



Cite this: *RSC Adv.*, 2018, 8, 37993

Production of cyclopentanone from furfural over Ru/C with Al_{11.6}PO_{23.7} and application in the synthesis of diesel range alkanes†

Tao Shen,^{ab} Ruijia Hu,^{ab} Chenjie Zhu,^{abc} Ming Li,^{ab} Wei Zhuang,^{ab} Chenglun Tang^{ab} and Hanjie Ying^{abc}

The bio-based platform molecule furfural was converted to the high value chemical cyclopentanone over Ru/C (0.5 wt%) and Al_{11.6}PO_{23.7} catalysts in good yield (84%) with water as the medium. After screening the reaction conditions, the selectivity for cyclopentanone and cyclopentanol could be controlled by adjusting the hydrogen pressure at the temperature of 433 K. Herein, we propose a new mechanism for the synergistic catalysis of a Bronsted acid and Lewis acid for the conversion of furfural to cyclopentanone through the cyclopentenone route, which is catalyzed by Ru/C and Al_{11.6}PO_{23.7}. In addition, based on cyclopentanone, higher octane number cyclic alkanes (>85% selectivity), which are used as hydrocarbon fuels, were synthesized *via* a C–C coupling reaction followed by hydrodeoxygenation.

Received 23rd October 2018
 Accepted 26th October 2018

DOI: 10.1039/c8ra08757a

rsc.li/rsc-advances

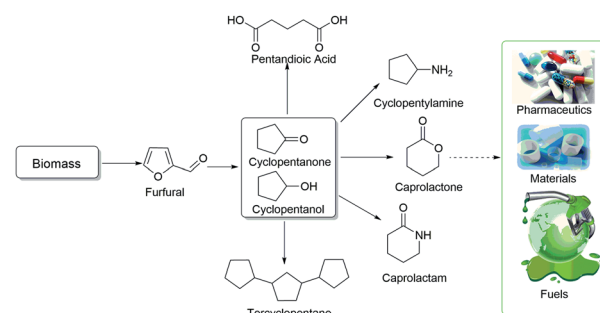
Introduction

With the depletion of petroleum resources, the exploitation of renewable resources has drawn increasing attention.^{1,2} Biomass is a renewable resource due to its abundant sources and short growth periods.^{3,4} Recently, accompanied by the successful synthesis of platform molecules from lignocellulose, the catalytic conversion technology of transforming biomass into high-value chemicals has shown great progress. Various furan-based derivatives can be produced *via* the acid-catalyzed dehydration of cellulose and hemicellulose.^{5–9} For example, furfural (FFA) can be produced on an industrial scale from biomass.¹⁰ Based on this, the catalytic hydrogenation and dehydration of furfural to a range of nonpetroleum-derived chemicals is significant, including 2-methyl furan (2-MF),¹¹ furfural alcohol (FAL),¹² tetrahydrofurfuryl alcohol (THFA),¹³ tetrahydrofuran (THF),¹⁴ 2-methyl tetrahydrofuran (MTHF),¹⁵ levulinic acid (LA),¹⁶ and pentanediol.^{17,18} These chemical intermediates can be used in the fields of materials, fuels and pharmaceuticals.^{19–23}

Cyclopentanone (CPO) is another hydrogenation product of furfural, and cyclopentanol (CPL) is the depth hydrogenation product of CPO. CPO and CPL are versatile chemical intermediates that can be used to synthesize medicines, rubber chemicals and fragrance chemicals, which are applied in pharmaceuticals,

fuel energy and materials (Scheme 1).^{24–29} Traditionally, CPO and CPL are synthesized *via* the ketonic decarboxylation of adipic acid or catalytic cyclization of 1, 6-hexanediol, followed by hydrogenation.^{30,31} Recently, based on lignocellulose, a new route was proposed, in which furfural was converted to CPL with no petroleum compounds as the substrates.

Inspired by the previous work of the Hronec group,^{32–34} new methods have been reported regarding furfural or furfuryl alcohol after hydrogenation and following rearrangement in aqueous media to synthesize CPO. These studies showed that hydrogenation metal catalysts (*e.g.*, Pt/C, Pd–Cu/C and Ni-based catalysts) have good selectivity for CPO. Besides, hydrogenation metal-based solid acid and solid base were also found to have good performance for the synthesis of CPO and CPL from furfural, for example, Ru/MIL-101 (Materials of Institute Lavoisier),³⁵ Ru/carbon nanotubes (CNTs),³⁶ Au/TiO₂,³⁷ Ni/CNTs,³⁸ and Ni/Cu–Mg–Al hydrotalcite.³⁹ In addition, alloy catalysts were also found to be efficient catalysts for the conversion of



Scheme 1 Methods for the conversion of CPO and CPL from biomass and their application.

^aCollege of Biotechnology and Pharmaceutical Engineering, Nanjing Tech University, Nanjing, China. E-mail: zhucj@njtech.edu.cn; yinghanjie@njtech.edu.cn

^bNational Engineering Technique Research Center for Biotechnology, Nanjing, China
^cJiangsu National Synergetic Innovation Center for Advanced Bio-Manufacture, Nanjing, China

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c8ra08757a



furfural converted CPO (*e.g.*, Ni–Cu/SBA-15,⁴⁰ Cu–Co alloy,⁴¹ CuZnAl and CuNiAl hydrotalcite^{42,43}). Considering the reported catalysts, higher selectivity for CPL can be obtained while in catalytic systems consisting of hydrogenation catalyst and solid acid.

Although some pioneering works have been performed in this area, this field is still lacking regarding some detailed processes. For example, the understanding of the mechanism in the cyclization process of the product is still in its infancy. Herein, we report the design of a new catalyst, aluminium phosphate ($\text{Al}_{11.6}\text{PO}_{23.7}$) and Ru/C, which is used in an aqueous environment to give a good yield of CPO and CPL. Additionally, the selectivity of the targeted product could be controlled by adjusting the hydrogen pressure. $\text{Al}_{11.6}\text{PO}_{23.7}$ is a bifunctional catalyst that has both an acid site and base site;⁴⁴ thus, we could adjust the mole ratio of Al and P to control the amount of acid and base, and also control the ratio of Lewis acid and Bronsted acid. According to these properties, different mole ratios of Al and P catalysts were prepared to study the influence factors and cyclization mechanism during the hydrogenation of furfural in aqueous media. This is a novel and efficient catalytic system in this process, which, to the best of our knowledge, has not been previously reported in this area.

CPO and 2-MF are novel products from the hydrogenation of furfural. Both are C5 feedstocks for the synthesis of long carbon cyclic alkanes. In our previous reports, carbonyl compounds through the C–C coupling reaction consisting of aldol condensation or HAA (hydroxyalkylation and alkylation) reaction with furan-based derivatives were prepared as fuel precursors, which were applied to the synthesis of liquid hydrocarbon fuels through hydrodeoxygenation.^{45–47} Here, we design a new route for the synthesis of cyclic alkanes for use in diesel range fuels from the hydrogenation product of furfural.

