

Cite this: *RSC Adv.*, 2017, 7, 16901

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

Wei Wang,^{*ab} Xiaohui Ji,^a Hongguang Ge,^a Zhizhou Li,^a Guanghui Tian,^a Xianzhao Shao^a and Qiang Zhang^a

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.

Received 26th February 2017
Accepted 13th March 2017

DOI: 10.1039/c7ra02396k

rsc.li/rsc-advances

Introduction

Utilization of renewable biomass for the production of fuels and chemicals has drawn worldwide attention as concerns grow over diminishing petroleum sources, greenhouse effect, and environmental pollution.^{1–6} Diesel and jet fuels are two kinds of frequently used transportation fuels mainly obtained from petrochemical engineering. In recent years, biomass diesel and jet fuels have been used as important fungible fuels owing to their renewability, low toxicity, low sulfur content, high octane number, and biodegradability.^{7–10} Lignocellulose is the major component of agriculture wastes or forest residues. Following the pioneering work of Dumesic *et al.*^{11–13} and Huber *et al.*,^{14,15} the synthesis of renewable diesel and jet-fuel-range alkanes with lignocellulose-derived platform chemicals has attracted increasing attention. Furfural is an important raw material obtained on an industrial scale by the hydrolysis/dehydration of hemicellulose.^{16–18} In recent studies, C₈ and C₁₃ oxygenates were produced through aldol condensation of furfural and acetone.^{14,19–22} Oxygenated derivatives of furfural were obtained by aldol condensation with methyl isobutyl ketone, pentanone, hexanone, and other biomass feedstock or hydroxyalkylation/alkylation with methyl furan.²³ These oxygenates can be converted to alkanes by low-temperature hydrogenation and hydrodeoxygenation (HDO).

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 furfural^{33,34} or itself.^{35–38} It can also react with 2-methyl furan through hydroxyalkylation/alkylation,^{9,39,40} 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

^aSchool of Chemistry and Environment Science, Shaanxi University of Technology, Hanzhong, 723001, China. E-mail: wangwei@sntu.edu.cn; Tel: +86 916 2641660

^bShaanxi Key Laboratory of Catalysis, Shaanxi University of Technology, Hanzhong, 723001, China

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c7ra02396k

compounds containing active α -hydrogen atoms (such as aldehyde, ketone, carboxylic acid, and ester), nucleophilic addition to obtain β -hydroxyl compounds, and then further dehydration to generate α , β -unsaturated carbonyl compounds. It could take place in homogeneous aqueous (or water/alcohol) solutions¹⁵ and biphasic systems.^{33,42} 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 (F₂Cp) 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- β , and SiO₂/Al₂O₃). Furthermore, we also studied the effects of catalyst dosage, reaction temperature, and time on the conversion of furfural and yields of F₂Cp 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 (SiO₂/Al₂O₃ = 12), ZSM-5 (SiO₂/Al₂O₃ = 25), and H- β (SiO₂/Al₂O₃ = 25) zeolites used in this work were provided by Catalyst Factory of Nankai University. SiO₂-Al₂O₃ (SiO₂/Al₂O₃ = 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. F₂Cp 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 reflex 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 F₂Cp

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 solid was humins.

Analysis

The concentrations of F₂Cp, FCp, and furfural were determined by an Agilent 1260 high performance liquid chromatography (HPLC) system, equipped with a ZORBAXSB-C₁₈ column (4.6 mm \times 150 mm, 5 μ 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 ¹H and ¹³C NMR sample preparation. Chemical shifts, quoted in ppm, are relative to the internal standards of the singlet at δ = 0 ppm for TMS for ¹H NMR and the middle peak of the CDCl₃ triplet at δ = 77 ppm for ¹³C 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 F₂Cp and FCp were calculated by the following formulas:

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

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

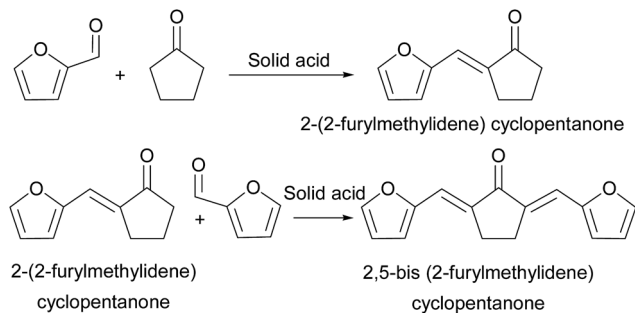
$$\text{Yield of F}_2\text{Cp (\%)} = \frac{2 \times \text{moles of F}_2\text{Cp}}{\text{moles of furfural input}} \times 100\%$$

