Supporting Information

Synthesis of renewable diesel with hydroxyacetone and 2-methyl-furan

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

[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*

* *Corresponding author: (+86)411-84379015, E-mail address: taozhang@dicp.ac.cn*

1. Experiment

1.1 Catalysts

Nafion-115 and Nafion-212 resins with average pore size about 4 nm[1] were supplied by DuPont Company. Amberlyst-15 and Amberlyst-36 resins were purchased from Sigma-Aldrich. According to the information offered by supplier， the average pore diameters of Amberlyst-15 and Amberlyst-36 resin are about 29 nm and 24 nm respectively. H-β (SiO_2/Al_2O_3 = 25), H-USY (SiO_2/Al_2O_3 = 12) and H-ZSM-5 (SiO_2/Al_2O_3 = 140) were provided by Nankai University. Sulfated active carbon, (denoted as AC-SO_3H) was homemade according to the method described in our previous work[2]. As the precursor, 2.0 g active carbon (supplied by NORIT Company) was added to 30 mL concentrated sulfuric acid (H_2SO_4, 98%) in a glass tube at room temperature. Then, the tube was heated at 523 K for 24 h under the protection of nitrogen flow (10 mL min^{-1}). After cooling down to room temperature and filtration, the solid was washed thoroughly with plenty of hot water (353 K) until no SO_4^{2-} was detected in the filtrate. Zirconium phosphate (ZrP) was obtained according to literature[3] by the precipitation of 1.0 mol L^{-1} $ZrCl_2O\cdot 8H_2O$ and 1.0 mol L^{-1} $NH_4H_2PO_4$ aqueous solution at a molar ratio of P/Zr = 2.0. The precipitate was filtrated, washed with water, dried at 373 K overnight and calcined in air at 673 K for 4 h.

The AC-SO_3H, ZrP, H-ZSM-5, H-USY, H-β catalysts used in this work were powders with particle size less than 0.4 mm. The Amberlyst-15 and Amberlyst-36 resins used in this work were beads with diameters around 0.7 mm and 0.4 mm respectively. The Nafion resins used in this work were films (thickness: 51 μm for

Nafion-212 and 127 μm for Nafion-115) which were cut into about 2×5 mm pieces by scissors before used for the reaction.

Pd/C catalyst used in HDO step was prepared by incipient wetness impregnation of the HNO_3 treated active carbon with the aqueous solutions of $PdCl_2$. The products were kept at room temperature for 12 h, dried at 393 K for 6 h, and then reduced by hydrogen flow (60 mL min^{-1} g_{cat}^{-1}) at 623 K for 2 h. After cooled down in hydrogen to room temperature, the catalysts were passivated with 1% O_2 in N_2 (V/V). The metal content in Pd/C catalyst was 5% by weight (denoted as 5 wt%).

1.2 Hydroxyalkylation/alkylation (HAA)

HAA reaction was carried out in a round-bottom flask equipped with a reflux condenser and a magnetic stirrer. The reaction temperature was controlled by water bath. Typically, 0.15 g catalyst, 3.28 g (40 mmol) 2-methylfuran (2-MF), 1.48 g (20 mmol) hydroxyacetone were used for each reaction. The mixture was stirred at set temperature, filtrated, and analyzed by an Agilent 1100 HPLC equipped with a ZORBAX SB-C18 (4.6 × 150 mm, 5 μm) column and refractive index detector (RID). A mixture of methanol and water (the volume ratio of methanol and water is 4:1) was used as mobile phase.

As we have reported previously,[4, 5] the conversion of 2-MF is higher than the yield of HAA products. The missing carbon in HAA reaction can be attributed to the large polymeric molecules (or coke) generated by over-alkylation. These compounds have high molecular weight (can't be analyzed by GC) and low solubility in the mobile phase of HPLC. Therefore, it is very hard to give quantitative information about them.

1.3 Hydrodeoxygenation (HDO)

The HDO reaction of HAA product was carried out in a 316L stainless steel tubular flow reactor described in our previous work.[4, 5] For each reaction, 1.8 g catalyst was used. The HAA product was feed into the reactor by a HPLC pump at 0.04 mL min^{-1} from the bottom along with hydrogen at a flow rate of 120 mL min^{-1}. The products from the reactor passed through a gas-liquid separator and became two phases. The gaseous products flowed through a back pressure regulator to maintain the pressure in reaction system and were analyzed online by an Agilent 6890N GC. Liquid products were drained periodically from the gas-liquid separator and analyzed by another Agilent 6890N GC.

