

# Synthesis of Diesel or Jet Fuel Range Cycloalkanes with 2-Methylfuran and Cyclopentanone from Lignocellulose

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## S Supporting Information

**ABSTRACT:** 2-Methylfuran (2-MF) and cyclopentanone (CPO) are the selective hydrogenation products of furfural, which can be produced in industrial scale with lignocellulose. In this work, renewable diesel or jet fuel range branched alkanes and cycloalkanes were first synthesized simultaneously by the solvent-free hydroxyalkylation/alkylation (HAA) of 2-MF and CPO followed by hydrodeoxygenation (HDO). Among the solid acid catalysts used in this work, Nafion-212 resin exhibited the best activity and selectivity for the HAA of 2-MF and CPO. The excellent performance of Nafion-212 resin can be attributed to the high acid strength of this catalyst. After the HDO of the HAA products of 2-MF and CPO over several nickel catalysts, a mixture of jet fuel range branched alkanes and cycloalkanes with relatively higher density was obtained at high carbon yield. Compared with Ni/SiO<sub>2</sub>, acidic support loaded nickel catalysts are more active in the HDO process, which may be attributed to the promotion effect of acid sites in dehydration and the ring opening reaction of furan compounds.

## 1. INTRODUCTION

As a solution to the energy and environmental problems we are facing today, the catalytic conversion of renewable biomass to fuels<sup>1–8</sup> and chemicals<sup>9–13</sup> has attracted great interest. Lignocellulose is the major ingredient of agriculture and forest wastes. Diesel and jet fuel are two kinds of often-used transportation fuels. In recent years, the synthesis of renewable diesel or jet fuel with the platform compounds from lignocellulose has drawn a lot of attention.<sup>14–19</sup>

Furfural is one of the most important chemicals that can be obtained from lignocelluloses.<sup>20–22</sup> In the previous works of the Dumesic group<sup>23,24</sup> and Huber et al.,<sup>25,26</sup> C<sub>8</sub>–C<sub>15</sub> straight alkanes were prepared by the aldol condensation of furfural (or 5-hydroxymethylfurfural) and acetone from the chemical treatment and acetone–*n*-butanol–ethanol (ABE) fermentation of lignocellulose, followed by hydrogenation and hydrodeoxygenation (HDO). In our recent work,<sup>27</sup> C<sub>10</sub> and C<sub>11</sub> branched alkanes were synthesized at high overall yield (~90%) by the aldol condensation of methyl isobutyl ketone and furfural, followed by the direct HDO. 2-Methylfuran (2-MF) is a selective hydrogenation product of furfural. In the very recent works of Corma et al.<sup>18,28</sup> and the Zhang group,<sup>29–33</sup> a series of C<sub>9</sub>–C<sub>16</sub> branched alkanes was synthesized by the hydroxyalkylation/alkylation (HAA) reaction of 2-MF and some lignocellulose-derived carbonyl compounds, followed by the direct HDO. So far, most of the reported works are concentrated on the production of diesel (C<sub>9</sub>–C<sub>21</sub>) or jet fuel (C<sub>8</sub>–C<sub>16</sub>) range straight-chain alkanes and/or branched-chain alkanes with the lignocellulose-based platform compounds. These alkanes have good thermal stability and excellent combustion efficiency. However, due to their lower densities

(~0.76–0.78 g mL<sup>−1</sup>), these alkanes must be blended with conventional jet fuel (a mixture of straight-chain alkanes, branched-chain alkanes, and cyclic hydrocarbons) to meet the specifications of aviation fuel. Compared with straight-chain alkanes and branched-chain alkanes, cycloalkanes have higher densities and volumetric heating values due to robust ring strain. To fulfill the need of aviation fuel, cycloalkanes or aromatics should also be synthesized and added to the biojet fuel to increase the density or volumetric heating of the fuel. As another possible application, the cycloalkanes can also be added into the biodiesel to increase its mileage per liter (or gallon).

Cyclopentanone (CPO) is a selective hydrogenation product of furfural<sup>34–36</sup> and a main component of bio-oil from the pyrolysis of biomass.<sup>37,38</sup> The cyclic structure of this compound makes it a promising feedstock in the production of cycloalkanes. To our knowledge, there is no report about the production of diesel or jet fuel range cycloalkane by the combination of HAA and HDO reactions. In this work, a mixture of C<sub>9</sub>–C<sub>15</sub> branched alkanes and cycloalkanes with relatively higher density was synthesized, for the first time, by the solid acid-catalyzed HAA reaction of 2-MF and CPO, which can be easily derived from lignocellulose, followed by the HDO over Ni-base catalysts.

