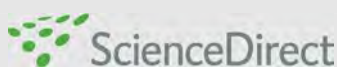
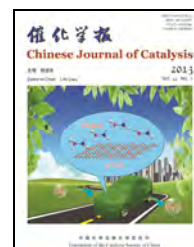




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Article

Dehydration of xylose to furfural using a Lewis or Brönsted acid catalyst and N₂ stripping

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ABSTRACT

The activity of Lewis (Nb₂O₅) and Brönsted (Amberlyst 70) acid catalysts for the cyclodehydration of xylose to furfural was studied. The nature of the acidity resulted in significant changes in the reaction mechanism. Lewis acid sites promote the formation of xylulose, while Brönsted acid sites are required to further dehydrate the sugar to furfural. Amberlyst 70 in water/toluene at 175 °C showed lower activity but gave a higher furfural yield. Using N₂ as the stripping agent considerably improved the furfural yield and product purity in the stripped stream. Catalyst stability was also studied.

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1. Introduction

Among the furan-based compounds, furfural (FUR) is one of the most interesting building-blocks to produce high added-value compounds. It is also used as an industrial solvent [1]. FUR is produced from pentosan-rich biomass by xylose cyclodehydration [2]. Current FUR production uses homogeneous catalysts, which lead to corrosion and toxic effluent issues as well as high separation and purification costs. Furfural condensation reactions that produce fragments and intermediates (rate constant k'_2) and resinification reactions (rate constant k'_3) occurring in the aqueous phase (Scheme 1(a)) can be largely avoided by using steam as a stripping agent [3].

Novel heterogeneous catalysts that have been used in water

or toluene include functionalized mesoporous supports [4–6], metal oxides [7], and zeolites [8,9]. Strong acid sites supported on materials that have suitable pore arrangements are essential to achieve high xylose conversion and FUR selectivity. Catalysts such as functionalized SBA-15 can give high FUR yields by the tuning of the pore structure [10] and Lewis/Brönsted ratio [11–13]. A drawback in the industrial use of these systems is that the biphasic process needs extra solvent/FUR separation stages, which is still a problem even if greener solvents than toluene are used [14]. For this reason, a novel separation technique using N₂ as the stripping agent [15] in combination with the use of a solid heterogeneous catalyst was studied here.

This work evaluated the use of solid heterogeneous Lewis and Brönsted acid catalysts in xylose dehydration in water as

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the solvent together with the use of N_2 stripping. Amberlyst 70 (A70) was selected as a representative Brønsted acid catalyst and niobium pentoxide (Nb_2O_5) on a mesoporous silica Cabosil named as Nb/Cab was the Lewis acid. The catalysts showed high activity and recyclability in transesterification reactions [16] and the dehydration of 5-hydroxymethyl-2-furaldehyde (HMF) from fructose [17]. The use of a combination of catalysts containing different acid types and a novel process engineering has interesting potential. The hydrothermal stability and regenerability of Nb/Cab were also studied.

2. Experimental

Nb/Cab was prepared by incipient wetness impregnation using an aqueous solution of niobium oxalate in 0.1 mol/L oxalic acid (12 wt%), dried in air at 60 °C and calcined at 550 °C for 6 h. Amberlyst 70 was supplied by Dow Chemicals.

N_2 isotherms of the catalysts were obtained at -196 °C using an Autosorb 1C (Quantachrome) apparatus. Samples were first degassed at 150 °C for 12 h. The specific surface area (A_{BET}) was calculated using BET method, and the micropore volume was estimated by the t -plot method. Temperature-programmed desorption of ammonia (NH_3 -TPD) was carried out as follows. The sample (0.2 g) was first heated under N_2 to 300 °C and then exposed to NH_3 at 120 °C. After flushing off excess NH_3 at 120 °C with N_2 for 1 h and cooling to 80 °C, the TPD program was performed (10 °C/min to 500 °C and kept for 30 min). Desorbed NH_3 was monitored by a TCD in an online gas chromatograph (Shimadzu GC-14A). Fourier transform infrared (FT-IR) spectra of adsorbed pyridine were recorded on a Shimadzu FT-IR instrument (FTIR 8300) using self supported wafers of 15 mg/cm² placed in a vacuum cell with greaseless stopcocks and CaF_2 windows. The sample was evacuated at 250 °C and 0.01 Pa overnight, exposed to pyridine at room temperature for 15 min, and outgassed at 200 °C.

