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One-pot Synthesis of Furfural from Xylose using Al_2O_3–Ni-Al Layered Double Hydroxide Acid-Base Bi-functional Catalyst and Sulfonated Resin

Mahiro Shirotori, Shun Nishimura, and Kohki Ebitani*

School of Materials Science, Japan Advanced Institute of Science and Technology, 1-1 Asahidai, Nomi, Ishikawa 923-1292

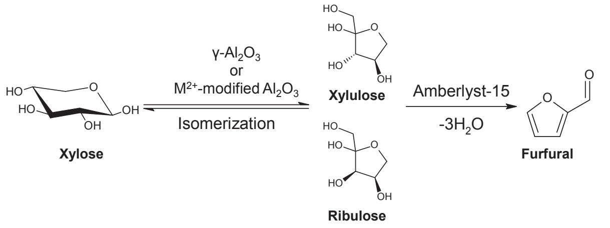
(E-mail: ebitani@jaist.ac.jp)

Furfural was effectively synthesized from xylose in a one-pot manner by the combined use of Ni^{2+}-modified γ-Al_2O_3 (Al_2O_3–Ni-Al layered double hydroxide (LDH)) and a sulfonated resin (Amberlyst-15) at 373 K (46% yield). The addition of Ni^{2+} onto γ-Al_2O_3 generated the bi-functional sites for Lewis acid γ-Al_2O_3 and Brønsted base Ni-Al LDH at close boundary, and these facilitate the xylose isomerization into xylulose and/or ribulose to afford good yield of furfural after successive dehydration of generated ketopentoses on Amberlyst-15.

Conversion of biomass resources into value-added chemicals/fuels is an important reaction to utilize renewable resources.[1–3] Cellulose and hemicellulose, the major component of lignocellulosic biomass, are the most abundant compounds that are mainly composed of monosaccharides.[4,5] Cellulose and hemicellulose can be converted into monosaccharides like glucose and xylose by the hydrolysis over activated carbons.[6–9] Therefore, successive chemical conversion of saccharides into value-added chemicals such as furans, sugar alcohols, levulinic acid, and γ-valerolactone has attracted much attention as one of the reactions worth conducting in biorefineries.

Furfural, a dehydration product of pentoses like xylose and arabinose, has great potential as non-petroleum building blocks in the production of polymers, pharmaceuticals, biofuels, and fine chemicals.[5,10–13] Conventionally, dehydration of xylose into furfural was examined using various solid acid catalysts such as sulfated zirconia,[14] porous niobium silicate,[15] sulfonic acid-modified mesoporous shell silica beads,[16] propylsulfonic SBA-15,[17] and zeolite-based catalysts.[18–21] However, due to the stability of xylose, these direct dehydrations need high reaction temperatures (>423 K).

To overcome this problem, one approach was developed, merging the isomerization of xylose (aldose) into unstable xylulose (ketose) before dehydration.[22,23] Dehydration of xylose via aldose–ketose isomerization over Lewis acid catalysts under a mild condition (373 K) has been reported by Binder et al.[23] and Suzuki et al.[24] using $CrCl_2$ with LiBr and SO_4^{2-}/SnO_2, respectively. As a different expedient, we have demonstrated that a combined use of the Brønsted solid base Mg-Al layered double hydroxide (Mg-Al LDH) and the Brønsted solid acid Amberlyst-15 efficiently afforded furfural from xylose in a one-pot manner. This reaction involves aldose–ketose isomerization by base LDH and successive dehydration of ketose by acid Amberlyst-15.[22] As advanced research studies, the bi-functional Cr/Mg-Al LDH surface, which consists of LDH-originated Brønsted base sites and Lewis acid sites on the dispersed Cr_2O_3, was a better isomerization catalyst than bare Mg-Al LDH, where the pair of Brønsted base and Lewis acid effectively promotes the aldose–ketose isomerization.[25]



Scheme 1. Possible reaction path for furfural synthesis via aldose–ketose isomerization over γ-Al_2O_3-based catalyst and successive dehydration on Amberlyst-15.

Herein, we focused on the modification of typical solid Lewis acid γ-Al_2O_3 with M^{2+} ion additions. M^{2+} species from aqueous solution onto γ-Al_2O_3 can generate M^{2+}-Al^{3+} LDH-type compounds,[26] thus, the addition of M^{2+} onto γ-Al_2O_3 would easily generate bi-functional Lewis acid γ-Al_2O_3–Brønsted base M-Al LDH sites. We investigated the modification effects of adding M^{2+} ions onto γ-Al_2O_3 in the one-pot synthesis of furfural from xylose with Amberlyst-15 (Scheme 1). The characterizations on crystal structure, crystallite size, and surface area of the M^{2+}-modified Al_2O_3 are demonstrated. The Lewis acidity is estimated by the Meerwein–Ponndorf–Verley (MPV) reduction of furfural to furfuryl alcohol in 2-propanol (see Supporting Information (SI)).