Results and discussion

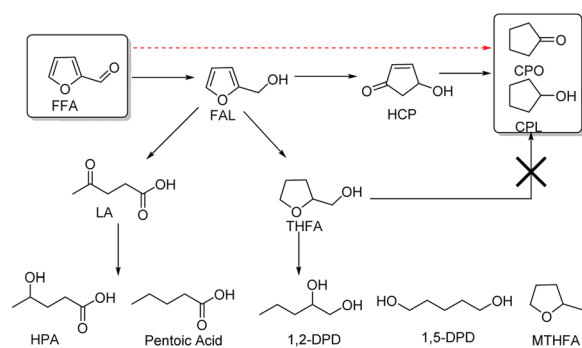
Hydrogenation of furfural to CPO or CPL

Building on the result of furfural after hydrogenation, FAL and THFA are the normal hydrogenation products.^{17,18} Under acidic and basic reaction conditions, dehydroxylation and ring opening rearrangement products (*e.g.*, FAL, THFA, MTHFA, LA, and pentanediol) can be obtained, respectively.^{16,19–23} CPO is the

hydrogenation and Piancatelli rearrangement product of furfural.³⁷ In this process (Scheme 2), furfural is firstly hydrogenated to furfuryl alcohol. If furfuryl alcohol undergoes a Piancatelli rearrangement, the product will be 4-hydroxy-2-cyclopentenone (HCP), which will then undergo in-depth hydrogenation and dehydroxylation to produce CPO or CPL. However, furfuryl alcohol in a Bronsted acid environment is dehydroxylated and undergoes a ring opening rearrangement reaction, and then, levulinic acid and in-depth hydrogenation compounds are obtained as the products.⁴⁹ Additionally, self-condensation of CPO can occur while in an acidic environment. These are the major factors that limit the yield of CPO. The hydrogenation metal catalyst is another factor that limits the yield of the product in this reaction. A higher hydrogenation efficiency catalyst would convert furfural into THFA, which is irreversibly transformed into CPO.³⁶ To our delight, after screening the hydrogenation metal and solid acid catalyst (entries 1–10), we found that aluminium phosphate and Ru/C were favorable catalysts for this reaction.

According to the previous research, solid acid is an important factor that influences the selectivity of LA and others. Considering all of the factors in the rearrangement process, we screened HfO_2 and TFA/ SiO_2 as well as different mole ratios of Al and P aluminium phosphate solid acid catalysts as ring opening and rearrangement catalysts. Among them, HfO_2 has a pure Lewis acid site, TFA/ SiO_2 is representative Bronsted acid catalyst, and aluminium phosphate has an adjustable ratio of L/B acid sites. From the results presented in Table 1 (entries 1–7), we found that HfO_2 and TFA/ SiO_2 had poor selectivity for CPO and CPL. This phenomenon illustrated that the cyclization rearrangement is not a simple Lewis or Bronsted acid catalyzed rearrangement reaction. However, after screening different mole ratios of Al- and P-type aluminium phosphate catalysts, we found that aluminium phosphate well-catalyzed the rearrangement. Additionally, the higher the molar ratio of the Al- and P-type aluminium phosphate catalyst, the better the selectivity for CPL and CPO. To determine the ultimate mole ratio of Al and P for this catalyst, we used 20 portions of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 1 portion of $(\text{NH}_4)_2\text{HPO}_4$ to prepare the aluminium phosphate catalyst. After XPS analysis of these catalysts (Fig. S1†), the maximum mole ratio of Al and P was determined to be 11.6 and the atomic levels of O 1s, Al 2p and P 2p were 50.33%, 24.75% and 2.12%, respectively (Fig. S1†).

Aluminium phosphate is a solid acid-base bifunctional catalyst, as discussed in our previous reports.⁴⁵ After NH_3 -TPD and CO_2 -TPD tests (Fig. S2†), the amount of acidic and basic $\text{Al}_{11.6}\text{PO}_{23.7}$ was found to be 1.211 mmol g^{-1} and 0.705 mmol g^{-1} , respectively. Also, the ratio of Lewis/Bronsted acid can be adjusted by changing the mole ratio of Al and P. Different mole ratios of Al and P (*e.g.*, 0.5, 1, 2, 5, and 20) aluminium phosphate catalysts were prepared to test in this reaction. After XPS analysis of these catalysts, the molecular formula of the different mole ratio Al and P aluminium phosphate catalysts were found to be $\text{AlP}_{1.2}\text{O}_4$, $\text{Al}_{1.1}\text{PO}_{4.2}$, $\text{Al}_{2.1}\text{PO}_{6.4}$, $\text{Al}_{5.3}\text{PO}_{12}$, $\text{Al}_{11.6}\text{PO}_{23.7}$. From the results presented in Table 1 (entries 3–7), the maximum mole ratio Al and P catalyst, $\text{Al}_{11.6}\text{PO}_{23.7}$, showed the best selectivity for CPO and CPL. Considering the influence of the



Scheme 2 Methods to obtain hydrogenation products from furfural.



Table 1 Results of the hydrogenation of furfural catalyzed by different catalysts^a

Entry	Catalyst	Solvent	Temp.	Con. (FFA)	Product (selectivity)				
					FAL	CPO	CPL	THFA	LA + others
1	Ru/C + TFA/SiO ₂	H ₂ O	433 K	100%	0%	0%	34%	27%	39%
2	Ru/C + HfO ₂	H ₂ O	433 K	100%	0%	5%	46%	32%	17%
3	Ru/C + AlP _{1,2} O ₄	H ₂ O	433 K	100%	0%	4%	47%	13%	36%
4	Ru/C + Al _{1,1} PO _{4,2}	H ₂ O	433 K	100%	0%	3%	64%	17%	19%
5	Ru/C + Al _{2,1} PO _{6,4}	H ₂ O	433 K	100%	0%	0%	72%	11%	17%
6	Ru/C + Al _{5,3} PO ₁₂	H ₂ O	433 K	100%	0%	0%	74%	10%	16%
7	Ru/C + Al _{11,6} PO _{23,7}	H ₂ O	433 K	100%	0%	0%	84%	6%	10%
8	RANEY® Ni + Al _{11,6} PO _{23,7}	H ₂ O	433 K	100%	0%	0%	56%	24%	20%
9	Pd/C + Al _{11,6} PO _{23,7}	H ₂ O	433 K	100%	0%	1%	68%	24%	17%
10 ^b	Pt/C + Al _{11,6} PO _{23,7}	H ₂ O	433 K	90%	0%	90%	0%	2%	8%
11 ^c	Ru/C + Al _{11,6} PO _{23,7}	H ₂ O	433 K	100%	0%	78%	4%	7%	11%
12 ^d	Ru/C + Al _{11,6} PO _{23,7}	H ₂ O	433 K	100%	0%	3%	74%	4%	19%
13 ^e	Ru/C + Al _{11,6} PO _{23,7}	H ₂ O	433 K	96%	0%	70%	5%	4%	21%
14	Ru/C + Al _{11,6} PO _{23,7}	MeOH	433 K	100%	0%	0%	0%	98%	2%
15	Ru/C + Al _{11,6} PO _{23,7}	THF	433 K	100%	0%	0%	0%	96%	4%
16 ^b	Ru/C + Al _{11,6} PO _{23,7}	H ₂ O	413 K	100%	0%	3%	78%	6%	13%
17 ^b	Ru/C + Al _{11,6} PO _{23,7}	H ₂ O	393 K	100%	0%	0%	3%	76%	21%
18	Ru/C + Al _{11,6} PO _{23,7}	H ₂ O	453 K	100%	0%	0%	72%	12%	16%

^a Reaction conditions: Furfural (20 mmol), hydrogenation metal catalyst (0.5 wt%, 0.25 g) and solid acid (0.25 g), 4 MPa H₂, reacted at the given temperature for 4 h. The products were analyzed and detected *via* HPLC. ^b Reacted for 8 hours. ^c Reacted at 2 MPa H₂ pressure.

