ sites as revealed by Acetonitrile adsorption followed by FT spectroscopy [10]. FT IR spectroscopy has also been applied, together with microcalorimetry, to analyze adsorption of probe molecule such as methanol, dimethylether and ammonia over NbOPO₄ catalysts, the strong interaction of such probe molecules, evidencing showing that NbOPO₄ is more acidic than pure Niobia; (Sun). Pyridine adsorption/desorption experiments -allows site-quantification of Bronsted and Lewis acidic sites [Bassan, M.H.C. de la cruz, J.F.C. da Silva, E.R.Lachter, Catalysis Today 118 (2006) 379-384], however its diagnostic bands fall in a spectral region which can be strongly perturbed by the signal of adsorbed organic species, i.e. heavy reaction byproducts over the spent catalyst. On the other side, to the best of our knowledge, pivalonitrile adsorption to characterize NpP surface, has not yet been reported, in spite of several advantages shown by this probe molecule, as recently underlined by several authors [J.Ni, F.C.Meunier, S.Robles-Manuel, J.Barrault, S.Valange, J.Phys. Chem. C 115 (2011) 24931-24936; 17]

In this work context we are now presenting a detailed spectroscopic study on the acidic surface properties of NbP catalyst, both in the fresh and used form, in order to explain its remarkable and prolonged activity and selectivity in xylose and corn stover hydrolized cyclodehydration. The evolution of acidic sites has been monitored by Acetonitrile and Pivalonitrile adsorption. Xylose thermal evolution in dry conditions and in the presence of water vapor has also been followed by in situ FT IR spectroscopy.

2. Experimental.

Niobium phosphate (NbOPO₄, NbP) ADF25 (surface area 180 m²/g) was supplied by CBMM (Companhia Brasileira de Metalurgia e Mineração) and was used mostly as received. Otherwise, when stated, NbP was treated at 255°C for 6 h under high vacuum (NbP_{vac}) resulting in an effective acidity of 0.33 meq/g determined by acid-base titration in water using 2-phenylethylamine as basic probe-[11, 12, P. Carniti, A. Gervasini, S. Biella and A. Auroux, Catal. Today, 2006, 118, 373–378-44]. This family of catalysts has been reported in the literature to posses mesoporosity, showing an average pore size which ranges from 2.5 nm to 6 nm ca (see for instance Carniti et al. Chem. Mater. 2005, de la Cruz)

Used NbP catalysts, obtained after subjection of fresh NbP_{vac} to cyclodehydration reaction of either xylose or corn stover hydrolysates at different conditions, were washed with water, dried overnight at 105°C and stored at ambient conditions before further characterizations. The analysis of surface species by FT IR spectroscopy evidenced that this treatment in very mild conditions preserved the presence of adsorbed species arising from consecutive catalytic runs. Spent (used) catalysts are noted as Spent-1 (Xylose conversion 150°C), Spent-2 (Xylose conversion 160°C), Spent-3 (Xylose conversion, three runs) and Spents CS (hydrolysate conversion).

Acetonitrile (AN, HPLC-grade) and pivalonitrile (PN; 98% purity) were supplied by Aldrich, and used after a distillation under vacuum, being weakly basic probe molecules with different steric hindrance. In particular, PN's critical dimension of ca.0.6 nm [13,14] is comparable with the molecular size of xylose. Xylose (Carlo Erba; reagent grade) was also used as received.

IR spectra were recorded by FT Thermo Nicolet Instrument 380 using self-supporting pressed disks of pure powders (20 mg average wt.), activated in the IR cell connected to a conventional gas-manipulation apparatus. Before any adsorption experiment, the fresh catalysts have been outgassed at 255°C for 1 hour, i.e. the activation temperature for catalytic tests, whereas the spent catalysts have been outgassed during 1 hour at 100°C in order to clean the surface from physisorbed water without changing the nature of residual adsorbed species. The adsorption procedure involves contact of the activated sample with AN or PN vapors and outgassing in steps from room temperature (r.t.) and up.

Skeletal spectrum of the fresh catalysts diluted in KBr (1% w/w) has been recorded and is reported in Supporting Informations (figure S1).

Experiments analyzing the working surface were performed by finely mixing fresh NbP_{vac} with a small amount of xylose (<10% w/w). Pressed self-supporting disks of the obtained mixture were outgassed at room temperature in the IR cell. Then, the sample was heated by step up to 140°C in the presence of water vapor, recording spectra of both surface and gas phase species at each temperature step.

[NH3-TPD analyses were performed in a home-made apparatus, using FT IR spectrometer Avatar 380 as detector.](#)

The [detailed](#) reaction conditions for the activity tests have been reported elsewhere [11]

3. Results and discussion

3.1. Characterization of fresh NbP catalyst

FT IR spectra of the sample after activation at different temperatures are reported in figure 1. Fresh niobium phosphate (NbP) was activated at 200°C and at 255°C during 1 hour ([reaction pretreatment temperature](#)) (~~reaction temperature~~). [The analysis of the OH stretching region, characterized by a broad and strong absorption between 3700 and 3000 cm⁻¹, shows that, Due to the relatively low activation temperature,](#) the resulting surface is still highly hydrated [due to the relatively low activation temperature.](#) Nevertheless, activated spectra display a sharp band at 3663 cm⁻¹ with a weak shoulder at ~3703 cm⁻¹. The former feature has been ascribed to OH stretching modes of surface hydrogenphosphate species and the latter to free Nb-OH groups [10]. The broad absorption at ~3380 as well as the band at 1612 cm⁻¹ correspond to adsorbed molecular water, stretching and scissoring modes of OH's, respectively. As expected, activation at 400°C results in the decreasing of the band due to H-bound hydroxyl groups, although also bands due to isolated Nb-OH and P-OH groups are reduced in intensity, pointing out the progressive dehydroxylation of the surface at increasing temperature.

Figure 1.

The spectrum of fresh NbP recorded in the presence of acetonitrile (AN) vapor displays the doublet components at 2317 and 2269 cm⁻¹, characteristic of AN and due to the Fermi resonance between C≡N stretching and $\delta_{\text{CH}_3} + \nu_{\text{C-C}}$ combination modes (figure 2). These components undergo a typical shift up of the

corresponding wavenumbers with respect to bands of the liquid molecule (2294 and 2254 cm^{-1} , table 1) along with a contemporary change of their relative intensity in favor of the higher frequency band and this behavior is due to the interaction with electron withdrawing centers. The higher the acidic site strength, the greater is the shift upward of the bands, reaching values higher than 30 cm^{-1} for strong Lewis acid such as transitional aluminas [10,15,16].