Preliminarily, we investigated the activity of combined use of γ-Al_2O_3 and Amberlyst-15 for xylose transformation (see Experimental procedure in SI). The time courses are shown in Figure 1. The use of γ-Al_2O_3 alone hardly yielded furfural at 373 K, whereas furfural was efficiently produced with the combined use of γ-Al_2O_3 and Amberlyst-15. In the latter case, the yield of furfural increased with time, and it became constant at ca. 45% after 17 h of the reaction. It is noteworthy that this value was higher than that in previous reports performed at 373 K using solid catalysts.[22,24] The HPLC profile of the reaction mixture at 8 h is shown in Figure S1. In the presence of γ-Al_2O_3 alone, three peaks were observed at retention times of 7.5, 7.7, and 8.0 min, which could be assigned to the xylose, xylulose and lyxose, and ribulose and arabinose, respectively. These results indicated that γ-Al_2O_3 significantly promoted the isomerization of xylose to such pentoses. For combined use with Amberlyst-15, very few amounts of such pentoses were detected because Amberlyst-15 is ineffective for dehydration of aldopentoses such as xylose and arabinose below 373 K,[22,25,27] the reaction path of one-pot synthesis of furfural from xylose is proposed as follows: first, γ-Al_2O_3 promoted the isomerization of xylose toward xylulose, lyxose, ribulose, and/or arabinose; thereafter, Amberlyst-15 effectively dehydrated xylulose and ribulose toward furfural.

In the next stage, we prepared various M^{2+}-modified Al_2O_3 catalysts (M^{2+}/Al^{3+} atomic ratio = 0.05, see SI) and evaluated

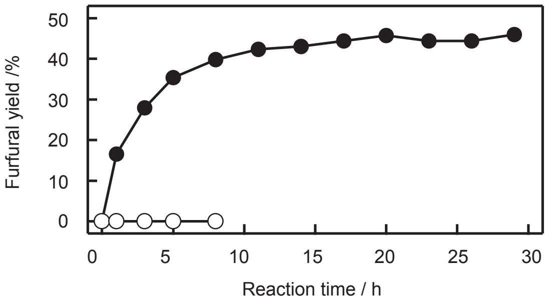


Figure 1. Time course of furfural yield from xylose on γ-Al_2O_3 (○) and combined use of γ-Al_2O_3 and Amberlyst-15 (●). *Reaction conditions:* xylose (0.67 mmol), γ-Al_2O_3 (0.2 g), Amberlyst-15 (0.1 g), DMF (3 mL), 373 K, 500 rpm, N_2 flow (30 mL min^{-1}).

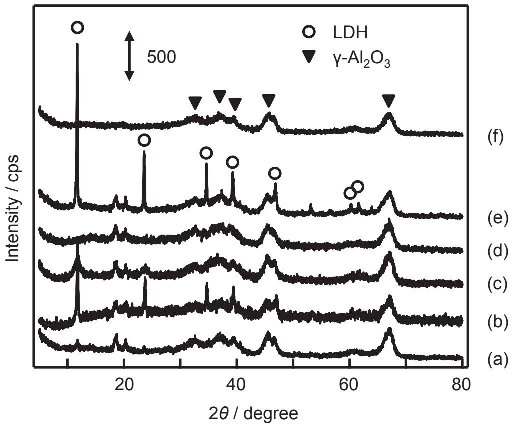


Figure 2. XRD patterns of γ-Al_2O_3 and various M^{2+}-modified Al_2O_3; (a) Mg^{2+}-modified Al_2O_3, (b) Co^{2+}-modified Al_2O_3, (c) Ni^{2+}-modified Al_2O_3, (d) Cu^{2+}-modified Al_2O_3, (e) Zn^{2+}-modified Al_2O_3, and (f) γ-Al_2O_3.

their catalytic performances and structural properties. The XRD patterns of various M^{2+}-modified Al_2O_3 and bare γ-Al_2O_3 are shown in Figure 2. All prepared M^{2+}-modified Al_2O_3 possessed the γ-Al_2O_3 phase. Interestingly, XRD patterns of LDH structure were also observed for Mg^{2+}, Co^{2+}, Ni^{2+}, and Zn^{2+}-modified Al_2O_3.