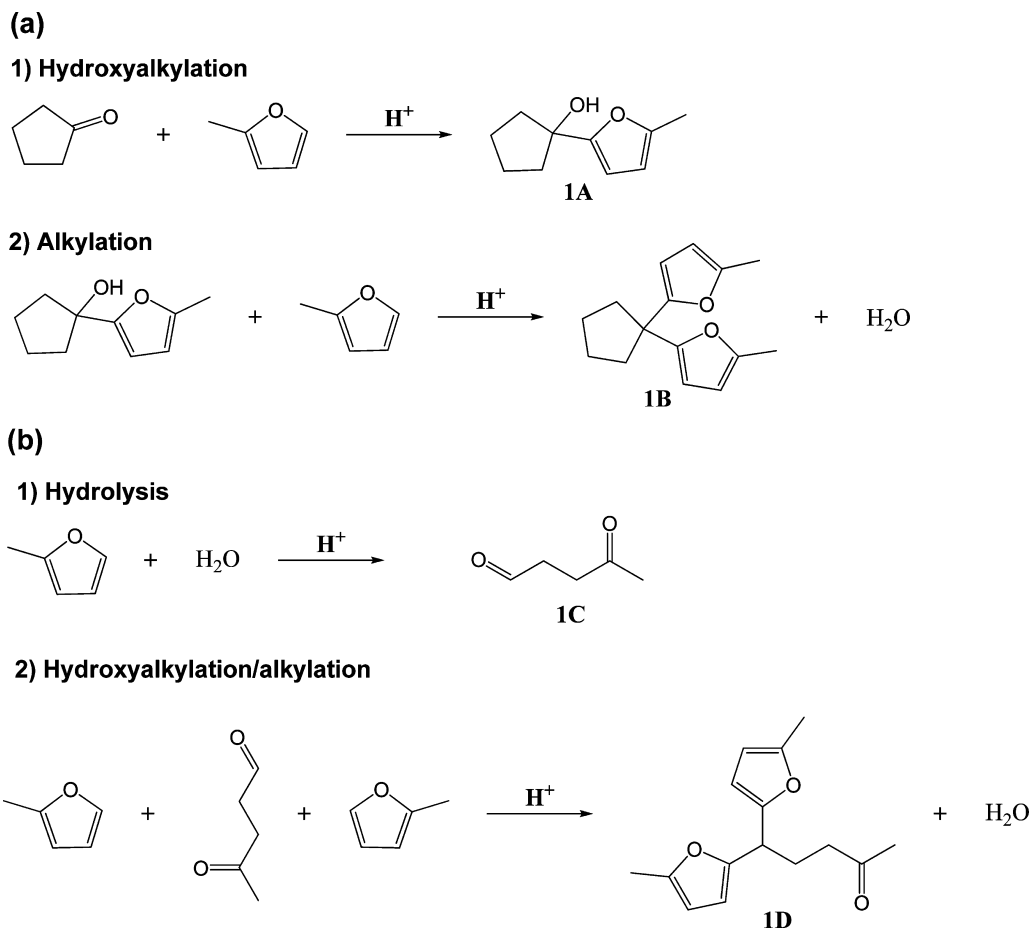
## 2. EXPERIMENTAL SECTION

**2.1. Materials.** Nafion-212 resin with a thickness of 51 μm was purchased from Dupont Company. Before being used for the reaction,

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Scheme 1. Pathways for the Generation of 1B (a) and 1D (b) during the Reactions between 2-MF and CPO



it was cut into about  $2 \times 5$  mm pieces. Amberlyst-36 and Amberlyst-15 resins were supplied by Sigma-Aldrich. H-USY ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 12$ ), H-ZSM-5 ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 140$ ), and H- $\beta$  ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 394$ ) zeolites used in this work were provided by Nankai University.  $\text{SiO}_2$  and  $\text{SiO}_2\text{--Al}_2\text{O}_3$  ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 25$ ) were purchased from Qingdao Ocean Chemical Ltd. Zirconium phosphate (ZrP) was prepared by a precipitation method reported previously.<sup>39</sup> An aqueous solution containing  $\text{ZrCl}_2\cdot 8\text{H}_2\text{O}$  ( $1.0 \text{ mol L}^{-1}$ ) and  $\text{NH}_4\text{H}_2\text{PO}_4$  ( $1.0 \text{ mol L}^{-1}$ ) at a P/Zr synthetic atomic ratio of 2.0 were precipitated at room temperature. The precipitates were filtered, washed thoroughly by water until no  $\text{Cl}^-$  was detected, dried at 373 K for 10 h, and calcined at 673 K for 4 h.

