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Synthesis of renewable diesel and jet fuel range alkanes using 2-methylfuran and cyclohexanone[†]

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New solid acid catalysts were prepared by bisphenol A, paraformaldehyde and chlorosulfonic acid, and applied to hydroxylalkylation/alkylation (HAA) of 2-methylfuran (2-MF) and cyclohexanone. After optimizing the reaction conditions, the conversion of 2-MF reached 99% and the yield of 5,5'-(cyclohexane-1,1-diy)bis(2-methylfuran) acquired 98%. The activity and catalytic efficiency were higher than those of Amberlyst 15 and Amberlyst 36 resins, which could be rationalized by high acid strength. At the same time, the catalysts were characterized by acid–base titration and FTIR. Hydrodeoxygenation (HDO) of HAA products of 2-methylfuran and cyclopentanone were processed on the Ni/SiO₂ catalyst prepared by wet impregnation method to further convert into aviation kerosene, and the yield reached 93%.

Introduction

Entering the 21st century, the aviation transportation industry has developed rapidly and occupies an important position in economic development and national security. Therefore, the safe and stable supply of high-quality aviation fuel is crucial. However, the substitutability of aviation fuel is poor. Aviation fuel is mainly derived from petrochemical-based fossil resources. Then, the combustion of petrochemical-based fuel also brings serious air pollution. So the development of renewable and environmentally friendly aviation fuel is the key to promote the sustainable development of the aviation industry.

In recent years, the use of renewable biomass resources to produce fuels^{1–3} and chemicals^{4–7} has attracted wide attention. Many works have confirmed the high potential of using lignocellulose to produce platform compounds. However, the carbon content of lignocellulose materials is generally C₅–C₆, which is far lower than the minimum carbon number of diesel fuel. Oxygenated compounds with long carbon chain of diesel or jet fuel are prepared by C–C coupling reaction of platform chemicals derived from lignocellulose. Subsequently, these oxygenated compounds were further hydrodeoxygenated to alkanes with high energy density.

2-Methylfuran (2-MF) is obtained the selective hydrogenation product of furfural, which is produced on an industrial scale through the hydrolysis and dehydration of hemicellulose in agricultural wastes and forest residues.^{8–10} High density biofuel precursors were generated by hydroxyl alkylation/alkylation of 2-

methylfuran and furfural, and hydrodeoxygenation. Alonso D. M.¹¹ and Yujia Luo *et al.*^{11,12} used Lewis acid Zr/SBA-15 catalyst to catalyze the hydroxylalkylation/alkylation of furfural and methylfuran. Methylfuran was hydroxylated (alkylated) with acetone, hydroxyacetone, mesityl oxide and butyraldehyde, and hydrodeoxygenated to synthesize renewable biomass diesel oil. High-density biofuel was synthesized using hydroxyl alkylation/alkylation of cyclopentanone/cyclohexanone and furfural. Wei Wang, *et al.*,^{13–17} reported renewable diesel were obtained with 2-methylfuran and angelica lactone under catalysts for the reaction include Nafion212, Amberlyst-36 and Amberlyst-15 resin. However, the high cost of Nafion212 resins may limit their use in industrial scale. In order to meet the needs of practical application, it is still necessary to develop cheaper and more accessible solid acid catalysts.

In this work, A novel sulfonated resin solid acid catalyst (SR180) was prepared using bisphenol A,¹⁸ paraformaldehyde and chlorosulfonic acid for the first time. Hydroxylalkylation/alkylation reaction of for cyclohexanone and 2-MF was implemented on the SR180 as catalyst for the solvent-free. The effects of calcination temperature, reaction temperature, reaction time and catalyst dosage on HAA reaction were studied. As the final purpose of this experiment, HAA products of 2-MF and cyclohexanone were further hydrodeoxygenated on Ni/SiO₂ catalyst to obtain alkanes in the range of diesel and jet fuel. In order to understand the catalytic performance of the catalyst, a series of methods were used to characterize the catalyst.

