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Synthesis of Furfural from Xylose by Heterogeneous and Reusable Nafion Catalysts

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Nafion 117 has been proven as a robust and reusable heterogeneous catalyst for the dehydration of 9.1% (w/w) xylose in dimethyl sulfoxide (DMSO) to yield 60% furfural in 2 h at 150 °C. The catalytic high activity promoted shorter reaction times to limit the formation of side-products which otherwise would lead to decreased yields. Within the allowable operating temperature range of Nafion (125 to 175 °C), the reaction was kinetically controlled. In corroboration with AFM and SEM

imaging, ATR–FTIR confirmed that the Nafion catalytic activity remained unchanged after 15 repeated uses. With excellent chemical and thermal stability under the conditions for xylose dehydration compared to existing solid acid catalysts, this reusable Nafion system could be a step towards the more economical production of furfural from renewable biomass, an intermediate chemical for the preparation of value-added chemicals.

Introduction

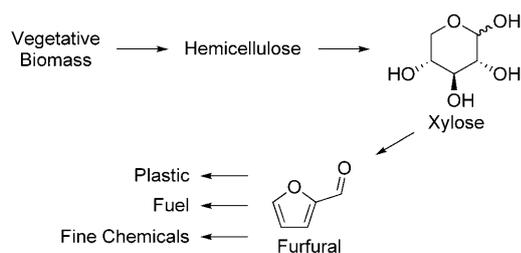
Owing to diminishing petrochemical resources, focus has turned to abundant biomass sources such as agricultural crops, forestry by-products and plant wastes rich in hemicellulose. Hemicellulose is a branched, heterogeneous polymer that comprises a backbone of pentose sugars such as xylose and mannose. Hemicellulose derived from hardwood trees and grass tends to be rich in xylose, while hemicellulose derived from softwood trees is rich in mannose. Organic acids and other sugars (such as arabinose, glucose, and rhamnose) can substitute for some of the pentose sugars in the hemicellulose backbone.^[1]

Hemicellulose-rich biomass can serve as alternative sustainable supplies for non-petroleum-derived chemicals. Furfural, an intermediate for the preparation of value-added products including plastics (furan-based polymers), pharmaceuticals, fuels, and fine chemicals,^[2] is produced from the acid-catalyzed dehydration of hemicellulose (Scheme 1).

To date, both batchwise and continuous acid hydrolysis are able to hydrolyze hemicellulosics to xylose, followed by dehydration of the latter to form furfural. At 170–185 °C, the reaction is complete within 3 h, yielding 40–50% furfural.^[2] Current commercial processes use concentrated inorganic acids (H₂SO₄

and HCl) that are highly toxic, corrosive, and difficult to handle. Other major drawbacks to mineral acids include: the occurrence of extensive side reactions from long reaction times that reduce furfural yield; neutralization of the spent acid; and technological challenges in the development, use, and maintenance of equipment exposed to the corrosive liquids. As part of a four-step process for the formation of jet- and diesel-fuel-range alkanes, Xing et al.^[3] reported the synthesis of furfural from HCl-catalyzed biphasic dehydration of hemicellulose extracts at 87% yield. However, they acknowledge that the high cost of producing such alkanes could be reduced by using solid acids in place of HCl.

Various materials have been tried as alternatives for the non-recoverable homogeneous catalysts currently used in furfural production. These heterogeneous catalysts are often solid acids characterized by strong Brønsted acidity, high surface area, and are thermally stable at the high temperatures required for rapid xylose dehydration to furfural. Zeolites generally produce lower reaction yields^[4–6] whereas heteropolyacids require lower substrate-to-catalyst loading to obtain moderate yields (63%).^[7] Sulfonic-acid-functionalized MCMs (Mobil catalytic materials) have 91% xylose conversion and 82% furfural selectivity, but require 24 h of reaction with diminishing catalyst activity for consecutive runs.^[8] In all cases, xylose dehydration is carried out at lower initial xylose concentrations (< 3.3 wt%), requiring the use of large solvent volumes on an industrial scale and costly isolation and distillation of furfural.



Scheme 1. Transformation of biomass into value-added chemical products.

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There is an urgent need to improve the cost-effectiveness of furan-based chemical industries.

This study demonstrates and optimizes the catalytic performance and reusability of Nafion, a sulfonated tetrafluoroethylene-based fluoropolymer-copolymer.^[9] Nafion has been known to withstand high temperatures (up to 190 °C) without any significant chemical degradation. As a superacid, Nafion has been used to catalyze various organic transformations including acylation, alkylation, and isomerization reactions.^[10] Indeed, Nafion has been used in the dehydration of fructose (hexose sugar) to produce hydroxymethylfurfural (HMF) with a 50% yield.^[11] To our knowledge, this study is the first systematic attempt to convert concentrated xylose (pentose sugar) to furfural using Nafion as a heterogeneous and reusable catalyst to facilitate product recovery. Mechanistic considerations towards selectivity and catalyst poisoning are suggested, and experimental data reveal the important role of water and the pore size of the catalyst in the formation of byproducts.

