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Exploitment of niobium oxide effective acidity for xylose dehydration to furfural

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ABSTRACT

Xylose together with other pentose and hexose sugars can be dehydrated to produce interesting platform chemical compounds, like 5-hydroxyfurfural (HMF) and furfural. This study continues our investigation on the niobium oxide based catalysts in connection with the research of adequate solvents systems to minimize catalyst deactivation and increase catalyst stability and durability during the dehydration of sugars. Silica-zirconia supported niobia samples (10 wt.% of Nb) prepared by impregnation or *sol–gel* in comparison with pure niobic acid are here presented for xylose dehydration. The reactions have been studied at different temperatures (130–180 °C) in batch or fixed bed continuous catalytic reactors in various solvents. Green solvents soluble in the aqueous solution of xylose or biphasic systems have been taken into account: water, water–isopropanol mixtures, water-γ-valerolactone, and water-cyclopentylmethyl ether. The surface acidities of the catalysts have been measured in cyclohexane (*intrinsic* acidity) and also in water to determine the *effective* catalyst acidity. The continuous tests and batch-recycling tests showed that the supported Nb-catalysts, even if initially less active, are more stable than niobic acid. The presence of isopropanol in water improves both the activity and stability of the catalysts in comparison with water and the use of cyclopentylmethyl ether gave the most interesting selectivity to furfural preserving the catalyst stability.

1. Introduction

Furfural is an important chemical species produced from pentosan-rich biomass, in particular by xylose dehydration. Currently, conventional processes of furfural production utilize mineral acids as catalysts but the development of more friendly acid solid catalysts with separable and reusable properties is required to prevent the environmental and economic drawbacks associated to homogeneous catalysis such as extreme corrosion, high toxicity, and excessive waste disposal.

In the past years, many solid acid catalysts have been developed and successfully applied in this reaction [1–11]. A problem arrives when water is concerned as reaction solvent; in water, or in general in highly protic and polar solvents, only very few solid acids can maintain the desirable acidity due to the solvent–surface interactions by solvation and coordination abilities of such solvents. The discovery of the water-tolerant properties of several solid acids containing niobium [12] has opened the possibility to use such materials as efficient catalysts in reactions where water is concerned as reactant, product, or solvent. Thus, different acid-catalyzed reactions, such as hydrolysis, dehydration, condensation, and esterification, among others, have been performed using niobium based catalysts [9,13,14].

In particular, the hydrated niobium pentoxide, $Nb_2O_5{\cdot}nH_2O$ (NBO), which is usually called niobic acid, is considered one of the most promising water-tolerant solid acid catalyst [15,16]. The lively acid properties of niobic acid, which can be maintained also in water, have been exploited in several reactions of biomass transformation as dehydration of pentoses and hexoses to obtain platform compounds such as furfural and 5-hydroxymethylfurfural (HMF), respectively [9,17,18].

The catalytic dehydration of pentoses and hexoses in water with niobic acid presents different disadvantages to overcome for practical application; in particular, low selectivity and yield to the main products (furfural and HMF) that are mainly associated to the formation of several side-products, as humins and other insoluble polymeric condensation by-products. These insoluble by-products cause activity declining and surface deactivation, as they deposit

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on the catalyst surface. Neither the routes through which humins are formed nor their molecular structure have yet been unequivocally established. Infrared spectroscopic experiments suggest that humins are formed via aldol addition/condensation involving the 2,5-dioxo-6-hydroxy-hexanal (DHH) species. From DHH, humins can grow as it is highly reactive and undergoes aldol addition/condensation with available aldehydes and ketones [19–21]. Both Lewis (LAS) and Brønsted (BAS) acid sites are involved in the mechanism of humin formation, and it seems that the strong acid site density of niobic acid is responsible for the fast decrease of activity observed [14,22]. In order to decrease the acid site density of the catalyst surfaces and to enhance the catalyst stability, supported or dispersed niobic acid on/in high surface area oxides have been already developed [11,23,24]. Good catalyst stability during long-term activity in the fructose dehydration has been observed on niobia deposited on silica [23]; unfortunately, fructose conversion was low likely due to the chemical inertness of silica. The choice of a more adequate support for niobia could improve catalyst activity in sugar dehydration reactions.

Moreover, the choice of the reaction solvent for the acid-catalyzed conversion of carbohydrate biomass is of high importance because it is desirable that the formed by-products are soluble, to improve the catalyst stability and durability. If water is the most frequently used solvent, due to its excellent substrate solubilization properties and to low cost, other friendly solvents are searched for improving the catalyst stability, in particular. Many different liquid solvents have been investigated as reaction medium instead of pure water, such as ionic liquid solvents [25], organic solvents [26,27] and water/organic solvent biphasic systems [28,29]. Different anhydrous solvents such as toluene [3], DMSO [1], methyl isobutyl ketone (MIBK) [30], or cyclopentyl methyl ether (CPME) [28] have been used as extracting solvent leading to furfural yields generally higher than the use of water. The use of solvents in homogeneous aqueous solution, such as water/1-butanol system, has been also suggested in different carbohydrate dehydration reactions in order to improve the selectivity toward the target product [2,27,31].

Therefore, the present study continues our investigation on hydrated niobium pentoxide and niobia-based catalysts in connection with the most exhaustive research of adequate monophase or biphase systems to minimize catalyst deactivation and increase catalyst stability and durability. Furthermore, silica-zirconia supporting niobia samples prepared by impregnation or sol–gel process, respectively, in comparison with pure NBO, are here presented for xylose dehydration studied at different temperatures (130–180 °C) in batch and fixed bed continuous reactors (to approach pilot plan conditions) using various solvents, to point out catalyst performances and limitations.

2. Experimental

2.1. Materials

D-(+)-Xylose (≥99%), anhydrous cyclopentyl methyl ether (CPME) (≥99.9%), octanoic acid (98%), γ-valerolactone (99%), 2-propanol (≥99.5%), 1-propanol (≥99.5%), niobium(V) ethoxide ($Nb(OCH_2CH_3)_5$, 99.95%, NBE), 2-phenylethylamine (PEA), and hydrochloric acid (37%) were purchased from Sigma–Aldrich. Ammonium hydroxide (NH_4OH) solution (purum, ~28% in water) was purchased from Fluka. Both hydrated niobium oxide (NBO) in pellets (with graphite) and in powder form and ammonium niobium oxalate complex $(NH_4)NbO(C_2O_4)_2\ nH_2O$, ANBO) were kindly furnished from Companhia Brasileira de Metalurgia e Mineraçao (CBMM, Brazil). Silica-zirconia (5 wt.% ZrO_2)was supplied from Grace Company.

