



# Silica–niobia oxides as viable acid catalysts in water: Effective vs. intrinsic acidity

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## ABSTRACT

By dispersing a niobia phase in/on silica matrix it was possible to maintain the catalytic activity in the dehydration of fructose in water for longer time without any deactivation, compared with the fast deactivation observed on bulk niobium oxide hydrate. The surface acidity of the bulk niobium oxide hydrate and silica-diluted niobia materials was responsible of the different catalytic performances observed. As the dehydration reaction can run in water, in agreement with the development of a green process, the acid properties of the catalysts were comparatively studied in water too, to find sound relations between acid and catalytic properties. On all the catalysts, the *effective* acidity, determined in water, was much lower compared with the *intrinsic* acidity determined in cyclohexane, as expected. A relation between the catalytic activity in the dehydration of fructose and the amount of *effective* acid sites of the samples was evidenced.

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## 1. Introduction

Niobium oxide hydrate or niobic acid ( $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ , hereafter called NBO) has received much attention as catalyst due to the presence of labile protons at its surface that give it strongly acidic properties ( $H_0 = -5.6$  [1,2]) that are maintained up to moderate temperatures (ca. 300 °C). This feature added to the water-tolerant property of niobic acid [3] opened many potential applications in acid catalysis for this material [4–8]. Of particular interest are the applications for some fine chemical acid-catalytic processes of renewable biomass transformation running in water, according with the request of green process developments. In particular, good catalytic activity in the dehydration fructofuranose reactions coupled with interesting selectivity to 5-hydroxymethyl-2-furaldehyde (HMF) has been presented in the literature [9–11]. HMF is one among the most interesting key products in the biobased transformations to fine chemicals, fibers, and polymers. Catalytic HMF formation has been demonstrated in water, traditional organic solvents, multiphase systems, and ionic liquid, also operating under non-conventional operative conditions [12–16]. For real catalytic applications, besides a balanced activity–selectivity pattern, the maintenance of a stable activity is an essential requisite. For example, during the reaction course of fructose dehydration over NBO, large amounts of solid products (humines or coke [9,10,17]) are formed decreasing the catalyst activity, compromising the catalyst

stability, and preventing the NBO use as effective catalyst in such reaction, despite its good activity [10,18]. The justification for this deactivation behaviour is far to be elucidated, it depends on reaction conditions such as contact time and temperature and in particular on the solvent nature. Based on chemical consideration on the acid-catalytic mechanism involved in the reaction, the strongly acid nature of the NBO sites could be responsible of such deactivation.

In the present investigation, we present our study on the long-term activity of series of niobia diluted in silica matrix samples, of which we have already reported the preparation and characterization [19] in the reaction of dehydration of fructose running in water in relation with their acid properties in comparison with the NBO activity and acidic feature.

It is well known that when different oxides are mixed together, the resultant oxides may possess higher or lower acid properties than the parent oxides [20]. Various attempts to rationalize the acidity of mixed oxides have appeared in the literature [21–26]. According with Tanabe's approach [20,21], introducing  $\text{Nb}^{5+}$  into silica, where Si cations are tetracoordinated, should induce Lewis or Brønsted acidity in the resultant silica–niobia oxide, depending on the tetrahedral or octahedral coordination of Nb, respectively, being the Nb coordination dependent also on the relative ratio of niobia to silica in the sample composition [27,28]. In fact, different Nb-coordinated species (monomeric, oligomeric fourfold-coordinated  $\text{NbO}_4$ , fivefold-coordinated  $\text{NbO}_5$ , and sixfold-coordinated polymeric  $\text{NbO}_6$  species [29–31]) have been recognized on supports of various nature. The complex behaviour of diluted Nb-species is expected influencing not only the acidity of the resultant surfaces but also their catalytic performances. Searching

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**Table 1**

Main properties of the studied catalysts: bulk and surface composition, and acidity.