Xylose dehydration batch reactor tests were performed in a 200 ml stainless steel reactor. The N_2 stripping tests were performed in a 2 L reactor. In a typical N_2 stripping test at 175 °C and 800 kPa, the reactor was first loaded with the catalyst and water. After heating, the xylose solution was fed from a N_2 pressurized vessel (to reach initial xylose load of 1 wt%). N_2 at

room temperature was bubbled into the liquid from the bottom at 150 ml/min. Stripped vapor containing FUR was condensed and separated from the stripping agent (N_2). Samples were taken at different intervals until the condensate was 80% of the initial reactor volume.

The products and remaining xylose were quantified using an HPLC module ICS-3000 from DIONEX coupled to an AS40 Autosampler. FUR was quantified after separation using a Kinetex C18-XB 150 mm × 4.6 mm column from Phenomenex kept at 40 °C. A UV-2070 Plus detector from JASCO at 280 nm wavelength was used. The mobile phase consisted of H_2SO_4 (0.01 mol/L) and acetonitrile aqueous solution (10%, v/v) at a flow rate of 1 ml/min. Xylose was quantified after separation using a CarboPac PA20 3 mm × 150 mm column at 30 °C with 0.5 ml/min of NaOH (8 mmol/L) as the mobile phase. Detection was performed using an electrochemical cell with integrated amperometry, and the standard Carbohydrate Quad method was used.

The xylose conversion was measured at different intervals. FUR yield was calculated as mole of FUR obtained per mole of converted xylose.

3. Results and discussion

From the characterization by N_2 physisorption, Nb/Cab has a specific surface area of 169 m²/g. Nb/Cab and A70 have low crystallinity (checked by XRD). The FT-IR spectra of pyridine saturated samples are shown in Fig. 1(a). The Nb/Cab sample showed only a Lewis site band at 1446 cm⁻¹, while the A70 showed only Brønsted sites at 1548 cm⁻¹. The peak at 1490 cm⁻¹ is due to both Lewis and Brønsted acid sites. The acidity data measured by NH_3 -TPD showed significant differences in the acid site amounts, of 2.55 and 0.045 mmol/g for A70 and Nb/Cab, respectively. The Nb_2O_5 content was 12 wt%, as determined by X-ray fluorescence spectroscopy.

The nature of the acid sites and strength determine xylose dehydration activity and furfural yield [12]. The batch reactor xylose dehydration catalytic tests at 175 °C (Batch W) showed that the Lewis sites gave a higher initial xylose conversion. Even with the two catalysts present with different total acid amounts, the xylose molecule was more easily adsorbed on the

