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One-pot Formation of Furfural from Xylose via Isomerization and Successive Dehydration Reactions over Heterogeneous Acid and Base Catalysts

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An efficient furfural formation from xylose, a major pentose in hemicellulose of biomass, was demonstrated using a pair of solid acid and base in one-pot. High furfural yield was obtained in polar aprotic solvents including *N*,*N*-dimethylformamide using Amberlyst-15 and hydrotalcite under moderate conditions. This efficient production of furfural was performed via aldose–ketose isomerization of xylose to xylulose by solid base and successive dehydration of xylulose to furfural by solid acid.

Production of chemicals and fuels from renewable resources has received considerable attention.[1,2] Lignocellulosic biomass, the most abundant biomass consists of cellulose (ca. 35–50%), hemicelluloses (ca. 25–30%), and lignin (ca. 15–30%).[1,2] Xylose, a major pentose, is involved as a form of xylan in hemicelluloses. Furan derivatives such as 5-(hydroxymethyl)-furfural (HMF) and furfural have great potentials as important platforms for a variety of chemicals including plastics, polymers, and pharmaceuticals.[3–6] They can be obtained by dehydration of monosaccharides of hexoses (glucose and fructose) and pentose (xylose). Efficient synthesis of furfural from xylose is strongly desirable as well as HMF synthesis from hexoses including glucose and fructose.

Heterogeneous acid catalysts have been examined for dehydration of xylose to furfural because of these advantages including easy separation, nontoxicity, and recyclability. H-mordenite and H-Y faujasite were found to exhibit dehydration at 433 K in water–methyl isobutyl ketone or water–toluene solution by Moreau et al.[7] Valente et al. have investigated the dehydration using a variety of solid acid catalysts including sulfonic acid appended porous silicas,[8] porous niobium silicates,[9] metal oxide nanosheets,[10] heteropolyacids,[11] sulfated zirconia,[12] and delaminated zeolites[13] in water–toluene biphase systems. Although good yield of furfural was obtained ($<47\%$), these reactions were performed at high temperature (433 K) and the dehydration mechanism still remains unknown.

In contrast, it is well known that aldoses such as glucose and mannose can be transformed into corresponding ketoses such as fructose by base-catalyzed isomerization.[14] We have very recently demonstrated that a pair of Amberlyst-15 as a solid acid and hydrotalcite as a base catalyst afforded efficient production from 5-(hydroxymethyl)furfural (HMF) of hexoses including glucose, sucrose, and cellobiose.[15] This one-pot reaction involves aldose–ketose isomerization by base and successive dehydration of ketose (fructose) by acid. Because xylose is an aldopentose, this one-pot system seems to be applicable for furfural formation from xylose as well as 5-(hydroxymethyl)furfural formation from glucose as shown in Figure 1, although there are no reports of xylulose as an important intermediate for furfural formation. One-pot reaction using heterogeneous catalysts afford environmentally-friendly benefits, including avoidance of isolation and purification of intermediate compounds, which saves time, energy, and solvent.[16–20]

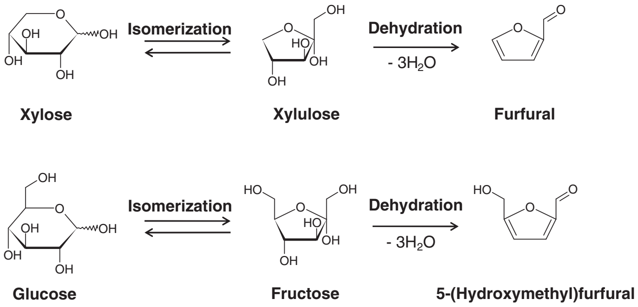

Figure 1. Possible reaction schemes for furfural formation via aldose–ketose isomerization and successive dehydration.

Here, we demonstrated an efficient production of furfural from xylose using a combination of solid acid and base catalysts in one-pot under moderate conditions. To our best knowledge, this is first example of furfural production from xylose via xylulose formation as an intermediate.

