Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Lignosulfonate-based acidic resin for the synthesis of renewable diesel and jet fuel range alkanes with 2-methylfuran and furfural

Shanshan Li,[a,b] Ning Li,*[a,c] Guangyi Li,[a] Lin Li,[a] Aiqin Wang,[a,c] Yu Cong,[a] Xiaodong Wang[a] and Tao Zhang*[a,c]

[a] *State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, No. 457 Zhongshan Road, Dalian 116023, China.*

[b] *Graduate School of Chinese Academy of Sciences, Beijing 100049, P. R. China*

[c] *Collaborative Innovation Center of Chemistry for Energy Materials (iChEM).*

*Corresponding author.

Prof. Tao Zhang; E-mail: taozhang@dicp.ac.cn; Tel.: +86 411 84379015; Fax: +86 411 84691570.

Dr. Ning Li; E-mail: lining@dicp.ac.cn; Tel.: +86 411 84379738; Fax: +86 411 84685940.

1. Method for the calculation of carbon yields in the HDO step:

The carbon yields of different alkanes in the HDO process were calculated according to the following formulas:

Carbon yield of C_9-C_{15} diesel and jet fuel range alkanes (%) = Total carbon of C_9-C_{15} alkanes in the liquid products/Total carbon of feedstock pumped into the reactor × 100%

Carbon yield of C_5-C_8 gasoline range alkanes (%) = Total carbon of C_5-C_8 alkanes in the gas products per unit time/Total carbon of feedstock pumped into the reactor per unit time × 100% + Total carbon of the C_5-C_8 alkanes in liquid phase products/Total carbon of feedstock pumped into the reactor × 100%

Carbon yield of C_1-C_4 light alkanes (%) = Total carbon of the C_1-C_4 alkanes in the gas products per unit time/Total carbon of feedstock pumped into the reactor per unit time × 100%

2. Characterization

2.1 N_2-adsorption

The physical adsorption of N_2 was conducted on ASAP 2010 (Micromeritics). The specific surface areas of the acidic resins (see Table S2) were measured by Brunauer–Emmett–Teller (BET) method via nitrogen adsorption at 77 K. The nitrogen sorption isotherms and pore size distributions were measured according to the Barrett–Joyner–Halenda (BJH) method from the desorption branch of the isotherms. Before each measurement, the sample was evacuated at 393 K to eliminate the adsorbents.

2.2 Fourier Transform Infrared Spectroscopy (FT-IR)

The FT-IR spectrum of LF resin was collected a Bruker Equinox 55 spectrometer equipped with a deuterated triglycine sulphate (DTGS) detector and extended KBr beam splitter. The spectrometer was operated in the absorbance mode at a resolution of 4 cm^{-1}. Before the test, the LF resin was mixed with KBr at a mass ratio of 1/100 and pressed to self-supporting tablets.

From the FT-IR spectrum of LF resin illustrated in Figure S3, we can see that this material has many functional groups. According to literature,[1] the peaks at 2847 cm^{-1} and 2939 cm^{-1} can be attributed to stretching vibration of $-CH_2-$ which was formed during the phenol-aldehyde condensation lignosulfonate and formaldehyde. The bands at 1218 cm^{-1} and 1034 cm^{-1} can be assigned to the sym-stretching of O=S=O and SO_3-H stretching in SO_3H groups, respectively.[2] The peaks at 1113 cm^{-1} and 1312 cm^{-1} represent the in-plane bending vibration of aromatic C-H[3] and syringyl ring breathing with C-O stretching,[4] respectively. The peaks at 1425 cm^{-1}, 1500 cm^{-1} and 1612 cm^{-1} can be attributed to the characteristic vibrations of benzene ring.[1, 3, 5] The wavenumber at 1709 cm^{-1} indicated the existence of COOH group on the surface of LF resin.[2c, 6] The broad peak at 3420 cm^{-1} can be attributed to the OH groups which are linked with the neighbor oxygen atom or SO_3H group by hydrogen-bond.[1] That is, the acidic groups (*i.e.* $-SO_3H$, -COOH and phenolic -OH) on the LF resin are adjacent to each other.

2.3 Titration of $-SO_3H$, -COOH and phenolic -OH

The amounts of acidic groups (*i.e.* -SO_3H, -COOH and phenolic -OH) on the surfaces of LF, Amberlyst-15, Amberlyst-36 and Nafion-212 resins (see Table S2) were measured by the acid-base titration method described in the literature.[1-2]

In the first step, we measured the amount of -SO_3H sites on the surface of catalyst. To do this, 0.1 g catalyst was dispersed into 20 mL 2 mol L^{-1} NaCl solution, sonicated for 1.5 h, and then centrifuged. The resulting liquid was titrated with 8 mmol L^{-1} NaOH solution (pre-calibrated with a standard potassium hydrogenphthalate solution) using phenolphthalein as indicator. The molar amount of -SO_3H sites per gram of catalyst was obtained according to consumption of NaOH solution.

In the second step, we measured the total amount of -SO_3H and -COOH sites on the surface of the catalyst. To do this, 0.05 g catalyst was dispersed into 20 mL 80 mmol L^{-1} $NaHCO_3$ solution. The liquid as obtained was titrated with 0.1 mol L^{-1} HCl (pre-calibrated by a standard NaOH solution) using methyl orange as indicator. The molar amount of -COOH sites per gram of catalyst was calculated by subtracting the molar amount of -SO_3H sites per gram of catalyst from the total amount of -SO_3H and -COOH sites per gram of catalyst.

In the third step, the overall amount of -SO_3H,-COOH and phenolic -OH sites on the surface of the catalyst was measured. To do this, 0.05 g catalyst was dispersed into 20 mL 8 mmol L^{-1} NaOH solution, sonicated for 1.5 h and then centrifuged. The resulting filtrate was titrated with 1 mmol L^{-1} potassium hydrogenphthalate solution using phenolphthalein as indicator. The molar amount of phenolic -OH sites per gram of catalyst was calculated by subtracting the total amount of -SO_3H and -COOH sites per gram of catalyst from the overall amount of -SO_3H, -COOH and phenolic -OH sites per gram of catalyst.

2.4 Microcalorimetric measurement of NH_3 adsorption

The microcalorimetric measurements of ammonia adsorption for the different solid acid catalysts used in the HAA reaction were performed at 353 K using a BT2.15 heat-flux calorimeter (France, Seteram) connected to a gas-handling and a volumetric system employing MKS Baratron Capacitance Manometers for precision pressure measurement ($\pm 0.5 \times 10^{-4}$ Torr). Before each measurement, ammonia (purity > 99.9%) was purified by successive freeze–pump–thaw cycles. The specific mass of sample with similar amount of acid sites was evacuated in a quartz cell at 353 K overnight under high vacuum to remove the physically adsorbed substance. The differential heat was measured as a function of acid site coverage by repeatedly introducing small dosage of ammonia onto the samples until the equilibrium pressure reached about 5-6 torr. Then the system was evacuated overnight to remove the physically adsorbed ammonia, and a second adsorption was performed. The amount of irreversible adsorbed ammonia was determined by the difference between the isotherms of the first and second adsorption cycles.