Prolonged outgassingEvacuation of the sample leads to the detection of a triplet, whose lower component band is centered at 2272 cm^{-1} and has been related to hydrogen bonding of AN with surface hydroxyl groups of NbP. This triplet results from the overlapping of two doublets due to AN coordinated over Lewis sites and AN interacting with OH groups. In particular, the second component of the AN-Lewis doublet and the first component of the AN-OH doublet are largely superimposed in the region 2295-2270 cm^{-1} . After prolonged outgassing, the latter doublet is strongly reduced in intensity and the absorption around 2295 cm^{-1} can be confidently assigned mainly to AN interacting with L sites (table 1). The features located at 2319 and 2293 cm^{-1} are typical of AN adsorbed on exposed Lewis acid sites with medium strength and are evident, although quite weakly, even after degassing at 200°C for 10 minutes. From literature data these sites should correspond to coordinatively unsaturated Nb^{+5} ions, well evident in spite of the high hydroxylation degree of the surface.

Table 1. IR frequencies (cm^{-1}) of AN adsorbed over NbP samples.

Sample	ev. r.t. 30 min.			ev. 100°C 10 min.	
	Lewis Sites		H-bonded	Lewis Sites	
Fresh NbP	2319	2295	2275	2319	2293
Spent-1	2319	2295	2269	2317	2291
Spent-2	2319	2292	2270, 2262	2317	2290
Spent-3	2318	2293	2265, 2259	2314	2292
Spent-CS	2316	2293	2265, 2259	2320	2290
$\gamma\text{-Al}_2\text{O}_3^*$	2330	2300			
Liquid AN*	2294,	2254			

* from ref. 13

The inset of figure 2 displays the high frequency region spectrum (in the subtracted form) of the fresh catalyst after AN adsorption and outgassing at room temperature for 30 minutes. It seems that AN adsorption mainly affects P-OH groups, which appear as negative band in the subtraction spectrum reported in the same figure, whereas the weak shoulder at 3700 cm^{-1} (Nb-OH stretching) seems to be less affected by adsorption. As it has been stated in a previous study [10], Brønsted acidity of POH groups seems to be stronger with respect to NbOH groups.

Figure 2.

Correspondingly, the broad band due to H-bound hydroxyl groups shows two components roughly centered at around 3370 and 3170 cm^{-1} which could correspond to perturbed OHs having different acidic strength (Nb-OH and P-OH respectively). This effect suggests that an interaction of AN with both exposed OH groups families occurs. Moreover, the shoulder at 3700 cm^{-1} seems to be quickly restored after degassing at 100°C, in agreement with its assignation to a weaker acidic site (spectra not shown). This behavior is another evidence of the weaker acidity of the NbOH sites compared to the POH sites.

In another set of experiments, PN has been adsorbed over the same fresh NbP samples. This probe molecule shows an increased steric hindrance [17], furthermore it allows a more straightforward insight on the Brønsted to Lewis sites ratio of the analyzed catalysts [in comparison with AN adsorption \[Meunier\]](#).

IR spectrum of PN is characterized by a single strong band observed in the liquid at 2235 cm^{-1} , due to the stretching vibration mode of the $\text{C}\equiv\text{N}$ triple bond. This band shifts to higher frequency when PN interacts with electron withdrawing centers through its nitrogen lone pair. The subtraction spectra of the $\text{C}\equiv\text{N}$ stretching region of PN adsorbed on the fresh catalyst are shown in figure 3. In presence of PN vapors three partially overlapped bands are clearly observed, the one with lowest frequency corresponds to physisorbed PN, a new band at 2276 cm^{-1} is formed after PN coordination with Lewis acid sites and the band at ~2260 cm^{-1} corresponds to PN H-bonded to OH groups (table 2). The intensities of these bands have been calculated after deconvolution (see also figure S2 in Supporting information as an example of deconvolution) and the Brønsted -to-Lewis intensity ratio [\(B/L\)](#) results higher than 1, which is in agreement with reports from Bassan et al. [18] claiming a prevailing Brønsted acidic character of this material. [B/L ratio parameter, characterizing the acidic nature of the surface, has also been reported as directly related to catalyst selectivity to furfural production \(Weingarten et al. J.Catal. 2012\).](#)

Subsequent outgassing at room temperature results in a net decrease of the H-bonded band displaying also a shoulder at lower frequencies. Correspondingly, in the high frequency region of the spectra, the OH stretching modes appear as negative bands after interaction with nitrile molecules (inset fig. 3). The PN coordinated band seems to maintain almost the same intensity even after outgassing at 100°C. At this temperature a broad and complex shoulder due to H-bound PN is still observed, possibly also showing two components centred at 3400 and 3170 cm^{-1} , as also reported after AN adsorption (inset figure 3).

Bands due to coordinated PN display a net decrease only after outgassing at 200°C, nevertheless both Lewis and Brønsted acid sites are evident even after outgassing at 300°C.

Figure 3.

[A following experiment has been preformed on PN adsorption over the catalyst surface previously slightly dehydrated heating in vacuum in the IR cell and after rehydration at room temperature and a short outgassing step. The surface spectrum shows a very strong and broad band characterizing bound-OHs, corresponding to a strong and complex peak centred at 1630 \$\text{cm}^{-1}\$, due to the deformation mode of the molecularly adsorbed](#)

[water \(Figure S3 in Supporting information\). PN adsorption and outgassing at room temperature evidenced a slightly increased ratio B/L sites, in comparison to the same ratio obtained after PN adsorption over the NbP sample, according to findings from West et al. \[5\] on the effect of vapour treatment on solid acidic catalysts. Nevertheless Lewis sites are still detected \(band at 2280 cm⁻¹\).](#)

In sum, the solid NbP catalyst shows the acidic properties arising from both exposed Brønsted and Lewis sites. In particular, the comparison with literature findings points out that the P-OH groups are slightly more acidic than Nb-OH groups, also over such a highly hydroxylated surface (i.e. activation temperature below 300°C before adsorption experiments).

Table 2. IR frequencies (cm⁻¹) and Brønsted to Lewis intensity ratio obtained after PN adsorption on different NbP samples

Sample	Lewis sites		Brønsted sites				B/L
	freq	area	freq	area	freq	area	
Fresh NbP _{vac}	2283	1,417	2261	1,4	2239	0,180	1,11
Fresh NbP	2283	1,080	2262	1,315	2240	0,056	1,26
Spent-3	2286	0,291	2263	0,245	2242	0,171	1,43
Spent-CS	2283	0,923	2259	0,690			0,75
γ-Al ₂ O ₃ *	2296						
Liquid PN*	2236						

* from ref. 13

The co-presence of Brønsted acidity (two different strength sites) but also Lewis acidity at the surface must act synergistically to allow the very good catalytic results reported in the furfural production [11,19]. In the following paragraph we will extensively analyze the surface modifications of the used catalysts, recovered after activity tests in different conditions and from different reactants.

