Electronic Supplementary Material (ESI) for Green Chemistry

Supporting Information

Synthesis of renewable diesel range alkanes by hydrodeoxygenation of furans over Ni/Hβ under mild condition

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Experimental

1. Materials

1.1 Catalysts

The Amberlyst-15 resin (dry) and Amberlyst-36 resin (wet) used in the production of precursors by hydroxyalkylation/alkylation (HAA) reaction were purchased from Sigma-Aldrich.

SiO_2 and SiO_2-Al_2O_3 (SiO_2/Al_2O_3 molar ratio: 37) were purchased from Qingdao Ocean Chemical Ltd.. Hβ zeolites with different SiO_2/Al_2O_3 molar ratios (indicated in bracket) and HUSY zeolite with the SiO_2/Al_2O_3 molar ratio of 12 were provided by Nankai University. The specific BET surface areas of different supports were shown in Table S2.

The catalysts used in hydrodeoxygenation (HDO) step was prepared by incipient wetness impregnation of the corresponding supports with the aqueous solutions of $H_2PtCl_6 \cdot 6H_2O$, $PdCl_2$, $RuCl_3 \cdot 3H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$, respectively. The products were kept at room temperature for 12 h, dried at 393 K for 6 h, and then calcined in air at 773 K for 2 h. To facilitate the comparison, the metal contents in all catalysts were fixed as 5% by weight (denoted as 5 wt%).

1.2 Precursors for diesel or jet fuel

In this work, a series of precursors for the renewable diesel or jet fuels were prepared by the HAA of 2-methylfuran (2-MF) and lignocellulose derived carbonyl compounds. The HAA reactions were carried out in a round-bottom flask equipped with a reflux condenser and a magnetic stirrer. The reaction temperature was controlled by water bath.

5,5'-(butane-1,1-diyl)bis(2-methylfuran) (simplified as BBM) used for the HDO process was synthesized according to the method described in our previous work[1] by the HAA of 2-MF and butanal. Typically, 1.5 g Amberlyst-15, 32.8 g (0.4 mol) 2-MF, 14.4 g (0.2 mol) butanal were used for each reaction. The mixture was stirred at 338 K for 2 h, filtrated, and purified by vacuum distillation. The ^{13}C and ^{1}H NMR spectra of the 5,5'-(butane-1,1-diyl) bis(2-methylfuran) as prepared were shown in Figure S6. According to the analysis of HPLC, the purity of BBM obtained by the vacuum distillation of the HAA product between 2-MF and butanal is higher than 95%. The purified BBM was liquid with good fluidity at room temperature. Therefore, it is easy to pump it into the fixed bed reactor.

5,5'-(propane-2,2-diyl)bis(2-methylfuran) (simplified as PBM) was synthesized according to the method described in our previous work[1] by the HAA of 2-MF and acetone. Typically, 1.5 g Amberlyst-15, 32.8 g (0.4 mol) 2-MF, 11.2 g (0.2 mol) acetone were used for each reaction. The mixture was stirred at 338 K for 2 h, filtrated, and purified by vacuum distillation. The ^{13}C and ^{1}H NMR spectra of 5,5'-(propane-2,2-diyl)bis(2-methylfuran) as prepared were shown in Figure S7.

5,5'-(furan-2-ylmethylene)bis(2-methylfuran) (simplified as FMBM) was prepared according to the method described in our previous work[2] by the HAA of 2-MF and furfural. Typically, 1.5 g Amberlyst-15, 32.8 g (0.4 mol) 2-MF, 19.3 g (0.2 mol) furfural were used for each reaction. The mixture was stirred at 338 K for 2 h, filtrated, and purified by vacuum distillation. The ^{13}C and ^{1}H NMR spectra of 5,5'-(furan-2-ylmethylene)bis(2-methylfuran) as prepared were shown in Figure S8.

Bis(5-methylfuran-2-yl)methane (simplified as BMM) was synthesized by the similar method by the HAA of 2-MF and formaldehyde. Typically, 3.0 g Amberlyst-36 (wet) (contain 50% water), 32.8 g (0.4 mol) 2-MF, 16.2 g 37% (0.2 mol) formaldehyde aqueous solution were used for each reaction. The mixture was stirred at 338 K for 2 h, filtrated, and purified by vacuum distillation. The ^{13}C and ^{1}H NMR spectra of bis(5-methylfuran-2-yl)methane as prepared were shown in Figure S9.

2. Activity test

The HDO of HAA products was carried out in a 316L stainless steel tubular flow reactor described in our previous work[1-3]. For each reaction, 1.8 g catalyst was used. Before the reaction, the catalysts were reduced *in-situ* in the reactor by an H_2 flow (at 160 mL min^{-1}) from the bottom at 723 K for 2 h. 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 at 6 MPa 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 range alkanes (%) = Sum of carbon in the C_9-C_{16} alkanes detected from the liquid phase products/Carbon fed into the reactor × 100%

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

3. Characterization

3.1 XRD

XRD patterns of different catalyst were obtained with a PW3040/60X' Pert PRO (PANalytical) diffractometer equipped with a Cu K_{α} radiation source (λ=0.15432 nm) at 40 kV and 40 mA.

3.2 N_2-adsorption

The specific BET surface areas of different supports were measured by nitrogen adsorption at 77 K using an ASAP 2010 apparatus. Before each measurement, the sample was evacuated at 573 K for 3 h.

3.3 Microcalorimetric measurement of ammonia adsorption

Microcalorimetric measurements of ammonia adsorption were performed at 423 K by 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 ($\pm 0.5\times10^{-4}$ Torr). Ammonia used for the measurements (purity > 99.999%) was purified by successive freeze–pump–thaw cycles. The samples (150-200 mg) were pretreated in a quartz cell at 773 K for 3 h under high vacuum. The differential heats were measured as a function of coverage by repeatedly introducing small doses of ammonia onto the samples until an equilibrium pressure of about 5-6 torr was reached. Then the system was evacuated overnight to remove the physisorbed ammonia, and a second adsorption cycle was performed. The amount of irreversible adsorbed ammonia was determined by the difference between the isotherms of the first and second adsorption cycles.