All the materials were used without further purification. Milli-Q H_2O was used for preparation of all aqueous solutions.

2.2. Catalyst preparation and characterization

Silica-zirconia (SZ) has been utilized as support of the NbO_x active phase, that has been deposited at 10 wt.% of Nb by classical wetness impregnation (Nb/SZ_i) and by a *sol–gel* like method (Nb/SZ_{sg}) modifying the procedures described in Ref. [32]. Ammonium niobium oxalate complex $(NH_4)\ NbO(C_2O_4)_2\ nH_2O$ (ANBO) and niobium (V) ethoxide ($Nb(OCH_2CH_3)_5$ (NBE)) were used as Nb sources, respectively.

For Nb/SZ_i preparation, a finite amount of SZ (ca. 15 g) was first dried at 120 °C for 4 h. The adequate amount of ANBO was dissolved in ca. 70 mL of water and it was added to SZ. The aqueous suspension of SZ in the presence of ANBO was kept overnight under vigorous stirring at room temperature. After 16 h of contact, water was mild evaporated in a rotavapor under vacuum between 40 and 50 °C for 5 h and eventually the solid obtained was dried in the oven at 120 °C overnight and calcined at 550 °C for 8 h.

For Nb/SZ_{sg} preparation, ca. 18 g of SZ was first dried at 120 °C for 4 h, then an amount of ca. 80 mL of 1-propanol was added under stirring, afterwards several drops of HCl 37% were added to the suspension (pH 1–2). After ca. 2 h, NBE (5 mL dissolved in ca. 10 mL of 1-propanol) was added to the slurry keeping it under stirring for other 2 h. Then, ammonium hydroxide (NH_4OH) solution (~20 mL) was added dropwise to obtain gelation. The unripe solid was aged at room temperature for two days, then it was dried in a rotavapor at r.t. for several hours, to eliminate the excess of propanol, dried at 120 °C overnight. Eventually, the solid was calcined at 550 °C for 8 h.

Thermal gravimetric analyses (TGA) were performed on the dried samples in a TGA analyzer from PerkinElmer (TGA7), with a scan of 10 °C min^{-1}, from 25 to 800 °C under flowing air. For better evidencing of the thermal events, differential thermogravimetric curves (DTGA) were also calculated from the parent TGA profiles.

Microstructure analysis of the samples have been determined by adsorption and desorption of nitrogen at −196 °C (Sorptomatic 1900 instrument) and successive numerical interpretation of the collected isotherms by BET and BJH models for the specific surface area and pore size distribution, respectively. Prior to measurement, the sample (ca. 0.1–0.3 g) crushed and sieved as 45–60 mesh particles was introduced in the sample holder and thermally activated at 350 °C for 16 h under vacuum.

Powder X-ray diffraction (XRD) patterns were recorded in the 15–80° 2θ range in scan mode (0.02° step, 1 s) using a X'Pert Pro PANalyticaldiffractometer with CuK_α radiation of 0.154046 nm. Diffractograms were analyzed with the X'PertHighScore Plus software.

Scanning electron micrographs (SEM) were collected by a LEO-1430 coupled with energy-dispersive X-ray spectroscopy (EDX) working with an accelerating voltage of 20 kV.

The acid titrations with PEA have been carried out at 30 °C in a recirculation chromatographic line (HPLC), comprising a pump (Waters 515) and a monochromatic UV detector (Waters, model 2487, $\lambda = 254$ nm) [23]. Successive dosed amounts of PEA solution in cyclohexane or in water were injected into the line in which cyclohexane or water continuously circulated. The attainment of the adsorption equilibrium was revealed by the attainment of stable UV-detector signal. The sample (ca. 0.1 g crushed and sieved as 80–200 mesh particles) was placed in a sample holder (stainless steel tube, 4 mm i.d. and 8 cm of length) between two sand pillows. Prior to the measurement, the sample was activated at 350 °C for 4 h in flowing air (8 mL min^{-1}) and then filled with the liquid.

After the collection of the first adsorption isotherm of PEA on the fresh sample (I run), pure solvent was allowed to flow for 30 min through the PEA-saturated sample, then a new adsorption of PEA was repeated (II run). The collected isotherms were interpreted following the Langmuir equation:

$$\frac{PEA_{ads}}{PEA_{ads,max}} = \frac{b_{ads}[PEA]_{eq}}{(1 + b_{ads}[PEA]_{eq})} \tag{1}$$

From the conventional linearized equation, reporting $[PEA]_{eq}/PEA_{ads}$ vs. $[PEA]_{eq}$, the values of $PEA_{ads,max}$ could be obtained. Assuming a 1:1 stoichiometry for the PEA adsorption on the acid site, the value of $PEA_{ads,max}$ obtained from the I run isotherm corresponded to the number of total acidic sites, while, the value of $PEA_{ads,max}$ obtained from the II run isotherm corresponded to the number of weak acidic sites. The number of strong acid sites was obtained as the difference between the number of total and of weak sites.

2.3. Catalytic tests of xylose dehydration

2.3.1. Catalytic tests of xylose dehydration with different solvents

All catalysts were tested in the dehydration of xylose to furfural in batch conditions with the different selected reaction solvents at lower (130 °C) and higher (160–180 °C) temperature.

Screening tests in different solvents were performed in amagnetically stirred (1500 rpm) Ace sealed pressure glass reactor (15 mL of volume) placed in a preheated oil bath at 130 °C for 6 h. Typical conditions used were: 4.5 wt.% of xylose and 3 wt.% of powder catalyst (catalyst/xylose wt. ratio, 0.67). The mass ratios of the solvents used were: for the biphasic water/CPME system, 3:7, for the monophasic water/γ-valerolactone, 1:9, and water/isopropanol (20% v/v), 8:2.