Results and Discussion

Initial screening of Nafion materials

Nafion polymers are commercially available in several forms, including beads, membranes, and solutions (in water/alcohol mixtures). Nafion 117 (polymeric membrane, 0.91 meqH⁺ g⁻¹) and SAC-13 (Nafion polymer on amorphous silica, 0.12 meqH⁺ g⁻¹) were selected because these physical forms can easily be recovered and reused for subsequent reactions. The two Nafion catalysts were used in the dehydration of 0.67 M xylose in DMSO. This solvent was specifically chosen as the test solvent to compare Nafion with other reported solid acid catalysts used in furfural synthesis. DMSO, being hygroscopic, is effective in suppressing condensation side products and the rehydration of sugars, resulting in improved selectivities and dehydration rates.^[12] Without the catalyst, only a 1% furfural yield was obtained. Table 1 shows the effects of reaction temperature on xylose dehydration.

Figure 1 shows representative reaction profiles for Nafion 117 and SAC-13 at 5 wt% loading (vs. xylose content).

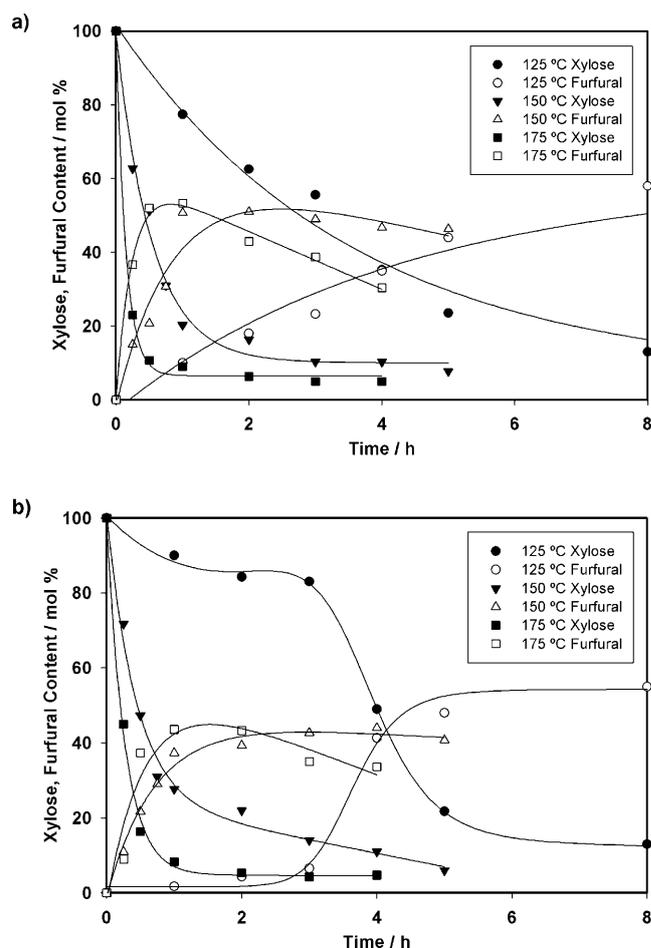


Figure 1. a) Reaction profiles for the dehydration of xylose with Nafion 117 (5 wt% loading vs. xylose) at different temperatures in DMSO. b) Reaction profiles for the dehydration of xylose with SAC-13 (5 wt% loading vs. xylose) at different temperatures in DMSO.

As expected, the rate of xylose conversion increases with increasing temperature. An induction period was observed for the conversion of xylose in Nafion SAC-13 at 125 °C. Although the effect was less pronounced with Nafion 117 at 125 °C, more than 3 h was required for either catalyst to convert 50% of the starting xylose. When the reaction temperature was increased from 125 °C to 150 °C, the turnover frequency (TOF) for xylose consumption also increased (Table 1). Above 150 °C, xylose conversion was far more rapid, where 90% of the initial xylose had already been converted to furfural and/or byproducts after 3 h. This effect was mirrored in the formation of furfural for both catalysts at 5 wt% loading versus xylose. Furfural production was relatively slow at 125 °C compared to 150 and 175 °C, with maximum yields of

