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Supporting Information

One-pot Conversion of the Biomass-derived Xylose and Furfural into Levulinate Esters via Acid Catalysis

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Experimental

All the chemicals used in this study were analytical grade. Dimethoxymethane, 5-hydroxymethylfurfural, xylose and furfural were purchased from Sigma Aldrich, Australia. Methanol was purchased from Merck Australia. The solid acidic resin catalyst, Amberlyst 70, purchased from Dow Chemical, was used as the catalyst for this study. Amberlyst 70 is a solid acidic resin catalyst with the maximum operating temperature of 190°C. The catalyst has an acid density of > 2.55 mmol/g and moisture content of ca. 55 wt%. The detailed technical data sheet for Amberlyst 70 can be found in reference [1].

The experiments were conducted in an EZE-Seal Stirred Reactor. The reactor system consists of a 100 ml EZE-Seal pressure reactor vessel, a high speed stirring device MAG075 MagneDrives® II, a body lift mechanism, a ceramic band heater and a Universal Reactor Controller (URC). The reactor vessel is made of Hastelloy. On the reactor head, the fittings and valves are used for gas and liquid sample port, cooling in- and outlet port, reactor gas inlet and release system. A pressure gage is installed on the reactor head for the reactor pressure monitoring purpose. Because of safety reason, a rupture disc is used to limit the pressure in the reactor. In order to cool down the stirring shaft during experiment, the water cooling channel is installed between reactor head and magnetic drive. A thermowell is installed behind the stirring shaft for measuring temperature of reaction medium with a thermocouple. The reactor is designed to work with the maximum pressure of 227 bar and maximum temperature of 454°C.

In a typical experiment, a certain amount of reactants (1.8 to 10.8 g), 3.6 g of Amberlyst 70 and a certain amount of solvent (40 to 80 mL) were used. Under the experimental conditions, xylose was fully dissolved in either DMM or DMM/methanol. The reactant mixture was mixed and loaded to the reactor at room temperature. After assembling the reactor, the reactor was purged with high-purity nitrogen for three times to remove the air residual inside. The purging process follows the procedure below: The reactor was pressurized with high-purity nitrogen to 40 bar and the pressurized gases were released via a needle valve slowly to atmospheric pressure. The same procedure was repeated for three times. After that, the autoclave was heated to the preset reaction temperature in ca. 10 min and held for typically 120 min with a stirring rate of 500 rpm under the autonomous vapour pressure. For some experiments, sampling was conducted while for some no sampling was conducted, which will be specified in the text. After the experiments, the reactor was cooling down to room temperature in ca. 30 min with cooling water running through a cooling coil installed inside the reactor. After that, the reactor was opened. The liquid products and the solid residual were collected and separated with filter paper (pore size of the filter paper: 2 μm). The liquid products were stored in a fridge before analysis. The solid products were washed with acetone thoroughly until the residual solution was colourless, in order to remove any organic residual absorbed on surface of the catalyst. After washing, the solid residual (catalyst plus polymer) was dried in oven at 105°C for 4 h to constant weight to measure the amount of insoluble polymer formed. The weight of the polymer formed (dry basis) equals to the weight of the solid residual (dry basis) minus the weight of the catalyst loaded (dry basis).

The acid catalysed conversion of xylose and furfural over Amberlyst 70 is heterogeneous reaction. To investigate the potential diffusion limitation, a series experiments with different stirring rate including 300, 500, 900 and 1200 rpm were performed at 160°C with furfural as the starting reactant in DMM/methanol. The detailed reaction conditions were depicted in the title of Figure S9. The results showed that the conversion and the yields of levulinic acid/ester were the similar under the varied stirring rates. This result indicated that the diffusion limitation is insignificant under the conditions employed in this study.

Agilent GC/MS (6890 series GC with a 5973 MS detector) equipped with a HP-INNOWax capillary column was used to analyse the products. The temperature for column was increased from 40 to 260°C at 10°C min^{-1} and helium (2.0 mL min^{-1}) was used as the carrier gas. The temperature for injection port was set at 250°C and acetone was used to dilute the samples before the analysis. The concentration of the sample in acetone is 10 wt.%.

Synchronous spectra of the polymers were recorded with a constant energy difference of –2800 cm^{-1} and a scan rate of 200 nm/min with a Perkin-Elmer LS50B UV-fluorescence spectrometer. The synchronous spectra reveal relative abundance and size of the π-conjugated structures in the polymers, giving direct information about when the polymerization starts. The wavelength of the UV fluorescence spectra could briefly indicate the ring size of the conjugated aromatic ring structures. Typically, the wavelength lower than 290 nm represent the mono aromatic ring structures, while the wavelength at 290 to 320 nm represents the aromatics with two fused rings. The wavelength higher than 320 nm represents the aromatics with three or more fused ring structures [2]. Thus, the longer the wavelength, the bigger the fused ring size. In addition, the height of the spectra represents the abundance of the aromatic ring structures. The higher the peak, the higher the abundance.

The insoluble polymers (mainly on/in catalyst) were characterized with a Perkin-Elmer Spectrum GX FT-IR/Raman Spectrometer. The polymer was mixed with KBr and milled together to prepare a sample with the concentration of the polymer of 1 wt.%. The milled sample was then pressed to round disc for the analysis. Each sample was scanned for 200 times and the baseline of the spectrum was then corrected for comparison.

Acid density of the catalyst was determined by a back titration method following basically the procedure in the literature [3].

Yield of the products (molar basis) is defined by the formula:

$$\text{Yield (mol \%)} = \frac{\text{amount of the product produced}}{\text{theoretical amount of the product from the reactant(s) loaded}} \times 100\%$$

Based on the results in Figure S5 and S6 (the data at the reaction time of 60 min, shown below), the Turnover Frequency (TOF) for the formation of levulinic acid/ester from xylose and furfural over A70 under the conditions employed were 0.87 and 2.04 h^{-1}, respectively. The formation of levulinic acid and methyl levulinate from xylose is slower than that from furfural. This is because from xylose to levulinic acid/ester has an additional step of dehydration of xylose to furfural, which is a relatively slow process. The TOF for the formation of levulinic acid from acid catalyzed conversion of glucose in water over the same Amberlyst 70 catalyst was 2.42 h^{-1} (the data at the reaction time of 60 min was used; Figure 1a in the reference) [4]. Huber et al performed the acid-catalyzed conversion of glucose to levulinic acid with zirconium phosphate as the catalyst. Based on the results in Figure 8 in the reference [5], the TOF for formation of levulinic acid over the Zr/P catalyst with only Brønsted acid sites was 1.94 h^{-1}. Rackemann et al performed acid-catalyzed conversion of glucose with methanesulfonic acid catalyst and the TOF for the formation of levulinic acid is 1.6 at the optimized conditions [6]. The above results showed that, with glucose as the initial reactant, Amberlyst 70 show comparable capacity for the formation of levulinic acid with the zirconium phosphate or methanesulfonic acid catalyst. In DMM/methanol, with furfural as the starting reactant, the TOF for the formation of levulinic acid is also comparable with that from the acid-catalyzed conversion of glucose in water.

[1] http://www.autoclaveengineers.com/products/stirred_reactors/SR_EZE_Seal_Stirred_Lab/index.html

[2] Yi Wang, Xiang Li, Daniel Mourant, Richard Gunawan, Shu Zhang, and Chun-Zhu Li, Energy Fuels 2012, 26, 241–247.

[3] A.Takagaki, M.Toda, M.Okamura, J.N.Kondo, S.Hayashi, K.Domen, M. Hara, Catal Today, 2006, 116,157–161.

[4] X. Hu, S. Wang, L. Wu, D. Dong, M. M. Hasan, C.-Z. Li, Fuel Process. Technol., 2014, 126, 315–323.

[5] R. Weingarten, Y. T. Kim, G. A. Tompsett, A. Fernández, K. S. Han, E. W. Hagaman, W. C. Conner Jr., J. A. Dumesic, G. W. Huber, J. Catal., 2013, 304, 123–134.

[6] D. W. Rackemann, J. P. Bartley, W. O. S. Doherty, Ind. Crop. Prod., 2014, 52, 46–57.

Table S1 Yields or conversion of furfural inacid catalyzed conversion of sugars and furans in DMM or DMM/co-solvent[a]

Entry	Reactant(s)	Typical reaction conditions	[b]Furfural yields/conversion
1	Xylose	T = 140°C, in DMM, t = 120 min , A70	9.5%
2	Xylose	T = 150°C, in DMM, t = 120 min , A70	4.5%
3	Xylose	T = 160°C, in DMM, t = 120 min , A70	1.4%
4	Xylose	T = 170°C, in DMM, t = 120 min , A70	1.8%
5	Xylose	T = 180°C, in DMM, t = 120 min , A70	0
6	Xylose	In DMM/water, T = 150°C, t = 120 min, A70	13.7%
7	Xylose	In DMM/DMSO, T = 150°C, t = 120 min, A70	32.9%
8	Xylose	In DMM/THF, T = 150°C, t = 120 min, A70	12.3%
9	Xylose	In DMM/diethyl ether, T = 150°C, t = 120 min, A70	7.1%
10	Xylose	In DMM/toluene, T = 150°C, t = 120 min, A70	10.1%
11	Xylose	In DMM/iso-propanol, T = 150°C, t = 120 min, A70	18.2%
12	Xylose	In DMM/methyl formate, T = 150°C, t = 120 min, A70	6.7%
13	Xylose	In DMM/methanol (25/15), T = 150°C, t = 120 min, A70	32.9%
14	Xylose	In DMM/ethanol, T = 150°C, t = 120 min, A70	22.5%
15	Xylose	In DMM/methanol (32.5/7.5), T = 150°C, t = 120 min, A70	14.9%
16	Xylose	In DMM/methanol (29/11), T = 150°C, t = 120 min, A70	26.0%
17	Xylose	In DMM/methanol (15/25), T = 150°C, t = 120 min, A70	36.4%

18	Xylose	In DMM/methanol(25/15), T = 150^{o}C, t = 360 min, A70	3.7%
19	Xylose	In DMM/methanol(25/15), T = 160^{o}C, t = 120 min, A70	15.4%
20	Xylose	In DMM/methanol, La(III) catalyst, T = 160^{o}C, t = 120 min	13.4%
21	Xylose	In DMM/methanol La(III) + A70 catalyst, T = 160^{o}C, t = 120 min	6.9%
22	Xylose	In acetaldehyde, T = 160^{o}C, t = 120 min, A70	20.6%
23	Xylose	In DEM/water, T = 160^{o}C, t = 120 min, A70	20.0%
24	Xylose	In DEM/methanol, T = 160^{o}C, t = 120 min, A70	17.5%
25	Xylose	In DEM/ethanol, T = 160^{o}C, t = 120 min, A70	11.8%
26	Xylose	In DMM/methanol, T = 160^{o}C, t = 120 min, A70	1.0%
27	Glucose	In DMM/methanol, T = 160^{o}C, t = 120 min, A70	14.8%
28	Glucose/xylose	In DMM/methanol, T = 150^{o}C, t = 120 min, A70	0
29	Furfural	In DMM/methanol, A70, T = 160^{o}C, t = 120 min	89.3%
30	Furfural	In DMM, A70, T = 160^{o}C, t = 120 min	98.9%
31	Furfural	In DMM/water, A70, T = 160^{o}C, t = 120 min	96.2%