Kinetic tests in water/γ-valerolactone at 160 °C and in water/CPME at 180 °C were carried out, with different amounts of catalyst and xylose respect to those used for the screening tests, following the reaction for 4 h.

The reaction started when the charged reactor was immersed in the oil bath (130 °C) and stopped by removing the reactor from the oil bath and rapidly cooled down by immersion in water at room temperature. Then, in case of biphasic systems, internal standards for organic phase (octanoic acid) and for aqueous phase (D (+)-glucose) were added to the quenched reaction mixture and after gently agitation for several minutes, ca. 2 mL aliquot was taken from the each phase for the analysis after filtration (polyethersulfone Millipore filter 0.22 μm).

Aqueous aliquots were analyzed with a HPLC Agilent 1200 series chromatograph equipped with a refraction index (RI) detector and a Bio-Rad Aminex HPX-87H column (300 × 7.8 mm) for analysis of xylose and furfural in aqueous phase. A 0.005 M H_2SO_4 mobile phase was employed as eluent with 0.4 mL min^{-1} flow rate and at 55 °C. In the case of organic aliquots, analysis of furfural in this phase was conducted by gas chromatography (CG) (Varian CP-3800) equipped with a ZB-WAX-Plus column (30 m × 0.32 mm × 0.25 μm) and a flame ionization detector (FID).

2.3.2. Catalyst stability tests

Recycling experiments of the catalysts were performed in a 100 mL Parr stainless steel reactor mechanically stirred at high temperature (180 °C) in water/CPME, 3:7 mass ratio, and 10 wt.% xylose and 5 wt.% catalyst. The reactor was first loaded with xylose and catalyst powder and the corresponding amount of solvent. After purging with N_2, the reactor was pressurized (500 kPa) and temperature increased to reach 180 °C without stirring. Once reached the stable reaction temperature, the mixture started reacting by stirring at 1000 rpm (zero time). The reaction was halted by stopping stirring and then the reactor was quenched to room temperature. The solution was taken out from the reactor and internal standards for aqueous and organic phase were added as above described before the analysis.

After the first reaction cycle, the catalyst inside the reactor was washed several times with the reaction solvent to eliminate the rests of xylose and organics weakly retained by the solid; the liquid was then removed from the reactor and the catalyst was left inside the reactor to dry for the next run.

Catalyst stability tests for long times on stream (up to 100 h) in water and water/isopropanol solution (20% v/v isopropanol) were carried out in a continuous reaction line equipped with a tubular catalytic reactor and a dosing pump (HPLC pump, Waters 501). The reactor and pre-heater were assembled in an oven with forced circulation of hot air in order to keep a constant temperature (130 °C). The catalyst sample (1 g), previously sieved to 25–45 mesh, was held in the middle of the reactor, between two sands beds (0.5 g, 45–60 mesh). The aqueous xylose solution (ca. 0.3 M) was continuously fed into the catalytic bed reactor. The feed flow rate was kept constant at 0.1 mL min^{-1} obtaining a contact time of 10 min g mL^{-1}. After starting the reaction, at least 100 mL of solution was left to flow before collecting samples for the analysis, so ensuring the stationary conditions to be obtained. The pressure in the reactor was kept between 10^3 and 2×10^3 kPa by means of a micrometric valve at the end of the reaction line. The products were analyzed in a liquid-chromatography apparatus (HPLC), consisting of a manual injector (Waters U6K), pump (Waters 510), heater (Waters CHM) for the column and refractive index detector (Waters 410). A sugar Pack I column operating at 90 °C and eluted with an aqueous solution of Ca-EDTA (10^{-4} M) was used.

3. Results and discussion

3.1. Characterization of materials

The two catalysts prepared by deposition of niobia over silica-zirconia (Nb/SZ_i and Nb/SZ_{sg}) were prepared starting from two different Nb precursors (ANBO and NBE) and employing two different preparation routes (impregnation and sol–gel, respectively). In both cases, calcination at 550 °C ensured the formation of a oxide sample. The calcination temperature was chosen based on the results obtained from the thermogravimetric analysis performed on the dried samples (Figure 1S, Supporting Information). Both the thermograms show at about 100 °C losses of mass associated to the physical desorption of water. The most intense losses of mass centered around 250–300 °C, could be attributed to the decomposition of ANBO and NBE. Quantitative evaluation of the mass losses were in agreement with the calculated amounts of carbon and nitrogen of the Nb-precursor used.

X-ray powder diffraction (P-XRD) of the supported catalysts on SZ support (Nb/SZ_i and Nb/SZ_{sg}) showed an amorphous halo centered at $2\theta = 22°$, typical of amorphous silica, indicating their main amorphous nature. Peaks related to the presence of Nb_2O_5 crystalline aggregates are detectable only for Nb/SZ_i (Fig. 1, top). It could be then inferred a higher Nb-dispersion on Nb/SZ_{sg} than on Nb/SZ_i. P-XRD of pure NBO (Figure 3S, Supporting Information) showed the typical crystalline pattern in which monoclinic H-Nb_2O_5 and T-orthorhombic phases can be distinguished. On Nb/SZ_i catalyst, the SEM-EDX analyses detected surface amounts of Nb_2O_5 of 17 ± 5 wt.% with the different areal zones more or less covered by Nb (Figure 2S, Supporting Information).

The main textural properties of all catalysts and support have been studied. Fig. 2 shows the N_2 adsorption–desorption isotherms of the two supported Nb-catalysts and bulk Nb_2O_5 (with graphite) and the silica-zirconia support. In Table 1, a summary of the main textural properties obtained is reported. SZ support shows type IV isotherm typical of the mesoporous solids: high specific

