Acid sites characterization of niobium phosphate catalysts and their activity in fructose dehydration to 5-hydroxymethyl-2-furaldehyde

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Abstract

The nature of different acid sites on the surface of various niobium-based catalysts has been spectroscopically investigated by means of FT-IR and UV–VIS techniques. Surface acidity has been further characterized by acetonitrile adsorption and subsequent FT-IR analysis. The catalytic activity of the different examined samples has been preliminarily tested in the fructose dehydration to 5-hydroxymethyl-2-furaldehyde, a reaction of relevant industrial interest. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Niobium phosphate; Phosphoric acid-treated niobium oxide; Heterogeneous catalysts; Acid sites characterization; Fructose dehydration; 5-Hydroxymethyl-2-furaldehyde

1. Introduction

Solid acids find relevant application in different fields of heterogeneous gas–solid and liquid–solid catalysis [1,2]. Protonic zeolites, silicaluminas, sulphuric acid treated oxides, tungsten oxide-containing materials, sulphonic acid resins represent examples of solid materials displaying strong to very strong Brønsted acidity. Weaker Brønsted acid solid catalysts are frequently based on phosphoric acid, such as the so-called solid phosphoric acid [3] and different metal phosphates [4]. Lewis acid solids are generally based on metal oxides characterized by cations with a high charge to diameter ratio [5], such as alumina or on metal halides. Hydrated niobium oxides (niobic acids) have also been investigated in the recent literature [6] and found to be interesting materials [7] displaying both Lewis and Brønsted acidity [1,8]. Proton NMR data indicate that Brønsted acidity of niobic acid is very high, almost comparable with that of protonic zeolites [9]. The products of the combination of niobium oxide and phosphoric acid are niobium phosphate [10] and phosphoric acid-

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treated niobic acid [11], both reported to be materials potentially useful in acid catalysis.

On the other hand, the request of renewable resources, such as biomass, as substitutes for mineral raw materials and their conversion in fine chemicals have received in the recent years an increasing interest. In this context, the selective acid dehydration of hexoses and polysaccharides to 5-hydroxymethyl-2-furaldehyde (HMF) has been particularly investigated [12–15]. This reaction is catalyzed by strong mineral acids [16], ammonium salts [17], zirconium phosphate [18,19], strong cation exchange resins [20], and more recently by H-form zeolites [21] and supported heteropolyacids [22]. All these catalysts promote the dehydration step to HMF but also, even if to a different extent, its subsequent rehydration to levulinic and formic acids, polymerization reactions also occurring to give soluble polymers and insoluble humins (Scheme 1).

All of the more recent processes studied for a possible industrial application were based on heterogeneous acid catalysts; however, their activity and selectivity were found to be still unsatisfactory. It is quite evident that both Brønsted and Lewis acid centers can promote carbohydrate dehydration, although no investigation of the nature of the acid sites of the applied catalysts has been reported up to now. Therefore, the characterization of niobium phosphate and phosphoric acid-treated niobic acid catalysts, in terms of Lewis and Brønsted surface sites, has been performed in order to optimize catalyst preparation conditions and reaction parameters; a preliminary investigation of their activity and selectivity in fructose dehydration to HMF is also reported.

2. Experimental

2.1. Materials

Niobic acid ($Nb_2O_5 \cdot nH_2O$, containing ca. 20 wt.% H_2O) and niobium phosphate ADF25 (NP1 sample) were supplied by CBMM (Companhia Brasileira de Metalurgia e Mineração).

P/N1 sample was prepared by stirring 6.35 g of niobic acid with 120 ml of 1 M H_3PO_4 aq. solution for 48 h at room temperature, followed by filtration and several water washings. Finally, the washed solid was transferred into a crucible and calcined by ignition with slow heating.

P/N2 sample was prepared starting from the same amounts of reagents as used for P/N1 but its flocculation was promoted by adding 30 ml of 5% NaCl aq. solution. The filtrated solid was washed with water until no chlorides were detected in the washing by the $AgNO_3$ test. Calcination was subsequently performed as described for P/N1.

NP2 sample was prepared by heating NP1 at 528 K for 6 h under high vacuum.

Niobium and phosphorus content of the catalytic samples was determined by gravimetric and titrimetric standard procedures, respectively [23].

The surface areas of catalysts were determined by the BET method.