Method for the calculation of carbon yield in HDO step:

Carbon yield of diesel (%) = Sum of carbon in the C_9-C_{16} alkanes detected from the liquid phase product/Carbon fed into the reactor × 100%

Carbon yield of gasoline (%) = Sum of carbon in the C_5-C_8 alkanes detected from the gas phase product in unit time/Carbon fed into the reactor in unit time × 100% + Sum of carbon in the C_5-C_8 alkanes detected from liquid phase products/Carbon fed into the reactor × 100%

Carbon yield of light alkanes (%) = Sum of carbon in the C_1-C_4 alkanes detected from the gas phase product in unit time/Carbon fed into the reactor in unit time × 100%

According to our analysis, the carbon balance for the HDO of 2-MF-Acetone HAA product and 2-MF-Hydroxyacetone HAA product were 84.6% and 92.1% respectively. The missing carbon may be explained by two possible reasons. One reason is the volatilization of gasoline range alkanes during the draining of liquid products from the gas-liquid separator and sample analyzing. Another reason is the coke formation on the surface of Pd/C catalyst. This is difficult to be proved because active carbon was used as the support.

2. Supporting figures

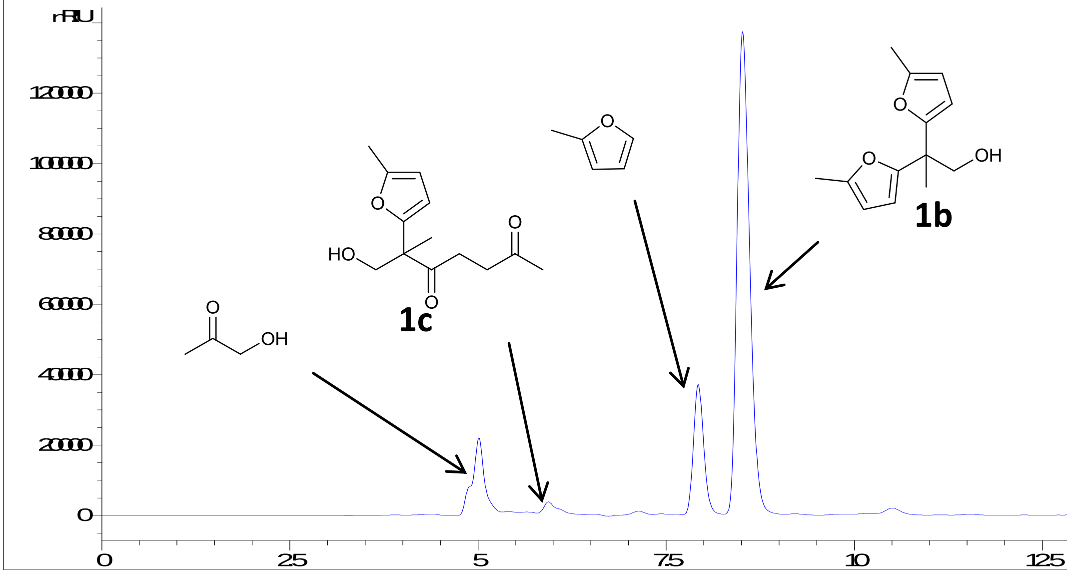
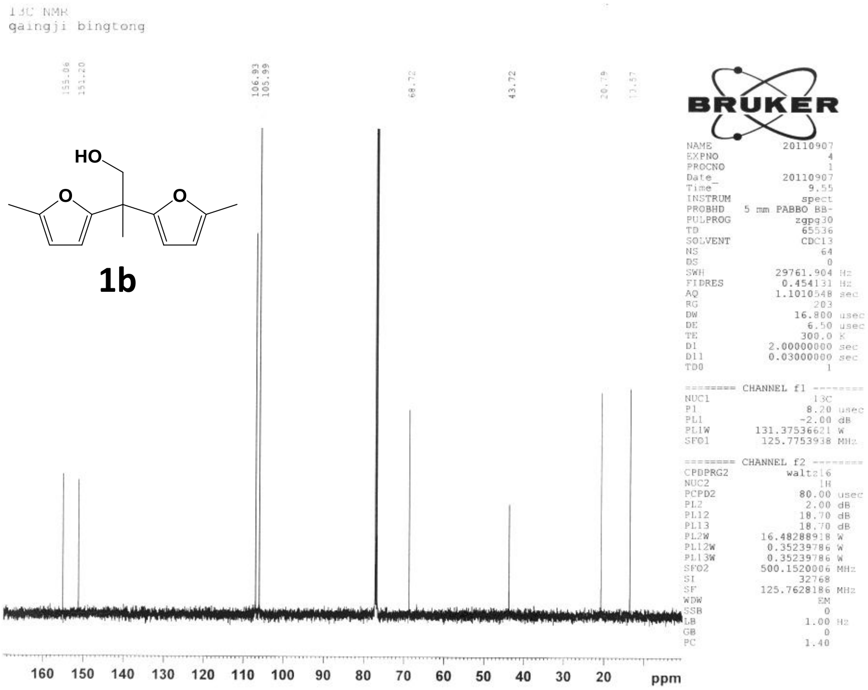
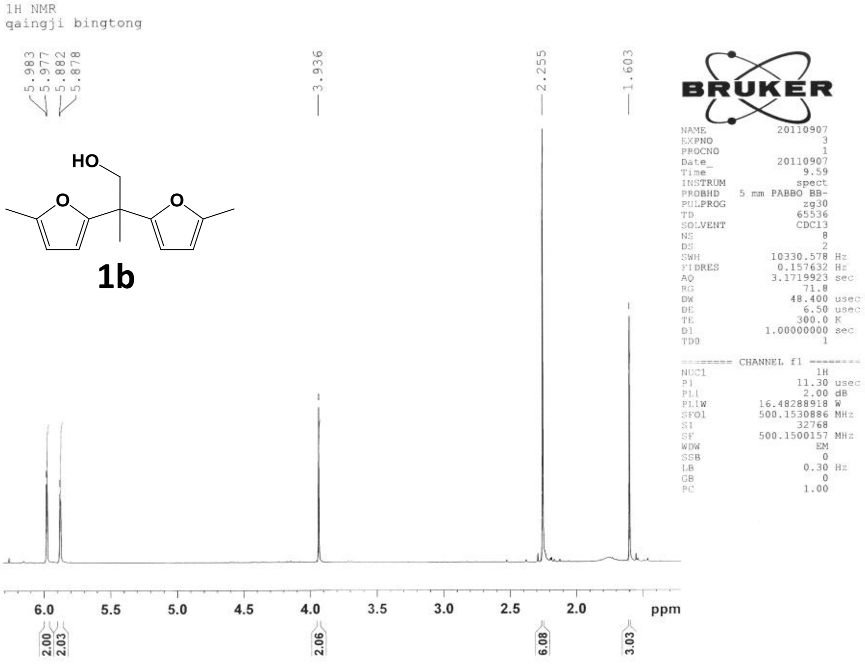


Figure S1. HPLC chromatogram of liquid products for the HAA of 2-methylfuranl (2-MF) with hydroxyacetone. Reaction conditions: 338 K, 2 h, 3.28 g 2-MF (40 mmol), 1.48 g hydroxyacetone (20 mmol) (2-MF: hydroxyacetone molar ratio was 2:1), 0.15 g Nafion-212.