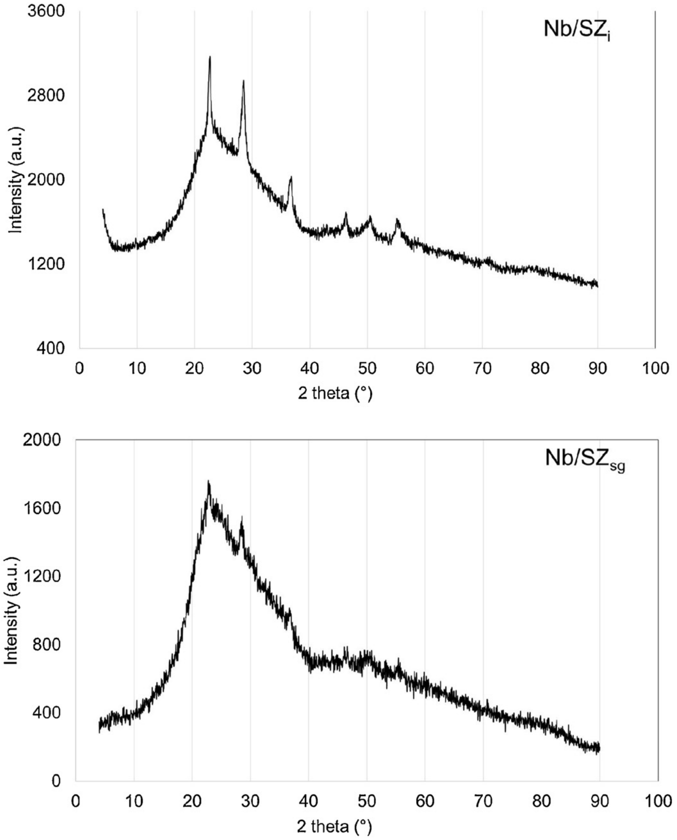

Fig. 1. P-XRD of Nb/SZ$_i$ (top) and Nb/SZ$_{sg}$ (bottom) (P-XRD of NBO is shown in Supporting Information section, Figure 3S).

surface area and pore volume with large pore diameter. The N_2 adsorption/desorption isotherms of Nb/SZ$_{sg}$ are also typical of a mesoporous solid. Any significant variation of pore size compared with the SZ support has not been observed, suggesting a uniform Nb-distribution on the support matrix. The same happens with Nb/SZ$_i$, which has high surface area and pore volume but a significant decrease of pore size compared with SZ. The results suggest that niobium has been deposited at the external and internal surface of SZ. Concerning Nb_2O_5, the results confirm the already reported morphologic features with the presence of pores with small size.

The surface acidity developed by the support and the prepared catalysts is expected to direct the activity and selectivity in the dehydration reaction of xylose. In view of the importance of the acidity of the catalysts manifested in the reaction medium, we have measured the intrinsic and effective acidities [23] of the catalyst samples, by determining the amount and strength of the acid sites. Starting from the determination of the *intrinsic* acidity of the samples, determined in cyclohexane (an aprotic and apolar liquid), we moved to the *effective* acidity determined in water (a protic and polar solvent with high solvating ability). We have chosen water because the reaction takes place in pure water and in some aqueous solutions (with γ-valerolactone and isopropanol). Also when the biphasic system water/CPME has been used, water, which has hydrophilic characteristics, is in contact with the catalyst oxide surfaces.

Table 1
Main textural properties of the studied samples.

Catalyst	BET surface area ($m^2\,g^{-1}$)	Pore volume ($cm^3\,g^{-1}$)	Average pore diameter (nm)
SZ	294	1.79	19.7
Nb/SZ$_{sg}$	217	1.21	18.1
Nb/SZ$_i$	262	0.95	13.6
NBO[a]	108	0.52	3.4

[a] Niobia in pellets.

Because it is known that water with its polar, protic, and solvating properties can interact with acid surfaces, modifying the number and strength of the acid sites (in general decreasing it). Therefore, a given acid surface can reconstruct itself in the presence of water. In order to find sound relations between the acid properties of the catalysts and their activity, the knowledge of the effective acidity seems more appropriate.

The *intrinsic* acidity of SZ is very high, but only the half of the sites are strong acid sites (Table 2 and Fig. 3). By covering part of SZ support with niobia phase, a decrease of surface acidity of the catalysts (Nb/SZ$_{sg}$ and Nb/SZ$_i$) has been obtained. This was expected due to the lower surface area values of Nb/SZ compared with the SZ support (Table 1). Interestingly, the percent of the strong acid sites of Nb/SZ$_{sg}$ and Nb/SZ$_i$ increases compared with SZ, likely due to the dispersed Nb-centers which can be associated to new LAS sites created on the catalyst surfaces [33].

The determination of the *effective* acidity, measured in water, shows a different *scenario* (Table 2 and Fig. 3). The catalyst prepared by sol–gel (Nb/SZ$_{sg}$) shows the highest amount of *effective* acid sites and it maintains in water ca. 65% of its *intrinsic* acid sites. In water, the acidity of SZ deeply decreases as well as the acidity of Nb/SZ$_i$ (only about 35% of acidity is retained in water for both the samples). In general, as known, the acid strength of the *effective* acid sites in water is low, the highest acid strength is associated to Nb/SZ$_{sg}$ surface (0.042 mequiv./g corresponding to 14% of the titrated acid sites in water).

The acidity determination of NBO confirmed the already known water-tolerant acid properties; ca. 90% of the acid sites titrated in cyclohexane are maintained in water and high percent (66%) of the *effective* acid sites are strong. Considering the lower surface area of NBO than that of Nb/SZ$_{sg}$ and Nb/SZ$_i$, the acid site density of NBO in water is very higher than that of the Nb/SZ catalysts.

3.2. Activity of xylose dehydration to furfural

Despite the apparent simplicity of the synthesis of furfural from xylose that consists only in a deep dehydration of the pentose, the reaction catalyzed by solid acids is far to be simple. Studies from literature have demonstrated that xylulose is a key intermediate that is formed from the xylose isomerization, by the catalytic action of LAS, and then it is dehydrated to furfural by BAS action [10]. However, excess of LAS on the catalyst surface causes side reactions to produce humins that decrease the furfural selectivity and yield and cause catalyst deactivation.

Our previous works [23,32] have shown that dispersed niobia systems on silica are more stable than bulk niobia in the dehydration of fructose to HMF, but conversion was low due to the inertness of silica surface. Taking into account these findings, for the xylose dehydration we have studied acid solid catalysts consisting of dispersed niobia phase onto an acidic oxide support. These systems might guarantee a convenient amount of acid sites with a balanced concentration of LAS and BAS sites [32,34] for a high xylose conversion and its selective transformation to furfural, according with the mechanistic findings of the literature [10].