^d Hydrogenation metal catalyst respect to 0.25 wt%. ^e Substrate furfural respect to 40 mmol.

ratio of Lewis/Bronsted acid and that Al_{11,6}PO_{23,7} had the best catalytic properties, the pyridine-adsorbed infrared spectra were analyzed to characterize the different molar ratio aluminium phosphate catalysts at temperatures of 313 K and 433 K (Fig. 1). From the results presented in Fig. 1 and Table S1,† we found that Al_{11,6}PO_{23,7} had the highest ratio of L/B at the reaction temperature. This result showed that a high amount of Lewis acid with a small amount of Bronsted acid can promote the cyclization rearrangement reaction. However, the pure Lewis acid catalyst HfO₂ had the poor selectivity for CPO. This phenomenon showed that the conversion of furfural to CPO occurs *via* the synergistic catalysis of a Lewis acid and Bronsted acid and that the catalyst must have a moderate ratio of L/B acid at the reaction temperature.

Besides the influence of the solid acid, the hydrogenation metal is another factor that limits the yield of CPL. As observed from Table 1 (entries 7–10), after comparing different hydrogenation metal catalysts, we found that Ru/C was the best catalyst for this reaction. RANEY® Ni and Pd/C had high hydrogenation activity, which was expressed as higher selectivity for THFA as the ultimate product. Furthermore, Pt/C had poor hydrogenation activity in this process since furfural was not completely converted and no CPL product was detected after 8 hours. In addition, different reaction conditions were tested for this reaction. From Table 1, Entry 11, we found CPO as the major product when the hydrogen pressure was

controlled at 2 MPa, which indicates that the selectivity of CPL or CPO can be controlled by adjusting the hydrogen pressure. Also, we decreased the amount of hydrogenation metal catalyst to 0.25 wt% and increased the amount of substrate to 40 mmol, as seen from Table 1, entries 12–13, and we found that a change in the amount of hydrogenation metal catalyst has little influence on the yield of CPL. However, CPO was detected as the major product and furfural had poor conversion with an

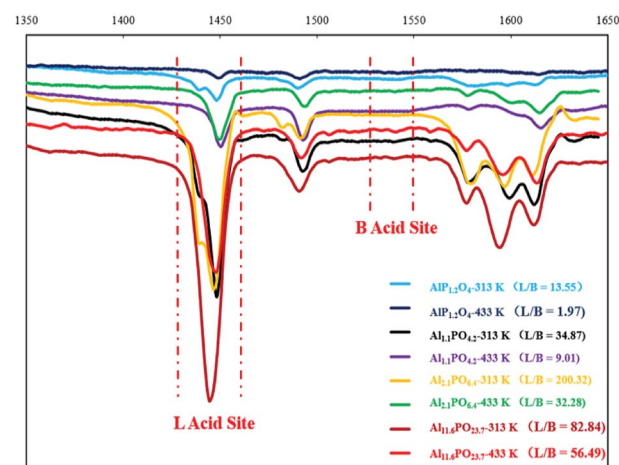


Fig. 1 Pyridine adsorption FT-IR spectroscopy result of different mole ratios of Al and P aluminium phosphate catalyst.



increase in the amount of substrate under the same reaction conditions. This phenomenon proved that hydrogen pressure is a major factor in the yield of CPO. Additionally, it was clearly found that the cyclization rearrangement occurred in the aqueous environment from the result in the Table 1, entries 8, 14–15. Herein, MeOH and THF, as a proton organic solvent and non-protonic organic solvent, were tested in this reaction, respectively. From the results, we found that THFA was the main product obtained in both solvents. Additionally, the reaction temperature is another factor that influenced the major products. From the result in Table 1, entries 8, 16–18, we found that the temperature determined the reaction speed and whether the reaction could be carried out or not. From Table 1, entries 16–17, we found that for the cyclization rearrangement to occur, the reaction temperature had to be over 393 K, and we also found that a higher temperature could increase the reaction speed.

Also, termination of this reaction did not occur during 4 hours at a temperature of 413 K. In addition, the higher temperature promoted the reaction process, but decreased the selectivity of the target product. For example, compared with the lower reaction temperature, more LA and other products were detected at the temperature of 453 K (Table 1, Entry 18). Hence, for the efficient catalysts Ru/C and $Al_{11.6}PO_{23.7}$ with water as the medium at the temperature of 433 K, CPL or CPO can be obtained as the main product. Furthermore, the catalysts can be recovered by filtration and washed with methanol after the reaction. From the results shown in Fig. S6,† it is observed that these catalysts can be reused six times and maintain their catalytic efficiency.

To research the in-depth process of the hydrogenation of furfural to CPO or CPL, different reaction conditions and substrates were used to examine the mechanism of the cyclization process at different reaction times. As observed from Fig. 2(a), an interesting phenomenon was found that differed from the previous report. In the previous work on the preparation of CPO and CPL, furfural was first converted to furfuryl alcohol, followed by Piancatelli rearrangement to HCP and converted to CPO *via* hydrogenation and dehydroxylation. However, from the result shown in Fig. 2(a), no CPO or CPL was obtained with furfuryl alcohol as the substrate at 433 K with Ru/C and $Al_{11.6}PO_{23.7}$ as the catalyst. The hydrogenation of furfuryl alcohol was very fast, and within 20 minutes all of the furfuryl alcohol was converted to levulinic acid (LA), tetrahydrofurfuryl alcohol (THFA) and others. This result is contrary with the previous mechanism of the hydrogenation of furfural to CPO. In addition, different temperatures and hydrogen pressures were tested using furfural as the substrate. From the results shown in Fig. 2(b), we found that at 393 K, furfural could not be converted to CPO. Also, we found that furfural was firstly completely converted to furfuryl alcohol in this process, followed by the conversion of furfuryl alcohol to THFA at a fast rate. Furthermore, conversion of furfuryl alcohol to LA and others was not restricted to these conditions, and the speed at which furfuryl alcohol was converted to LA and others was promoted by a high temperature. Comparing Fig. 2(a) and (b), we can infer that FAL converted to THFA and others at a fast speed under the heating reactor conditions, which is the reason why no targeted products were obtained using FAL as the substrate. In addition, from