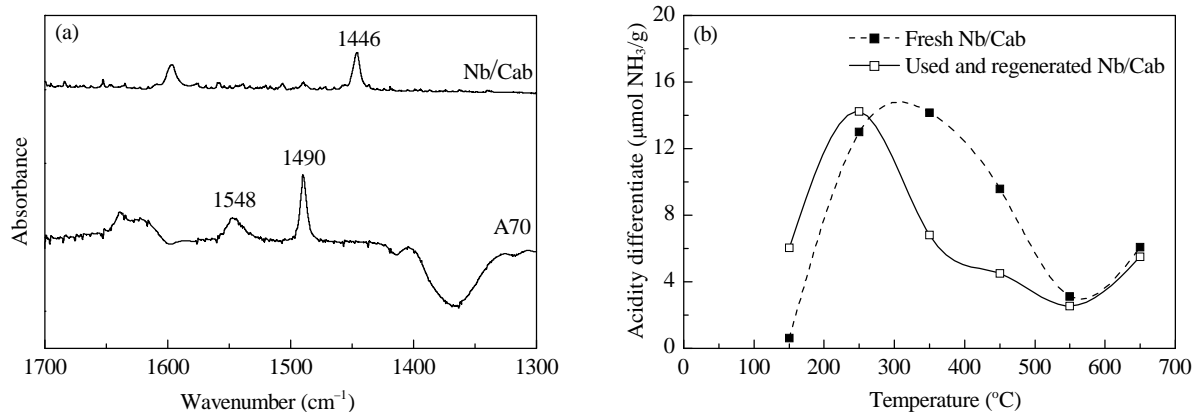


Fig. 1. (a) Acid site characterization of Amberlyst 70 (A70) and Nb_2O_5 on mesoporous silica cabosil (Nb/Cab) by pyridine-FTIR; (b) NH_3 -TPD profiles of Nb/Cab.

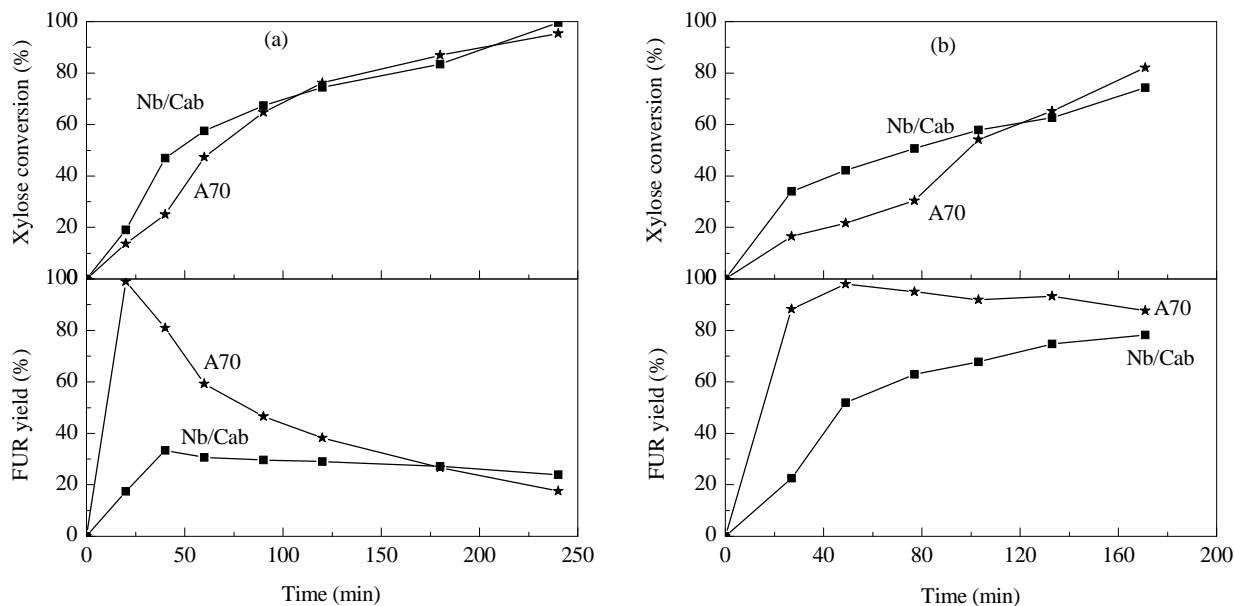


Fig. 2. Evolution of xylose conversion and FUR yield during batch reactor tests at 175 °C (a) and N₂ stripping at 175 °C using 150 ml/min of N₂ at 800 kPa bar (absolute pressure) (b).