3.2.1. Catalytic tests of xylose dehydration at low temperatures with different solvents

First of all, all the catalysts were tested in batch experiments for dehydration of xylose to furfural in different reaction solvents at low temperature (130 °C). Besides water, a biphasic system,

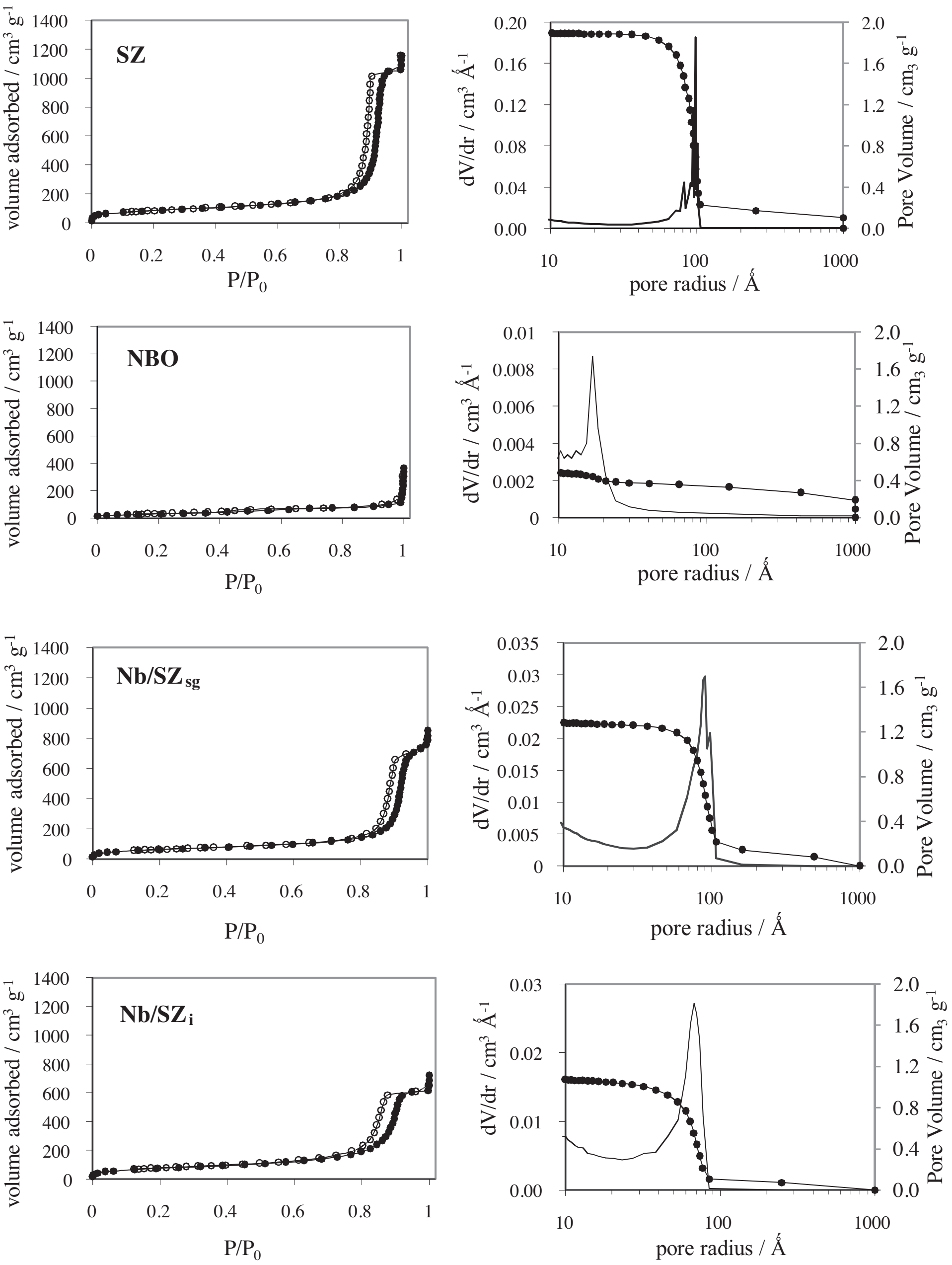

Fig. 2. N_2 adsorption/desorption isotherms (left side) and BJH pore volume distribution (right side) of all the catalyst samples.

water/CPME, and two aqueous solutions, water/γ-valerolatone and water/isopropanol, were employed. The goodness of CPME, a highly hydrophobic ether, as green solvent for carbohydrate biomass conversion has been already recognized [28]. γ-Valerolactone, too, is an interesting solvent as it can be produced from lignocellulose, it has been also used in dehydration of sugars with interesting performances [26,27,31,35]. Also aqueous mixtures containing isopropanol could improve the stability of the catalyst by improving solubility of some of the condensation products formed during the reaction.

Table 2
Summary of the *intrinsic* and *effective* acidities of the Nb-catalysts measured by PEA titration in cyclohexane (I.A.) and in water (E.A.), at 30 °C.[a]

Catalyst	Intrinsic acidity (mequiv./g) in cyclohexane				Effective acidity (mequiv./g) in water			
	Total sites (mequiv./g)	Weak sites (mequiv./g)	Strong sites (mequiv./g)	Strong sites (%)	Total sites (mequiv./g)	Weak sites (mequiv./g)	Strong sites (mequiv./g)	Strong sites (%)
SZ	0.76	0.40	0.36	47	0.27	0.26	0.005	2
Nb/SZ_{sg}	0.47	0.16	0.31	66	0.30	0.25	0.042	14
Nb/SZ_i	0.59	0.12	0.47	80	0.22	0.20	0.013	6
NBO	0.21	0.07	0.14	66	0.19	0.07	0.12	64

[a] Total acid sites (determined from the I run isotherm), weak acid sites (determined from the II run isotherm) and strong acid sites (determined by difference); see Experimental.