Some relevant characteristics of the above samples are summarized in Table 1.
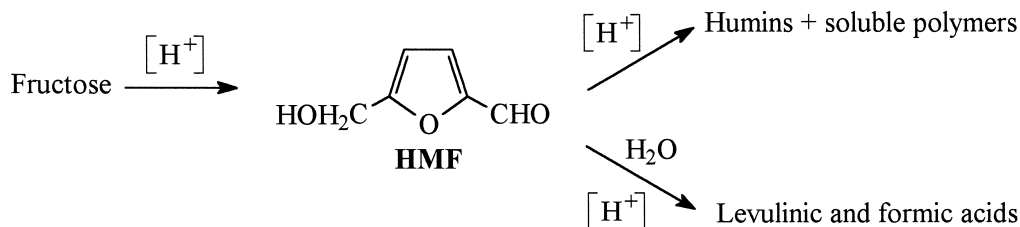
Scheme 1.

Table 1
Niobium-based catalytic systems applied for fructose dehydration

Sample	Type	P/Nb (g at./g at.)	Surface area (m^2/g)	Remarks
Niobic acid	$Nb_2O_5 \cdot nH_2O$	0.0	–	H_2O 20 wt.%
P/N1	H_3PO_4-treated niobic acid	0.61	170	–
P/N2	H_3PO_4-treated niobic acid	1.92	170	NaCl as flocculation agent
NP1	Niobium phosphate	0.45	180	–
NP2	Niobium phosphate	0.45	150	Degassed at 528 K for 6 h

D-Fructose (Fluka) and acetonitrile (Carlo Erba) were used as received.

2.2. Catalytic experiments and analyses

Catalytic experiments were carried out in batch, under nitrogen, on aq. 6 wt.% fructose solutions in a stirred glass vessel equipped with a condenser and heated with a thermostated oil bath at 110°C. The proper amount of catalyst was added to the substrate solution and the reaction was allowed to proceed for a prefixed duration. Intermediate samplings of the reaction mixture were accomplished and analyzed. HMF and 2-furaldehyde (2FA) were directly analyzed, after calibration with pure standards, by GC on a Perkin-Elmer Sigma 3B gas-chromatograph, equipped with a Tenax packed column (2 m), a flame ionization detector and a Carlo Erba DP 700 integrator. Residual fructose was determined by GC analysis, according to the literature procedure [16]. Polymeric by-products were determined by difference.

2.3. Physicochemical measurements

IR spectra were recorded on a Nicolet Magna 750 Fourier transform instrument, using pressed disks of pure catalysts powders, eventually activated by outgassing at different temperatures into the IR cell.

UV spectra were recorded with a Jasco V-570 spectrometer using a diffuse reflectance attachment.

XRD were recorded with a Siemens D500 (CuKα radiation).

3. Results and discussion

3.1. Structural characterization

The XRD analysis of all samples show that they are fully amorphous.

The skeletal IR spectra are reported in Fig. 1. Niobic acid presents a main strong band centered at 622 cm^{-1}, with an evident shoulder at ca. 920 cm^{-1} and FIR bands at 410 and 250 cm^{-1}. These spectra are consistent with the skeletal IR spectra previously reported for niobic acid [24]. The comparison of the skeletal spectra of our samples with those of two polymorphs of Nb_2O_5 reported in the literature [25,26] does not reveal the presence of crystalline phases, in agreement with XRD analysis. The IR spectrum can be discussed in comparison with the vibrational spectra of niobic acid [27] and of amorphous [27] and crystalline Nb_2O_5 [27,28] as well as with the vibrational spectra of several metal niobates [29,30]. The broad IR band near 920 cm^{-1}, corresponding to a very broad Raman feature in the 1000–800 cm^{-1} range, is likely associated to the stretching mode of quite short ''terminal'' Nb=O bonds, while the stronger band near 620 cm^{-1} can be assigned to the stretchings of longer bridging Nb–O–Nb bonds. This agrees with a structure predominantly composed of condensed distorted NbO$_6$ octahedra.
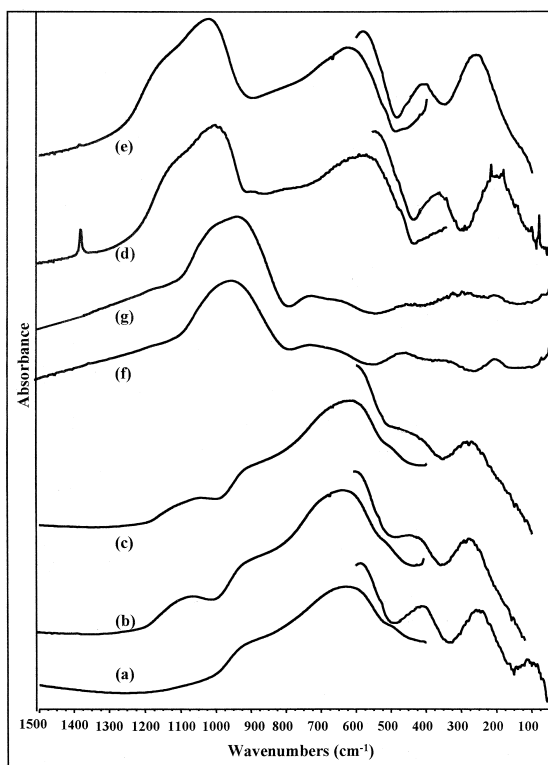
Fig. 1. FT-IR skeletal spectra (KBr pressed disks): (a) niobic acid, (b) P/N1, (c) P/N2, (d) NP1, (e) NP2, (f) subtraction spectra [P/N1-niobic acid], (g) subtraction spectra [P/N2-niobic acid].