2.5 X-ray Diffraction (XRD)

XRD patterns of different catalysts were recorded with a PW3040/60X' Pert PRO (PANalytical) diffractometer using a Cu Kα radiation source ($\lambda = 0.15432$ nm) at 40 kV and 40 mA. From the XRD patterns of Ni catalysts (see Figure S9 in supporting information), we can only observe the peaks of H-ZSM-5 support and metallic Ni. No peak of nickel oxide was noticed.

2.6 H_2-O_2 titration

The nickel dispersions (ratio of surface nickel atoms to the total amount of nickel atoms in each catalyst) of the Ni catalysts were obtained with a Micromeritics AutoChem II 2920 Automated Catalyst Characterization System by H_2-O_2 titration. In a typical measurement, the sample was firstly reduced in H_2 flow at 773 K for 2 h and then purged in Ar flow at 783 K for 30 min to remove adsorbed H_2. After that, the catalyst was cooled down in Ar flow to 393 K and purged with a constant flow of 2% O_2/He (V/V) for 30 min for O_2 adsorption. Subsequently, the sample was heated to 773 K in a constant Ar flow. After the stabilization of baseline, the H_2 adsorption was then conducted by dosage of 10% H_2/Ar (V/V) pulse at 773 K. Finally, the metal dispersion of Ni catalyst was calculated on the basis of the amounts of adsorbed H_2 and total Ni loading under the assumption that the stoichiometry of H_2 to surface Ni atom is 1.5 (mol/mol).

2.7 Transmission Electron Microscopy (TEM)

The TEM images of the Ni-based HDO catalysts were obtained by a FEI TECNAI G^2 Spirit Transmission Electron Microscope operated at an accelerating voltage of 120 kV. Before the tests, the catalysts were reduced by H_2 at 773 K for 2 h. From the TEM images showed in the Figure S10, the utilization of complex agents obviously decreases the Ni particle sizes over the Ni/H-ZSM-5 catalysts. This result is consistent with what we observed in H_2-O_2 titration tests.

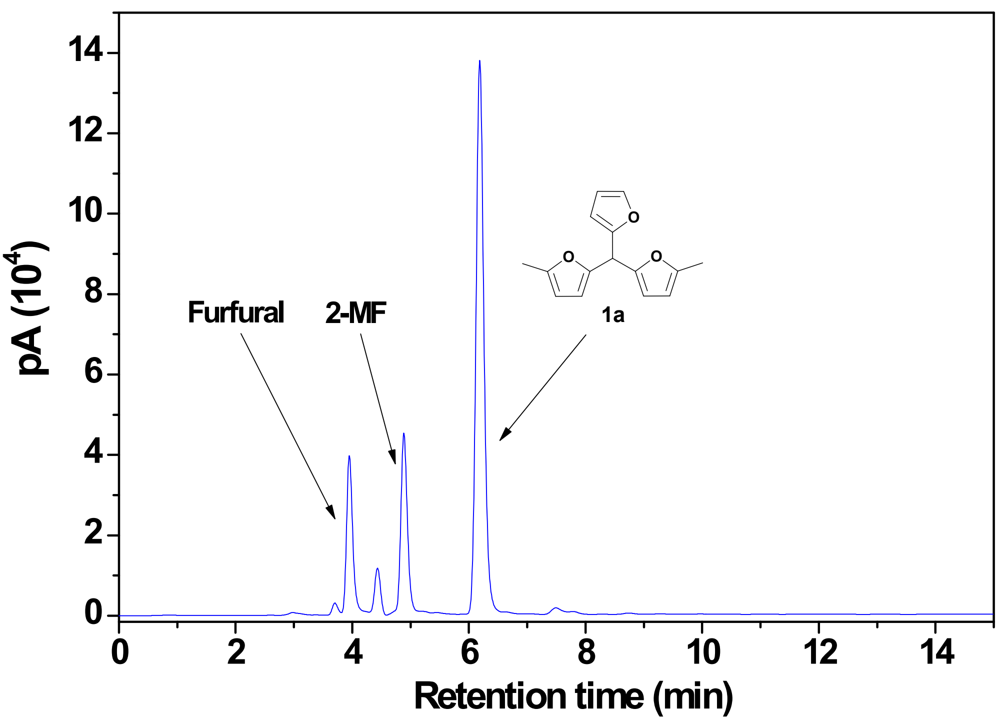
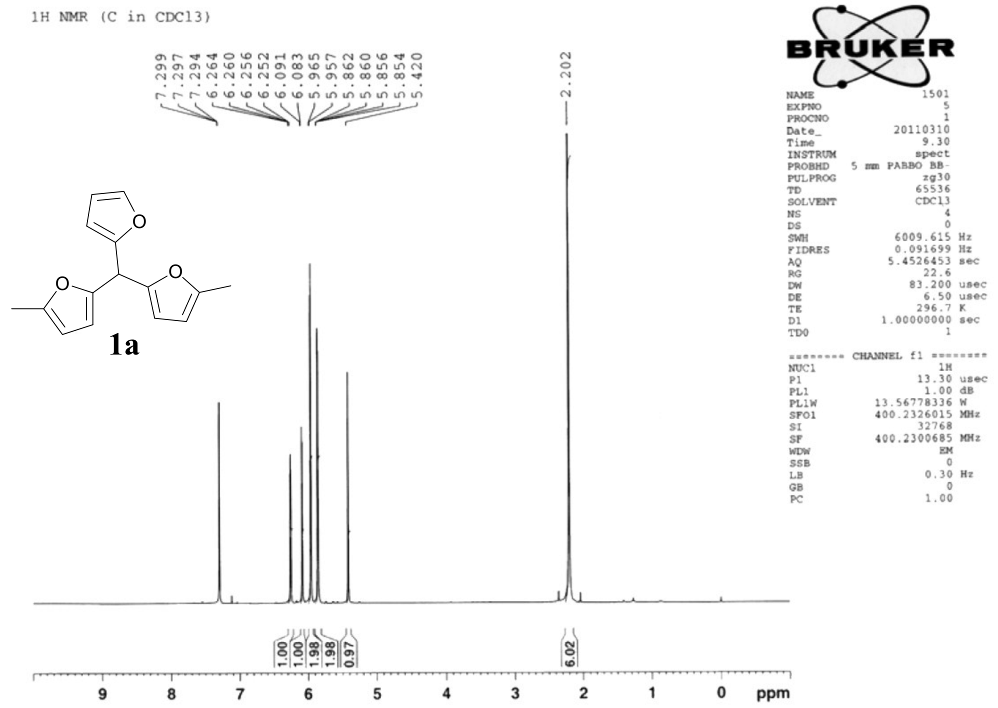
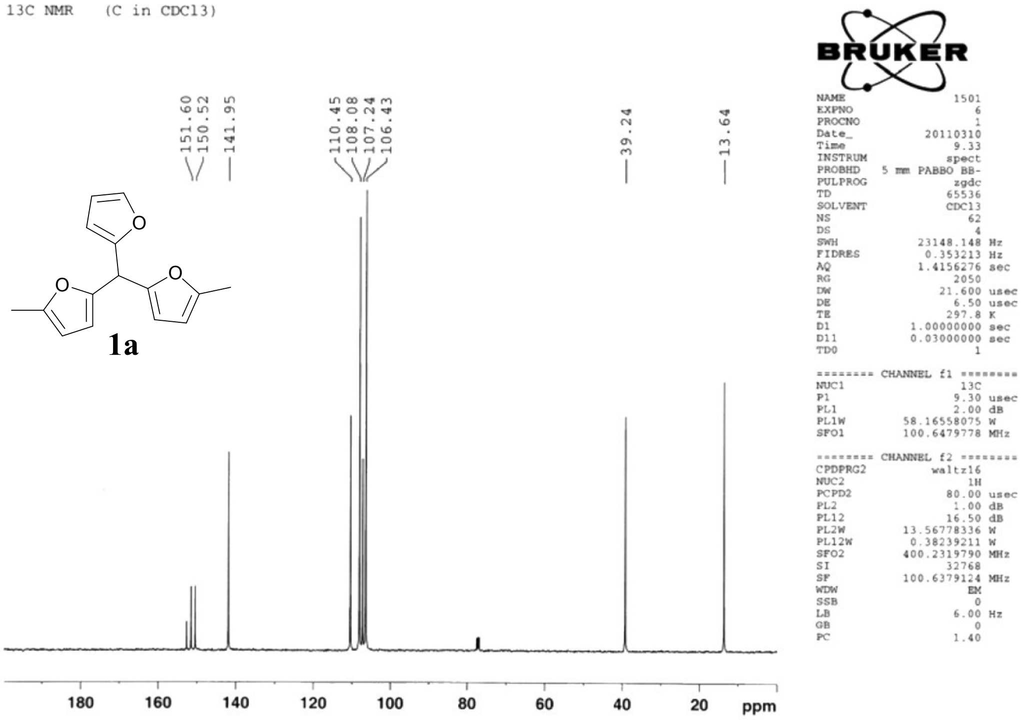