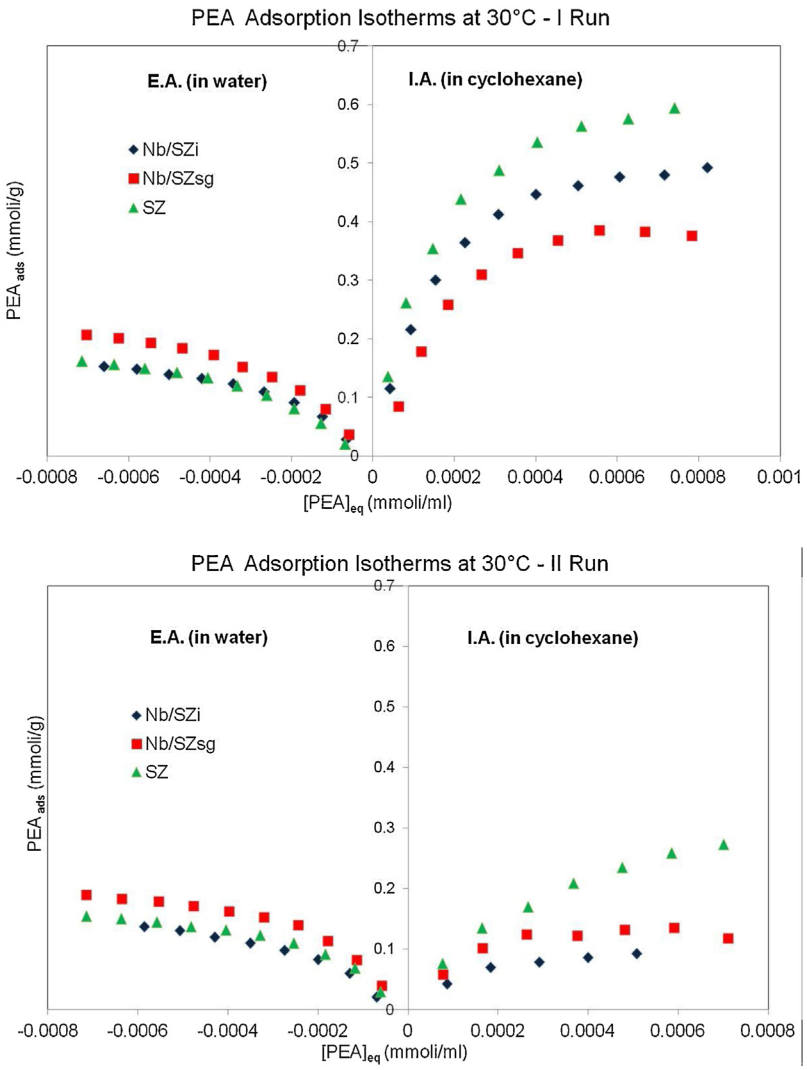

Fig. 3. *Intrinsic* (in cyclohexane) and *effective* (in water) acidities of the samples: adsorption isotherms of PEA at 30 °C. I° run collected on fresh and activated sample and II° run collected on the previously sample saturated by PEA and eluted with solvent.

Fig. 4 shows the results of xylose conversion and furfural yield obtained for both NBO and the two supported Nb-catalysts (Nb/SZ$_i$ and Nb/SZ$_{sg}$). In all the solvents, NBO was more active than the other supported niobia catalysts; this was expected due to the lower amount of niobia on the supported catalysts and to the higher acid site density of NBO in comparison with the diluted Nb/SZ catalysts [23]. However, Nb/SZ$_i$ and Nb/SZ$_{sg}$ show similar catalytic behavior, disregarding the solvent used, it seems that the method of preparation does not have a crucial influence in the final catalytic activity but the solvent nature directs both xylose conversion and yield to furfural obtained. Comparing the results obtained in the different solvents, both xylose conversion and furfural yield are higher than those obtained when pure water was used, for all the catalysts. The biphasic system water/CPME appeared the best solvent by balancing the results obtained in terms of xylose conversion and selectivity. It is also worthy to mention that the supported niobia catalysts show the highest conversion in presence of γ-valerolactone compared with the other solvents.

Continuous catalytic tests in a flow fixed bed reactor have been made aimed to study the stability of the catalysts for long time on stream; we have chosen to compare water and isopropanol/water as solvents (Fig. 5). The continuous tests showed that NBO was more active than the supported niobia catalysts in both the solvents tested, confirming what has been observed in batch reactor tests.

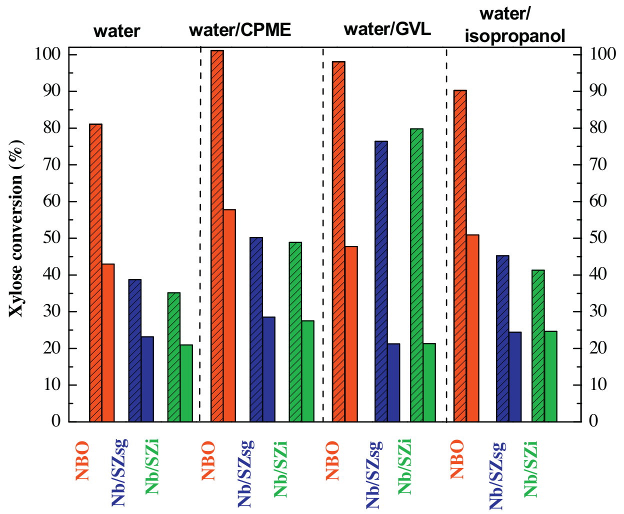

Fig. 4. Xylose conversion (dashed bars) and furfural yield (filled bars) for the NBO and Nb/SZ catalysts in different reaction solvents. Reaction conditions: batch reactor; 4.5 wt.% xylose, 3 wt.% catalyst; 5 g total solution; γ-valerolactone (GVL)/aqueous mass ratio, 9; CPME/aqueous mass ratio, 2.33; water/isopropanol 20% v/v; reaction temperature, 130 °C; tos, 360 min.