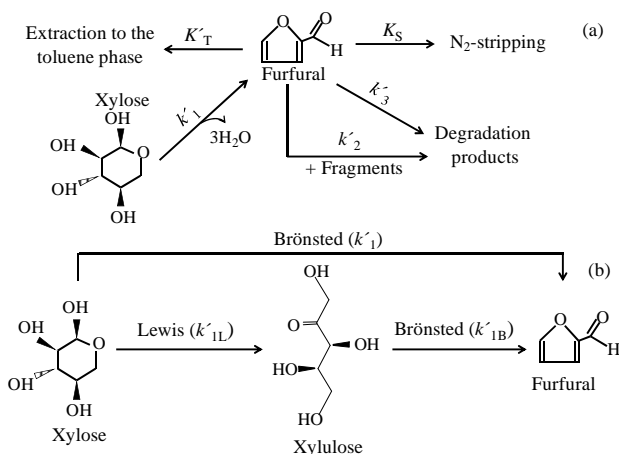
Lewis acid sites and converted at higher rates (Fig. 2(a)). Average TOF values (based on converted xylose) in the first 60 min were 4.28 and 0.06 mmol/(meq H⁺·min) for Nb/Cab and A70, respectively. It has been reported in the literature [18] that Lewis sites are suppressed in water. However, if all the Nb/Cab acid sites (0.045 mmol/g) were converted to Brønsted acid sites, the Nb/Cab should show a lower activity than A70 (acidity of 2.55). Because both catalysts showed similar conversion rates, it was improbable that the Lewis sites were converted to Brønsted sites.

On the other hand, it is noteworthy that the presence of Lewis acid sites clearly changed the mechanism of FUR production from xylose as compared to that on Brønsted acid sites. The dehydration of xylose on Lewis acid sites occurs in two consecutive steps, as shown in Scheme 1(b). The presence of small amounts of xylulose in the HPLC analysis (not quantified)

suggested that xylose was first isomerized to xylulose and then further dehydrated to furfural. The reactions on Nb/Cab were first catalyzed by the uncoordinated metal sites on Nb₂O₅, and the xylulose was dehydrated mainly by the H₃O⁺ in water. The direct conversion of xylose to furfural on a Brønsted acid (A70) requires a high activation energy, while the Lewis acids can lower this activation energy by 59% [11]. The xylose dehydration activity is determined by the structural porosity [10] and type of acid site [19]. In our case, even if xylose diffusion in the pores might be limited by the porosity of the Cabosil support (diffusivity of 0.011 cm²/s), this was offset by the presence of active Lewis sites that can convert xylose at a higher rate than A70.

On the other hand, the FUR yield differed greatly in the initial stages, reaching a maximum (99%) at 14% xylose conversion for A70 (Fig. 2(a)). Because H₃O⁺ protons at 160 °C are not as strong an acid as the SO₃H⁻ groups on A70, the xylulose intermediate on Nb/Cab was dehydrated at a lower rate than when A70 was used, which opened a route to faster condensation reactions with FUR and thus a lower FUR yield than that obtained with A70 (Fig. 2(a)). The presence of H₃O⁺ is required to further dehydrate xylulose to furfural. At 160 °C, water can self-ionize and form the H₃O⁺ hydronium form and be used as a Brønsted acid. These results clearly confirmed the different activities of the Lewis and Brønsted acid sites for the decomposition reactions. As shown in Table 1, the final FUR yield in water (Batch WT) did not exceed 25%. Under biphasic water/toluene (1:1 v/v) conditions (Batch WT), the FUR yields were increased by ~40%. In addition, the data were modeled to get a K'_T value (distribution coefficient between the aqueous and organic phases) of 4.6 (min·g_{CAT})⁻¹.

The presence of Lewis acid sites in solvents other than water would considerably change the reaction mechanism. Organic solvents such as DMSO gave lower yields than water but had higher acid site stability [10]. For an understanding of this,



Scheme 1. (a) Kinetic and diffusion rate constants during xylose dehydration to furfural. (b) Mechanism and reaction pathways using Lewis and Brønsted acid catalysts in the xylose dehydration in water.

Table 1Acid site stability and catalytic activity of Nb/Cab and A70 at 175 °C under batch reaction and N₂ stripping conditions.