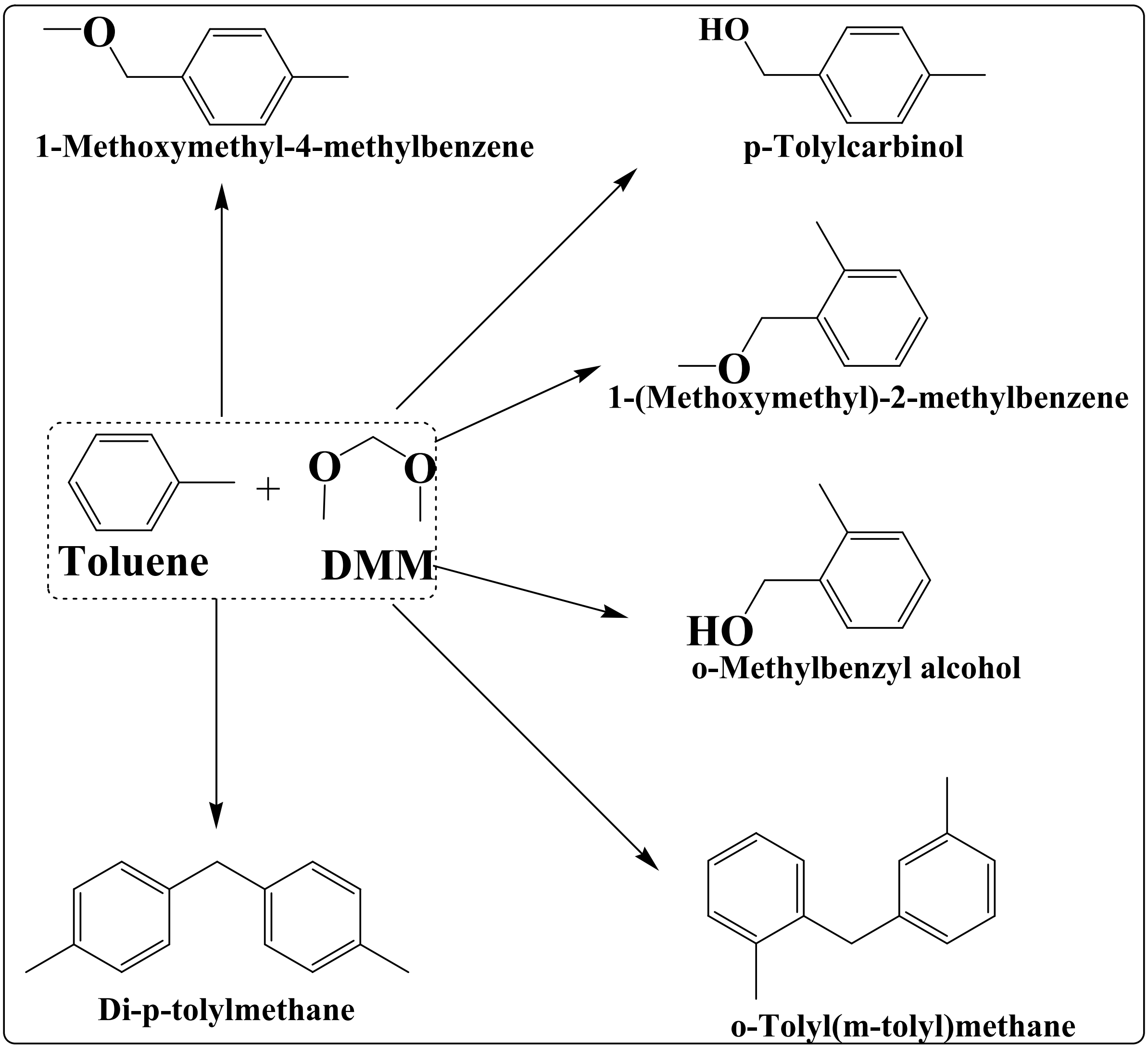
[a] Only typical reaction conditions are specified in Table S1. In general, the experiments were performed at the following conditions: reactant(s): 1.8 g, catalyst: 3.6 g; DMM/co-solvent: 40 mL; p = autogenous vapour pressure.

[b] If the reactant was not furfural, the data was the yield of furfural. If furfural was the starting reactant, the data was the conversion of furfural.

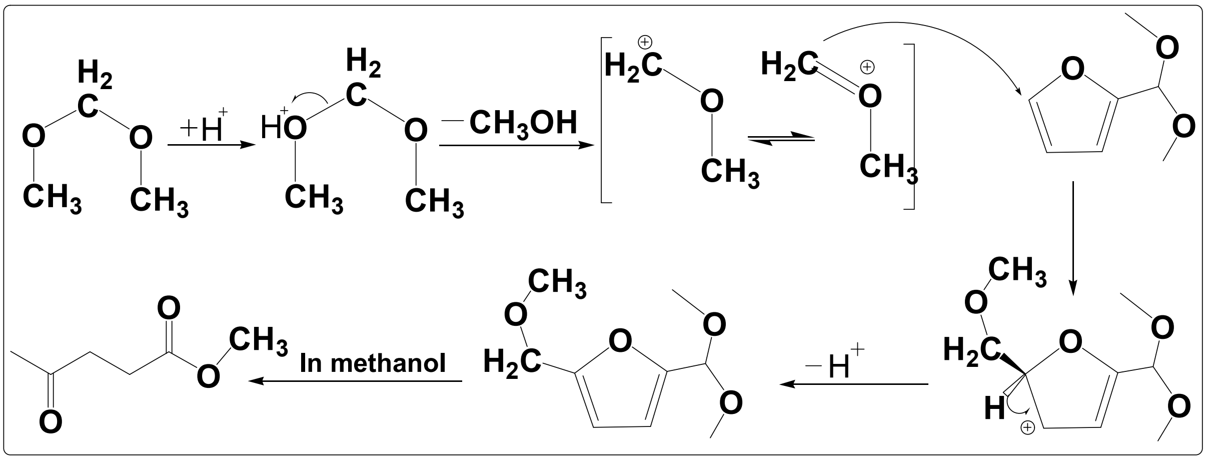
Table S2 Conversion of methyl levulinate in DMM/co-solvent[a]

Entry	Key parameters			Abundance (a. u.)	
	Reactan	Solvents	t (min)	MMO	MOA
1	MLE	DMM	50	7.77E+0	3.65E+0
2	MLE	DMM	100	3.32E+0	1.19E+0
3	MLE	DMM/water	50	2.07E+0	1.67E+0
4	MLE	DMM/water	100	3.42E+0	1.56E+0
5	MLE	DMM/methano	50	1.81E+0	1.66E+0
6	MLE	DMM/methano	100	5.07E+0	2.87E+0

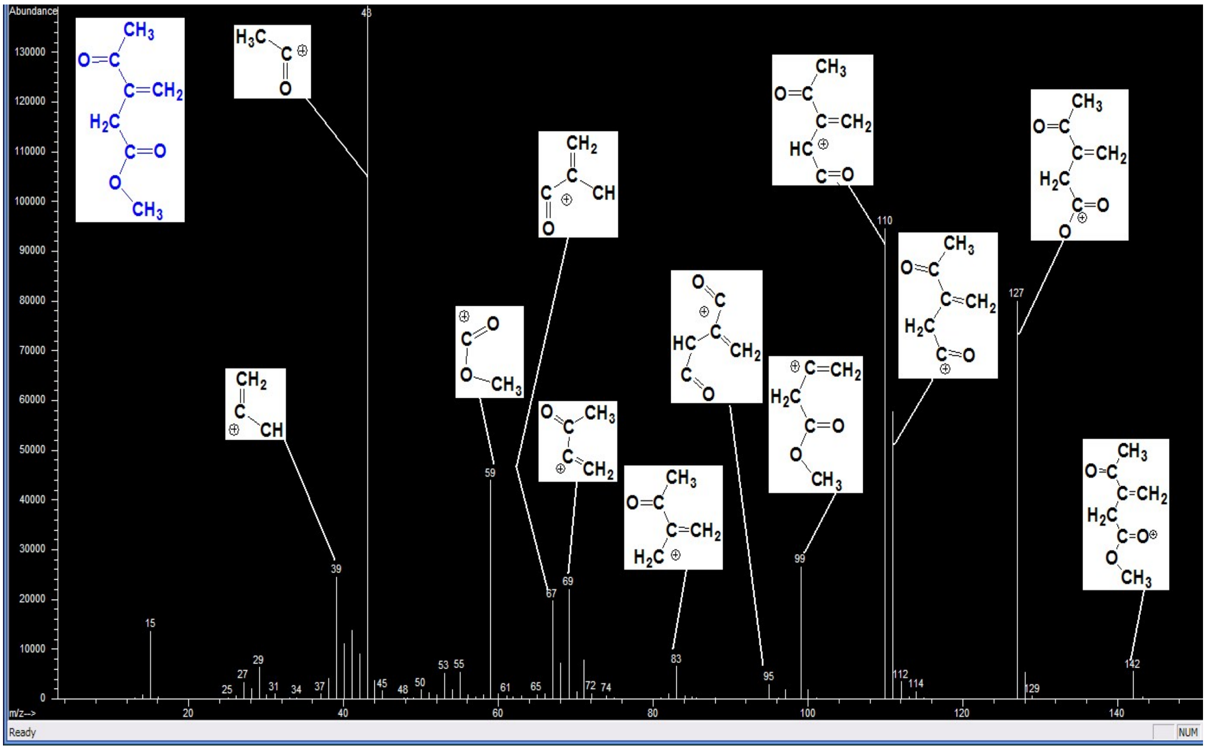
[a] Reaction conditions: methyl levulinate: 1.8 g; A70: 3.6 g; DMM/co-solvent: 40 mL (volume ratio; 25: 15); T = 160°C. [b] ”X(%)” stands for conversion (%).