3.2. Characterization of used NbP catalysts.

Niobium phosphate catalysts used in the dehydration of xylose and of corn stover hydrolyzate in pure aqueous medium to produce furfural at different reaction conditions were characterized by AN and PN adsorption followed by IR spectroscopy. Table 3 presents all the used catalysts analyzed and the reaction conditions to which they were subjected. Niobium phosphate has proven to be an active catalyst in sugar dehydration (either pentoses or hexoses), as reported previously [10,11,20]. Also, recyclability of used catalysts has been evaluated in a sole aqueous system resulting in good performance after two recycles at the optimized reaction conditions. The comparison with results reported for the fresh catalyst [11] shows that yields of furfural remained high, decreasing only around 5% after the second recycle. Yield was maintained between 43 and 36% in all three runs and xylose conversion was lowered only in the second recycle.

Table 3. Used NbP samples, reaction conditions, conversion (X) and yields to furfural (Y) obtained [11].

Sample	Reaction conditions	X _{reached} (%)	Y _{reached} (%)
Spent-1	Xy ^a ; 150°C, 15 min	44	23
Spent-2	Xy ^a ; 160°C, 15 min	63	31
Spent-3		82	43
	Xy ^a ; 160°C, 30 min;	80	40
	3 runs	70	36
Spent-CS	Hy ^b ; 170°C, 30 min		23

^a Xylose as reagent; ^b Corn stover hydrolysate as source of pentosans.

These catalysts have changed color from white to dark brown most likely due to deposition of humins, insoluble carbonaceous materials formed during xylose cyclodehydration, since this reaction presents low selectivity specially when performed in sole aqueous medium. After outgassing at 100°C, the presence of such degradation products on the spent catalysts is ascertained by a broad complex IR band at 1708 cm⁻¹ corresponding to stretching of C=O species (figure 4,B), as referenced in ref. 21. The sharp band at 1610 cm⁻¹ is due to adsorbed water, stable at the surface at such low activation temperature. The broad and ill-defined absorption between 1300 and 1450 cm⁻¹ can be assigned to CH deformations and is more evident in the spectrum of the sample Spent-3, which has been recovered after three consecutive catalytic runs. This spectrum is also more noisy, showing low transmittance with bands close to the saturation of the IR signal as a consequence of the increased amount of organic material deposited at the surface.

Unlike the spent samples tested in xylose conversion, the spectrum of sample spent-CS (which has been tested with corn stover hydrolysate) only shows a main band due to molecularly adsorbed water, and some new very weak components below 1600 cm⁻¹, which have been evidenced in the subtraction spectrum [spent-CS] – [spent-1] (inset in figure 4B, broken line). These components, centered around 1550, 1500 and 1460 cm⁻¹ correspond to aromatic ring vibrational modes and could be due to residual organic species having an increased content of aromatic rings such as the phenolic compounds usually present in the water-extractable fraction of this biomass which accounts for ~11% of its dry weight [11].

Figure 4

The analysis of the OH stretching region (figure 4A) indicates that, as observed in the activated fresh sample spectrum, both the used catalysts after one run still display a weak shoulder due to residual POH species at 3667 cm⁻¹, and possibly an even weaker component at 3700 cm⁻¹ (Nb-OH) whereas there is no evidence of isolated OH groups in the spectrum of the spent-3 sample (3 catalytic runs), whose surface is heavily covered by organic degradation products. Furthermore, in all the spectra the presence of high amounts of adsorbed

molecular water is observed as a broad absorption at 3400 cm^{-1} corresponding to stretching modes of H-bound OH groups. From these data it seems that the reaction strongly affects the P-OH groups, having the highest Brønsted acidity. However it is remarkable that this effect is reversible and does not involve all the exposed hydroxyl groups, thus explaining the high activity observed for this catalyst even in consecutive runs.

It is worth noticing that even after the reaction with corn stover hydrolysate (sample Spent-CS), in spite of the evident deposition of organic matter at the catalyst surface, isolated P-OHs are still clearly detectable, suggesting that the catalyst can be as reusable in this case as after reaction with xylose model molecule.

Sample spent-1 has also been submitted to an oxidative treatment directly in the IR cell, heating in air at 400°C and outgassing at the same temperature (this spectrum was multiplied by a factor of 10 so as to highlight the OH groups). This treatment results in an almost clean surface in the low frequency region (figure 4B) and in the detection of sharp bands due to both Nb-OH and P-OH groups, completely recovered in the high frequency region (figure 4A, broken line).

AN was also adsorbed on the spent catalysts followed by outgassing at increasing temperatures. Spectra resulting from AN adsorption and desorption upon outgassing at increasing temperature on Spent-1 catalyst are reported in figure 5A and B.

Figure 5.

Figure 5 B presents the enlarged $\text{C}\equiv\text{N}$ stretching region: a triplet band of lower intensity and slightly lower frequency, as compared to the fresh catalyst, is observed after degassing AN vapors. As stated before for the fresh catalyst, the features now located at 2317 and 2295 cm^{-1} characteristic of Lewis acid sites with medium strength are evident only up to 100°C (table 1). The lower frequency band (2267 cm^{-1}) due to AN interacting with Brønsted sites is shifted to lower frequency than for the fresh NbP catalyst, and somehow becomes more complex, possibly showing two components. This should indicate that a heterogeneous population of OH groups having lower acidic strength are still exposed. A possible explanation is the selective poisoning of the stronger acidic sites by degradation products, but we cannot rule out the formation of hydrophilic byproducts at the surface, namely humin species, contributing to the increase of H-bound AN. Upon outgassing at 100°C only AN coordinated over Lewis sites is detected. Following outgassing at higher temperatures, also exceeding activation temperature, the absorptions due to molecular water decrease as well as the bands in the region from 1750 to 1400 cm^{-1} related to the organic matter deposited on NbP.

The Spent-1 sample has then been submitted to different activation procedures before AN adsorption, namely: i) outgassing at 400°C and ii) calcination and outgassing at 400°C , in order to study the effect of oxidative regeneration of the surface on the acidity. Subtraction spectra are reported in figure 6 in comparison to the fresh and untreated spent-1 sample corresponding spectra.

High temperature treatment of the spent sample results in a more dehydroxylated surface in both cases (outgassing and calcination) with a consequent decrease in the amount of organic matter deposited on the surface, by far more evident in the calcined sample as observed at frequencies from 1700 – 1300 cm^{-1} .