| Entry | Catalyst | Catalyst loading [wt%] (vs. xylose) | <i>T</i> [°C] | <i>t</i> [h] | Conversion [%] | Selectivity [%] | Yield [%] | TOF ^[a] [mmol g _{cat} ⁻¹ h ⁻¹] | TOF ^[a] [mmol meq ⁻¹ h ⁻¹] |
|-------|----------|-------------------------------------|---------------|--------------|----------------|-----------------|-----------|---|--|
| 1 | 117 | 5 | 125 | 8 | 87 | 67 | 58 | 31 | 34 |
| 2 | 117 | 5 | 150 | 2 | 84 | 61 | 51 | 131 | 143 |
| 3 | 117 | 5 | 175 | 0.5 | 89 | 58 | 52 | 212 | 233 |
| 4 | 117 | 20 | 125 | 8 | 91 | 62 | 56 | 16 | 18 |
| 5 | 117 | 20 | 150 | 2 | 91 | 66 | 60 | 49 | 53 |
| 6 | 117 | 20 | 175 | 0.5 | 91 | 65 | 59 | 59 | 65 |
| 7 | SAC-13 | 5 | 125 | 8 | 87 | 63 | 55 | 13 | 111 |
| 8 | SAC-13 | 5 | 150 | 2 | 78 | 50 | 39 | 139 | 1155 |
| 9 | SAC-13 | 5 | 175 | 0.5 | 84 | 45 | 37 | 234 | 1954 |
| 10 | SAC-13 | 38 | 125 | 8 | 92 | 57 | 52 | 3 | 25 |
| 11 | SAC-13 | 38 | 150 | 2 | 93 | 57 | 49 | 21 | 172 |
| 12 | SAC-13 | 38 | 175 | 0.5 | 90 | 56 | 51 | 32 | 263 |

[a] Initial xylose concentration of 9.1 wt% [b] TOF for 125 °C calculated at 1 h, other temperatures at 0.5 h.

58% and 55% at 8 h for Nafion 117 and SAC-13, respectively (Table 1, entries 1 and 7). Peak furfural yields were achieved within 3 h at 150 and 175 °C, but began decreasing with prolonged reaction time.

Figure 2 shows the reaction profiles for Nafion 117 and SAC-13 at 20 and 38 wt% loading versus xylose. The xylose conversion rate was faster at these higher catalyst loadings. Similar to

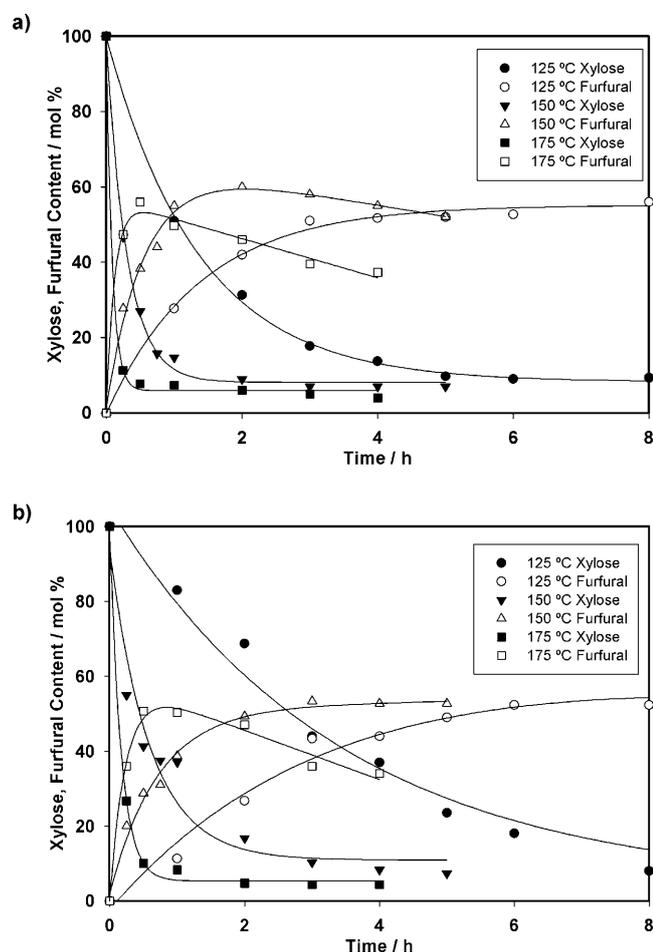


Figure 2. a) Reaction profiles for the dehydration of xylose with Nafion 117 (20 wt% loading vs. xylose) at different temperatures in DMSO. b) Reaction profiles for the dehydration of xylose with Nafion SAC-13 (38 wt% loading vs. xylose) at different temperatures in DMSO.

reactions conducted at 5 wt% loading, a decrease in furfural yield was observed at 150 and 175 °C for the higher catalyst loading with extended reaction times. Nafion 117 (20 wt% loading vs. xylose) produced the highest furfural yield at 60%, with a selectivity of 66% in 2 h at 150 °C (Table 1, entry 5), although a yield of 59% was also achieved at 175 °C after only 0.5 h with 20 wt% catalyst loading versus xylose (Table 1, entry 6). The higher yield of Nafion 117 with increasing catalyst loading can be attributed to the greater number of available sulfonic acid sites^[13,14] per unit weight relative to SAC-13, the weight of which mainly comprises the amorphous silica support. Also, the reduced yield of SAC-13 compared to Nafion 117 might be due to the interaction of the Nafion poly-

mer with the silanol groups, which would decrease the availability of the sulfonic acid groups to participate in catalysis.^[14] Notably, furfural, with a boiling point of 162 °C, could be separated from DMSO (boiling point 189 °C) by distillation, allowing the reuse of this solvent.

