Synthesis of C15 and C10 fuel precursors with cyclopentanone and furfural derived from hemicellulose†

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Fuel precursors 2,5-bis(2-furylmethylidene)cyclopentanone (F2Cp) and 2-(2-furylmethylidene)cyclopentanone (FCp) were obtained through aldol condensation of cyclopentanone and furfural over solid acid catalysts under solvent-free conditions. Nafion exhibited the best performance among the investigated catalysts (Nafion, Amberlyst-15, Amberlyst-36, H-USY, ZSM-5, H-β, and SiO2/Al2O3). Under optimized conditions, yields of F2Cp and FCp were 37.48% and 23.77%, respectively. Selectivities of F2Cp and FCp were 50.74% and 32.18%, respectively. Nafion showed good stability and did not deactivate during 4 runs. Meanwhile, a certain amount of humin was also generated during the reaction. The reaction mechanism for the aldol condensation of cyclopentanone and furfural and the formation mechanism of humin were also proposed.

Cyclopentanone can be obtained from a furfural and furfural alcohol selective hydrogenation and rearrangement reaction.24-31 Zhang and his group studied selective conversion of furfural to cyclopentanone with CuZnAl catalysts, where the yield obtained was 62%.24 Furfural and furfural alcohol selective hydrogenation and rearrangement reaction can be catalyzed with Ni, Pt, Pd, Pt–Ru, and Ru catalysts by using water as the solvent, with a yield of cyclopentanone up to 76.5%.28 Fu et al. reported the selective conversion of furfural to cyclopentanone with Cu–Co catalysts with a 67% yield of cyclopentanone.29 Xu’s group reported conversion of furfural into cyclopentanone over Ni–Cu bimetallic catalysts at a 62% yield.30 Xiao et al. reported selective hydrogenation of furfural to cyclopentanone over hydrotalcite-based Cu–Ni–Al catalysts with a yield of up to 95.8%.31

Cyclopentanone can undergo condensation with valeraldehyde,32 furfural33,34 or itself.35-38 It can also react with 2-methyl furan through hydroxalkylation/alkylation,39,40 generating C10–C15 oxygen-containing compounds, and then the C10–C15 oxygen-containing compounds can be converted into high-density diesel or jet fuel by hydrodeoxygenation. Aldol condensation of cyclopentanone and furfural by sodium hydroxide in solution free system achieved 2,5-bis(2-furylmethylidene)cyclopentanone yield of 96.0%.41 Aldol condensation of cyclopentanone and furfural in an aqueous solution of sodium hydroxide gave a 2,5-bis(2-furylmethylidene)cyclopentanone yield of more than 95%.33,34 However, the reaction yields a large amount of wastewater and thus was not environmentally benign, additionally, the used sodium hydroxide could not be effectively recycled.

Aldol condensation is an important organic synthetic reaction catalyzed by acid or alkali. It involves transforming of
compounds containing active \( \alpha \)-hydrogen atoms (such as aldehyde, ketone, carboxylic acid, and ester), nucleophilic addition to obtain \( \beta \)-hydroxyl compounds, and then further dehydration to generate \( \alpha, \beta \)-unsaturated carbonyl compounds. It could take place in homogeneous aqueous (or water/alcohol) solutions\(^{15,42} \) and biphasic systems.\(^{15,42} \) To simplify the process, new solid base catalysts have also been developed.\(^{22,43-46} \)

In this work, fuel precursors 2,5-bis(2-furylmethylidene)cyclopentanone (F\(_2\)Cp) and 2-(2-furylmethylidene)cyclopentanone (FCp) were obtained from aldol condensation of cyclopentanone and furfural over solid acids catalyst under solvent-free conditions. Nafion exhibited the best performance among investigated catalysts (Nafion, Amberlyst-15, Amberlyst-36, H-USY, ZSM-5, H-\( \beta \), and SiO\(_2\)/Al\(_2\)O\(_3\)). Furthermore, we also studied the effects of catalyst dosage, reaction temperature, and time on the conversion of furfural and yields of F\(_2\)Cp and FCp over the Nafion catalyst under solvent-free conditions. We also investigated the stability of the Nafion catalyst. Finally, the reaction mechanism of aldol condensation of cyclopentanone and furfural and the formation mechanism of humins were also proposed.