The transition metal (Fe, Co, Ni, Cu)-based HDO catalysts used in this work were obtained by the incipient wetness impregnation of different supports with the solutions of corresponding metal nitrates. To facilitate the comparison, the theoretical metal contents in all catalysts were fixed at 5 wt %. The catalysts were prepared in three steps. In the first step, we measured the specific water absorption of each support. According to these values, we prepared the metal nitrate solutions and added them to the corresponding supports. After being aged at room temperature for 5 h, the products were dried in an oven at 393 K for 8 h and calcined at 773 K for 3 h.

**2.2. Hydroxyalkylation/Alkylation (HAA).** The HAA reaction of 2-MF and CPO was performed in a flask connected to a reflux condenser. To facilitate the mass transfer, the reactants and catalyst were agitated by a magnetic stirrer. The temperature of the reaction system was regulated by water bath. For each reaction, 3.28 g (40 mmol) of 2-MF, 1.68 g (20 mmol) of CPO, and 0.15 g of catalyst were used. After the reaction, the product was filtered and then analyzed by a high performance liquid chromatography (HPLC) with a refractive index detector and a Zorbax SB-C18 column. A mixture of methanol and water at the volume ratio of 9:1 was used as mobile phase.

The  $^{13}\text{C}$  and  $^1\text{H}$  NMR spectra were recorded on a Bruker AVANCE 500 MHz NMR spectrometer (11.7 T). Before the tests, the products from the reaction of 2-MF and CPO were separated by column chromatography with silica gel (purchased from Merck) as stationary phase, and the mixture of ethyl acetate and petroleum ether (at the volume ratio of 1:20) was used as the mobile phase. Chloroform- $d$  (99.8% atom D with 0.1% v/v tetramethylsilane (TMS)) from Aldrich was used as a solvent for  $^1\text{H}$  and  $^{13}\text{C}$  NMR sample preparation. Chemical shifts, quoted in ppm, are relative to the internal standards, namely, the singlet  $\delta = 0$  ppm of TMS for  $^1\text{H}$  NMR and the middle of  $\text{CDCl}_3$  triplet  $\delta = 77$  ppm for  $^{13}\text{C}$  NMR.

**2.3. Hydrodeoxygenation (HDO).** The HDO of the diesel or jet fuel precursors from the HAA of 2-MF and CPO was conducted in a fixed-bed reactor, which has been described in our previous work.<sup>30</sup> Catalyst (1.8 g) was used for each test. Before the reaction, the catalysts were reduced *in situ* by hydrogen at 773 K for 2 h. Under the assistance of an HPLC pump, the HAA products (purified by vacuum distillation) were fed into the stainless steel tubular reactor at  $0.04 \text{ mL min}^{-1}$  from the bottom along with hydrogen at  $120 \text{ mL min}^{-1}$ . The gas and liquid products that flowed through the tubular reactor (at 6 MPa and 533 K) became two phases in a gas–liquid separator. The gas-phase products passed a back-pressure regulator and were analyzed by a GC equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID). The liquid-phase products were collected from the bottom of the separator and analyzed by another GC equipped with an FID and an autosampler. The carbon yields of the different alkanes were calculated by following equations:

carbon yield of diesel range alkanes (%)

$$= \frac{\text{sum of carbon in the } \text{C}_9\text{--C}_{15} \text{ alkanes detected from the liquid phase product}}{\text{carbon fed into the reactor}} \times 100$$

carbon yield of gasoline range alkanes (%)

$$= \frac{\text{sum of carbon in the } C_5-C_8 \text{ alkanes detected from the gas phase product in unit time} / \text{carbon fed into the reactor in unit time} \times 100 + \text{sum of carbon in the } C_5-C_8 \text{ alkanes detected from liquid phase products} / \text{carbon fed into the reactor} \times 100}{2}$$

carbon yield of light alkanes (%)

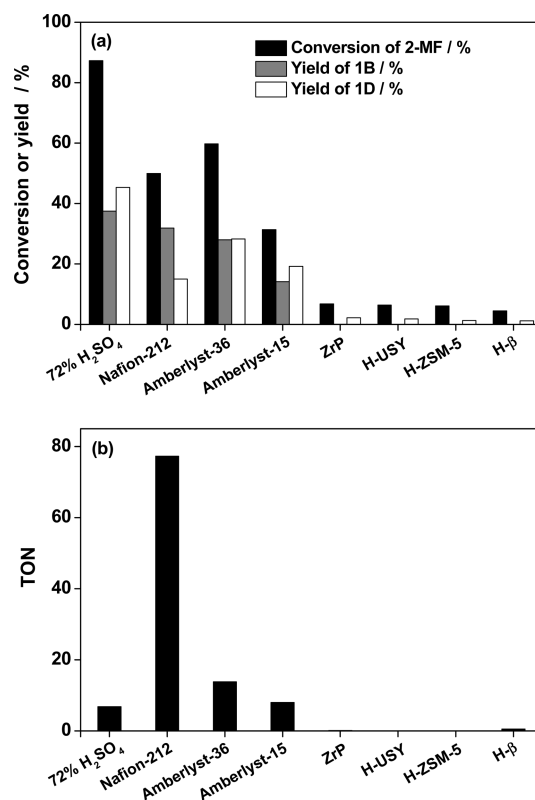
$$= \frac{\text{sum of carbon in the } C_1-C_4 \text{ alkanes detected from the gas phase product in unit time} / \text{carbon fed into the reactor in unit time} \times 100}{2}$$

