Supporting Information for

Cooperative catalysis of Pt/C and acid resin for the production of 2,5-dimethyltetrahydrofuran from biomass derived 2,5-hexanedione under mild condition

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1. Experimental Section

1.1 Catalyst preparation

The supports, activated charcoal and Amberlyst® 15H, were thoroughly washed with water and ethanol, and then dried under 100 ºC overnight before use. The preparation process of Pd/C (1 wt%) was as following: 4.33 mL of 0.01 g/mL $Pd(NO_3)_2$ stock solution was dropped onto 2 g activated charcoal under stirring, and the slurry was continuely stirred under 60 ºC to remove extra water. The obtained powder was dried under 110 ºC overnight, and then reduced by H_2 under 300 ºC, 5 ºC/min for 2 h. Ru/C (1 wt%) was prepared by a similar process with $RuCl_3$ as the precursor. Pt/AM-1 was prepared as following: 2.1 mL 0.01 g/mL H_2PtCl_6 was dropped onto 1 g dried AM-1, and the mixture was stirred overnight. Water was evaporated via continuely stirring under 60 ºC. The obtained catalyst precursor was dried under 110 ºC overnight, and then reduced under H_2 atmosphere, 150 ºC, 5 ºC/min, 1 h. The metal loadings on the supports were analyzed on ICP-AES (VISTA-MPX).

1.2 Acid strength of the acid catalyst

The acid strength of the acid resin, including Amberlyst®15(H) (AM-1), Amberlite®IR-120(H) (AM-2), and Nafion®SAC-13 (NS) was measured by the titration method according to the reported literature.[1] Typically, 0.5 g acid resin was thoroughly washed with water, dried under 100 ºC, and then suspended into 20 mL of 0.01 M NaOH solution. The mixture was stirred overnight. Then the particles were separated out by filtration, and the filtrate was titrated with 0.01 M HCl using methyl orange as indicator. The acid strength was calculated according to the amounts of consumed NaOH. The results were

expressed in the form of acid density (mmol H^+/g catalyst). The acid properties of the molecular sieve, Zeolite Y (hydrogen, the framework Si/Al ratio=35), were studied by Pyridine Adsorbed Fourier Transformed Infrared method in the recent work of our group and the data were used directly.[2] For the heteropoly acids, silicotungstic acid and phosphomolybdic acid, due to their special structures, the acid density was calculated according to the structure in the reported literatures.[3]

1.3 Conversion of 2,5-HDO

0.5 g 2,5-HDO, 2 g water and 0.05 g AM-2 were introduced into a 10 mL Teflon-lined stainless steel autoclave equipped with a magnetic stirrer. After removing the air via vacuum, nitrogen was charged into the reactor. The reaction was conducted under 90 ºC for 2 h. After reaction, the reactor was cooled in ice-water to quench the reaction and the organic phase was diluted by ethanol. The sample was analyzed by gas chromatograph (GC, HP 4890) equipped with a flame ionization detector (FID), and THFAL was used as the internal standard. Identification of the products and reactant was done using a GC-MS (SHIMADZU-QP2010) as well as by comparing the retention times to respective standards in GC traces.

1.4 Conversion of DMF to DMTHF via 2,5-HD

0.43 g DMF and 0.1 g AM-2 were added into the mixture of 0.2 ml H_2O and 2 ml THF, and the reaction was conducted under 90 ºC for 24 h. After reaction and cooling down, 0.05 g Pt/C and 3.0 MPa H_2 were charged into the reaction solution directly. The mixture was maintained under 90 ºC for 10 h. The product was analysed by gas chromatograph (GC, HP 4890) equipped with a flame ionization detector (FID), and THFAL was used as the internal standard.

2. Results and Discussion

2.1 Acid strength of the acid catalyst

Table S1. The acid density of acid catalysts used in this work[a]

Entry	Catalyst	Acid density mmol H^+/g
1[b]	Am-1	4.2
2[b]	Am-2	2.5
3[b]	NS	0.13
4[c]	MS	0.22
5[d]	SA	1.3
6[d]	PA	1.5

[a]AM-1=Amberlyst®15(H); AM-2=Amberlite®IR-120(H); NS=Nafion®SAC-13; MS=Molecular sieve (Zeolite Y); SA=Silicotungstic acid; PA=Phosphomolybdic acid. [b]The acid density was measured by the titration method. [c]The acid property was detected in our recent work, and the value was the sum of the amounts of Brønsted acid and Lewis acid sites.[2] [d]The acid densities were calculated according to the reported literature.[3] The amounts of protons in one structure unit (Keggin unit) for SA and PA were 3.6 and 2.8, respectively. The composition of one Keggin unit for SA and PA was $H_4W_{12}O_{40}Si$ and $H_3Mo_{12}O_{40}P$, corresponding to the acid density of 1.3 and 1.5, respectively.

References:

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