Figure S1. HPLC chromatogram of the liquid products from the HAA of 2-MF with furfural.



```
NAME               1501
EXPNO                 5
PROCNO                1
Date_          20110310
Time               9.30
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                    4
DS                    0
SWH            6009.615 Hz
FIDRES         0.091699 Hz
AQ            5.4526453 sec
RG                 22.6
DW               83.200 usec
DE                 6.50 usec
TE                296.7 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                13.30 usec
PL1                1.00 dB
PL1W        13.56778336 W
SFO1        400.2326015 MHz
SI                32768
SF          400.2300685 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```



```
NAME               1501
EXPNO                 6
PROCNO                1
Date_          20110310
Time               9.33
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zgdc
TD                65536
SOLVENT           CDCl3
NS                   62
DS                    4
SWH           23148.148 Hz
FIDRES         0.353213 Hz
AQ            1.4156276 sec
RG                 2050
DW               21.600 usec
DE                 6.50 usec
TE                297.8 K
D1           1.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                 9.30 usec
PL1                2.00 dB
PL1W        58.16558075 W
SFO1        100.6479778 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2                1.00 dB
PL12              16.50 dB
PL2W        13.56778336 W
PL12W        0.38239211 W
SFO2        400.2319790 MHz
SI                32768
SF          100.6379124 MHz
WDW                  EM
SSB                   0
LB                 6.00 Hz
GB                    0
PC                 1.40
```

Figure S2. ^{13}C and ^{1}H NMR spectra of the **1a** produced by HAA of 2-MF with furfural.

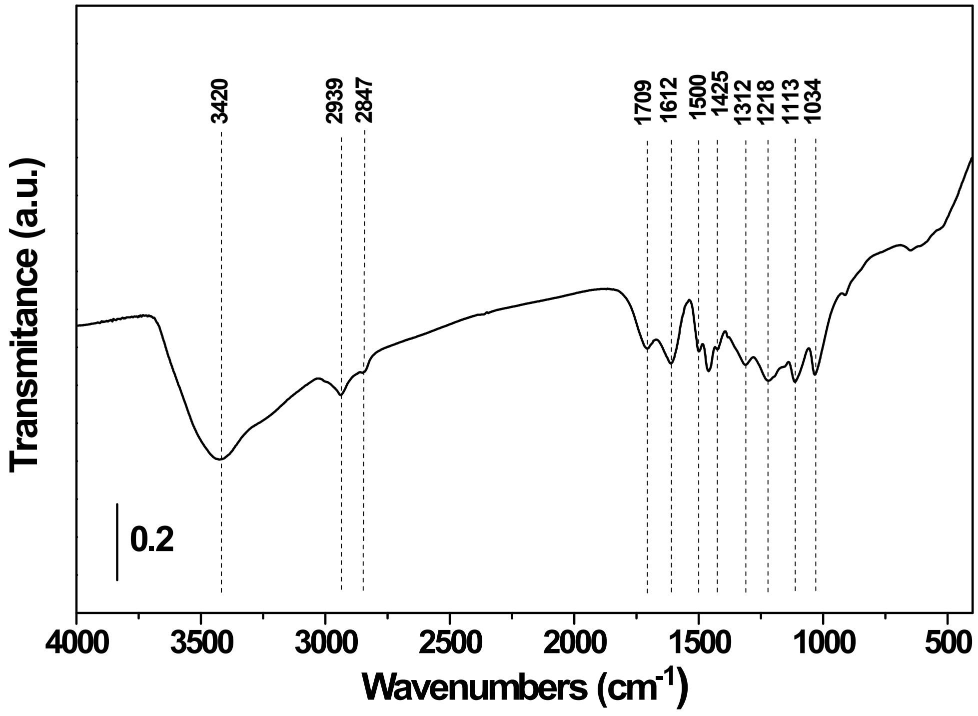


Figure S3. FT-IR spectrum of LF resin which was prepared by the protonation of the condensation product of sodium lignosulfonate and formaldehyde.

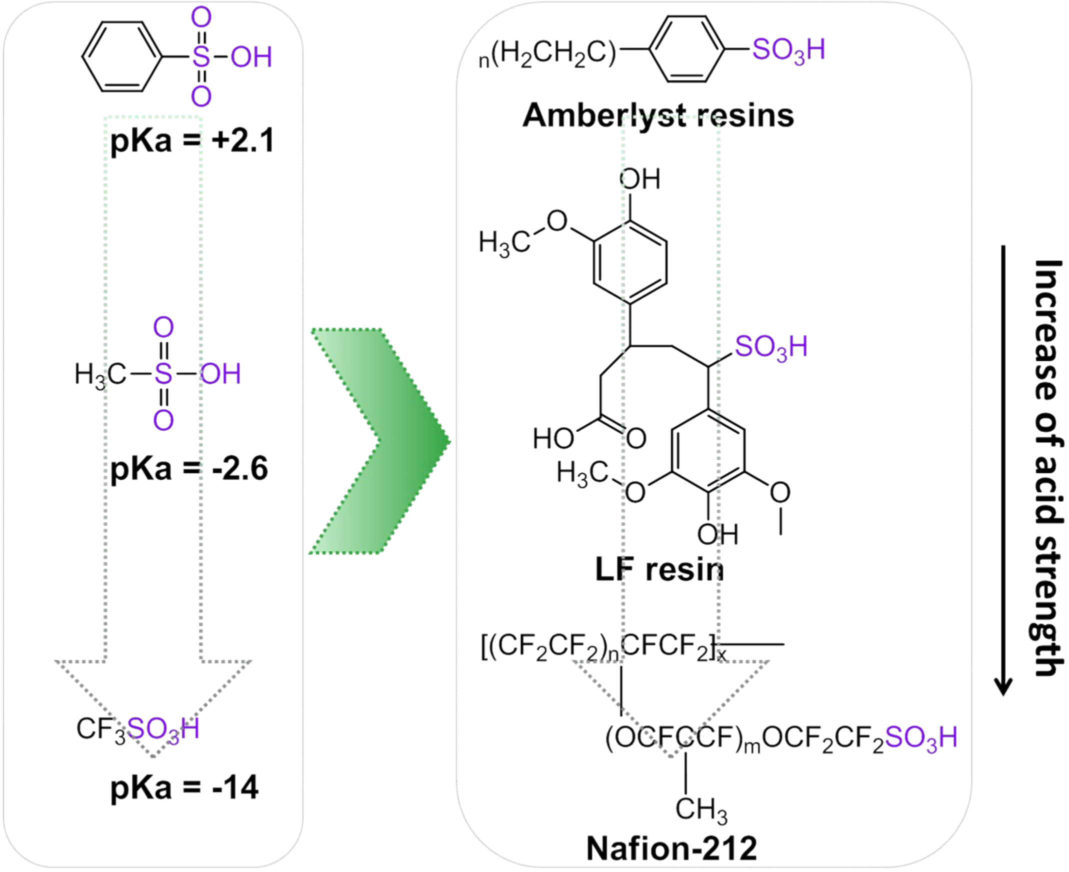
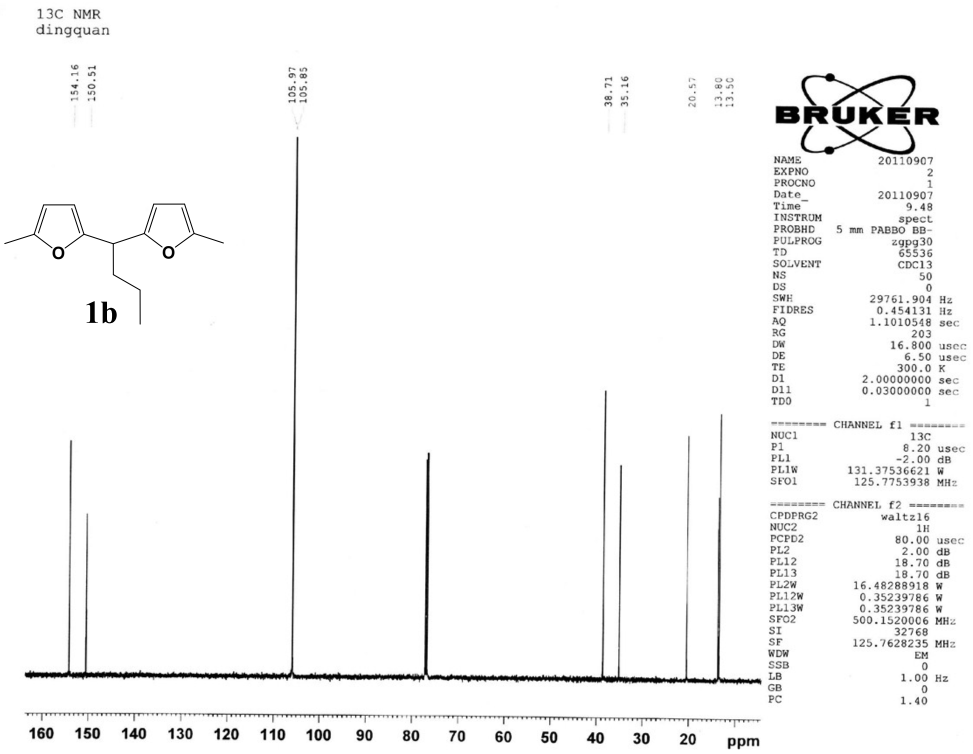
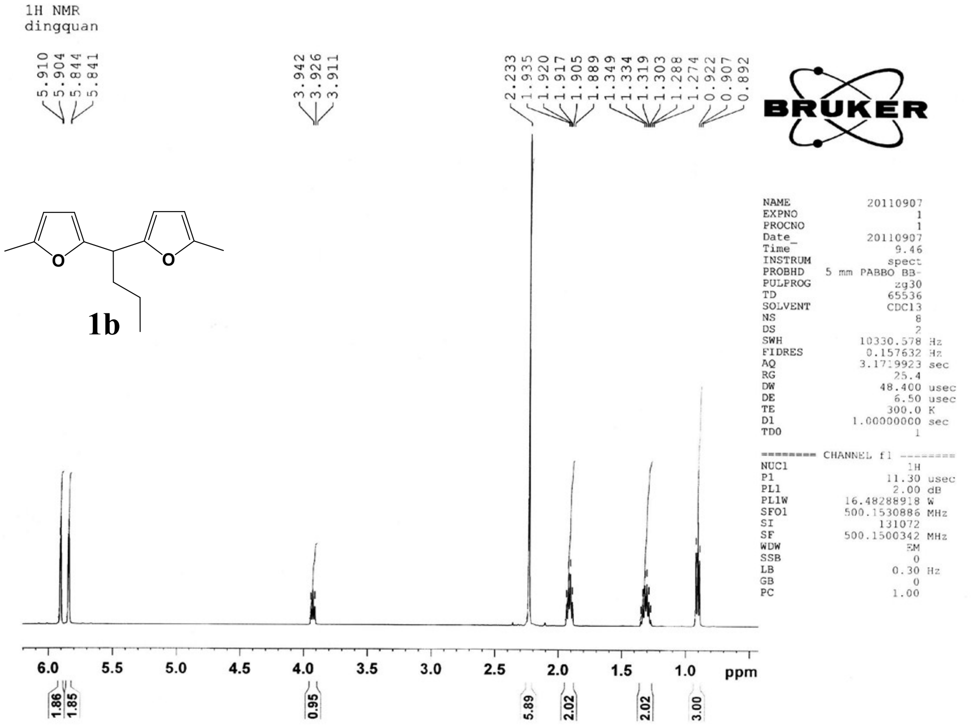


Figure S4. Chemical structures and the acid strengths of different organic acids and solid acids.[7]

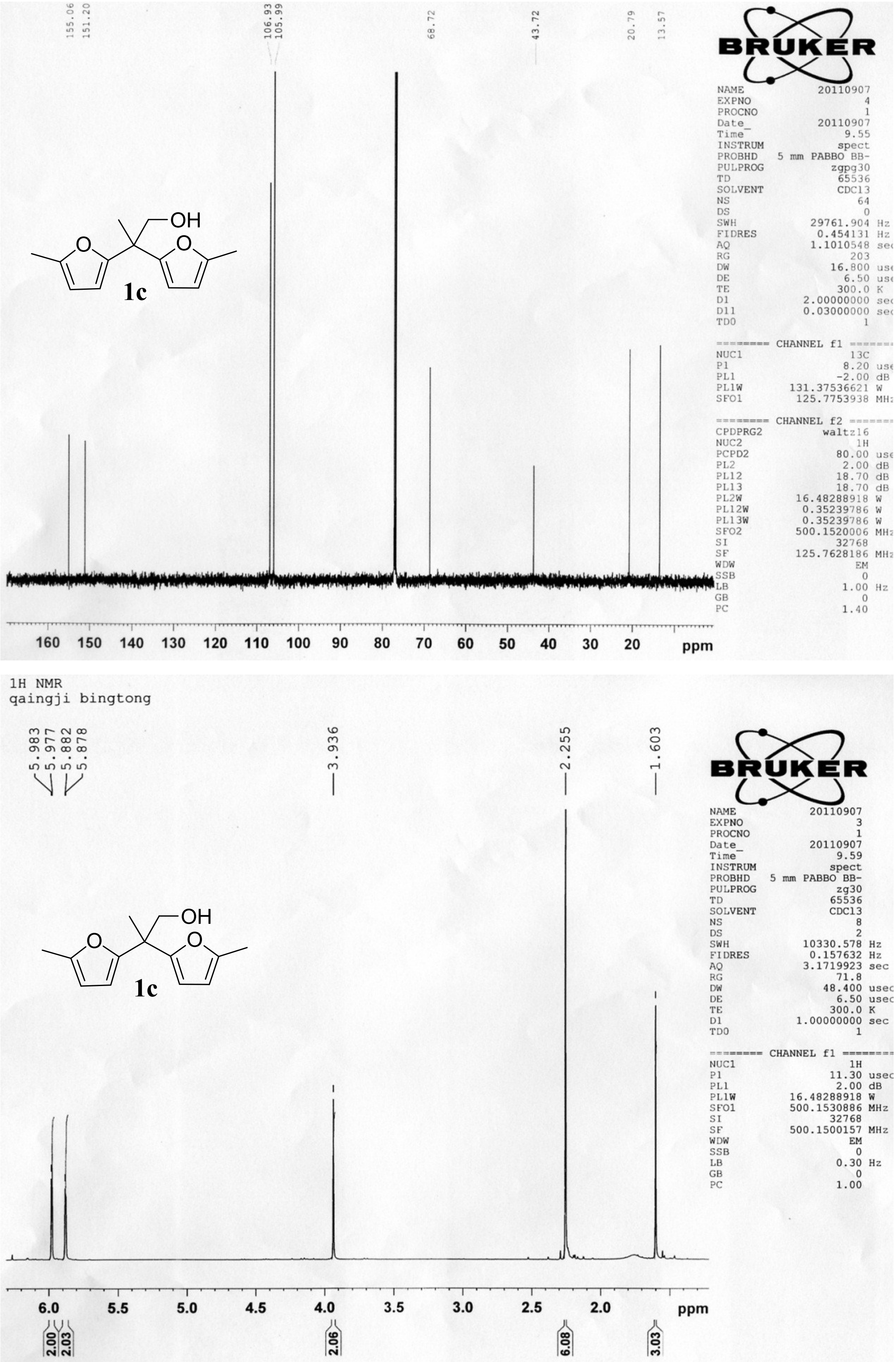