Moreover, after AN adsorption over the calcined sample the same triplet of bands appears, as for AN adsorption over the fresh catalyst, pointing out that acidic sites can be effectively restored once the organic surface materials have been removed. The lower frequency band due to AN interacting with Brønsted sites appears more complex, and this is in agreement with the detection of more defined Nb-OH groups (figure 4A) possibly evidenced by the high calcination temperature. It is worth to note that also the high temperature vacuum treatment seems to expose such NbOH sites, although in lesser extent, as can be detected in the high frequency region of the spectrum (not shown). A quite sharp band at 2350 cm^{-1} corresponds to stretching vibrational modes of molecular CO_2 enclosed in the oxide structure and arising from organic species combustion. Lewis sites are also restored after calcinations, strong enough to be detected even after outgassing at 160°C.

Figure 6

AN adsorption has also been carried out in the same conditions over all the spent catalysts reported in table 3. In figure 7 two series of spectra are reported: after prolonged outgassing at room temperature and after outgassing at 100°C. The corresponding bands wavenumbers are summarized in table 1. In spite of the residual organic species adsorbed after reaction, in the spectra recorded at room temperature the main bands are due to AN interacting with Lewis and Brønsted sites, as detailed in the previous section. Furthermore, the comparison among spectra shows that all the bands are consistent with features of the fresh catalyst spectrum reported in the same figure.

The presence of OH groups having Brønsted acidity is revealed by the bands of H-bound AN in the range 2270-2255 cm^{-1} (figure 7,A). The complexity of these bands and the slightly lower frequencies observed in the spectra of the spent catalysts (table 1) suggest that different OH groups are still exposed at the surface after reaction, possibly having lower acidity than the fresh sample, in agreement with the spectra reported in figure 4. In detail: sample Spent-1 shows the best defined band at 2267 cm^{-1} due to AN interacting with Brønsted sites which are almost unperturbed by the catalytic run at 150°C; the increase in reaction temperature (160°C, sample Spent-2) leads to small changes in the spectrum where possibly Brønsted sites are slightly reduced in quantity. Furthermore, three catalytic runs at 160°C do not affect significantly the acidity of the spent catalyst (sample Spent-3), in agreement with activity data (table 3): Brønsted acidic sites are still exposed, although the corresponding AN bands are weaker. Moreover, we must underline that isolated hydroxyl groups were not clearly detectable in the OH stretching region (figure 4A), which mostly consisted in a broad and not resolved absorption, therefore OH groups are strongly perturbed after reaction, by the deposited organic species, nevertheless Brønsted acidity is still available.

Remarkably, also the spectrum of the catalyst recovered after reaction with the corn stover hydrolysate (Spent-CS sample) shows features completely consistent with the fresh catalyst.

Figure 7

Lewis acidity can be selectively studied in the second series of spectra recorded after AN adsorption and outgassing at 100°C (figure 7,B). From these spectra it is clear that also Lewis sites are still exposed after reaction, characterized by bands in the range 2320-2290 cm^{-1} . The bands of coordinated AN over the used catalysts show a small but continuous shift to lower frequencies, but the spectrum of Spent-CS sample. Possibly, as we reported for the Brønsted sites, weaker Lewis sites are exposed, corresponding to Nb ions whose acidity can be somehow lowered by the presence of adsorbed organic byproducts, for instance oxygen-rich humin polymers.

Also PN was adsorbed over the spent catalysts. Figure 8 displays the subtraction spectra of PN adsorption and outgassing over the spent-3 and spent-CS along with the fresh NbP for comparison. Interestingly, bands due to PN interacting with Brønsted and Lewis centres are detected even after 3 catalytic runs, however are by far reduced in intensity. It seems that PN adsorption is more hindered than AN adsorption over the Spent-3 catalyst, where organic deposition built up during consecutive runs. The same effect does not occur over the Spent-CS catalyst, which is loaded with organic byproducts of slightly different chemical nature (as discussed above).

The B/L ratios have been calculated as bands area ratio, from the deconvolution of PN bands recorded after prolonged outgassing at room temperature (see [example](#) of bands deconvolution in figure S2) and are reported in table 2. This ratio, although not an absolute measure of the acidic sites number, allows us to characterize the acidic character of the surface. The comparison of data from Spent-3 with the fresh catalyst apparently shows that spent catalyst keeps mostly Brønsted acidic properties. This effect can be explained considering the accumulation of strongly adsorbed byproducts, such as carbonyl compounds and phenol-like compounds, since all these are electron rich compounds that can easily coordinate over Lewis sites hindering PN adsorption.

Figure 8.

The quite unexpected low B/L ratio observed for the Spent-CS sample can be due to the very low intensity and high complexity of the corresponding bands (see figure 8), whose ratio is indeed difficult to evaluate.

3.3. Working surface

In this set of experiments, NbP catalyst has been finely mixed with a small amount of xylose (<10% w/w), pressed in self supporting disks and outgassed for one hour at room temperature in the IR cell (Figure 9).

Then the sample has been heated by step up to 120°C and then 140°C in the presence of water vapor, recording spectra of both surface and gas phase species at each temperature step. The IR spectrum of the mixture NbP/xylose after outgassing at room temperature shows a very strong band centered at 1620 cm⁻¹ and assigned to the H-O-H deformation mode of molecularly adsorbed water, characterizing the highly hydrated catalyst surface. In the range 1500-1200 cm⁻¹ several bands due to xylose molecule almost unperturbed can be detected: a broad triplet at 1476, 1462, 1452 cm⁻¹, sharp bands at 1395, 1372, 1357, 1339 cm⁻¹, a doublet of bands at 1312-1306 cm⁻¹. This spectral region comprises the bending modes of CH₂, CCH, OCH and COH groups, and these modes are mainly mixed vibrational motion [22, 23]. Unfortunately, due to the high cut off limit of the catalyst itself, we are not able to analyze the region below 1200 cm⁻¹, where CC and CO stretching modes fall. At the same time, in the high frequency region, a negative weak band appears at 3660 cm⁻¹, already at room temperature, suggesting that first H-bonds are involved in the interaction of xylose with the catalyst surface. Indeed, at this stage, the bands we detected are mainly due to the mechanical mixture of the xylose molecule with the catalyst and no specific interaction can be envisaged.