Experimental

Material

p-Toluene sulfonic acid was purchased from Tianjin Damao Chemical Reagent Factory. Paraformaldehyde was provided

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from Tianjin Kemiou Chemical Reagent Factory. Bisphenol A was purchased from Tianjin Institute of Photoing Fine Chemistry. A total of 3.05 g bisphenol A was weighed, and 10 mL of *n*-butanol was placed in a round-bottom flask with a condenser tube and a thermometer, and heated in a constant temperature oil bath at 80 °C. When bisphenol A was completely dissolved, the solution was transparent. Then 1.88 g paraformaldehyde and 0.28 g *p*-toluene sulfonic acid were added, and the reaction mixture was heated to 90 °C for 6 h. After the reaction was completed, the *n*-butanol solvent was evaporated by a rotary evaporator, and then calcined at 150 °C for two hours. The carrier was obtained by grinding, sieving and calcination. Then 1.00 g of solid acid catalyst carrier was weighed and placed in a round-bottom flask. 1 mL of chlorosulfonic acid was added and stirred evenly. The mixture was stirred in an oil bath at 50 °C for 4 h. After the reaction was complete, it was quenched with ice water and filtered. The deionized water was washed until the pH of the washing solution was neutral. The mixture was dried overnight at 80 °C in an oven and packaged for use.

H-Y ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 4$), H β ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 4$), H-ZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 50$) were purchased from Nankai University, nano-SiO₂ was supplied from The Aladdin reagent factory. Hydrodeoxygenation catalysts of Ni/H-ZSM-5, Ni/H β , Ni/HY, Ni/SiO₂ were prepared. The saturated water absorption of H-ZSM-5, H β , HY, SiO₂ molecular sieves were 1.5, 1.6, 1.65, 2.5 mL g⁻¹, respectively. A certain concentration of nickel nitrate solution was prepared, and it was impregnated on different molecular sieves (molecular sieves need to be calcined at 773 K for 4 h before impregnation), stirring evenly, standing at room temperature for 24 h, 393 K overnight drying. Then the catalyst was calcined at 773 K for 4 h in air. The catalyst was reduced under condition of 120 mL min⁻¹ H₂, at 773 K during 2 h. The loading of Ni is 5 wt%.

Instrument measurement

Accurately weigh 2 mg of SR resin to be tested and 200 mg of vacuum-dried KBr, mix them uniformly in a 2 mL sample tube, and then pour them into an agate mortar and repeatedly grind and press them into tablets.

Measuring the number of $-\text{SO}_3\text{H}$ sites on the catalyst surface. Firstly, 0.1 g catalyst was dispersed in 20 mL 2 mol L⁻¹ NaCl solution and ultrasonicated for 1.5 h, then centrifuged. The obtained liquid was titrated with 8 mmol L⁻¹ NaOH solution (pre-calibrated with standard potassium hydrogen phthalate solution) and phenolphthalein was used as indicator. The $-\text{SO}_3\text{H}$ molar amount per gram catalyst is calculated according to the consumption of NaOH solution.

Catalytic tests

Hydroxyalkylation/alkylation reaction (HAA) reaction of 2-methylfuran (2-MF) with furfural was carried out in a 35 mL pressure tube. The reaction temperature was controlled by oil bath method. 2-MF and cyclohexanone are purchased in <https://www.Aladdin-E.com> and used directly without further purification. 0.98 g cyclohexanone (10 mmol), 1.68 g 2-MF (20 mmol) and 0.10 g catalyst were placed in a 35 mL pressure

tube and stirred for 2 h in solvent-free setting temperature for HAA reaction of 2-MF and cyclohexanone. The product analysis showed that the HAA product mainly contained C₁₆ intermediate by NMR analysis, indicating that 2-MF and cyclohexanone could be effectively transferred to the target product in the presence of sulfonic acid solid acid catalyst. After the reaction, the sample was centrifuged and quantitatively determined by gas chromatography (Agilent 7890 B). The gas chromatography analysis of liquid products was carried out on Agilent 7890 B chromatograph under the meteorological condition, using HP-INNOWAX capillary column (30 m, 0.25 mm ID, 0.5 mm membrane) and FID detector. The column temperature was maintained at 40 °C for 2 min, and rose to 280 °C at 15 °C min⁻¹ for 5 min. The injection port and FID were set at 250 °C and 320 °C, respectively. Hydrogen flow 30 mL min⁻¹, air flow 400 mL min⁻¹ and tail blowing 25 mL min⁻¹.