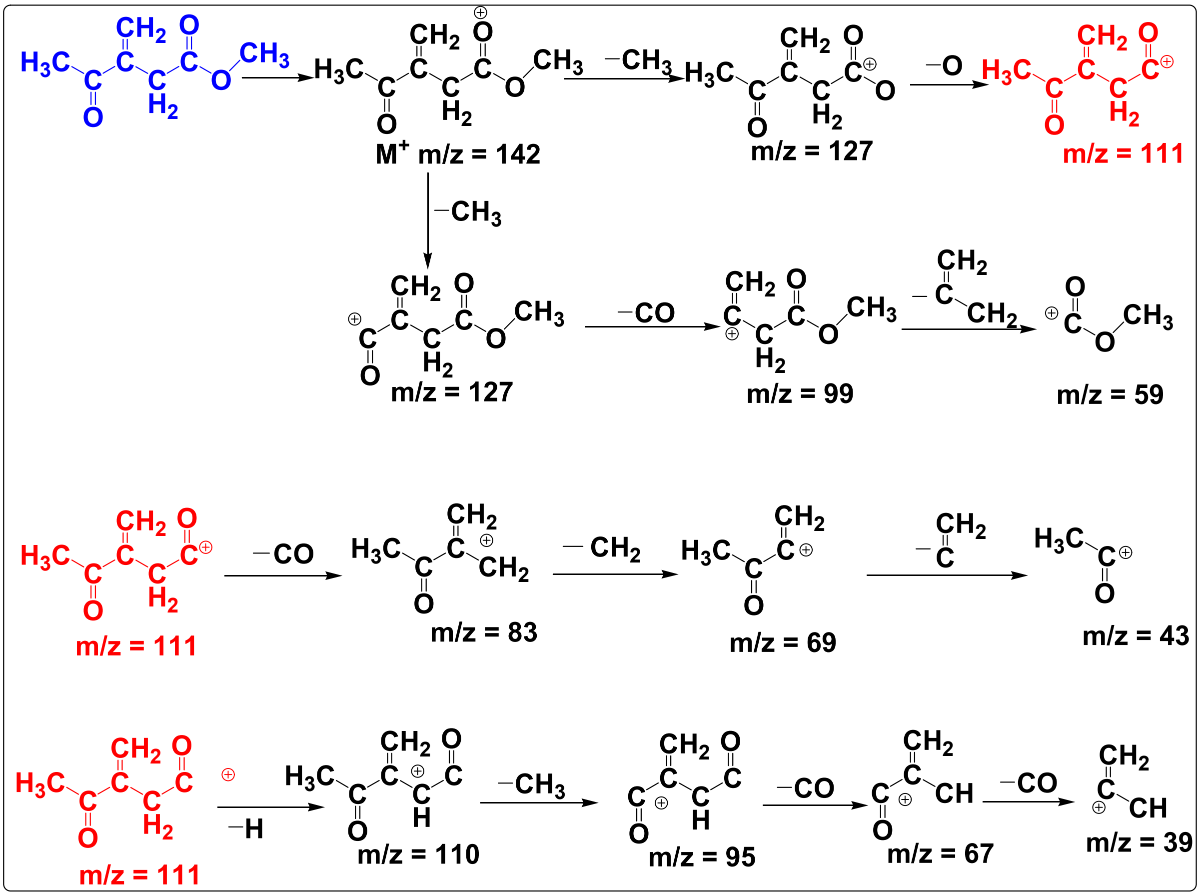
Scheme S1 Conversion of toluene in DMM into the aromatic compounds via the electrophilic substitutions. The identification of the compounds was confirmed by injecting standards.



Scheme S2 The proposed routes for the formation of methyl levulinate from furfural in DMM. The above charged intermediates were not detected with GC-MS. The derivatives of HMF can also be in other forms such as the acetal of HMF.



Scheme S3 The mass spectrum of methyl 3-methylene-4-oxopentanoate (MMO).



Scheme S4 The proposed routes for the fragmentation of methyl 3-methylene-4-oxopentanoate (MMO) in the mass spectrometer.

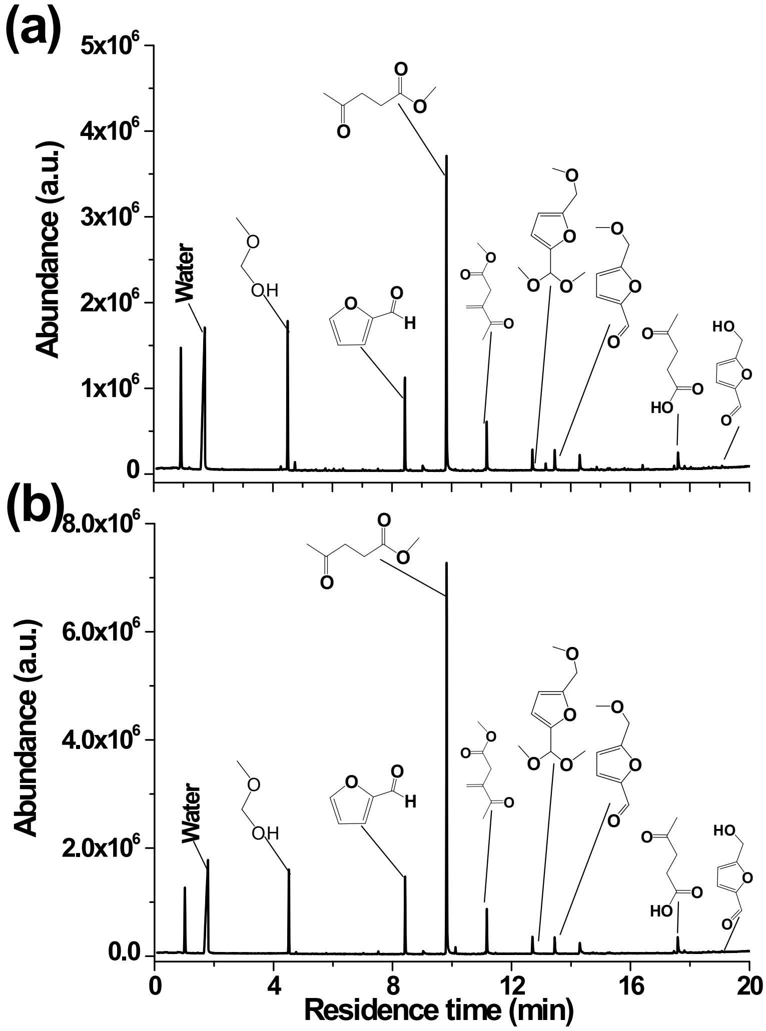


Figure S1 Typical mass spectrum for the conversion of (a) xylose and (b) furfural in DMM/methanol.

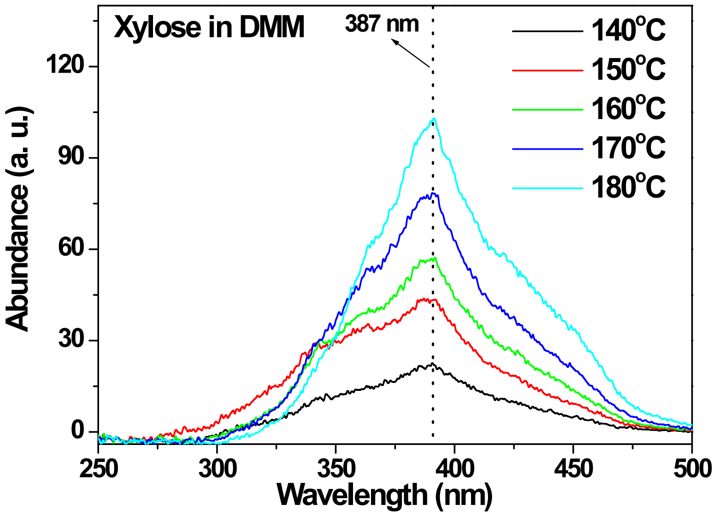


Figure S2 Constant energy (− 2800 cm^{-1}) synchronous spectra for the soluble polymers from the acid-catalyzed conversion of xylose in DMM. The samples were diluted to 3200 ppm in methanol before the analysis.

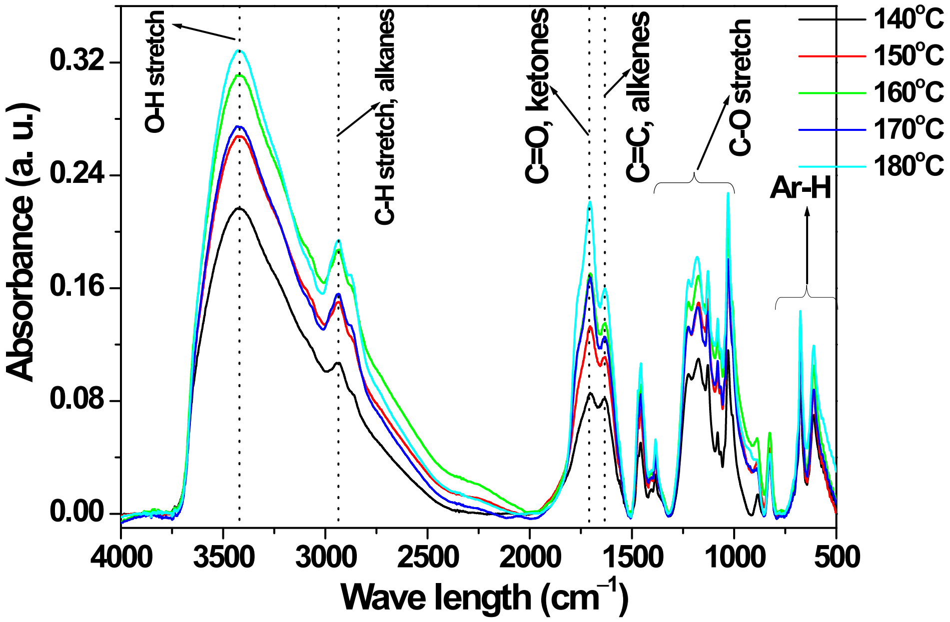


Figure S3 FT-IR characterization of the used catalysts in the acid-treatment of xylose in DMM at the different reaction temperatures.

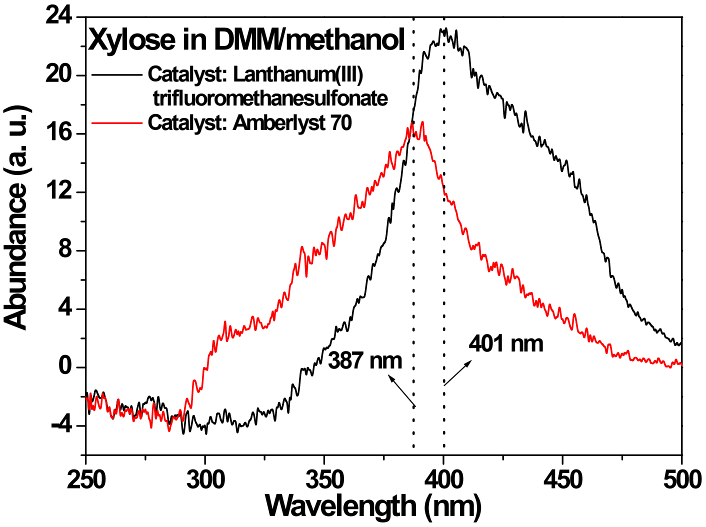


Figure S4 Constant energy (− 2800 cm^{-1}) synchronous spectra for the soluble polymers from the acid-catalyzed conversion of xylose in DMM/methanol over lanthanum (III) trifluoromethanesulfonate and Amberlyst 70. The samples were diluted to 3200 ppm in methanol before the analysis.