```
NAME          20110907
EXPNO                2
PROCNO               1
Date_         20110907
Time              9.48
INSTRUM          spect
PROBHD   5 mm PABBO BB-
PULPROG         zgpg30
TD               65536
SOLVENT          CDC13
NS                  50
DS                   0
SWH          29761.904 Hz
FIDRES        0.454131 Hz
AQ           1.1010548 sec
RG                 203
DW              16.800 usec
DE                6.50 usec
TE               300.0 K
D1          2.00000000 sec
D11         0.03000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1               13C
P1                8.20 usec
PL1              -2.00 dB
PL1W      131.37536621 W
SFO1       125.7753938 MHz

======== CHANNEL f2 ========
CPDPRG2        waltz16
NUC2                1H
PCPD2            80.00 usec
PL2               2.00 dB
PL12             18.70 dB
PL13             18.70 dB
PL2W       16.48288918 W
PL12W       0.35239786 W
PL13W       0.35239786 W
SFO2       500.1520006 MHz
SI               32768
SF         125.7628235 MHz
WDW                 EM
SSB                  0
LB                1.00 Hz
GB                   0
PC                1.40
```



```
NAME          20110907
EXPNO                1
PROCNO               1
Date_         20110907
Time              9.46
INSTRUM          spect
PROBHD   5 mm PABBO BB-
PULPROG           zg30
TD               65536
SOLVENT          CDC13
NS                   8
DS                   2
SWH          10330.578 Hz
FIDRES        0.157632 Hz
AQ           3.1719923 sec
RG                25.4
DW              48.400 usec
DE                6.50 usec
TE               300.0 K
D1          1.00000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1                1H
P1               11.30 usec
PL1               2.00 dB
PL1W       16.48288918 W
SFO1       500.1530886 MHz
SI              131072
SF         500.1500342 MHz
WDW                 EM
SSB                  0
LB                0.30 Hz
GB                   0
PC                1.00
```

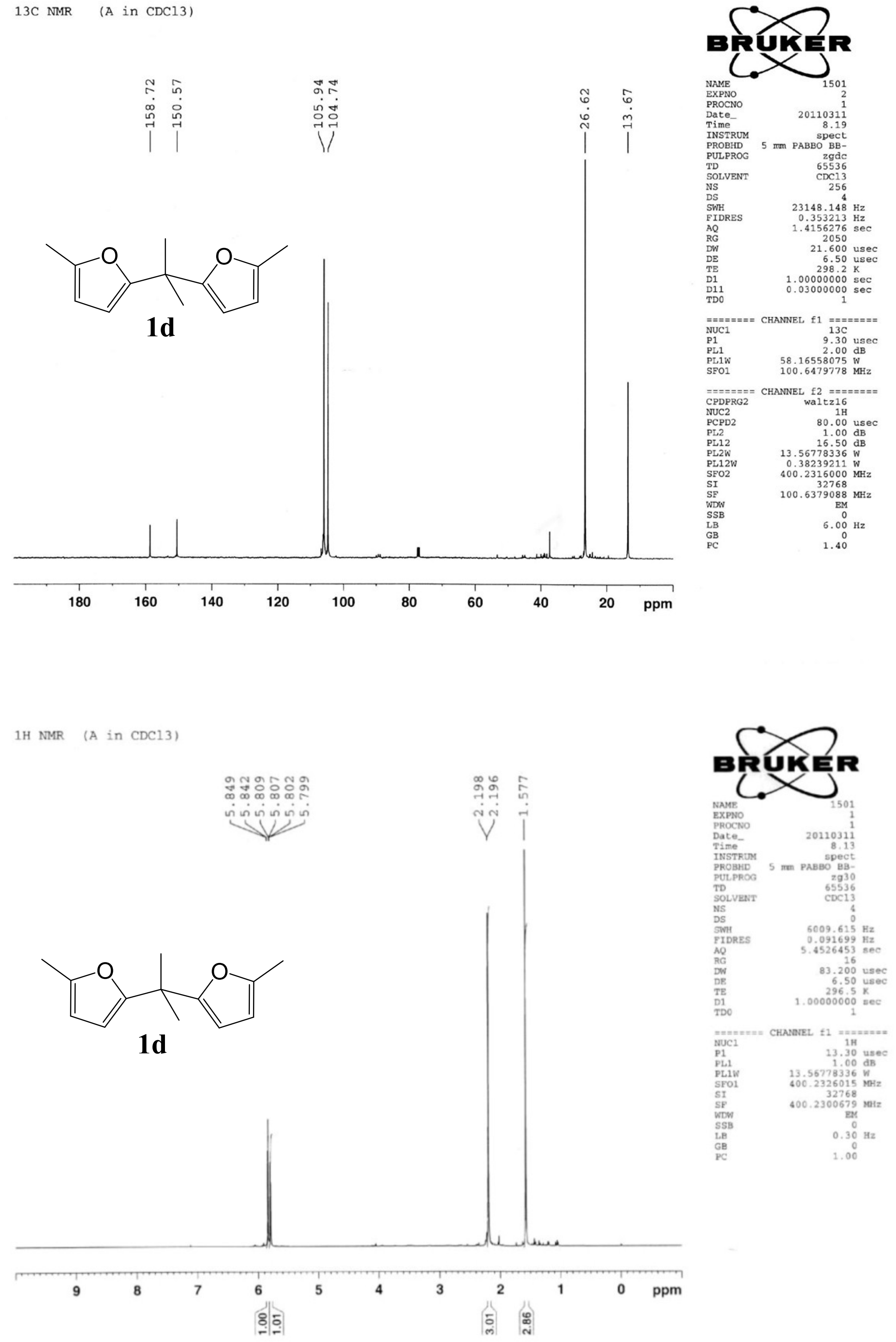
Figure S5. ^{13}C and ^{1}H NMR spectra of the **1b** produced by HAA of 2-MF with *n*-butanal.