The catalytic reaction was carried out in a 100 mL stainless steel autoclave equipped with a mechanical agitator, a pressure gauge and an automatic temperature control device. In this experiment, 500 mg HAA product, 200 mg hydrodeoxygenation catalyst and 10 mL cyclohexane were added to the reactor. After sealing, the reactor was purged with hydrogen 4–5 times and pressurized to 4 MPa. Then the reactor was heated to the required temperature and stirred continuously at 800 rpm. After the reaction was completed, the samples were cooled to room temperature and centrifuged for quantitative determination by Agilent 7890 B.

Results and discussion

Catalyst characterization

The calcination temperature of the catalyst precursor was investigated, and the volatile components were removed to obtain a stable solid acid precursor. The determination results of solid acid content obtained by sulfonation of precursor chlorosulfonic acid at different calcination temperatures are shown in Table 1. It can be seen from Table 1 that when the calcination temperature of the solid acid precursor is from 100 to 300 °C, the acid content of the prepared solid acid increases first and then decreases. At 150 °C and 180 °C, the acid content of catalysts of SR150 and SR180 were 2.74 mmol g⁻¹ and 2.79 mmol g⁻¹. The acid amount of SR150 is equivalent to that of SR180.

Infrared spectra of the prepared solid acid catalysts of SR100, SR150, SR180, SR200 and SR300 resin were shown in Fig. 1. It

Table 1 Acid values of the catalysts different calcination temperature used in HAA of 2-MF and cyclohexanone

Calcination	Temperature (°C)	Acid value (mmol g ⁻¹)
SR100	100	2.16
SR150	150	2.74
SR180	180	2.79
SR200	200	2.06
SR300	300	1.98



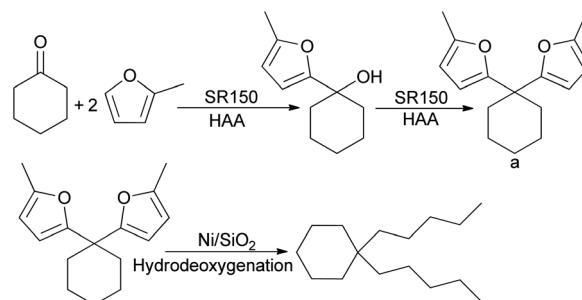
can be seen that the material has many functional groups. The broad peak at 3420 cm^{-1} can be attributed to OH groups adjacent to oxygen atoms or SO_3H groups *via* hydrogen bonds. According to ref. 19, the peaks at 2847 cm^{-1} and 2939 cm^{-1} can be attributed to the stretching vibration of $-\text{CH}_2-$ in catalysts. The bands at 1218 cm^{-1} and 1034 cm^{-1} can be attributed to the symmetric stretching of $\text{O}=\text{S}=\text{O}$ and SO_3-H in the SO_3H group, respectively.²⁰ Peaks at 1425 cm^{-1} , 1500 cm^{-1} and 1612 cm^{-1} can be attributed to the characteristic vibrations of benzene rings.^{21,22}

Hydroxyalkylation/alkylation

The hydroxyalkylation/alkylation of 2-methylfuran with cyclohexanone is carried out over a series solid acid catalysts. The hydroxyalkylation/alkylation reaction between 2-methylfuran and cyclohexanone is shown in Scheme 1. The NMR spectra of hydroxylation/alkylation product of 2-methylfuran with cyclohexanone are shown as p. S1 and p. S2 in ESI† respectively. The NMR spectrum of a (p. S1 in ESI†) shows the following peaks ^1H NMR ($\text{CDCl}_3\text{-d}$), δ : 5.99 (s, 2H), 5.96 (s, 2H), 2.30 (s, 6H), 2.09 (d, 4H, $J = 12$), 1.51 (m, 6H); ^{13}C NMR ($\text{CDCl}_3\text{-d}$), δ : 154.8 (2C), 150 (2C), 106.2 (2C), 105.6 (2C), 45.7 (1C), 36.1 (2C), 25.1 (1C), 18 (2C), 13.7 (2C). Based on $^1\text{HNMR}$ and $^{13}\text{CNMR}$ spectra analysis, 5,5'-(cyclohexane-1,1-diyl)bis(2-methylfuran) (a) was identified as the major product.

HAA of 2-MF and cyclohexanone solvent-free were carried out on acidic catalysts by acidification of phenolic condensation products of bisphenol A and paraformaldehyde. 5,5'-(Cyclohexane-1,1-diyl)bis(2-methylfuran) is the main product.

