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Synthesis of Renewable Triketones, Diketones and Jet Fuel Range Cycloalkanes with 5-Hydroxymethylfurfural and Ketones

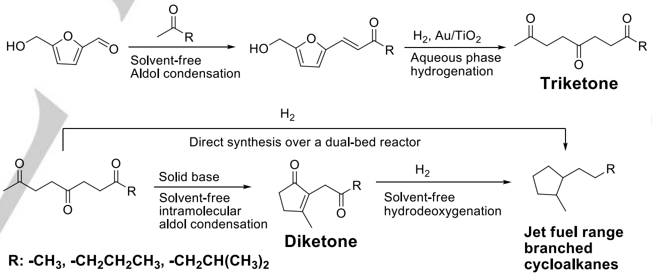
Shanshan Li,†[a,b] Fang Chen,†[a,b] Ning Li,*[a,c] Wentao Wang,[a] Xueru Sheng,[a,b] Aiqin Wang,[a,c] Yu Cong,[a] Xiaodong Wang,[a] and Tao Zhang*[a,c]

Abstract: For the first time, a series of renewable C_9-C_{12} triketones with repeating [$COCH_2CH_2$] units were synthesized in high carbon yields (~90%) by the aqueous phase hydrogenation of the aldol condensation products of 5-hydroxylmethylfurfural (HMF) and ketones over the Au/TiO_2 catalyst. Compared with the reported routes, this new route has many advantages such as environmental friendly, fewer steps, using a cheaper easier separation and reusable catalyst, *etc.*. The triketones as obtained can be used as feedstocks in the production of conducting or semi-conducting polymers. By the solvent-free intramolecular aldol condensation over solid base catalysts, these triketones were selectively converted to diketones which can be used as the intermediates in synthesis of useful chemicals or polymers. As another application, the triketones and diketones can also be utilized as precursors for the synthesis of jet fuel range branched cycloalkanes which have low freezing points (224-250 K) and high densities (~0.81 g mL^{-1}).

Introduction

Due to the increase of social concern about the renewable energy and environmental problems, the catalytic conversion of biomass has become a very hot research topic.[1] Lignocellulose is the main component of agricultural and forestry waste. Compared with the other forms of biomass, lignocellulose is much cheaper and more abundant. During the past years, the catalytic conversion of lignocellulosic platform compounds to fuels[2] and useful chemicals[3] has drawn a lot of attention.

Polyketones with repeating [$COCH_2CH_2$] units are important feedstocks in the synthesis of conducting or semi-conducting polymers which have repeating [$C(NR_2)_2CH_2CH_2$] units.[4] 5-Hydroxymethylfurfural (HMF) is a platform compound which can be produced by the hydrolysis/dehydration of cellulose.[5] Acetone is the by-product in the manufacture of bio-butanol and bio-ethanol by the Acetone-Butanol-Ethanol (ABE) fermentation of lignocellulose.[6] 2-Pentanone is a by-product in the selective hydrogenation of furfural to 2-methylfuran,[7] a fuel additive or feedstock in the production of diesel and jet fuel range branched alkanes.[8] Methyl isobutyl ketone (MIBK) is an important chemical which has been produced in industrial scale by the one-step self-aldol condensation/hydrogenation of acetone.[9] In this work, a series of C_9-C_{12} triketones with repeating [$COCH_2CH_2$] units were first synthesized in high carbon yields (~90%) by the aqueous phase hydrogenation of the aldol condensation products of HMF and acetone, 2-pentanone or MIBK over a cost-effective and reusable Au/TiO_2 catalyst. To expand their application scope, we investigated the solid base catalysed solvent-free intramolecular aldol condensation of these triketones to C_9-C_{12} diketones which can be used as feedstocks in the production of many useful chemicals[10] or renewable polymers.[11] Furthermore, we also explored the possiblity to synthesize jet fuel range branched cycloalkanes which have low freezing points (224~250 K) and high densities (~0.81 g mL^{-1}) with the C_9-C_{12} diketones and triketones as obtained. The strategy of this work is illustrated in Scheme 1.



Scheme 1. Reaction pathways for the synthesis of renewable C_9-C_{12} triketones, diketones and jet fuel range branched cycloalkanes with HMF and ketones which can be derived from lignocellulose.

Results and Discussion

In the first part of this work, we investigated the solvent-free aldol condensation of HMF and acetone, 2-pentanone or MIBK over CaO, a cheap solid base catalyst which has been produced in industrial scale by the calcination of limestone at high temperature. The detail information was given in supporting information. According to the analysis of the products, HMF was completely converted, high carbon yields (91.2-94.0%) of 4-(5-(hydroxymethyl)furan-2-yl)but-3-en-2-one, 1-(5-(hydroxymethyl)furan-2-yl)hex-1-en-3-one and 1-(5-(hydroxymethyl)furan-2-yl)-5-methylhex-1-en-3-one (*i.e.* the **1A**, **1B** and **1C** in Scheme 2) were obtained from the solvent-free aldol condensation of HMF and acetone, 2-pentanone or MIBK over CaO under mild conditions (413 K or 403 K, 6 h). The reaction pathways for the generation of the **1A**, **1B** and **1C** were illustrated in Scheme 2. Taking into consideration of the low

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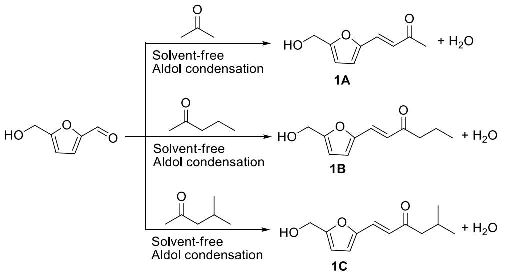
price and high activity of CaO, we think it is a promising catalyst in future application.



Scheme 2. Reaction pathways for the generation of **1A**, **1B** and **1C** from the solvent-free aldol condensation of HMF with acetone, 2-pentanone, and MIBK.

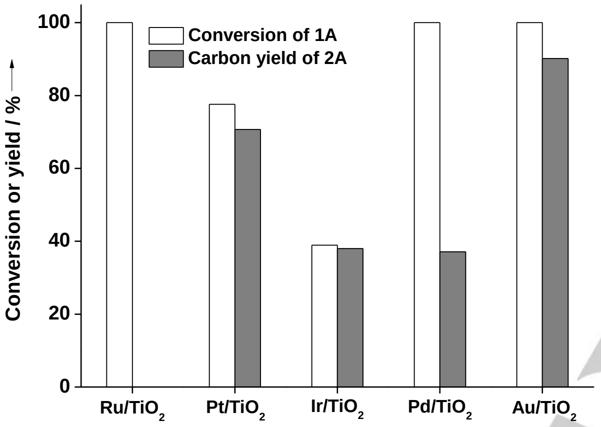
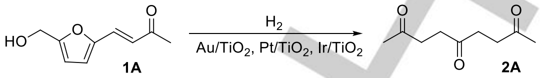


Figure 1. Conversion of **1A** (white bar) and carbon yield of **2A** (grey bar) over the TiO_2 supported noble metal catalysts. Reaction conditions: 0.2 g **1A**, 0.04 g catalyst, 15 mL H_2O, 5 mL THF; 393 K, 6.5 MPa H_2, 800 rpm, 6 h.