### 3. RESULTS AND DISCUSSION

**3.1. Hydroxyalkylation/Alkylation (HAA).** According to the analysis by HPLC and NMR (see Figures S1–S3 in Supporting Information) of liquid products from the reaction of 2-MF with CPO over several solid acids, 5,5'-(cyclopentane-1,1-diyl)bis(2-methylfuran) (**1B** in Scheme 1) was detected in the liquid products. This compound was generated by the HAA of 2-MF and CPO. Besides **1B**, 5,5-bis(5-methylfuran-2-yl)pentan-2-one (**1D** in Scheme 1) was also identified. According to the previous work of Corma et al.,<sup>18</sup> this compound is generated by the trimerization reaction of 2-MF. The reaction pathways for the generation of **1B** and **1D** are illustrated in Scheme 1.

From Figure 1a, it is clear that the HAA of 2-MF and CPO can be catalyzed by H<sub>2</sub>SO<sub>4</sub> and acidic resins, while the H-ZSM-5, H-USY, and H- $\beta$  zeolites were inactive for this reaction. The lower activities of zeolite catalysts can be explained by their smaller pore diameters (see Table 1), which are comparable to or even smaller than the sizes of **1B** (0.72  $\times$  0.55 nm) and **1D** (0.83  $\times$  0.66 nm), which were estimated by the software of Materials Studio (see Figure S4 in Supporting Information).

The sequence for the yield of **1B** over the solid acid catalysts is Nafion-212 > Amberlyst-36 > Amberlyst-15 > ZrP, H-USY, H-ZSM-5, H- $\beta$ . According to the yields of **1B** in Figure 1a and the amount of acid sites (measured by NH<sub>3</sub>-chemisorption described in our previous work<sup>33,40</sup>) over different catalysts, we calculated the turnover numbers (TONs) of 2-MF to **1B** (dividing the mol of **1B** in the product by the mol of acid sites over the catalyst). From the results illustrated in Figure 1b, the TON for the conversion of 2-MF to **1B** over the nonzeolite catalysts decreases in the order of Nafion-212 > Amberlyst-36 > Amberlyst-15 > ZrP. This sequence is consistent with that of the Hammett acidity function ( $-H_0$ ) values of these catalysts (see Table 1). Therefore, the higher catalytic efficiency of Nafion-212 resin can be attributed to the higher strength of acid sites on this catalyst. To further prove this speculation, we compared the activities of H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub>, and CH<sub>3</sub>COOH. From Figure 2, the sequence for the yield of **1B** is H<sub>2</sub>SO<sub>4</sub> (2.6%) > H<sub>3</sub>PO<sub>4</sub> (0.1%) > CH<sub>3</sub>COOH (0%), which is consistent with the acid strength of these acids. The higher acid strength of Nafion-212 resin is determined by its structure. As we know, Nafion is a perfluorinated sulfonic acid resin,<sup>41</sup> while Amberlyst resins are sulfonic-acid-functionalized cross-linked polystyrene.<sup>42</sup> The presence of fluorine on Nafion resin greatly enhances the acid strength of the  $-SO_3H$  group. As a result, the strength of the acid sites over Nafion resin is higher than that of H<sub>2</sub>SO<sub>4</sub> and Amberlyst resins.



**Figure 1.** 2-MF conversions, the yields of **1B** and **1D**, the TONs of 2-MF to **1B** over different acid catalysts. Reaction conditions: 338 K, 2 h; 3.28 g of 2-MF, 1.68 g of CPO (2-MF/CPO molar ratio = 2), and 0.15 g of catalyst.