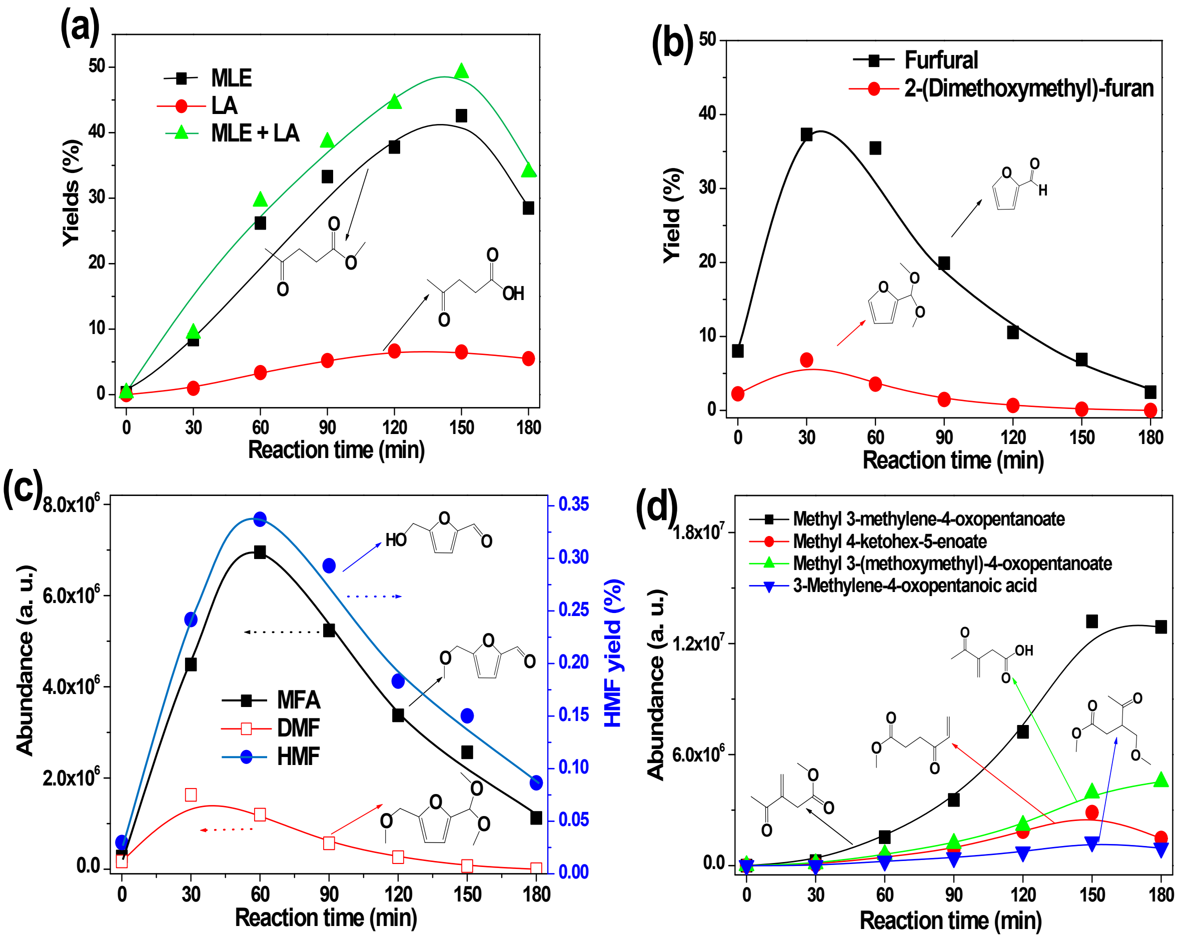


Figure S5 Product distributions in the acid-catalyzed conversion of xylose in DMM/methanol. Reaction conditions: xylose; 3.6 g; Amberlyst 70: 7.2 g; DMM/methanol: 80 mL (DMM: 50 mL, methanol: 30 mL); T = 160^{o}C; t = 180 min; p = autogenous vapour pressure. “0 min” in the x-axis meant the reaction temperature just reached 160°C in ca. 10 min.

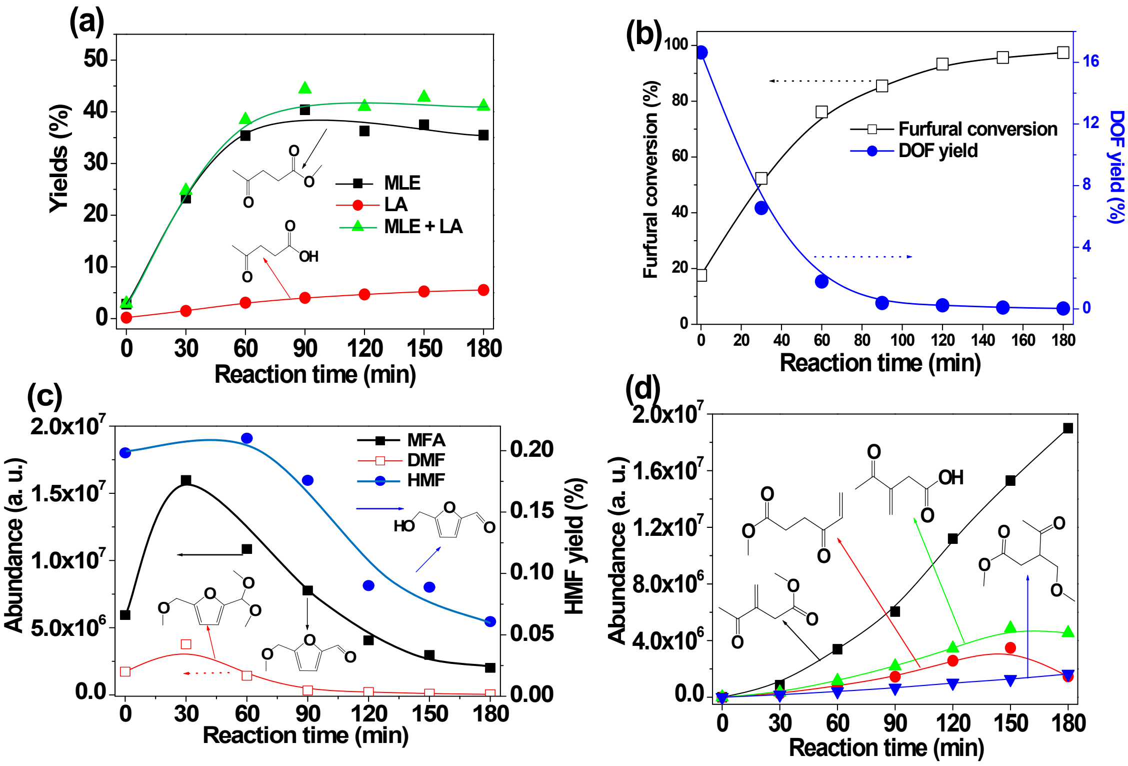


Figure S6 Product distribution in the acid-catalyzed conversion of furfural in DMM/methanol. Reaction conditions: furfural; 3.6 g; Amberlyst 70: 7.2 g; DMM/methanol: 80 mL (DMM: 50 mL, methanol: 30 mL); T = 160°C; t = 180 min; p = autogenous vapour pressure. "0 min" in the x-axis meant the reaction temperature just reached 160°C in ca. 10 min.

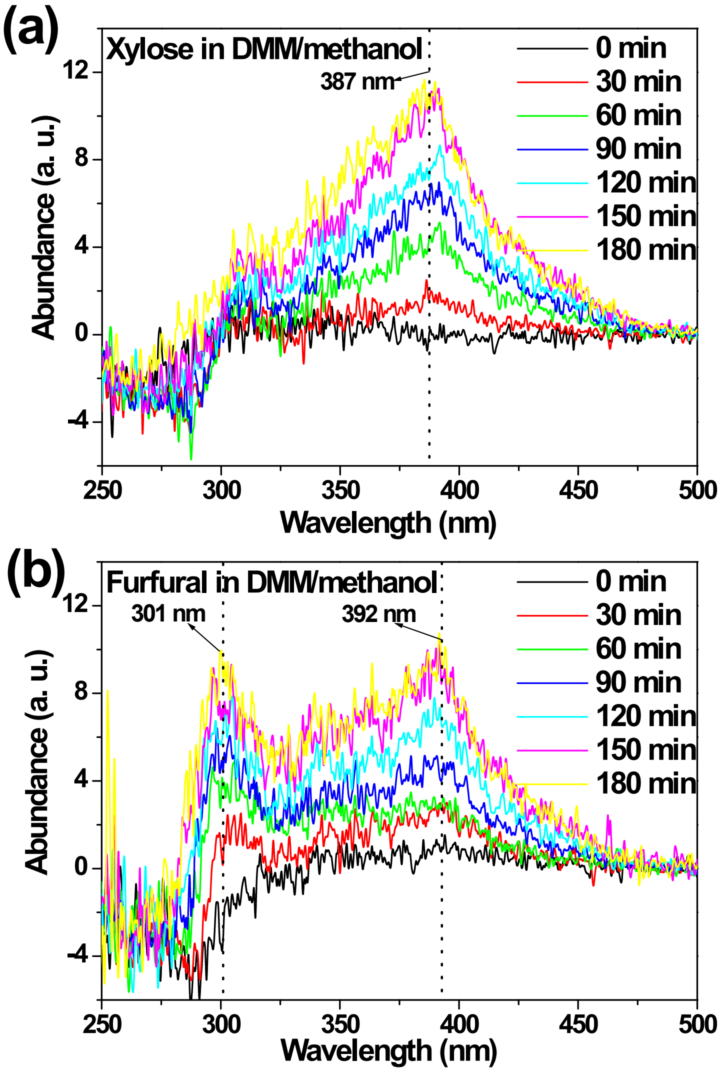


Figure S7 Constant energy (− 2800 cm^{-1}) synchronous spectra of the soluble polymers from the acid-catalyzed conversion of xylose and furfural in DMM/co-solvent versus the reaction time. The samples were diluted to 400 ppm in methanol before the analysis.