Taking **1A** for example, we investigated the aqueous phase hydrogenation of the aldol condensation product over a series of TiO_2 loaded noble metal catalysts. To increase the solubility of substrate in water, tetrahydrofuran (THF) was used as a co-solvent. From the analysis of hydrogenation products, it was noticed that the chemical property of noble metal has strong influence on its catalytic performance in the aqueous phase hydrogenation of **1A**. Over the Au/TiO_2, Pt/TiO_2 and Ir/TiO_2 catalysts, **1A** was selectively converted to nonane-2,5,8-trione (*i.e.* the **2A** in Scheme 3). In contrast, lower carbon yields (or selectivity) of **2A** were obtained over the Pd/TiO_2 or Ru/TiO_2 catalysts. This can be explained by the selectivity of different noble metal catalysts to furan ring opening reaction versus furan ring saturation during the hydrogenation of **1A**. As what has been reported by Bell *et al.* in their recent work on the hydrogenolysis 2,5-dimethylfuran to hexanone and hexanol,[12] the Pd/TiO_2 or Ru/TiO_2 exhibited higher selectivity for furan ring hydrogenation products (see Figure S1 and Table S1 in supporting information) than those of the Au/TiO_2, Pt/TiO_2 and Ir/TiO_2 catalysts, which may be the reason for their lower selectivity for the hydrogenation of **1A** to **2A**. Based on the result illustrated in Figure 1, we can see that the Au/TiO_2 catalyst is more active than the Pt/TiO_2 and Ir/TiO_2 catalysts for the hydrogenation of **1A** to **2A**. Over the Au/TiO_2 catalyst, high carbon yield (90.1%) of **2A** can be achieved under mild conditions (393 K, 6.5 MPa H_2). Taking into consideration of the lower price and higher activity of Au catalyst than those of Pt or Ir catalysts, we think the Au/TiO_2 is a promising catalyst for the production of **2A**.



Scheme 3. Reaction pathway for the generation of **2A** from the aqueous phase hydrogenation of **1A** over different noble metal catalysts.

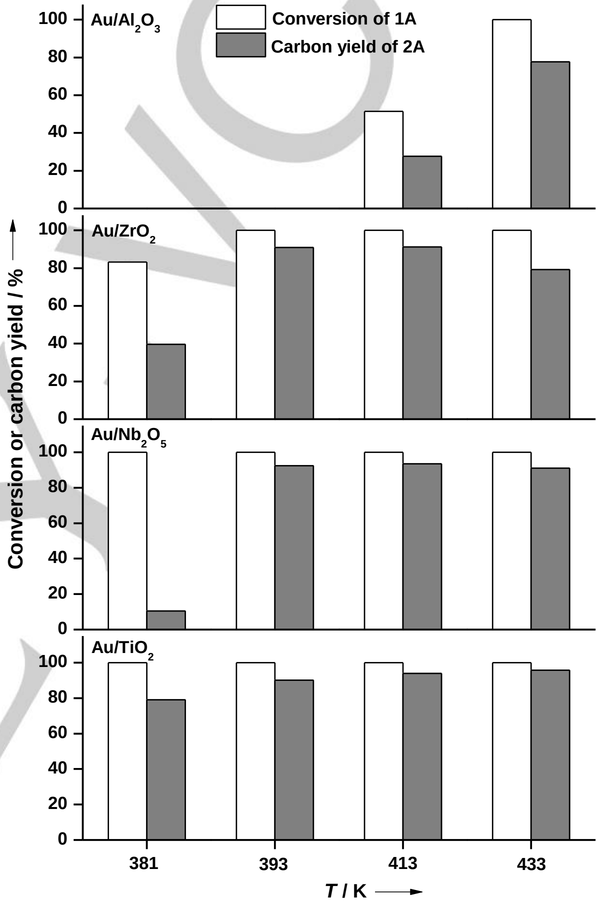
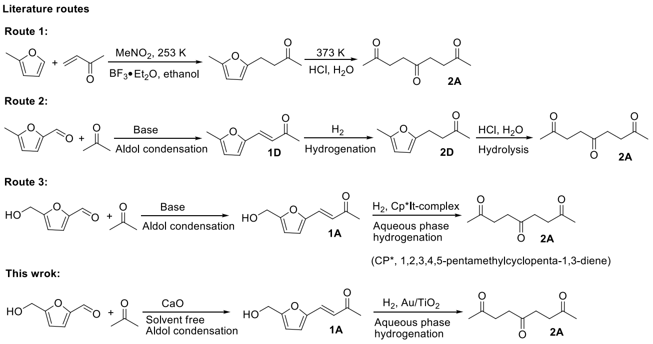


Figure 2. Conversion of **1A** (white bar) and carbon yield of **2A** (grey bar) over the Au catalysts loaded on different supports. Reaction conditions: 0.2 g **1A**, 0.04 g catalyst, 15 mL H_2O, 5 mL THF, 6.5 MPa H_2, 800 rpm, 6 h.

Subsequently, we also studied the effect of support on the aqueous phase hydrogenation of **1A** over Au catalyst. Amongst the investigated Au catalysts, Au/TiO_2 is the most selective one to **2A** (see Figure 2). The activities of the investigated Au catalysts decrease in the order of Au/TiO_2 > Au/ZrO_2 > Au/Nb_2O_5 > Au/Al_2O_3. The advantage of the Au/TiO_2 catalyst is more significant at low temperature (such as 381 K). In addition to its low price and wide availability, we think that TiO_2 is a good support for the Au catalyst which used in the production of **2A**. According to the statistical results based on the TEM images of Au catalysts (see Figure S2 in supporting information), the average sizes of Au particles on the Au/TiO_2 (5.15±2.58 nm) and Au/ZrO_2 (5.20±2.67 nm) catalysts are very close, which may be the reason for the similar activity of these catalysts in the aqueous phase hydrogenation of **1A**. Moreover, it was also noticed that the average sizes of Au particles on the Au/TiO_2 and Au/ZrO_2 catalysts are lower than that on the Au/Nb_2O_5 catalyst (6.37±2.69 nm) but evidently higher than that on the Au/Al_2O_3 catalyst (1.98±0.65 nm), which may be a possible reason for the relatively lower activity of Au/Nb_2O_5 and Au/Al_2O_3 catalysts in the aqueous phase hydrogenation of **1A**. As we know, the particle size has strong influence on the activity of Au catalyst, volcanic type relationship was observed between the particle size of Au catalysts and their activity in many reactions.[13]



Scheme 4. Synthetic routes for the renewable **2A** reported in literature and this work.