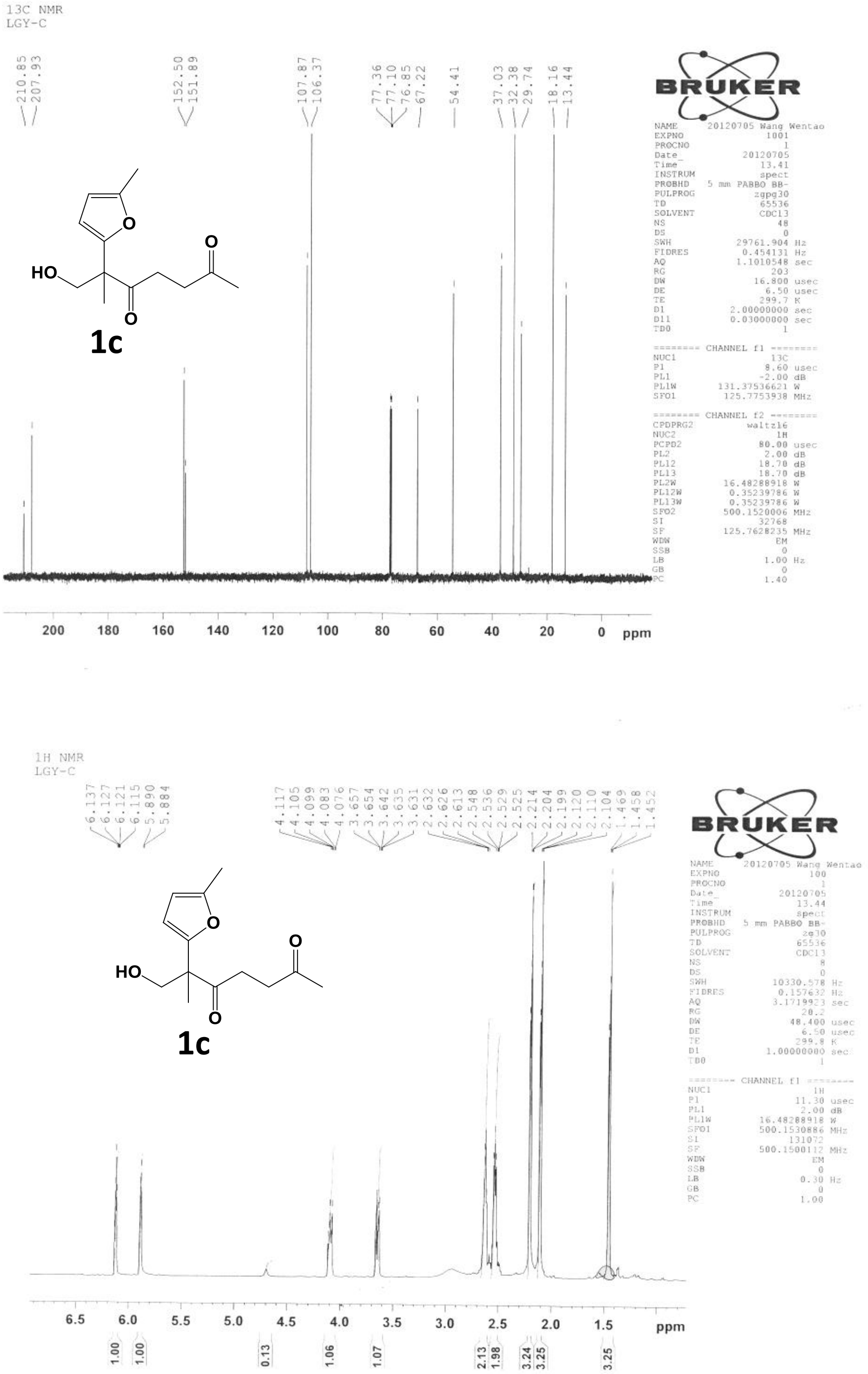


```
NAME            20110907
EXPNO                  4
PROCNO                 1
Date_           20110907
Time                9.55
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT            CDCl3
NS                    64
DS                     0
SWH            29761.904 Hz
FIDRES          0.454131 Hz
AQ             1.1010548 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           125.7628186 MHz
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 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                 32768
SF           500.1500157 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

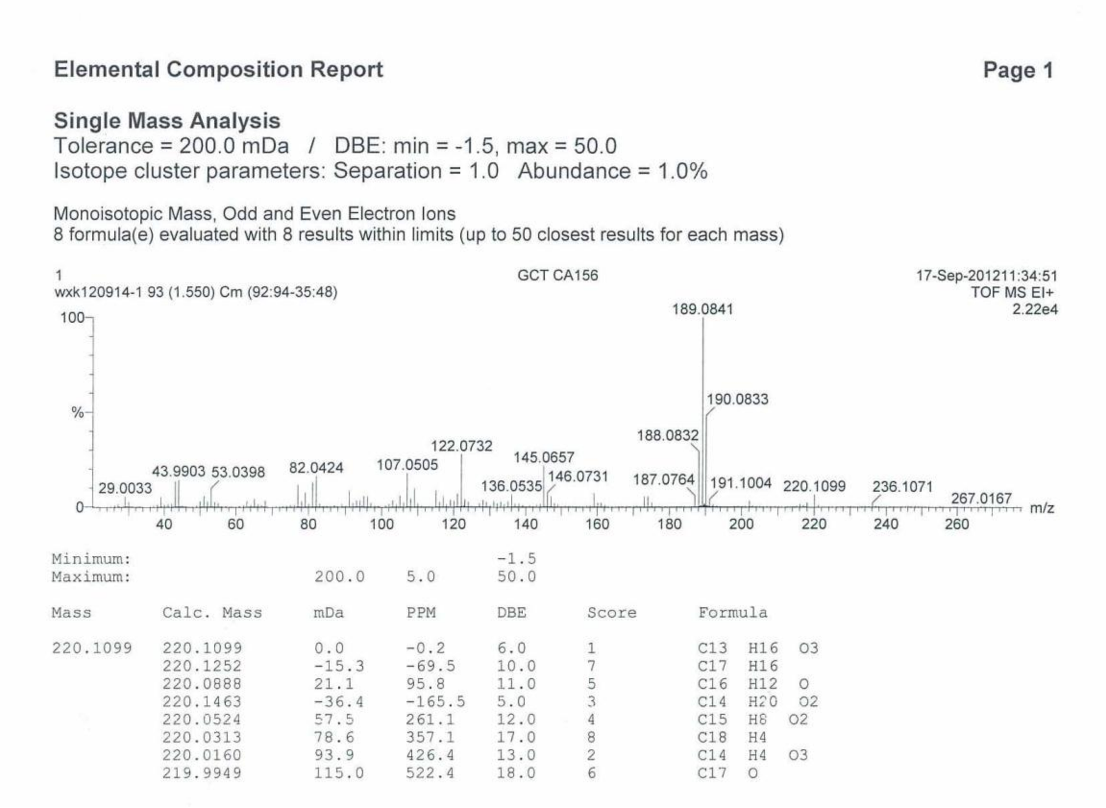
Figure S2. ^{13}C and ^{1}H NMR spectra of the **1b** produced by the HAA of 2-MF and hydroxyacetone.



