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Synergy effect between solid acid catalysts and concentrated carboxylic acids solutions for efficient furfural production from xylose

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ABSTRACT

An efficient furfural formation from xylose was demonstrated combining a concentrated aqueous solution of acetic acid and solid acid catalysts. Higher furfural yields and selectivities were obtained by comparison to the catalytic performances obtained in pure water. The evident synergy effect observed at 150 °C between the aqueous carboxylic acid solution and the solid acid catalysts is tentatively explained by the occurrence of two phenomena: 1) the contribution of Lewis acid sites which would operate in cooperation with the homogeneous weak Brønsted acidity brought by the aqueous acetic acid solution. According to the literature, the two steps mechanism involving the xylose-xylulose isomerization over Lewis acid sites and the successive Brønsted acid catalyzed cyclodehydration to furfural would be the prevailing reaction pathway in the heterogeneous–homogenous catalytic system at 150 °C. 2) an enhancement of the surface solid acid coverage by the carbohydrate and furfural owing to the presence of carboxylic acid in the aqueous solution as shown by comparative liquid phase adsorption experiments done in pure water and in aqueous acetic acid solutions. Among a series of solid acid catalysts, ZrW, $Cs_2HPW_{12}O_{40}$, HY (Si/Al = 15), K10 and NbOH, the latter one, NbOH used non-calcinated was shown to be active, selective and stable in the aqueous acetic acid media. HY and K10 are as active and selective for furfural formation but suffer for a strong Al leaching which precludes their utilization as true solid acid catalyst in acetic acid media.

1. Introduction

Upgrading the carbohydrates biomass into high value-added chemicals is a current research topic of high interest [1]. Among the principal sources of carbohydrates, cellulose, a hexose biopolymer, has already well established applications, mainly in the paper industry. By contrast, hemicelluloses have limited identified applications and are still considered as an agriculture waste for example in bagasse sugarcane. In this xylan rich biomass, hemicelluloses are composed mainly of pentoses and the principal commercial product derived from them is furfural, obtained from the dehydration of the C5 units forming the polysaccharide (Scheme 1). This is an industrial process known since the earlier 1900, and the world production is about 250,000 tons annually. The potential of the furfural yield depend on the composition of the biomass and may ranges from 150 to 220 kg of furfural produced per metric ton of dry biomass [2].

Today, the most widely used process in the industry is the Quaker Oats process, which uses sulphuric acid as catalyst and a furfural steam distillation. This process is characterized by a limited yield in furfural, 35% due to side reactions and by an excessive water vapour consumption [3]. Other new processes have been developed but are not yet commercialized such as the SupraYield process which claims a furfural production (up to 50%) thanks to a discontinuous reactor working at high temperatures (200–225 °C) and high pressures (15–30 bars) but at a low contact time [4]. Nowadays, there is a need to develop a sustainable process which might avoid the use of strong mineral acids, such as sulphuric acid, and their drawbacks: low selectivity, equipment corrosion, health and environmental issues, impossibility of catalyst recycling. This justifies the growing interest in the search for heterogeneous acid catalysts for conducting in an efficient and sustainable way the furfural production from xylose dehydration.

One of the first reports on the use of a heterogeneous catalyst for the transformation of xylose in furfural is from Moreau et al. in 1998 [5]. They reported the use of H-mordenite and H-faujasite zeolites in a biphasic medium composed of water and toluene or MIBK (methyl isobutyl ketone) as furfural extractive solvent. This methodology allows the furfural extraction from the water phase, in order to avoid its degradation. The furfural selectivity achieved 82% for a xylose conversion of 51%. Since this pioneering work, others zeolites such as ZSM-5 [6], HUSY, H-Beta [7–9], H-mordenite

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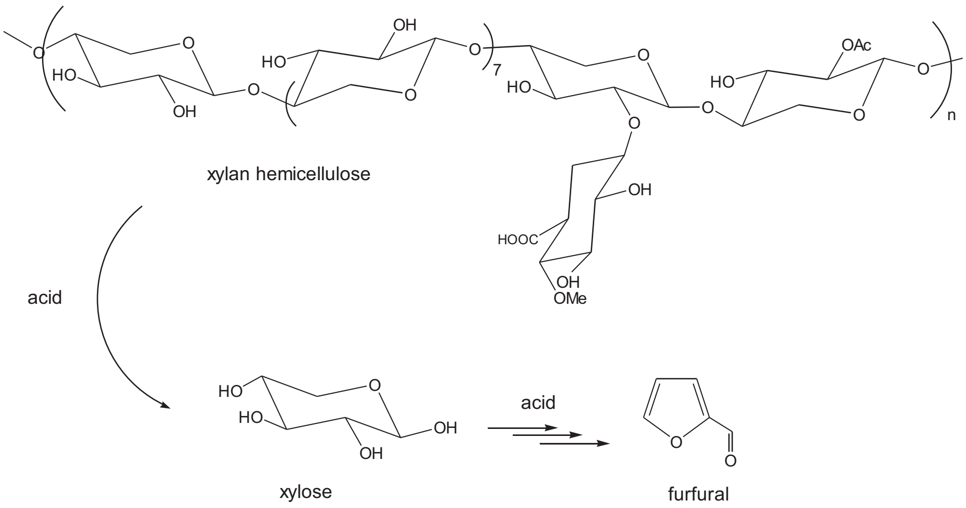

Scheme 1. Furfural formation from xylan hemicelluloses.

[7,10], SAPO-11 [8,9] and solid acids like niobic acid [11] or even sulphonated graphenes [12] have been introduced for this reaction. It can be mainly concluded from all these studies that zeolites with small pore size and a low mesoporous volume, are more effective for the dehydration of xylose and more selective when used in the presence of an extractive solvent, leading to high furfural yields.

Indeed, as evocated above, in the more general field of catalytic sugars cyclodehydration, most of the studies have been carried out in the presence of an extractive solvent to increase the furanic derivatives yields. Cabezas et al. and Corker et al. studied the influence of the solvent employed during the extractive reaction. They reported that furfural is easily degradable due to side reactions forming humins when the reaction occurs in water, at high temperature [13,14]. Thus, various systems have been evaluated in order to determinate the benefit of using either MIBK, toluene, isobutyl acetate or alcohols such as methyl-2-butanol and 2-ethyl-1-hexanol. Alkyl-phenols are also applied with success to get high furfural yields [15]. Toluene appeared to be the most efficient solvent, leading to the highest furfural yields up to 80%. Despite its toxicity and unlikely industrial large scale application, this solvent has been further studied with different catalytic systems. Dias et al. used this solvent, in proportion of 70 wt%/water to explore the activity of several solid catalysts. Whatever their catalytic activity and selectivity in furfural in pure water, heteropolyacids (PW, SiW and PMo) [16,17], cesium-based heteropolyacids [18], titanium and niobium nanosheets [19], niobium-based silicates [20] and silica supported sulphated zirconia [21] have greater catalytic performances when used with toluene as extractive solvent. Note that DMSO, when used as co-solvent added to the aqueous phase, has also a positive influence to the furanic derivatives yields. Its role is less documented, but it was proposed in the similar reaction of glucose dehydration into 5-hydroxymethyl furfural (5-HMF), that adding DMSO to water might favor the furanose form of hexoses which exists in negligible proportion in pure water. It was also proposed that DMSO addition to water could reduce the condensation reactions and the successive rehydration of 5-HMF associated by the reduced proportion of water [22]. However, beside the efficiency of the extractive reaction methodology applied to sugar dehydration, it is scarcely underlined that due to the low partition coefficient of furfural to the organic solvent, its efficient extraction depends on salts addition in high amounts leading to complex reaction media [15]. If this methodology can suit well to the use of homogeneous mineral acids, it will not be compatible with the use of a heterogeneous solid acid, due to the possible solid acid catalyst deactivation via cationic exchange as evocated recently by Dumesic et al. [23].