During the past years, three routes have been developed for the synthesis of renewable **2A**. In the previous work of Poirier[14] and Alder[4] and their co-workers (see Route 1 in Scheme 4), **2A** was produced by the HCl catalysed hydrolysis of 4-(5-methylfuran-2-yl)butan-2-one which can be obtained by the alkylation of 2-methylfuran and methyl vinyl ketone (from the aldol condensation of acetone and formaldehyde[15] or the decarboxylation of levulinic acid[16]). As we know, the methyl vinyl ketone is highly toxic. Therefore, the exploration of environmental friendly synthetic route is highly expected. In the previous work of Gordon and Silks *et al.* [17] (see Route 2 in Scheme 4), **2A** was prepared by acid catalysed hydrolysis of the 4-(5-methyl-a-furyl)-2-butanone (*i.e.* **2D** in Scheme 4) from the hydrogenation of the aldol condensation product of methylfurfural and acetone (*i.e.* **1D** in Scheme 4). In the recent work of Zhang *et al.*,[18] a new method (*i.e.* Route 3 in Scheme 4) was developed for the synthesis of **2A** by the aqueous phase hydrogenation of **1A** under the catalysis of bipyridine coordinated Cp*-Iridium(III) complexes (Cp*, 1,2,3,4,5-pentamethylcyclopenta-1,3-diene). Compared with the previous two routes, this new route is environmental friendly and contains few steps. However, the high price of the Cp*-Iridium(III) complexes catalyst is the bottleneck for the real application of this route. As a solution to this problem, we developed a much cheaper and easily separated heterogeneous Au/TiO_2 catalyst which is advantageous in future application.

The catalytic performances of the Au/TiO_2 catalyst for the aqueous phase hydrogenation reactions of other aldol condensation products of HMF (*i.e.* the **1B** and **1C** in Scheme 4) were explored. According to the analysis of products, the **1B** and **1C** were totally converted, high carbon yields (~90%) of undecane-2,5,8-trione and 10-methylundecane-2,5,8-trione (*i.e.* the **2B** and **2C** in Scheme 5) were achieved over the Au/TiO_2 catalyst under the same reaction conditions as we used for the aqueous phase hydrogenation of **1A**. Both **2B** and **2C** have repeating [$COCH_2CH_2$] units. Therefore, they can be used as feedstocks for the synthesis of conducting or semi-conducting polymers with repeating [$C(NR_2)_2CH_2CH_2$] units. The reaction pathways for the generation of **2B** and **2C** from the aqueous phase hydrogenation of **1B** and **1C** over the Au/TiO_2 catalyst were proposed in Scheme 5.

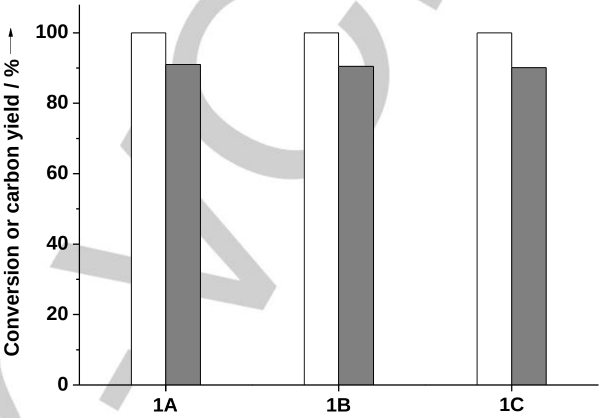
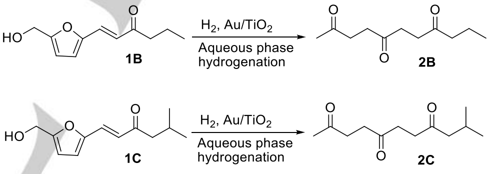
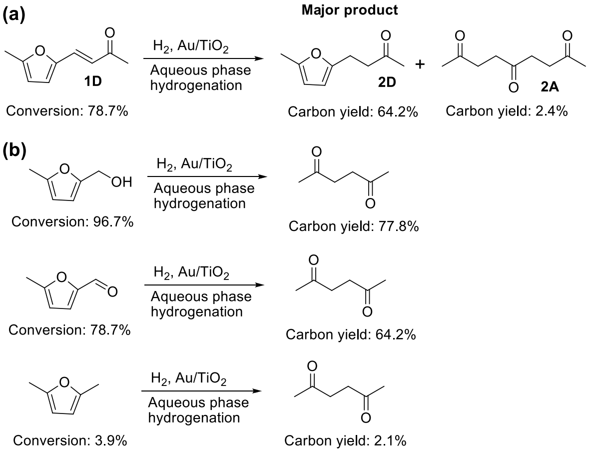


Figure 3. Conversion of **1A**, **1B** and **1C** (white bar) and carbon yields of **2A, 2B** and **2C** (grey bar) over the Au/TiO_2 catalyst. Reaction conditions: 0.2 g substrate, 0.04 g catalyst, 15 mL H_2O, 5 mL THF; 393 K, 6.5 MPa H_2, 800 rpm, 6 h.



Scheme 5. Reaction pathways for the generation of **2B** and **2C** from the aqueous phase hydrogenation of **1B** and **1C** over the Au/TiO_2 catalyst.



Scheme 6. Reaction pathways for the generation of different products from the aqueous phase hydrogenation of 4-(5-methylfuran-2-yl)but-3-en-2-one, 5-methylfurfural and 2,5-dimethylfuran over the Au/TiO_2 catalyst. Reaction conditions: (a) 0.2 g 4-(5-methylfuran-2-yl)but-3-en-2-one, 0.04 g catalyst, 10 mL H_2O, 10 mL THF; 413 K, 6.5 MPa H_2, 800 rpm, 4 h. (b) 5.2 mmol 5-methylfurfuryl alcohol, 5-methylfurfural or 2,5-dimethylfuran, 0.25 g catalyst, 30 mL water and 10 mL THF; 413 K, 6.5 MPa H_2, 800 rpm, 3 h.