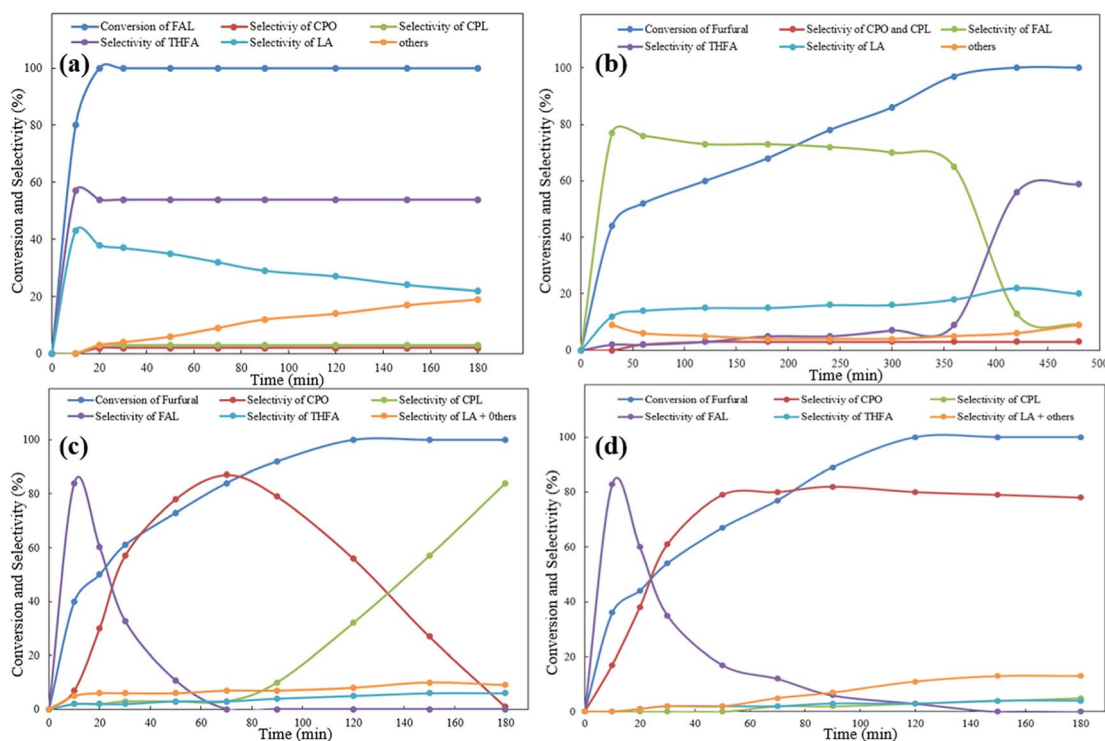


Fig. 2 Conversion and selectivity of different reaction conditions at different times. (a) Furfuryl alcohol (FAL) as the substrate, reacted at the temperature of 433 K, 4 MPa H₂; (b) furfural as the substrate, reacted at the temperature of 393 K, 4 MPa H₂; (c) furfural as the substrate, reacted at the temperature of 433 K, 4 MPa H₂; and (d) furfural as the substrate, reacted at the temperature of 433 K, 2 MPa H₂.



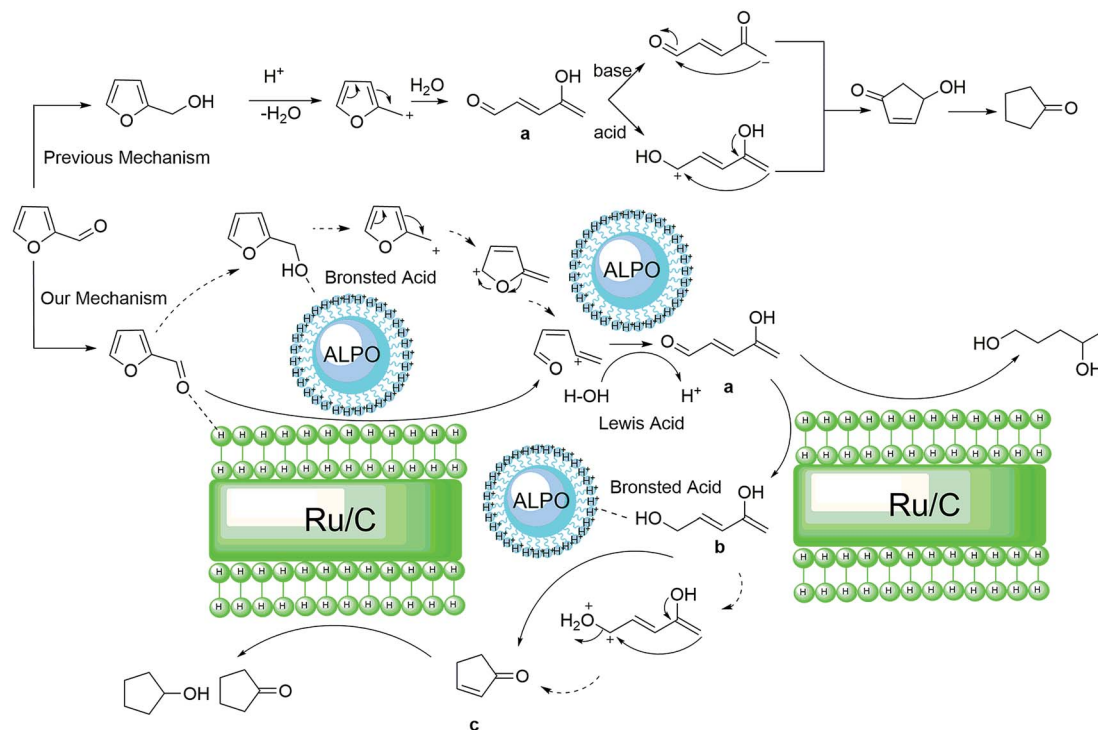


Fig. 3 Mechanism for the conversion of furfural to CPO.

the result shown in Fig. 2(c) and (d), within 10 minutes, the slight conversion of furfural and higher selectivity for FAL were detected in this process. Furthermore, in the following few minutes, the selectivity of FAL decreased acutely, and the selectivity for CPO increased. This phenomenon demonstrated that furfural was converted to FAL, and then FAL converted to CPO immediately in this catalytic system. Additionally, the selectivity for CPO and CPL can be controlled by adjusting the hydrogen pressure.

Encouraged by the previous report, we know that CPO is the hydrogenation and Piancatelli rearrangement product of furfural. During the rearrangement process, furfural is first hydrogenated to furfuryl alcohol. 4-Hydroxy-2-cyclopentenone is the intermediate product, which forms after the Piancatelli rearrangement of furfural alcohol, and then following in-depth hydrogenation and dehydroxylation, cyclopentanone or cyclopentanol is produced. From the previous report,⁵⁰ there are two methods for the formation of 4-hydroxy-2-cyclopentenone (HCP) (Fig. 3). One is the acid catalyzed enol attack of the aldehyde carbocation, followed by cyclization to HCP, and the other is *via* base-catalyzed aldol condensation. However, from the result show in Fig. 2, there no HCP and a little FAL were detected in this process. Hence, furfuryl alcohol conversion to HCP during Piancatelli rearrangement may not be an exclusive method to produce CPO from furfural.