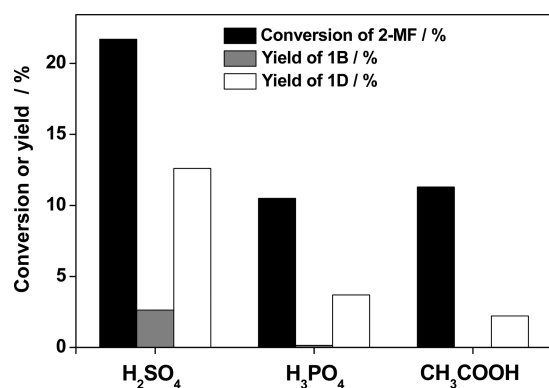
**Table 1.** Average Pore Diameters and Hammett Acidity Function ( $-H_0$ ) Values of the Solid Acid Catalysts Used in the Alkylation of 2-MF with CPO

catalyst	average pore diameters, nm	$-H_0$
Nafion-212	4 <sup>a</sup>	11–13 <sup>45</sup>
Amberlyst-15	29 <sup>a</sup>	2.2 <sup>45</sup>
Amberlyst-36	24 <sup>a</sup>	2.2–2.65 <sup>45</sup>
ZrP	7.2 <sup>b</sup>	–1.0 to ca. –2.8 <sup>46</sup>
H-USY	~0.7 <sup>47</sup>	3.0–4.4 <sup>45,48</sup>
H- $\beta$	~0.6 <sup>47</sup>	4.4–5.7 <sup>48</sup>
H-ZSM-5	~0.5 <sup>47</sup>	5.6–5.7 <sup>45,48</sup>

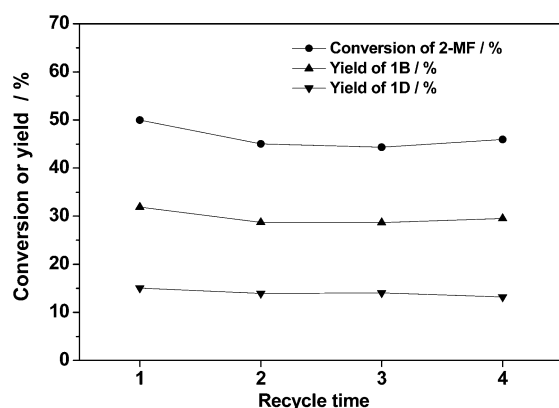
<sup>a</sup>According to the information provided by supplier. <sup>b</sup>Measured by N<sub>2</sub> physical adsorption.

Another advantage of Nafion-212 resin is the higher selectivity for **1B**. As we can see from Figure 1a, the carbon yield of **1B** (31.9%) over Nafion-212 resin is about twice that of **1D** (15.0%) under the same reaction conditions. In contrast, the carbon yields of **1B** over other solid acids are similar as (Amberlyst-36) or even lower than those of **1D**. From this result, we believe that the HAA of 2-MF and CPO is more sensitive to the strength of acid site than the trimerization reaction of 2-MF.

The stability of Nafion-212 resin in the HAA of 2-MF and CPO was explored. To eliminate the influence of residues, the catalysts were repeatedly rinsed with methanol and then dried at 353 K for 1.5 h after each usage. From the results shown in Figure 3, Nafion-212 resin has good stability in the HAA of 2-MF and CPO. No evident activity change was noticed over this catalyst after it was used 4 times. Considering the excellent



**Figure 2.** 2-MF conversions and the yields of **1B** and **1D** under the catalysis of different acid solutions. Reaction conditions: 338 K; 2 h; 3.28 g of 2-MF (40 mmol), 1.68 g of CPO (20 mmol) (2-MF/CPO molar ratio = 2), and 0.15 mL of catalyst. The concentrations of the H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub>, and acetic acid solution were 5 N.



**Figure 3.** 2-MF conversion, the yields of **1B** and **1D** over Nafion-212 resin as the function of recycle time. Reaction conditions: 338 K; 2 h; 3.28 g of 2-MF, 1.68 g of CPO (2-MF/CPO molar ratio was 2), and 0.15 g of Nafion-212 resin.

catalytic performance and the good stability of Nafion-212 resin, we believe it is a promising catalyst in future applications.

The influences of reaction conditions on the **1B** and **1D** yields in the presence of Nafion-212 resin were also investigated. From Table 2, we can see that the **1B** yield on Nafion-212 resin increased when the reaction temperature was increased from 273 to 323 K. Further increasing the reaction temperature from 323 to 353 K led to the decrease of **1B** yield. It was also noticed that the yield of **1D** monotonously increased with reaction temperature. On the basis of these results, we can see that higher temperatures are beneficial to the trimerization reaction of 2-MF. The increase of **1D** yield with temperature can be rationalized because high reaction temperature is favorable for the hydrolysis of 2-MF (or the generation of **1C**), which is the first step for production of **1D** (see Scheme 1). The effect of catalyst amount on the **1B** and **1D** yields over Nafion-212 resin was also explored (see Table 2). At lower catalyst dosages, the **1B** and **1D** yields increased when more catalyst was used in the reaction. This result can be understood by the presence of additional active sites. When the dosage of Nafion-212 resin is higher than 0.15 g, the further increment of catalyst amount had no significant influence on the yield of **1B** and **1D**. Moreover, it is observed that the yield of **1B** increased with time in the first 12 h and then stabilized. In contrast the yield of **1D** continuously increased with the reaction time. After