The reaction profiles of Nafion 117 (5 wt% loading versus xylose) and SAC-13 (38 wt% loading versus xylose) at 175 °C were compared on the basis of equivalent number of H⁺ sites (4.55×10^{-3} meqH⁺, determined by ion-exchange-capacity titrations) in Figure 3.

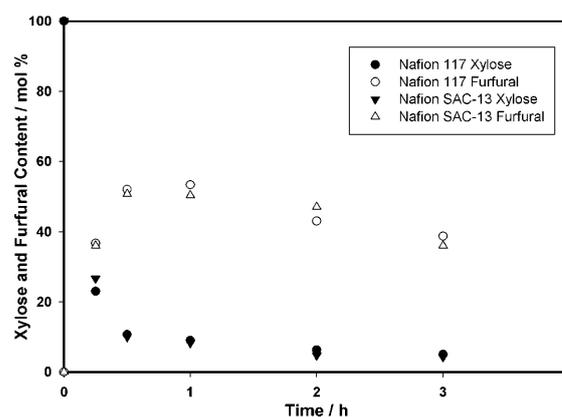


Figure 3. Reaction profiles for the dehydration of xylose with Nafion 117 (5 wt% catalyst loading versus xylose) versus Nafion SAC-13 (38 wt% catalyst loading versus xylose) at 175 °C.

Similar yields were achieved for Nafion 117 and SAC-13 when equivalent protons were compared. For Nafion SAC-13, the TOF for xylose consumption expressed on a weight basis was lower than that observed for Nafion 117 (Table 1, entries 1–3, 10–12). However, if the TOF was expressed as a relationship of the catalyst acid content, the activities of Nafion 117 and SAC-13 were very similar. In all cases, the TOF increased with increasing temperature. Nafion 117 for the dehydration of xylose to furfural was compared with other reported heterogeneous catalysts (Table 2). Although the furfural yield of Nafion 117 (20 wt% loading vs. xylose) was similar to that of Amberlyst-15 or the heteropolyacid H₃PW₁₂O₄₀, the reaction was performed at higher initial xylose concentrations, at a higher xylose/catalyst ratio, and with shorter reaction times. Consequently, the remaining work in this study was conducted with Nafion 117 because it achieved the highest yields.

Reactivity of the Nafion 117 catalyst

Acid-catalyzed dehydration of xylose is postulated to involve successive protonation of the xylose hydroxyl groups, leading to the release of three water molecules and the formation of furfural.^[15] The cluster-channel model for Nafion shows hydrophilic clusters of sulfonic acid groups (4 nm in diameter)^[16] that are dispersed through the hydrophobic semicrystalline perfluorocarbon matrix.^[9,17] Apparently, xylose migrates to these hydrophilic clusters where sulfonic acid groups catalyze the xylose dehydration.

| Table 2. Comparison of heterogeneous catalysts used in the dehydration of xylose to furfural. | | | | | | | | |
|---|---------------------|-------------|------------|-------------------|--------------------|--------------|--------------------------------|--------------------------|
| Catalyst | Solvent | T [°C] | t [h] | Conversion [%] | Selectivity [%] | Yield [%] | Initial xylose conc. [wt %] | Xylose/catalyst [w/w] |
| HY faujasite ^[a] | Water/toluene (1:3) | 175 | 0.83 | 66 | 64 | 42 | 3.3 | 3.75 |
| Delaminated H-Nu6(2) ^[b] | Water/toluene (3:7) | 150 | 4 | 90 | 53 | 48 | 2.7 | 1.5 |
| H ₃ PW ₁₂ O ₄₀ ^[c] | DMSO | 150 | 4 | 94 | 67 | 63 | 2.7 | 1.5 |
| MCM-41-SO ₃ Hc ^[d] | DMSO | 175 | 4 | 91 | 82 | 75 | 2.7 | 1.5 |
| Amberlyst-15 ^[d] | DMSO | 140 | 4 | 87 | 68 | 59 | 2.7 | 1.5 |
| Nafion 117 | DMSO | 150 | 2 | 91 | 66 | 60 | 9.1 | 5 |

[a] Reference [4]. [b] Reference [5]. [c] Reference [7]. [d] Reference [8].