According to the results shown in Fig. 2 and the characterization of the $\text{Al}_{11.6}\text{PO}_{23.7}$ catalyst, we inferred the mechanism of the hydrogenation of furfural to CPO as follows (Fig. 3). Initially, furfural is converted to FAL, which is catalyzed by Ru/C in the hydrogen environment, and then dehydroxylation of FAL occurs

to form the furan methyl carbocation, which is catalyzed by the Bronsted acid site in $\text{Al}_{11.6}\text{PO}_{23.7}$. After that, intermediate **a** (4-hydroxypenta-2,4-dienal) is formed through the carbocation rearrangement, which is catalyzed by the Lewis acid site in $\text{Al}_{11.6}\text{PO}_{23.7}$. In the following step, intermediate **a** is catalyzed by Ru/C and converted to **b** (penta-2,4-diene-1,4-diol) in the hydrogen environment. Finally, dehydroxylation occurs and the hydroxyl group in **b** is catalyzed by $\text{Al}_{11.6}\text{PO}_{23.7}$. Then the cyclopentenone **c** intermediate is formed through the enol attack on the carbocation after dehydroxylation, and CPO is obtained *via* hydrogenation in this process at last. This mechanism is consistent with the result shown in Fig. 2. Additionally, the cyclopentenone **c** was detected at the reaction time of 70 min, and no HCP and FAL were detected at that time (see Fig. 4). This phenomenon is attributed to the Bronsted acid site in $\text{Al}_{11.6}\text{PO}_{23.7}$, which promoted the formation of the furan methyl carbocation. Also, the in-depth hydrogenation product (1,4-

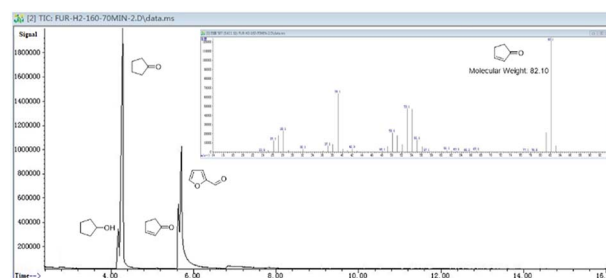
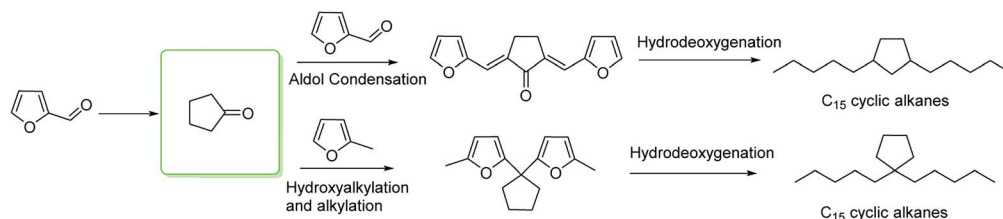


Fig. 4 GC-MS result of furfural conversion to CPO.





Scheme 3 Method for the synthesis of diesel range alkanes based on CPO from hemicellulose.

pentanediol) of intermediate **b** was detected by GC-MS (see Fig. S7†) at a higher hydrogen pressure. This phenomenon demonstrated that intermediates **b** and **c** were formed during this process, and the process of rearrangement was not through the HCP route. This result is consistent with the previous report,³⁴ where cyclopentanone **c** was a promising intermediate in the conversion of furfural to CPO. In addition, based on previous reports,^{51–54} HCP would have been formed at a high temperature with FAL as the substrate. However, as this process was carried out at 433 K during, it is hard to prove that furfuryl alcohol as the substrate through HCP was converted to CPO. Hence, this cyclization reaction is a Bronsted acid and Lewis acid synergistic catalytic process *via* dehydroxylation and hydrogenation.

Hydrodeoxygenation of C–C coupling reaction product


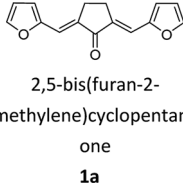
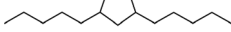

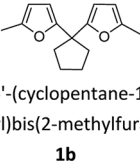

CPO and CPL are versatile chemical intermediates that are applied in various fields of daily life. Inspired by our previous work,^{45–47} cyclopentanone can be used as a substrate to synthesize diesel range fuels due to its carbonyl group. This process consists of two steps. The first step is a C–C coupling reaction (*e.g.*, hydroxyalkylation and alkylation or aldol condensation) to increase the carbon number and octane value. Then, hydrocarbon fuels were obtained after the hydrodeoxygenation of the C–C coupling products (Scheme 3). According to the carbon numbers of the alkanes, we divided these products into light alkanes (C1–C4), gasoline range alkanes (C5–C8) and diesel range alkanes (C9–C16). Herein, we chose furfural and 2-methyl furan as the substrates to couple with CPO for the synthesis of diesel range hydrocarbon fuels, and all of the substrates came from hemicellulose.⁵⁵

Aldol condensation of bio-based carbonyl compounds and furfural was carried out in our previous report.⁴⁷ After comparing mineral bases, organic bases and solid bases, we found that organic amines were efficient catalysts to control the single and double aldol condensation products. TBD (1,5,7-triazabicyclo[4.4.0]dec-5-ene) was identified as an efficient and reusable catalyst for this reaction. Herein, the experiments were carried out in a methanol environment at room temperature, and 10% equivalent catalyst to cyclopentanone was used to catalyze the aldol condensation. To our surprise, a greater than 95% yield of **1a** was obtained after 10 minutes (Table 2, Fig. S9†), and the product was isolated after filtration with no further purification. Furthermore, the catalyst in the solvent could be reused for the next reaction. Hydroxyalkylation and alkylation of cyclopentanone with 2-methylfuran were carried

out to synthesize another fuel precursor. Encouraged by the previous result,^{56–59} the hydroxyalkylation and alkylation reactions were sensitive to the acid strength of the catalyst. A strong acid was more active than weak acid for this reaction. Using *para*-toluenesulfonic acid as a commercially available and efficient catalyst for this reaction, more than 90% yield of **1b** was obtained when 10% equivalent catalyst to cyclopentanone was used at 333 K for 6 hours (Table 2, Fig. S10†). After the reaction, the catalyst and product were separated after extraction with water and ethyl acetate. After concentrating the ethyl acetate and water phases, the catalyst and product were obtained, respectively.