In order to go further in the development of an environment-friendly process, we decided to study sugars cyclodehydration in aqueous media without resort to an organic extractive solvent with potential toxicity. Previous works from our group have shown the benefit to perform hexoses dehydration in concentrated aqueous solutions of carboxylic acids. From fructose, 5-HMF yields of 60% were achieved in concentrated aqueous solutions of lactic acid. In pure water, from the screening of a large panel of solid acid catalyst, we have shown that the most efficient one was niobium hydroxide acid (NbOH) which led to a maximum 5-HMF yield of 30% [24]. Notably, this 5-HMF yield was obtained only when a high catalyst to sugar ratio was used. When NbOH was used in catalytic proportion, 5 wt%, the 5-HMF yield was limited to 10%.

To go further in the development of an efficient and green way to dehydrate monosaccharides, the present work aims to evaluate a large panel of different solid acid catalysts for xylose cyclodehydration in pure water and to perform an comparative evaluation of a concentrated aqueous solution of acetic acid as reactive medium, in the absence or in the presence of added solid acids. It was expected from this methodology to evidence or not, the occurrence of a synergy effect between the homogeneous weak Brønsted acid, acetic acid and the solid acid catalysts.

2. Experimental

2.1. Catalysts

Tungstated zirconia (ZrW) was prepared by anionic exchange according to an optimized method [25]. The acidic cesium salt of phosphotungstic acid $Cs_2HPW_{12}O_{40}$ (Cs_2HP) was prepared by precipitation through a previously reported procedure [26]. Niobium hydroxide (NbOH) was obtained from CBMM (Brazil) and used as received without calcination. Zeolites HY (Si/Al = 15), ZSM-5 (Si/Al = 40) were provided by IFPEN. K10 was purchased from Aldrich.

2.2. Catalysts characterization

The specific surface areas were determined by nitrogen adsorption at −196 °C using a Micrometrics ASAP 2020 equipment. Samples were previously degassed at 150 °C under vacuum (10^{-3} Pa) for 5 h. Surface areas were calculated using the Brunauer–Emmett–Teller (BET) methods.

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Ammonia adsorption was measured by gravimetry using a Setaram DTA-DTG 92-12 apparatus. 25 mg of the sample was weighed in a platinum holder and in situ pre-treated under helium flow (40 cm^3 min^{-1}) at 150 °C for 3 h. After cooling the solid down to 80 °C under helium flow, the solid was saturated with ammonia using an ammonia stream diluted in helium (1%), and then a pure helium flow was introduced at 80 °C to remove the reversible ammonia uptake. The total amount of acid sites was deduced from the irreversible ammonia adsorption at 80 °C.

FTIR spectra of self-supported pellets (ZrW, NbOH, K10, HY) or of $Cs_2HPW_{12}O_{40}$ spread on a silicon plate were recorded with a Brucker Vector 22 spectrometer in the absorption mode with a resolution of 2 cm^{-1}. The samples were placed in an IR cell equipped with CaF_2 windows and treated in situ. The wafers of ZrW, K10, HY and NbOH samples were pretreated under vacuum at respectively at 400 °C or 150 °C for the later one. The heteropolyacid dispersed on the silicon plate was vacuum treated at 200 °C. Pyridine was adsorbed under saturation vapor pressure at ambient temperature then desorbed at 150 °C for 1 h in order to remove the physisorbed species.

Calorimetry of NH_3 adsorption: The acid properties were measured by NH_3 adsorption at 80 °C, using a **TianCalvet calorimeter** coupled with a volumetric equipment. The catalysts samples of NbOH and $Cs_2HPW_{12}O_{40}$ (0.1 g) were evacuated at 150 °C and 200 °C respectively for 1 h under secondary vacuum. The others samples, ZrW and HY were pretreated at 400 °C in the same conditions. Then, the pre-treated samples were placed into the calorimeter up to the stabilization of the temperature (one night), then contacted with small doses of gas up to equilibrium and the differential enthalpy of adsorption was recorded together with the amount of adsorbed NH_3.

2.3. *Xylose dehydration reactions*

The catalytic conversion of xylose (Sigma–Aldrich, >99%) into furfural was studied in a magnetically stirred 100 mL autoclave, heated with a controlled heating envelop. In a typical procedure, xylose (0.6 g), powdered catalyst (30 mg), water (60 mL), or in the case of 20 wt% of acetic acid solution, water (48 mL) and acetic acid (12 mL), were introduced into the autoclave. The reactor was flushed and pressurized with argon, and then heated to the desired temperature. Zero time was the instant where the internal temperature of the vessel reached the target temperature. At the end of a run the autoclave was cooled down to room temperature using ice bath, the solid catalyst and possibly solid humins were filtered off (0.45 μm Teflon filter) and the liquid phase were recovered for analysis.

The identification and quantification of the reaction products in the aqueous phase were conducted by Shimadzu LC-20AD HPLC (COREGEL 87C column, 80 °C) equipped with a refractive index detector using water as eluent (0.6 mL min^{-1}). Authentic samples of xylose, furfural and levulinic acid (Sigma–Aldrich, 99%) were used for calibration. Levulinic acid is the main by-product identified when the reaction is performed in water; the presence of acetic acid prevents its identification by HPLC due to overlapping peaks.

Xylose conversion, furfural yield and selectivity were calculated as follows:

$$\text{Conversion}\,(\%) = \frac{\text{mol of initial xylose} - \text{mol of unreacted xylose}}{\text{mol of initial xylose}} \times 100$$

$$\text{Yield}\,(\%) = \frac{\text{mol of furfural}}{\text{mol of initial xylose}} \times 100$$

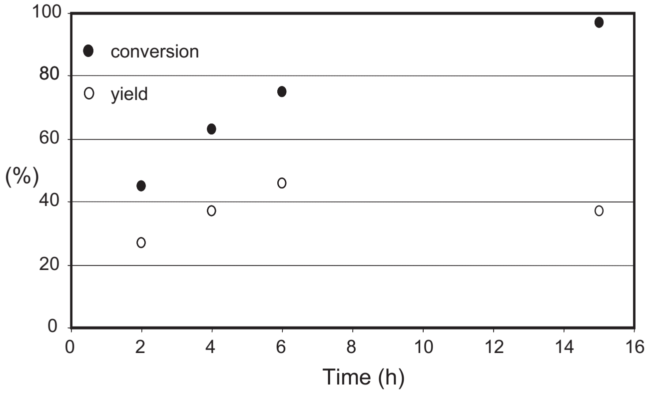

Fig. 1. Kinetic of xylose dehydration into furfural performed in 20 wt% acetic acid solution in the presence of NbOH. Conditions: Xylose 1%wt, solvent 60 mL (20 wt% of acetic acid in water), 150 °C, NbOH: 5 wt%/xylose.

$$\text{Selectivity}\,(\%) = \frac{\text{Yield}\,(\%)}{\text{Conversion}\,(\%)} \times 100$$

Few preliminary experiments were performed in order to set some conditions, and especially the reaction time. For that we studied the influence of the presence of one of the reported most active catalyst, the Nb based catalyst, NbOH, in 20 wt% aqueous acetic acid solution. The temperature was first set up at 150 °C as reference to literature data. Due to the volatility of furfural/water azeotrop as regard xylose, the progress of the reaction was not followed by taking liquid samples at regular times, but we performed distinct reactions at various reaction times for kinetic studies. The xylose conversion and the furfural yield are shown in Fig. 1.