```
NAME        20120705 Wang Wentao
EXPNO                   1001
PROCNO                     1
Date_               20120705
Time                   13.41
INSTRUM                spect
PROBHD      5 mm PABBO BB-
PULPROG              zgpg30
TD                    65536
SOLVENT                CDCl3
NS                        48
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                   299.7 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                     13C
P1                  8.60 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        20120705 Wang Wentao
EXPNO                    100
PROCNO                     1
Date_               20120705
Time                   13.44
INSTRUM                spect
PROBHD      5 mm PABBO BB-
PULPROG                 zg30
TD                    65536
SOLVENT                CDCl3
NS                         8
DS                         0
SWH             10330.578 Hz
FIDRES           0.157632 Hz
AQ              3.1719923 sec
RG                      20.2
DW                48.400 usec
DE                  6.50 usec
TE                   299.8 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           500.1500112 MHz
WDW                       EM
SSB                        0
LB                   0.30 Hz
GB                         0
PC                      1.00
```

Figure S3. ^{13}C and ^{1}H NMR spectra of the **1c** produced by the HAA of 2-MF and hydroxyacetone.



Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 200.0 mDa / DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
8 formula(e) evaluated with 8 results within limits (up to 50 closest results for each mass)

1 GCT CA156 17-Sep-201211:34:51
wxk120914-1 93 (1.550) Cm (92:94-35:48) TOF MS EI+
2.22e4

```
Minimum:                                    -1.5
Maximum:                   200.0    5.0     50.0