After heating at 120°C, we detected a general broadening and weakening of these bands, especially the components below 1400 cm⁻¹, whose maxima are also slightly shifted upwards and split. This effect is even more evident at 140°C. Some new weak features also appear at 1430 and 1365 cm⁻¹. The band at 1450 cm⁻¹ (CH deformation mode) disappears (enlargement in Figure S3S4). The perturbation of the adsorbed xylose spectrum can be related to the coordination of the molecule with electron withdrawing centers at the catalyst surface, for instance, Lewis acidic centers. Correspondingly the relative intensity of the adsorbed water deformation and stretching bands (1620 cm⁻¹ and 3650 cm⁻¹, broad) are increasing, suggesting that dehydration activity is already starting at this temperature, i.e. just below the best reaction temperature, as defined in table 3. On the other hand, the multiplicity of bands detected in the low frequency region after heating could be due to the formation of some isomerization products at the surface, namely xylulose, in agreement with the reaction mechanism proposed to occur during furfural production in presence of Lewis acids [24].

Figure 9

After heating in the range 120-140°C, new bands appear in the gas phase spectra (figure 10), at 1710 cm⁻¹ (C=O stretching), 1450 cm⁻¹ (CH deformation), 750 cm⁻¹ (ring CC stretching), corresponding to the spectrum of furfural [25]. Some other features are also detected in the spectrum, in the CH stretching region above 3000 cm⁻¹ and in the CC/CO stretching region at 1100 cm⁻¹, possibly due to light reaction byproducts, already desorbed in the gas phase at such low temperature, for instance alcohols and alkenes. The intensity of bands assigned to furfural in the gas phase increases with increasing reaction temperature, but also with increasing contact time, see inset in figure 10 focusing on the band at 753 cm⁻¹. The intensity of this band is also reported in figure S4S5, as a function of reaction temperature and contact time.

Figure 10.

At 140°C, beside bands due to adsorbed xylose, in the condensed phase new bands are detected, some of them corresponding to adsorbed furfural (for instance the broad band at 1730 cm⁻¹ characterizing the aldehyde group) and some corresponding to reaction products or byproducts, for instance the weak band at 1780 cm⁻¹ which could be assigned to adsorbed carboxylic acids and/or anhydride-like species. On the other hand, the broad and strong absorption tailing below 1700 cm⁻¹ is assignable to C=O stretching mode of a mixture of carbonylic compounds (figure 9, inset). The bands are still detectable in the spectrum of the catalyst surface after prolonged outgassing. These features should correspond to species which are the likely precursors of humin and polymeric degradation byproducts detected at the catalyst surface after catalytic runs, arising from further reaction of furfural molecules tightly held at the surface through coordination at Lewis sites. These findings support the reaction path suggested by Weingarten et al. who pointed out the role of Lewis sites for several solid catalysts in lowering the selectivity to furfural production, by forming stable surface adduct with furfural itself, which undergoes degradation to complex byproducts [19].

PN adsorption has been then carried out over the surface of the same catalyst after a brief outgassing at room temperature and the resulting spectra are reported in figure 11. At room temperature only one complex band appears centered at 2235 cm⁻¹ (liquid-like PN) with shoulders at 2245 and 2254 cm⁻¹ (H-bound PN). Outgassing at room temperature completely removes all these weakly adsorbed species. Therefore PN interaction occurs only over very weak Brønsted sites, whereas Lewis sites are not anymore available to coordination. Therefore, both the more acidic Brønsted and Lewis sites are involved in the xylose conversion, but the low amount of water vapor in the IR cell does not allow the reconstruction of these sites and the “cleaning” of the catalyst surface, as can be performed in the reactor in the aqueous medium.

Xylose conversion in the IR cell has been also tested on NbP without the addition of water vapor ([solid state spectra in figure S6](#)~~not reported~~); ~~but and~~ only traces of furfural formation could be detected in the gas phase above 150°C, showing that the hydroxylated surface can supply only a limited amount of acidic sites in such conditions, although the reaction itself is actually starting. Indeed the treatment with water has been reported to increase the surface concentration of Brønsted sites over solid acid catalyst [5] ~~and in a following experiments we confirmed that admission of humid air into the IR cell after outgassing the catalyst at 200°C (i.e. after depleting the amount of OH groups) restores Brønsted acidic sites characterized by the CN stretching band at 2260 cm⁻¹ ca.~~

The adsorption of xylose onto NbP catalyst from an aqueous solution (20% xylose wt) has also been attempted. After impregnation of the catalyst powder with the solution, the disk has been heated at 150°C, obtaining a spectrum which is very similar to the one obtained in the experiment with solid xylose/NbP mixture ~~and the corresponding spectra are reported in~~ (Supporting Information, figure [S5S7](#)). Therefore our reaction conditions at different hydroxylation degrees of the catalyst surface can be representative of the catalytic activity.

Figure 11.

From these data we can suggest that over NbP catalyst exposed Lewis sites, for instance Nb ions, are likely the first coordination sites, activating the reactants (xylose or oligomers) through the coordination of electron lone pairs of oxygen atoms. The broadening and shifting of the CC/CO stretching bands observed in the in situ IR experiments can be an indication of such an interaction. After this initial step, the activated reactants molecules can undergo the protonation of oxygen atoms from the acidic P-OH, mainly, resulting in carbocations formation, in agreement with the mechanism proposed by Bassan et al. for the esterification of fatty acids [18]. Likely, water in the reaction environment favors the desorption of furfural, that can be detected either as adsorbed species (see the carbonyl band in figure 9) either in vapor phase in the IR cell at the reaction temperature (figure 10). Beside this main reaction pathways, acidic sites should catalyze also polymerization reactions, whose heavy products are characterized mainly by a complex envelop of bands in the 1800-1700 cm^{-1} region, typical of $>\text{C}=\text{O}$ and $-\text{OC}=\text{O}$ stretching modes. Lewis acidic sites seem to be involved also in this step, favoring the formation of heavy byproducts detrimental to selectivity to furfural.

CONCLUSIONS

The results discussed above allow us to propose the following conclusions.

- At the fresh Niobium Phosphate catalyst surface, AN and PN adsorption evidences P-OH and Nb-OH groups acting as Bronsted acidic sites, whereas Nb^{5+} ions behave as Lewis exposed sites, showing medium strength acidity. Both Bronsted sites and Lewis acidic sites detected over the hydroxylated surface can act synergistically explaining the reported good catalytic results in xylose and corn stover hydrolysates conversion.
- Degradation products characterized by strong carbonyl stretching bands are detected over the spent catalysts after xylose conversion and these adsorbed species can be oxidized to CO_2 by thermal treatment in air, leading to an almost clean surface and also recovering surface hydroxyl groups. On the other side, tests carried out in the presence of real corn stover hydrolysis lead to the deposition of different kind of organic species, characterized by an increased amount of aromatic rings, likely phenolic compounds.
- The careful characterization of the spent catalysts surface, after different reactivity tests, shows that the strongest acidic P-OH groups are detectable at the catalyst surface without any kind of regeneration procedure. Correspondingly, nitriles adsorption shows that after reaction, both Lewis sites and, mainly, Bronsted sites are still exposed at the spent catalyst surface, although slightly weaker and heterogeneous, therefore explaining the remarkably high reusability of this material. This aspect is fundamental for the sustainability of the novel approach which proposes the conversion of the hemicelluloses fraction of raw biomass in the absence of mineral acids, following a two stage cascade process in water in presence of sole niobium phosphate (NbP) as catalyst.

