

Supporting Information for

One-Pot Synthesis of Furfural Derivatives from Pentoses using Solid Acid and Base Catalysts

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Table S1. Structural properties and activities for one-pot synthesis of **2** from xylose and/or arabinose.

Entry	M/HTs	Yield ^a /%		$S_{\text{BET}}^c / \text{m}^2 \text{g}^{-1}$
		furfural	2	
1	HT	0, 0 ^b	21, 17 ^b	45
2	Cr/HT	3, 3 ^b	44, 42 ^b	130
3	Sn/HT	1, 1 ^b	34, 34 ^b	95
4	Zr/HT	1	25	89
5	Ni/HT	0	24	53
6	La/HT	0	23	46
7	Fe/HT	2	19	124
8	Cu/HT	1	13	62

^aYield for one-pot synthesis of **2** from xylose and/or arabinose. Reaction conditions: Step 1) xylose (0.67 mmol), M/HTs (0.2 g), Amberlyst-15 (0.1 g), DMF (3 mL), 373 K, N₂ flow (30 mL min⁻¹). Step 2) After the step 1, the reaction mixture was cooled down to room temperature without stirring. Then 0.8 mmol of **1** was added and restarted the reaction. ^bArabinose (0.67 mmol) was used as the substrate. ^cBET surface area.

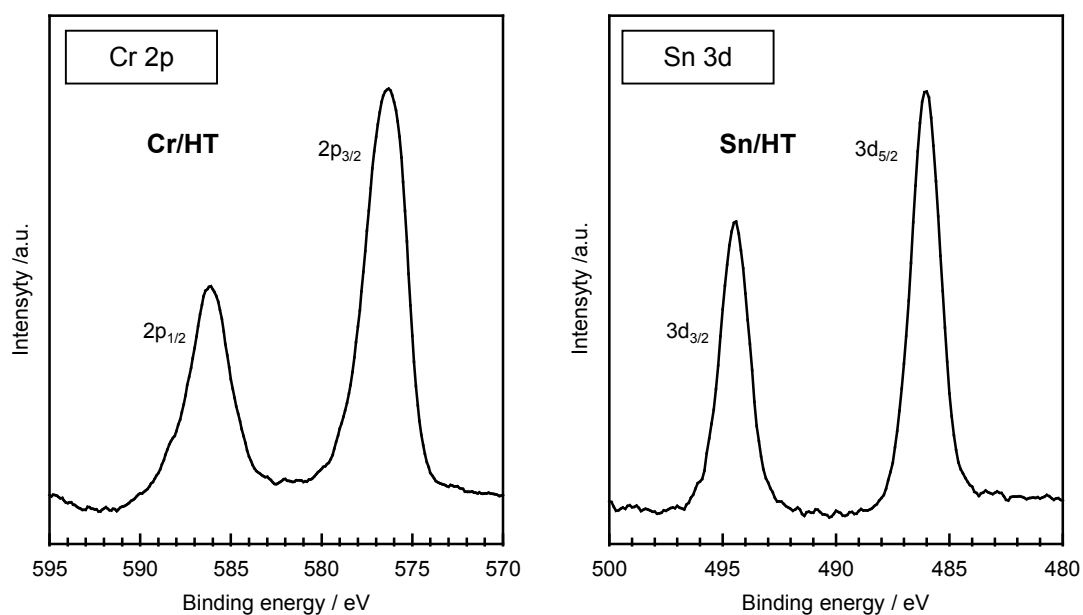


Figure S1. XPS spectra of Cr/HT and Sn/HT.