Catalyst	Acidity ^a (mmol/g)		Batch W ^b		Batch WT ^b		N ₂ -stripping ^b	
	Fresh	Used-stripping	Xylose conversion (%)	FUR yield (%)	Xylose conversion (%)	FUR yield (%)	Xylose conversion (%)	FUR yield (%)
Nb/Cab	0.045	0.039	99	24	99	35	74	78
A70	2.550	1.531	95	17	95	46	82	87

^a Measured by NH₃-TPD for Nb/Cab and equilibration with NaNO₃ and titration with NaOH for A70.^b Test reactions performed with 1% of initial xylose load and 60 wt% of catalyst with respect to xylose load. The average standard deviation in the tests was 4%.

the effect of water on the hydrolysis and Lewis acidity of Nb₂O₅ needs to be further studied. Catalysts that have optimized Lewis/Brønsted ratios and suitable textural properties are the best for studying xylose dehydration to FUR in water. Also, from a consideration of industrial application, different extraction configurations such as N₂ stripping are a better approach than using extra solvents.

In order to model the experimental data, the kinetic constants (Scheme 1(a)) were simplified and split into three equations and iterated until the tolerance range specified (10⁻⁹) for the sum of least squares was reached. Xylose was directly dehydrated to furfural by A70, and it can also be further condensed with xylose intermediates or fragments. As shown in Scheme 1(b), the Lewis acid sites isomerized xylose to produce xylulose with a rate constant k'_{1L} , and this was then dehydrated to FUR catalyzed by a Brønsted site with a rate constant k'_{1B} . These constants were lumped as k'_1 in the kinetic model, and k'_3 was obtained from the resinification reactions of FUR and catalyst. The constants showed slight differences for k'_1 (6.8×10^{-3} and 6.6×10^{-3} (min·g_{CAT})⁻¹ for Nb/Cab and A70, respectively), but significant differences for k'_2 (6.4×10^{-4} and 3.1×10^{-4} L/(min·g·g_{CAT})⁻¹). Obviously, the differences in the condensation reactions (k'_2) had the biggest influence on FUR yield reduction on Nb/Cab.

During the initial stage of the process operated with N₂ stripping, xylose dehydration activity was faster with Nb/Cab than with A70 (Fig. 2(b)). This gave higher FUR concentrations in the reactor (FUR_R). The stripped and condensed FUR (FUR_C) showed the same trend. N₂ was a very efficient stripping agent and was able to achieve FUR_C/FUR_R ratios of 6–8. In the first 90 min, the condensate concentrations showed FUR concentration maxima for both catalysts. During N₂ stripping, the liquid volume in the reactor decreased, so the catalysts required enough acid capacity to be able to convert xylose and thus achieve a constant xylose concentration profile. However, the molar conversion rate of xylose with Nb/Cab was not as high as with A70, which was due to the blockage of the active sites by deposited humins. This decreased its dehydration activity by the end of the tests. This acid site blockage enhanced the occurrence of side reactions and reduced the FUR yield to 78%. This phenomenon has been previously reported [20]. The tests performed in the absence of a catalyst gave lower FUR yield compared to the heterogeneously catalyzed systems. When the Nb/Cab catalyst was deactivated by deposited humins, it showed a similar conversion to the non-catalyzed systems, and thus a lower FUR yield. As shown in the initial N₂ stripping stages in Fig. 2(b), the Nb/Cab FUR yield was low due to the

slow dehydration of xylulose to FUR. However, longer reaction periods favored the formation of FUR and N₂ can be used to strip it and avoid its further degradation by condensation reactions (such as the ones reducing the FUR yield under the batch reactor conditions). On the other hand, the A70 acid amount was maintained higher than that of Nb/Cab in the tests, and A70 showed a more constant xylose conversion rate. Moreover, due to the higher FUR yield from the Brønsted acid sites (shown in the batch reactor tests) and its higher acid amount, the A70 FUR yield was increased up to 87%. The results clearly confirmed that the activity is dependent on the operational configuration. Moreover, clear FUR yield differences between the use of batch reaction and N₂ stripping were observed.