### Experimental

#### Materials

Nafion resin with a diameter ball of 0.2 mm was provided by JiangSu Success Resin Ltd. Amberlyst-36 and Amberlyst-15 resins were purchased by Sigma Aldrich. H-USY (SiO\(_2\)/Al\(_2\)O\(_3\) = 12), ZSM-5 (SiO\(_2\)/Al\(_2\)O\(_3\) = 25), and H-\( \beta \) (SiO\(_2\)/Al\(_2\)O\(_3\) = 25) zeolites used in this work were provided by Catalyst Factory of Nankai University. SiO\(_2\)/Al\(_2\)O\(_3\) (SiO\(_2\)/Al\(_2\)O\(_3\) = 25) was purchased from Qingdao Ocean Chemical Ltd. Furfural (99%) and cyclopentanone (99%) were purchased from Sigma Aldrich. Furfural was purified by vacuum distillation and stored in a refrigerator at 0°C. F\(_2\)Cp was prepared following a typical process in the literature.\(^{31} \) FCp produced from the reaction of furfural and cyclopentanone was further separated by column chromatography with silica gel (purchased from Merck) as the stationary phase, and a mixture of ethyl acetate and petroleum ether (at a volume ratio of 1 : 15) was used as the mobile phase. Thin layer chromatography (TLC) was used for detection of FCp, and the collected effluent containing FCp was concentrated through vacuum distillation.

#### Aldol condensation

The reactions were carried out in a 50 mL batch reactor with a reflux condenser and a magnetic stirrer at atmospheric pressure. The temperature was controlled by a pre-heated oil bath. In a typical reaction, 0.40 g of catalyst, 1.92 g of furfural (20 mmol), and 5.04 g of cyclopentanone (60 mmol) were added to the reactor and then the mixture was stirred at 60°C for 6 h.

#### Separation of humins

The crude product in the reactions was then mixed with 200 mL of anhydrous ethanol under refluxing for 30 min. Unreacted furfural, cyclopentanone, and the products of FCp and F\(_2\)Cp were separated from insoluble residue through filtering at a high temperature (~78°C). The residue was treated twice with 200 mL of anhydrous ethanol to completely removed the soluble substances. The residue was solid humins.

#### Analysis

The concentrations of F\(_2\)Cp, FCp, and furfural were determined by an Agilent 1260 high performance liquid chromatography (HPLC) system, equipped with a ZORBAXSB-C\(_{18}\) column (4.6 mm \( \times \) 150 mm, 5 \( \mu \)m) and a refractive index detector (RID). A solution of methanol and water (9 : 1 v/v) was used as the eluent.

The products were verified with a Bruker AVANCE 500 MHz NMR spectrometer, with chloroform-d (99.8% atom D with 0.1% v/v tetramethylsilane (TMS)) from Aldrich was used as the solvent for \(^1\)H and \(^{13}\)C NMR sample preparation. Chemical shifts, quoted in ppm, are relative to the internal standards of the singlet at \( \delta = 0 \) ppm for TMS for \(^1\)H NMR and the middle peak of the CDCl\(_3\) triplet at \( \delta = 77 \) ppm for \(^{13}\)C NMR.

Infrared (IR) spectra were measured with a Bruker Vertex 70 Infrared spectrometer using a pressed disc method with potassium bromide. The instrumental resolution was set to at 4 cm\(^{-1}\). The IR spectrum of air was recorded as the background, and then samples were placed in a holder for transmittance measuring. Scan time of 60 s were used for both the background and the samples.