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 (p S2 in ESI†) and NMR (p S3, S4 in ESI†) spectra, F₂Cp (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 F₂Cp was the product of aldol condensation between FCp further with furfural. The NMR spectra (p S3 in ESI†) of F₂Cp show the following peaks: ¹H NMR (CDCl₃-d), δ : 7.80 (s, 2H), 7.56 (s, 2H), 6.90 (t, 2H), 6.75 (m, 2H), 3.28 (t, 4H); ¹³C NMR (CDCl₃-d), δ : 195 (1C), 152 (2C), 144 (2C), 135 (2C), 119 (2C), 116 (2C), 112 (2C),





Scheme 1 Reaction route of aldol condensation of furfural and cyclopentanone.

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 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 Nafion, Amberlyst-15, and Amberlyst-36 resins than under catalysis by H-USY, HZSM-5, H- β , SiO₂/AlO₃ under the same reaction conditions.

The sequence for the yield of F₂Cp, FCp over the solid acid catalysts was Nafion > Amberlyst-15 > Amberlyst-36 > H- β , H-USY, ZSM-5, SiO₂/Al₂O₃. This sequence is consistent with that of the Hammett acidity function ($-H_o$) values of these catalysts (see Table 1). Therefore, the higher catalytic efficiency of Nafion resin can be attributed to the higher strength of acid sites on this catalyst. The higher acid strength of Nafion resin is dependent on by its structure. As we know, Nafion is

Table 1 Average pore sizes, acid amounts and Hammett acidity function ($-H_o$) values of the different solid acid catalysts used in the aldol condensation of furfural and cyclopentanone^a

Catalyst	Acid amount (mmol g ⁻¹)	Average pore size (nm)	$-H_o$
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. 50)
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)

^a According to the information provided by supplier.

a perfluorinated sulfonic acid resin,⁴⁷ while Amberlyst resins are sulfonic-acid-functionalized cross-linked polystyrene.⁴⁸ The presence of fluorine on the Nafion resin greatly enhances the acid strength of the $-SO_3H$ 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

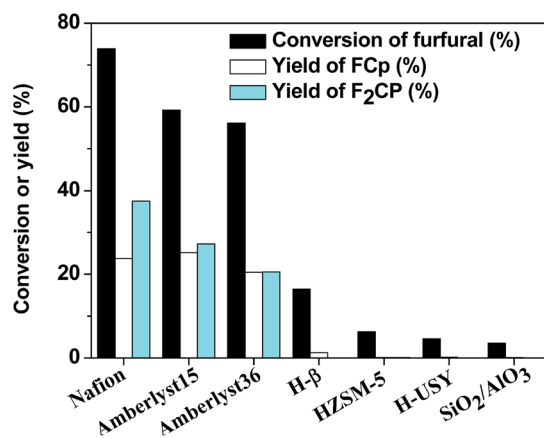


Fig. 1 The aldol condensation of furfural and cyclopentanone over various heterogeneous catalysts. Reaction conditions: 60 °C, 6 h; 1.92 g (20 mmol) furfural, 5.04 g (60 mmol) cyclopentanone, 0.40 g catalyst.

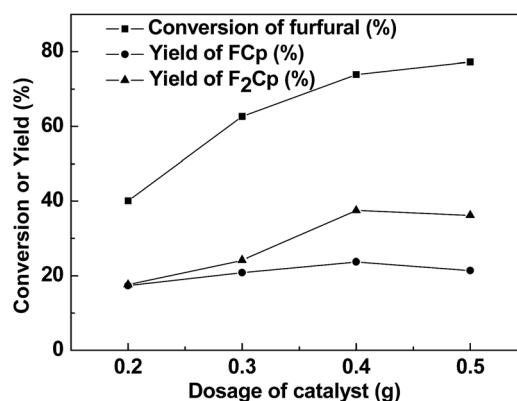


Fig. 2 The effect of the catalyst dosage on the aldol condensation. Reaction conditions: 60 °C, 6 h; 1.92 g (20 mmol) furfural, 5.04 g (60 mmol) cyclopentanone.