The GC-MS analysis of the reactor liquid sample showed a broad range of degradation products from undesired reactions, such as pyruvaldehyde, dihydroxypropanone, and acetic acid. However, the stripped condensate sample showed a FUR selectivity of 98% for both catalysts, suggesting that N₂ can effectively strip FUR from the reaction medium. From the modeled data, a K_S interphase separation value of 0.041 L/min was estimated.

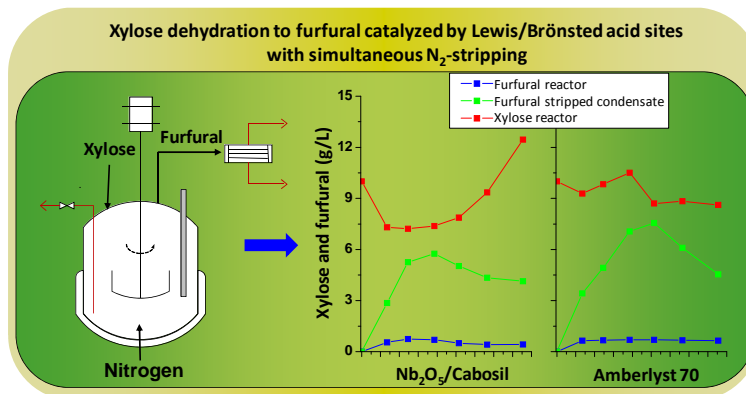
The regeneration of acid catalysts after xylose dehydration reactions is common [20]. In the Nb/Cab case, the non-treated catalyst showed a considerably lower catalytic activity, suggesting that deposited coke should be removed from the surface. The acid amount of the used catalysts was also evaluated after coke oxidation using a thermal treatment at 550 °C. As shown in Fig. 1(a), a reduction of adsorbed NH₃ on the strong Lewis acid sites at 250–500 °C occurred, while the weaker acid site amounts were still the same. The overall desorbed NH₃ amount showed small acid amount differences with respect to the fresh sample (Table 1). This observation proved the hydrothermal stability of the uncoordinated Nb₂O₅ even at high reaction temperatures. On the other hand, 40% of the sulfonic sites on the A70 sample were leached into the reaction medium. In spite of having less reaction acid site stability than Nb/Cab (1.53 mmol/g), it showed higher accessibility and more acid amount than Nb/Cab. This allowed it to effectively dehydrate the xylose during all the N₂ stripping tests. Amberlyst 70 is a commercial catalyst that can be used in non-aggressive solvents, such as dimethylsulfoxide. However, the presence of water in the reaction considerably reduces acid site stability. A new approach to enhance the hydrothermal stability is to modify the synthesis conditions. In a recent publication [20], an increase of the synthesis aging temperature was reported to induce higher sulfonic stability. This approach can also be applied to Amberlyst catalysts.

Graphical Abstract

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Dehydration of xylose to furfural using Lewis or Brönsted acid catalyst and N₂ stripping

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The present work studied the change of the xylose dehydration mechanism and furfural yield using Lewis (Nb₂O₅/Cabosil) or Brönsted (Amberlyst 70) acid catalysts in combination with simultaneous discontinuous N₂-stripping.

4. Conclusions

Xylose dehydration activity showed differences on niobium pentoxide (Nb₂O₅/Cabosil) or sulfonic site (Amberlyst 70) catalysts. Lewis acid sites converted xylose at a higher rate than Brönsted acid sites, while strong Brönsted sites such as those on Amberlyst 70 gave a higher furfural yield. N₂ stripping achieved better extraction efficiency than the use of toluene as a co-solvent. The use of N₂ stripping with a solid heterogeneous catalyst has several environmental advantages with respect to the use of co-solvents, such as easier product-solvent separation, lower furfural dilution due to the use of non-condensable N₂ and higher product purity. This advantage was obtained with both of the solid acid Brönsted or Lewis acid catalyst.

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