Mass       Calc. Mass      mDa      PPM     DBE      Score      Formula

220.1099   220.1099        0.0      -0.2    6.0      1          C13  H16  O3
           220.1252        -15.3    -69.5   10.0     7          C17  H16
           220.0888        21.1     95.8    11.0     5          C16  H12  O
           220.1463        -36.4    -165.5  5.0      3          C14  H20  O2
           220.0524        57.5     261.1   12.0     4          C15  H8  O2
           220.0313        78.6     357.1   17.0     8          C18  H4
           220.0160        93.9     426.4   13.0     2          C14  H4  O3
           219.9949        115.0    522.4   18.0     6          C17  O
```

Figure S4. HR-GC-MS spectra of the **1b** produced by the HAA of 2-MF and hydroxyacetone.

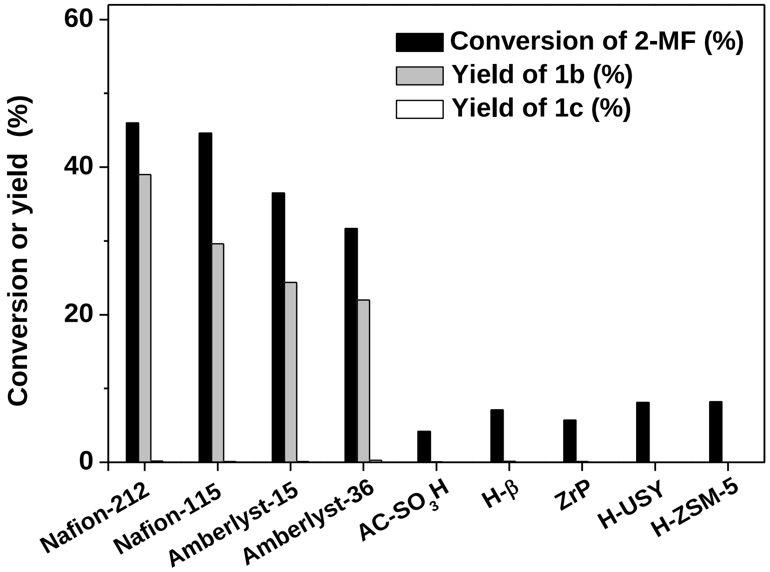


Figure S5. Conversion of 2-MF (black bars) and yields of HAA products (gray bars) over different solid acid catalyst. Reaction conditions: 338 K, 2 h, 3.28 g 2-MF (40 mmol), 1.48 g hydroxyacetone (20 mmol) (2-MF: hydroxyacetone molar ratio was 2:1), 0.015 g catalyst.

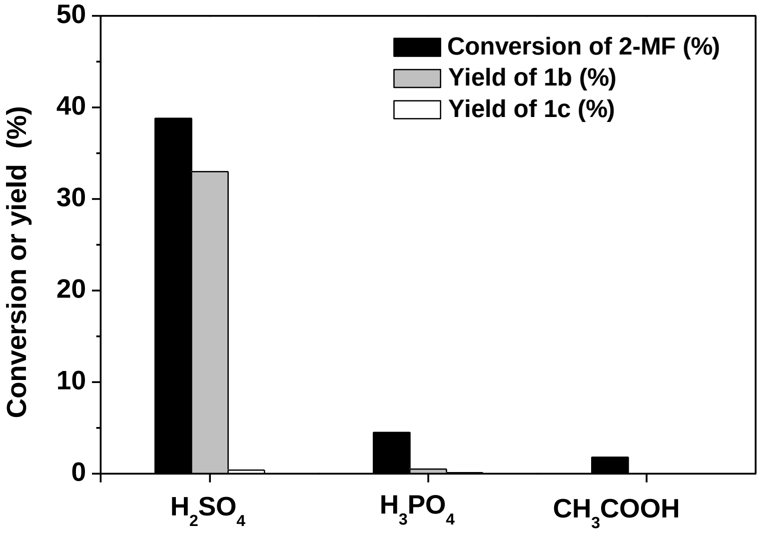