The effect of catalysts at different calcination temperatures on the hydroxyalkylation/alkylation reaction of 2-methylfuran and cyclohexanone was shown Fig. 2. It can be seen from the Fig. 2 that with the increased in calcination temperature, the product yield first increased and then decreased, which is consistent with the acid amount of catalysts of the acid–base titration. When the calcination temperature is $150\text{ }^\circ\text{C}$, the 5,5'-(cyclohexane-1,1-diyl)bis(2-methylfuran) yield is 93.95% over



Scheme 1 Reaction route of alkanes in the range of synthetic diesel or aviation kerosene fuels using 2-MF and cyclohexanone.

SR150. When the calcination temperature is $180\text{ }^\circ\text{C}$, the yield of 5,5'-(cyclohexane-1,1-diyl)bis(2-methylfuran) is 94.26%.

It can be seen from Fig. 3 that the activity of acidic resins decreased in the order of SR150 > Nafion212 > Amberlyst15 > Amberlyst36. This can be explained by the chemical structure of these acidic resins. According to literature^{22,23} only $-\text{SO}_3\text{H}$ is the active centre catalyzing the HAA reaction of 2-methylfuran and cyclohexanone, and the number of $-\text{SO}_3\text{H}$ acidic sites for Amberlyst15, Amberlyst36 (ref. 24) and Nafion212 are 4.43, 3.52 and 1.08 mmol g^{-1} . Water is formed during HAA of 2-MF and cyclohexanone. Under the catalysis of acidic sites, the water produced by the HAA reaction can further react with the furan functional groups in the HAA product, and this continuous HAA-hydrolysis-HAA reaction (or excessive condensation) will lead to the production of large polymer molecules, which will block Holes in Amberlyst resin. The order of activity is therefore as above. The HAA yields of 2-MF and cyclohexanone catalyzed by Nafion212 and amberlyst15 were consistent with the results reported in the literature.²⁵

According to ref. 26–30, the HAA reaction of 2-MF was very sensitive to the acidity of the catalyst. In the HAA reaction of 2-MF, strong acid was more active than weak acid. The HAA

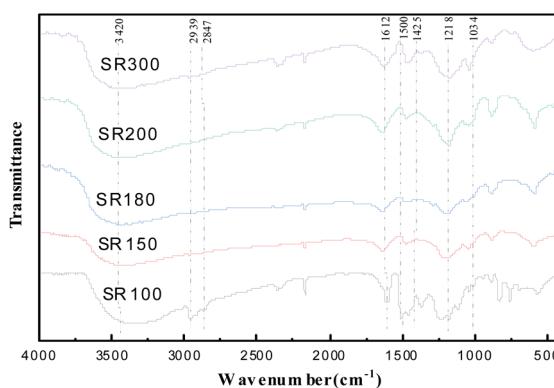


Fig. 1 IR spectra of solid acid catalysts over SR180. However, the 5,5'-(cyclohexane-1,1-diyl)bis(2-methylfuran) yield decreases over SR200 and SR300 with the increase of calcination temperature. When the calcination temperature of $300\text{ }^\circ\text{C}$, the 5,5'-(cyclohexane-1,1-diyl)bis(2-methylfuran) yield was decreased to 78% over SR300.

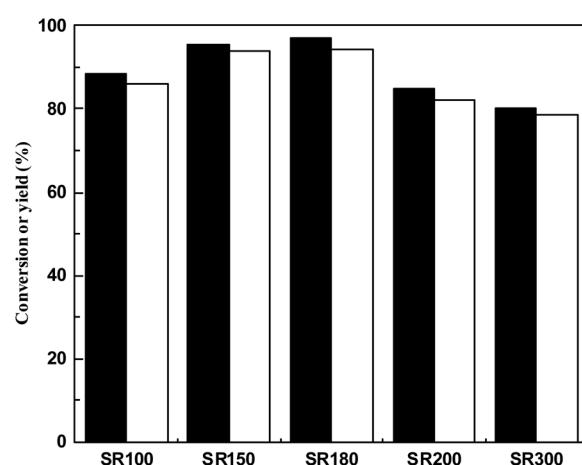


Fig. 2 Changes of conversion of 2-MF (black bar) and carbon yield of a (white bar) under different calcination temperatures. Reaction conditions: $60\text{ }^\circ\text{C}$, 2 hours; 0.98 g cyclohexanone and 1.68 g 2-MF, different SR catalysts 0.10 g.