We note that, while the xylose conversion increased regularly with time, the furfural yield started to decrease in the second part of the reaction. As already evocated above, this is most likely due to furfural degradation after prolonged reaction times in the absence of extraction solvents. From these preliminary experiments done on one of the most active solid catalyst, we decided to fix the reaction times at 6 h or 15 h for the following studies. The data obtained at 6 h will be used to calculate the rate of xylose conversion and the furfural production although the slight decrease of the reaction rate after 6 h of the reaction observed for one of the most active catalyst (Fig. 1). Reaction performed for 15 h will be especially useful to compare the less active catalysts.

3. Results and discussion

3.1. *Catalysts characterization*

The main acidic features of these solid acids, such as the nature of acidity (Lewis/Brønsted) determined by IR of Py adsorption and their strength, measured by calorimetry of ammonia adsorption (Q_{diff} NH_3) were already reported in our previous publications [24,27–29]. These data are summarized in Table 1, together with the total number of acid sites determined by irreversible NH_3 adsorption monitored by gravimetry and the BET surface areas.

The catalyst selection contains two strong solid acids: a tungstated zirconia, dominated by the Lewis acidity and the acidic cesium salt of 12-tungstophosphoric acid which contains exclusively Brønsted acid sites. The three others solids, K10, HY and NbOH are weaker acids. While K10 and HY are dominated by the Brønsted acidity, NbOH presents more Lewis acid sites than Brønsted ones (Fig. 2). Notably, NbOH presents the highest acid sites density.

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Table 1
BET surface area and acidic features of the solid catalysts used in this study.

Catalyst	Acidity[a]	BET surface area ($m^2\ g^{-1}$)	Total acid sites[b] ($\mu mol\ g^{-1}$)	Acid sites density ($\mu mol\ m^{-2}$)	Qdiff[c] NH_3 adsorption ($kJ\ mol^{-1}$)
ZrW	**Lewis** (Brønsted)	118	189	1.6	160
Cs_2HP	**Brønsted**	105	189	1.8	200
K10	**Brønsted** (Lewis)	233	129	0.6	–
HY(Si/Al = 14)	**Brønsted** (Lewis)	718	187	0.3	140
NbOH	**Lewis** (Brønsted)	144	469	3.3	150

[a] Determined by in situ IR spectroscopy of pyridine adsorption. The dominant nature of acidity is written in bold letters.
[b] Measured by NH_3 adsorption monitored by gravimetry as described in the experimental part.
[c] Measured by calorimetry of NH3 adsorption

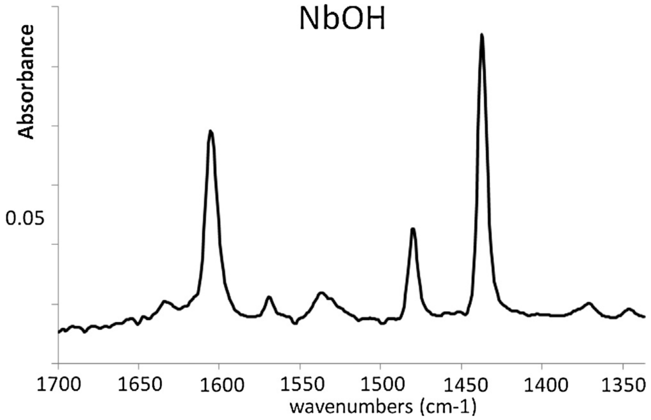

Fig. 2. Infrared spectrum of pyridine adsorption on NbOH then vacuum treated at 150 °C.

3.2. Catalytic studies

3.2.1. Comparison of solid acid catalysts for xylose cyclodehydration in furfural in pure water or in concentrated acetic acid solution (20 wt%)

The catalytic performances of the selected solid acid catalysts were evaluated in pure water first (Fig. 3) and then in a concentrated aqueous solution of acetic acid (Fig. 4).

In the absence of solid catalyst, the xylose conversion is limited to 10% after 6 h of reaction in pure water at 150 °C with a furfural yield of 6% (Fig. 3).

Higher xylose conversion and furfural yield are observed in acetic acid solution, respectively 17% and 11% (Fig. 4). Thus, at 150 °C, a 20 wt% aqueous solution of acetic acid is only slightly a more reactive media than pure water as regards to xylose dehydration. One can consider that these conditions are convenient to evaluate the promotion effects of solid acids addition since the xylose conversion is limited in these both homogeneous liquid media under these conditions of reaction.

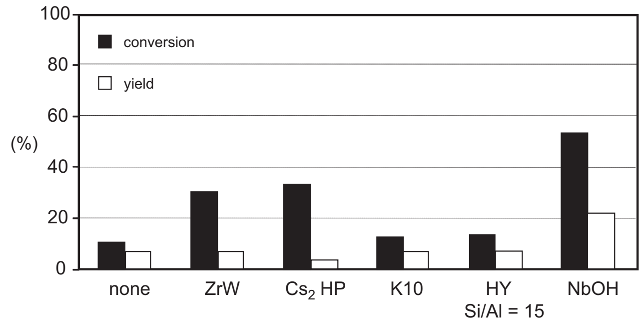

Fig. 3. Xylose dehydration into furfural performed in pure water. Influence of solid acid catalysts. Xylose 0.6 g, catalyst 30 mg, water 60 mL, 150 °C, 6 h.

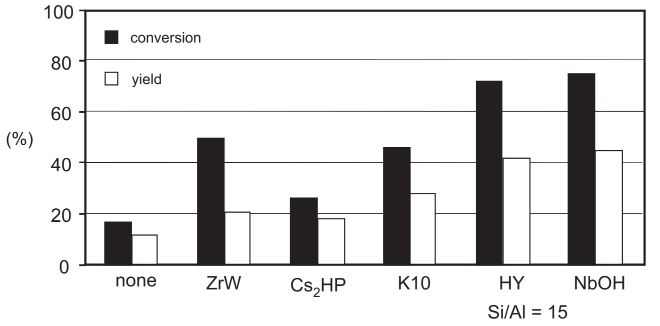

Fig. 4. Xylose dehydration into furfural performed in 20 wt% acetic acid. Influence of solid acid catalysts. Xylose 0.6 g, catalyst 30 mg, solvent 60 mL, 150 °C, 6 h.