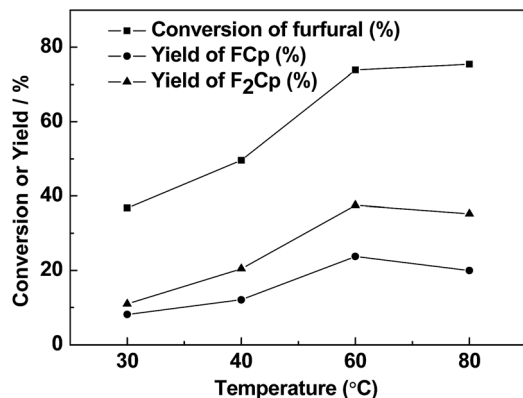


Fig. 3 The effect of reaction temperature on the aldol condensation. Reaction conditions: 0.40 g Nafion catalyst, 6 h; 1.92 g (20 mmol) furfural, 5.04 g (60 mmol) cyclopentanone.

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 Nafion 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, Nafion 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 Nafion 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 Nafion catalyst in solvent-free conditions gave a conversion of

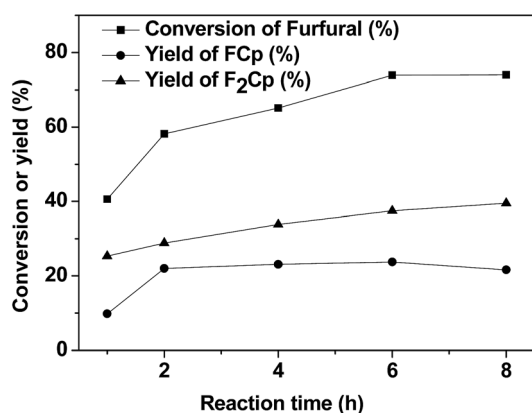


Fig. 4 The effect of reaction time on the aldol condensation. Reaction conditions: 0.40 g Nafion catalyst, 1.92 g (20 mmol) furfural, 5.04 g (60 mmol) cyclopentanone at 60 °C.

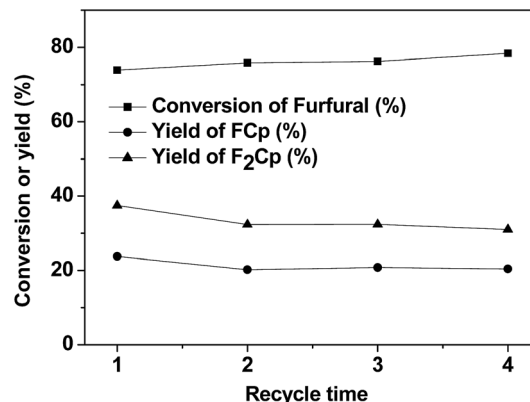
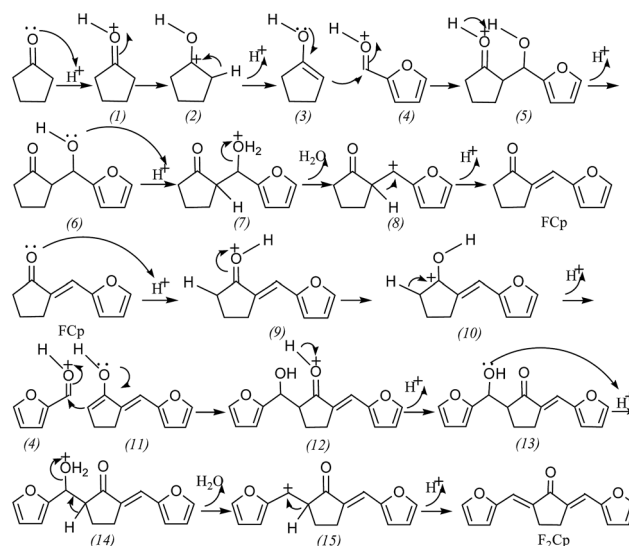


Fig. 5 The recyclability of Nafion resin for the aldol condensation. Reaction conditions: 60 °C, 6 h; 1.92 g (20 mmol) furfural, 5.04 g (60 mmol) cyclopentanone, and 0.40 g of Nafion.

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 carbocation (2). Carbanion and H⁺ were gained by electron heterolytic formation of α -C-H σ bond of carbocation. 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



Scheme 2 Reaction mechanism of aldol condensation from furfural and cyclopentanone by solid acid catalysis.