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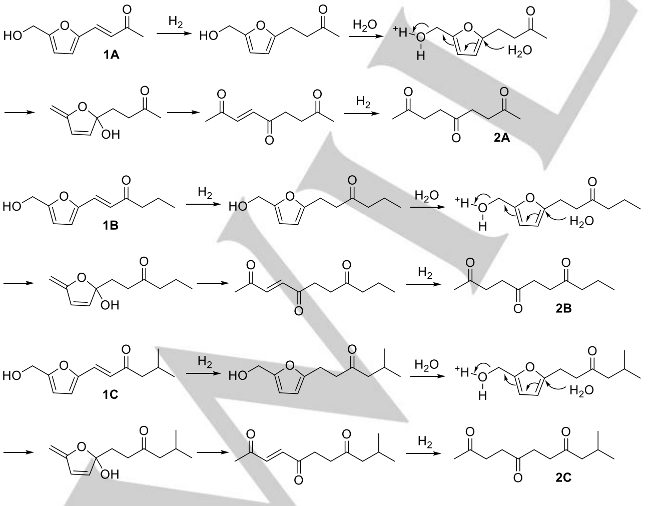
To get deeper insight of this reaction, we studied the aqueous phase hydrogenation of some model compounds over the Au/TiO_2 catalyst. It is very interesting that when we used 4-(5-methylfuran-2-yl)but-3-en-2-one (*i.e.* **1D** in Scheme 6) to replace **1A** as the feedstock in the aqueous phase hydrogenation, evidently lower substrate conversion (78.7%) and carbon yield of **2A** (2.4%) were obtained over the Au/TiO_2 catalyst even at higher reaction temperature (413 K vs. 393 K). The main product from the aqueous phase hydrogenation of **1D** over the Au/TiO_2 catalyst was identified as 4-(5-methyl-a-furyl)-2-butanone (*i.e.* the **2D** in Scheme 6). Based on this result, two conclusions can be drawn. 1) The **2D** is not the intermediate which was generated during the aqueous phase hydrogenation of **1A** to **2A** over the Au/TiO_2 catalyst. That is, the aqueous phase hydrogenation of **1A** to **2A** follows a reaction pathway other than the hydrolysis of **2D**. 2) The presence of hydroxyl group on the methyl group adjacent to the furan ring in **1A** molecule is favourable for the production of **2A** from aqueous phase hydrogenation over the Au/TiO_2 catalyst. To verify this speculation, we also compared the aqueous phase hydrogenation of 5-methylfurfuryl alcohol, 5-methylfurfural and 2,5-dimethylfuran over the Au/TiO_2 catalyst. It was noticed that all of these reactions lead to the generation of hexane-2,5-dione as the major product. However, evidently higher carbon yields of hexane-2,5-dione (77.8% and 64.2% vs. 2.1%) were obtained when 5-methylfurfuryl alcohol and 5-methylfurfural were used as the substrates. From the result in Scheme 6, we can also see that the reactivity of 5-methylfurfuryl alcohol is higher than that of 5-methylfurfural. According to this result, we think 5-methylfurfuryl alcohol is the intermediate between 5-methylfurfural and hexane-2,5-dione. In the recent work of Zhang *et al.*,[18] similar results were observed over the Cp*-Iridium(III) complex catalyst. It was suggested that the presence of hydroxyl group promotes the hydrolysis of furan ring. Based on the experimental facts which were obtained in this work and the literature about similar reaction system,[18] the reaction mechanism for the aqueous phase hydrogenation of **1A** to **2A** over the Au/TiO_2 catalyst was proposed in Scheme 7.



Scheme 7. Reaction mechanism for the aqueous phase hydrogenation of **1A**, **1B** and **1C** to **2A**, **2B** and **2C** over the Au/TiO_2 catalyst.

To fulfil the need of real application, we also checked the reusability of the Au/TiO_2 catalyst in the aqueous phase hydrogenation of **1A** to **2A**. According to Figure 4, the Au/TiO_2 catalyst is stable under the investigated conditions. No evidently change in the activity or selectivity of the catalyst was observed during the three usages.

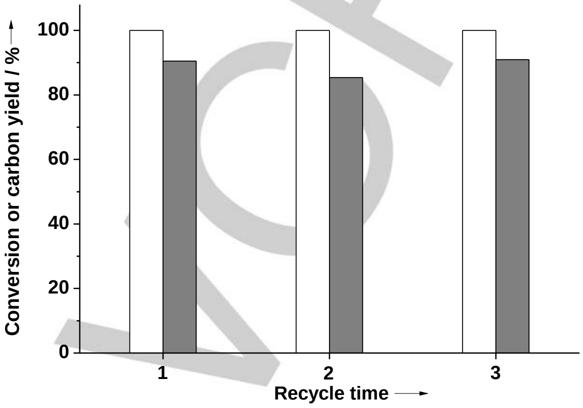


Figure 4. Conversion of **1A** (white bar) and carbon yield of **2A** (grey bar) over the Au/TiO_2 catalyst as the function of recycle time. Reaction conditions: 0.2 g **1A**, 0.04 g catalyst, 15 mL H_2O, 5 mL THF; 393 K, 6.5 MPa H_2, 800 rpm, 6 h.

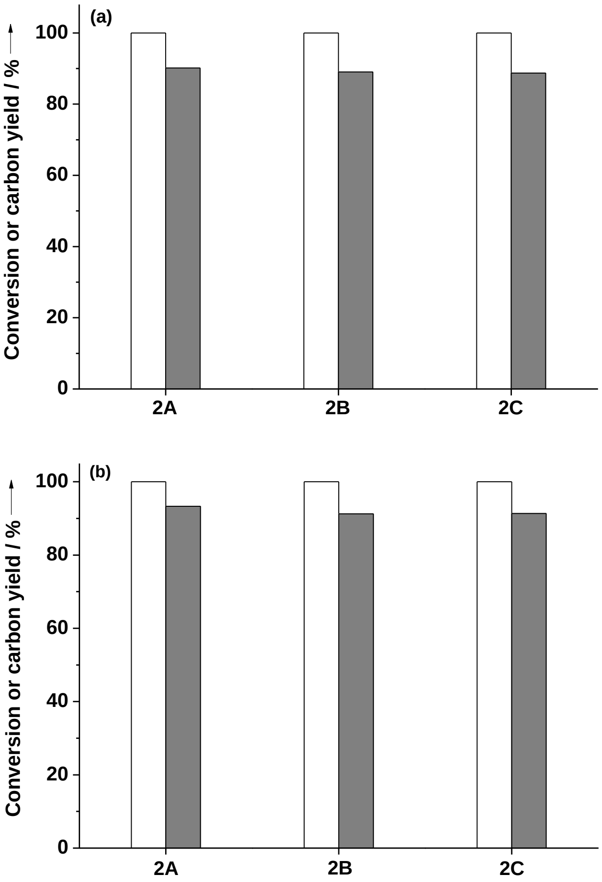
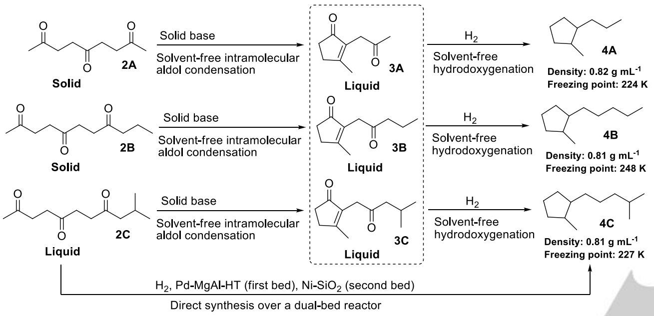


Figure 5. Conversions of **2A**, **2B** and **2C** (white bars) and the carbon yields of **3A**, **3B** and **3C** (grey bars) over the CaO (a) and MgAl-HT (b) catalysts under N_2 atmosphere. Reaction conditions: 1.5 g substrate, 0.2 g CaO or MgAl-HT catalyst, 423 K, 800 rpm, 6 h.