Sample	Nb <sub>2</sub> O <sub>5</sub> concentration (mol%)		BET surface (m <sup>2</sup> g <sup>-1</sup> )	Intrinsic acidity (IA) <sup>c</sup>		Effective acidity (EA) <sup>d</sup>		R <sub>EA/IA</sub> <sup>e</sup>
	Bulk <sup>a</sup>	Surface <sup>b</sup>		mequiv. g <sup>-1</sup>	μequiv. m <sup>-2</sup>	mequiv. g <sup>-1</sup>	μequiv. m <sup>-2</sup>	
NBO <sup>f</sup>	–	–	105	0.149	1.419	0.123	1.171	0.83
Samples prepared by co-precipitation (aqueous series)								
Si–Nb/5 <sub>aq</sub>	1.2	0.57	274	0.550	2.007	0.078	0.285	0.14
Si–Nb/15 <sub>aq</sub>	3.8	2.15	200	0.422	2.110	0.061	0.305	0.14
Si–Nb/30 <sub>aq</sub>	8.8	4.82	165	0.322	1.952	0.046	0.279	0.14
Si–Nb/45 <sub>aq</sub>	15.6	7.03	141	0.251	1.780	0.067	0.475	0.27
Si–Nb/60 <sub>aq</sub>	25.3	15.93	93	0.207	2.226	0.037	0.398	0.18
Samples prepared by sol–gel (organic series)								
Si–Nb/5 <sub>org</sub>	1.2	0.67	317	0.450	1.420	0.095	0.300	0.21
Si–Nb/15 <sub>org</sub>	3.8	2.77	434	0.656	1.512	0.131	0.302	0.20
Si–Nb/30 <sub>org</sub>	8.8	7.13	448	0.639	1.426	0.147	0.328	0.23
Si–Nb/45 <sub>org</sub>	15.6	12.63	262	0.474	1.809	0.168	0.641	0.35
Si–Nb/60 <sub>org</sub>	25.3	20.97	134	0.141	1.052	0.084	0.627	0.60
Samples prepared by wet impregnation								
Si–Nb/5 <sub>wi</sub>	1.2	0.70	193	0.336	1.741	–	–	–
Si–Nb/10 <sub>wi</sub>	2.2	1.24	234	0.356	1.521	0.124	0.530	0.35
Si–Nb/20 <sub>wi</sub>	4.3	1.42	184	0.340	1.848	0.111	0.630	0.33

<sup>a</sup> Obtained from preparation data.<sup>b</sup> Obtained from XPS analyses, computing Nb-concentration in terms of Nb<sub>2</sub>O<sub>5</sub> [19].<sup>c</sup> Determined in cyclohexane, at PEA concentration, of  $1 \times 10^{-4}$  M.<sup>d</sup> Determined in water, at PEA concentration of  $1 \times 10^{-4}$  M.<sup>e</sup> Ratio between effective to intrinsic acid sites.<sup>f</sup> Nb<sub>2</sub>O<sub>5</sub>, commercial sample from Companhia Brasileira de Metalurgia e Mineração (CBMM).

for sound relations between the catalyst activity and acidity of the studied samples, besides the *intrinsic* acidity, determined in apolar solvent (cyclohexane), the *effective* acidity of the surfaces, performing the titrations in water, was measured, pursuing our studies on the *intrinsic* and *effective* acidity of solid catalysts [32,33].

## 2. Experimental

### 2.1. Material

The catalysts used in this study were already described in Ref. [19] and they are presented in Table 1. They all were silica–niobia oxides (Si–Nb) containing different amount of Nb (from 5 to 60 mass% of Nb<sub>2</sub>O<sub>5</sub> corresponding to 1 to 25 molar% of Nb<sub>2</sub>O<sub>5</sub>, respectively). The first and second Si–Nb sample series were prepared by co-precipitation in water (*aqueous route* synthesis, Si–Nb/*X*<sub>aq</sub>, with  $5 < X/\text{mass\%} < 60$ ) and sol–gel (*organic route* synthesis, Si–Nb/*X*<sub>org</sub>, with  $5 < X/\text{mass\%} < 60$ ). A third sample series was prepared by wet impregnation on a home-made silica (Si–Nb/*X*<sub>wi</sub> with  $5 < X/\text{mass\%} < 20$ ). The Nb source was NH<sub>4</sub>[NbO(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>·(H<sub>2</sub>O)]·(H<sub>2</sub>O)<sub>m</sub> (ANBO) for the Si–Nb/*X*<sub>aq</sub> and Si–Nb/*X*<sub>wi</sub> series samples, while Nb(OCH<sub>2</sub>CH<sub>3</sub>)<sub>5</sub> (NBE) was used for the Si–Nb/*X*<sub>org</sub> sample synthesis.