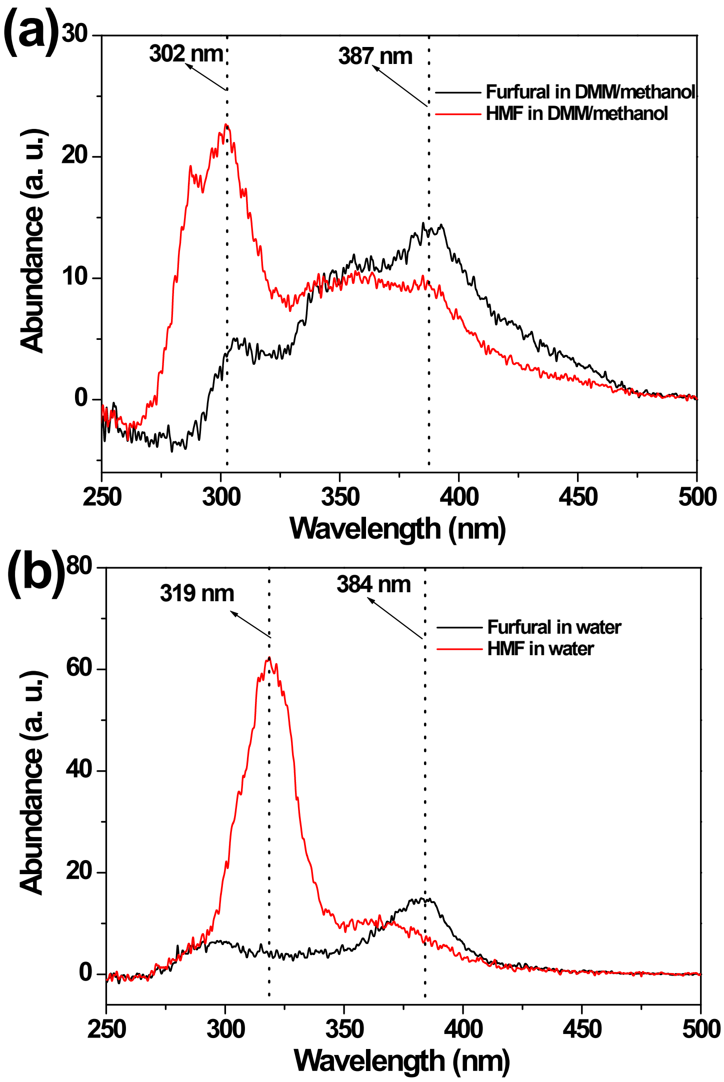


Figure S8 Constant energy (− 2800 cm^{-1}) synchronous spectra for the soluble polymers from the acid-catalyzed conversion of furfural and HMF in DMM/methanol (reaction conditions: furfural or HMF: 1.8 g; Amberlyst 70: 3.6 g; DMM/methanol: 40 mL (DMM: 25 mL, methanol: 15 mL); T= 160°C; t = 120 min; p = autogenous vapour pressure) and in water (reaction conditions: furfural or HMF: 6 g; Amberlyst 70: 18 g; water: 60 mL; T= 190°C; t = 100 min; p = autogenous vapour pressure). The samples were diluted to 3200 ppm in methanol before the analysis.

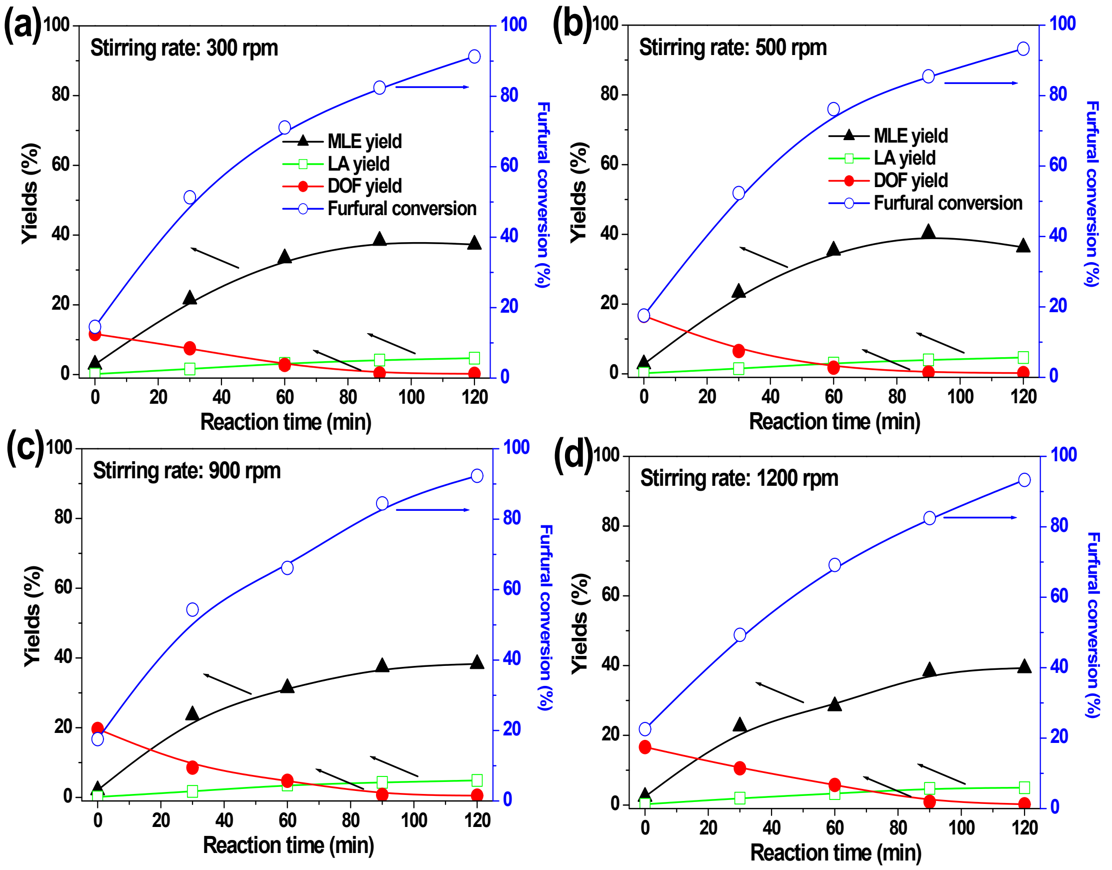


Figure S9 Product distribution in the acid-catalyzed conversion of furfural in DMM/methanolversus stirring rate. Reaction conditions: furfural: 1.8 g; Amberlyst 70: 3.6 g; DMM/methanol: 80 mL (DMM: 50 mL, methanol: 30 mL); T = 160^{o}C; t = 120 min; p = autogenous vapour pressure. “0 min” in the x-axis meant the reaction temperature just reached 160°C in ca. 10 min.

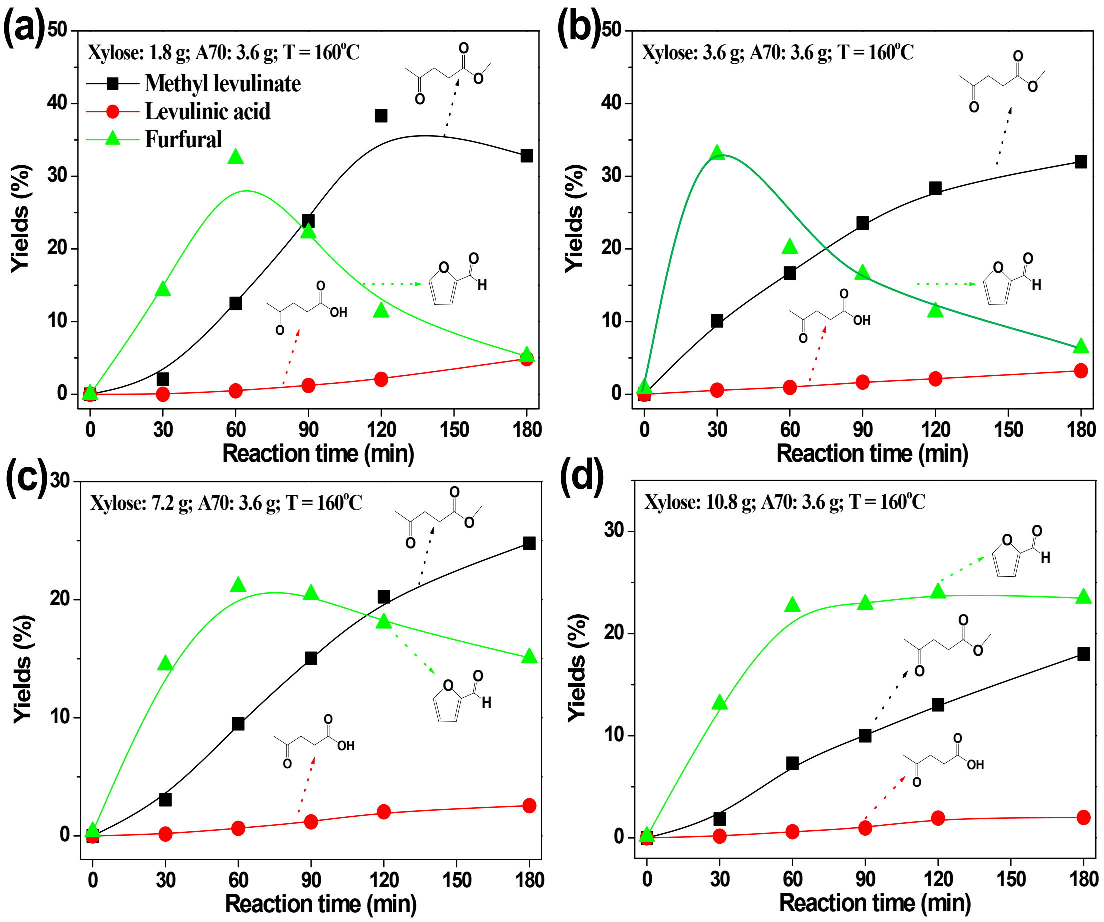


Figure S10 Product distribution versus xylose loading and reaction time in the acid-catalyzed conversion of xylose in DMM/methanol. Reaction conditions: xylose: (a)1.8 g; (b) 3.6 g; (c)7.2 g; (d)10.8 g. Amberlyst 70: 3.6 g; DMM/methanol: 80 mL (DMM: 50 mL, methanol:; 30 mL); T = 160^{o}C; t = 180 min; p = autogenous vapour pressure. “0 min” in the x-axis meant the reaction temperature just reached 160°C in ca. 10 min. Xylose conversion at the end of the tests was 100% for Figure (a), 82% for Figure (b), 61% for Figure (c), 47% for Figure (d), respectively.

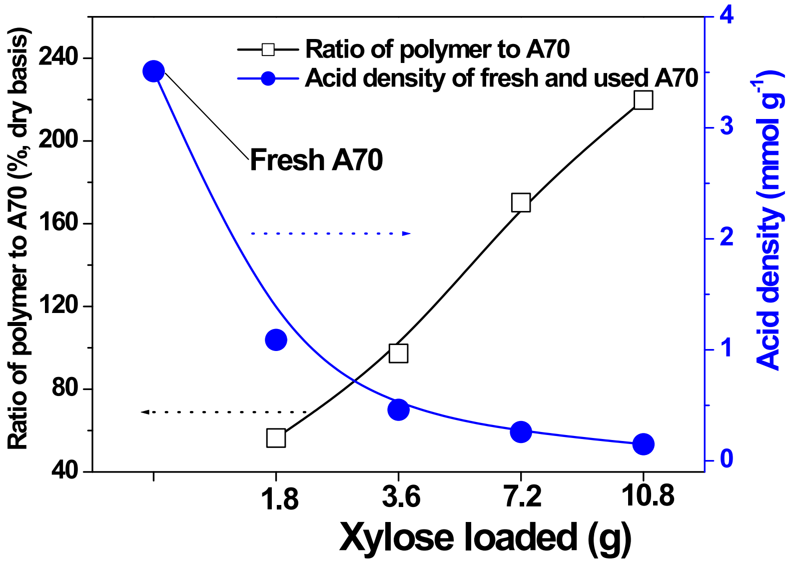


Figure S11 Formation of coke and acid density of the used Amberlyst 70 in the acid-catalyzed conversion of xylose with different loadings in DMM/methanol. The catalyst together with the solid residual were collected by filtration after the experiment and was then dried in an oven operated at 105°C to a constant weight to measure the polymer formed on/in catalyst. A back titration method was used to measure the acid density on catalyst surface.