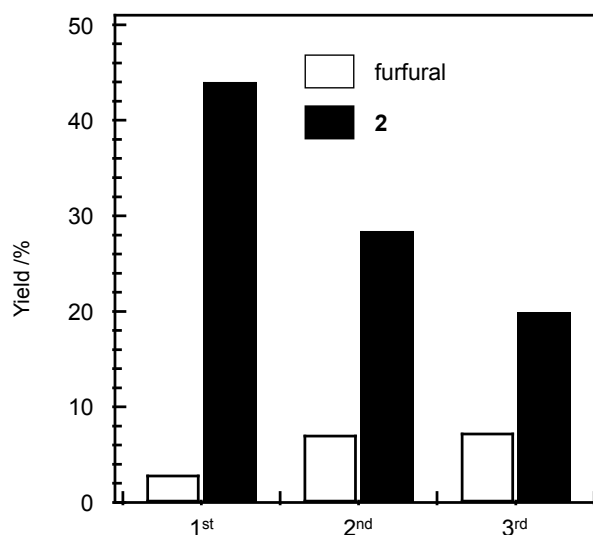


Figure S2. Recyclability of Cr/HT and Amberlyst-15 for the one-pot synthesis of **2** from xylose.

Reaction conditions: Step 1) xylose (0.67 mmol), Cr/HT (0.2 g), Amberlyst-15 (0.1 g), DMF (3 mL), 373 K, N₂ flow (30 mL min⁻¹). Step 2) After the step 1, the reaction mixture was cooled down to room temperature without stirring. Then 0.8 mmol of malononitrile (**1**) was added, and the following reaction was started.

After the reaction, catalysts were collected and washed with DMF and water for several times, and then reused for the next reaction. As shown in Figure S2, the yield of **2** (black) gradually decreased from 44% to 28% (for 2nd run) and 20% (for 3rd run). In contrast, the yield of furfural (white), an intermediate of one-pot synthesis of **2**, increased from 3% to 7% (for 2nd and 3rd runs). These results clearly showed that step 2, the Knoevenagel condensation of furfural catalyzed by base, became slower in reuse runs. In the same time, color of the Cr/HT was changed from green to dark-brown before and after the reaction. Thus, we supposed that some of base sites of Cr/HT became covered by the adsorbents of intermediate and/or other by-products, and those caused decrease of catalytic activity for the further one-pot reactions.

It is notable that even though Cr/HT and Amberlyst-15 in second reaction gave a decrease to 27% of furfurals yield, which is higher value in comparison with 21% for the pair of fresh HT and Amberlyst-15 (See Table S1, entry 1).

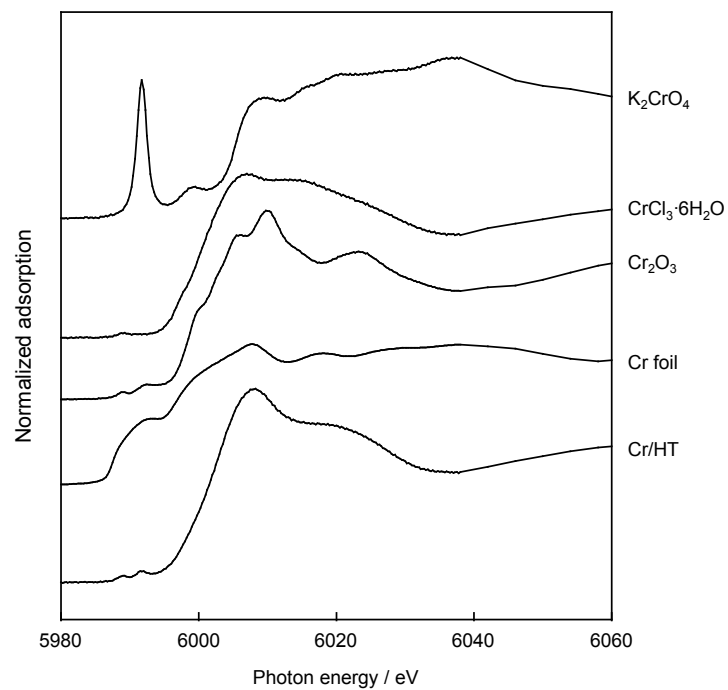


Figure S3. Cr *K*-edge XANES spectra of reference samples and Cr/HT.