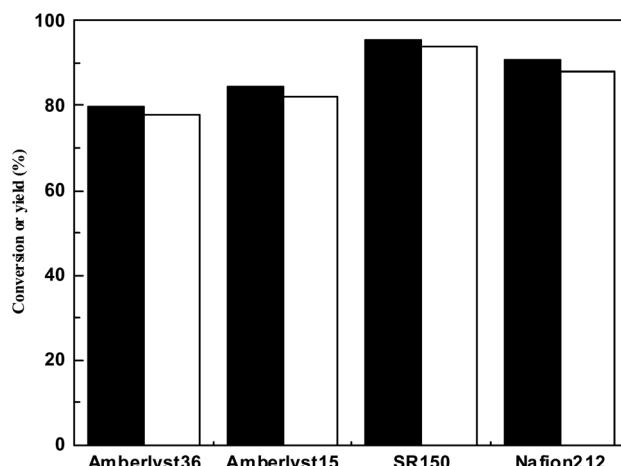


Fig. 3 Conversion of 2-MF (black bar) and carbon yield of a (white bar) catalyzed by different acidic resins. Reaction conditions: 60 °C, 2 h; 0.10 g SR150, 0.98 g cyclohexanone and 1.68 g 2-MF

reaction of 2-MF and cyclohexanone was easier due to the electrophilicity of cyclohexanone.

The activity of different acidic resins in 2-MF and cyclohexanone HAA is related to the acid strength of these catalysts. The acid strength of different resins can be rationalized by the chemical environment of $-\text{SO}_3\text{H}$ groups. According to ref. 30, Nafion resin is a perfluorosulfonic acid resin, commonly known as superacid. Amberlyst resin is a kind of sulfonic acid functionalized crosslinked polystyrene resin. We can also attribute the excellent performance of SR150 in the HAA reaction of 2-MF and cyclohexanone to its relatively high acid strength.

It can be seen from Fig. 4 that the catalytic efficiency increases with the increase of catalyst dosage. When the catalyst dosage of 0.01 g, the 5,5'-(cyclohexane-1,1-diyl)bis(2-methylfuran) yield is 32.86%, and the catalytic effect increased with the increase of catalyst dosage. When the catalyst dosage increased 0.01 g, the 5,5'-(cyclohexane-1,1-diyl)bis

(2-methylfuran) yield increases slowly. Therefore, in the follow-up study, the amount of catalyst is 0.01 g.

The effect of reaction temperature on HAA reaction of 2 MF and cyclohexanone is shown in Fig. 5. Fig. 5 showed that when the reaction temperature is from 40 °C to 60 °C, the catalytic efficiency of is improved. While the reaction temperature is 40 °C, the yield of the 5,5'-(cyclohexane-1,1-diyl)bis(2-methylfuran) is 61%, and when the temperature is higher than 60 °C, the yield of the 5,5'-(cyclohexane-1,1-diyl)bis(2-methylfuran) yield increased only from 93% to 96%. Based on green energy saving, 60 °C is the best reaction temperature.

The effect of reaction time on HAA reaction of 2 MF and cyclohexanone is shown in Fig. 6. It can be seen from Fig. 6 that the yield of the 5,5'-(cyclohexane-1,1-diyl)bis(2-methylfuran) is 40% when the reaction time is 15 min, the yield of the 5,5'-(cyclohexane-1,1-diyl)bis(2-methylfuran) increased significantly to 93% with the extension of reaction time up to 2 h. Then the yield of 5,5'-(cyclohexane-1,1-diyl)bis(2-methylfuran) changes gently with the extension of reaction time. The yield of 5,5'-(cyclohexane-1,1-diyl)bis(2-methylfuran) is 98% when the reaction time of 6 h.

We also study the reusability of SR150 for HAA of 2-MF and cyclohexanone. Therefore, SR150 was reused under optimal conditions (0.10 g catalyst, 60 °C, 2 h). In order to eliminate the influence of residues (including HAA products, unreacted 2-MF and cyclohexanone) on the used catalysts, the catalysts were fully washed and soaked with methanol and dried at 60 °C for 2 h. From the results shown in Fig. 7, SR150 is very stable under the conditions studied, the catalyst is reused four times.