Table 1 summarizes the catalytic activities for one-pot synthesis of furfural from xylose using M^{2+}-modified Al_2O_3 and Amberlyst-15. Catalytic activity of M^{2+}-modified Al_2O_3 for the MPV reduction was estimated based on the initial rate for the hydrogenation of furfural. BET specific surface areas of M^{2+}-modified Al_2O_3 are also listed in Table 1. It remarkably indicated that the pairs of Ni^{2+}-modified Al_2O_3 and Amberlyst-15 showed better catalytic activities for furfural synthesis than that of γ-Al_2O_3 and Amberlyst-15. Since the BET surface areas of M^{2+}-modified Al_2O_3 were almost the same values (136–158 $m^2\,g^{-1}$), no significant correlation between catalytic activity for furfural synthesis and surface area were expected in these catalysts.

In contrast, the good correlation was observed between the catalytic activities of γ-Al_2O_3 and Mg^{2+}-, Co^{2+}-, Cu^{2+}-, and Zn^{2+}-modified Al_2O_3 for furfural synthesis and MPV reduction, as shown in Figure 3 (open circle); the activity for furfural synthesis increased with increasing activity for MPV reduction.

Table 1. Catalytic activities and surface area of M^{2+}-modified Al_2O_3

Modified metal ion	Furfural yield[a,b]/%	Initial rate for furfural synthesis[a,c] /mmol $g^{-1}\,h^{-1}$	Initial rate for MPV reduction[d] /mmol $g^{-1}\,h^{-1}$	S_{BET}[e]/$m^2\,g^{-1}$
Mg^{2+}	38	0.36	2.32	154
Co^{2+}	37	0.30	2.22	155
Ni^{2+}	46	0.45	2.25	158
Cu^{2+}	25	0.21	0.47	153
Zn^{2+}	33	0.32	1.82	136
—	40	0.37	2.92	193

[a]*Reaction conditions:* xylose (0.67 mmol), M^{2+}-modified Al_2O_3 (0.2 g), Amberlyst-15 (0.1 g), DMF (3 mL), 373 K, N_2 flow (30 mL min^{-1}). [b]8 h. [c]1 h. [d]*Reaction conditions:* furfural (1.3 mmol), 2-propanol (83 mmol), M^{2+}-modified Al_2O_3 (0.1 g), 355 K, 1 h. [e]BET specific surface area.

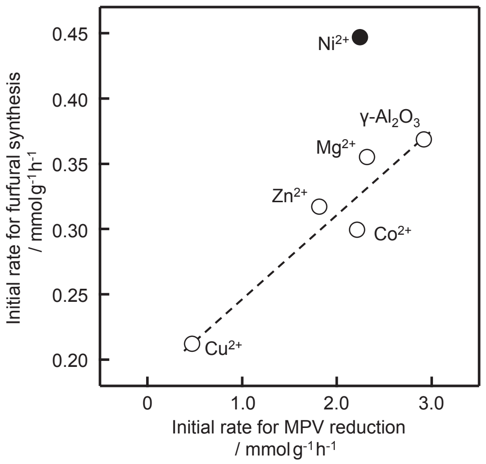


Figure 3. Correlation of activities for MPV reduction and furfural synthesis over various M^{2+}-modified Al_2O_3 catalysts.

Román-Leshkov et al. have reported that the isomerization of aldose into ketose over Lewis acid catalysts like tin-containing zeolite proceeded via MPV reduction under hydride shift mechanism.[28] Therefore, Lewis acidity is an important factor in M^{2+}-modified Al_2O_3 catalysts. In fact, a linear trend ($R^2 = 0.90$) was assigned in Figure 3 except for Ni^{2+}-modified Al_2O_3 (closed circle); i.e. the initial rate for furfural production of Ni^{2+}-modified Al_2O_3 is faster than Mg^{2+}- or Co^{2+}-modified Al_2O_3, whereas MPV reduction occurs with almost the same rate. This result suggested that the improvement of activity for furfural synthesis in Ni^{2+}-modified Al_2O_3 catalyst was hardly explained by Lewis acidity alone. Indeed, the activity for MPV reduction on Ni^{2+}-modified Al_2O_3 (2.25 mmol $g^{-1}\,h^{-1}$) was slower than that on γ-Al_2O_3 (2.92 mmol $g^{-1}\,h^{-1}$).[29] Thus, the effects of generated Ni-Al LDH need to be considered.