Niobium oxide hydrate (NBO) was kindly furnished from Companhia Brasileira de Metalurgia e Mineração (CBMM) and used without any further treatment.

On fresh and several selected used catalyst samples, several analyses of characterization were performed. BET surface area was determined by N<sub>2</sub> adsorption/desorption at –196 °C using a Carlo Erba Sorptomatic 1900 instrument. Thermogravimetric analyses (TGA) were performed in a TGA 7 PerkinElmer thermal analyzer. Quantitative evaluation of coke deposited on the surface catalysts after reaction was obtained by PE 2400 Series II PerkinElmer CHNS/O analyzer. UV–vis diffuse reflectance spectroscopy (UV–DRS) measurements were performed by a PerkinElmer Lambda 35 instrument equipped with an integrating sphere and Spectralon<sup>®</sup> as reference material.

### 2.2. Intrinsic and effective acidity determination

The experiments of acid titrations of the samples by 2-phenylethylamine (PEA, pK<sub>a</sub> = 9.90) probe were performed in solvents of different characteristics: cyclohexane (aprotic/apolar), and water (protic/polar), using a HPLC line, comprising a pump (Waters, model 515) and a monochromatic UV detector (Waters, model 2487, λ = 254 nm), coupled to a personal computer for the collection, storage, and processing of the data [19,32,33]. The line used worked according to a recirculating method (Fig. 1).

The sample (0.050–0.100 g, crushed and sieved as 80–200 mesh particles) was placed in a sample holder consisting of a small stainless steel tube (i.d. 2 mm, length 12 cm), between two sand pillows. The sample was successively activated at 350 °C for 16 h in flowing air (8 ml min<sup>-1</sup>), then evacuated and eventually filled with the solvent (cyclohexane or water). The sample holder, inserted in a glass jacket connected with a water thermostat to maintain a constant temperature (±0.1 °C), was mounted in place of the chromatographic column.

The acid titrations were carried out at temperature interval from 17 to 77 °C. Successive dosed amounts of PEA in cyclohexane or water (20–50 μl, 0.10–0.15 M) were injected into the line in which the solution continuously circulated. For each injection, the PEA solution recirculated onto the sample until adsorption equilibrium was achieved, revealed by the attainment of the UV-detector signal stability. Fig. 2 shows a typical example of raw data obtained from the titration experiments, consisting on a series of increasing steps, each one representing the attainment of the adsorption equilibrium. Assuming a 1:1 stoichiometry for the PEA adsorption on the acid site, the number of acid sites *per* sample mass (mequiv. g<sup>-1</sup>) titrated at each equilibrium PEA concentration was evaluated, obtaining adsorption isotherms for the various samples.

### 2.3. Fructose dehydration reaction

D(–)-Fructose (RPE C. Erba) was used as substrate.

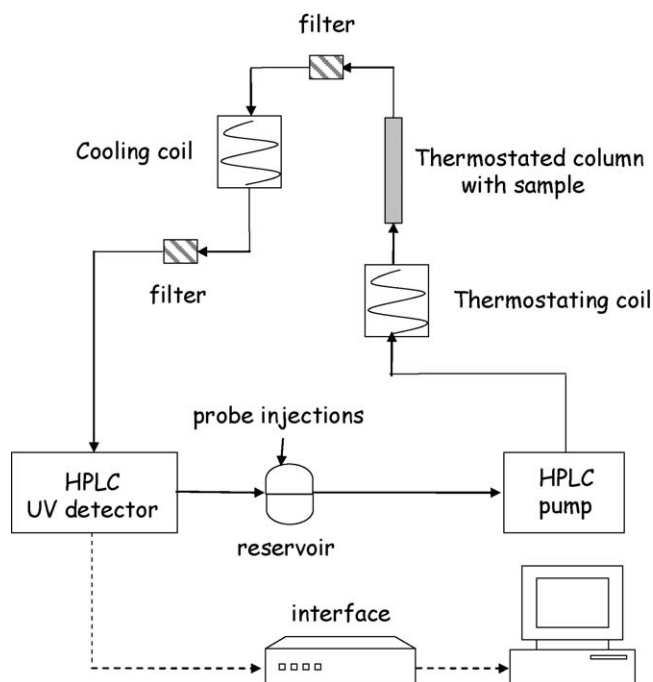


Fig. 1. Scheme of the apparatus used for the acidity determination in liquid.