3.4 H_2-O_2 titration

The Ni dispersions of various Ni catalysts (corresponding to the ratio of surface Ni atoms to total Ni atoms) were measured with a Micromeritics AutoChem II 2920 Automated Catalyst Characterization System by H_2-O_2 titration assuming that the stoichiometry of H_2 to surface Ni atom is 1.5. Before each test, the sample was reduced in 10% H_2/Ar flow at 773 K for 2 h, purged in Ar flow at 783 K for 0.5 h and cooled down in Ar flow to 393 K. The O_2 adsorption was carried out by the constant flow of 2% O_2 in He for 0.5 h. Then, the sample was purged and heated in Ar flow to 773 K. After the stabilization of baseline, the H_2 adsorption was carried out by the pulse adsorption of 10% H_2/Ar at 773 K.

3.5 TEM

The TEM images of the Ni/Hβ catalysts were obtained on a with a TECNAI G^2 Spirit FEI Transmission Electron Microscopy operating at 120 kV. Before the test, the catalysts were reduced *in-situ* by an H_2 flow at 723 K for 2 h. According to Figure S10, the average sizes of Ni particles on Ni/Hβ-(25), Ni/Hβ-(160) and Ni/Hβ-(394) catalysts were estimated as 9 nm, 53 nm and 50 nm, respectively. This result means all the Ni particles are loaded on the outside surface of Hβ zeolites (pore size: 6.6×6.7 Å, 5.6×5.6 Å; internal pore space: 6.68 Å according to literature[4]) rather than in their pores.

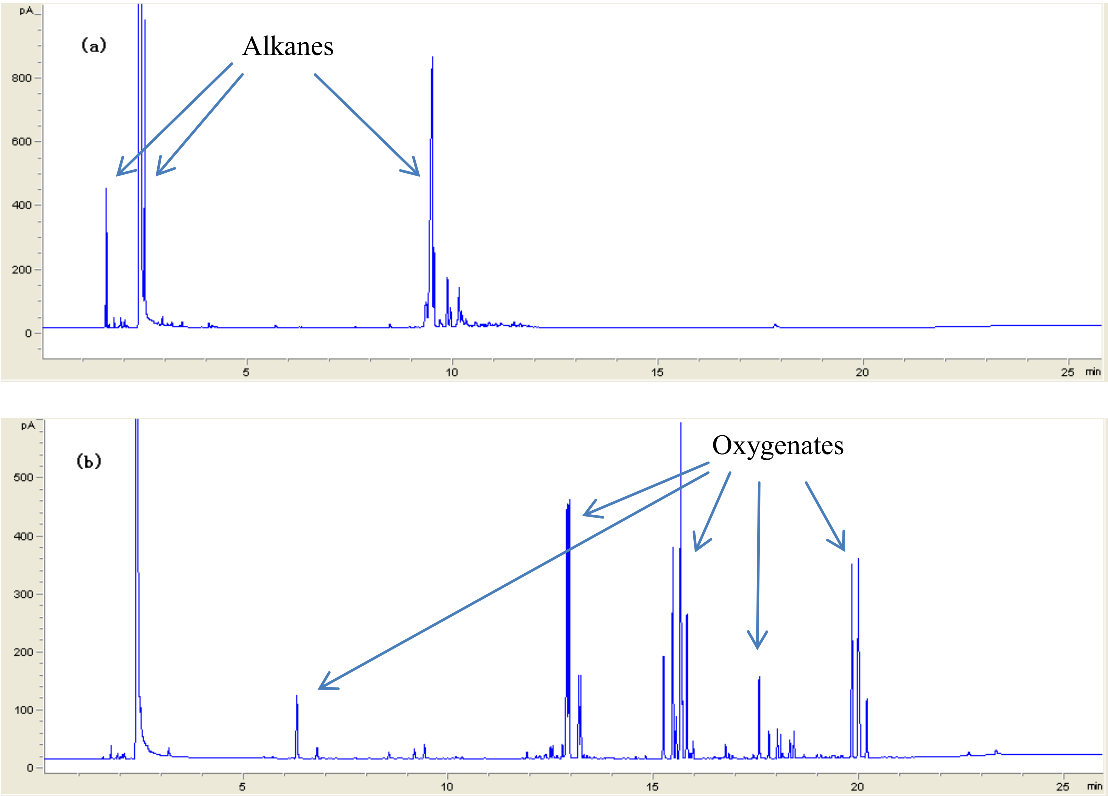


Figure S1. Gas chromatograms of the liquid products from the HDO of 5,5'-(butane-1,1-diyl)bis(2-methylfuran) (BBM) over (a) Ni/Hβ-(394) and (b) Ni/SiO_2. Reaction conditions: 1.8 g catalyst; liquid feedstock flow rate 0.04 mL min^{-1} (WHSV = 1.3 h^{-1}); hydrogen flow rate: 120 mL min^{-1}.