-Experiments of xylose conversion carried out in the IR cell suggest that exposed Lewis sites are likely coordination sites for xylose model molecule, which can successively undergo isomerization to xylulose, a likely intermediate to furfural production, but also polymerization to heavy reaction byproducts.

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FIGURE CAPTIONS

Figure 1. FT IR spectra of fresh NbP catalyst after outgassing at increasing temperatures. Spectra from top to bottom outgassed at: 200°C; 255°C; 400°C.

Figure 2. FT-IR subtraction spectra of fresh NbP after outgassing at 255°C for 1 hour and subsequent contact with AN vapors. Spectra from top to bottom: in presence of AN vapor; evacuated (ev.) at room temperature (r.t.); ev. for 30 min. r.t.; ev. at 100°C; ev. at 200°C. Inset: high frequency region subtracted spectrum of the fresh NbP after AN adsorption and outgassing at r.t. for 30 min.

Figure 3. FT-IR subtraction spectra of PN adsorbed on Fresh NbP. Spectra from top to bottom: in presence of PN vapor; ev. r.t.; ev. r.t. for 30min; ev. 100°C; ev. 200°C; ev. 300°C. Inset: subtraction of the high frequency region after PN adsorption and evacuation at r.t. for 30 min. and 100°C, from top to bottom, respectively.

Figure 4. FT IR spectra of fresh and spent catalysts after mild activation in vacuum (fresh NbP was activated at 255°C while all the spent catalysts were activated at 100°C). (A) Straight lines spectra from top to bottom: Fresh NbP activated at 255°C; Spent-1; Spent-2, Spent-CS; Spent-3. all the spent samples were activated at 100°C. Broken line: Spent-1 calcined 400°C (multiplied by a factor of 10). OH stretching region; (B) Straight lines spectra from bottom to top: Fresh NbP; Spent-1 calcined 400°C; Spent-1; Spent-2; Spent-3; Spent-CS. Broken line spectrum: subtraction spectrum [Spent-CS] – [Spent-1]. Low frequency region.

Figure 5. (A) FT IR spectra of spent-1 catalyst from top to bottom: activated at 100°C for 1hr; in presence of AN vapor; ev. r.t.; ev. 30 min. r.t.; ev. 100°C; ev. 200°C; ev. 300°C; ev. 400°C. (B) Subtraction spectra from top to bottom: in presence of AN vapor; ev. r.t.; ev. 30' r.t.; ev. 100°C, enlargement of the CN stretching region.

Figure 6. FT-IR subtraction spectra of fresh NbP and spent-1 catalysts with different treatments after contact with AN and outgassing at r.t. for 30 min. These spectra were normalized to wafers of 15 mg to allow easier comparison and are ordered from top to bottom as follows: Fresh NbP, spent-1, Spent-1 calcined 400°C 1hr.

Figure 7. FT-IR spectra of different spent NbP samples after contact with AN and outgassing at different conditions: A) outgassing at r.t. for 30 min. B) outgassing at 100°C for 10 min. These spectra were normalized to wafers of 15 mg to allow easier comparison and are ordered from top to bottom as follows: Fresh NbP, spent-1, spent-2, spent-3 and spent-CS.

Figure 8. FT-IR subtraction spectra of different NbP samples after contact with PN and outgassing at: A) r.t. for 30 min. B) 100°C. These spectra were normalized to wafers of 15 mg to allow easier comparison and are ordered from top to bottom as follows: fresh NbP; spent-CS; spent-3.

Figure 9. FT IR subtraction spectra of the condensed phase species arising from contact of NbP catalyst with xylose and water vapor. The spectrum of NbP catalyst has been subtracted. Inset: subtraction spectrum [NbP+ xylose at 150°C] – [NbP spectrum]. Broken line: solid xylose spectrum.

Figure 10. FT IR spectrum of the gas phase species arising from xylose conversion over NbP catalyst at 140°C (in the presence of water vapor). Inset: detail of the low frequency region.

Figure 11. FT IR spectrum of surface species arising from PN adsorption at room temperature after experiment of xylose conversion (fig. 9 and 10)