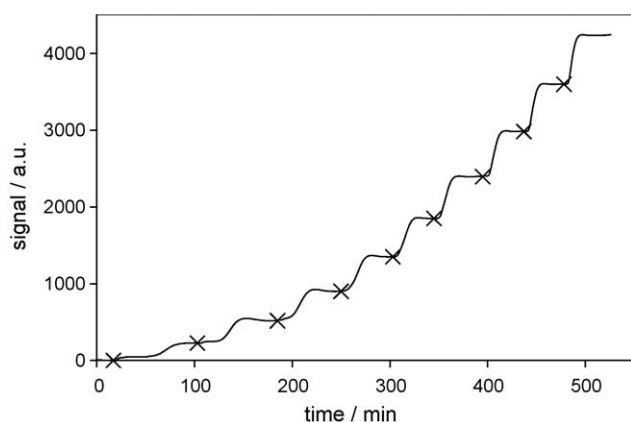


Fig. 2. Example of raw data obtained from the acid–base titration in liquid in the HPLC line. The points representing the probe injection are indicated by a cross (x).

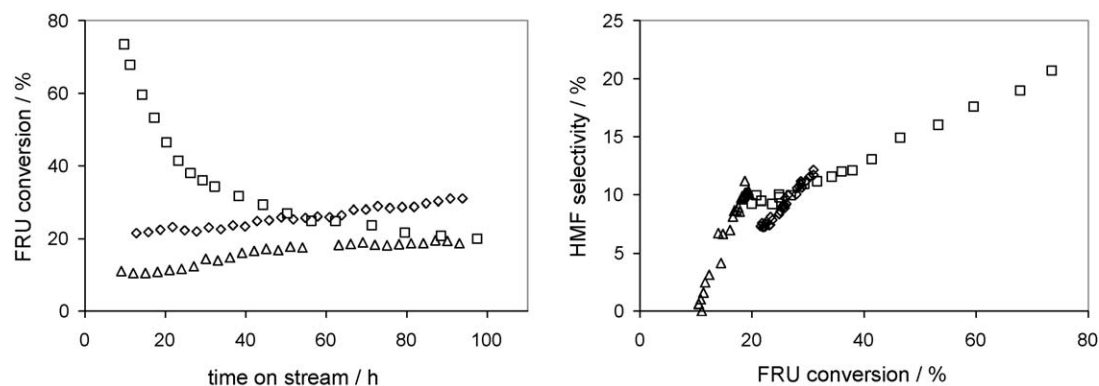


Fig. 3. Stability tests in the fructose dehydration reaction in water on NBO ( $\square$ ) and on two Si–Nb samples: Si–Nb/60<sub>aq</sub> ( $\diamond$ ) and Si–Nb/15<sub>org</sub> ( $\triangle$ ). Reaction conditions: temperature of 100 °C and contact time of 21, 27, and 40 g min ml<sup>−1</sup> for Si–Nb/15<sub>org</sub>, Si–Nb/60<sub>aq</sub>, and NBO, respectively. Left side, FRU conversion as a function of time on stream; right side, selectivity to HMF as a function of FRU conversion.

The catalytic test of fructose (FRU) dehydration to 5-hydroxymethyl-2-furaldehyde (HMF) was performed in a continuous reaction line in water at fixed temperature of 100 °C and contact time (20–40 min ml<sup>−1</sup> g), under a pressure of ca. 3 bar.

The fructose solution was continuously fed (0.1 ml min<sup>−1</sup>, 0.3 M) to the catalyst by a HPLC pump (Waters, mod. 501). The powder catalyst (2–4 g, sieved as 20–45 mesh particles) was placed in a stainless steel tubular fixed-bed reactor (volume 7 cm<sup>3</sup>). The reaction line is described in detail in Ref. [11].