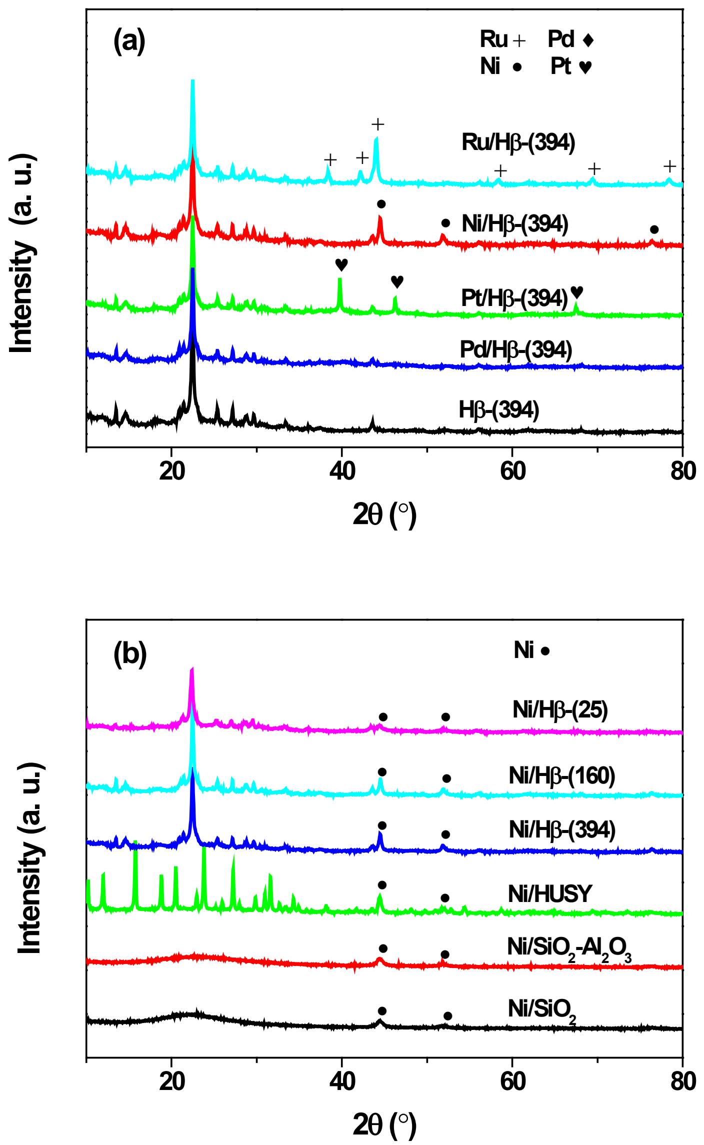
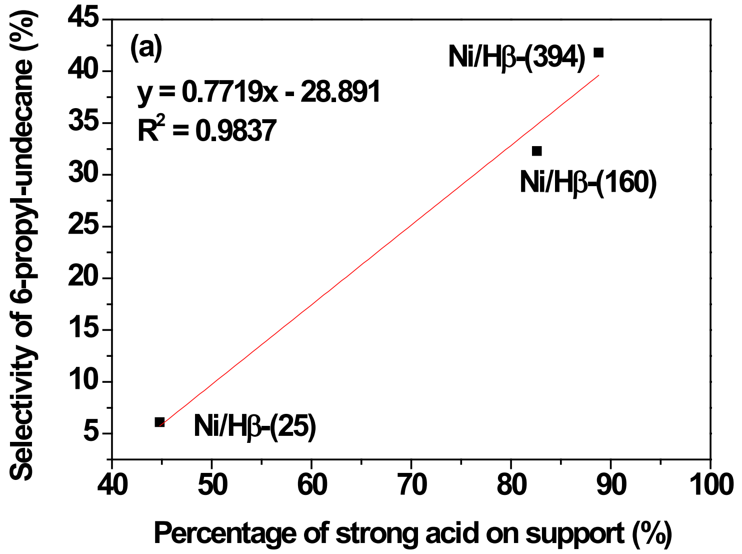


Figure S2. XRD patterns of (a) different metal loaded Hβ-(394) catalysts and (b) Ni catalysts loaded on different supports.



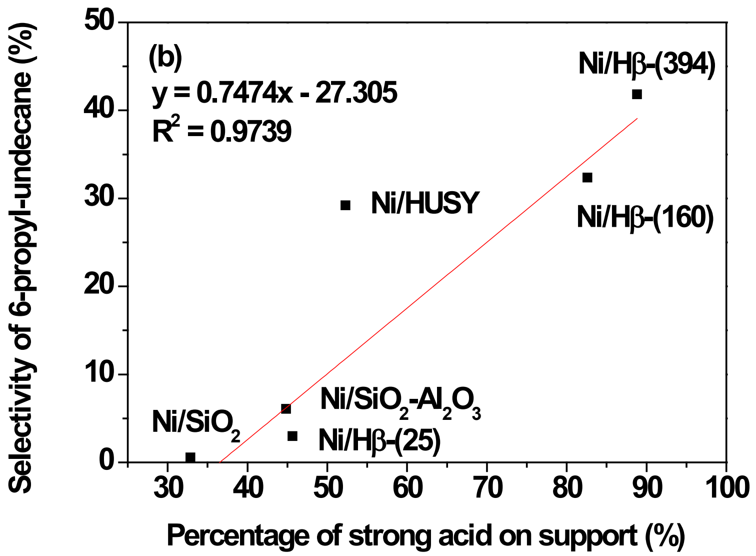


Figure S3 Relationship between the selectivity of 6-propyl-undecane over different Ni catalysts and the percentages of strong acid on the supports.

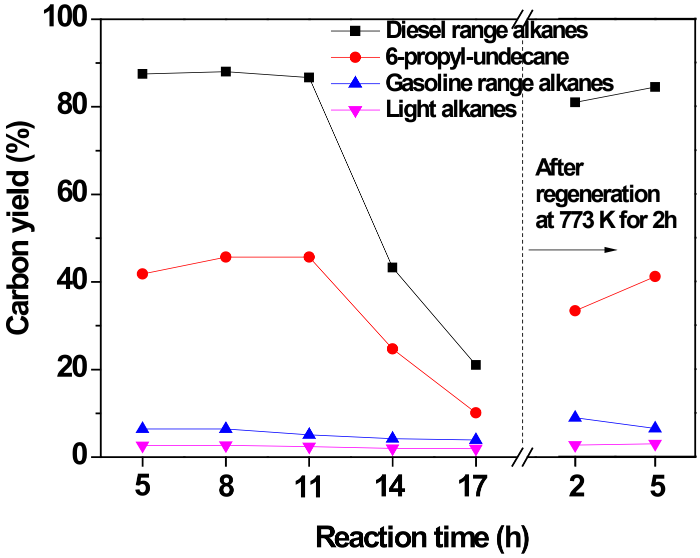


Figure S4. Carbon yields of different alkanes from the HDO of BBM over Ni/Hβ-(394). Reaction conditions: 503 K, 6 MPa, 1.8 g Ni/Hβ-(394) catalyst; BBM flow rate: 0.04 mL min^{-1} (WHSV = 1.3 h^{-1}); hydrogen flow rate: 120 mL min^{-1}. The diesel range alkanes, gasoline range alkanes and light alkanes account for C_9-C_{15}, C_5-C_8 and C_1-C_4 alkanes, respectively.