The reaction was typically performed using 0.1 g of solid acid catalyst and/or 0.2 g of solid base catalyst, 0.1 g of substrate (xylose) and 3 mL of *N*,*N*-dimethylformamide at 353–403 K for 3 h.[21] The experiments were carried out in a Schlenk tube attached with reflux condenser under an N_2 atmosphere. The conversions and yields were estimated using high-performance liquid chromatography (HPLC) (Waters) with an Aminex HPX-87H column from Bio-Rad Laboratories, Inc. Samples were diluted with water before HPLC measurement. The products were analyzed using a refractive index (RI) detector. The analysis conditions were set as follows: eluent, 10 mM H_2SO_4; flow rate, $0.5\,mL\,min^{-1}$; column temperature, 323 K. For separation of xylose and xylulose, a Shodex Asahipak NH2P-50 4E column (eluent; water:acetonitrile = 25:75) was used.

Table 1 shows furfural formation from xylose (pentose) using solid acid and/or base catalysts at 373 K for 3 h. The individual use of Amberlyst-15 gave 51% xylose conversion, but negligible yield and poor selectivity of furfural as a desired product (below 1%) (Entry 1). In the presence of hydrotalcite, no production of furfural was observed (Entry 2). An efficient production of furfural was obtained in the presence of Amberlyst-15 and hydrotalcite (Entry 3). 42% furfural selectivity at high xylose conversion (57%) has been achieved using 0.1 g of Amberlyst-15 and 0.1 g of hydrotalcite in *N*,*N*-dimethylformamide at 373 K for 3 h, much higher than those of *para*-toluenesulfonic acid (p-TsOH•nH$_2$O) (Entry 6) and sulfuric acid (Entry 7). This clearly indicates that one-pot reaction using a combination of solid acid and base is a powerful

Table 1. Furfural formation from xylose using Amberlyst-15 and hydrotalcite[a]

Entry	Acid	Base	Xylose conv./%	Furfural selec./%
1	Amberlyst-15	—	51	<1
2	—	Hydrotalcite	60	0
3	Amberlyst-15	Hydrotalcite	57, 72[b]	42, 51[b]
4[b]	Amberlyst-15	Amberlyst A26 OH	61	29
5[b]	Amberlyst-15	Amberlyst A21	23	52
6	p-TsOH•nH$_2$O[c]	—	62	25
7	H$_2$SO$_4$[c]	—	81	18
8[d]	—	—	0	0

[a]*Reaction conditions*: xylose (0.1 g), Amberlyst-15 (0.1 g), hydrotalcite (0.1 g), *N*,*N*-dimethylformamide (3 mL), 373 K, 3 h. [b]Amberlyst-15 (0.1 g), solid base (0.2 g). [c]0.5 mmol. [d]Blank.

approach for efficient production of furfural from pentose as well as that of 5-(hydroxymethyl)fufural from hexose. Other characteristic peaks except for furfural were not detected by HPLC, suggesting that undesired by-products seem to be complex compounds which were formed by successive condensation of furfural and intermediates of xylose transformation.[8–13] It should be noted that the one-pot synthesis of furfural could be applied using other combinations of solid acid and base. The pairs of ion-exchangre resins of Amberlyst-15 acid resin and commercial anion-exchange base resins including Amberlyst A26 OH (OH form) and Amberlyst A 21 (tertiary amine form) also gave furfural (Entries 4 and 5). Furfural was also produced in other polar aprotic solvents including *N*,*N*-dimethylacetamide, dimethyl sulfoxide, and acetonitrile (see SI, Table S1).[21] Furfural selectivity was ca. 50% for *N*,*N*-dimethylformamide, *N*,*N*-dimethylacetamide, and dimethyl sulfoxide whereas xylose conversion depended on those of solvents, suggesting that isomerization of xylose by base might be affected by solvents. This one-pot reaction, however, could not proceed in water because of difficulty of dehydration by a solid acid as previously reported.[15]