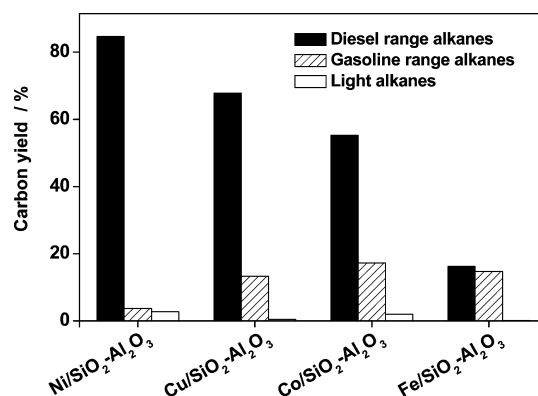
**Table 2.** 2-MF Conversion and the Yields of **1B** and **1D** over Nafion-212 Resin

temperature (K)	mass of catalyst (g)	reaction time <sup>a</sup> (h)	conversion (%)		yield (%)	
			2-MF	CPO	1B	1D
338	0.015	2	13.5	8.3	8.2	2.9
338	0.05	2	35.1	23	21.6	9.1
338	0.10	2	42.7	28.9	26.8	12.7
338	0.15	2	50.0	34.3	31.9	15
338	0.30	2	53.8	34.5	32.4	17.7
273	0.15	2	4.5	0.9	0.4	3.1
303	0.15	2	10.0	3.8	3.5	1.6
323	0.15	2	26.3	18.5	16.1	5.6
338	0.15	2	50.0	34.3	31.9	15.0
353 <sup>b</sup>	0.15	2	41.6	24.9	22.7	19.8
338	0.15	0.5	17.0	9.5	8.8	4.9
338	0.15	2	50.0	34.3	31.9	15
338	0.15	6	74.1	46.8	46.6	22.9
338	0.15	12	93.3	61.7	56.7	34.6
338	0.15	24	97.9	61.7	54.6	40.4

<sup>a</sup>Reaction conditions: 3.28 g of 2-MF, 1.68 g of CPO (2-MF/CPO molar ratio = 2). <sup>b</sup>The reaction at 353 K was conducted in the autoclave.

reaction at 323 K for 24 h, 2-MF was almost completely converted, the sum of **1B** and **1D** yield up to 95% was reached.

**3.2. Hydrodeoxygenation (HDO).** The HDO of the HAA products of 2-MF and CPO was carried out over a series of transition metal-loaded SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalysts. From the results illustrated in Figure 4, the Ni/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> demonstrated the

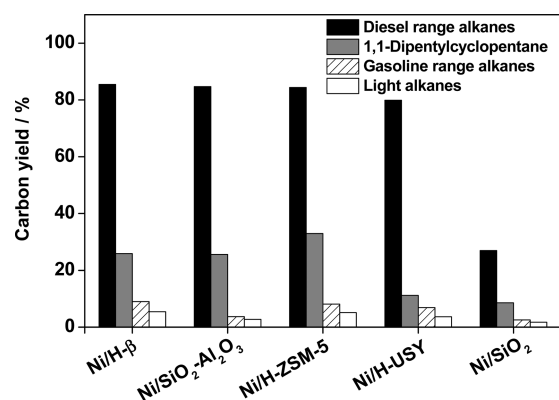


**Figure 4.** Carbon yields of different alkanes obtained by the hydrodeoxygenation (HDO) of HAA products of 2-MF and CPO over the M/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> (M = Fe, Co, Ni, Cu) catalysts. Reaction conditions: 533 K, 1.8 g of catalyst; liquid flow rate = 0.04 mL min<sup>-1</sup> (weight-hourly space velocity (WHSV) = 1.3 h<sup>-1</sup>); H<sub>2</sub> flow rate = 120 mL min<sup>-1</sup>. The diesel range alkanes, gasoline range alkanes, and light alkanes account for C<sub>9</sub>-C<sub>15</sub>, C<sub>5</sub>-C<sub>8</sub>, and C<sub>1</sub>-C<sub>4</sub> alkanes, respectively.

best performance among the investigated M/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> (M = Fe, Co, Ni, Cu) catalysts. Over it, evidently higher carbon yield to diesel or jet fuel range alkanes was achieved, which can be explained by the higher hydrogenation activity of Ni.