The products were analyzed in a liquid chromatography apparatus (HPLC) consisting of a pump (Waters, mod. 510), an injector (Waters UK6), a heater (Waters CHM) for the column, and a refractive index detector (Waters, mod. 410). A SugarPak-1 column (Waters) was used, packed with a microparticulate cation-exchange gel in calcium form, operating at 90 °C and eluted with a solution of Ca-EDTA 10<sup>−4</sup> M in water (0.5 ml min<sup>−1</sup>).

### 3. Results and discussion

We have already reported about the catalytic activity of NBO in water in the dehydration reaction of fructose [11], according with other literature findings [9,10]. Unfortunately, the initial good activity of NBO was fast lost and a decreasing exponential trend of fructose conversion against reaction time was observed [11]. This behaviour reflects a fast deactivation of a part of active acid sites, likely the most strongly acidic ones. The observed loss of activity could be attributable to deposition of insoluble humines and coke on the catalyst surface [9,10,17,34], which is a favoured phenomenon on fixed bed of packed catalyst [11].

Surprisingly, a very different observation was revealed when measuring long-term activity of diluted niobia phases in silica matrix (Si–Nb samples) in the same reaction. Fig. 3 reports the direct comparison of the curves of fructose conversion as a function of time on stream for NBO and two selected Si–Nb samples differently prepared and containing lower or higher Nb-concentration. Over both the Si–Nb catalysts, initial conversion was much lower than on NBO, as expected, due to the very low amount of surface Nb-concentration, because of the silica dilution effect (see Table 1), while no deactivation effect was observed; even a slight conversion increasing could be observed. In Fig. 3 it also reported the HMF selectivity as a function of fructose conversion. A regular increasing trend was observed for all the three catalyst samples. Such a trend suggests a reaction mechanism, quite similar for all the catalysts, with the formation of intermediate products, leading to HMF through a consecutive reaction, or with a pre-equilibrium step involving fructose as already observed on Nb-oxide and Nb-phosphate catalysts [11].

The considerable difference observed in the long-term activity of the diluted niobia phases in silica matrix (Si–Nb samples) compared with bulk NBO phase could be related with different amount, structure, and composition of the insoluble carbonaceous species formed on the surfaces. Following the indication of Sahoo et al. [35], we investigated by TGA analysis the presence of *soft* and *hard* carbon deposits on the used catalyst samples. A TGA analysis in air atmosphere of the three samples, whose long-term activity is above described, was performed. In any case, decreasing mass profiles against temperature were observed, indicating the presence of coke on all the three catalysts. The ratio between the *soft* coke, determined in the temperature interval from 180 to 330 °C, and *hard* coke, from 330 to 800 °C, was higher on NBO (0.9) than on Si–Nb/60<sub>aq</sub> and Si–Nb/15<sub>org</sub> (0.5–0.6). Elemental analysis (C, H, and N mass percent determination) of the carbonaceous deposits indicated differences in terms of H/C ratio for the three catalysts. Higher H/C ratios were observed on the Si–Nb samples than on NBO. This observation agreed with the larger presence of *hard* coke on the Si–Nb samples, as emerged from TGA analysis. Coke deposits on the used catalyst samples were also observed by UV-DRS measurements. A broad band at wavelength from 400 to 700 nm appeared on the used samples, indicative of aromatic and polyaromatic compounds. Concerning the inorganic phases, any difference could not be observed by UV-DRS comparing the fresh [19] and the used samples (after treatment of coke removal at 350 °C for 16 h). Also morphology, surface area and porosity, of NBO and Si–Nb/60<sub>aq</sub> and Si–Nb/15<sub>org</sub> was not different comparing the fresh and the used samples [36].

The above reported different behaviour of the catalysts is likely due to the different acidic properties. Then, we wanted to deepen the study of the acid properties of the Si–Nb catalysts in comparison with those of NBO to find out reasons for their different long-term activity behaviour.