The conversions of furfural and the yields of F\(_2\)Cp and FCp were calculated by the following formulas:

\[
\text{Conversions of furfural} (\%) = \frac{\text{moles of furfural consumed}}{\text{moles of furfural input}} \times 100\%
\]

\[
\text{Yield of FCp} (\%) = \frac{\text{moles of FCp}}{\text{moles of furfural input}} \times 100\%
\]

\[
\text{Yield of F}_2\text{Cp} (\%) = \frac{2 \times \text{moles of F}_2\text{Cp}}{\text{moles of furfural input}} \times 100\%
\]

### Results and discussion

#### Aldol condensation of furfural with cyclopentanone

The aldol condensation of furfural with cyclopentanone was carried out over solid acid catalysts. According to the analysis of HPLC (in Scheme 1) was identified as the main product. In addition, FCp (in Scheme 1) was also detected in the reaction mixture. As shown in Scheme 1, FCp was the product of the aldol condensation of furfural with cyclopentanone, and F\(_2\)Cp was the product of aldol condensation between FCp further with furfural. The NMR spectra (p S3 in ESI†) of F\(_2\)Cp show the following peaks: \(^1\)H NMR (CDCl\(_3\)-d): \( \delta = 7.80 \) (s, 2H), 7.56 (s, 2H), 6.90 (t, 2H), 6.75 (m, 2H), 3.28 (t, 4H); \(^{13}\)C NMR (CDCl\(_3\)-d): \( \delta = 195 \) (1C), 152 (2C), 144 (2C), 135 (2C), 119 (2C), 116 (2C), 112 (2C),
25 (2C). The F₂Cp obtained was in the form of yellow needles crystal. The NMR spectra (p S4 in ESI†) of FCP show the following peaks: 1H NMR (CDCl₃-d), δ: 7.71 (s, 1H), 7.37 (d, 1H, J = 4), 6.87 (t, 1H), 6.72 (d, 1H, J = 4), 3.20 (t, 2H), 2.59 (t, 2H), 2.26 (m, 2H); 13C NMR (CDCl₃-d), δ: 207 (1C), 152 (1C), 144 (1C), 133 (1C), 118 (1C), 115 (1C), 112 (1C), 37 (1C), 28 (1C), 19 (1C). The F₂Cp obtained was in the form of yellow needles crystal. The NMR spectra (p S4 in ESI†) of FCP show the following peaks: 1H NMR (CDCl₃-d), δ: 7.71 (s, 1H), 7.37 (d, 1H, J = 4), 6.87 (t, 1H), 6.72 (d, 1H, J = 4), 3.20 (t, 2H), 2.59 (t, 2H), 2.26 (m, 2H); 13C NMR (CDCl₃-d), δ: 207 (1C), 152 (1C), 144 (1C), 133 (1C), 118 (1C), 115 (1C), 112 (1C), 37 (1C), 28 (1C), 19 (1C). The FCP was a yellow-brown solid.

The catalytic performances of different solid acids for the aldol condensation of furfural with cyclopentanone are shown in Fig. 1, which shows that solid acid catalysts can promote the aldol condensation of furfural with cyclopentanone. Higher yields of F₂Cp and FCP could be achieved over Na⁺-USY, Amberlyst-15, and Amberlyst-36 resins than under catalysis by H-ZSM-5, H-USY, H-β, SiO₂/Al₂O₃ under the same reaction conditions.

The sequence for the yield of F₂Cp, FCP over the solid acid catalysts was Na⁺-USY > Amberlyst-15 > Amberlyst-36 > H-β, H-USY, ZSM-5, SiO₂/Al₂O₃. This sequence is consistent with that of the Hammett acidity function (−Hₒ) values of these catalysts (see Table 1). Therefore, the higher catalytic efficiency of Na⁺-USY resin can be attributed to the higher strength of acid sites on this catalyst. The higher acid strength of Na⁺-USY resin is dependent on its structure. As we know, Na⁺ is a perfluorinated sulfonic acid resin,⁴⁷ while Amberlyst resins are sulfonic acid-functionalized cross-linked polystyrene.⁴⁸ The presence of fluorine on the Na⁺-USY resin greatly enhances the acid strength of the −SO₃H group.