Subsequently, we compared the performances of several Ni catalysts for the HDO of the HAA products of 2-MF and CPO. From Figure 5, a significant support effect can be observed. Over the nickel catalysts loaded on solid acid support, the HAA products (including **1B** and **1D**) were completely converted to



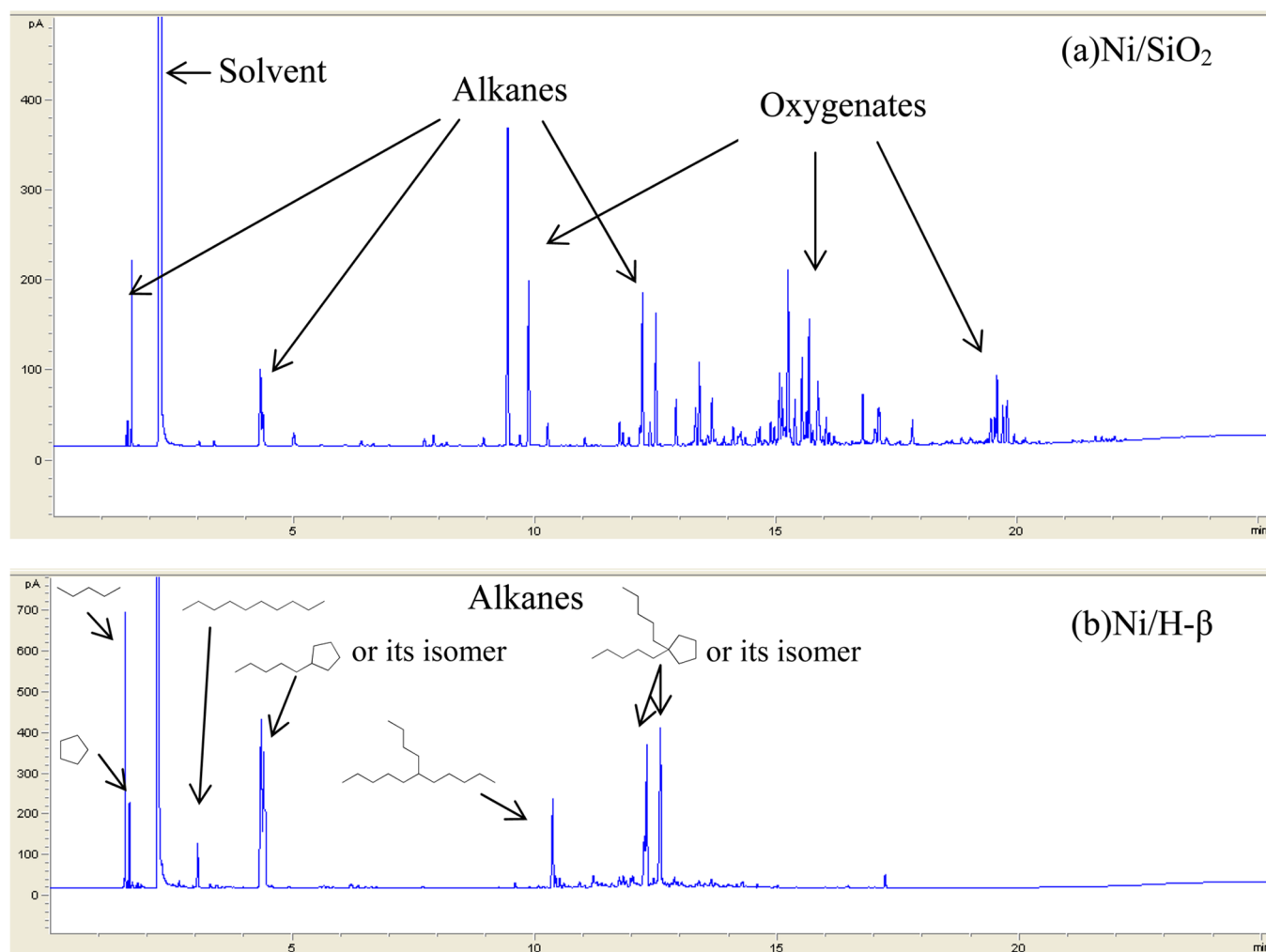


**Figure 5.** Carbon yields of different alkanes obtained by the HDO of HAA products of 2-MF and CPO over the nickel catalysts. Reaction conditions: 533 K, 1.8 g of catalyst; liquid flow rate = 0.04 mL min<sup>-1</sup> (WHSV = 1.3 h<sup>-1</sup>); H<sub>2</sub> flow rate = 120 mL min<sup>-1</sup>. The diesel range alkanes, gasoline range alkanes, and light alkanes account for C<sub>9</sub>–C<sub>15</sub>, C<sub>5</sub>–C<sub>8</sub>, and C<sub>1</sub>–C<sub>4</sub> alkanes, respectively.