Table 1 lists the samples studied in this work and presents some of their main properties: bulk and surface composition, and surface area values. The three different series of Si–Nb samples were prepared by different preparation routes using tetraethylorthosilicate, TEOS, as Si-precursor, ANBO or NBE, as Nb-fonts. The Si–Nb samples prepared by co-precipitation (aqueous series) and by sol-gel method (organic series) contained Nb<sub>2</sub>O<sub>5</sub> concentration from 5 to 60 mass%, corresponding to 1.2 to 25 mol%, respectively. The surface composition of the samples, as measured from XPS measurements, regularly got richer in Nb (from 0.7 to 21 mol%, calculated as Nb<sub>2</sub>O<sub>5</sub>, Table 1) increasing the Nb-bulk concentration. The samples of the organic series had higher Nb surface concentration than those of aqueous series. The samples prepared by wet impregnation on a sol-gel synthesized silica [37] contained Nb from 1 to 4 mol% in terms of Nb<sub>2</sub>O<sub>5</sub> and their surfaces contained 0.7–1.4 mol% in terms of Nb<sub>2</sub>O<sub>5</sub>.

The *intrinsic* acidic properties of all the samples were measured in apolar solvent (cyclohexane) by titration with the PEA basic probe, able to titrate all the surface acid sites of any acid strength. The main results obtained are reported in Table 1 as amount of acid sites per unit mass (mequiv. g<sup>−1</sup>) as well as per surface area (μequiv. m<sup>−2</sup>), titrated at a fixed equilibrium PEA concentration (1 × 10<sup>−4</sup> M). For the Si–Nb samples of the aqueous and organic series, the amount of acid sites reflected the trend of surface area of the samples. For the samples prepared by impregnation, the small differences of surface area of the samples do not allow to evidence the same trend. In the titration of *intrinsic* acidity all the sites present on the surface are titrated, as a consequence wider is the surface higher is the number of sites.

A different trend emerged when the acid sites titration of the samples by PEA was performed in water. Due to the polar and protic properties of water, some of the acidic groups at the surface can interact with the water molecules preventing from their

titration. PEA could only displace the adsorbed water molecules from the most acidic sites. The acid–base titration in water leads to the *effective* acid sites determination, which is tightly related to the catalytic action occurred in water. Also in this case, a comparison is possible at PEA fixed equilibrium concentration (1 × 10<sup>−4</sup> M). As shown in Table 1 the number of the *effective* acid sites does not follow the trend of surface area of the samples. Looking in particular at the acidity per surface area (μequiv. m<sup>−2</sup>) but also at the ratio between *effective* to *intrinsic* acid sites, it seems evident for both the aqueous and the organic series samples that the

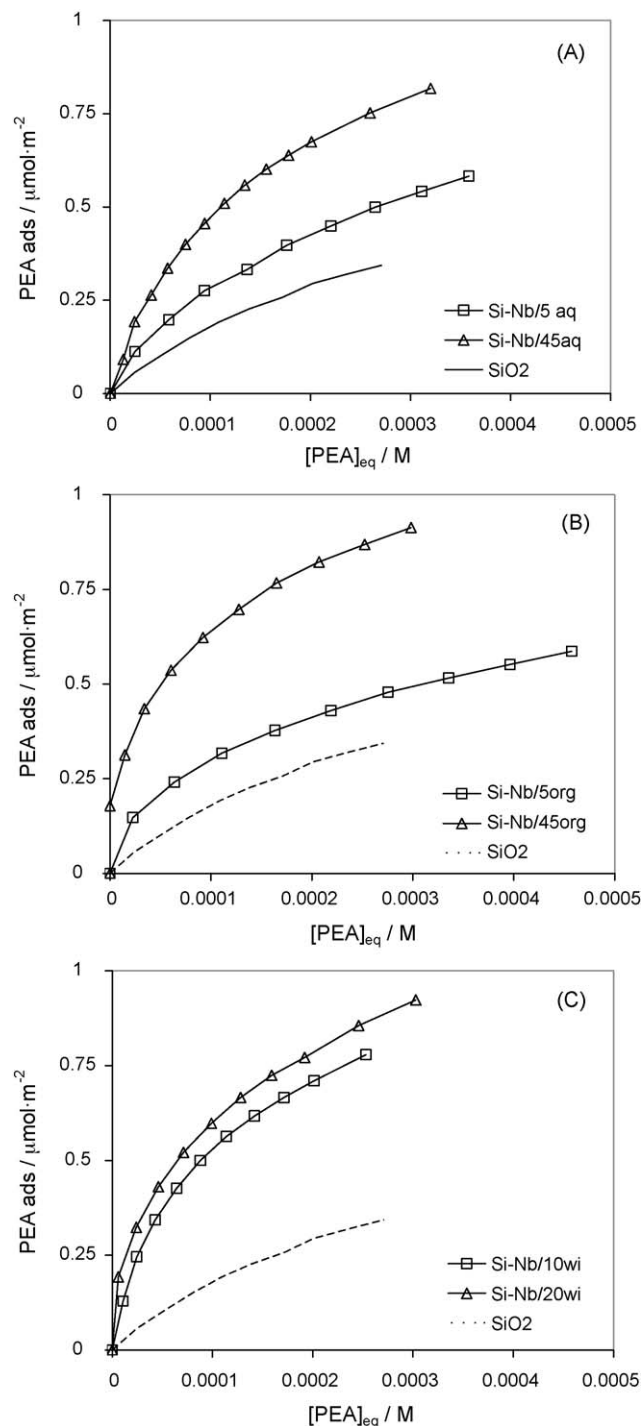
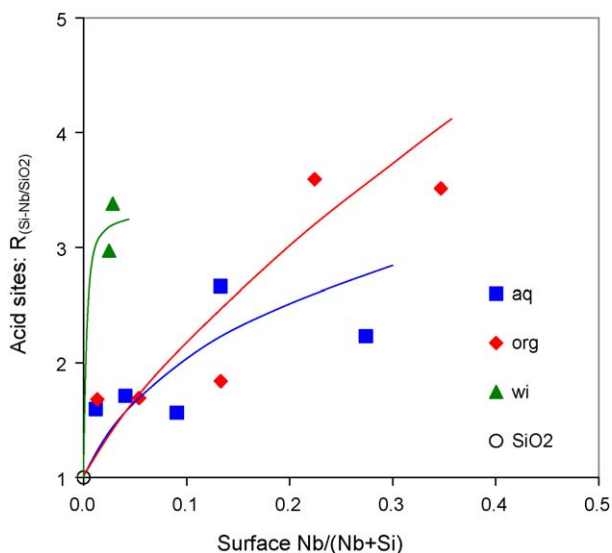