Impregnation of niobic acid with phosphoric acid results in the formation of an additional broad band apparently located at 1040 cm^{-1}, certainly due to the O=P=O asymmetric stretching modes of phosphate or polyphosphate species. The subtraction spectra actually show this band centered at 1080 cm^{-1} for the sample P/N1, and at 1070 cm^{-1} with a shoulder at 1100 cm^{-1} for the sample P/N2.

The spectra of the niobium phosphate catalysts show a strong band due to the asymmetric stretching modes of phosphate ions with a maximum at 1024 cm^{-1} and an evident shoulder at 1130 cm^{-1}. An additional strong band is found at 620 cm^{-1} which, in agreement with the spectrum of niobic acid, could be mainly due to Nb–O stretching modes. A component near 940 cm^{-1} could be assigned to the stretching mode of Nb=O niobyl species. These IR spectra,

simpler than those of crystalline NbOPO$_4$ [10,31], suggest that the basic structural units of our amorphous sample could be again NbO$_6$ distorted octahedra and tetrahedral orthophosphate species, similar to those present in the bulk of crystalline NbPO$_5$ [32].

UV–VIS spectra (Fig. 2) of NP1 and NP2 are similar each other and quite different from those of P/N1 and P/N2 which, in turn, are identical each other and similar to the spectrum of niobic acid. In all cases, an absorption edge is observed, certainly due to the charge transfer transitions $O^{2-} \rightarrow Nb^{5+}$ which can be associated to the energy gap between the O 2p valence band and the Nb 4d conduction band.

In the case of niobic acid (Fig. 2, trace a) the threshold energy is found at 25 600 cm^{-1} with a flexure point at ca. 31 500 cm^{-1} and a maximum of absorption at 34 400 cm^{-1}. The threshold limit seems to be shifted a little bit up for P/N samples (27 300 cm^{-1}, Fig. 2, traces b and c). These spectra are similar to those reported for different Nb$_2$O$_5$ preparations [33–35] and
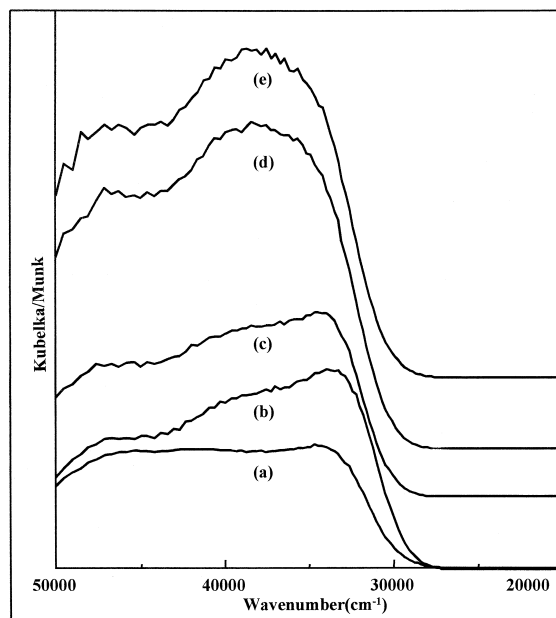

Fig. 2. UV–VIS spectra: (a) niobic acid, (b) P/N1, (c) P/N2, (d) NP1 and (e) NP2. Spectral intensities are expressed by Kubelka/Munk function.

for niobates with perovskite-related structures [36], showing that Nb is totally in the pentavalent state in a distorted octahedral coordination. The position of the edge suggests that these octahedra are predominantly corner-sharing [36].