The influence of catalyst dosage on aldol condensation of furfural and cyclopentanone is shown in Fig. 2. It can be seen that conversion of furfural was increased as the amount of catalyst was raised from 0.2 to 0.5 g. Meanwhile, yields of F₂Cp and FCP increased with the catalyst dosage first, and then leveled off. When the catalyst amount of 0.40 g, yields of F₂Cp and FCP maximized. Hence, the catalyst amount was 0.40 g in the following parts.

Temperature is an important parameter for any chemical reaction. Thus, the effect of the reaction temperature on the conversion of furfural, yields of F₂Cp and FCP were studied and the results were shown in Fig. 3. The conversion of furfural increased first, and then remained constant as the reaction temperature increased further. Moreover, yields of F₂Cp and FCP increased at first with the reaction temperature, and then decreased. Therefore, the chosen reaction temperature was 60 °C.

The impact of reaction time on the conversion of furfural, yields of F₂Cp and FCP was then examined. The experimental

![Fig. 1](image1.png) The aldol condensation of furfural and cyclopentanone over various heterogeneous catalysts. Reaction conditions: 60 °C, 6 h; 1.92 g (20 mmol) furfural, 5.04 g (60 mmol) cyclopentanone, 0.40 g catalyst.

![Fig. 2](image2.png) The effect of the catalyst dosage on the aldol condensation. Reaction conditions: 60 °C, 6 h; 1.92 g (20 mmol) furfural, 5.04 g (60 mmol) cyclopentanone.

![Table 1](table1.png) Average pore sizes, acid amounts and Hammett acidity function (−Hₒ) values of the different solid acid catalysts used in the aldol condensation of furfural and cyclopentanone.⁴⁹

| Catalyst     | Acid amount (mmol g⁻¹) | Average pore size (nm) | −Hₒ     |
|--------------|------------------------|------------------------|---------|
| Nafion       | 3.0                    | 4.0                    | 11–13 (ref. 45) |
| Amberlyst-15 | 4.7                    | 29                     | 2.2 (ref. 49)   |
| Amberlyst-36 | 5.4                    | 24                     | 2.2–2.65 (ref. 50) |
| H-ZSM-5      | 0.43                   | 0.5                    | 5.6–5.7 (ref. 50) |
| H-USY        | 0.44–0.48              | 0.7                    | 3.0–4.4 (ref. 49) |
| H-β          | 0.2                    | 0.6 × 0.67, 0.56 × 0.56 | 4.4–5.7 (ref. 49) |
| H-Y          | 0.9                    | 0.74 × 0.74            | −1.5 to 5.6 (ref. 49) |

⁴⁷ According to the information provided by supplier.
results were shown in Fig. 4. It can be seen that conversion of furfural first increased and then remained constant as the reaction time was prolonged from 0.5 to 8 hours. The conversion of furfural was 73.86% at 6 h. Meanwhile, yields of F2Cp and FCP increased at first, and then remained constant. At 6 h, yields of F2Cp and FCP were 37.48% and 23.77%, respectively. Thus, the reaction time of 6 h was better.

The stability of Naion in the aldol condensation of furfural and cyclopentanone was implemented. To eliminate the influence of residues, the catalysts were regenerated with a 10% H2O2 aqueous solution at 80 °C for 2.0 h. Then, the mixture was filtered and the catalyst was dried at 80 °C for 2.0 h after each usage. According to the results shown in Fig. 5, Naion showed good stability in the aldol condensation of furfural and cyclopentanone. No evident activity change was noticed over this catalyst after it was used 4 times. Considering the excellent catalytic performance and good stability of Naion resin, we consider it a promising catalyst in future applications.