The triketones (*i.e.* **2A**, **2B** and **2C**) which were obtained from the aqueous phase hydrogenation reactions can be further converted to diketones over the solid base catalysts under solvent-free conditions. According to Figure 5, both CaO and magnesium-aluminium hydrotalcite (MgAl-HT) catalysts exhibited high activities for the solvent-free intramolecular aldol condensation. Over them, the **2A**, **2B** and **2C** were completely converted, high carbons yields (88.7-93.3%) of 3-methyl-2-(2-oxopropyl)cyclopent-2-enone, 3-methyl-2-(2-oxopentyl)cyclopent-2-enone and 3-methyl-2-(4-methyl-2-oxopentyl)cyclopent-2-enone (*i.e.* **3A**, **3B** and **3C** in scheme 7) were achieved at 423 K. According to literature, these diketones can be used as the feedstock in the manufacture of valuable chemicals, such as amines, cycloketones, pyrrolidine *etc*..[10] Furthermore, these diketones can also be hydrogenated to diols which are widely used as feedstocks in polymer industry.[11]



Scheme 8. Reaction pathways for the production of diketones and jet fuel range cycloalkanes with **2A**, **2B** and **2C**.

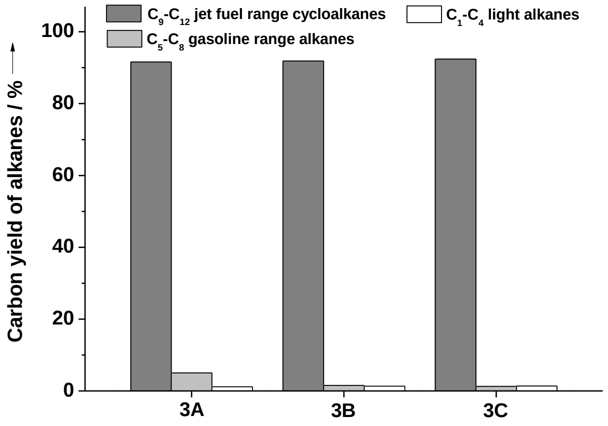


Figure 6. Carbon yields of jet fuel range C_9-C_{12} cycloalkanes (grey bar), C_5-C_8 gasoline range alkanes (light grey bar) and C_1-C_4 light alkanes (white bar) from the solvent-free hydrodeoxygenation (HDO) of **3A**, **3B** and **3C** over the Ni-SiO_2 catalyst. Reaction conditions: 533 K, 6 MPa H_2; 1.80 g Ni-SiO_2 catalyst, liquid feedstock flow rate: 0.04 mL min^{-1} (WHSV = 1.4 h^{-1}); hydrogen flow rate: 120 mL min^{-1}.

The cyclic diketones (*i.e.* **3A**, **3B** and **3C** in scheme 7) as obtained are liquid at room temperature. As another potential application, they can be converted to jet fuel range branched alkanes with high densities and low freezing points by solvent-free hydrodeoxygenation (HDO). According to Figure 6, high carbon yields (>90%) of jet fuel range C_9-C_{12} branched cycloalkanes (*i.e.* **4A**, **4B** and **4C** in Scheme 8) can be obtained from the solvent-free HDO of **3A**, **3B** and **3C** over the Ni-SiO_2 catalyst which was prepared by a deposition-precipitation method developed by Lercher *et al.*.[19] According to our measurement (see the results listed in Scheme 8), these cycloalkanes have high densities (0.81-0.82 g mL^{-1}) and low freezing points (224-248 K). Therefore, they can be used as additives to increase the volumetric heat values of conventional bio-jet fuel.[20]

The stability of the Ni-SiO_2 catalyst in the HDO process was also checked. Taking the solvent-free HDO of **3A** for example (see Figure 7), no evident change in the carbon yields of different alkanes was observed during the 24 h time on stream, which means that this catalyst is stable under the investigated conditions. This result is consistent with what we have observed in the solvent-free HDO of other biomass derived cyclketone.[21]

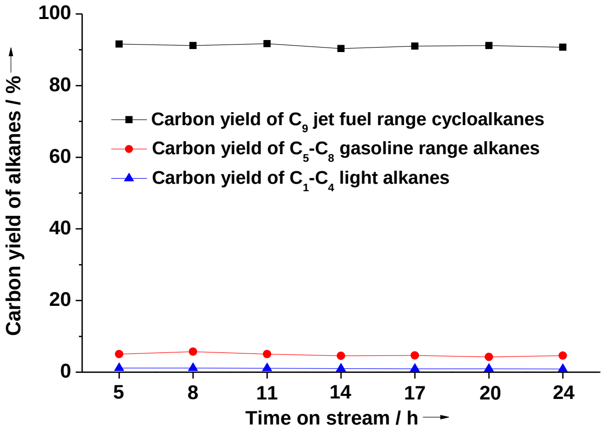


Figure 7. Carbon yields of C_9 jet fuel range branched cycloalkanes (■), C_5-C_8 gasoline range alkanes (●) and C_1-C_4 light alkanes (▲) from the solvent-free HDO of **3A** over the Ni-SiO_2 catalyst as the function of reaction time. Reaction conditions: 533 K, 6 MPa H_2, 1.80 g Ni-SiO_2 catalyst; liquid feedstock flow rate 0.04 mL min^{-1} (WHSV = 1.4 h^{-1}); H_2 flow rate: 120 mL min^{-1}.

Taking into consideration of the fact that the **2C** also exists as liquid at room temperature (this may be explained by the branched carbon chain structure of this compound), we also explored the direct synthesis of jet fuel range branched cycloalkanes with **2C** and hydrogen over a dual-bed catalyst system which had been used in our recent work.[22] The detail information about the dual-bed catalyst system was given in the supporting information. In the first bed, Pd-MgAl-HT catalyst was used for the intramolecular aldol condensation/hydrogenation of **2C**. In the second bed, the condensation product from the first bed was further hydrodeoxygenated over the Ni-SiO_2 catalyst. As we expected, 89.0% carbon yield of **4C**, 1.3% carbon yield of C_5-C_8 gasoline range alkanes and 2.3% carbon yield of C_1-C_4 light alkanes can be directly obtained by the reaction of **2C** and hydrogen at 543 K and 0.5 MPa H_2 over such a dual bed catalyst system. These values are very close to what have been achieved by the solvent free HDO of **3C** over Ni-SiO_2 catalyst. Based on this result, we think it is possible to integrate the intramolecular aldol condensation step and HDO step into a one-step process which will lead to the higher efficiency and lower energy consumption in real application.