In the case of NP1 and NP2 samples (Fig. 2, traces d and e) the thresholds are at the same energy, but the absorption edges are broader and the flexure points as well as the absorption maxima are shifted to higher energies (the maximum for both samples is located at 38,000 cm^{-1}).

The spectra differ also for the pattern in the $50\,000–40\,000$ cm^{-1} region where an erosion of the absorption, resulting by impregnation of phosphoric acid over niobic acid (samples P/N1 and P/N2), is observed. This can be ascribed to the presence of absorptions of Nb^{5+} ions in the state of low coordination near the surface of the niobic acid support, whose coordination would be completed by the $H_2PO_4^-$ or HPO_4^{2-} in the P/N samples.

3.2. Surface hydroxy-groups

FT-IR spectra of the samples, after activation at 473 K and 673 K, are reported in Fig. 3. The spectrum of niobic acid, after outgassing at 473 K, shows a quite sharp peak at 3708 cm^{-1}, perhaps with a shoulder near 3735 cm^{-1}, and a broad absorption centered near 3300 cm^{-1}. Outgassing at 673 K causes not only a significant decrease of the broad absorption but also a relevant reduction of the sharper components, which however still retain the same frequency. The analysis of the lower frequency region shows that, after outgassing at 473 K, a weak band is still present at 1610 cm^{-1}, due to the scissoring mode of adsorbed molecular water. The behaviour of this band seems to be parallel to that of the broad absorption centered near 3300 cm^{-1}, so that it seems reasonable to assign both to adsorbed molecular water. On the contrary, the weak bands at 3735 (shoulder) and 3708 cm^{-1} could be reasonably assigned to the O–H stretching modes of free Nb–OH groups.
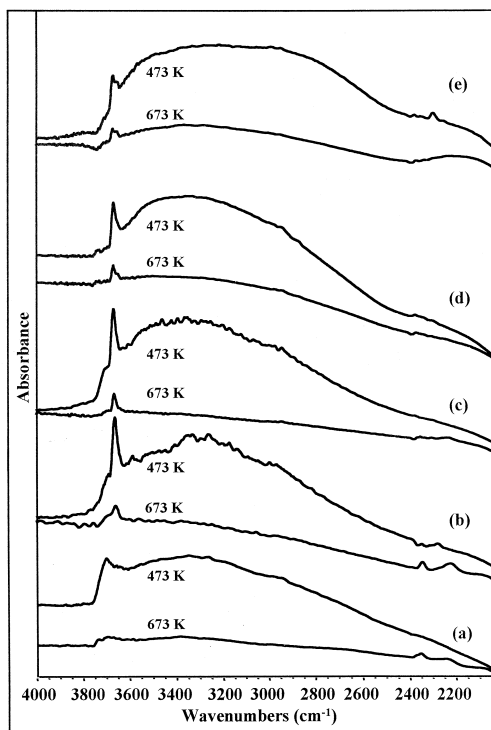

Fig. 3. FT-IR spectra (O–H stretching region) of the samples (pure powder pressed disks) after activation by outgassing for 1 h at 473 K and 673 K: (a) niobic acid, (b) P/N1, (c) P/N2, (d) NP1 and (e) NP2.

Impregnation of phosphoric acid strongly modifies the spectrum. Indeed, after outgassing at 473 K, both P/N samples show a very strong sharp band at 3666–3662 cm^{-1} and the appearance of an even more prominent broad absorption centered again near 3300 cm^{-1}. Actually, a shoulder near 3700 cm^{-1} seems to be still present. Further outgassing at 673 K causes the almost complete disappearance of the broad absorption, again assigned to water molecules (a parallel behaviour is again observed for the band near 1605 cm^{-1}, due to the scissoring mode). The band at about 3665 cm^{-1} is stronger for the P/N 2 sample and it corresponds to the sharp band always present on the surface of metal phosphates, pyrophosphates [37,38] as well as of silica, alumina, titania and zirconia where phosphoric acid is supported [39,40]. This band is assigned to the OH stretching mode of surface hydrogenphosphate species. The detec-

tion also of the band near 3700 cm^{-1} suggests that Nb–OH groups still exist on the surface of the P/N samples.