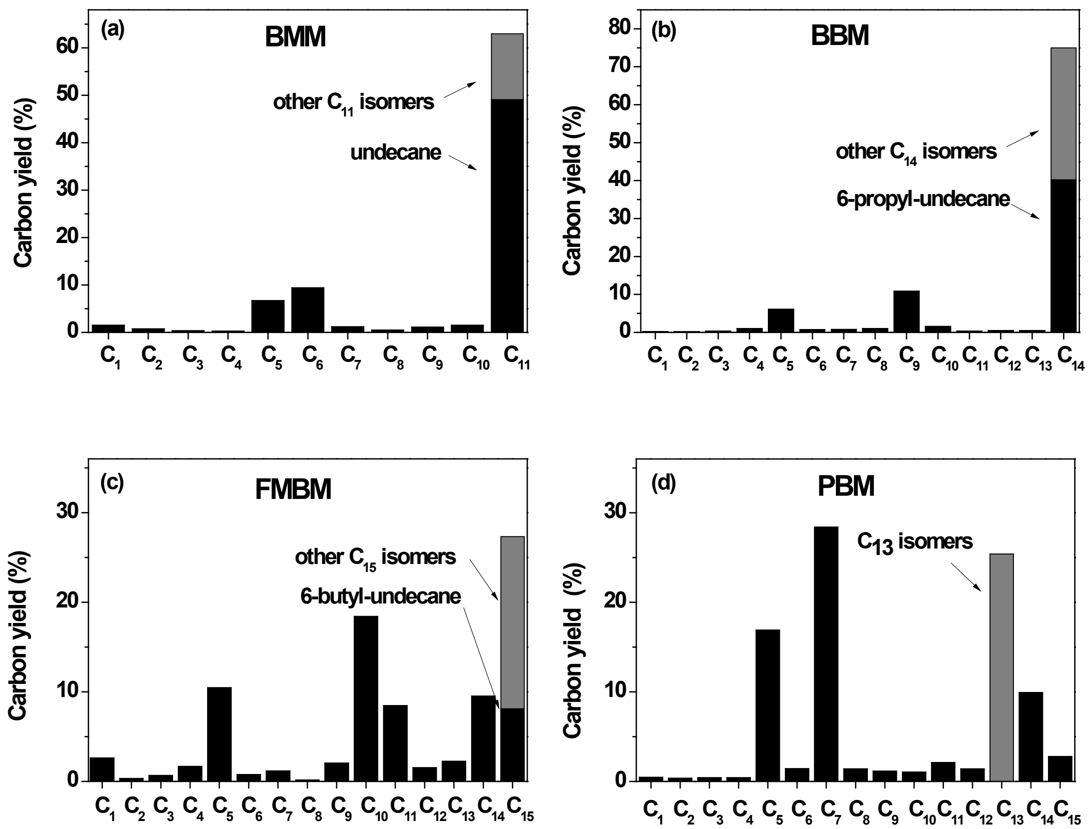
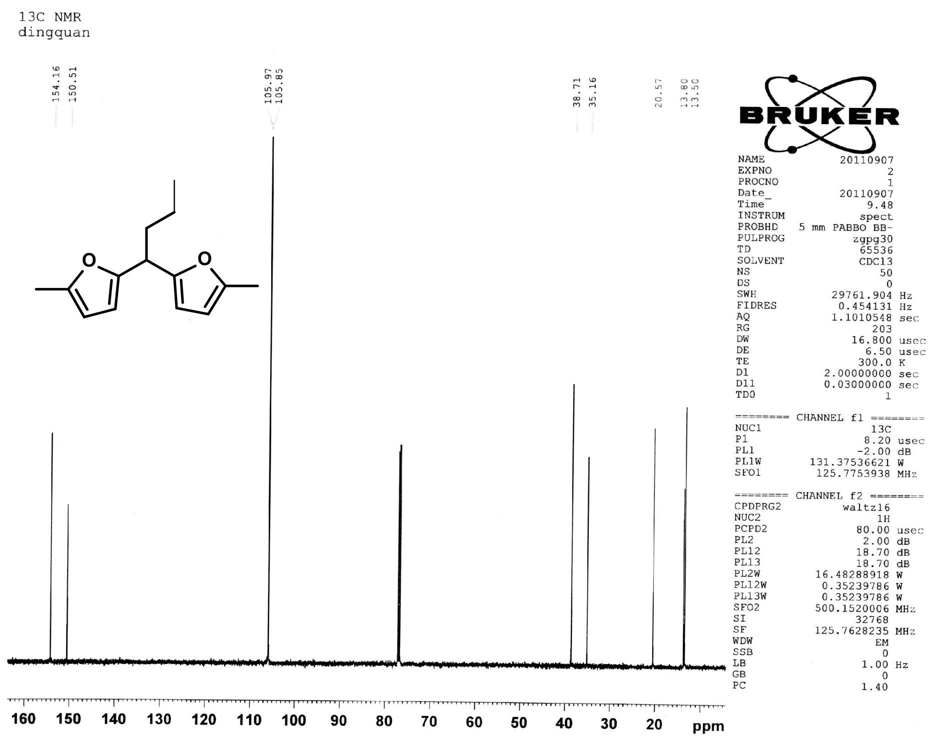


Figure S5. The carbon distributions of the alkanes obtained by the HDO of different HAA products over the Ni/Hβ-(394) catalyst. Reaction conditions: 533 K, 6 MPa, 1.8 g catalyst; liquid feedstock flow rate 0.04 mL min^{-1} (WHSV = 1.3 h^{-1}); hydrogen flow rate: 120 mL min^{-1}. The diesel range alkanes, gasoline range alkanes and light alkanes account for C_9-C_{15}, C_5-C_8 and C_1-C_4 alkanes respectively.