The amount of hydrotalcite plays an important role in the one-pot reaction although most of previous examples of one-pot reaction using a combination of acid and base did not mention about it in detail. Figure 2 shows the furfural formation from xylose using various amount of hydrotalcite in the presence of Amberlyst-15. It appears that the addition of hydrotalcite significantly increases furfural yield and selectivity. The use of 0.05 g of hydrotalcite in the presence of Amberlyst-15 afforded 34% furfural selectivity whereas the absence of hydrotalcite gave less than 1% selectivity. Both furfural selectivity and xylose conversion increased with increasing hydrotalcite amount, affording 51% selectivity at 72% xylose conversion using 0.2 g of hydrotalcite in the presence of Amberlyst-15 (Table 1, Entry 3). Excess addition of hydrotalcite (0.3 g), however, resulted in decreases of both furfural yield and xylose conversion probably due to inefficient contacts of substrate and solid catalysts by poor stirring. Other possibility of decrease of xylose conversion is adsorption of intermediates onto hydrotalcite, which was clearly observed by color change of solid hydrotalcite from white to dark-brown.

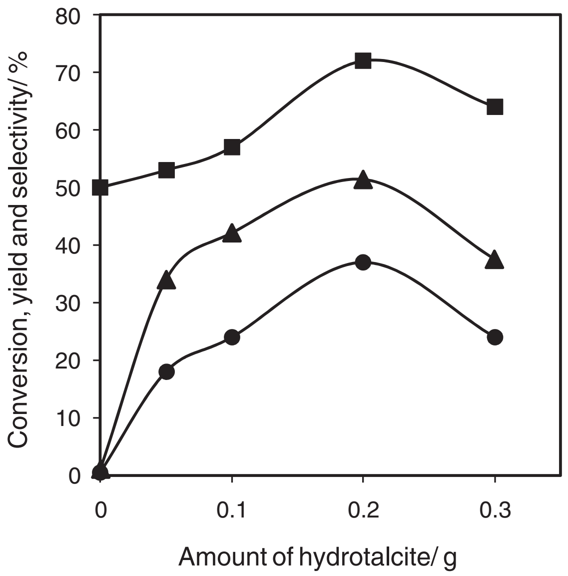

Figure 2. Effect of amount of hydrotalcite on furfural production from xylose in one-pot reaction. Xylose conversion (square), furfural yield (circtle), and furfural selectivity (triangle). *Reaction conditions*: xylose (0.1 g), Amberlyst-15 (0.1 g), hydrotalcite (0–0.3 g), *N*,*N*-dimethylformamide (3 mL), 373 K. 3 h.

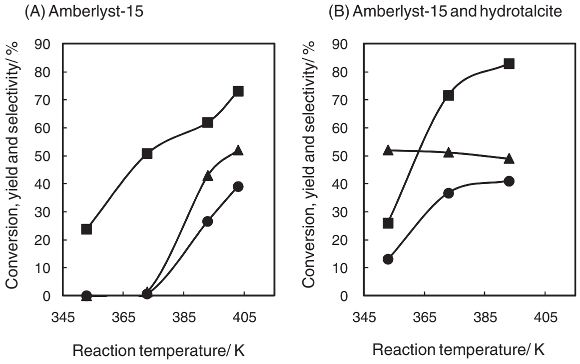

Figure 3. Dependence of xylose dehydration over (A) Amberlyst-15 and (B) a combination of Amberlyst-15 and hydrotalcite on reaction temperature. Xylose conversion (square), furfural yield (circle), and furfural selectivity (triangle). *Reaction conditions*: xylose (0.1 g), Amberlyst-15 (0.1 g), hydrotalcite (0.2 g), *N*,*N*-dimethylformamide (3 mL), 353–403 K, 3 h.