Conclusions

In summary, new synthetic routes for the renewable C_9-C_{12} triketones, diketones and jet fuel range branched cycloalkanes were developed using lignocellulose derived HMF and ketones (such as acetone, 2-pentanone and MIBK) as the feedstocks. In the first step of this route, a series of C_9-C_{12} furan compounds were obtained in high carbon yield (~90%) by the solvent-free aldol condensation of HMF and ketones over CaO catalyst. In the second step, the furan compounds as obtained in the first step were further converted to C_9-C_{12} triketones with repeating [$COCH_2CH_2$] units by the aqueous phase hydrogenation over noble metal catalyst. Due to their special chemical structure, these C_9-C_{12} triketones can be used as the feedstocks in the production of conducting or semi-conducting polymers which have repeating [$C(NR_2)_2CH_2CH_2$] units. Among the investigated catalysts, the Au/TiO_2 catalyst exhibited the highest activity, good selectivity and stability for the production of triketones from the aqueous phase hydrogenation reactions. The presence of hydroxyl group on the methyl group adjacent to the furan ring is favorable for the ring-opening reactions of the furan compounds during the aqueous phase hydrogenation. The triketones as obtained can be further converted to cyclic diketones by the solvent-free intramolecular aldol condensation of triketones over the MgAl-HT and CaO catalysts. The diketones as obtained can be used as the intermediates in the production of many useful chemicals or polymers. By the solvent-free HDO over the Ni-SiO_2 catalyst, these diketones (exist as liquid at room temperature) can also be converted to jet fuel range branched cycloalkanes which have high densities (~0.81 g mL^{-1}) and low freezing points (224-250 K). As another option, the jet fuel range branched cycloalkanes can also be directly produced by the reaction of triketone and hydrogen over a dual-bed catalyst system of Pd-MgAl-HT and Ni-SiO_2. This work paves a new way for the synthesis of renewable polyketones and jet fuel range cycloalkanes with lignocellulosic platform compounds.

Experimental Section

Preparation of catalysts: The CaO catalyst was purchased from Aladdin Reagent Company. Before being used for the solvent-free aldol condensation reactions, the CaO catalyst was calcined in nitrogen flow at 873 K for 4 h. The magnesium-aluminium hydrotalcite (MgAl-HT) catalyst with an Mg/Al atomic ratio of 3 was prepared by the method which was reported in literature.[2a, 22a] Typically, 53.8 g $Mg(NO_3)_2 \cdot 6H_2O$ (0.21 mol) and 26.3 g $Al(NO_3)_3 \cdot 9H_2O$ (0.07 mol) was dissolved in 200 mL deionized water and this mixture was marked as Solution-A. Then 17.5 g NaOH and 12.0 g Na_2CO_3 was dissolved in 200 mL deionized water and this mixture was named as Solution-B. Then Solution-A was added into Solution-B at a rate of 2 mL min^{-1}. The mixture was vigorously stirred at 343 K for 16 h. The solid as obtained was filtered, washed with deionized water until filtrate pH became 7 and dried overnight at 353 K. Before being used in the activity test, the dried precursor was calcined in nitrogen flow at 723 K for 8 h. The Pd doped modified magnesium-aluminium hydrotalcite (Pd-MgAl-HT) catalyst was prepared by the same method (simply adding $Pd(NO_3)_2 \cdot xH_2O$ in the Mg/Al aqueous solution). The theoretical Pd/Al atomic ratio in the Pd-MgAl-HT catalyst was controlled as 0.02:1.

The Au/TiO_2 catalyst used in the aqueous phase hydrogenation reactions was prepared by the ion-exchanging TiO_2 P25 (Degussa) with an aqueous solution of $HAuCl_4 \cdot 4H_2O$ according to the method described in literature.[23] Typically, 0.99 g TiO_2 P25 was added to 278 mL aqueous solution of $HAuCl_4 \cdot 4H_2O$ (2.3 mmol L^{-1}). The mixture was vigorously stirred at 343 K for 1 h, filtrated, thoroughly washed with distilled water and dried at 353 K for 12 h. Before the activity test, the Au/TiO_2 catalyst was reduced in hydrogen flow at 473 K for 2 h, cooled down to room temperature in hydrogen flow, then passivated by 1vol.% O_2 in nitrogen flow for 4 h. According to the analysis of ICP, the Au content in the reduced Au/TiO_2 catalyst was measured as 0.81wt.%. For comparison, we also prepared the Au/ZrO_2, Au/Nb_2O_5 and Au/Al_2O_3 catalysts by the same method using ZrO_2, Nb_2O_5 and γ-Al_2O_3 as the supports, respectively. The Pd/TiO_2, Pt/TiO_2, Ir/TiO_2 and Ru/TiO_2 catalysts were prepared by the incipientwetness impregnation of TiO_2 P25 with the aqueous solutions of $PdCl_2$, H_2PtCl_6, H_2IrCl_6 and $RuCl_3$. The theoretical noble metal contents in the catalysts were controlled as 0.8wt.%. Before the activity tests, the Pd/TiO_2, Pt/TiO_2, Ir/TiO_2 and Ru/TiO_2 catalysts were reduced in hydrogen flow at 573 K for 2 h, cooled down to room temperature in hydrogen flow, then passivated by 1vol.% O_2 in nitrogen flow for 4 h.

The Ni-SiO_2 catalyst used in HDO test was prepared by the deposition-precipitation method reported by Lercher *et al*.[19] Typically, 250 mL of 0.14 M $Ni(NO_3)_2 \cdot 6H_2O$ aqueous solution was divided into two parts. Urea (0.42 mol L^{-1}, 6.3 g) was added to one portion (50 mL) to make Part-C. SiO_2 (1.9 g) and HNO_3 (65%, 0.02 mol L^{-1}, 0.32 mL) were added to the other portion (200 mL) under vigorous stirring to make Part-D. Then Part-D was put into a flask which is put in a water bath at 353 K. After the slow addition of Part-C to the flask, the as-obtained suspension was heated to 363 K and stirred for 10 h. The suspension was then cooled to room temperature, filtrated, washed and dried at 363 K for 24 h. The as-prepared solid was then calcined in air flow at 973 K and reduced in flowing H_2 (120 mL min^{-1}) at 733 K for 2 h. According to the ICP analysis, the actual Ni content in the Ni-SiO_2 catalyst was measured as 34.0wt.%.