Figure S6. Conversion of 2-MF, yields of **1b** and **1c** under the catalysis of different acids. Reaction conditions: 338 K; 2 h; 3.28 g 2-MF (40 mmol), 1.48 g hydroxyacetone (20 mmol) (2-MF: hydroxyacetone molar ratio was 2:1) and 0.15 mL catalyst. The concentrations of the three acids were 5 N.

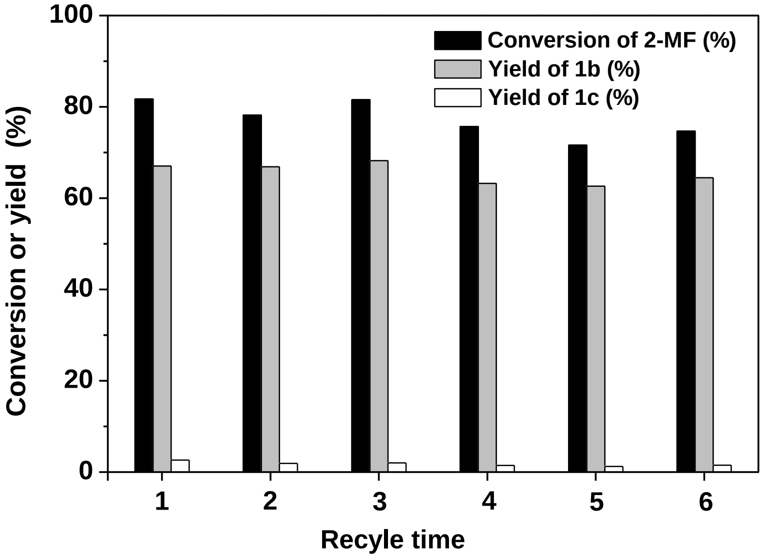


Figure S7. Conversion of 2-MF, the yields of **1b** and **1c** over Nafion-212 resin. Reaction conditions: 338 K, 2 h; 3.28 g (40 mmol) 2-MF, 1.48 g (20 mmol) hydroxyacetone (2-MF: hydroxyacetone molar ratio was 2:1), and 0.15 g catalyst.

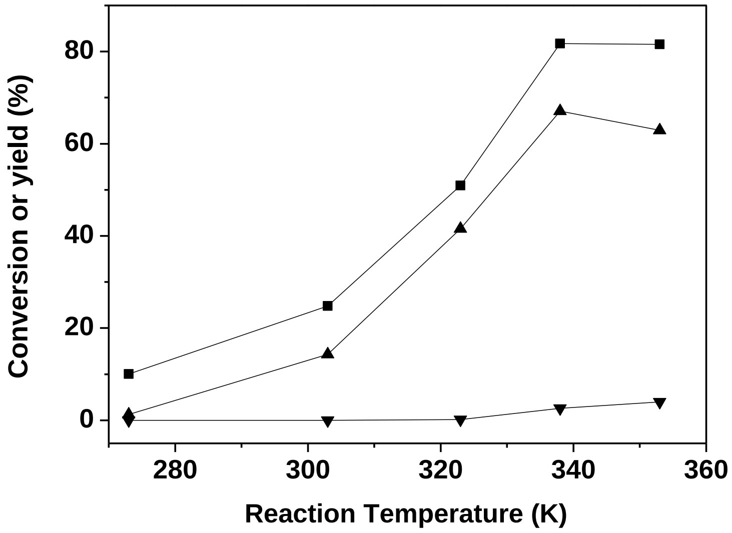


Figure S8. Conversion of 2-MF (■), yields of **1b** (▲) and **1c** (▼) over Nafion-212 resin. Reaction conditions: 2 h; 3.28 g 2-MF (40 mmol), 1.48 g hydroxyacetone (20 mmol) (2-MF: hydroxyacetone molar ratio was 2:1) and 0.15 g catalyst. The reaction at 353 K was carried out in the autoclave.

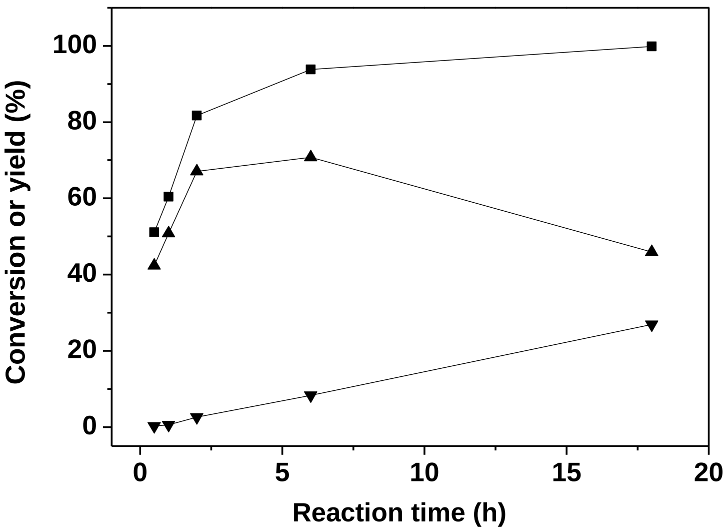


Figure S9. Conversion of 2-MF (■), yields of **1b** (▲) and **1c** (▼) over Nafion-212 resin. Reaction conditions: 338 K; 3.28 g 2-MF (40 mmol), 1.48 g hydroxyacetone (20 mmol) (2-MF: hydroxyacetone molar ratio was 2:1) and 0.15 g catalyst.