FT-IR spectra of the NP samples also show the sharp band of the POH groups as well as a weak band at 3700 cm^{-1} assigned to Nb–OH groups. Additionally, they also display a broad absorption with a minimum near 2500 cm^{-1} and two maxima in the 3200–3300 cm^{-1} range as well as at about 2100 cm^{-1}.

This pattern is typical of species involving quasi symmetrical H-bonds according to what reported for phosphoric acid supported on silica. It is likely due to water molecules strongly interacting with hydrogenphosphate species.

All the above spectral data indicate that both P/N and NP samples are characterized by the presence of hydrogenphosphate species and NbOH groups on their surface, retaining water molecules even after degassing. However, a more important interaction of water molecules with surface hydrogenphosphate species seems to occur in the case of NP samples.

3.3. Characterization of the surface acidity by acetonitrile adsorption

Previous studies [1] reported IR spectra of pyridine adsorbed over niobium compounds. However, the use of the above base did not result very useful for distinguish sites with medium-strong acidity. In order to have a more detailed characterization of the above acid sites we have therefore used the weaker acetonitrile base as probe molecule. The FTIR spectra of the different samples, after degassing and adsorption of acetonitrile, are reported in Figs. 4–6, as far as the C$\equiv$N stretching region is concerned. In this region liquid acetonitrile shows a strong doublet at 2294 and 2254 cm^{-1}, the intensity of the latter band being definitely stronger. This doublet is due to the Fermi resonance between the C$\equiv$N stretching and a δ_{CH3} + ν_{C-C} combination [41–44].

When an interaction between C$\equiv$N groups of acetonitrile and electron-withdrawing centers
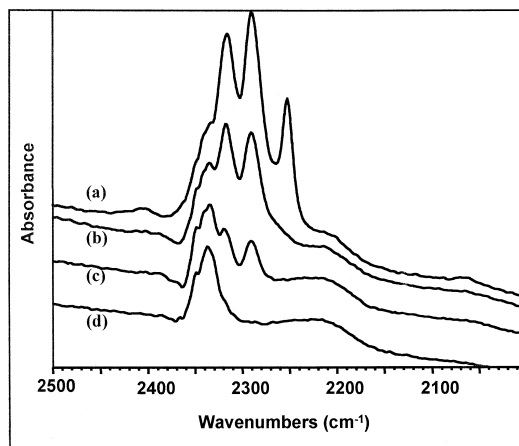

Fig. 4. FT-IR spectra of niobic acid (pure powder pressed disks) after outgassing at 673 K and following contact with acetonitrile vapors (5 Torr) (a) and successive outgassing at 298 K (b), 373 K (c), 573 K (d) for 10 min. The gas-phase spectra have been subtracted.

occurs, a typical shift up of the doublet components with respect to the liquid molecule is observed, a contemporary change of their relative intensity in favour of the higher frequency band being evidenced [43,44]. For this reason, the use of undeuterated acetonitrile was preferred.

Indeed, three bands are actually found in all the investigated samples. These triplets actually result from the superimposition of two doublets. The doublet related to the more weakly adsorbed species in all cases is characterized by a band which represents the triplet component always located at the lowest frequency region (in the 2252–2260 cm^{-1} range), the other one contributing to the triplet intermediate band at ca. 2290 cm^{-1}. In fact, by degassing the sample already at room temperature, the triplet, at least in the cases of niobic acid and P/N samples (Figs. 4 and 5, respectively) substantially evolves in a doublet, due to the disappearing of the two contributions of the more weakly adsorbed species. Accordingly, in these cases the lower frequency band is observed (Figs. 4 and 5, traces a) near 2253 cm^{-1}, almost the same frequency as that of the liquid acetonitrile. By contrast, on niobium phosphates (NP1 and NP2
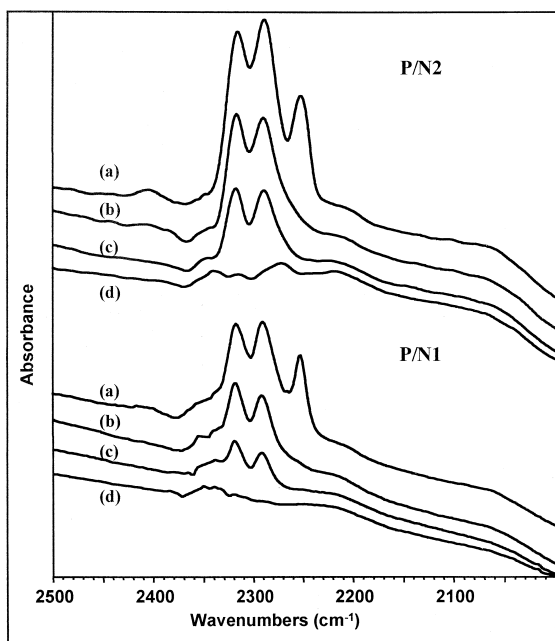
Fig. 5. FT-IR spectra of P/N1 and P/N2 (pure powder pressed disks) after outgassing at 673 K and following contact with acetonitrile vapors (5 Torr) (a) and successive outgassing at 298 K (b), 373 K (c), 573 K (d) for 10 min. The gas-phase spectra have been subtracted.