```
NAME            20110907
EXPNO                  4
PROCNO                 1
Date_           20110907
Time                9.55
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    64
DS                     0
SWH            29761.904 Hz
FIDRES          0.454131 Hz
AQ             1.1010548 se
RG                   203
DW                16.800 us
DE                  6.50 us
TE                 300.0 K
D1            2.00000000 se
D11           0.03000000 se
TD0                    1

======== CHANNEL f1 =====
NUC1                 13C
P1                  8.20 us
PL1                -2.00 dB
PL1W        131.37536621 W
SFO1         125.7753938 MH

======== CHANNEL f2 =====
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 us
PL2                 2.00 dB
PL12               18.70 dB
PL13               18.70 dB
PL2W         16.48288918 W
PL12W         0.35239786 W
PL13W         0.35239786 W
SFO2         500.1520006 MH
SI                 32768
SF           125.7628186 MH
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

```
NAME            20110907
EXPNO                  3
PROCNO                 1
Date_           20110907
Time                9.59
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     2
SWH            10330.578 Hz
FIDRES          0.157632 Hz
AQ             3.1719923 sec
RG                  71.8
DW                48.400 use
DE                  6.50 use
TE                 300.0 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 11.30 use
PL1                 2.00 dB
PL1W         16.48288918 W
SFO1         500.1530886 MHz
SI                 32768
SF           500.1500157 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

Figure S6. ^{13}C and ^{1}H NMR spectra of the **1c** produced by the HAA of 2-MF with acetol.



```
NAME                1501
EXPNO                  2
PROCNO                 1
Date_           20110311
Time                8.19
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zgdc
TD                 65536
SOLVENT            CDCl3
NS                   256
DS                     4
SWH            23148.148 Hz
FIDRES          0.353213 Hz
AQ             1.4156276 sec
RG                  2050
DW                21.600 usec
DE                  6.50 usec
TE                 298.2 K
D1            1.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.30 usec
PL1                 2.00 dB
PL1W         58.16558075 W
SFO1         100.6479778 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 1.00 dB
PL12               16.50 dB
PL2W         13.56778336 W
PL12W         0.38239211 W
SFO2         400.2316000 MHz
SI                 32768
SF           100.6379088 MHz
WDW                   EM
SSB                    0
LB                  6.00 Hz
GB                     0
PC                  1.40
```

```
NAME                1501
EXPNO                  1
PROCNO                 1
Date_           20110311
Time                8.13
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     4
DS                     0
SWH             6009.615 Hz
FIDRES          0.091699 Hz
AQ             5.4526453 sec
RG                    16
DW                83.200 usec
DE                  6.50 usec
TE                 296.5 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 13.30 usec
PL1                 1.00 dB
PL1W         13.56778336 W
SFO1         400.2326015 MHz
SI                 32768
SF           400.2300679 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

Figure S7. ^{13}C and ^{1}H NMR spectra of the **1d** produced by HAA of 2-MF with acetone.

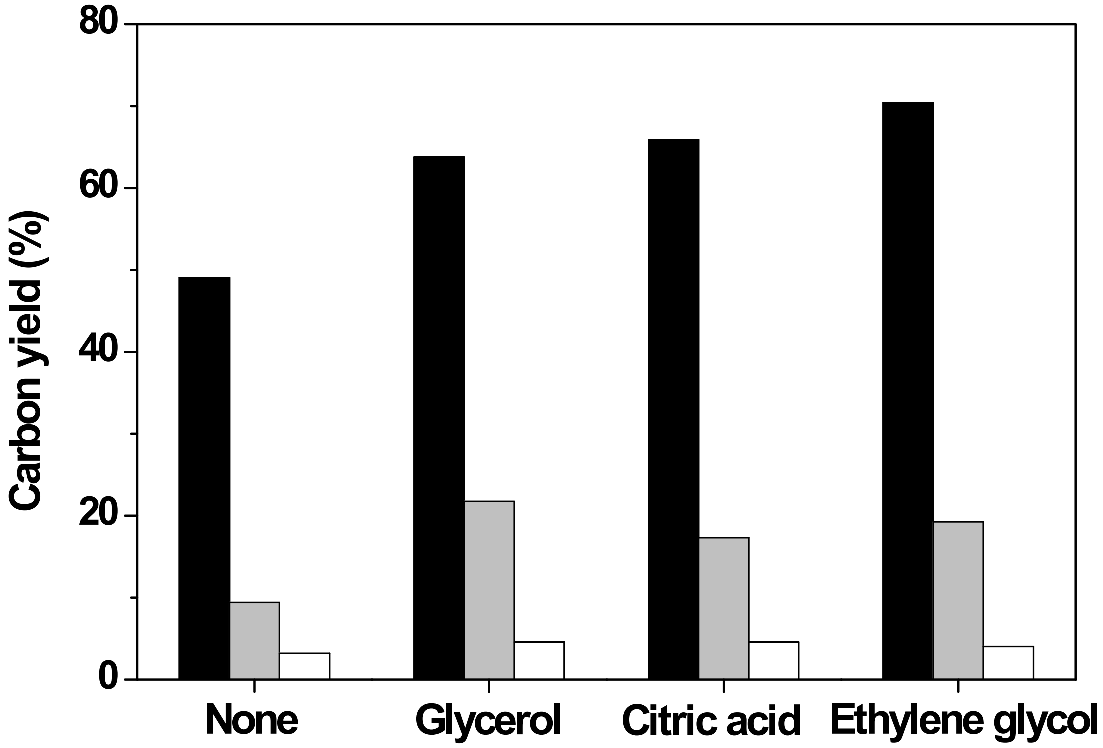


Figure S8. Carbon yields of C_9-C_{15} diesel and jet fuel range alkanes (black bars), C_5-C_8 gasoline range alkanes (grey bars) and C_1-C_4 light alkanes (white bars) over the Ni/H-ZSM-5 catalysts prepared with different complex agents. Reaction conditions: 533 K, 6 MPa, 1.8 g HDO catalyst; flow rate of liquid feedstock: 0.04 mL min^{-1} (WHSV = 1.3 h^{-1}); H_2 flow rate: 120 mL min^{-1}.