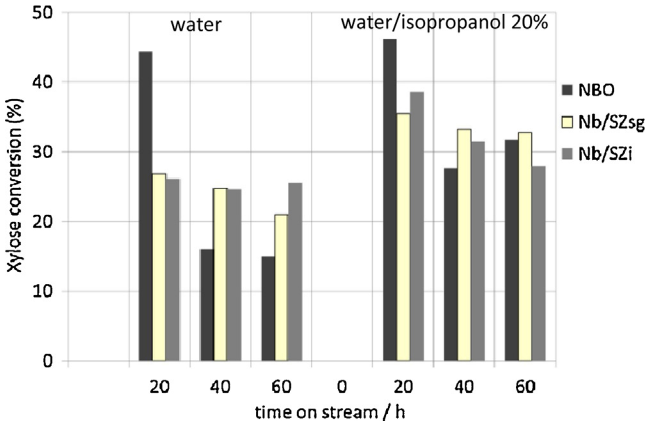

Fig. 5. Xylose conversion for different time on stream for the NBO and Nb/SZ catalysts. Reaction conditions: fixed bed reactor; 4.5 wt.% xylose, 3 wt.% catalyst; contact time, 6–10 min g mL^{-1}; reaction temperature, 130 °C.

Concerning the supported catalysts, even if initially less active, they are more stable; only a little loss of activity was observed up to 60 h of activity. In addition, the presence of isopropanol in water improved the activity of the catalyst, even if a certain degree of activity loss was still present.

3.2.2. Catalytic tests of xylose dehydration at high temperatures with selected reaction solvents

On the basis of the results obtained from the tests of xylose dehydration at low temperatures (130 °C), emerged that the biphasic system water/CPME and the monophasic γ-valerolatone in mixture with water seemed to be the most interesting solvents for the studied reaction. The key role of the solvent in the conversion of carbohydrate biomass has been recently pointed out also by Perez and Fraga [36]. Therefore, all the catalysts were tested again in the two selected solvents at higher temperatures (160 °C for water/γ-valerolatone and 180 °C for water/CPME) and following the reaction as a function of time.

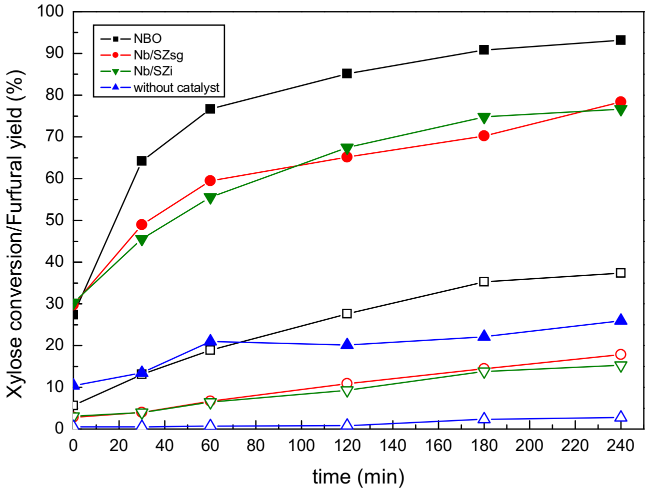

Fig. 6. Comparison of the xylose conversion (filled markers) and furfural yield (empty markers) with reaction time on NBO and Nb/SZ catalysts and without catalyst (blank test). Reaction conditions: batch reactor; 2 wt.% xylose and 0.2 wt.% of catalyst; γ-valerolactone/aqueous mass ratio, 9; 50 g total solution; reaction temperature,160 °C.

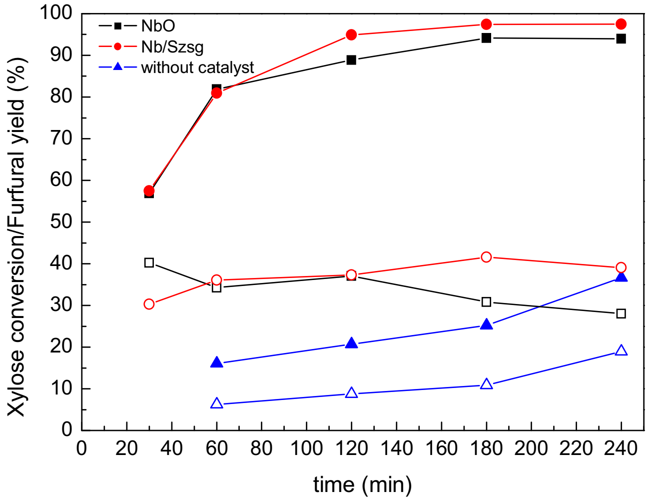

Fig. 7. Comparison of the xylose conversion (filled markers) and furfural yield (empty markers) for NBO and Nb/SZ$_{sg}$ catalysts and without catalyst (blank test) vs. reaction time. Reaction conditions: 10 wt.% of xylose and 5 wt.% of catalyst in the aqueous phase, CPME/aqueous phase mass ratio, 2.33; 50 g total solution; reaction temperature, 180 °C.

Fig. 6 shows the results obtained in γ-valerolactone as solvent and Fig. 7 those obtained in water/CPME biphasic system, in terms of xylose conversion and furfural yield, in comparison with the blank test carried out without catalyst. The results confirm the ranking of activity observed at low reaction temperature. Moreover, on all the catalysts xylose conversion and furfural yield can be described by increasing curves, suggesting that the activity loss is weak. Moreover, when plotting the selectivity to furfural against xylose conversion, exponential curves could be observed on all the catalysts, indicating that under the used experimental conditions, furfural is a final and stable product of reaction (Figure 4S, Supporting Information). The most interesting results (both conversion and furfural yield) have been observed in water/CPME system (Fig. 7). In this solvent, Nb/SZsg had quite complete xylose conversion while yield to furfural was not higher than 40% after 240 min of reaction, with a poor increasing trend with reaction time. At this high temperature (180 °C), resinification reactions could be very fast with high amount of by-product formation.

In water/CPME biphasic system, besides catalytic activity, also the stability of the NBO and Nb/SZ catalysts has been studied by performing recycling experiments at 180 °C for various reaction times (60 min, 120 min, and 240 min of reaction time for NBO and 240 min for Nb/SZ catalysts). The catalytic runs were carried out for short periods of time to facilitate the observation of any activity decline.

Fig. 8 shows the xylose conversion and furfural yield for several consecutive runs for each catalyst tested. Nb/SZ$_{sg}$ and Nb/SZ$_{i}$ have a quite stable production of furfural with yield around 45–50% and selectivity of almost 80% after 7 runs, while xylose conversion is roughly constant. This means that the presence of by-products also deposited on the catalyst surface do not completely deactivate the catalyst surfaces. On the opposite, a regular deactivate trend of xylose conversion was observed on NBO, while once again, furfural yield production is more stable. By increasing the reaction time (recycling tests each 120 min and 240 min), the conversion and furfural yield increased suggesting that the NBO surface is not completely deactivated.