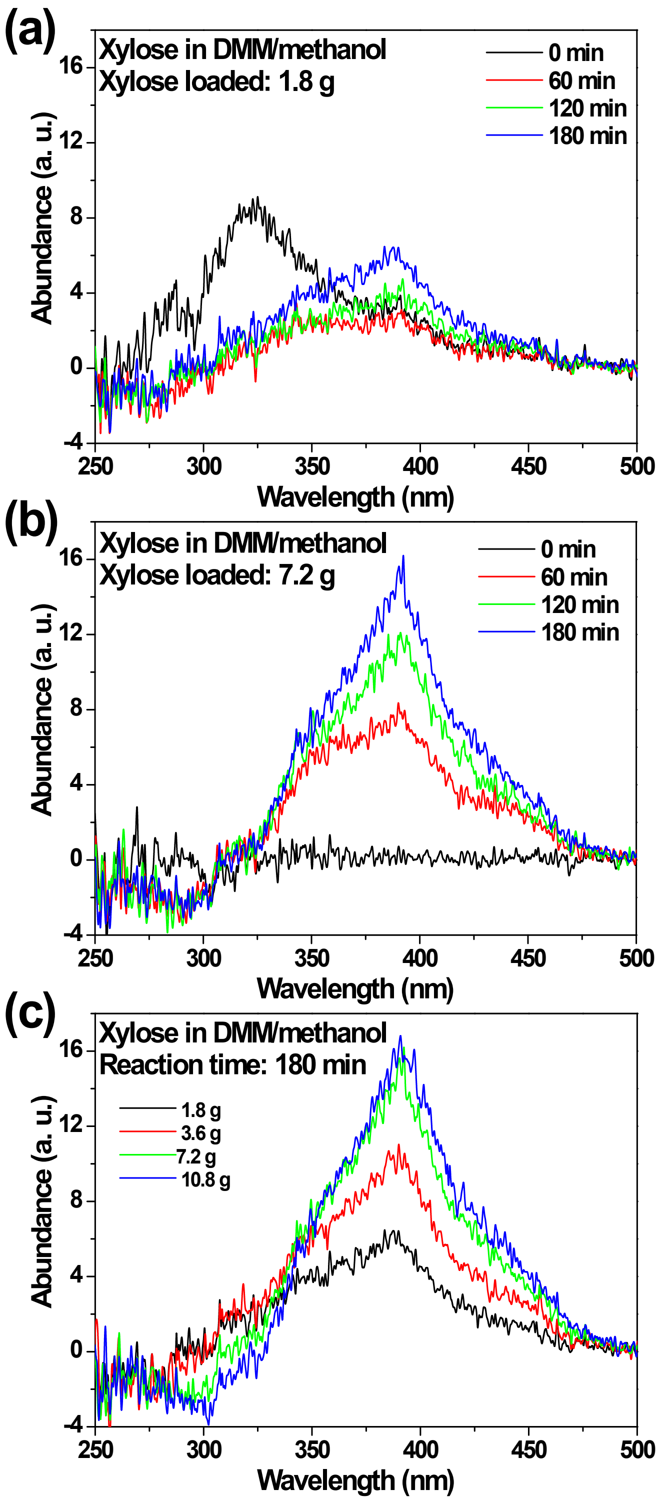


Figure S12 Constant energy (− 2800 cm^{-1}) synchronous spectra of the soluble polymers from the acid-catalyzed conversion of xylose with different loadings in DMM/methanol. The polymer was produced under the conditions specified in the title of Figure S10. The samples were diluted to 400 ppm in methanol before the analysis.

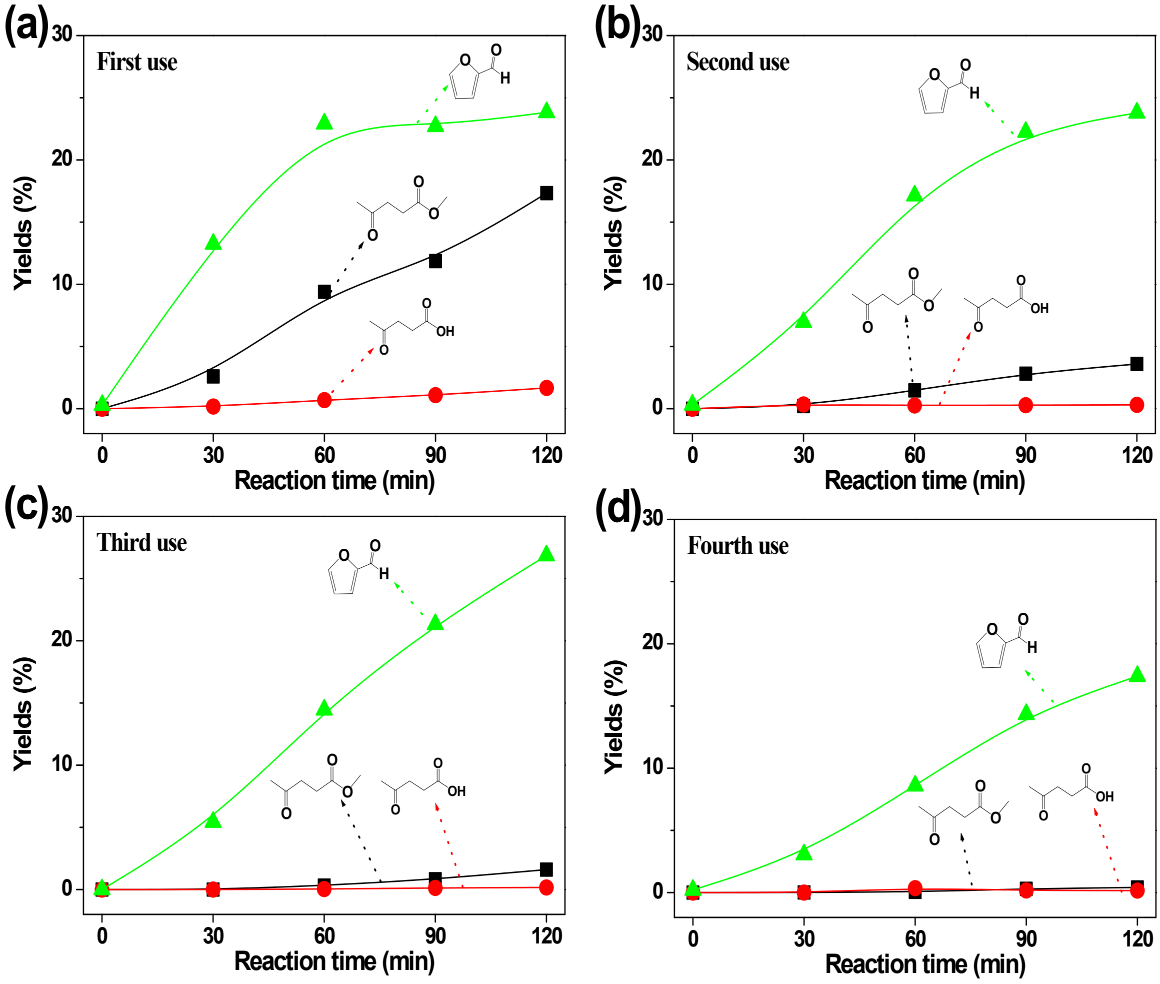


Figure S13 Product distribution in the acid-catalyzed conversion of xylose in DMM/methanol over a recycled Amberlyst 70 catalyst. Reaction conditions: xylose: 9 g; Amberlyst 70: 3.6 g; DMM/methanol: 80 mL (DMM: 50 mL, methanol: 30 mL); T = 160°C; t = 180 min; p = autogenous vapour pressure. “0 min” in the x-axis meant the reaction temperature just reached 160°C in ca. 10 min. Specifically, 3.6 g of fresh A70 was used. After the first use, the same catalyst was then filtered and washed with methanol and dried at 80°C for 4 hours before the second use. The same procedure was repeated for the third and fourth use.