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Figure 1

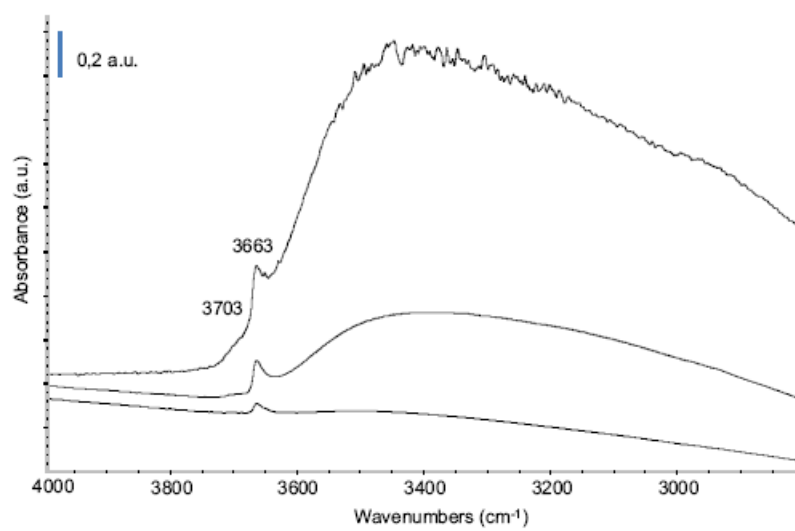


Figure 2

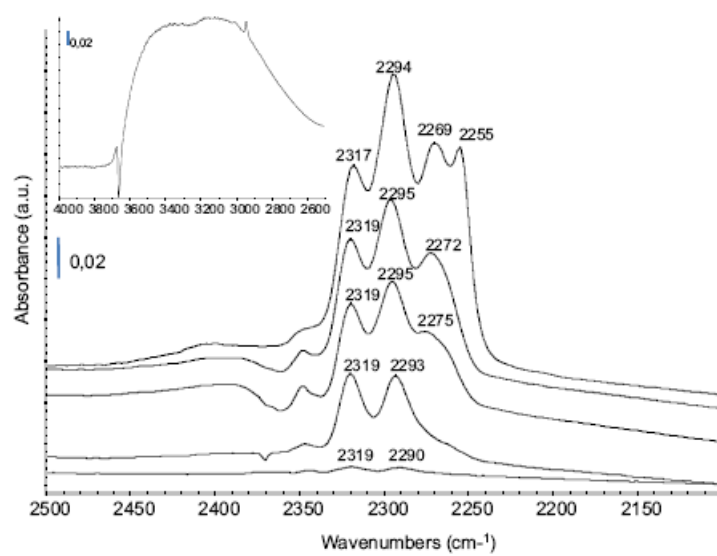


Figure 3

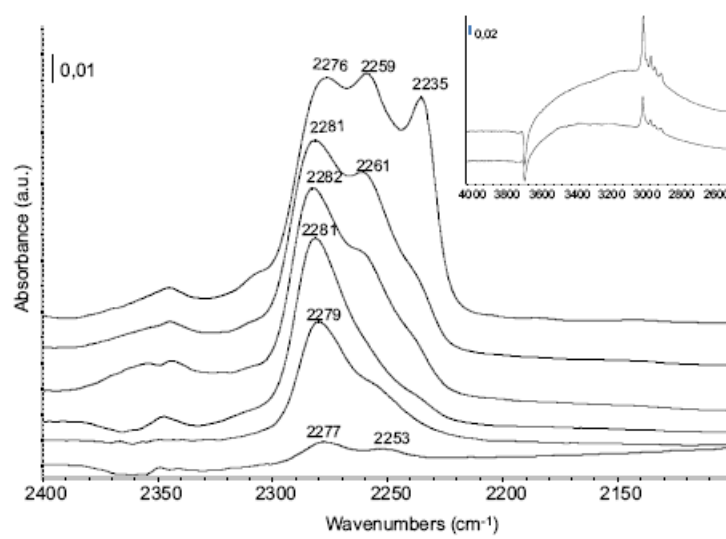


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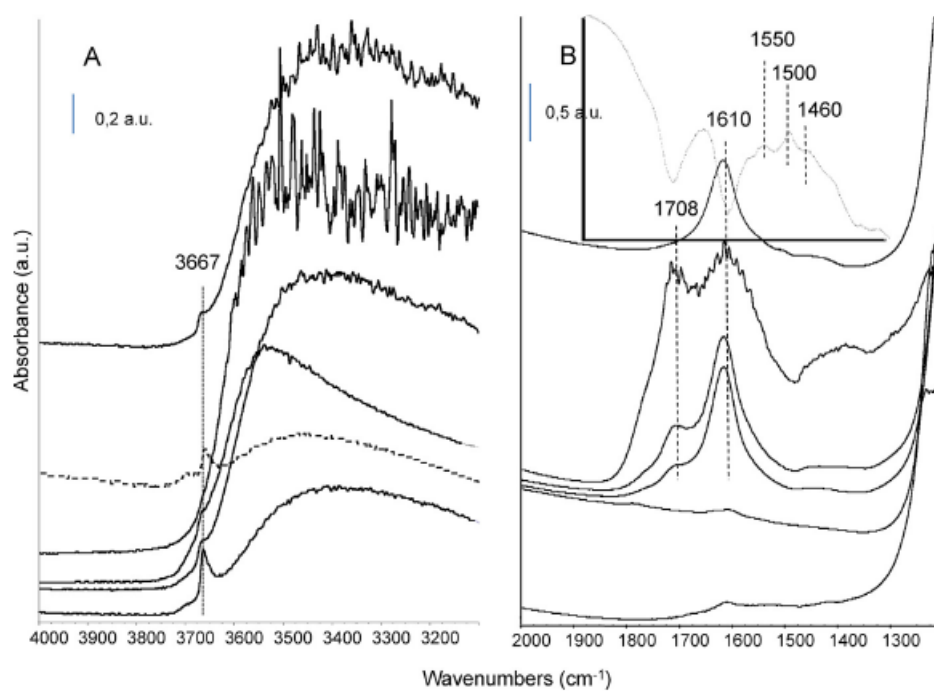