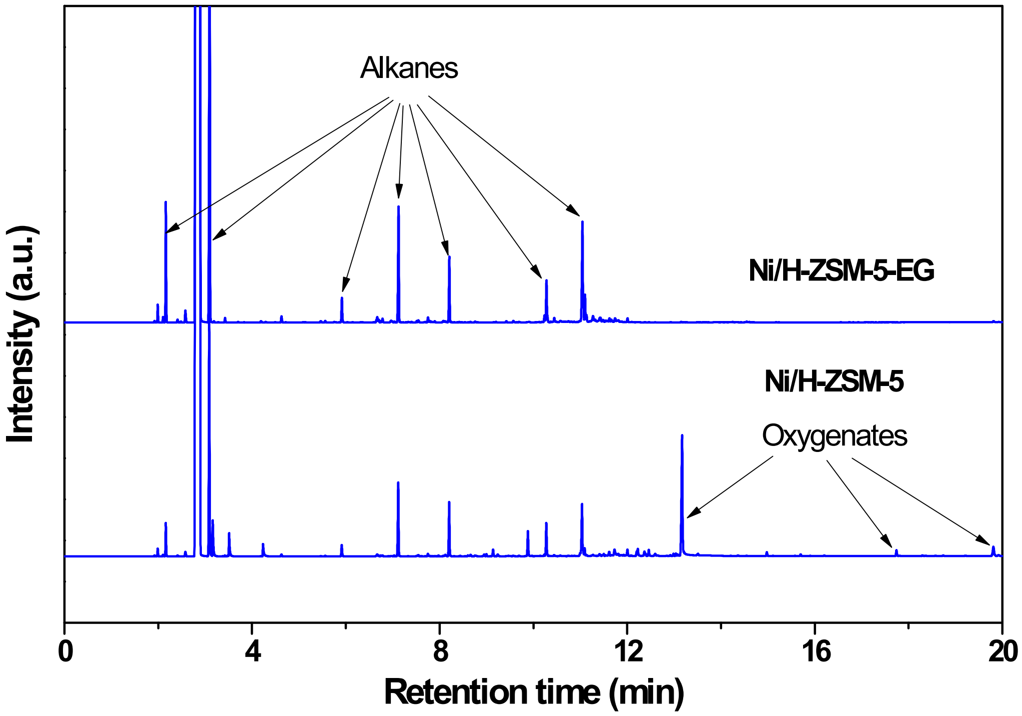


Figure S9. Gas chromatograms of the liquid products from the HDO of **1a** over the Ni/H-ZSM-5 and Ni/H-ZSM-5-EG catalysts. Reaction conditions: 533 K, 6 MPa H_2, 1.8 g catalyst; liquid feedstock flow rate of 0.04 mL min^{-1} (WHSV = 1.3 h^{-1}); H_2 flow rate of 120 mL min^{-1}.

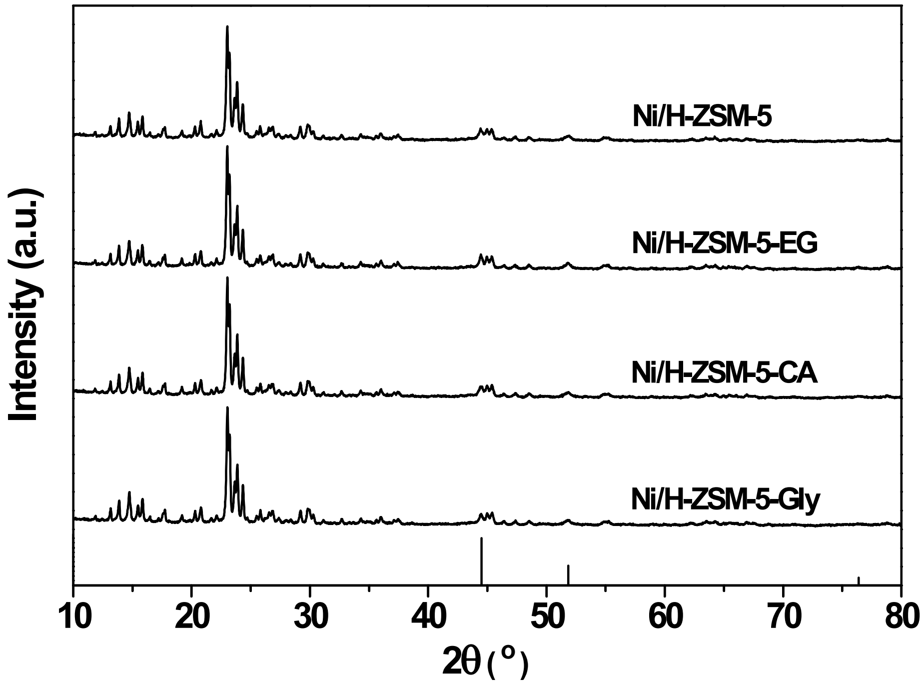


Figure S10. XRD patterns of different Ni/H-ZSM-5 catalysts. Ni/H-ZSM-5, Ni/H-ZSM-5-EG, Ni/H-ZSM-5-CA and Ni/H-ZSM-5-Gly denote the Ni/H-ZSM-5 catalyst prepared by conventional incipient wetness impregnation method (without using complex agent) and the Ni/H-ZSM-5 catalysts prepared by incipient wetness complexation impregnation method using ethylene glycol, citric acid or glycerol as the complex agent, respectively. The pattern at the bottom is that of metallic nickel from the JCPD standards (No. 00-004-0850).

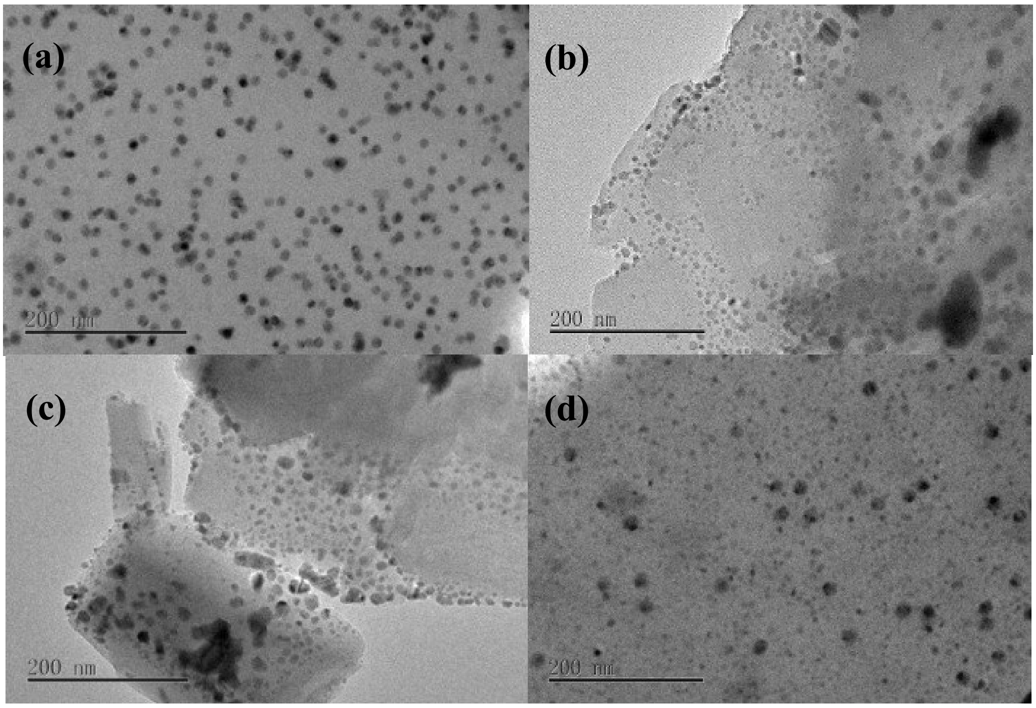


Figure S11. TEM images of the Ni/H-ZSM-5 (a), Ni/H-ZSM-5-Gly (b), Ni/H-ZSM-5-CA (c) and Ni/H-ZSM-5-EG (d) catalysts.