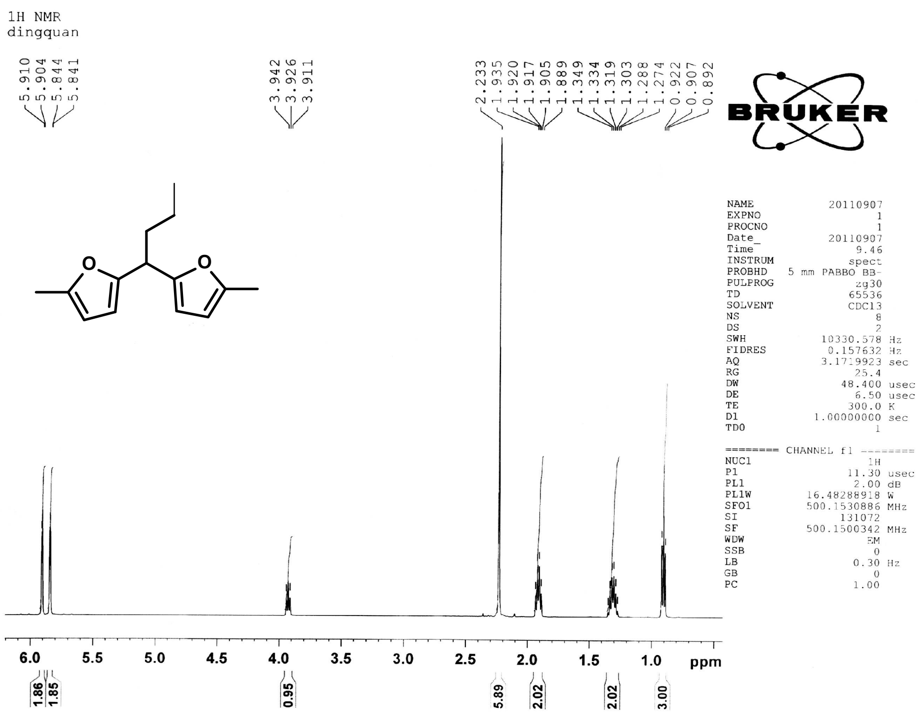
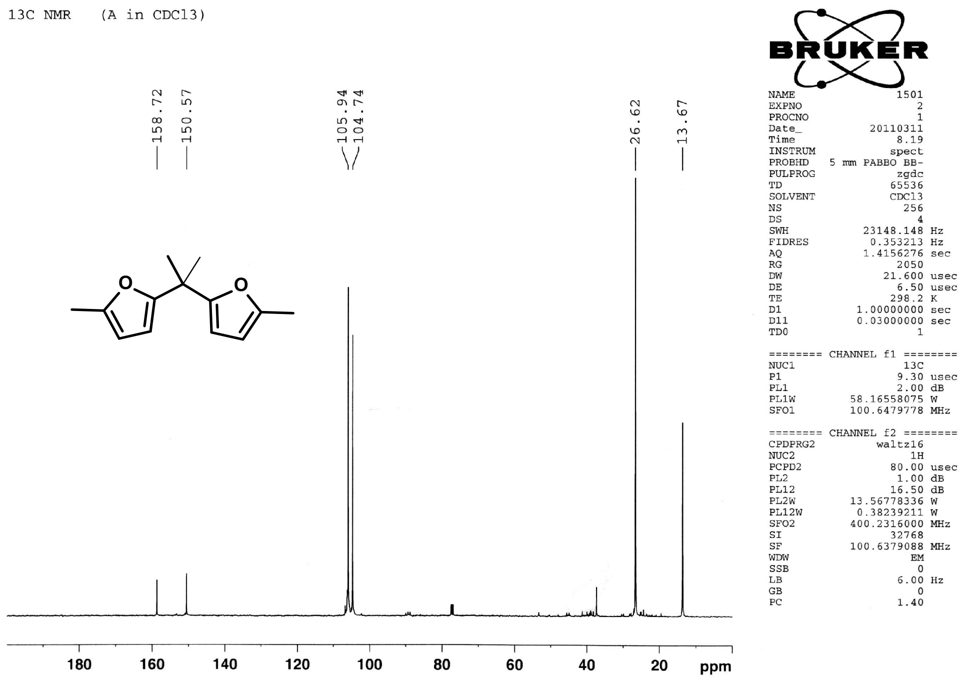


Figure S6. ^{13}C and ^{1}H NMR spectra of 5,5'-(butane-1,1-diyl)bis(2-methylfuran) prepared by the HAA of 2-MF with butanal.



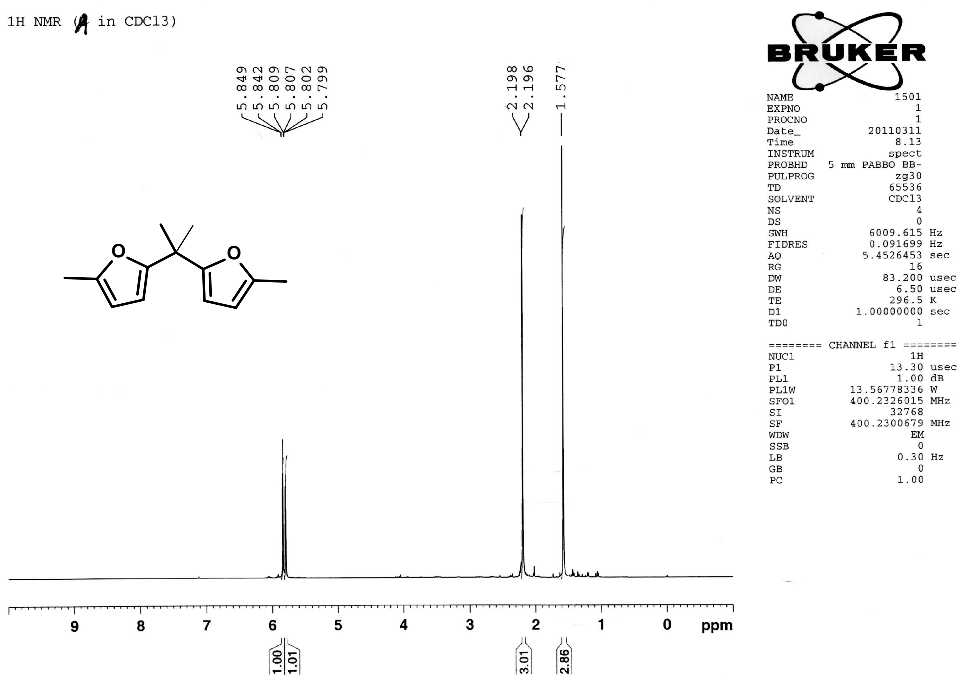


Figure S7. ^{13}C and ^{1}H NMR spectra of 5,5'-(propane-2,2-diyl)bis(2-methylfuran) produced by the HAA of 2-MF and acetone.