The pore size of the Nafion catalysts may play a significant role in the formation of byproducts. The size of a furfural molecule along its longest axis is 0.57 nm.^[18] The relatively large pore sizes of Nafion 117 (> 10 nm) could allow for furfural to have a substantial residence time within the catalyst, leading to condensation reactions with xylose intermediates to form furfural-based dimers, trimers, and oligomers.^[19] As such, mor-denites with 0.7 nm pore size tend to exhibit higher selectivity than faujasites with 1.3 nm pore sizes.^[4] For heterogeneous zeolite ZSM-5 (1.2 nm pore size)^[6] and faujasites, the deposition of furfural oligomers inside catalyst pores is the primary source of catalyst deactivation. However, even with the deposition of carbonaceous materials on the surface of the Nafion, the reactivity and reusability of the catalyst remained high after repeated runs (vide infra).

A maximum furfural yield was achieved in 2 h at 150 °C with 91 % xylose conversion for Nafion 117 (20 wt% loading vs. xylose). However, as the reaction was prolonged, oligomeric side products began to form, decreasing the yield from 60% to 45–50% after 6 h of reaction. The reaction of furfural in DMSO (0.67 M) with Nafion 117 (20 wt% loading vs. xylose, 150 °C) was conducted to determine whether the formation of by-products was due to the self-polymerization of furfural. After 6 h of reaction, > 99% of the starting furfural was recovered, confirming that the presence of the starting xylose was required for the byproduct formation process to occur.^[15]

In xylose dehydration, the conversion rate may be determined by the rate of transport of the xylose involved in the diffusion of the bulk fluid to the active site of the Nafion sulfonic acid sites, located either on the surface or within the pores of the catalyst. The rate of xylose conversion is independent of furfural loss reactions.^[15] For Nafion catalysts, increasing temperatures produce an exponential rise in the initial rate of xylose conversion, similar to heteropolyacids.^[7]

The kinetics for xylose conversion was carried out using the method of initial rates. The $\ln k$ vs. $1/T$ Arrhenius plots (Figure 4) produced activation energy values of 86.4 and 89.3 kJ mol⁻¹, respectively, for Nafion 117 at 5% and 20% catalyst weight loading. These energy values are lower than other liquid acid catalysts such as H₂SO₄ (134 kJ mol⁻¹)^[20] and HCl (142 kJ mol⁻¹)^[21] and the heterogeneous catalyst zeolite ZSM-5 (134 kJ mol⁻¹)^[6] used in xylose conversion. Nafion 117 could accelerate the reaction due to its high acidity as a superacid and its ability to stabilize the protonated xylose transition state

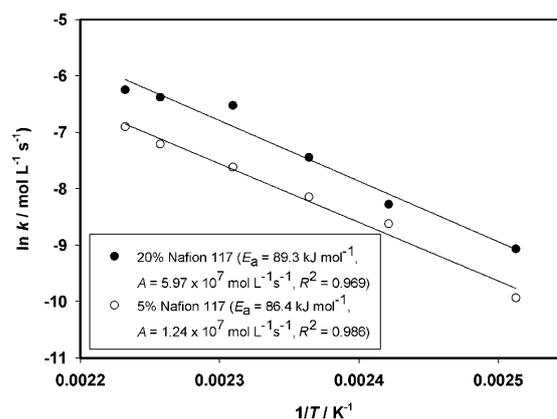


Figure 4. Arrhenius plots of xylose conversion using the Nafion 117 catalyst at 5 wt% and 20 wt% catalyst loading versus xylose.

through coordination to the polyanionic Nafion network.^[15,22] Solid catalysts can be subjected to diffusion and mass transfer effects.^[23] However, the linear Arrhenius plots demonstrated that between 125 to 175 °C, the conversion of xylose by Nafion was not affected by mass-transfer-related effects and that the reaction was kinetically controlled.^[23] The optimal reaction temperature range for using Nafion catalysts for xylose dehydration is unlikely to be outside of these temperatures. At reaction temperatures below 125 °C, the rate of xylose dehydration was slow, and at temperatures above 175 °C, particularly > 190 °C, the degradation of the Nafion polymer would occur, hampering its reusability.

Batch processes using mineral acids for the production of furfural are often inefficient because furfural can react with xylose intermediates in the liquid phase, forming unwanted byproducts. In addition to using biphasic solvent systems, most notably water and tetrahydrofuran,^[3] processes such as Suprayield^[15] aim to produce high yields of furfural by rapidly removing furfural vapor away from xylose as it is being formed by adiabatic distillation. Presently, only orthophosphoric acid is used as the catalyst in the Suprayield process due to corrosion problems associated with other mineral acids. Solid acids could be used as an alternative to orthophosphoric acid for such a process, providing the benefits of a reusable, nontoxic catalyst. However, the ability of solid acids to interact with slurries of biomass material to produce furfural is currently unknown.