These results may suggest that the selective acid sites for the furfural formation, still lively in water and associated with the dispersed niobia phase, are not deactivated during the course of reaction, while the rest of the acid surface is mainly involved in the unselective conversion of xylose. Concerning the role of the reaction solvent, it clearly appears that water and water solutions can modulate the catalyst acidity decreasing the acid site density of the surfaces. This leads to a positive effect on the catalyst stability.

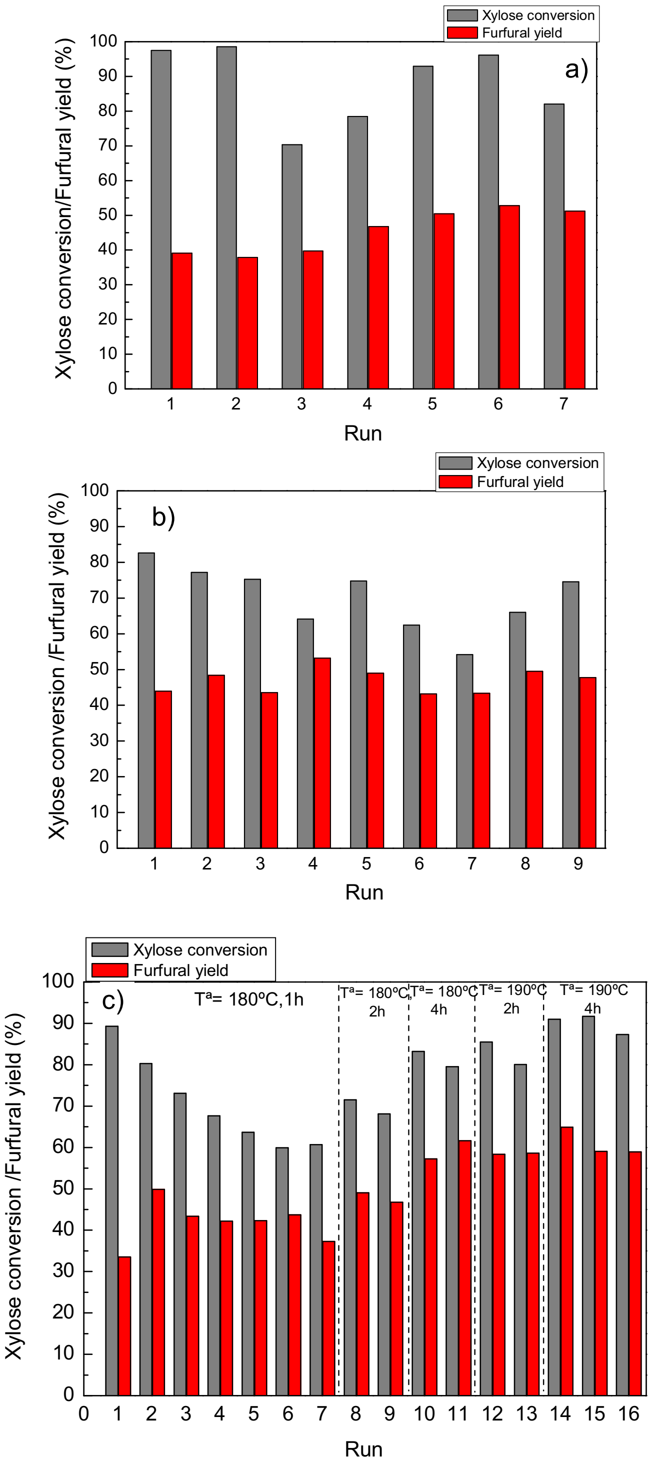

Fig. 8. Recycling tests on NBO and Nb/SZ catalysts: a) Nb/SZ$_{sg}$, b) Nb/SZ$_i$, c) NBO. Reaction conditions: 10 wt.% xylose and 5 wt.% catalyst in the aqueous phase, CPME/aqueous phase mass ratio, 2.33; 50 g total solution, reaction temperature, 180 °C, time of reaction, 240 min for the supported catalysts.

4. Conclusive remarks

In this work, we have shown that niobia phase dispersed over an acid oxide support, like silica-zirconia, is effective for the acid conversion of xylose to furfural, due to the *water-tolerant* acid properties of the niobia phase, as proved by our acidity measurements carried out in water.

The niobia supported catalysts have lower activity than bulk niobia but higher stability during the reaction course, as proved by the recycling tests and continuous catalytic tests. The catalyst with the highest niobia dispersion (prepared by *sol–gel*) showed the most interesting performances, which can be associated with the highest amount of strong *effective* acid sites. Moreover, a crucial role of the reaction solvent has been enlightened; the wise choice of solvent prevents a severe catalyst deactivation and maintains the selective conversion of xylose to furfural. By using a biphasic system, it is possible extracting the final furfural product from aqueous phase and avoid side-reactions or/and lowering the formation of humins. It is also worth noticing that by using aqueous solutions (with alcohol or lactone), catalyst stability improves thanks to an increase of solubility of the formed humins, so avoiding that they can deposit on the catalyst surface and deactivate it.

Our future activity will be directed toward the development of an optimized catalyst *plus* solvent system, with catalyst acid sites of adequate nature for isomerize and dehydrate monosaccharides and with more solubility of the formed by-products in the selected solvent. These are the two key factors to obtain a successful catalytic process in the sugar conversion.

Supplementary information

SEM image of Nb/SZ$_i$ showing a morphology characterized by polyhedra of irregular shape; thermogravimetric profiles of the dried catalysts (Nb/SZ); XRD patterns of fresh Nb_2O_5; trend of the selectivity to furfural vs. xylose conversion on the different Nb-catalysts, reaction carried out in γ-valerolactone:water monophasic system at 160 °C in the batch reactor; explicative note on the properties of 2-phenylethyl amine used as basic probe in the acidity measurements and on the method of acid–base titration in liquid.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cattod.2015.01.018.

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