Hydrodeoxygenation reaction

As the ultimate goal of this work, alkanes in the range of renewable biomass diesel or aviation fuel were produced. We also studied the hydrodeoxygenation (HDO) of HAA products of 2-MF and cyclohexanone. HDO was reacted in a 100 mL stainless steel axe reactor with cyclohexane as solvent. After the reaction, the samples were cooled to room temperature and

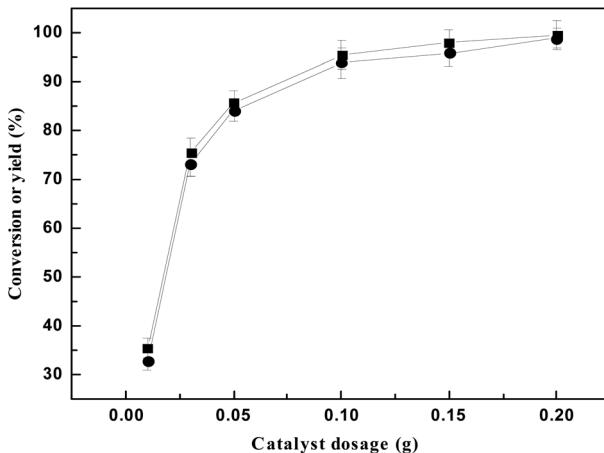


Fig. 4 The conversion of 2-MF (■) and the carbon yield of a (●) varied with the amount of catalyst. Reaction conditions: 60 °C, 2 hours; 0.98 g cyclohexanone and 1.68 g 2-MF.

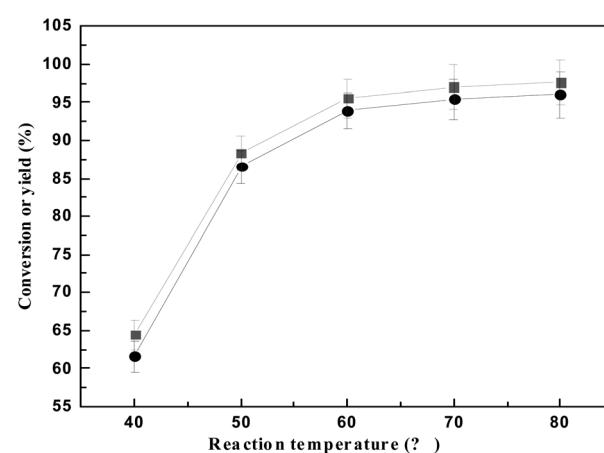


Fig. 5 The conversion of 2-MF (■) and the carbon yield of a (●) varied with reaction temperature. Reaction conditions: 2 h, 0.10 g SR150; 0.98 g cyclohexanone and 1.68 g 2-MF.

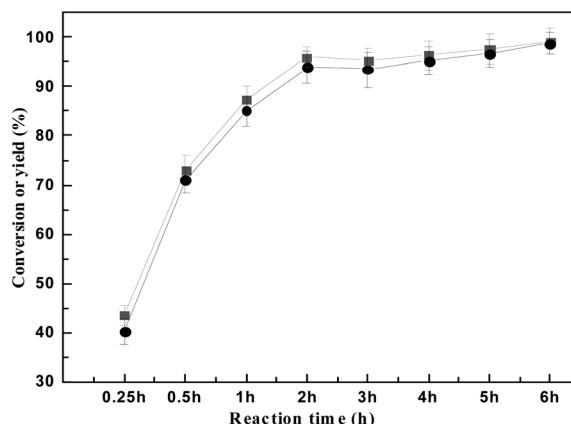


Fig. 6 The conversion of 2-MF (■) and the carbon yield of a (●) varied with reaction time. Reaction conditions: 60 °C, 0.10 g SR150; 0.98 g cyclohexanone and 1.68 g 2-MF.