Preparation of the 1A, 1B and 1C: The **1A**, **1B** and **1C** used in the aqueous phase hydrogenation tests were obtained by the solvent-free aldol condensation of HMF and acetone, 2-pentanone and MIBK, respectively. The detail information for the preparation of these compounds was given in the supporting information.

Aqueous phase hydrogenation of the furan-base ketones: The aqueous hydrogenation reactions of the **1A**, **1B** and **1C** from the solvent-free aldol condensation of HMF and acetone, 2-pentanone and MIBK were carried out in a stainless steel batch reactor. To increase the solubility of these substrates in water, tetrahydrofuran (THF) was added as a co-solvent. For each test, 0.2 g substract, 0.04 g catalyst, 15 mL H_2O and 5 mL THF were used. The reactions were conducted at 393 K under 6.5 MPa H_2 for 6 h, then stopped by quenching the reactor to room teperature by cool water. After releasing of unreacted hydrogen, the products were taken out from the reactor, diluted and analyzed by an Agilent 7890 GC equipped with a HP-INNOWAX capillary column (30 m, 0.25 mm I.D., 0.5 μm film) and FID detector.

Solvent-free intramolecular aldol condensation of triketones: The solvent-free intramolecular aldol condensation reactions of the triketones (*i.e.* **2A**, **2B** and **2C**) were carried out in a stainless steel batch reactor in N_2 atmosphere. For each test, 1.5 g triketone, 0.2 g CaO or MgAl-HT catalyst were used. The reactions were conducted at 423 K for 6 h, then stopped by quenching the reactor to room teperature by cool water. The products were taken out from the reactor, diluted and analyzed by the Agilent 7890 GC.

Hydrodeoxygenation (HDO): The solvent-free HDO of the diketones (*i.e.* **3A**, **3B** and **3C**) was carried out by a stainless steel tubular flow reactor described in our previous work. For each test, 1.8 g Ni-SiO_2 catalyst was used. Before the HDO process, the catalysts were reduced *in-situ* by hydrogen flow at 773 K for 2 h. After the reactor temperature was cooled down to 533 K and kept at this value for 0.5 h, the diketones were pumped into the reactor at 0.04 mL min^{-1} from the bottom along with hydrogen at a flow rate of 120 mL min^{-1}. After coming out from the tubular reactor, the products became two phases in a gas-liquid separator. The gaseous products flowed through a back pressure regulator to maintain the system pressure at 6 MPa and were analyzed online by an Agilent 6890N GC. The liquid products were drained periodically from the gas-liquid separator and analyzed by an Agilent 7890A GC.

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[1] a) G. W. Huber, S. Iborra, A. Corma, *Chem. Rev.* **2006**, *106*, 4044-4098; b) D. M. Alonso, S. G. Wettstein, J. A. Dumesic, *Chem. Soc. Rev.* **2012**, *41*, 8075-8098; c) X. Wang, R. Rinaldi, *Angew. Chem. Int. Ed.* **2013**, *52*, 11499-11503; d) K. Barta, P. C. Ford, *Acc. Chem. Res.* **2014**, *47*, 1503-1512; e) M. Besson, P. Gallezot, C. Pinel, *Chem. Rev.* **2014**, *114*, 1827-1870.

[2] a) G. W. Huber, J. N. Chheda, C. J. Barrett, J. A. Dumesic, *Science* **2005**, *308*, 1446-1450; b) C. Zhao, Y. Kou, A. A. Lemonidou, X. B. Li, J. A. Lercher, *Angew. Chem. Int. Ed.* **2009**, *48*, 3987-3990; c) J. Q. Bond, D. M. Alonso, D. Wang, R. M. West, J. A. Dumesic, *Science* **2010**, *327*, 1110-1114; d) N. Yan, Y. Yuan, R. Dykeman, Y. Kou, P. J. Dyson, *Angew. Chem. Int. Ed.* **2010**, *49*, 5549-5553; e) B. G. Harvey, R. L. Quintana, *Energy Environ. Sci.* **2010**, *3*, 352-357; f) A. Corma, O. de la Torre, M. Renz, N. Villandier, *Angew. Chem. Int. Ed.* **2011**, *50*, 2375-2378; g) A. D. Sutton, F. D. Waldie, R. L. Wu, M. Schlaf, L. A. Silks, J. C. Gordon, *Nature Chem.* **2013**, *5*, 428-432; h) Q.-N. Xia, Q. Cuan, X.-H. Liu, X.-Q. Gong, G.-Z. Lu, Y.-Q. Wang, *Angew. Chem. Int. Ed.* **2014**, *53*, 9755-9760; i) M. Mascal, S. Dutta, I. Gandarias, *Angew. Chem. Int. Ed.* **2014**, *53*, 1854-1857; j) S. Sankaranarayanapillai, S. Sreekumar, J. Gomes, A. Grippo, G. E. Arab, M. Head-Gordon, F. D. Toste, A. T. Bell, *Angew. Chem. Int. Ed.* **2015**, *54*, 4673-4677.

[3] a) A. Fukuoka, P. L. Dhepe, *Angew. Chem. Int. Ed.* **2006**, *45*, 5161-5163; b) N. Ji, T. Zhang, M. Y. Zheng, A. Q. Wang, H. Wang, X. D. Wang, J. G. G. Chen, *Angew. Chem. Int. Ed.* **2008**, *47*, 8510-8513; c) Y. T. Cheng, J. Jae, J. Shi, W. Fan, G. W. Huber, *Angew. Chem. Int. Ed.* **2012**, *51*, 1387-1390; d) Y. T. Cheng, Z. P. Wang, C. J. Gilbert, W. Fan, G. W. Huber, *Angew. Chem. Int. Ed.* **2012**, *51*, 11097-11100; e) Y. L. Wang, W. P. Deng, B. J. Wang, Q. H. Zhang, X. Y. Wan, Z. C. Tang, Y. Wang, C. Zhu, Z. X. Cao, G. C. Wang, H. L. Wan, *Nat. Commun.* **2013**, *4*, 2141; f) F. Liu, M. Audemar, K. D. Vigier, D. Cartigny, J. M. Clacens, M. F. C. Gomes, A. A. H. Padua, F. De Campo, F. Jerome, *Green Chem.* **2013**, *15*, 3205-3213; g) F. Liu, M. Audemar, K. De Oliveira Vigier, J.-M. Clacens, F. De Campo, F. Jerome, *Green Chem.* **2014**, *16*, 4110-4114; h) P. Sun, G. Gao, Z. Zhao, C. Xia, F. Li, *ACS Catal.* **2014**, *4*, 4136-4142; i) T. Prasomsri, M. Shetty, K. Murugappan, Y. Roman-Leshkov, *Energy Environ. Sci.* **2014**, *7*, 2660-2669.