As mentioned in previous research on furfural synthesis using solid acid catalysts,[7–13] individual use of an acid catalyst actually gave furfural at high temperature. Furfural formation using individual Amberlyst-15 and a combination of Amberlyst-15 and hydrotalcite are compared as a function of reaction temperature (Figure 3). Although no or negligible yield of furfural was obtained below 373 K in the presence of Amberlyst-15, the yield increased with increase in reaction temperature, reached 39% at 403 K. This high temperature, however, has a significant drawback for reuse of the ion-exchange resin. The yield of furfural drastically decreased from 39% to 18% for 1st reuse and 10% for 2nd reuse (see SI, Figure S1).[21]

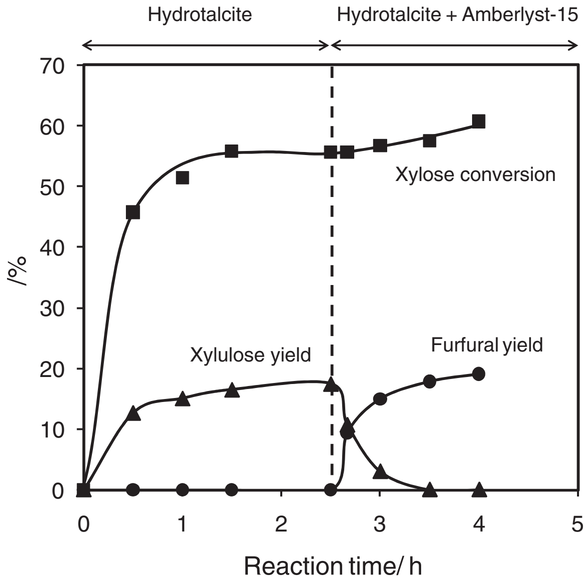

Figure 4. Plot of xylose conversion (square), xylulose yield (triangle), and furfural yield (circle) for the transformation of xylose as a function of reaction time. Amberlyst-15 was added after 2.5 h. *Reaction conditions*: xylose (0.1 g), hydrotalcite (0.2 g), Amberlyst-15 (0.1 g), *N*,*N*-dimethylformamide (3 mL), 353 K.

A combination of Amberlyst-15 and hydrotalcite exhibits comparable activity even at 373 K (37% furfural yield) to using Amberlyst-15 at 403 K. This one-pot reaction afforded furfural even at 353 K with high selectivity (ca. 50%), much different from that using individual solid acid. Owing to the activity at moderate temperature, recyclability of catalysts was improved (see SI, Figure S1).[21]

The appearance of the ketose, xylulose, via isomerization of xylulose by base catalyst has been confirmed by the occurrence of sequential reactions as shown in Figure 4. In the presence of hydrotalcite, xylulose yield gradually increased with increasing reaction time to 2.5 h. After the addition of a solid acid, xylulose was successfully transformed into furfural. It should be noted that this reaction pathway is much different from that using individual acid catalyst, where furfural could be formed by a direct intramolecular rearrangement of the protonated pyranose proposed by quantum mechanical calculations,[22] resulting in the difference of furfural yield between individual use of an acid catalyst and a combination of acid and base catalysts under moderate temperature as shown in Figure 3.

This behavior of sequential reaction is similar to 5-(hydroxymethyl)furfural formation from glucose using the combination of Amberlyst-15 and hydrotalcite. Therefore, 5-(hydroxymethyl)furfural and furfural could be formed together from mixtures of hexose and pentose in this one-pot system. Table 2 lists the results of dehydration of glucose and xylose in the presence of Amberlyst-15 and hydrotalcite. The pair afforded 5-(hydroxymethyl)furfural and furfural from glucose and xylose, respectively whereas individual use of Ambelyst-15 gave negligible activity.

In conclusion, an efficient production of furfural from xylose has been achieved using a pair of solid acid and base catalysts under moderate conditions. This one-pot reaction involves xylose–xylulose isomerization and successive dehydration of xylulose to furfural as well as 5-(hydroxymethyl)furfural formation from glucose.

Table 2. 5-(Hydroxymethyl)furfural and furfural formation from mixture of glucose and xylose using Amberlyst-15 and hydrotalcite[a]

Acid	Base	Yield/%	
		HMF	Furfural
Amberlyst-15	—	0	1
Amberlyst-15	Hydrotalcite	48	41

[a] *Reaction conditions*: glucose (0.05 g), xylose (0.05 g), Amberlyst-15 (0.1 g), hydrotalcite (0.2 g), *N*,*N*-dimethylformamide (3 mL), 373 K, 3 h.

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References and Notes

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