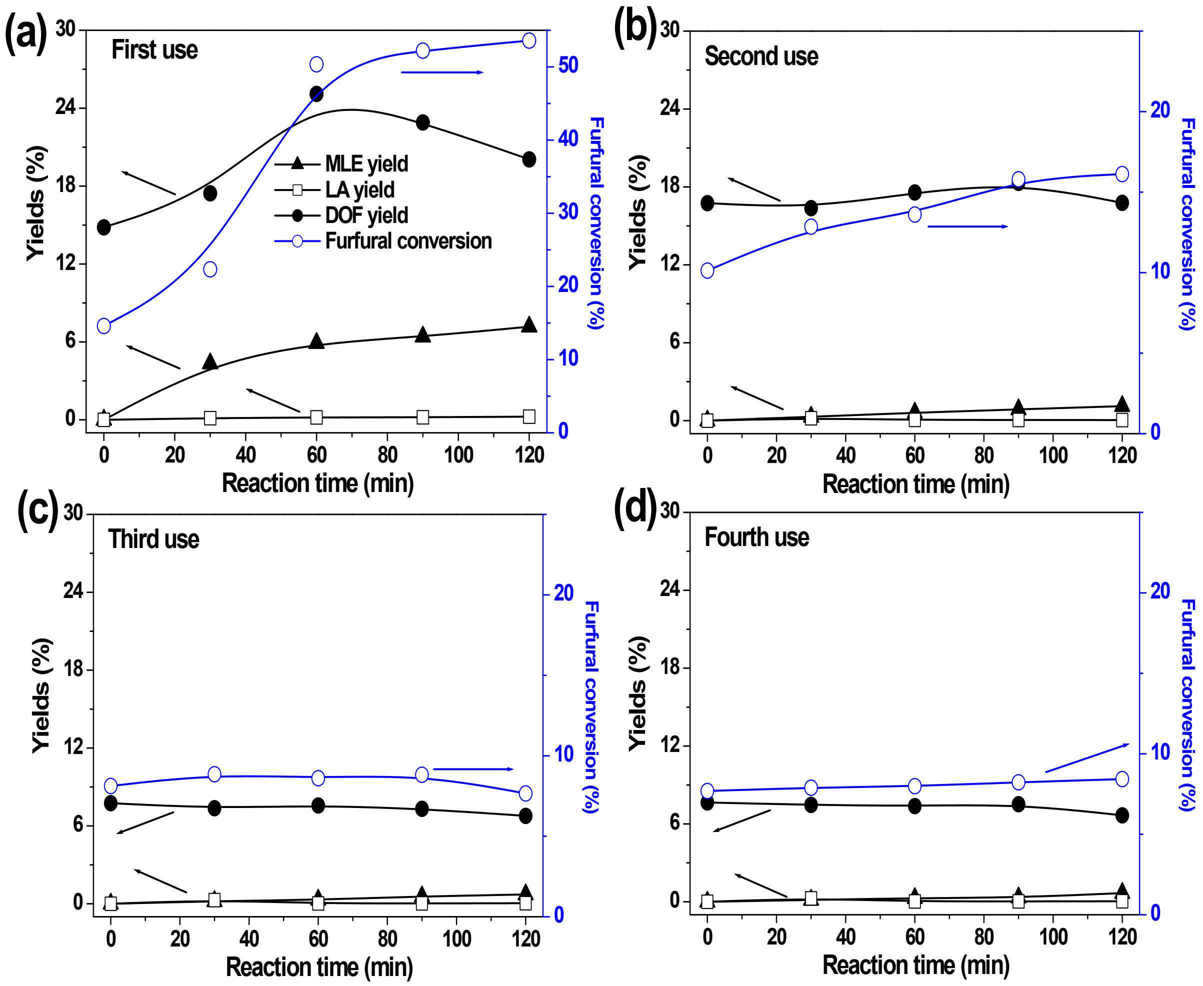


Figure S14 Product distribution in the acid-catalyzed conversion of furfural in DMM/methanol over a recycled Amberlyst 70 catalyst. Reaction conditions: furfural: 9 g; Amberlyst 70: 3.6 g; DMM/methanol: 80 mL (DMM: 50 mL, methanol:; 30 mL); T = 160°C; t = 180 min; p = autogenous vapour pressure. “0 min” in the x-axis meant the reaction temperature just reached 160°C in ca. 10 min. Specifically, 3.6 g of fresh A70 was used. After the first use, the same catalyst was then filtered and washed with methanol and dried at 80°C for 4 hours before the second use. The same procedure was repeated for the third and fourth use.

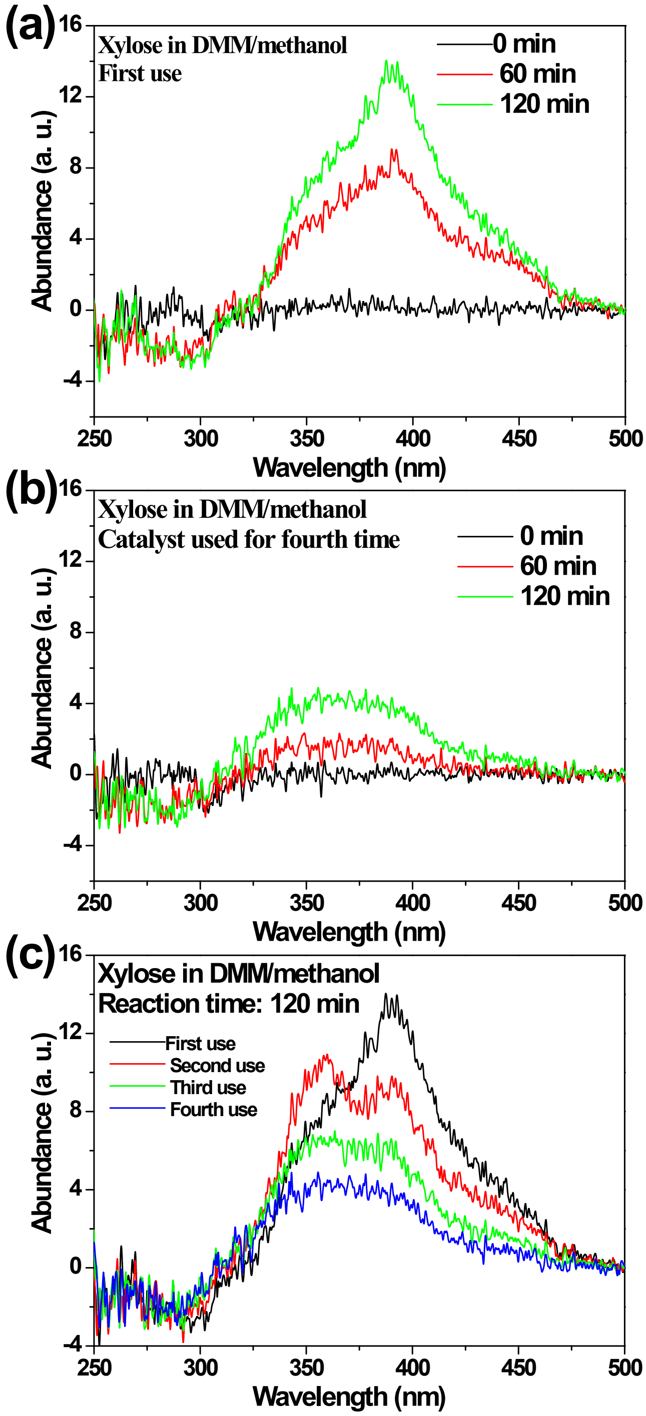


Figure S15 Constant energy ($-$ 2800 cm^{-1}) synchronous spectra of the soluble polymers from the acid-catalyzed conversion of xylose in DMM/methanol over Amberlyst 70 with different recycled times. The polymer was produced under the conditions specified in the title of Figure S13. The samples were diluted to 400 ppm in methanol before the analysis.

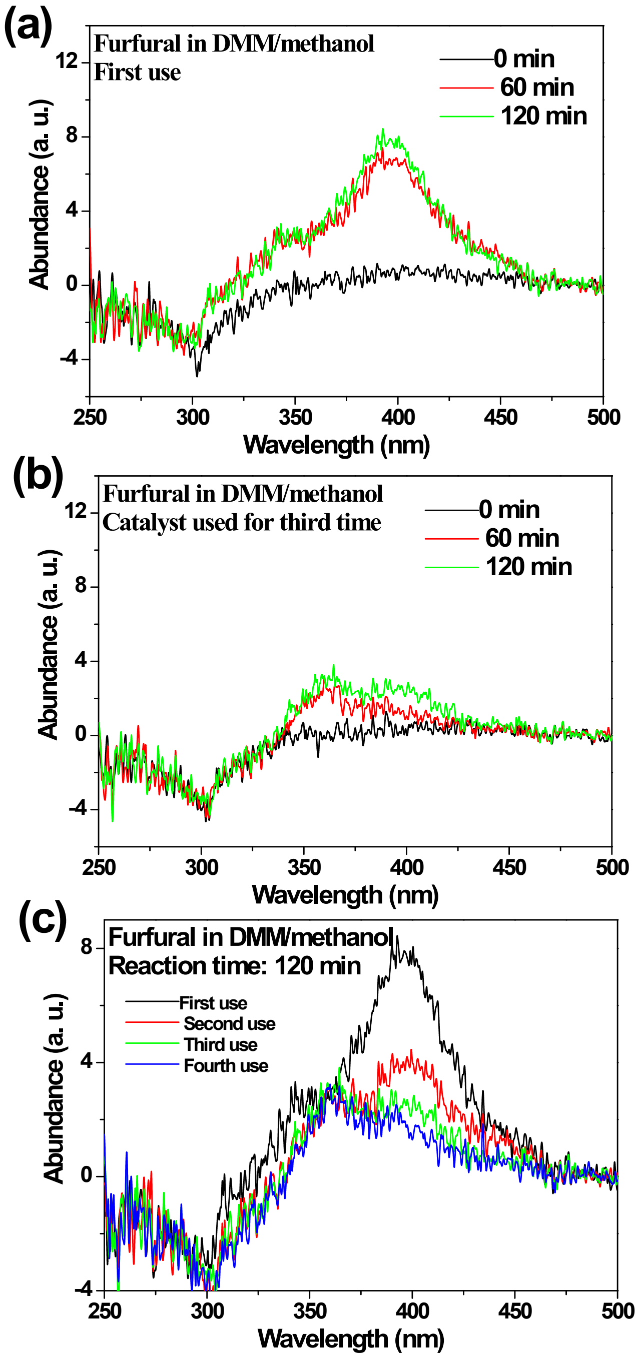


Figure S16 Constant energy (− 2800 cm^{-1}) synchronous spectra of the soluble polymers from the acid-catalyzed conversion of furfuralin DMM/methanol over Amberlyst 70 with different recycled times. The polymer was produced under the conditions specified in the title of Figure S14. The samples were diluted to 400 ppm in methanol before the analysis.

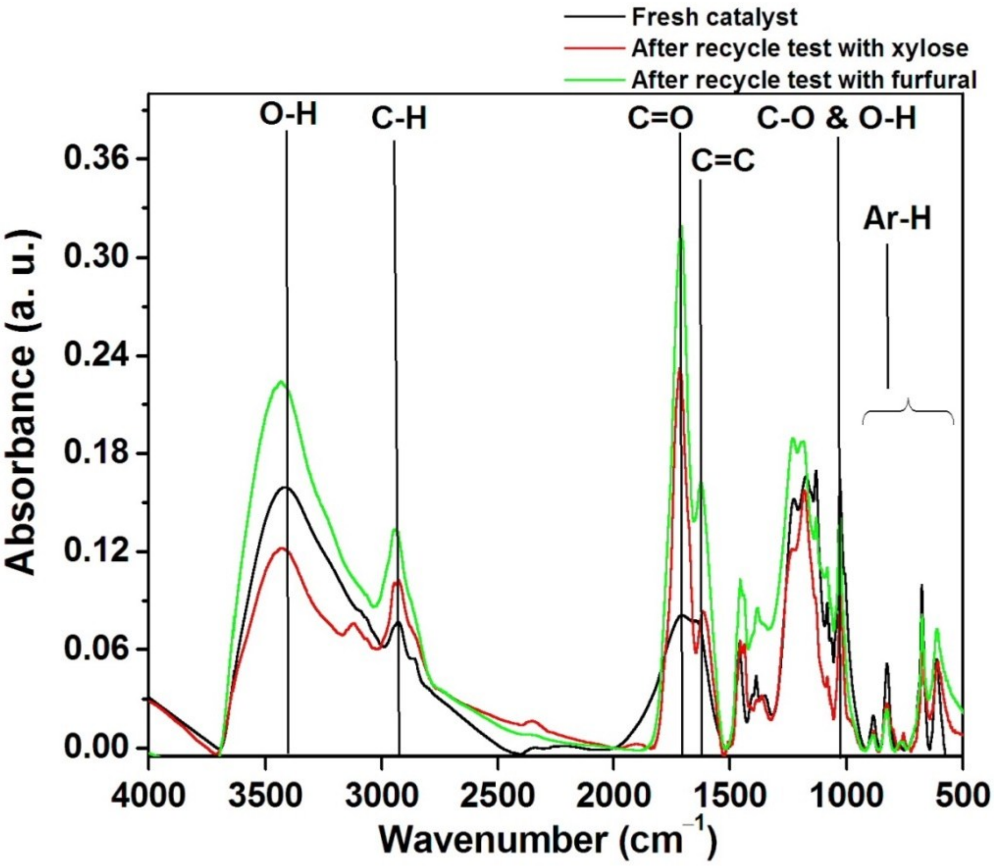


Figure S17 FT-IR characterization of the Fresh A70 and the A70 catalysts after the recycle tests with xylose or furfural as the starting reactants.