[4] R. W. Alder, N. P. Hyland, J. C. Jeffery, T. Riis-Johannessen, D. J. Riley, *Org. Biomol. Chem.* **2009**, *7*, 2704-2715.

[5] a) H. Zhao, J. E. Holladay, H. Brown, Z. C. Zhang, *Science* **2007**, *316*, 1597-1600; b) R. Weingarten, A. Rodriguez-Beuerman, F. Cao, J. S. Luterbacher, D. M. Alonso, J. A. Dumesic, G. W. Huber, *ChemCatChem* **2014**, *6*, 2229-2234.

[6] B. G. Harvey, H. A. Meylemans, *J. Chem. Technol. Biotechnol.* **2011**, *86*, 2-9.

[7] H.-Y. Zheng, Y.-L. Zhu, B.-T. Teng, Z.-Q. Bai, C.-H. Zhang, H.-W. Xiang, Y.-W. Li, *J. Mol. Catal. A: Chem.* **2006**, *246*, 18-23.

[8] A. Corma, O. de la Torre, M. Renz, *Energy Environ. Sci.* **2012**, *5*, 6328-6344.

[9] a) P. Wang, S. Bai, J. Zhao, P. Su, Q. Yang, C. Li, *ChemSusChem* **2012**, *5*, 2390-2396; b) P. V. R. Rao, V. P. Kumar, G. S. Rao, K. V. R. Chary, *Catal. Sci. Tech.* **2012**, *2*, 1665-1673.

[10] a) E. O'Reilly, C. Iglesias, D. Ghislieri, J. Hopwood, J. L. Galman, R. C. Lloyd, N. J. Turner, *Angew. Chem. Int. Ed.* **2014**, *53*, 2447-2450; b) S. Kotani, S. Aoki, M. Sugiura, M. Ogasawara, M. Nakajima, *Org. Lett.* **2014**, *16*, 4802-4805; c) T. A. Minard, C. T. Oswin, F. D. C. Waldie, J. K Howell, B. M. T. Scott, D. D. Mondo, R. J. Sullivan, B. Stein, M. Jennings, M. Schlaf, *J. Mol. Catal. A: Chem.* **2016**, *422*, 175-187; d) P. Li, J. Zhao, C. Xia, F. Li, *Org. Lett.* **2014**, *16*, 5992-5995.

[11] G. Li, N. Li, M. Zheng, S. Li, A. Wang, Y. Cong, X. Wang, T. Zhang, *Green Chem.* **2016**, *18*, 3607-3613.

[12] Y. L. Louie, J. Tang, A. M. L. Hell, A. T. Bell, *Appl. Catal. B: Environ.* **2017**, *202*, 557-568.

[13] M. Haruta, M. Daté, *Appl. Catal. A: Gen.* **2001**, *222*, 427-437.

[14] J. M. Poirier, G. Dujardin, *Heterocycles* **1987**, *25*, 399-407.

[15] J. Mei, J. Mao, Z. Chen, S. Yuan, H. Li, H. Yin, *Chem. Eng. Sci.* **2015**, *131*, 213-218.

[16] Y. Gong, L. Lin, B. X. Zhang, *Chin. J. Chem.* **2012**, *30*, 327-332.

[17] C. R. Waidmann, A. W. Pierpont, E. R. Batista, J. C. Gordon, R. L. Martin, L. A. Silks, R. M. West, R. L. Wu, *Catal. Sci. Tech.* **2013**, *3*, 106-115.

[18] Z. Xu, P. Yan, W. Xu, X. Liu, Z. Xia, B. Chung, S. Jia, Z. C. Zhang, *ACS Catal.* **2015**, *5*, 788-792.

[19] J. He, C. Zhao, J. A. Lercher, *J. Am. Chem. Soc.* **2012**, *134*, 20768-20775.

[20] a) G. Li, N. Li, X. Wang, X. Sheng, S. Li, A. Wang, Y. Cong, X. Wang, T. Zhang, *Energy Fuels* **2014**, *28*, 5112-5118; b) X. Zhang, Q. Deng, P. Han, J. Xu, L. Pan, L. Wang, J.-J. Zou, *AIChE J.* **2016**, n/a-n/a; c) J. Yang, S. Li, N. Li, W. Wang, A. Wang, T. Zhang, Y. Cong, X. Wang, G. W. Huber, *Ind. Eng. Chem. Res.* **2015**, *54*, 11825-11837; d) Q. Deng, G Nie, L. Pan, J.-J. Zou, X. Zhang, L. Wang, *Green Chem.* **2015**, *17*, 4473-4481.

[21] J. Yang, N. Li, G. Li, W. Wang, A. Wang, X. Wang, Y. Cong, T. Zhang, *Chem. Commun.* **2014**, *50*, 2572-2574.

[22] a) X. Sheng, G. Li, W. Wang, Y. Cong, X. Wang, G. W. Huber, N. Li, A. Wang, T. Zhang, *AIChE J.* **2016**, *62*, 2754-2761; b) X. Sheng, N. Li, G. Li, W. Wang, A. Wang, Y. Cong, X. Wang, T. Zhang, *Green Chem.* **2016**, *18*, 3707-3711; c) S. S. Li, N. Li, W. T. Wang, L. Li, A. Q. Wang, X. D. Wang, T. Zhang, *Sci Rep* **2016**, *6*, 7.

[23] S. Ivanova, C. Petit, V. Pitchon, *Appl. Catal. A: Gen.* **2004**, *267*, 191-201.

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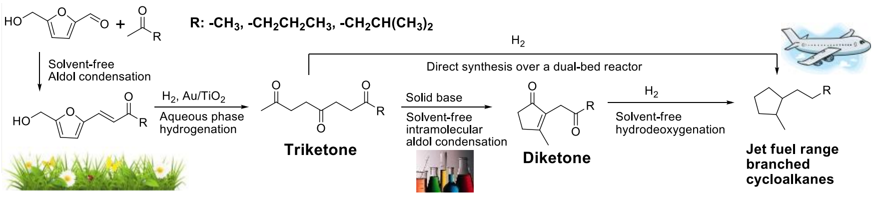

Renewable C_9-C_{12} triketones with repeating [$COCH_2CH_2$] units were synthesized in high carbon yields (~90%) over a cost-effective and reusable Au/TiO_2 catalyst. The triketones as obtained can be used as feedstocks in the production of conducting or semi-conducting polymers. Furthermore, these triketones can also be converted to diketones or jet fuel range branched cycloalkanes with high density and low freezing points.

Shanshan Li, Fang Chen, Ning Li, Wentao Wang, Xueru Sheng, Aiqin Wang, Yu Cong, Xiaodong Wang, and Tao Zhang**

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Synthesis of Renewable Triketones, Diketones and Jet Fuel Range Cycloalkanes with 5-Hydroxymethylfurfural and Ketones