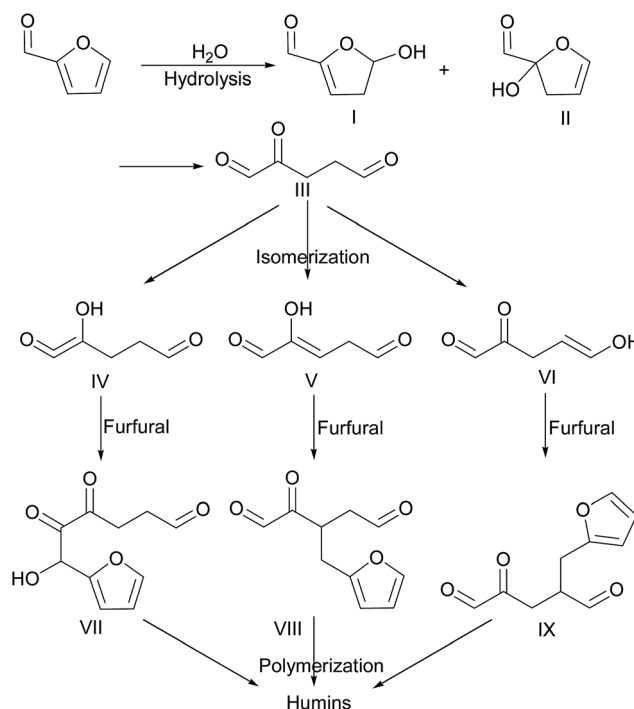


transferred to the electron-deficient oxygen of carbonyl. At the same time, the C=C π electrons of intermediate (3) attack the electron-deficient carbon of intermediate (4) to form a C-C bond and the lone pair on the oxygen atom transferred to the adjacent carbon atoms to form C=C gave rise to the structure 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 σ bond is transferred and proton is released to form the product FCp.

The carbonyl of FCp is protonated to obtain intermediate (9), and the π 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 proton and forms intermediate (13). The intermediate (13) is protonated to form intermediate (14), and then releases a water molecule to form intermediate (15) (σ bond shift). At the same time, proton is removed to form the product F₂Cp. This reaction mechanism is similar to that of acetophenone and benzaldehyde under the catalysis of sulfuric acid.⁵¹

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.^{52–54} The open ring of intermediates I and II generate 2-oxo pentanedial (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 hexanal (VII), 2-oxo-3-tetrahydrofuran methylene pentanedial (VIII), and 2-oxo-4-tetrahydrofuran methylene pentanedial (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 F₂Cp and FCp were 37.48% and 23.77%, respectively. Selectivities of F₂Cp 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



Scheme 3 Formation mechanism of humins.

film formed on the surface of the Nafion 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 CH₂ bond stretching vibration owing to polymerization. The weak absorption peak at 1735 cm^{-1} is due to the stretching vibration of the C=O bonds in aldehyde groups. The strong absorption peaks at 1707 cm^{-1} and 1681 cm^{-1} are caused by the stretching vibration of C=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

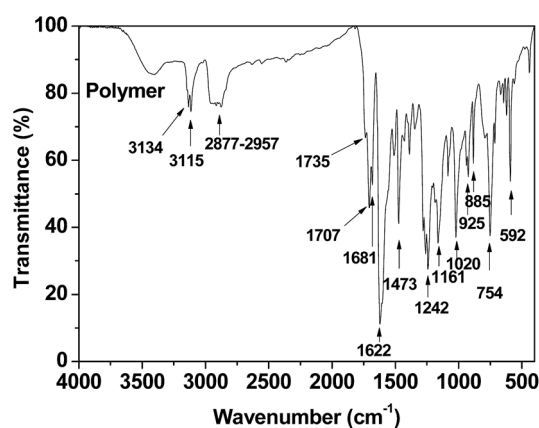


Fig. 6 Infrared spectra of furfural polymers.



bending vibrations in CH₂ 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 F₂Cp 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, SiO₂/Al₂O₃). 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 F₂Cp 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.

Acknowledgements

This study was supported by the Education Department of Shaanxi Provincial Government Research Project (No. 16JK1146), the National Natural Science Foundation of China (No. 21503125, 21502109), and the Funds of Research Programs of Shaanxi University of Technology (No. SLGQD13(2)-1).