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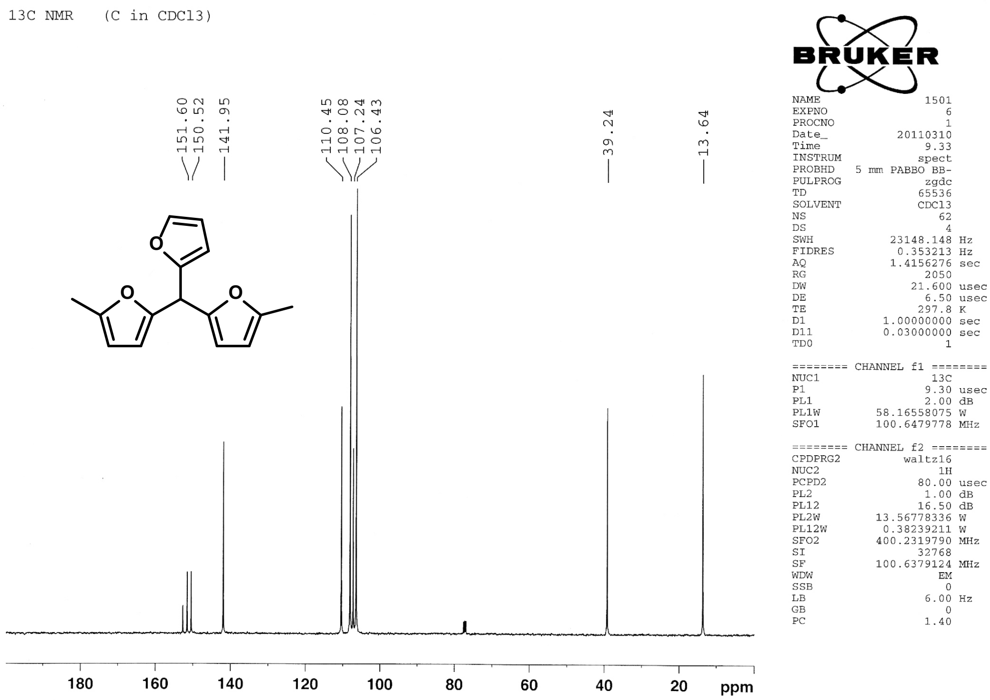


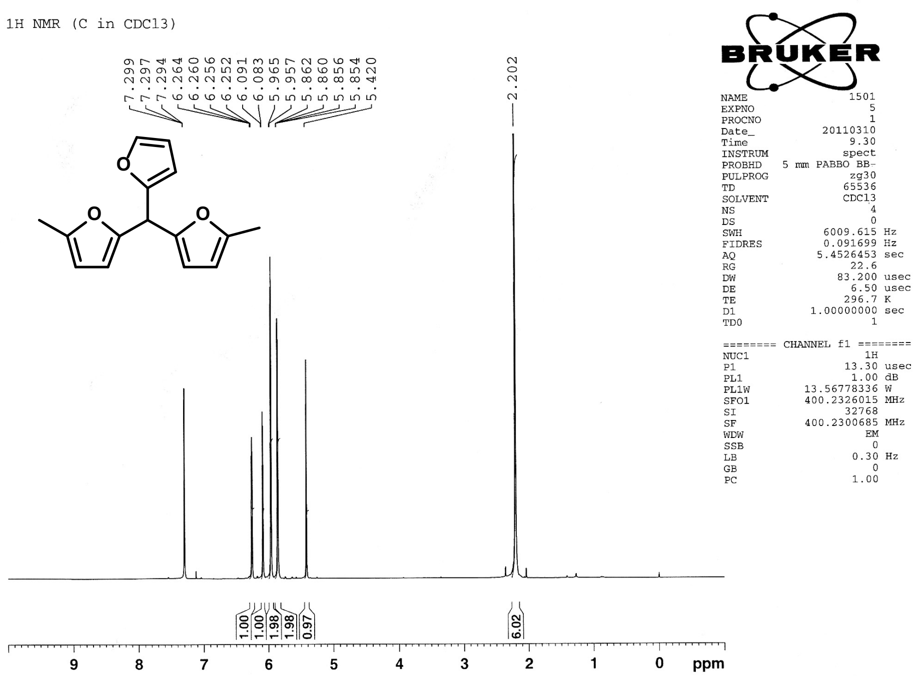
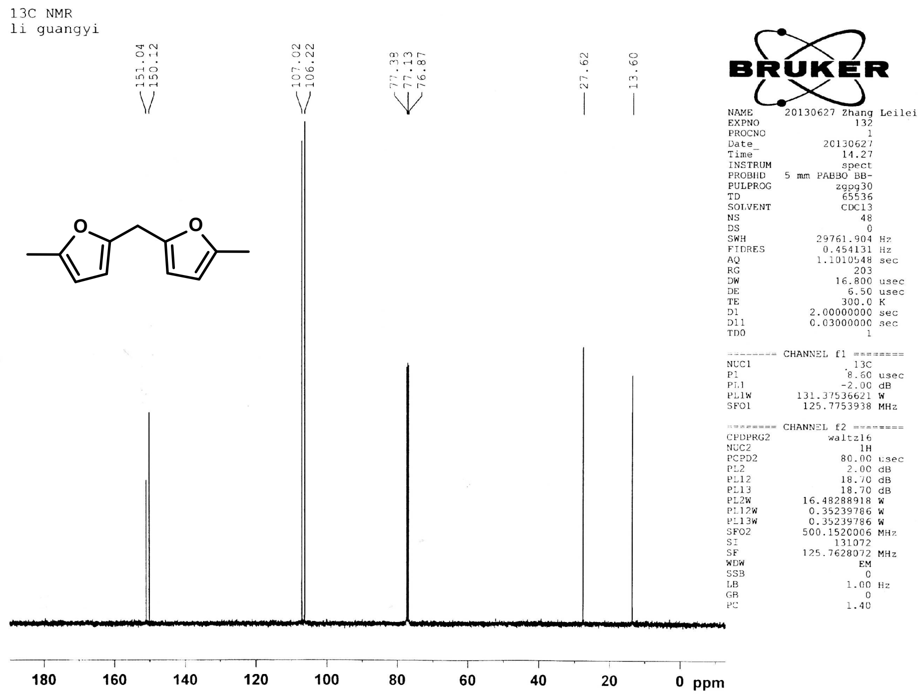