Figure 5

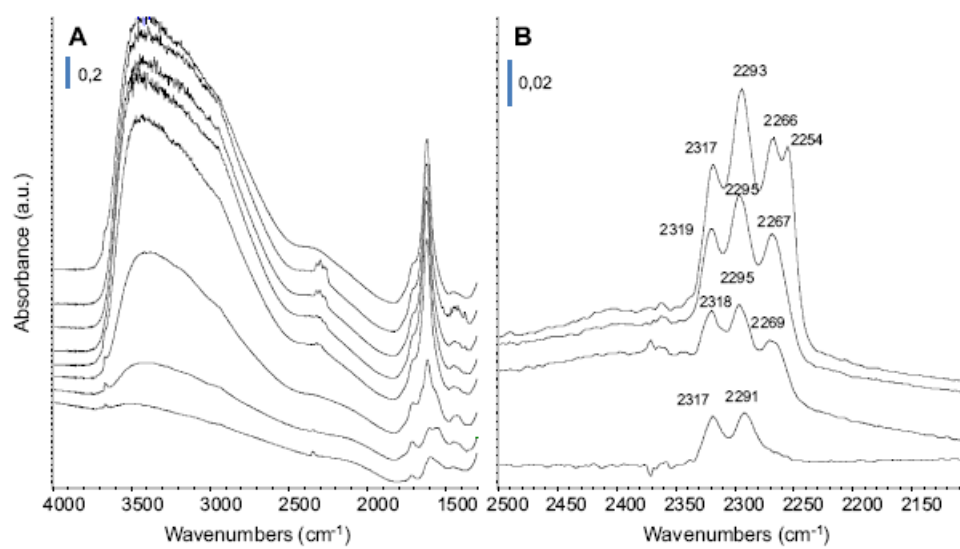


Figure 6

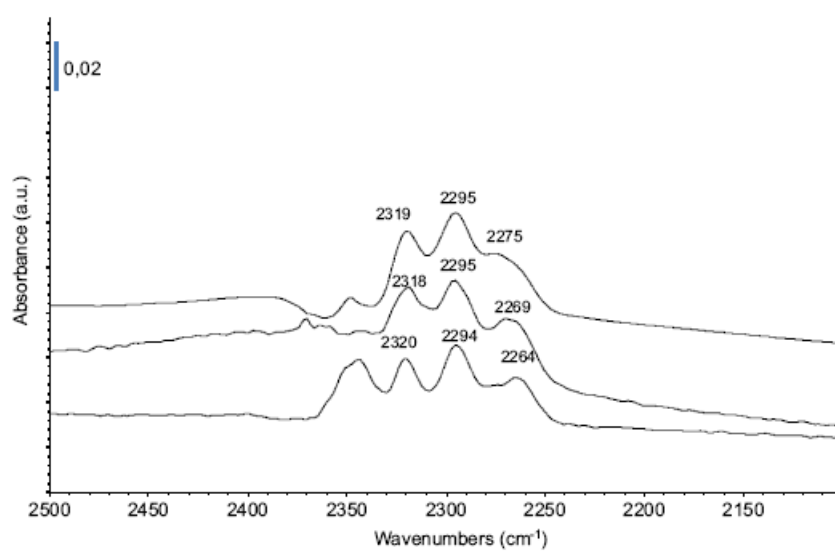


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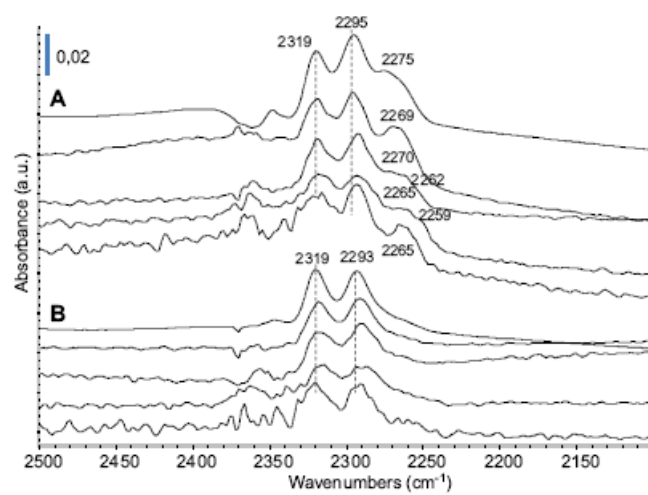


Figure 8

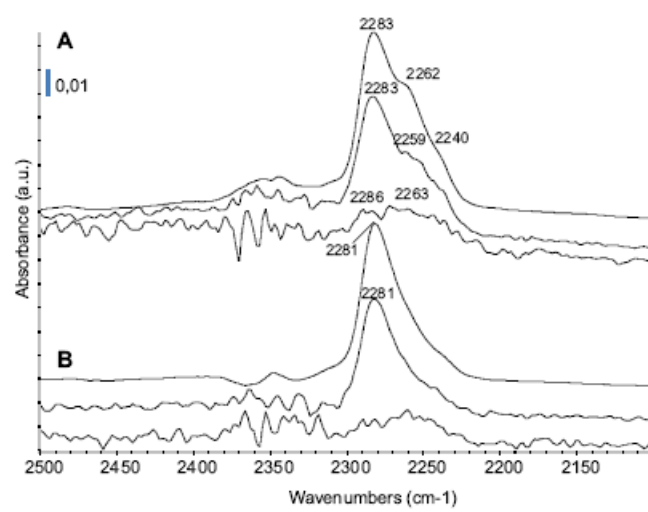


Figure 9

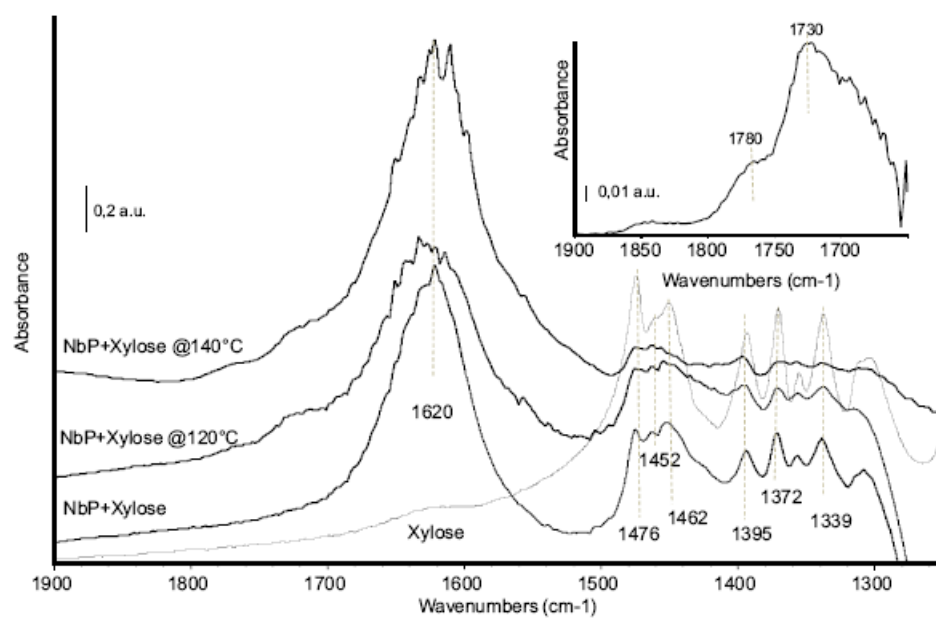


Figure 10

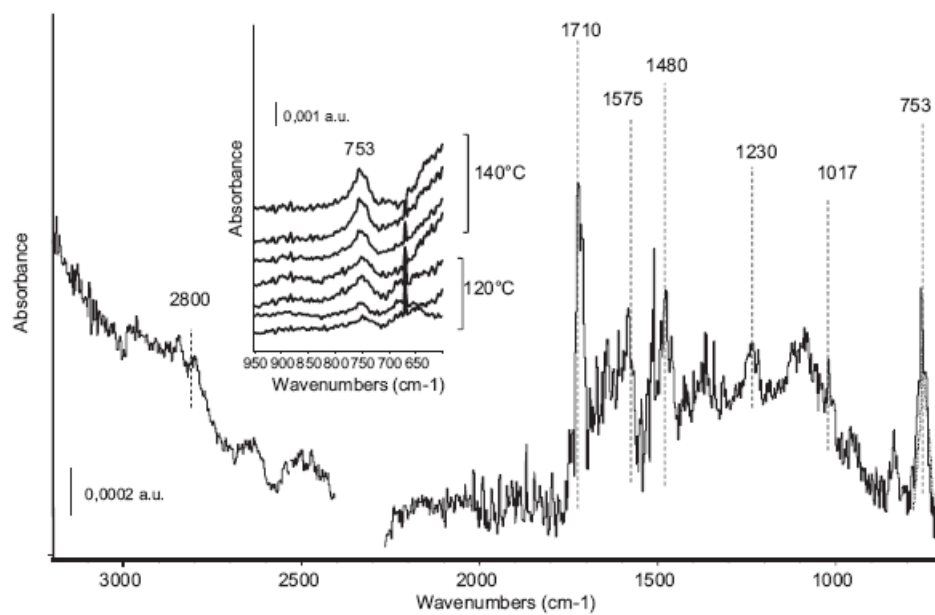


Figure 11