Under the optimum conditions (60 °C, 6 hours, and 0.40 g catalyst), aldol condensation of furfural and cyclopentanone on Naion catalyst in solvent-free conditions gave a conversion of 73.86% for furfural and yields of 37.48% and 23.77% for F2Cp and FCP, respectively. Selectivities of F2Cp and FCP were 50.74% and 32.18%, respectively.

**Reaction mechanism of furfural with cyclopentanone**

The reaction mechanism of aldol condensation using furfural and cyclopentanone by solid acid catalysis is shown in Scheme 2. Cyclopentanone is first protonated by a proton (H+) over solid acid to form an electron-deficient intermediate (1). The π electron of C==O double bonds is transferred to the electron-deficient atom of oxygen to form carboxylation (2). Carbanion and H+ were gained by electron heterolytic formation of α C–H bond of carboxylation. The lone pair electrons of the carbanion are split and transfer to the carbocation, and the C=C bond-containing enol structure (3) is formed. The negatively charged carbon of (3) attacked the C atom of C==O of the same protonated furfural. The π electron of intermediate (4) is

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**Fig. 3** The effect of reaction temperature on the aldol condensation. Reaction conditions: 0.40 g Naion catalyst, 6 h; 1.92 g (20 mmol) furfural, 5.04 g (60 mmol) cyclopentanone.

**Fig. 4** The effect of reaction time on the aldol condensation. Reaction conditions: 0.40 g Naion catalyst, 1.92 g (20 mmol) furfural, 5.04 g (60 mmol) cyclopentanone at 60 °C.

**Fig. 5** The recyclability of Naion resin for the aldol condensation. Reaction conditions: 60 °C, 6 h; 1.92 g (20 mmol) furfural, 5.04 g (60 mmol) cyclopentanone, and 0.40 g of Naion.

**Scheme 2** Reaction mechanism of aldol condensation from furfural and cyclopentanone by solid acid catalysis.
transferred to the electron-deficient oxygen of carbonyl. At the same time, the C–C \( \sigma \) electrons of intermediate (3) attack the electron-deficient carbon of intermediate (4) to form a C–C bond and the lone pair on the oxygen atom transferred to the adjacent carbon atoms to form C=C gave rise to the structure of the intermediate (5). The intermediate (5) released protons to form intermediate (6). Hydroxyl groups of intermediate (6) are protonated to form intermediate (7) under acidic conditions. Then, one molecule of water is released to form intermediate (8). Meanwhile, the C–H \( \sigma \) bond is transferred and proton is released to form the product FCp.

The carbonyl of FCp is protonated to obtain intermediate (9), and the \( \pi \) electron of C=O in intermediate (9) transferred to the carbonyl oxygen atom to form a carbon cationic structure (10), which undergoes heterolytic electron transfer to form the enol structure (11). The negative charge of the carbon with a protonated enol structure (11) attacks the protonated carbonyl of furfural in intermediate (4), forming a C–C bond to obtain the intermediate (12). Intermediate (12) releases protons and forms intermediate (13). The intermediate (13) is protonated to form intermediate (14), and then releases a water molecule to form intermediate (15) (\( \sigma \) bond shift). At the same time, proton is removed to form the product F_2Cp. This reaction mechanism is similar to that of acetophenone and benzaldehyde under the catalysis of sulfuric acid.\(^\text{31}\)