samples) the lowest frequency component partially resists on degassing at room temperature and is observed at 2256–2260 cm^{-1}, slightly but definitely shifted upwards (Fig. 6). These data indicate that the hydrogen bonding of acetonitrile with the surface hydroxy groups of the NP samples is significantly stronger than that with P/N samples and niobic acid.

In all cases, by outgassing the samples at a temperature equal to 373 K or even higher, the spectra evolve into a doublet arising from a resisting species. The components of the doublet, having now nearly the same intensity, are located at 2317 ± 2 and 2292 ± 2 cm^{-1} (Figs. 4–6). These features are typical of acetonitrile molecules adsorbed on Lewis acid sites with medium strength [6]. The position of the bands is nearly the same for niobic acid and P/N samples, while is shifted of no more than 3 cm^{-1} upwards for the NP samples. This indicates that sites of similar strength are present in

all cases, although those on the surface of NP samples seem to be slightly more acidic. In any case, the Lewis strength of these sites is still not very high in comparison not only with very acidic surfaces such as aluminas [45] but also with vanadium pentoxide [46] and vanadyl pyrophosphate [37].

With the aim to gain a deeper insight on the interaction of acetonitrile with the surface OH groups of the different samples, the strength of the resulting hydrogen bonds has been investigated. In Fig. 7, the subtraction spectra recorded upon interaction of the catalysts with acetonitrile are reported in the overall spectral region. In the region near 3700 cm^{-1}, the absorptions due to the OH stretchings of the free surface OH groups of the catalysts, which vanish upon adsorption of acetonitrile, appear as negative bands. At lower frequency, the OH stretching absorptions of the hydroxy groups interacting
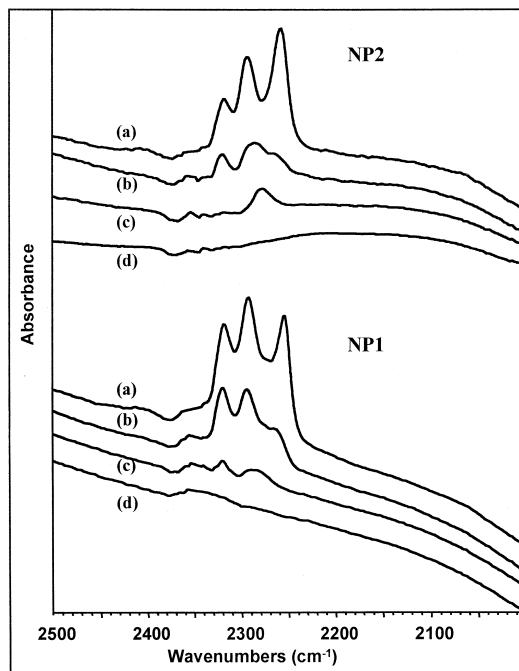