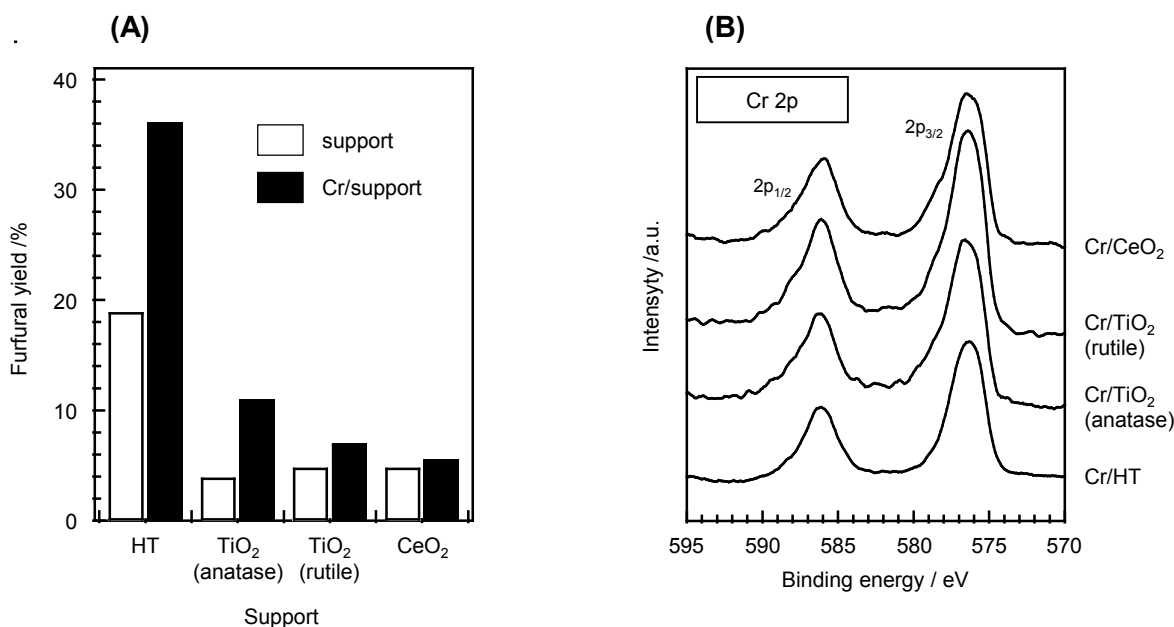


Figure S4. (A) Furfural yields for one-pot conversion of xylose using Cr-supported various metal oxides and Amberlyst-15,* and (B) Cr 2p XPS spectra of the Cr-supported various metal oxides.

*Reaction conditions: xylose (0.67 mmol), support or Cr/support (0.2 g), Amberlyst-15 (0.1 g), DMF 3 mL, 373 K, 3 h, N₂ flow.

TiO₂ (anatase and rutile) and CeO₂ supported Cr catalysts were prepared by an impregnation method (adsorption) in the presence of urea, and applied for the one-pot conversion of xylose to furfural. In these cases, XPS analysis of Cr 2p_{3/2} also supported the presence of Cr₂O₃ species on the Cr-supported various metal oxides similar to Cr/HT (See Figure S4(B)). As shown in Figure S4(A), though the addition of Cr₂O₃ on various supports improved the activity for the one-pot synthesis of furfural from xylose comparing from each support itself, the Cr/HT or the HT itself showed the best activity among Cr/TiO₂ and Cr/CeO₂ or TiO₂ and CeO₂. These results strongly supported our suggestion; the dispersed Cr₂O₃ itself on support was effective for this one-pot reaction (working as the co-catalyst for improvement); however, the main activity was due to the Brønsted base on HT surface in the case of Cr/HT. Thus, we proposed that the isomerization reaction over the Cr/HT mainly occurred through the proton shift on Brønsted base site on HT rather than the hydride shift on Lewis acid Cr₂O₃ sites.