With the aim of synthesizing hydrocarbon fuels, hydrodeoxygenation of C–C coupling products was performed in a batch reactor. Hydrodeoxygenation is both hydrogenation and deoxygenation. This process requires synergistic catalysis between the hydrogenation catalyst and solid acid. Encouraged by our previous work,^{45–47} we found that the commercial catalyst Pd/C added zeolite (H-beta) had the best selectivity for alkanes. During this experiment, 5% equivalent Pd with 0.5 g H-beta (Si/Al = 40) to 5 mmol C–C coupling products was used as the catalyst and reacted at 473 K, and water as the solvent and 3 MPa hydrogen pressure were required simultaneously. After hydrodeoxygenation, the gas product was detected by GC with a TCD detector and the liquid product was extracted with ethyl acetate and detected with GC-MS (Fig. S8†). From the result in Fig. 5 and 6, hydrodeoxygenation of the aldol condensation product gives more than 50% yield of theoretical product, which

Table 2 Structures of the fuel precursors and their theoretical HDO products

Substrate	Fuel precursor	Theoretical alkane product
 Furfural	 2,5-bis(furan-2-ylmethylene)cyclopentan-1-one 1a	 C ₁₅ H ₃₀ cyclic alkane 2a
 2-methylfuran	 5,5'-(cyclopentane-1,1-diy)bis(2-methylfuran) 1b	 C ₁₅ H ₃₀ cyclic alkane 2b



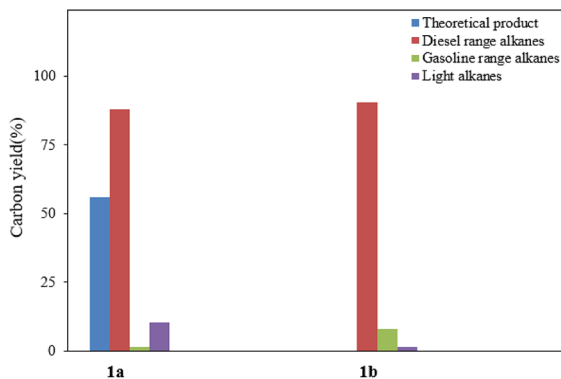


Fig. 5 Carbon yield of different alkanes from the HDO of different precursors over the Pd/C + H-beta system. The diesel range alkanes, gasoline range alkanes and light alkanes represent C₉–C₁₈, C₅–C₈ and C₁–C₄ alkanes, respectively.

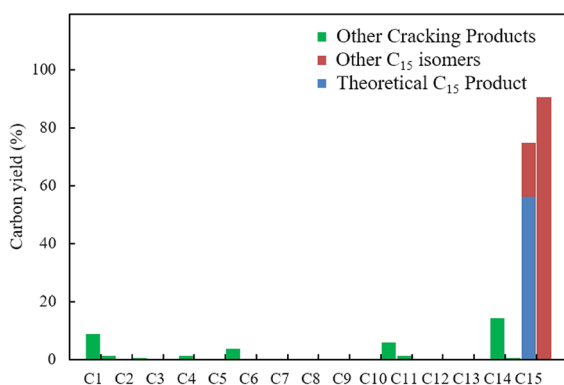


Fig. 6 Product distribution of alkanes from the HDO of the fuel precursors (left: 1a and right: 1b).

is also accompanied by isomerization and decarbonylation. To our delight, a small amount of C11 and C14 cyclic alkanes was detected, which belong to the diesel range alkanes. However, it is unfortunate that there was no theoretical product produced after hydrodeoxygenation of the hydroxyalkylation and alkylation product. This phenomenon is attributed to the stability of the carbocation, where C–C cleavage of 2 at the carbon atom adjacent to the furan ring generated a tertiary carbocation, and the formation of the most stable tertiary carbocation led to the C–C cleavage products during hydrodeoxygenation. From the results shown in Fig. 5 and S12,[†] according to the different cracking cleavage, more than 85% yield of C15 isomer alkanes were obtained. To our delight, regarding the specificity of cyclopentyl, hexatomic ring cyclic alkanes were obtained from the cracking of cyclopentyl and subsequent rearrangement, and the final products C10 and C15 cyclic alkanes in the range of diesel fuels. Hence, based on cyclopentanone, the C–C coupling reaction followed by hydrodeoxygenation is an effective method to prepared cyclic alkanes. Compared to straight chain alkanes, cyclic alkanes have higher densities and volumetric heating values due to the strong ring strain. Also, cyclic alkanes are the second most abundant component in commercial and military jet fuels, at a mass percent of 20–50 wt%.^{60–63}

Experimental

Catalyst preparation

All reagents used in this work were of analytical reagent grade, commercially available and used without further purification. Amorphous aluminium phosphate (AlPO) was prepared according to the reported procedure.⁴⁸ In a typical synthesis of AlPO (Al/P = 1), Al(NO₃)₃·9H₂O and (NH₄)₂HPO₄ based on a mole ratio of Al/P = 1 were dissolved in water acidified with nitric acid. Concentrated ammonia was added to this solution, and a hydrogel was achieved at pH = 8. The above hydrogel solution was stirred for 1 h and then the solvent was filtered, and the hydrogel was washed with distilled water twice. The hydrogel was dried at 120 °C for 12 h and calcined at 550 °C at a heating rate of 5 °C min^{−1} in air for 30 min. The other AlPO catalyst with different mole ratios of Al/P (*e.g.*, Al₁₀PO, Al₅PO, Al₂PO, AlP₂O) were prepared according to the abovementioned method, but using different mole ratios of Al(NO₃)₃·9H₂O and (NH₄)₂HPO₄.

Hafnium oxide was prepared *via* calcination of hafnium hydroxide hydrate. Typically, the hydrogel was prepared *via* the dropwise addition of a concentrated ammonia solution to an aqueous solution of HfCl₄ (10 mmol in 50 mL deionized water). The mixture was stirred for 2 h at room temperature, after which a pH of 8–9 was reached, and then aged at 120 °C for 6 h. The catalyst was obtained through filtration and then dried at 50 °C overnight after removing excess ions *via* thorough washing with water. The samples were then calcined at 550 °C for 4 h.

Trifluoromethanesulfonic acid-based silicon dioxide (TFA/SiO₂ (30%)) was prepared using 7 g nano silica dispersed in 100 mL isobutanol and 3 g trifluoromethanesulfonic acid dissolved in 20 mL dichloromethane, which were added dropwise to aqueous isobutanol aqueous with violent stirring at a temperature of 353 K for 6 hours. Subsequently, the TFA/SiO₂ (30%) catalyst was obtained after filtration and dried at 333 K under vacuum.

Experimental

Hydrogenation of furfural to cyclopentanone or cyclopentanol. Generally, furfural (20 mmol, 1.92 g) was added to a solution of 50 mL deionized water and then transferred to a 100 mL Parr pressure reactor. Then the hydrogenation metal catalyst (0.25 g, 0.5% hydrogenation metal to furfural) and solid acid catalyst (0.25 g) were added to the reactor. The reactor was purged three times with nitrogen and charged with a given pressure of H₂. Then, the reactor was heated to a given temperature with vigorous stirring for 4 h. After completion, the mixture was directly analyzed by HPLC. Finally, the mixture was filtered. The catalysts were recovered by filtration and washed with MeOH or EtOAc, and the filtrate was extracted with EtOAc. Finally the obtained organic layer was evaporated to provide the product.