Fig. 6. FT-IR spectra of NP1 and NP2 (pure powder pressed disks) after outgassing at 673 K and following contact with acetonitrile vapors (5 Torr) (a) and successive outgassing at 298 K (b), 373 K (c), 573 K (d) for 10 min. The gas-phase spectra have been subtracted.
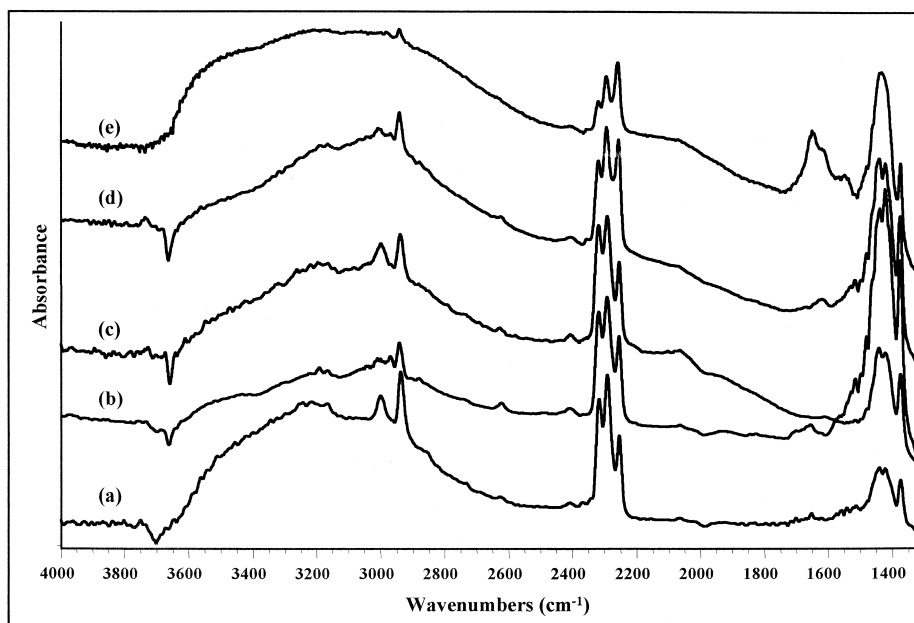
Fig. 7. Subtraction spectra recorded upon contact of the catalysts activated by outgassing at 673 K for 1 h with acetonitrile vapors (5 Torr): (a) niobic acid, (b) P/N1, (c) P/N2, (d) NP1 and (e) NP2. The gas-phase spectra have been subtracted.

with acetonitrile via H-bonding are observed as a broad positive band with a maximum frequency depending on the nature of the catalyst sample. In fact, the extent of the shift undergone upon adsorption is typically used to measure the strength of the H-bond [6]. The positive band is centered near 3250 cm^{-1} in the case of niobic acid (Fig. 7a), and near 3000 cm^{-1} for P/N samples (Fig. 7, traces b and c). NP samples show the same band at a slightly lower frequency than P/N samples (Fig. 7, traces d and e), thus providing evidence for the stronger Brønsted acidity of POH with respect NbOH groups, as well as for a slightly stronger acidity of NP with respect to P/N samples.

3.4. Catalytic activity

The catalytic activity of niobium phosphate in the dehydration of fructose and polysaccharides to HMF was firstly evidenced by us [47]. Due to the increased interest towards this type of reaction, particularly when carried out with

heterogeneous catalysts, further experiments were accomplished by using the above spectroscopically characterized catalytic samples. Water was used in all the cases as reaction medium because it is an excellent and cheap solvent for fructose. A substrate/catalyst weight ratio, analogous to that previously employed in the same reaction by using other heterogeneous catalysts such as zeolites [15,21], zirconium phosphate [18,19] and cation exchange resins [20], was adopted. Some selected results are reported in Table 2.

When P/N1 and P/N2 catalysts were used, a high selectivity to HMF was observed (entries 1 and 2, respectively) in the first half an hour of reaction, i.e., for fructose conversion near 30%. Moreover, no detectable amounts of levulinic and formic acids were observed in the reaction aqueous medium, the resulting catalysts unable to rehydrate HMF, contrarily to what was previously found in the presence of homogeneous proton acids [13] or of heterogeneous catalysts such as acid ion exchange resins [48] or zeolites

Table 2
Fructose dehydration to HMF in the presence of different heterogeneous niobium-based catalysts[a]

Entry	Catalyst	R^b (wt./wt.)	Time (h)	Conversion (%)	Selectivity (%)[c]		T.N.[d]
					HMF	2FA[e]	
1	P/N1	1.7	0.5	31.2	93.3	Traces	5.1
			1.0	33.3	30.3	Traces	0.9
			2.0	61.5	12.4	Traces	0.3
2	P/N2	1.6	0.5	28.5	97.8	2.2	5.1
			1.0	55.0	39.6	2.5	1.9
			2.0	61.4	35.1	2.7	1.0
3	NP1	1.4	1.0	25.1	91.8	0.5	1.8
			2.0	39.0	71.2	0.9	1.2
			3.0	48.0	67.4	1.4	0.7
4	NP2	1.4	0.5	28.8	100.0	0.0	4.6
			1.0	29.3	85.2	0.9	1.9
			2.0	33.3	71.9	Traces	0.9