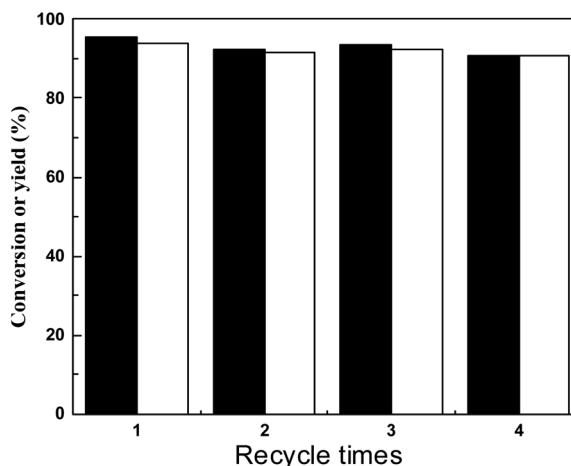


Fig. 7 Number of catalyst recycles, conversion of 2-MF (black bar) and carbon yield of a (white bar). Reaction conditions: 60 °C; 0.10 g SR150; 0.98 g cyclohexanone and 1.68 g 2-MF.

centrifuged for quantitative determination by GC (p. S3 in ESI[†]) and GC-MS (p. S4 in ESI[†]). According to GC and GC-MS analysis, 5,5'-(cyclohexane-1,1-diyl)bis(2-methylfuran) was completely converted to alkanes on non-noble metal supported molecular sieves, with 1,1-dipentylcyclohexane as the main product.

Hydrodeoxygenation of HAA product of 2-MF and cyclohexanone was implemented over molecular sieve loaded non-noble metal catalysts. For comparison, the loading amount of metal nickel in the catalyst is 5%. It can be seen from Fig. 8 that the carbon yield (80.97%) of C₈–C₁₆ alkanes in diesel and jet fuels over Ni/SiO₂ was higher than that over the catalysts of Ni/HY (73.51%), Ni/HZSM5 (60.13%) and Ni/H β (35.35%). Under this reaction condition, Ni/HZSM5 was not completely hydrodeoxygenated, and the product of Ni/H β had 45% naphtha.

After hydrodeoxygenation mixture of 5,5'-(cyclohexane-1,1-diyl)bis(2-methylfuran) was distilled under reduced pressure, the obtained biofuel has a density of 0.83 g mL⁻¹.

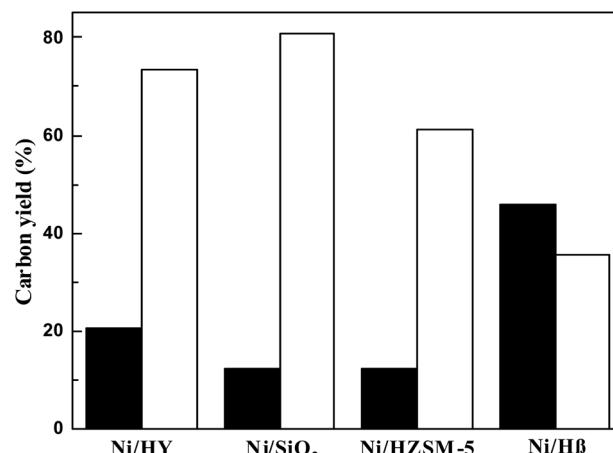


Fig. 8 Carbon yields of C₈–C₁₆ diesel range alkanes (white bars), C₅–C₇ gasoline range alkanes (black bars), over molecular sieve loaded non-noble metal catalysts. Reaction conditions: 500 mg HAA product, 200 mg catalyst, 280 °C, 24 h.

Conclusions

In this work, a new solid acid resin catalyst was prepared by bisphenol A, paraformaldehyde and chlorosulfonic acid, and applied to the hydroalkylation/alkylation of 2-methylfuran and cyclohexanone. The conversion of 2-MF reached 99% and the yield of 5,5'-(cyclohexane-1,1-diyl)bis(2-methylfuran) acquired 98%, under optimizing the reaction conditions. At the same time, hydrodeoxygenation of HAA products of 2-MF and cyclohexanone were executed over non-noble metal-supported molecular sieve catalysts. 5,5'-(Cyclohexane-1,1-diyl) bis(2-methylfuran) was completely converted to alkanes over Ni/SiO₂, with 1,1-dipentylcyclohexane as the main product. The carbon yield of C₈–C₁₆ alkanes in diesel and jet fuels reached 80.97%. Acquired cycloalkanes has 0.83 g mL⁻¹. It can be used as high-density fuel or additive in other diesel or aviation kerosene fuels.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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