Notes and references

- G. W. Huber and A. Corma, *Chem. Rev.*, 2006, **106**, 4044–4098.
- C. Zhao, Y. Kou, A. A. Lemonidou, X. Li and J. A. Lercher, *Angew. Chem., Int. Ed.*, 2009, **48**, 3987–3990.
- D. M. Alonso, J. Q. Bond, J. C. Serrano-Ruiz and J. A. Dumesic, *Green Chem.*, 2010, **12**, 992–999.
- M. J. Climent, A. Corma and S. Iborra, *Green Chem.*, 2014, **16**, 516–547.
- C. Zhao and J. A. Lercher, *Angew. Chem., Int. Ed.*, 2012, **51**, 5935–5940.
- T. D. Matson, K. Barta, A. V. Iretskii and P. C. Ford, *J. Am. Chem. Soc.*, 2011, **133**, 14090–14097.
- S. Li, N. Li, G. Li, A. Wang, Y. Cong, X. Wang and T. Zhang, *Catal. Today*, 2014, **234**, 91–99.
- G. Li, N. Li, S. Li, A. Wang, Y. Cong, X. Wang and T. Zhang, *Chem. Commun.*, 2013, **49**, 5727–5729.
- G. Li, N. Li, X. Wang, X. Sheng, S. Li, A. Wang, Y. Cong, X. Wang and T. Zhang, *Energy Fuels*, 2014, **28**, 5112–5118.
- G. Nie, X. Zhang, P. Han, J. Xie, L. Pan, L. Wang and J.-J. Zou, *Chem. Eng. Sci.*, 2017, **158**, 64–69.
- J. Q. Bond, D. M. Alonso, D. Wang, R. M. West and J. A. Dumesic, *Science*, 2010, **327**, 1110–1114.
- D. A. S. Edward, L. Kunkes, R. M. West, J. C. Serrano-Ruiz, C. A. Gärtner and J. A. Dumesic, *Science*, 2008, **322**, 417–421.
- G. W. Huber, J. N. Chheda, C. J. Barrett and J. A. Dumesic, *Science*, 2005, **308**, 1446–1450.
- H. Olcay, A. V. Subrahmanyam, R. Xing, J. Lajoie, J. A. Dumesic and G. W. Huber, *Energy Environ. Sci.*, 2013, **6**, 205–216.
- R. Xing, A. V. Subrahmanyam, H. Olcay, W. Qi, G. P. van Walsum, H. Pendse and G. W. Huber, *Green Chem.*, 2010, **12**, 1933–1946.
- I. Agirrezabal-Telleria, J. Requies, M. B. Güemez and P. L. Arias, *Appl. Catal., B*, 2012, **115–116**, 169–178.
- P. Azadi, R. Carrasquillo-Flores, Y. J. Pagán-Torres, E. I. Gürbüz, R. Farnood and J. A. Dumesic, *Green Chem.*, 2012, **14**, 1573–1576.
- E. I. Gürbüz, S. G. Wettstein and J. A. Dumesic, *ChemSusChem*, 2012, **5**, 383–387.
- Q. N. Xia, Q. Cuan, X. H. Liu, X. Q. Gong, G. Z. Lu and Y. Q. Wang, *Angew. Chem., Int. Ed.*, 2014, **53**, 9755–9760.
- W. Shen, G. A. Tompsett, K. D. Hammond, R. Xing, F. Dogan, C. P. Grey, W. C. Conner, S. M. Auerbach and G. W. Huber, *Appl. Catal., A*, 2011, **392**, 57–68.
- R. M. West, Z. Y. Liu, M. Peter, C. A. Gärtner and J. A. Dumesic, *J. Mol. Catal. A: Chem.*, 2008, **296**, 18–27.
- M. Chatterjee, K. Matsushima, Y. Ikushima, M. Sato, T. Yokoyama, H. Kawanami and T. Suzuki, *Green Chem.*, 2010, **12**, 779–782.
- G. Li, N. Li, Z. Wang, C. Li, A. Wang, X. Wang, Y. Cong and T. Zhang, *ChemSusChem*, 2012, **5**, 1958–1966.
- J. Guo, G. Xu, Z. Han, Y. Zhang, Y. Fu and Q. Guo, *ACS Sustainable Chem. Eng.*, 2014, **2**, 2259–2266.
- M. Hronec, K. Fulajtárová and T. Liptaj, *Appl. Catal., A*, 2012, **437–438**, 104–111.
- M. Hronec, K. Fulajtárová and M. Mičušík, *Appl. Catal., A*, 2013, **468**, 426–431.
- M. Hronec, K. Fulajtárová, I. Vávra, T. Soták, E. Dobročka and M. Mičušík, *Appl. Catal., B*, 2016, **181**, 210–219.
- M. Hronec and K. Fulajtárová, *Catal. Commun.*, 2012, **24**, 100–104.
- X.-Y. Li, R. Shang, M.-C. Fu and Y. Fu, *Green Chem.*, 2015, **17**, 2790–2793.
- Y. Yang, Z. Du, Y. Huang, F. Lu, F. Wang, J. Gao and J. Xu, *Green Chem.*, 2013, **15**, 1932–1940.
- H. Zhu, M. Zhou, Z. Zeng, G. Xiao and R. Xiao, *Korean J. Chem. Eng.*, 2014, **31**, 593–597.
- M. Hasni, G. Prado, J. Rouchaud, P. Grange, M. Devillers and S. Delsarte, *J. Mol. Catal. A: Chem.*, 2006, **247**, 116–123.
- M. Hronec, K. Fulajtárová, T. Liptaj, M. Štolcová, N. Prónayová and T. Soták, *Biomass Bioenergy*, 2014, **63**, 291–299.
- M. Hronec, K. Fulajtárová, T. Liptaj, N. Prónayová and T. Soták, *Fuel Process. Technol.*, 2015, **138**, 564–569.
- J. Yang, N. Li, G. Li, W. Wang, A. Wang, X. Wang, Y. Cong and T. Zhang, *Chem. Commun.*, 2014, **50**, 2572–2574.
- X. Sheng, N. Li, G. Li, W. Wang, J. Yang, Y. Cong, A. Wang, X. Wang and T. Zhang, *Sci. Rep.*, 2015, **5**, 9565.