In pure water, we can observe from Fig. 3 that, ZrW, $Cs_2HPW_{12}O_{40}$ and the niobium hydroxide are active catalysts leading respectively to xylose conversions of 30, 33 and 53%. The niobium hydroxide, which was used without preliminary calcination step, is by far the catalyst leading to the highest furfural production in pure water, reaching up to 22% yield in furfural. On the contrary, ZrW and $Cs_2HPW_{12}O_{40}$ have a very low selectivity in furfural, leading mostly to the formation of levulinic acid and humins. The HY zeolite and the K10 clay exhibit a reduced activity equivalent to that measured in the blank experiment. To go further in the understanding of the catalysts reactivity, let us consider the catalysts acidic features presented in Table 1. It seems that the acid sites density might be correlated with the catalysts activity for xylose conversion in pure water. The most active catalysts, ZrW, Cs_2HP, NbOH are all of them characterized by a significant highest acid sites density compared to K10 and HY which are, comparatively, not efficient catalysts in these conditions. The nature of the acidity Lewis/Brønsted and the acid strength do not find clear correlations with the xylose conversion nor the furfural selectivity in pure water. We can just underline that the most efficient solid catalyst to produce furfural in pure water is, within our catalysts selection, NbOH and this catalysts is characterized by the highest density of acid sites of medium strength with a low Brønsted/Lewis acid sites ratio. The present study does not confirm a previous one which reported the required high Brønsted/Lewis acid sites ratio to get selectively furfural from xylose in water [30].

The solid acids series has been evaluated **in concentrated aqueous acetic acid media**, in the same conditions, for 6 h at 150 °C (Fig. 4). In the absence of solid acids, by changing the reaction medium from water to the aqueous solution of acetic acid (20 wt%), the xylose conversion was raised from 10 to 17% and furfural yield from 6 to 11% only. Thus, these conditions, 6 h of reaction at 150 °C, are convenient to evidence the occurrence of a beneficial effect of the addition of a heterogeneous acid function to the homogeneous weak Brønsted acidity brought by the concentrated aqueous acetic acid medium. Starting from glucose, we reported recently that glucose is not dehydrated in 20 wt% acetic acid solution after 2 h of reaction at 150 °C, but upon addition of a strong solid Lewis acids

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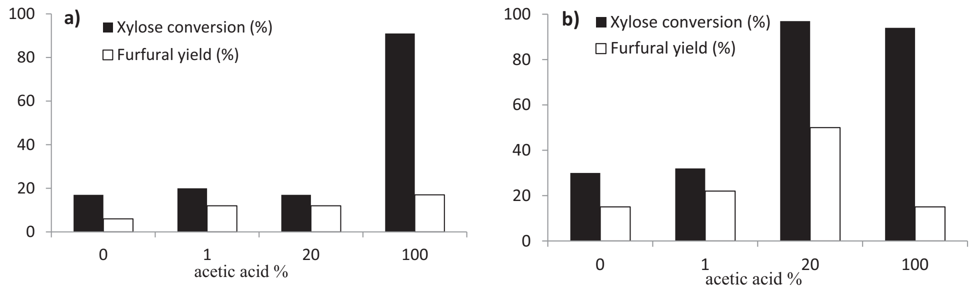

Fig. 5. Xylose cyclodehydration into furfural- Influence of acetic acid concentration in the absence (a) or presence of solid acid catalyst (b). Conditions: Xylose 0.6 g, water 60 mL, 150 °C, 6 h. Catalyst: H-ZSM-5, (Si/Al = 40) 30 mg (a).

Table 2
Rate of xylose conversion in pure water or in aqueous solution of acetic acid. Influence of the presence of solid acids.

Catalyst	Rate of xylose conversion[a] (10^{-4} mol h^{-1})	
	Water 100%	Acetic acid 20%
None	0.7	1.1
ZrW	**2.0**	**3.3**
Cs_2HP	2.2	1.8
NbOH	**3.6**	**5.0**
K10	**0.8**	**3.1**
HY Si/Al = 15	**0.9**	**4.8**

[a] Calculated after 6 h of reaction. Xylose 0.6 g, catalyst 30 mg, solvent 60 mL, 150 °C.

such as tungstated alumina (AlW), a promoting effect was observed, leading to a glucose conversion of 25% in the case of AlW but unfortunately to a low selectivity into 5-HMF [24]. These solids were assumed to isomerize glucose into fructose, the latter being more easily converted in the reactive aqueous acetic acid medium, shown to be very efficient to dehydrate selectively fructose into 5-HMF. In the present work, we observe from Fig. 4 that when the homogeneous acetic acid medium is combined to a heterogeneous acid catalyst, the xylose conversion and the furfural yields are promoted in a general rule, but this is not true for Cs_2HP. For NbOH, HY and K10 the xylose conversion and the furfural yields overreached the sum of the contribution of the solid acids in water in one part and the homogeneous acetic acid solution in another part. This is indicative of a synergy effect between the homogenous reactive phase, 20 wt% aqueous solution of acetic acid, and the heterogeneous solid acid sites. In order to quantify the synergy effect observed between the acetic acid solution and the different heterogeneous acid catalysts, the rates of xylose conversion have been calculated in both media, in the presence and absence of added solid catalysts (Table 2). It is shown that this synergy effect is marked for ZrW, NbOH, K10 and HY catalysts.

It is noteworthy that the catalysts which were the most active in water, ZrW and Cs_2HP, respectively strong Lewis and Brønsted acids, are still active in acetic acid media but more selective into furfural, 41 and 65% respectively (Fig. 4). Niobium hydroxide becomes also more selective into furfural in the acetic acid medium and then becomes one of the most efficient catalyst for furfural production from xylose giving a furfural yield up to 46% (60% selectivity) after 6 h of reaction at 150 °C. The same remark holds true for HY and K10.

3.2.2. *Influence of the acetic acid concentration*

To investigate how the concentration of acetic acid solutions affect the furfural yield, two series of experiments were performed: the first one using different concentration of acetic acid in the absence of added solid catalyst (Fig. 5a), the second one in the presence of an added solid catalyst, H-ZSM-5 (Si/Al = 40) and different concentration of acetic acid (Fig. 5b).

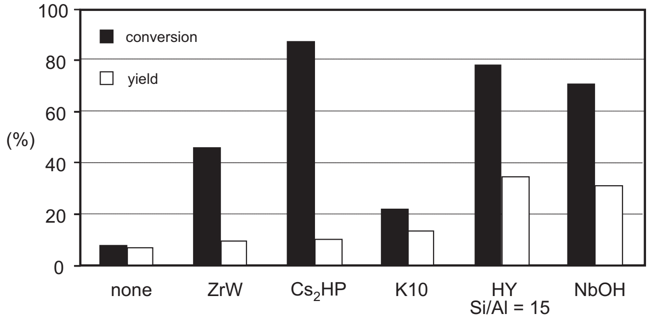

Fig. 6. Xylose dehydration into furfural performed in pure water. Xylose 0.6 g, catalyst 30 mg, water 60 mL, 150 °C, 15 h.

From Fig. 5a, one can deduce that the aqueous solutions of acetic acid are not efficient to catalyze the cyclodehydration of xylose in furfural at 150 °C, nor the anhydride acetic acid which leads to a full xylose conversion, but a limited amount of furfural. Other products were detected by HPLC but not identified. From the experiments done in the presence of the acidic zeolite, H-ZSM-5, it is seen in Fig. 5b that an improved yield in furfural is obtained only when the zeolite is used together with a concentrated solution of acetic acid, of 20 wt%.

3.2.3. *Impact of more severe conditions: increase of the reaction time and temperature*

A longer reaction time of 15 h has been tested on all the catalysts, in both media, pure water and 20 wt% aqueous acetic acid.