Hydroxyalkylation and alkylation of cyclopentanone and 2-methyl furan. 5,5'-(Cyclopentane-1,1-diyl)bis(2-methylfuran) was prepared *via* a typical method. To a solution of 2-methylfuran (25 mmol, 2.05 g) and cyclopentanone (10 mmol, 0.84 g)



para-toluene sulfonic acid (1 mmol, 0.25 g) was added at 333 K under solvent-free conditions for 6 h. Then, the mixture was diluted with water and extracted with EtOAc. The combined organic extracts were concentrated under vacuum and purified by column chromatography to provide the analytically pure product **1a** (2.116 g, 92%), which was isolated as a light brown oil. ¹H NMR (400 MHz, MeOD) δ 5.85 (d, J = 3.1 Hz, 2H), 5.83 (d, J = 3.0 Hz, 2H), 2.20 (s, 6H), 2.16 (d, J = 6.8 Hz, 4H), 1.73–1.67 (m, 4H). ¹³C NMR (100 MHz, MeOD) δ 158.32, 151.62, 106.70, 50.06, 37.81, 24.80, 13.47.

Aldol condensation of cyclopentanone and furfural. 2,5-Bis(furan-2-ylmethylene)cyclopentan-1-one was prepared *via* a typical method. Cyclopentanone (10 mmol, 0.84 g) and furfural (20 mmol, 1.92 g) were diluted with MeOH to 10 mL solution. The catalyst TBD (1 mmol, 0.139 g) was added to this solution, and the reaction was carried out at room temperature for 2 minutes. The product was separated from the solvent by filtration and then desiccated to afford 2.394 g (96%) of product **2a** as a yellow solid; ¹H NMR (400 MHz, CDCl₃) δ 7.59 (d, J = 1.3 Hz, 2H), 7.35 (s, 2H), 6.69 (d, J = 3.4 Hz, 2H), 6.53 (dd, J = 3.4, 1.7 Hz, 2H), 3.07 (s, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 195.5, 152.9, 145.2, 136.0, 120.0, 116.1, 112.8, 25.9.

Hydrodeoxygenation of the C–C coupling reaction product. Typically, **1a** (5 mmol, 1.15 g) was dissolved in 50 mL distilled water and transferred to a 100 mL Parr pressure reactor. To this reactor Pd/C (5 wt%, 0.5 g) and H-beta (Si/Al = 40) zeolite (0.5 g) were added. The reactor was purged three times with nitrogen and charged to 4 MPa H₂. The reactor was heated to 473 K with vigorous stirring for 8 h. After the system cooled to room temperature, the gas was collected in a gas cylinder of known volume and the pressure of the gas cylinder was adjusted to 1 atm using high purity nitrogen as a makeup gas. The gaseous products were analyzed by GC using a methanizer (for CO and CO₂) and TCD analyzer (for other gaseous hydrocarbons), and the overall gas yield was determined. Then, the catalysts were removed by centrifugation, and the liquid solution was extracted with EtOAc and analyzed by GC-MS. Alkane selectivity was reported based on the percentage of peak areas measured by GC. Total organic carbon (TOC) analysis was performed on the final concentrated liquid organic products to quantify the total carbon present and calibrate the GC for reaction products.

Conclusions

In this study, the commercial hydrogenation catalyst Ru/C with Al_{11.6}PO_{23.7} was validated as a novel and efficient catalyst system for the synthesis of cyclopentanone or cyclopentanol from furfural. In this process, a new mechanism for the conversion of furfural to cyclopentanone catalyzed by Ru/C and Al_{11.6}PO_{23.7} was proposed. Additionally, with cyclopentanone as the building block, the C–C coupling reaction and hydrodeoxygenation was an excellent route to synthesize cyclic alkanes (diesel range cyclic alkanes, selectivity > 85%). Hence, based on furfural, we not only provide an efficient catalytic system to produce cyclopentanol, but also offer a novel route for the synthesis of cyclic alkanes as hydrocarbon fuels without phenyl compounds.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by the Program for the National Natural Science Foundation of China (Grant No: 21776132); the Young Elite Scientist Sponsorship Program by CAST; the Changjiang Scholars and Innovative Research Team in University (Grant No: IRT_14R28); the Major Research Plan of the National Natural Science Foundation of China (Grant No: 21390204); the Jiangsu National Synergetic Innovation Center for Advanced Bio-Manufacture.

Notes and references

- G. W. Huber, S. Iborra and A. Corma, *Chem. Rev.*, 2006, **106**, 4044–4098.
- D. M. Alonso, J. Q. Bond and J. A. Dumesic, *Green Chem.*, 2010, **12**, 1493–1513.
- C. Zhou, X. Xia, C. Lin, D. Tong and J. Beltramini, *Chem. Soc. Rev.*, 2011, **40**, 5588–5617.
- Y. Lin and G. W. Huber, *Energy Environ. Sci.*, 2009, **2**, 68–80.
- Y. Román-Leshkov, J. N. Chheda and J. A. Dumesic, *Science*, 2006, **312**, 1933–1937.
- T. S. Hansen, J. Mielby and A. Riisager, *Green Chem.*, 2011, **13**, 109–114.
- S. Q. Hu, Z. F. Zhang, J. L. Song, Y. X. Zhou and B. X. Han, *Green Chem.*, 2009, **11**, 1746–1749.
- G. Marcotullio and W. De Jong, *Green Chem.*, 2010, **12**, 1739–1746.
- J. N. Chheda, Y. Román-Leshkov and J. A. Dumesic, *Green Chem.*, 2007, **9**, 342–350.
- D. T. Win, *Aust. J. Biotechnol.*, 2005, **8**, 185–190.
- Y. Roman-Leshkov, C. J. Barrett, Z. Y. Liu and J. A. Dumesic, *Nature*, 2007, **447**, 982–985.
- B. M. Nagaraja, A. H. Padmasri, B. David Raju and K. S. Rama Rao, *J. Mol. Catal. A: Chem.*, 2007, **265**, 90–97.
- V. V. Ordonsky, J. C. Schouten, J. van der Schaaf and T. A. Nijhuis, *Appl. Catal., A*, 2013, **451**, 6–13.
- E. J. García-Suárez, A. M. Balu, M. Tristany, A. B. García, K. Philippot and R. Luque, *Green Chem.*, 2012, **14**, 1434–1439.
- K. Yan, J. Y. Liao, X. Wu and X. M. Xie, *RSC Adv.*, 2013, **3**, 3853–3856.
- X. Hu, S. Jiang, L. Wu, S. Wang and C. Z. Li, *Chem. Commun.*, 2017, **53**, 2938–2941.
- T. Mizugaki, T. Yamakawa, Y. Nagatsu, Z. Maeno, T. Mitsudome, K. Jitsukawa and K. Kaneda, *ACS Sustainable Chem. Eng.*, 2014, **2**, 2243–2247.
- S. Liu, Y. Amada, M. Tamura, Y. Nakagawa and K. Tomishige, *Green Chem.*, 2014, **16**, 617–626.
- G. Li, N. Li, M. Zheng, S. Li, A. Wang, Y. Cong, X. Wang and T. Zhang, *Green Chem.*, 2016, **18**, 3607–3613.
- S. Dutta, *RSC Adv.*, 2012, **2**, 12575–12593.