alkanes, and high carbon yields (80–85.5%) of diesel or jet fuel range alkanes were achieved. These carbon yields are similar to the best result we got for the HDO of HAA products over Ni-

base catalyst (when the HAA product of 2-MF and butanal was used as feedstock).<sup>32</sup> According to our measurement, the diesel or jet fuel range alkanes as obtained (a mixture of branched alkanes and cycloalkanes) have densities around 0.82 g mL<sup>-1</sup>, which is higher than those of straight or branch alkanes (~0.76–0.78 g mL<sup>-1</sup>). In the recent works of our group, a series of synthetic routes for diesel and jet fuel alkanes was developed by the combination of HAA reactions of 2-MF with lignocellulose-derived carbonyl compounds, followed by HDO.<sup>29–33</sup> Among them, the 2-MF–furfural route was considered as the most promising one for two reasons, namely, (1) furfural is the feedstock for the production of 2-MF, which facilitates industrial integration and (2) furfural can be directly obtained from biomass. Compared with the 2-MF–furfural route, the 2-MF–CPO route contains more steps and has higher cost, because CPO is the selective hydrogenation product of furfural. However, these shortages of the 2-MF–CPO route can be partially made up considering of the higher carbon yield to diesel or jet fuel range alkanes and the higher density of alkane products, which are favorable for aviation fuel.

In contrast to what we observed over nickel-loaded solid-acid catalysts, lower carbon yield of alkanes (27%) was achieved over Ni/SiO<sub>2</sub>. From the chromatogram of the liquid sample from the HDO of HAA products over Ni/SiO<sub>2</sub> (see Figure 6),



**Figure 6.** Chromatograms of liquid samples from the HDO of HAA products of 2-MF and CPO over Ni/SiO<sub>2</sub> and Ni/Hβ catalysts. Reaction conditions: 533 K, 1.8 g of catalyst; liquid feedstock flow rate = 0.04 mL min<sup>-1</sup> (WHSV = 1.3 h<sup>-1</sup>); hydrogen flow rate = 120 mL min<sup>-1</sup>.

evident peaks of oxygenates can be observed. The low HDO activity of Ni/SiO<sub>2</sub> can be explained by the lower acidity of SiO<sub>2</sub> than other supports. It is well-known that acid sites play an important role in the HDO of biomass derived oxygenates. (1) Acid sites can promote the dehydration. It was suggested that the dehydration followed by the hydrogenation is the major pathway for the C–O cleavage reaction during the HDO of biomass-derived oxygenates.<sup>43</sup> (2) Acid sites can promote the ring-opening reaction of furan compounds, which can greatly decrease the reaction temperature for the HDO of furan compounds to alkanes.<sup>44</sup> Compared to weak acid site, strong acid site is more active for the dehydration and ring-opening reaction of furans,<sup>44</sup> which may be reason for the higher activity of acidic support loaded Ni catalysts than that of Ni/SiO<sub>2</sub>.

From chemical structures of the major alkane products labeled in Figure 6 (according to the GC-MS analysis), it is also noticed that the alkane products obtained in this work are mainly composed of branched alkanes and cycloalkanes. As we know, branched alkanes have relatively higher cetane values, which are favorable for diesel fuel. In contrast, the cycloalkanes have higher densities and volume heat values, which are desirable for aviation fuel.

## CONCLUSIONS

A new route for the simultaneous production of renewable diesel or jet fuel range cycloalkanes was developed by the HAA of 2-MF and CPO followed by the HDO process. Among the solid acid catalysts used in this work, Nafion-212 resin demonstrated the best performance and good stability in the HAA of 2-MF and CPO, which can be attributed to the higher acid strength of this catalyst. Solid acid loaded Ni catalysts were found to be effective in HDO of HAA products under milder conditions, which makes them promising catalysts in future applications.

## ASSOCIATED CONTENT

### Supporting Information

HPLC chromatogram and the <sup>13</sup>C and <sup>1</sup>H NMR spectra of the liquid products from the HAA of 2-methylfuran (2-MF) with cyclopentanone (CPO); molecular dimensions of different products from the reaction of 2-MF and CPO. These materials are available free of charge via the Internet at <http://pubs.acs.org>.

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### Author Contributions

Prof. T. Zhang and Dr. N. Li designed the experiments, analyzed the data. G. Li performed the experiments under the help of X. Sheng, S. Li, and Dr. X. Wang. Prof. A. Wang, Prof. Y. Cong, and Prof. X. Wang analyzed the data. All authors discussed the results and wrote the manuscript together.

### Notes

The authors declare no competing financial interest.

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## ABBREVIATIONS

HAA=hydroxyalkylation/alkylation

2-MF=2-methylfuran

CPO=cyclopentanone

HDO=hydrodeoxygenation

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