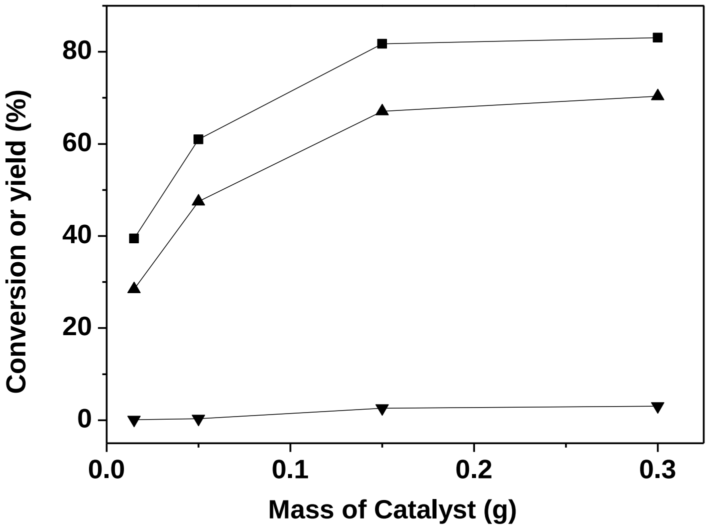


Figure S10. Conversion of 2-MF (■), yields of **1b** (▲) and **1c** (▼) over Nafion-212 resin. Reaction conditions: 338 K, 2 h; 3.28 g 2-MF, 1.48 g hydroxyacetone (2-MF: hydroxyacetone molar ratio was 2:1).

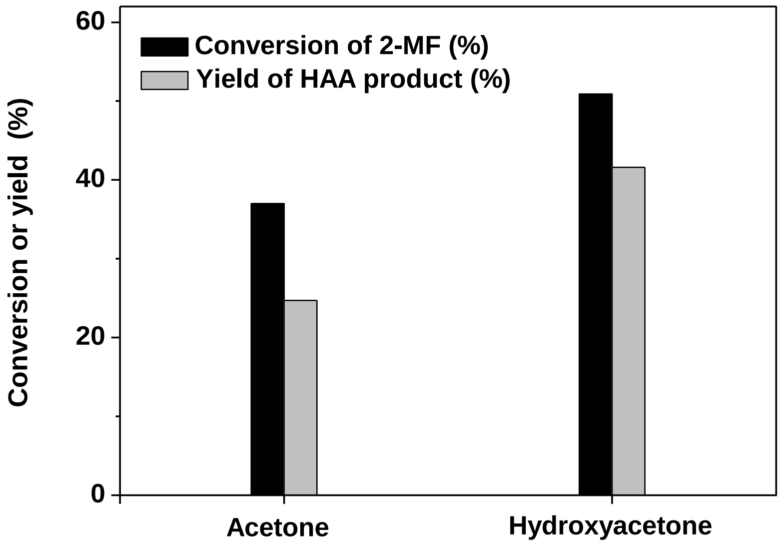


Figure S11. Conversion of 2-MF (black bars) and yield of HAA products (gray bars) over Nafion-212 resin. Reaction conditions: 323 K, 2 h, 3.28 g 2-MF (40 mmol), 1.16 g acetone or 1.48 g hydroxyacetone (20 mmol) (2-MF: acetone or hydroxyacetone molar ratio was 2:1) and 0.15 g Nafion-212.

References

1. W. Y. Hsu and T. D. Gierke, *J. Membr. Sci.*, 1983, **13**, 307-326.
2. J. F. Pang, A. Q. Wang, M. Y. Zheng and T. Zhang, *Chem. Commun.*, 2010, **46**, 6935-6937.
3. Y. Kamiya, S. Sakata, Y. Yoshinaga, R. Ohnishi and T. Okuhara, *Catal. Lett.*, 2004, **94**, 45-47.
4. G. Li, N. Li, Z. Wang, C. Li, A. Wang, X. Wang, Y. Cong and T. Zhang, *ChemSusChem*, 2012, **5**, 1958-1966.
5. G. Li, N. Li, J. Yang, A. Wang, X. Wang, Y. Cong and T. Zhang, *Bioresour. Technol.*, 2013, **134**, 66-72.