- 37 W. Wang, N. Li, G. Li, S. Li, W. Wang, A. Wang, Y. Cong, X. Wang and T. Zhang, *ACS Sustainable Chem. Eng.*, 2017, **5**, 1812–1817.
- 38 Q. Deng, G. Nie, L. Pan, J.-J. Zou, X. Zhang and L. Wang, *Green Chem.*, 2015, **17**, 4473–4481.
- 39 X. Zhang, Q. Deng, P. Han, J. Xu, L. Pan, L. Wang and J.-J. Zou, *AIChE J.*, 2017, **63**, 680–688.
- 40 Q. Deng, P. Han, J. Xu, J.-J. Zou, L. Wang and X. Zhang, *Chem. Eng. Sci.*, 2015, **138**, 239–243.
- 41 Q. Deng, J. Xu, P. Han, L. Pan, L. Wang, X. Zhang and J.-J. Zou, *Fuel Process. Technol.*, 2016, **148**, 361–366.
- 42 J. N. Chheda, G. W. Huber and J. A. Dumesic, *Angew. Chem., Int. Ed.*, 2007, **46**, 7164–7183.
- 43 L. Faba, E. Diaz and S. Ordonez, *ChemSusChem*, 2013, **6**, 463–473.
- 44 J. Yang, N. Li, G. Li, W. Wang, A. Wang, X. Wang, Y. Cong and T. Zhang, *ChemSusChem*, 2013, **6**, 1149–1152.
- 45 J. Yang, N. Li, S. Li, W. Wang, L. Li, A. Wang, X. Wang, Y. Cong and T. Zhang, *Green Chem.*, 2014, **16**, 4879–4884.
- 46 R. E. O'Neill, L. Vanoye, C. De Bellefon and F. Aiouache, *Appl. Catal., B*, 2014, **144**, 46–56.
- 47 K. A. M. a. R. B. Moore, *Chem. Rev.*, 2004, **104**, 4535–4586.
- 48 R. Weingarten, G. A. Tompsett, W. C. Conner and G. W. Huber, *J. Catal.*, 2011, **279**, 174–182.
- 49 M. Cadenas, R. Bringué, C. Fité, E. Ramírez and F. Cunill, *Top. Catal.*, 2011, **54**, 998–1008.
- 50 J. Jae, G. A. Tompsett, A. J. Foster, K. D. Hammond, S. M. Auerbach, R. F. Lobo and G. W. Huber, *J. Catal.*, 2011, **279**, 257–268.
- 51 D. S. Noyce and W. A. Pryor, *J. Am. Chem. Soc.*, 1955, **77**, 1397–1401.
- 52 S. K. R. Patil, J. Heltzel and C. R. F. Lund, *Energy Fuels*, 2012, **26**, 5281–5293.
- 53 S. K. R. Patil and C. R. F. Lund, *Energy Fuels*, 2011, **25**, 4745–4755.
- 54 I. van Zandvoort, Y. Wang, C. B. Rasrendra, E. R. H. van Eck, P. C. A. Bruijninx, H. J. Heeres and B. M. Weckhuysen, *ChemSusChem*, 2013, **6**, 1745–1758.