In pure water (Fig. 6), in the absence of solid acid, the xylose conversion is not favored at longer reaction time. It is the opposite in the presence of most of the solid acid catalysts except for K10. For ZrW and Cs_2HP, the xylose conversion increased, particularly for Cs_2HP, but the furfural yields did not. This may be explained by their too strong acidity which might promote successive transformation of adsorbed intermediates and favor some kind of polymer and/or humins formation more or less soluble. This was supported by the fact that carbon balances generally higher than 80% were obtained from Total Organic Carbon (TOC) analysis for the reaction performed in water. Note also that TGA-DTA analysis done on the used catalysts recovered by filtration, evidenced the presence of carboneous compounds and/or deposit. The yield of solid humins deduced from the TGA experiment is between 3 and 5 wt%, without significant differences between the two liquid media nor the nature of the catalyst. When NbOH is used, the furfural yield grows up to 31%, without noticeable decrease of the selectivity. The HY zeolites presents a peculiar behavior with a marked enhancement of its catalytic activity when the reaction time increased from 6 to 15 h: after 15 h of reaction, the furfural yield achieved 35% with a furfural selectivity of 46%, which represents even a better performance than NbOH for xylose dehydration in pure water. As a

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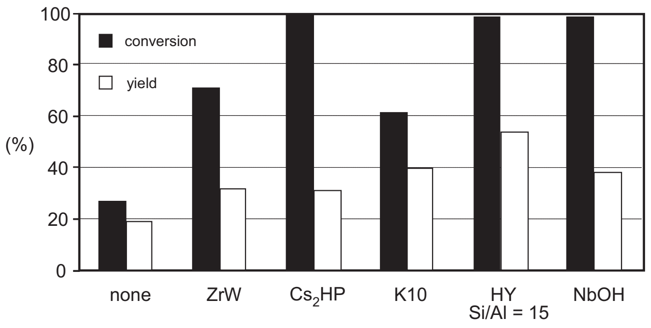

Fig. 7. Xylose dehydration into furfural performed in 20 wt% acetic acid. Xylose 0.6 g, catalyst 30 mg, solvent 60 mL, 150 °C, 15 h.

general remark, if for a category of catalysts, such as strong Lewis or Brønsted acids, longer reaction times have increased the formation of by-products such as levulinic acid and humins, for weaker solid acids, presenting Lewis/Brønsted acid sites, such as HY and NbOH, prolonged reaction times in water at 150 °C is not detrimental for the furfural selectivity.

In 20 wt% acetic acid solution (Fig. 7), a longer reaction time in the absence of solid catalyst enhanced the xylose conversion and the furfural yield up to 27% and 19%, respectively. Again, addition of ZrW and Cs_2HP, raised the xylose conversion as regards to the pure water medium together with the furfural yield and selectivity. This tendency is not observed in pure water, the general rule in water medium over ZrW and Cs_2HP is to observe a decrease of the furfural selectivity when the conversion increases. Again, as regard to the pure water medium, for longer reaction time over K10, HY and NbOH, the improved activity is not accompanied by an enhancement of the furfural selectivity.

The xylose dehydration was also investigated at a higher temperature, 180 °C, in the two media. At this temperature, the blank experiments, done without solid catalyst, shows that the two media catalyze xylose dehydration into furfural, in water a xylose conversion higher than 40% was obtained with a furfural yield of 27% (Fig. 8), the acetic acid medium led to a complete xylose conversion with a furfural yield of 44% (Fig. 9). As a general comment, one can observe that in acetic acid solution high xylose conversions are observed, >90%, with furfural yield equals or higher than 40%. Note that in the presence of the following catalysts, Cs_2HP, K10 and HY, furfural yields close to 55% are achieved. In water, lower conversion levels are observed together with lower furfural yields, usually less than 40% (Fig. 8). Therefore, at 180 °C, we can still underline the positive impact of the aqueous acetic acid medium to limit by-products formation at the expense of furfural. Experiments were also conducted for longer reaction times at 180 °C. In both liquid media, 100% water and the aqueous acetic acid solution, almost total xylose conversions were obtained with in general a decrease of furfural yields accounting for the likely furfural degradation in these severe conditions. However, higher furfural yields are still observed in the acetic acid medium, i.e. the furfural yield is still close 50% after 15 h of reaction at 180 °C, in the aqueous acetic acid solution over K10.

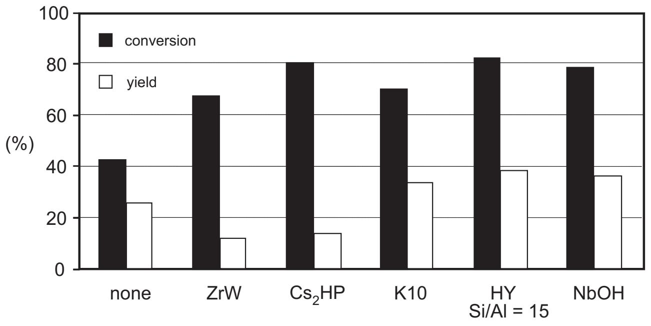

Fig. 8. Xylose dehydration into furfural performed in pure water. Xylose 0.6 g, catalyst 30 mg, water 60 mL, 180 °C, 6 h.

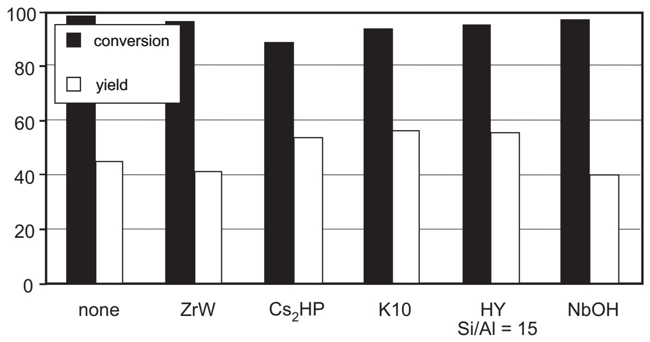

Fig. 9. Xylose dehydration into furfural performed in 20 wt% acetic acid. Xylose 0.6 g, catalyst 30 mg, solvent 60 mL, 180 °C, 6 h.

Table 3
Furfural stability in different media and conditions.

Medium	Temperature (°C)	Time (h)	Furfural loss (%)[a]
Water	150	6	5
Water + 30mgNbOH	***150***	***6***	***15***
Water	150	15	15
20% Acetic acid	150	6	15
20% Acetic acid + 30mgNbOH	***150***	***6***	***10***
20% Acetic acid	150	15	22
Water	180	6	22
Water	180	15	39
20% Acetic acid	180	6	12
20% Acetic acid	180	15	64

[a] Calculated introducing 100 mg of furfural in 60 mL of water or 20 wt% acetic acid in water.

3.2.4. Evaluation of furfural stability as a function of the medium, temperature, time and NbOH addition

Most of the data provided here correspond to the composition of the reaction medium at a given time since we did not perform specific kinetic studies. Only the data obtained at the lowest temperature, 150 °C, and short reaction time, 6 h, where the xylose conversion is limited, can be considered as “initial data” with a limited influence of the products adsorption/transformation. Indeed, in the preliminary experiments, we have evidenced over NbOH, in acetic acid medium, that the maximum furfural yield is reached between 6 h and 15 h (Fig. 1). Thus, to clarify the impact of the furfural instability on the data presented above, this was investigated in the different media and in the various used conditions. Results are presented in Table 3.