Effect of water content on Nafion 117

Water can lead to undesirable condensation side products and the rehydration of furfural.^[6,7,12] Indeed, water played an important role in xylose dehydration by Nafion 117, as shown in Figure 5. Nafion 117 could tolerate a water content of up to

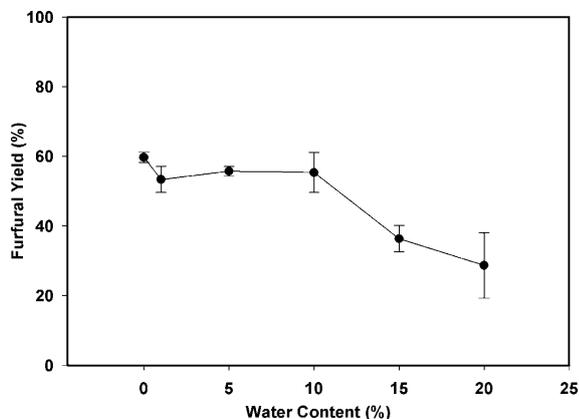


Figure 5. Effects of water content on dehydration of xylose with Nafion 117 (20 wt% loading versus xylose, 150 °C, 2 h) in DMSO.

10% in DMSO without significant loss of activity, as an average furfural yield of 56% was obtained with 89% xylose conversion. However, the furfural yield decreased significantly to 36% and 29% when the water content increased to 15 and 20%. The dehydration of xylose to furfural releases three equivalents of water for every equivalent of xylose, that is, the maximum water content added to the reaction mixture would be around 3.5%. The experiments conducted in this study with varying water content intend to show that water tolerance granted by the catalyst is acceptable within the range of water produced by the dehydration reaction. Notice also that many other solid acid catalysts are also affected by the presence of water.^[22] In the case of Nafion, water may also lead to the solvation of sulfonic acid groups which reduces the number of participating acidic sites, thereby reducing the rate at which xylose dehydration occurs.^[24]

Catalyst poisoning of Nafion 117

Deprotonation of the sulfonic acid groups of Nafion 117 would deactivate the catalyst by reducing the number of available acid sites for xylose dehydration. Monovalent and divalent cations can readily exchange with the H⁺ of the sulfonic acid groups of Nafion.^[25] Sulfonic acid groups can also react with bases, such as triethylamine (NEt₃) to form triethylammonium sulfonate salts,^[26] which may also result in a similar catalyst-deactivating effect.

To confirm the effects of sulfonic acid exchange and neutralization on the Nafion catalyst, NaCl and NEt₃ were added to 2.5 M aqueous solutions of xylose (Table 3). These solutions were diluted in DMSO to yield 10% water and 3.8% initial xylose content. Both NaCl and NEt₃ adversely affected the fur-

| Poison | Conversion [%] | Selectivity [%] | Yield [%] |
|------------------|----------------|-----------------|-----------|
| None | 92 | 63 | 58 |
| NaCl | 86 | 15 | 13 |
| NEt ₃ | 45 | 3 | 1 |

[a] Dehydration of 0.25 M xylose in 9:1 v/v DMSO/H₂O, 20 wt% catalyst loading vs. xylose, at 150 °C in 2 h. Poison = 0.07 mmol, xylose = 0.25 mmol, available H⁺ = 0.007 mmol

fural yield, 13% and 1% respectively, compared to 58% for the control. Poisons can play a role in reducing the effectiveness of the catalyst, particularly in real-world industrial applications where the xylose source material may be alkaline or contain significant quantities of cations.

Catalyst recyclability of Nafion 117

A series of experiments (20 wt% loading versus xylose, 2 h, 150 °C) was conducted to assess the reusability of Nafion 117. The catalyst was removed from the reaction mixture after each run by filtration and reused without any treatment. After each run, the Nafion catalyst slowly changed in color, from colorless to brown, with minute amounts of organic residue coated on the catalyst surface.

Scanning electron microscopy—energy dispersive X-ray (SEM–EDX) analysis was conducted on the pristine catalyst and after three reaction runs. A cross-sectional image of the pristine catalyst (Figure 6a) shows striations along the edge of the membrane. After three runs, the roughness along the edge of the membrane surface has been significantly reduced, possibly due to the deposition of organic residues (Figure 6b). Minimal membrane swelling was observed after each run. EDX analysis (Figure 6c) provided further information about the elemental composition of the Nafion material. A slight increase in carbon