To discuss the singularity of Ni^{2+} modification, basic density of Ni^{2+}-modified Al_2O_3 and crystallite size of generated Ni-Al LDH on γ-Al_2O_3 were investigated. An increase of base density of Ni^{2+}-modified Al_2O_3 (0.71 nm^{-2}) from γ-Al_2O_3 (0.59 nm^{-2}) owing to generation of Ni-Al LDH on γ-Al_2O_3 was determined by N_2 adsorption and titration with benzoic acid. Interestingly, it was observed that the generated LDH (003) plane crystallite size over Ni^{2+}-modified Al_2O_3 was obviously smaller (7 nm) than Mg^{2+}-modified Al_2O_3 (25 nm), Co^{2+}-

modified Al_2O_3 (33 nm), and Zn^{2+}-modified Al_2O_3 (43 nm) (see SI, Figure S2). These suggested the possibility that xylose is successfully converted using coexistence of small basic Ni-Al LDH with γ-Al_2O_3.

To verify this hypothesis, we prepared the physically mixed catalyst of small Ni-Al LDH (5 nm) and γ-Al_2O_3 following to the estimation; viz. the weight ratio of Ni-Al LDH and γ-Al_2O_3 in the Ni^{2+}-modified Al_2O_3 is 0.16 by the XRD peak intensities for Ni-Al LDH (003) and γ-Al_2O_3 (440) plane (see SI, Figure S3), and then applied it to furfural synthesis with Amberlyst-15. Initial rate of the physically mixed catalyst (0.34 mmol g^{-1} h^{-1}) is almost similar to that of bare γ-Al_2O_3, and significantly smaller than Ni^{2+}-modified Al_2O_3 (0.45 mmol g^{-1} h^{-1}). Furthermore, when the physical mixture of γ-Al_2O_3 and Ni-Al LDH was applied to the MPV reduction, the initial rate for furfuryl alcohol was 2.22 mmol g^{-1} h^{-1}, similar to that of Ni^{2+}-modified Al_2O_3 (2.25 mmol g^{-1} h^{-1}). Therefore, the enhanced activity for xylose conversion by the Ni^{2+}-modified Al_2O_3 could not be explained in terms of the Lewis acidity or simple coexistence of fine Ni-Al LDH and γ-Al_2O_3.

Figure S4 shows TEM images of γ-Al_2O_3 and Ni^{2+}-modified Al_2O_3. Ni^{2+}-modified Al_2O_3 possess a morphology in which acicular γ-Al_2O_3 and flat plate Ni-Al LDH are mixed uniformly. Caillerie et al. have reported that the breaking of Al–O bonds of γ-Al_2O_3 can be promoted by Ni^{2+} or Co^{2+} ions at neutral pH, thus the adsorption of Co^{2+} or Ni^{2+} complexes from aqueous solution onto γ-Al_2O_3 can generate Ni-Al and Co-Al hydrotalcite-type compounds via three simultaneous phenomena at the oxide/water interface; the adsorption of ions, the alumina dissolution, and the coprecipitation of M^{2+} with Al^{3+} ions extracted from support.[26] Accordingly, we considered that Ni^{2+}-modified Al_2O_3 possess boundaries between Al_2O_3 and LDH more abundantly than a simple mixture of γ-Al_2O_3 and Ni-Al LDH. In addition, since the crystallite size of Ni-Al LDH in Ni^{2+}-modified Al_2O_3 was much smaller than that of Mg^{2+}-, Co^{2+}-, and Zn^{2+}-modified Al_2O_3, the Ni^{2+}-modified Al_2O_3 would possess a lot of close boundaries compared to other M^{2+}-modified Al_2O_3. Therefore, we suggested that the close boundaries between γ-Al_2O_3 and Ni-Al LDH facilitated the isomerization xylose into xylulose as bi-functional Lewis acid–Brønsted base active sites. Finally, it was noted that the combined use of Ni^{2+}-modified Al_2O_3 and Amberlyst-15 yielded 46% furfural from xylose in 8 h, though the pair of bare γ-Al_2O_3 and Amberlyst-15 needed 17 h (yield = 45%).

In conclusion, one-pot synthesis of furfural from xylose efficiently proceeded by a combined use of Ni^{2+}-modified Al_2O_3, which contains fine Ni-Al layered double hydroxide (LDH) crystal, and Amberlyst-15. The close boundaries between Lewis acid γ-Al_2O_3 and Brønsted base Ni-Al LDH facilitated the isomerization of xylose into xylulose and ribulose, which in turn is dehydrated into furfural catalyzed by Brønsted acid Amberlyst-15.

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Supporting Information is available on http://dx.doi.org/10.1246/cl.151064.

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