From these data, it is clear that furfural is less stable in the aqueous acetic acid medium than in pure water. However, to our surprise, this difference of furfural stability in these two media does not seem to be enhanced at higher temperature and prolonged reaction time. If after 6 h of reaction at 150 °C, a maximum of 15% of furfural has reacted in aqueous acetic acid medium and only 5% in water, at 180 °C after 15 h, the loss in furfural achieved 64% in aqueous acetic acid against 39% in water. Notably, upon NbOH addition, the furfural stability was increased in acetic acid media and the contrary is true in pure water.

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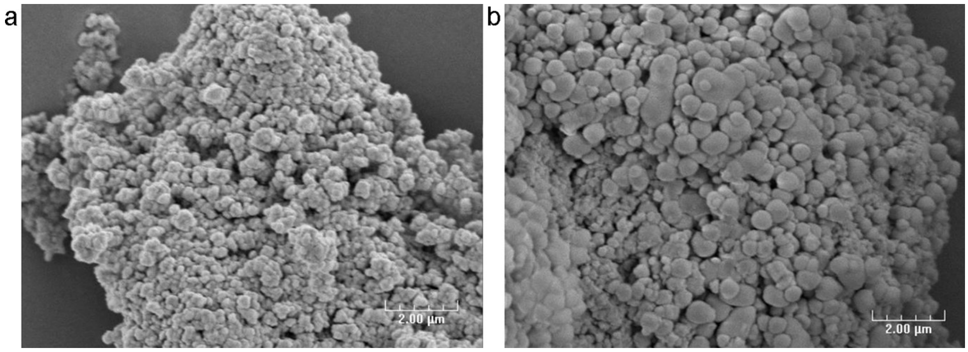

Fig. 10. (a) SEM image of fresh NbOH. (b) SEM image of used NbOH.

Table 4
Catalyst leaching given in terms of % of the leached elements.

Catalyst	100% water (metal)	20% acetic acid (metal)
ZrW	2.3 (W)	2.7 (W)
Cs_2HP[a]	–	–
NbOH	<0.2 (Nb)	0.2 (Nb)
K10	3 (Al)	25 (Al)
HY Si/Al = 15	15 (Al)	61 (Al)

Data obtained from the catalyst composition and the chemical analysis of the reaction liquid media recovered after filtration of the used catalyst. Reaction conditions: 150 °C for 15 h.

[a] $Cs_2HPW_{12}O_{40}$ catalyst cannot be separated by filtration.

3.2.5. Catalysts stability

To assess the stability of the catalysts, we have studied the leaching of the catalysts using elemental analysis of the recovered reaction liquid after filtration. Results are given in Table 4. Evaluations of the leaching were based on the analysis of the main elements: W, Nb and Al for ZrW, NbOH, K10 and HY, respectively.

This study shows that the K10 clay and the HY zeolite are not stable in pure hot water, nor in the aqueous acetic acid medium; the worst conditions being the hot aqueous acetic acid medium. Fortunately, ZrW and NbOH present a relative stability in these media and this is particularly true for NbOH, a selective catalyst into furfural from xylose cyclodehydration.

The morphology of fresh and used NbOH was observed SEM. Fig. 10 shows the presence of additional spherical particles, characteristic of the formation of solid humins.

3.3. Discussion

In an attempt to rationalize the impact of the two liquid media, we plotted in Fig. 11 the furfural selectivities as a function of xylose conversions, in the presence of solid acid catalysts, at 150 °C and for 6 h of reaction time (conditions which do not lead to significant xylose conversion without solid catalysts).

This figure evidences that the aqueous acetic acid solution is a more adequate medium than pure water to produce selectively furfural from xylose. For each medium, the promoting effect depends on the nature of the solid acids.

In **pure water**, Fig. 11 shows the negative impact of strong solid acid addition, such as ZrW and Cs_2HP. On the opposite, weaker acids such as NbOH and HY favor the furfural formation from xylose in pure water, with a furfural selectivity higher than 40% at high conversion, 80%.

In concentrated aqueous solutions of acetic acid, it is also clearly evidenced that the use of solid acids of moderate strength such as HY, K10 or NbOH enhances the furfural selectivity at high xylose conversion level (a maximum selectivity of 54% at full conversion for HY). We can consider that these three solids provide as well Lewis and Brønsted sites of moderate strength. Indeed, NbOH provides heterogeneous superficial acid sites with a dominant Lewis acidity since NbOH is stable is the acetic acid media. On the contrary, HY and K10, known as mainly Brønsted solid acids, are not stable in the acetic acid medium, they release important amount of Al species which might act as soluble Lewis species.

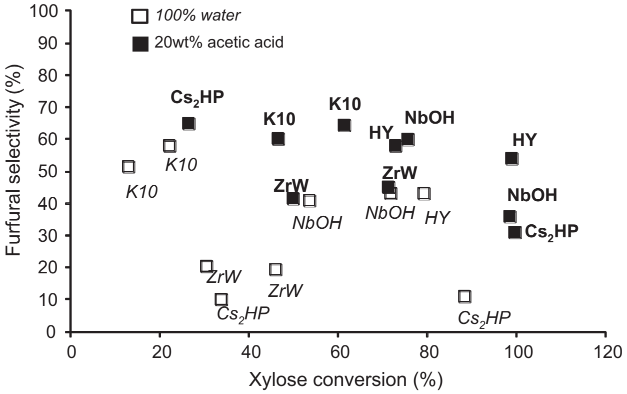

Fig. 11. Furfural selectivities as a function of xylose conversion. Dependence on the liquid medium: 100% water versus 20 wt% aqueous acetic acid solution. Xylose 0.6 g, catalyst 30 mg, solvent 60 mL, 150 °C, 6 or 15 h.

It was recently proposed that xylose dehydration into furfural might proceed efficiently via an intermediate aldose-ketose isomerization (xylose to xylulose) promoted by a solid base, and further cyclodehydration of xylulose, a ketopentose, into fufural [31,32].

Such a picture is now well accepted for glucose dehydration into 5-HMF which requires the intermediate isomerization of glucose into fructose, the aldohexose which is easily dehydrated into 5-HMF. Also, it is known for a long time that the glucose isomerization step is catalyzed by bases [33,34], but recently, the efficiency of Lewis solid acids has been demonstrated even in water medium [35]. In a similar way, the participation of Lewis acid sites to the efficient furfural production from xylose was recently proposed by Stein et al. [36] and Yang et al. [37] Thus, in the present work, by combining different solid acid catalysts to the concentrated aqueous carboxylic acid solution, resulting in high selectivities and furfural yields, a reasonable explanation is to ascribe the synergic effect to the Lewis acidity of moderate strength of the solid acid catalysts in the case of NbOH or of the leached Al species for K10 and YH which have lost 25% and 61% of their Al content in the acetic acid solution. Indeed, these solids could provide the Lewis acid sites of adequate strength to assist the aldose-ketose isomerization and therefore accelerate the rate of furfural formation by cyclodehydration, a Brønsted acid catalyzed step (route 2, Scheme 2). Over NbOH, a stable catalyst in the acetic acid medium, the aldose-ketose