- 21 N. Li, G. A. Tompsett and G. W. Huber, *ChemSusChem*, 2010, **3**, 1154–1157.
- 22 M. J. Climent, A. Corma and S. Iborra, *Green Chem.*, 2014, **16**, 516–547.
- 23 A. B. Gawade and G. D. Yadav, *Curr. Catal.*, 2017, **6**, 193–200.
- 24 L. Rokhum and G. Bez, *Synth. Commun.*, 2011, **41**, 548–552.
- 25 G. Liang, A. Wang, L. Li, G. Xu, N. Yan and T. Zhang, *Angew. Chem.*, 2017, **129**, 3096–3100.
- 26 J. Zhu, Z. Tan and W. Yang, *Macromol. Res.*, 2017, **25**, 792–798.
- 27 S. Madabhushi, N. Chinthala, V. S. Vangipuram, K. R. Godala, R. Jillella, K. K. R. Mallu and C. R. Beeram, *Tetrahedron Lett.*, 2011, **52**, 6103–6107.
- 28 L. K. Sharma, K. B. Kim and G. I. Elliott, *Green Chem.*, 2011, **13**, 1546–1549.
- 29 X. Sheng, N. Li, G. Li, W. Wang, J. Yang, Y. Cong, A. Wang, X. Wang and T. Zhang, *Sci. Rep.*, 2015, **5**, 9565.
- 30 M. Renz, *Eur. J. Org. Chem.*, 2005, **6**, 979–988.
- 31 T. Akashi, S. Sato, R. Takahashi, T. Sodesawa and K. Inui, *Catal. Commun.*, 2003, **4**, 411–416.
- 32 M. Hronec, K. Fulajtarova and T. Liptaj, *Appl. Catal., A*, 2012, **437**, 104–111.
- 33 M. Hronec and K. Fulajtarova, *Catal. Commun.*, 2012, **24**, 100–104.
- 34 M. Hronec, K. Fulajtarova, I. Vavra, T. Sotak, E. Dobrocka and M. Micusik, *Appl. Catal., B*, 2016, **181**, 210–219.
- 35 R. Fang, H. Liu, R. Luque and Y. Li, *Green Chem.*, 2015, **17**, 4183–4188.
- 36 Y. Liu, Z. Chen, X. Wang, Y. Liang, X. Yang and Z. Wang, *ACS Sustainable Chem. Eng.*, 2017, **5**, 744–751.
- 37 G. Zhang, M. Zhu, Q. Zhang, Y. Liu, H. He and Y. Cao, *Green Chem.*, 2016, **18**, 2155–2164.
- 38 M. Zhou, H. Zhu, L. Niu, G. Xiao and R. Xiao, *Catal. Lett.*, 2014, **144**, 235–241.
- 39 M. Zhou, Z. Zeng, H. Zhu, G. Xiao and R. Xiao, *J. Energy Chem.*, 2014, **23**, 91–96.
- 40 Y. Yang, Z. Du, Y. Huang, F. Lu, F. Wang, J. Gao and J. Xu, *Green Chem.*, 2013, **15**, 1932–1940.
- 41 X. Li, J. Deng, J. Shi, T. Pan, C. Yu, H. Xu and Y. Fu, *Green Chem.*, 2015, **17**, 1038–1046.
- 42 J. Guo, G. Xu, Z. Han, Y. Zhang, Y. Fu and Q. Guo, *ACS Sustainable Chem. Eng.*, 2014, **2**, 2259–2266.
- 43 H. Zhu, M. Zhou, Z. Zeng, G. Xiao and R. Xiao, *Korean J. Chem. Eng.*, 2014, **31**, 593–597.
- 44 M. J. Climent, A. Corma, H. Garcia, R. Guil-Lopez, S. Iborra and V. Fornés, *J. Catal.*, 2001, **197**, 385–393.
- 45 C. Zhu, T. Shen, D. Liu, J. Wu, Y. Chen, L. Wang, K. Guo, H. Ying and P. Ouyang, *Green Chem.*, 2016, **18**, 2165–2174.
- 46 T. Shen, C. Zhu, C. Tang, Z. Cao, L. Wang, K. Guo and H. Ying, *RSC Adv.*, 2016, **6**, 62974–62980.
- 47 T. Shen, J. Tang, C. Tang, J. Wu, L. Wang, C. Zhu and H. Ying, *Org. Process Res. Dev.*, 2017, **21**, 890–896.
- 48 T. Lindblad, B. Rebenstorf, Z.-G. Yan and S. L. T. Andersson, *Appl. Catal., A*, 1994, **112**, 187–208.
- 49 Y. Xu, J. Shi, W. Wu, R. Zhu, X. Li, J. Deng and Y. Fu, *Appl. Catal., A*, 2017, **543**, 266–273.
- 50 D. Ren, Z. Song, L. Li, Y. Liu, F. Jin and Z. Huo, *Green Chem.*, 2016, **18**, 3075–3081.
- 51 T. Kumaraguru, P. Babita, G. Sheelu, K. Lavanya and N. W. Fadnavis, *Org. Process Res. Dev.*, 2013, **17**, 1526–1530.
- 52 K. Ulbrich, P. Kreitmeier and O. Reiser, *Synlett*, 2010, **2010**, 2037–2040.
- 53 M. Hronec, K. Fulajtarová and T. Soták, *J. Ind. Eng. Chem.*, 2014, **20**, 650–655.
- 54 G. Li, N. Li, M. Zheng, S. Li, A. Wang, Y. Cong, X. Wang and T. Zhang, *Green Chem.*, 2016, **18**, 3607–3613.
- 55 K. J. Zeitsch, in *The Chemistry and Technology of Furfural and its Many By-Products, Sugar Series*, Elsevier Science, Dordrecht, 2000, vol. 13, pp. 229–230.
- 56 G. Li, N. Li, S. Li, A. Wang, Y. Cong, X. Wang and T. Zhang, *Chem. Commun.*, 2013, **49**, 5727–5729.
- 57 S. Li, N. Li, G. Li, A. Wang, Y. Cong, X. Wang and T. Zhang, *Catal. Today*, 2014, **234**, 91–99.
- 58 G. Li, N. Li, Z. Wang, C. Li, A. Wang, X. Wang, Y. Cong and T. Zhang, *ChemSusChem*, 2012, **5**, 1958–1966.
- 59 K.-I. Shimizu and A. Satsuma, *Energy Environ. Sci.*, 2011, **4**, 3140–3153.
- 60 E. Corporan, T. Edwards, L. Shafer, M. J. DeWitt, C. Klingshirn, S. Zabarnick, Z. West, R. Striebich, J. Graham and J. Klein, *Energy Fuels*, 2011, **25**, 955–966.
- 61 P. Bi, J. Wang, Y. Zhang, P. Jiang, X. Wu, J. Liu, H. Xue, T. Wang and Q. Li, *Bioresour. Technol.*, 2015, **183**, 10–17.
- 62 H. A. Meylemans, R. L. Quintana, B. R. Goldsmith and B. G. Harvey, *ChemSusChem*, 2011, **4**, 465–469.
- 63 J. Yang, N. Li, G. Li, W. Wang, A. Wang, X. Wang, Y. Cong and T. Zhang, *Chem. Commun.*, 2014, **50**, 2572–2574.