**Formation mechanism of humins**

Water is continuously produced from aldol condensation of furfural and cyclopentanone on solid acid conditions. Under these conditions, furfural can be easily polymerized through hydrolysis. The conversion process is shown in Scheme 3. Furfural is first hydrolyzed to produce 5-hydroxy-4,5-dihydrofuran-2-carbaldehyde (I) or 2-hydroxy-2,3-dihydrofuran-2-carbaldehyde (II). The hydrolysis mechanism of furfural is similar to that of 5-hydroxymethyl furfural.\(^\text{32-34}\) The open ring of intermediates I and II generate 2-oxo pentanoidal (III). Isomerization and rearrangement of intermediate III provided 4-hydroxy-5-oxo-4-pentene aldehyde (IV), 2-hydroxy-2-ene glutaraldehyde (V), or 5-hydroxy-2-oxo-4-aldehyde (VI). Then the aldol condensation of IV, V, and VI with furfural forms 4,5-dioxo-6-hydroxy-6-tetrahydrofuran hexanoid (VII), 2-oxo-3-tetrahydrofuran methylene pentanedial (VIII), and 2-oxo-4-tetrahydrofuran methylene pentanoidal (IX). VII, VIII, and IX will polymerize by themselves or interaction each other to form a polymer with high viscosity (humins). The humins can easily cover the catalyst surface form a membrane. Leading to the active centers of the catalyst are completely isolated from the feedstock (cyclopentanone and furfural). The catalyst subsequently will loss of activity, and therefore the reaction cannot complete thoroughly. Intermediate III can also generate humins through self-condensation or condensation with furfural. This is the reason why, under the optimized conditions, conversion of furfural was 73.86% and the yields of F_2Cp and FCp were 37.48% and 23.77%, respectively. Selectivities of F_2Cp and FCp were 50.74% and 32.18%, respectively. At the same time, we also found that, during the regeneration process of the catalyst, a layer of thin film formed on the surface of the Naion ball. It is consistent with formation polymer of hydrolysis reaction.

The infrared spectrum of the polymer is shown in Fig. 6. The weak absorption at 3134 cm\(^{-1}\) and 3115 cm\(^{-1}\) belong to the C–H bond stretching vibration of the furan ring. The weak absorption bands at 2877–2957 cm\(^{-1}\) are attributed to CH\(_2\) bond stretching vibration owing to polymerization. The weak absorption peak at 1735 cm\(^{-1}\) is due to the stretching vibration of the \( \text{C}=\text{O} \) bonds in aldehyde groups. The strong absorption peaks at 1707 cm\(^{-1}\) and 1681 cm\(^{-1}\) are caused by the stretching vibration of \( \text{C}=\text{O} \) bonds in unsaturated aldehyde and ketone. The strong absorption peaks at 1622 cm\(^{-1}\) and 1604 cm\(^{-1}\) correspond to the C–C stretching vibration and those at 1473 cm\(^{-1}\), 1388 cm\(^{-1}\), and 1348 cm\(^{-1}\) are attributed to the C–H

![Scheme 3](image-url)
bending vibrations in CH$_2$ bonds. Absorption peaks at 1280 cm$^{-1}$, 1261 cm$^{-1}$, 1205 cm$^{-1}$, and 1161 cm$^{-1}$ corresponded to C–O bond stretching vibrations, while those at 3134 cm$^{-1}$, 3115 cm$^{-1}$, 1622 cm$^{-1}$, 1604 cm$^{-1}$, 1485 cm$^{-1}$, 1161 cm$^{-1}$, 1020 cm$^{-1}$, 754 cm$^{-1}$, and 592 cm$^{-1}$ are caused by the vibrations of the furan ring.

**Conclusions**

A series of solid acid catalysts were firstly used for the synthesis of fuel precursors F$_2$Cp and FCp from cyclopentanone and furfural derived from hemicellulose in a solvent free system. Nafion exhibited the best performance among the investigated catalysts (Nafion, Amberlyst-15, Amberlyst-36, H-USY, ZSM-5, H–β, SiO$_2$/Al$_2$O$_3$). The effects of dosage of catalyst, reaction temperature, and time are studied. Under the optimized conditions, conversion of furfural was 73.86%, the yields of F$_2$Cp and FCp were 37.48% and 23.77%, respectively. No deactivation was observed during 4 continuous runs. Mechanism of aldol condensation of furfural and cyclopentanone was proposed in detail. Meanwhile, a certain amount of humins also formed in the reaction process, and the products were characterized using FT-IR spectra.

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