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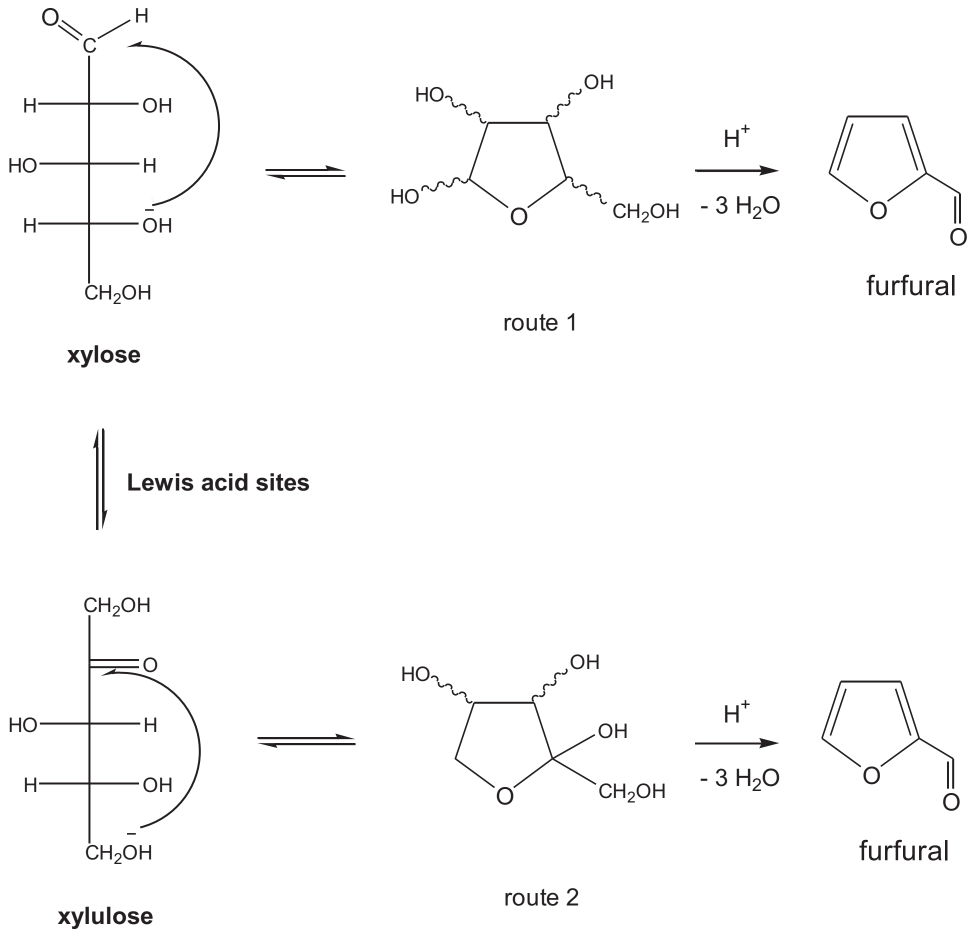

Scheme 2. Possible pathways for catalytic furfural synthesis from xylose.

isomerization would occur on the solid catalyst surface, while over HY and K10, leached Al species might also catalyze this isomerization step.

At high temperatures, 180 °C, it is seen that high rates of furfural formation are obtained even without out added solid catalysts. This indicates that a direct pathway, involving a unique step, the direct xylose cyclodehydration into fufural is a pure Brønsted acid catalyzed step but a more energy demanding pathway (route 1, in Scheme 2).

A last but not least phenomenon might also contribute to this synergic effect between the concentrated aqueous acetic acid solution and the solid acid catalysts at 150 °C. Indeed, from the literature data it is generally reported that over-catalytic amounts of solid catalysts were systematic used to observe an effect of the solid catalyst. It became more and more evident that the limited sugar affinity with the catalyst surface might be the key issue which infer the control of the sugar transformation on the catalyst surface when the reaction is done in water. One can anticipate that the carbohydrates molecules, which are highly hydroxylated organic molecules with high affinity with the liquid water molecules, must be adsorbed in a limited way from an aqueous solution to a solid surface. Thus the peculiar activity of NbOH (not calcinated) in water could find an explanation in its high hydroxylated form and its high acidic density which might favor the carbohydrate adsorption. Moreover, the question raised by the synergy effect observed by combining the aqueous concentrated acetic acid solution and solid acids could account for an enhanced solid surface coverage by the carbohydrates, a consequence of the high concentration of the carboxylic acid which would lower the bonding interaction between the carbohydrates and the water molecules.

Table 5
Adsorption of xylose and furfural over NbOH from solutions of xylose and furfural in 100% water or 20 wt% acetic acid.

Components	Liquid media	Total adsorption (μmol g^{-1})[a]
Xylose	Pure water	28
Xylose	20 wt% acid acetic in water	37
Furfural	Pure water	129
Furfural	20 wt% Acid acetic in water	2430

1 g of NbOH in suspension in 25 mL of xylose and furfural solutions (10 g L^{-1}). Agitation of the suspension for 4 h, under isothermal conditions at 30 °C. Determination of xylose and furfural adsorption by HPLC analysis.

[a] Adsorbed amount per gram of catalyst.

This idea has prompted us to compare the adsorption of xylose, and furfural on NbOH, in water or in 20 wt% acetic acid solution. The adsorption data are reported in Table 5.

The adsorption of furfural is by far higher than that of xylose. Interestingly, the addition of acetic acid significantly enhanced the adsorption of furfural on NbOH while the effect is rather limited on the xylose adsorption. This might be due to distinct intermolecular interaction between carbohydrates or furfural molecules with the liquid media ascribed to distinct polarities and hydrogen bonding network. Note that the total amount of furfural adsorbed on NbOH in aqueous solution of acetic acid over-reaches the total number of acid sites of NbOH, the adsorption measured in liquid phase involves the irreversible and reversible adsorption.

These data suggest that a higher catalyst surface coverage with xylose and furfural exists and may contribute to the synergy effect between the carboxylic acid solution and the solid acids, at the origin of the enhanced furfural formation from xylose. However, if

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the favored xylose adsorption account for the conversion increase, the enhanced furfural adsorption on NbOH would have a negative impact on the furfural production considering that further formation of levulinic acid and humins might be favored. Interestingly, the results do not support this scheme. Indeed, in Figs. 3 and 4, we can see that upon acetic acid addition, the xylose conversion was increased **together with the furfural selectivity**. Let us recall that, unfortunately, levulinic acid cannot be quantified due to overlapping peaks with acetic acid in the HPLC chromatogram. Then, to clarify the impact of acetic acid on the selectivity, we have also quantify by TGA, the weight amount of solid humins recovered with the aged catalysts by filtration: the yields in solid humins are similar in both liquid media in presence of NbOH, close to 4 wt%. These data preclude the favored successive formation of by-products caused by the improved adsorption of furfural on the catalyst surface. To strengthen this proposition, the furfural stability was also evaluated in the presence of NbOH in water and in acetic acid solution (see Table 3). We show that, upon NbOH addition in water, the furfural stability was decreased while in acetic acid aqueous solution, in presence of NbOH, the furfural stability was improved by 30% after 6 h of reaction at 150 °C: 15% of furfural were lost in water against 10% in acetic acid solution. Therefore, according to the unchanged solid humins yield upon acetic acid addition, to the enhanced furfural adsorption on NbOH in the presence of acetic acid and to the proved enhanced furfural stability, it seems reasonable to propose that the degradation reactions of furfural on the NbOH surface are slow down compared to the furfural degradation occurring in the homogeneous aqueous acetic acid liquid medium. In other words, the observed phenomenon seems to be caused by the furfural and xylose partition between the homogeneous phase and the catalyst surface, which was changed upon reactive co-solvent addition, acetic acid, in favor of the catalyst coverage. Accordingly, the superficial reactions would be favored at the expense of the un-selective homogeneous reactions.