Table S1. Conversions of 2-methylfuran (2-MF) and carbon yields of **1a** under the catalysis of *p*-toluenesulfonic acid, acetic acid and phenol. Reaction conditions: 3.28 g (40 mmol) 2-MF, 1.92 g (20 mmol) furfural, 0.1 mL catalyst; 323 K, 2 h.

Catalyst[a]	Mole of acid (mmol)	Conversion of 2-MF (%)	Carbon yield of **1a** (%)
p-Toluenesulfonic acid	0.2	57.1	45.9
Acetic acid	0.2	4.9	0
Phenol	0.2	3.8	0

[a] The concentrations of the acid solutions are 2 mol L^{-1}.

Table S2. Specific BET surface areas, average pore sizes and the amount of acid sites of the LF, Amberlyst-15, Amberlyst-36, and Nafion-212 resins which were used as catalysts for the hydroxyalkylation/alkylation (HAA) of 2-MF and furfural.

Catalysts	Specific BET surface area (m^2 g^{-1})	Average pore size (nm)[a]	Amount of acid sites on the surface of catalyst (mmol g_{cat}^{-1})[b]		
			-SO_3H group	-COOH group	Phenolic -OH group
LF	2	5.7	1.02	0.25	1.11
Amberlyst-15	41	29	4.61 (4.7)	—	—
Amberlyst-36	13	24	5.33 (5.4)	—	—
Nafion-212	2	4.0	1.08 (1.1)	—	—

[a] Average pore sizes were measured by N_2-adsorption according to the Barrett–Joyner–Halenda (BJH) method. [b] The amounts of acid sites were obtained by titration method. The values in the brackets were the ones provided by supplier.

Table S3. Effect of calcium lignosulfonate concentration on the conversion of 2-MF and the carbon yield of **1a** over the LF resin. Reaction conditions: 3.28 g (40 mmol) 2-MF, 1.92 g (20 mmol) furfural, 0.15 g catalyst; 323 K, 2 h.

Catalyst[a]	Amount of acid sites on the surface of catalyst (mmol g_{cat}^{-1})[b]	Conversion of 2-MF (%)	Carbon yield of **1a** (%)
LF	1.02	70.4	65.4
LF-Ca-1	0.97	64.4	60.9
LF-Ca-5	0.93	63.4	59.4
LF-Ca-10	0.87	58.9	55.1

[a] LF-Ca-1, LF-Ca-5 and LF-Ca-10 denote the LF resins prepared with the mixture of sodium lignosulfonate and calcium lignosulfonate at the mass ratio of 99:1, 19:1 and 9:1, respectively.

[b] Measured by the chemical titration described in the supporting information.

Table S4. Effect of sugar concentration on the conversion of 2-MF and the carbon yield of **1a** over the LF resin. Reaction conditions: 3.28 g (40 mmol) 2-MF, 1.92 g (20 mmol) furfural, 0.15 g catalyst; 323 K, 2 h.

Catalyst[a]	Amount of acid sites on the surface of catalyst (mmol g_{cat}^{-1})[b]	Conversion of 2-MF (%)	Carbon yield of **1a** (%)
LF	1.02	70.4	65.4
LF-Sugars-1	1.00	64.7	62.2
LF-Sugars-5	0.92	62.2	58.6
LF-Sugars-10	0.79	57.6	54.1

[a] LF-Sugars-1, LF-Sugars-5 and LF-Sugars-10 denote the LF resins prepared with the mixture of sodium lignosulfonate, glucose and xylose at the mass ratio of 198:1:1, 38:1:1 and 18:1:1, respectively.

[b] Measured by the chemical titration described in the supporting information.

Table S5. Metal dispersions and the amounts of chemical accessiable Ni sites over the different catalyst measured by H_2-O_2 titration.

Catalyst[a]	Metal dispersion (%)	Amount of chemical accessible Ni sites (μmol g^{-1})
Ni/H-ZSM-5	6.7	64.1
Ni/H-ZSM-5-Gly	10.0	77.4
Ni/H-ZSM-5-CA	9.8	76.1
Ni/H-ZSM-5-EG	11.4	96.8

[a] The theoretical content of Ni in each catalyst was 5 wt.%. Ni/H-ZSM-5, Ni/H-ZSM-5-Gly, Ni/H-ZSM-5-CA, Ni/H-ZSM-5-EG account for the Ni/H-ZSM-5 catalysts prepared by conventional impregnation method or complexation impregnation method in the presence of glycerol, citric acid and ethylene glycol, respectively.

References

1. X. Zhang, Z. Zhang, F. Wang, Y. Wang, Q. Song and J. Xu, *J. Mol. Catal. A: Chem.*, 2013, **377**, 102-107.
2. a) S. Suganuma, K. Nakajima, M. Kitano, D. Yamaguchi, H. Kato, S. Hayashi and M. Hara, *J. Am. Chem. Soc.*, 2008, **130**, 12787-12793; b) X. Li, Y. Jiang, L. Shuai, L. Wang, L. Meng and X. Mu, *J. Mater. Chem.*, 2012, **22**, 1283-1289; c) D. Lee, *Molecules*, 2013, **18**, 8168-8180.
3. W. Bai, Y. Wang, X. Song, X. Jin and X. Guo, *J. Macromol. Sci. Part A*, 2014, **51**, 737-742.
4. Y. Ge, Z. Li, Y. Pang and X. Qiu, *Int. J. Biol. Macromol.*, 2013, **52**, 300-304.
5. X.P. Ouyang, L.X. Ke, X.Q. Qiu, Y.X. Guo and Y.X. Pang, *J. Dispersion Sci. Technol.*, 2009, **30**, 1-6.
6. R. Demir-Cakan, N. Baccile, M. Antonietti and M.-M. Titirici, *Chem. Mater.*, 2009, **21**, 484-490.
7. a) K.A. Mauritz and R.B. Moore, *Chem. Rev.*, 2004, **104**, 4535-4586; b) B.G. Harvey, M.E. Wright and R.L. Quintana, *Energy & Fuels*, 2010, **24**, 267-273; c) J. Zakzeski, P.C.A. Bruijnincx, A.L. Jongerius and B.M. Weckhuysen, *Chem. Rev.*, 2010, **110**, 3552-3599; d) R. Weingarten, G.A. Tompsett, W.C. Conner and G.W. Huber, *J. Catal.*, 2011, **279**, 174-182.