Figure S8. ^{13}C and ^{1}H NMR of 5,5'-(furan-2-ylmethylene)bis(2-methylfuran) prepared by the HAA of 2-MF and furfural.



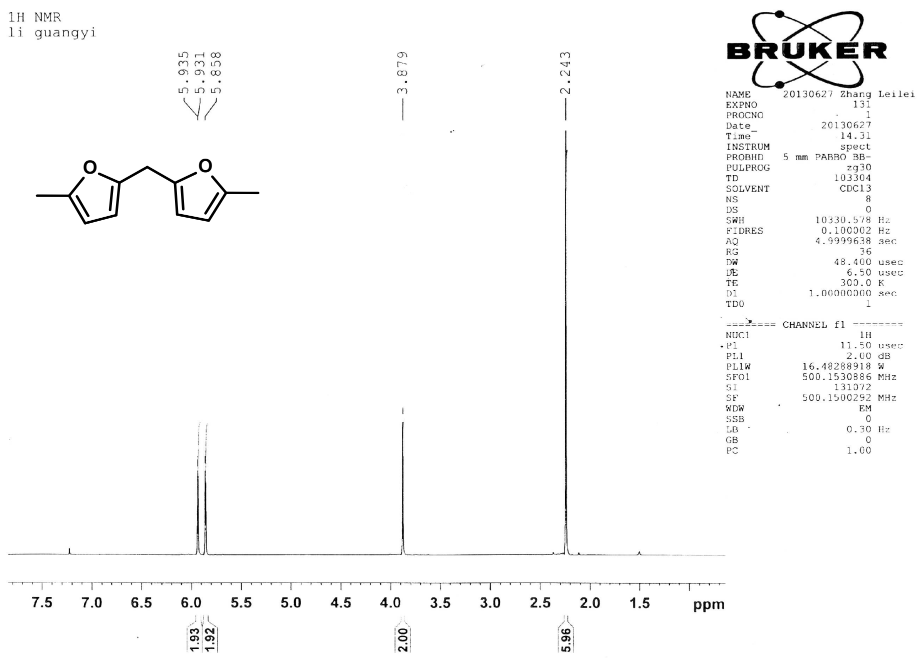


Figure S9. ^{13}C and ^{1}H NMR of bis(5-methylfuran-2-yl)methane prepared by the HAA of 2-MF and formaldehyde.

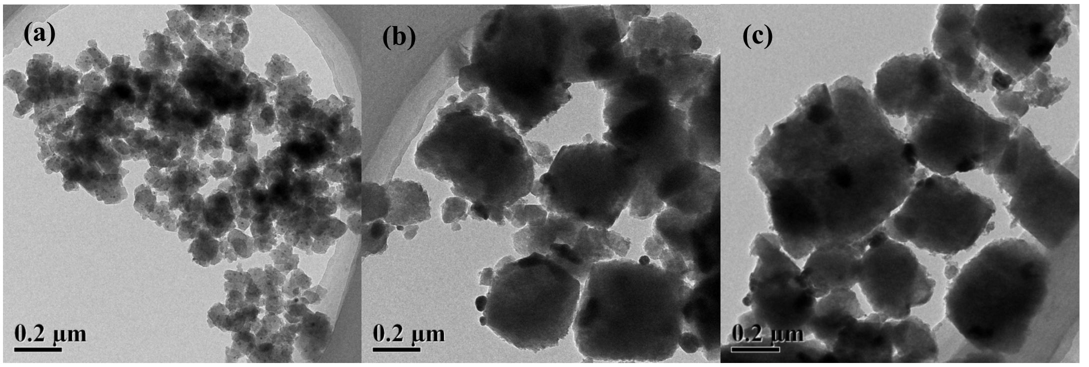
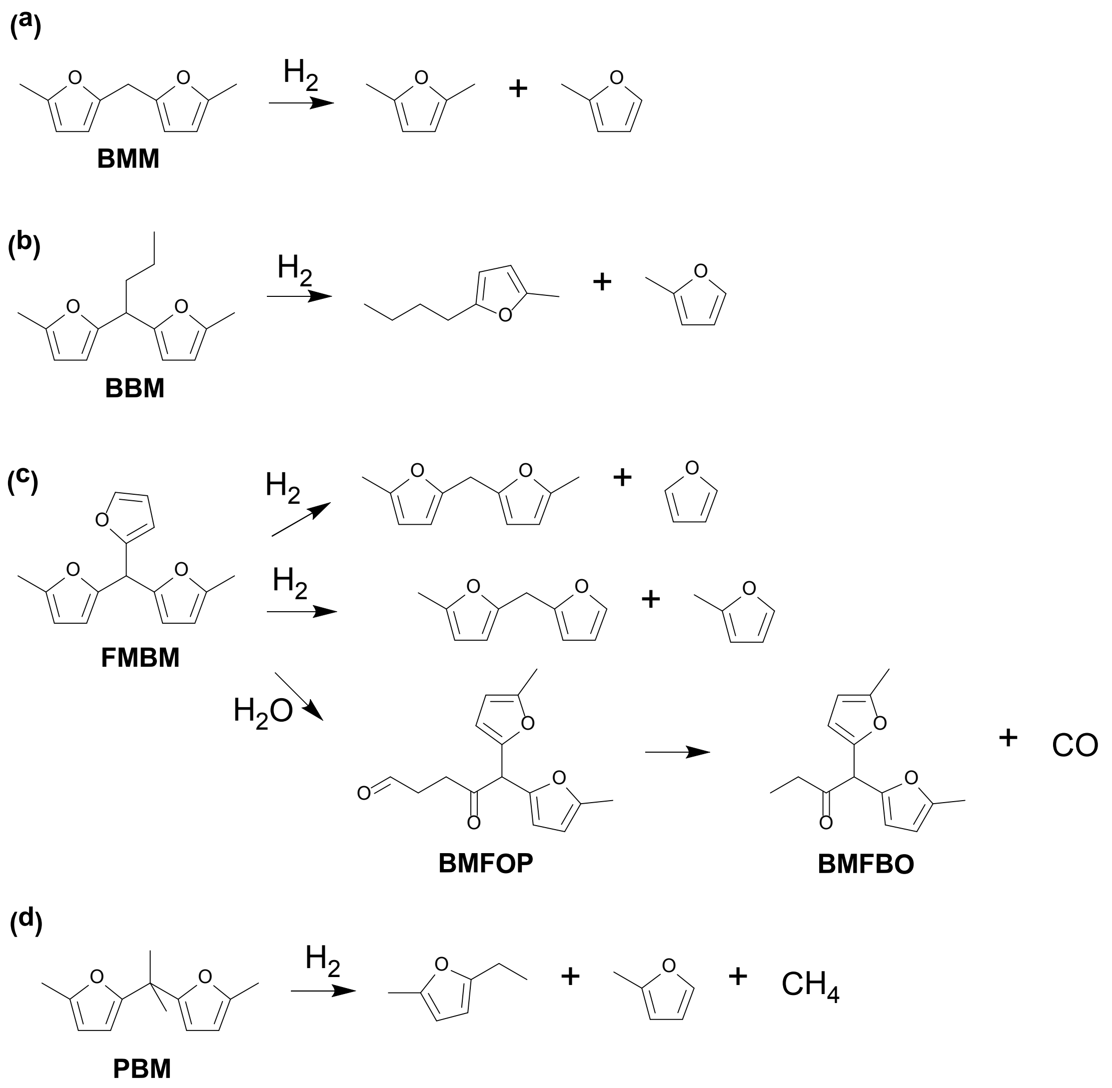