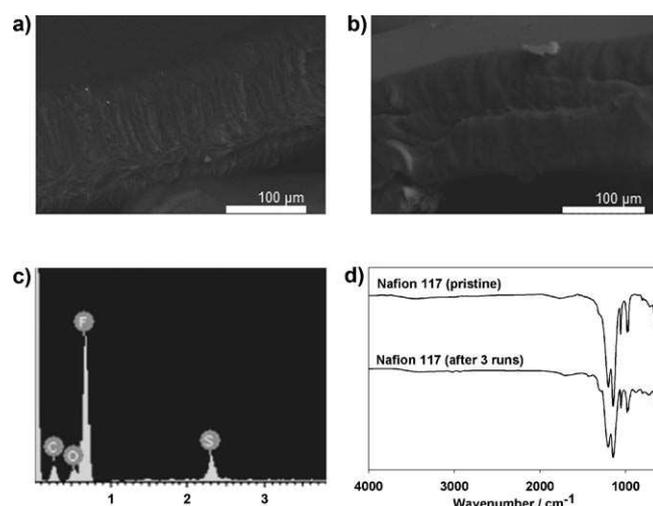


Figure 6. SEM images of Nafion 117 a) before, and b) after reaction. c) EDX spectrum of Nafion 117 membrane after reaction. d) IR spectra of pristine Nafion 117 and post-reaction Nafion 117 (after three recycling runs).

and oxygen content, along with a decrease in sulfur and fluorine content after the reaction runs, showed that non-Nafion carbonaceous matters were deposited on the membrane's surface (Table 4).

| Element | Pristine Nafion 117 [wt%] | Post-reaction Nafion 117 [wt%] |
|---------|---------------------------|--------------------------------|
| C | 22.7 | 23.9 |
| O | 5.4 | 5.6 |
| S | 1.0 | 0.9 |
| F | 70.8 | 70.6 |

For the attenuated total reflectance–infrared (ATR–IR) spectra of the membrane samples (Figure 6d), characteristic peaks for Nafion are listed in Table 5. The lack of peak shifts between

| Peak | Pristine Nafion 117 [cm ⁻¹] | Post-Reaction Nafion 117 [cm ⁻¹] ^[a] |
|-------------------------|---|---|
| $\nu_{as}(\text{CF}_2)$ | 1201 | 1203 |
| $\nu_s(\text{CF}_2)$ | 1146 | 1146 |
| $\nu_s(\text{SO})$ | 1057 | 1052 |
| $\nu_s(\text{CFRCF}_3)$ | 982 | 981 |
| $\nu_s(\text{COC})$ | 969 | 968 |

[a] After 3 runs.

the pristine and used membrane show that there are no significant changes to the chemical environment of the used Nafion,^[27] even after thermal treatment at 150 °C in DMSO over three consecutive runs. The ATR–IR spectrum of the used catalyst was also clear of any bands that would suggest furfural was coated on the surface of the catalyst. Atomic force microscopy (AFM) images of the fresh and used catalyst are shown in Figure 7. In Figure 7a, the surface of the Nafion is smooth, but in Figure 7b, the surface of the catalyst is covered with localized regions of nanoparticle-sized organic residue deposits.

After 15 consecutive runs at the optimized reaction conditions, the Nafion membrane remained intact with furfural yields ranging from 58 to 62% (Figure 8). Xylose conversion was >90% in all 15 runs after 2 h. Such a result clearly demonstrates the stability and reusability of the Nafion 117 catalyst

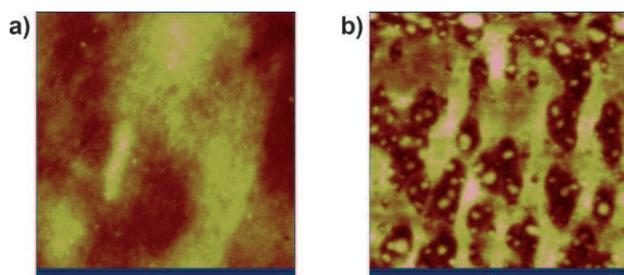


Figure 7. AFM images of Nafion 117 a) before and b) after reaction.

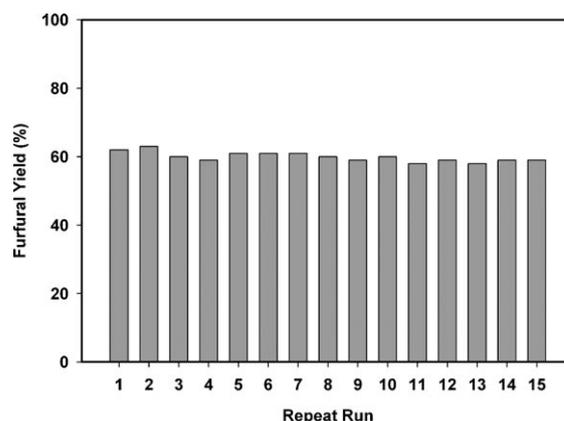


Figure 8. Furfural yield from recycling of Nafion 117 (20 wt% loading versus xylose, 150 °C, 2 h).

even in the presence of organic impurities that could block the catalytically active acidic sites, leading to catalyst deactivation. This is in contrast to other solid acid catalysts such as sulfonic-acid-functionalized MCM or delaminated zeolites, which employed catalyst regeneration procedures and still experienced reduced activity with consecutive runs. Although Nafion 117 activity remains high after 15 runs, treatment with dilute hydrogen peroxide and acid could regenerate the catalyst^[28] back to a tan-colored membrane, if desired. Annealing^[29] is another means to improve catalyst longevity by altering the physical properties of Nafion, such as proton conductivity, water permeability and water sorption, a subject of future endeavors.