[a]Reaction conditions; substrate: 6 wt.% fructose aq. solution; T: 100°C; amount of catalyst: 0.7 g.
[b]Substrate to catalyst weight ratio.
[c]Expressed for each product as: (mol of product/mol of reacted fructose) $\times$ 100; when HMF + 2FA < 100 polymeric by-products are also present.
[d]Turnover number expressed as: (mmol of HMF/g of catalyst $\times$ h).
[e]2-Furaldehyde.

[15]. On the other hand, a small amount (< 3%) of 2-furaldehyde (2FA) was found, according to what has been very recently reported [49]. It is worth mentioning that only few heterogeneous catalysts were able to achieve similar performances, but this behaviour was obtained exclusively by using a mixed water/organic medium where a large excess of organic component was necessary [15]. The turnover number (T.N.) values (Table 2) obtained (about 5) are significantly higher than those previously reported for other heterogeneous catalysts tested in the same reaction [50]. However, for longer reaction times (1–2 h), a drop of selectivity to HMF was observed, particularly in the case of P/N1 catalyst. This indicates that, under the adopted reaction conditions, HMF further evolves to polymeric by-products. In the presence of NP1 and NP2 catalysts, characterized by active sites with a little higher Brønsted and Lewis acidity as compared with P/N samples, similar activity and selectivity to HMF were ascertained (entries 3 and 4, Table 2) at comparable fructose conversion (about 30%). However, at longer reaction times, these catalysts allow to maintain a higher selectivity to HMF (> 70% after 2 h)

although it is accompanied by a progressive catalysts deactivation, probably due to the interaction of reaction products with the stronger acid sites leading to a surface loading. From a comparison that takes into account all the above catalytic features, NP samples seem to be more promising catalysts than P/N ones. In order to overcome the drawback of sites deactivation in NP samples, experiments providing a subsequent organic solvent extraction of the reaction products are in progress. Indeed, this approach would permit reduction of the residence time of HMF in the reactor and hence on the catalyst, thus decreasing site loading and at the same time improving their productivity.

4. Conclusions

On the basis of the results obtained, the following conclusions can be drawn.
– Skeletal IR spectra show that the ''surface'' phosphate species of P/N samples differ for coordination from the bulk phosphate species of amorphous niobium phosphate NP.

– UV spectra also show that coordination at niobium is octahedral in all cases, but with relevant differences in the coordination sphere. Low coordination Nb species probably exist in niobic acid, which are converted into higher coordination species after impregnation with phosphoric acid.

– Outgassed niobic acid shows OH stretching bands at 3735 and 3708 cm^{-1}, assigned to terminal NbOH groups.

– All phosphate containing samples, both P/N and NP, show, after activation by outgassing, a strong sharp OH stretching band near 3665 cm^{-1}, assigned to terminal POH groups together with weaker features assignable to NbOH groups.

– Acetonitrile adsorption shows that in all samples medium strong protonic centers and medium strong Lewis acid sites exist at the surface.

– The Lewis acidity strength is similar in all the catalysts examined here and it can be assigned to coordinatively unsaturated Nb^{+5} sites.

– The H-bonding with acetonitrile indicates that the POH groups of amorphous niobium phosphates NP are characterized by a slightly stronger Brønsted acidity than those of P/N samples, NbOH sites appearing to be weaker as Brønsted acids than POH groups.

– All the examined catalyst samples afford the dehydration of fructose to HMF in aqueous medium with a significant improvement of performances, in terms of selectivity and productivity, at least in experiments carried out at low conversion, as compared with previously reported heterogeneous catalysts even working in organic solvents or in mixed organic/water medium.

– All the samples show a similar catalytic behaviour, batch experiments being unable to evidence their subtle differences. However, the lower reactivity of HMF towards polymerization processes in the presence of NP catalysts, makes them more promising from applicative point of view. In this respect, further investigations on fructose dehydration to HMF by NP

catalysts in aqueous medium followed by an extraction step with an organic solvent are in progress.

Acknowledgements

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