4. Conclusion

In this work, we have studied the influence of the presence of solid acid catalysts in aqueous acetic acid solution for the transformation of xylose into furfural. Depending on the acidic features of the solid catalyst, especially the presence of Brønsted and Lewis acid sites, eventually provided by the leached Al element in some cases, we observed a synergy effect between the reaction medium and the added solid acid catalyst. This synergy effect is tentatively explained by two different phenomenons:

- The participation of the Lewis acid sites provided by the solid catalysts itself or by the leached Al species in the overall reaction pathway. These sites might assist the aldose-ketose isomerization and makes the successive Brønsted acid catalyzed dehydration step to occur faster at the moderate temperature of 150 °C.
- The presence of high concentration of acetic acid in water was proposed to enhance the surface catalyst coverage with the carbohydrate and furfural. We think that upon acetic acid addition a simple solvent effect may intervene, producing weaker intermolecular interactions between carbohydrates or furfural molecules with the acetic acid/water media due to distinct polarities and hydrogen bonding network. Therefore the partition of xylose and furfural between the liquid phase and the surface can be changed in favor of an improved surface coverage, as shown by the adsorption measurements. Consequently, the more selective heterogeneous catalyzed steps could occurred at the expense of the uncontrolled homogenous ones since it was shown that upon NbOH addition, the furfural stability was improved in acetic acid medium.

We think that the use of water-acetic acid reactive media in the presence of solid acid catalysts offer a new sustainable possibility for furfural production.

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References

[1] P. Gallezot, Chem. Soc. Rev. 41 (2012) 1538–1558.
[2] A.S. Mamman, J.M. Lee, Y.C. Kim, I.T. Hwang, N.J. Park, Y.K. Hwang, J.S. Chang, J.S. Hwang, Biofuels Bioprod. Biorefining 2 (2008) 438–454.
[3] H.J. Brownlee, C.S. Miner, Ind. Eng. Chem. 40 (1948) 201–204.
[4] D.R. Arnold, A novel Process for Furfural Production in School of Chemical Engineering, University of Natal, South Africa, 2003.
[5] C. Moreau, R. Durand, D. Peyron, J. Duhamet, P. Rivalier, Ind. Crop. Prod. 7 (1998) 95–99.
[6] R. O'Neill, M.N. Ahmad, L. Vanoye, F. Aiouache, Ind. Eng. Chem. Res. 48 (2009) 4300–4306.
[7] P.L. Dhepe, R. Sahu, Green Chem. 12 (2010) 2153–2156.
[8] S. Lima, M.M. Antunes, A. Fernandes, M. Pillinger, M.F. Ribeiro, A.A. Valente, Appl. Catal. A 388 (2010) 141–148.
[9] S. Lima, A. Fernandes, M.M. Antunes, M. Pillinger, F. Ribeiro, A.A. Valente, Catal. Lett. 135 (2010) 41–47.
[10] J. Lessard, J.F. Morin, J.F. Wehrung, D. Magnin, E. Chornet, Top. Catal. 53 (2010) 1231–1234.
[11] S. Lima, M. Pillinger, A.A. Valente, Catal. Commun. 9 (2008) 2144–2148.
[12] E. Lam, J.H. Chong, E. Majid, Y.L. Liu, S. Hrapovic, A.C.W. Leung, J.H.T. Luong, Carbon 50 (2012) 1033–1043.
[13] J.L. Cabezas, L.A. Barcena, J. Coca, M. Cockrem, J. Chem. Eng. Data 33 (1988) 435–437.
[14] J.R. Croker, R.G. Bowrey, Ind. Eng. Chem. Fundam 23 (1984) 480–484.
[15] E.I. Gurbuz, S.G. Wettstein, J.A. Dumesic, ChemSusChem 5 (2012) 383–387.
[16] A.S. Dias, M. Pillinger, A.A. Valente, Appl. Catal. A 285 (2005) 126–131.
[17] A.S. Dias, M. Pillinger, A.A. Valente, Micro. Meso. Mater. 94 (2006) 214–225.
[18] A.S. Dias, S. Lima, M. Pillinger, A.A. Valente, Carbohydr. Res. 341 (2006) 2946–2953.
[19] A.S. Dias, S. Lima, D. Carriazo, V. Rives, M. Pillinger, A.A. Valente, J. Catal. 244 (2006) 230–237.
[20] A.S. Dias, S. Lima, P. Brandao, M. Pillinger, J. Rocha, A.A. Valente, Catal. Lett. 108 (2006) 179–186.
[21] A.S. Dias, S. Lima, M. Pillinger, A.A. Valente, Catal. Lett. 114 (2007) 151–160.
[22] J.N. Chheda, Y. Roman-Leshkov, J.A. Dumesic, Green Chem. 9 (2007) 342–350.
[23] E.I. Gurbuz, J.M.R. Gallo, D.M. Alonso, S.G. Wettstein, W.Y. Lim, J.A. Dumesic, Angew. Chem. Int. Ed. 52 (2013) 1270–1274.
[24] R. Lopes de Souza, H. Yu, F. Rataboul, N. Essayem, Challenges 3 (2012) 212–232.
[25] F. Figueras, N. Essayem, C. Feche, S. Loridant, J. Palomeque, G. Gelbard, WO 2004/004893.
[26] N. Essayem, G. Coudurier, M. Fournier, J.C. Vedrine, Catal. Lett. 34 (1995) 223–235.
[27] F. Chambon, F. Rataboul, C. Pinel, A. Cabiac, E. Guillon, N. Essayem, Appl. Catal. B 105 (2011) 171–181.
[28] B. Hamad, R.O.L. de Souza, G. Sapaly, M.G.C. Rocha, P.G.P. de Oliveira, W.A. Gonzalez, E.A. Sales, N. Essayem, Catal. Commun. 10 (2008) 92–97.
[29] A.L. Mota Salinas, G. Sapaly, Y. Ben Taarit, J.C. Vedrine, N. Essayem, Appl. Catal. A 336 (2008) 61–71.
[30] R. Weingarten, G.A. Tompsett, W.C. Conner, G.W. Huber, J. Catal. 279 (2011) 174–182.
[31] A. Takagaki, M. Ohara, S. Nishimura, K. Ebitani, Chem. Lett. 39 (2010) 838–840.
[32] V. Choudhary, S.I. Sandler, D.G. Vlachos, ACS Catalysis 2 (2012) 2022–2028.
[33] C. Moreau, R. Durand, A. Roux, D. Tichit, Appl. Catal. A 193 (2000) 257–264.
[34] R.O.L. Souza, D.P. Fabiano, C. Feche, F. Rataboul, D. Cardoso, N. Essayem, Catal. Today 195 (2012) 114–119.
[35] Y. Roman-Leshkov, M. Moliner, J.A. Labinger, M.E. Davis, Angew. Chem. Int. Ed. 49 (2010) 8954–8957.
[36] T. vom Stein, P.M. Grande, W. Leitner, P.D. de Maria, ChemSusChem 4 (2011) 1592–1594.
[37] Y. Yang, C.W. Hu, M.M. Abu-Omar, ChemSusChem 5 (2012) 405–410.

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