Fig. 4. Catalyst *effective* acidity: isotherms of PEA adsorption at 17 °C in water. (A) Si–Nb/5<sub>aq</sub> (□), Si–Nb/45<sub>aq</sub> (△), and SiO<sub>2</sub> (—); (B) Si–Nb/5<sub>org</sub> (□), Si–Nb/45<sub>org</sub> (△), and SiO<sub>2</sub> (---); and (C) Si–Nb/10<sub>wi</sub> (□), Si–Nb/20<sub>wi</sub> (△), and SiO<sub>2</sub> (---).





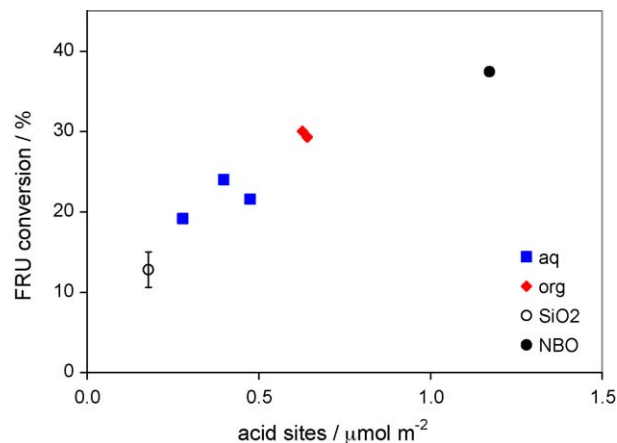
**Fig. 5.** Ratio between the *effective* acid sites of Si-Nb samples and those of SiO<sub>2</sub>, determined at PEA concentration of  $1 \times 10^{-4}$  M (see Table 1), as a function of surface Nb-concentration (as determined from XPS, see Table 1): aq, samples prepared by *aqueous route* synthesis; org, samples prepared by *organic route* synthesis; wi, samples prepared by wet impregnation.

*effective* acidity is increasing with the niobia concentration. This behaviour is expected as the niobia surface sites are stronger than those of the silica phase.