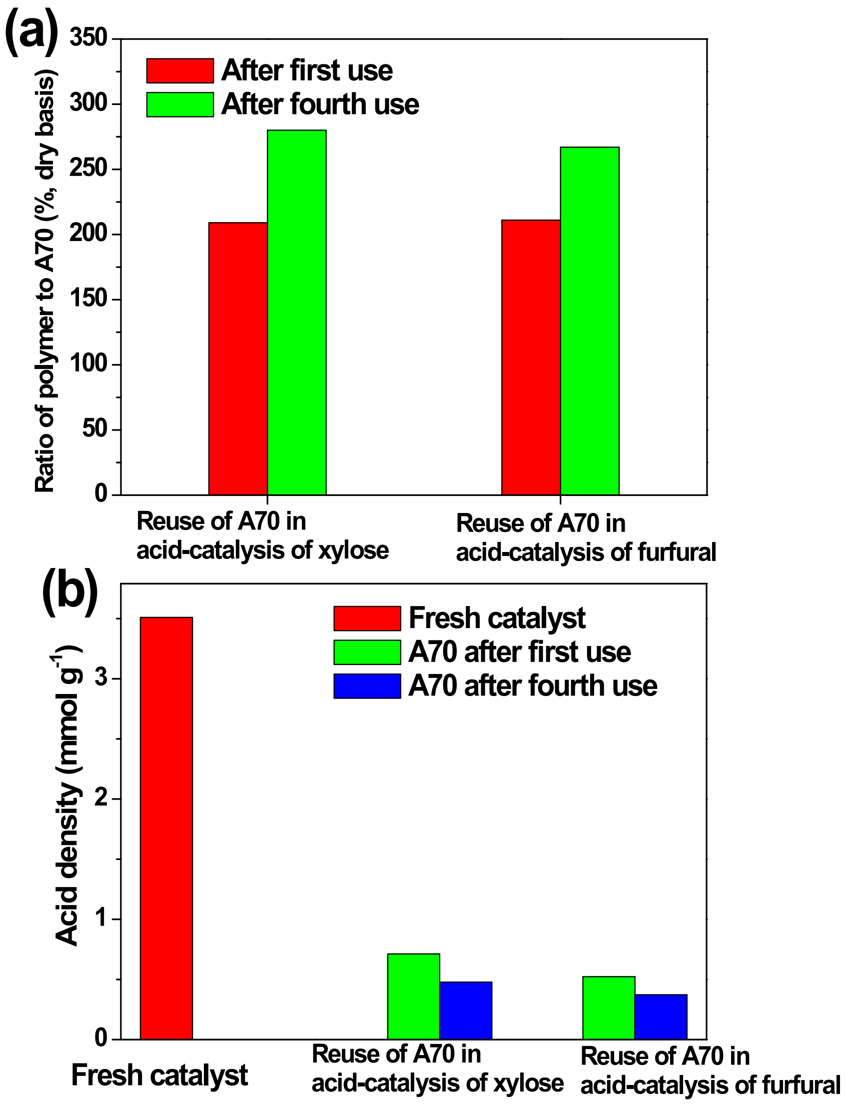


Figure S18 Formation of coke and acid density of the used Amberlyst 70 with different recycled times in the acid-catalyzed conversion of xylose and furfural in DMM/methanol. The same batch of Amberlyst 70 was recycled for four times in acid-catalyzed conversion of xylose or furfural at the conditions specified in the title of Figure S13 and S14. Amberlyst 70 after recycled for one time was also prepared separately under the conditions specified in the title of Figure S13 and S14.

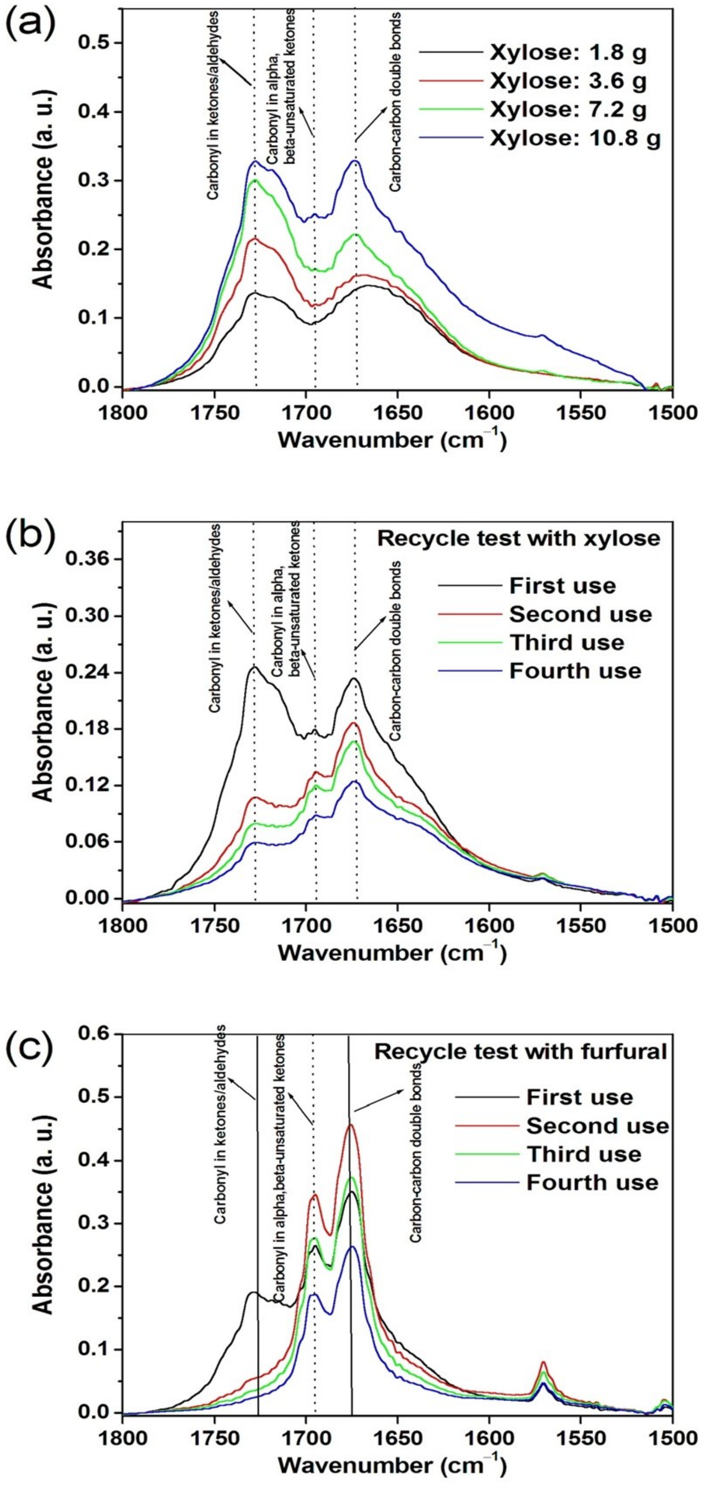


Figure S19 FT-IR characterization of the liquid samples in acid-treatment of (a) xylose with different loadings; (b) recycle test with xylose as starting reactant; (c) recycle test with furfural as starting reactant. The liquid sample was the last sample during the corresponding experiment. The detailed conditions were depicted in the titles of Figure 10, 13 and 14, respectively.

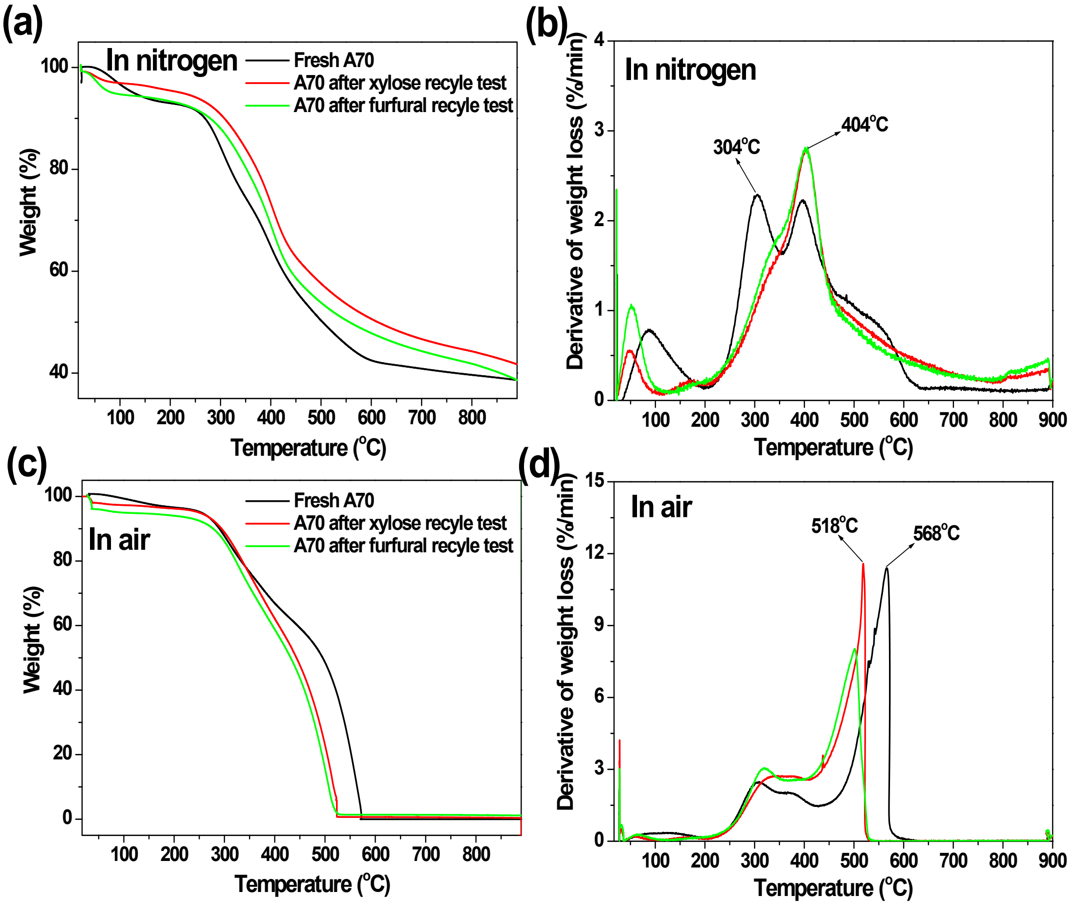


Figure S20 TGA and DTG curves for the fresh A70 and the A70 catalysts after the recycle test with xylose or furfural as the starting reactants. The catalysts were dried to constant weight before the tests.