Figure S10 TEM images of Ni/Hβ-(25) (a), Ni/Hβ-(160) (b) and Ni/Hβ-(394) (c) catalysts.



Scheme S1. Possible C-C cracking fragments in HDO of different HAA products.

Table S1. Carbon yields of alkanes and oxygenates over different catalysts. Reaction conditions: 6 MPa, 1.8 g catalyst; liquid feedstock flow rate 0.04 mL min^{-1} (WHSV = 1.3 h^{-1}); hydrogen flow rate: 120 mL min^{-1}.

Entry	Catalyst	Feedstock	Temperature (K)	Carbon yield (%)	
				Alkanes	Oxygenates
1	Pd/Hβ-(394)	BBM	503	99	0
2	Ru/Hβ-(394)	BBM	503	100	0
3	Pt/Hβ-(394)	BBM	503	99	0
4	Ni/Hβ-(394)	BBM	503	97	0
5	Ni/HUSY	BBM	503	82	~18[a]
6	Ni/SiO_2-Al_2O_3	BBM	503	17	~83[a]
7	Ni/SiO_2	BBM	503	2	~98[a]
8	Ni/Hβ-(25)	BBM	503	59	~41[a]
9	Ni/Hβ-(160)	BBM	503	97	0
10	Ni/Hβ-(394)	BBM	473	47	~53[a]
11	Ni/Hβ-(394)	BBM	533	100	0
12	Ni/Hβ-(394)	BBM	573	99	0
13	Ni/Hβ-(394)	BMM	533	86	0
14	Ni/Hβ-(394)	FMBM	533	88	0
15	Ni/Hβ-(394)	PBM	533	94	0

a: The carbon yield of oxygenates intermediates was estimated by (100 minus carbon yield percentage of alkane products)%.

Table S2. Specific surface areas and total acid concentrations of different supports.

Support	S_{BET} (m^2 g^{-1})[a]	Total acid concentration (μmol g^{-1})[b]
SiO_2	384	19.6
SiO_2-Al_2O_3	505	251.9
HUSY	641	870.4
Hβ-(394)	435	30.0
Hβ-(160)	610	129.4
Hβ-(25)	588	545.2

[a]S_{BET} was determined by N_2 adsorption at 77 K using a Micromeritics ASAP 2010 apparatus.

[b]Total acid concentrations were determined by the microcalorimetric measurements of ammonia adsorption.

Table S3. Dispersions and average particle sizes of Ni in different catalysts.

Catalyst	Dispersion (%)[a]	Average size of Ni particle (nm)[b]
Ni/SiO_2	10.9	12
Ni/SiO_2-Al_2O_3	3.4	12
Ni/HUSY	0.7	26
Ni/Hβ-(394)	7.9	33
Ni/Hβ-(160)	10.5	32
Ni/Hβ-(25)	4.3	15

[a]The dispersion of Ni in each catalyst was measured by H_2-O_2 titration.

[b]Average size of Ni particles in each catalysts was estimated according to XRD results (by Debye-Scherrer equation).

Table S4. Effect of reaction time on the carbon yields of alkanes and oxygenates over Ni/Hβ-(394) catalyst. Reaction conditions: 533 K, 6 MPa, 1.8 g Ni/Hβ-(394) catalyst; BBM flow rate 0.04 mL min^{-1} (WHSV = 1.3 h^{-1}); hydrogen flow rate: 120 mL min^{-1}.

Reaction time (h)	Carbon yield (%)	
	Alkanes	Oxygenates
5	100	0
8	97	0
11	100	0
14	100	0
17	97	0
20	96	0
24	99	0

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