Conclusions

Nafion 117 is a robust and reusable heterogeneous catalyst for the dehydration of concentrated xylose to yield 60% furfural in 2 h at 150 °C. A negligible mass transfer effect is noted at 125 to 175 °C, that is, the reaction is virtually kinetic-controlled. The catalyst is reused multiple times without loss of activity, a significant achievement over existing solid acid catalysts. Considering its chemical and thermal stability under the reaction conditions for xylose dehydration, this reusable catalyst could be a potential catalytic system for the industrial production of furfural, an important chemical with diversified applications, from renewable xylose-containing biomass. From a practical viewpoint, it is desirable to evaluate the applicability of Nafion for the synthesis of furfural from different sources of hemicellulose including xylan; a subject of future endeavor.

Experimental Section

Materials: D-(+)-Xylose (BDH), Nafion SAC-13, furfural, dimethyl sulfoxide (DMSO), phloroglucinol (Sigma–Aldrich), acetonitrile (J. T. Baker), hydrochloric acid (Fisher), and glacial acetic acid (EMD) were used as received. Nafion 117 (Sigma–Aldrich) was purified by treatment with hot hydrogen peroxide (3%) to remove organic impurities and 1 M hot sulfuric acid to remove metallic/ionic impurities.^[28] Catalytic acid sites of the Nafion species were determined by titration.^[30]

Analytical methods: Furfural concentration was determined by high-performance liquid chromatography (HPLC) at 25 °C using a spectrophotometer (Waters Lambda-Max Model 487) set at 250 nm, equipped with a pump (Waters Model 590), and a Beckman Ultrasphere (235330) 5 µm column. An acetonitrile/water (10:90 v/v) mixture was used as the mobile phase at 2.0 mL min⁻¹. The furfural concentration was estimated from a calibration curve. The unreacted xylose content was determined by a colorimetric assay using a Beckman DU 640 spectrophotometer.^[31] In brief, xylose samples were reacted with phloroglucinol in acidic media at 100 °C for 4 min. Absorbances were measured at 554 nm with the xylose concentration calculated from a calibration curve. Xylose conversion [Eq. (1)] and furfural selectivity [Eq. (2)]^[32] were calculated as:

$$\text{Conversion} = \frac{\text{initial xylose [mol]} - \text{unreacted xylose [mol]}}{\text{initial xylose [mol]}} \quad (1)$$

$$\text{Selectivity} = \frac{\text{furfural [mol]}}{\text{initial xylose [mol]} - \text{unreacted xylose [mol]}} \quad (2)$$

Procedure for the conversion of xylose to furfural: D-(+)-Xylose (100 mg), DMSO (1 mL), and an acid catalyst, were loaded into a 5 mL vial with a magnetic stir bar and sealed. The mixture was stirred at 300 rpm and heated in a constant temperature oil bath after a certain reaction time. In general, three replicates were taken for each data point. Zero time was taken to be the instant the vial was immersed in the oil bath. After reaction, the vial was cooled to room temperature and the sample was analyzed for furfural and unreacted xylose by HPLC and UV/vis spectroscopy, respectively.

Characterization of Nafion 117: SEM–EDX analysis was performed on a Hitachi S 2600N SEM (Hitachi Scientific Instruments, Tokyo, Japan) equipped with a microanalysis detector for EDX (Inca x-act, Oxford Analytical Instruments, Abington, UK). Nafion samples (pristine and post-reaction) were glued on double-sided carbon tape and mounted on a sample holder. EDX spectra were collected at 30° angle, 20 kV accelerating voltage and 20 nm working distance. EDX results were analyzed using incorporated Inca, Point and Analyze software. SEM micrographs acquired in backscattered electron mode were obtained at low vacuum of 15 Pa, 25 kV of accelerating voltage with a 12 mm working distance.

ATR–FTIR spectra were collected (Bruker Tensor 27 FTIR spectrophotometer) from 4000 to 600 cm⁻¹ for 64 scans and 4 cm⁻¹ resolution using a zinc selenide (ZnSe) crystal. AFM (atomic force microscopy) measurement was performed using tapping mode at scan rates of 0.5 Hz with 512×512 pixels on a Dimension 3100 with a NanoScope IV controller (Veeco Digital Instruments, Santa Barbara, CA). All measurements were made using a silicon cantilever (MPP-11100, spring constant ca. 40 Nm⁻¹, resonance frequency ca. 300 kHz, NanoDevices, CA).

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