In Fig. 4, are drawn some examples of isotherms of PEA adsorption obtained at 17 °C in water for the different series of samples, compared with the isotherm relevant to SiO<sub>2</sub>. As above underlined, higher values of adsorbed PEA were obtained with samples at higher concentration of Nb. Starting from the isotherms, the adsorption constants (or Langmuir constant *b*) were evaluated. The *b* values can account for the average strength of interaction between the acid sites and the PEA probe. An increasing trend of the *b* values with increasing Nb loading was obtained (*b* values from 5000 to 7300 M<sup>-1</sup>, from 7800 to 19,000 M<sup>-1</sup>, from 11,000 to 12,000 M<sup>-1</sup>, for the aqueous, organic, and impregnated series, respectively, and 3000 M<sup>-1</sup> for SiO<sub>2</sub>). The average strength of the surface is increasing with the surface enrichment of Nb. An analogous trend was observed in cyclohexane [19].

In Fig. 5, on the basis of the data of Table 1, the ratio between the number of *effective* acid sites ( $\mu\text{equiv. m}^{-2}$ ) of the Si-Nb samples and those of SiO<sub>2</sub>, is reported as a function of surface Nb-concentration determined by XPS analysis [19]. In every case, the amount of *effective* acidic sites was increasing with the surface Nb-concentration. The highest values were obtained for the impregnated series samples and the lowest for the aqueous series samples.

A series of PEA titration in water at different temperatures (up to 77 °C) is in progress to better study the surface heterogeneity of the samples. Preliminary results were obtained on Si-Nb/45<sub>aq</sub>, Si-Nb/45<sub>org</sub>, Si-Nb/20<sub>wi</sub>, and NBO samples. Experimental isotherms were transformed into the corresponding isosters for surface coverages in the range 0.01–0.09 mmol<sub>PEA</sub> g<sup>-1</sup>. The isosteric heats of adsorption (*Q<sub>st</sub>*) were evaluated from the slopes of the lines obtained by plotting  $\ln [\text{PEA}]_{\text{eq}}$  vs.  $1/T$ , in accordance with a van 't Hoff type equation. Lower values of *Q<sub>st</sub>* were calculated for Si-Nb/45<sub>aq</sub> and Si-Nb/45<sub>org</sub> (12 and 11 kJ mol<sup>-1</sup>, respectively) than for Si-Nb/20<sub>wi</sub> (32 kJ mol<sup>-1</sup>). All the *Q<sub>st</sub>* values obtained are lower than that obtained for NBO (68 kJ mol<sup>-1</sup>). The *Q<sub>st</sub>* values have to be considered as average values of acid strength. The lowest *Q<sub>st</sub>* values were obtained for the mixed oxides of the aqueous and organic



**Fig. 6.** Fructose conversion as a function of the amount of *effective* acid sites (determined at PEA concentration of  $1 \times 10^{-4}$  M, see Table 1) for selected catalyst samples (aq, samples prepared by *aqueous route* synthesis; org, samples prepared by *organic route* synthesis). Reaction conditions: temperature of 100 °C and contact time comprised between 25 and 30 g min ml<sup>-1</sup>. Silica: value extrapolated from lower contact times.

series at low Nb-concentration. A value nearer to the one of NBO was obtained for the impregnated sample in which Nb<sub>2</sub>O<sub>5</sub> aggregates are present.

A set of activity tests of fructose conversion was carried out in water with the catalysts of the aqueous and organic series. The results are summarized in Fig. 6, compared with results obtained with SiO<sub>2</sub> and NBO. The temperature of reaction was 100 °C and contact time comprised between 25 and 30 g min ml<sup>-1</sup>. All the data reported in the figure evidenced a clear unique dependence of the catalytic activity from the surface acidity, expressed as *effective* acidic sites concentration. In this case too, the increasing of fructose conversion played along with the HMF selectivity increasing.

#### 4. Conclusion

On the basis of the reported results, we can conclude that the *effective* acidity is related with the niobia centres present on the catalyst surface in silica-diluted niobia catalysts. Also the catalytic activity for fructose dehydration is strictly related with the surface concentration of niobia, that seems to be the *effective* active phase in the samples.

The low or absent deactivation of the Si-Nb catalysts can likely be attributed to the dilution and dispersion of the niobia centres. The presence of strong Nb-acid centres close the ones to the others, as in the case of NBO, probably is the cause of the formation great amounts of humines or other insoluble residues on its surface responsible of the observed deactivation.

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