Supporting Information

# Synthesis of jet fuel range cycloalkanes with diacetone alcohol from lignocellulose

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#### 1. Experimental

#### **1.1 Preparation of catalysts**

Nafion resin was supplied by Jiangsu Success Resin Corporation. Amberlyst-45 and Amberlite IRC 76CRF resins were purchased from the Dow Chemical Company.

Activated carbon loaded noble metal (M/C, M = Ru, Pt, Rh, Ir, Pd) catalysts were prepared by the classical wet impregnation method using an activated carbon supplied by Guanghua activated carbon company. To facilitate the comparison, the theoretical contents of noble metals in the catalysts were controlled as 5% by weight (denoted as 5wt.%). Taking the preparation of 5wt.%Ru/C catalyst for example: 3.88 g 10wt.% RuCl<sub>3</sub>•3H<sub>2</sub>O aqueous solution was added dropwise into a suspension of 3 g activated carbon and 30 mL water. After being stirred at 318 K for 1 h, the pH of the mixture was adjusted to 9-10 by 1 mol L<sup>-1</sup> NaOH. Then 20 g 40wt.% formaldehyde solution was added dropwise into the mixture. After being stirred at 358 K for 70 min, the mixture was filtered, washed with deionized water until no Cl<sup>-</sup> ion was detected in the filtrate and dried at 353 K for 3 h.

#### **1.2.** Activity test

#### **1.2.1 Hydrogenation of diacetone alcohol**

The solvent-free hydrogenation of diacetone alcohol was carried out in a stainless steel tubular flow reactor described in our previous work.<sup>1</sup> For each test, 1.0 g catalyst was used. The diacetone alcohol was pumped into the reactor at 0.08 mL min<sup>-1</sup> from the top of the reactor, along with hydrogen at a flow rate of 120 mL min<sup>-1</sup>. After passing a

gas-liquid separator, the liquid products were drained periodically from the gas-liquid separator and analyzed by an Agilent 7890B GC equipped with a HP-INNOWAX capillary column ( $30 \text{ m} \times 0.25 \text{ mm} \times 0.5 \text{ \mum}$ , FID detector).

#### 1.2.2 Dehydration/Diels-Alder reaction of 2-methyl-2,4-pentanediol

The solvent-free dehydration/Diels-Alder reaction of 2-methyl-2,4-pentanediol was performed in a stainless steel batch reactor. Typically, 4.5 g 2-methyl-2,4-pentanediol and 0.45 g solid acid catalyst (or 0.45 mL acid solution) were used for each test. The mixture was stirred at 443 K for 6 h. After being cooled down to room temperature, the products became two phases. The organic phase and aqueous phase were separated, diluted and analyzed by an Agilent 7890A GC equipped with a HP-5 capillary column.

#### 1.2.3 Hydrogenation of the dehydration/Diels-Alder reaction products

The solvent-free hydrogenation of the dehydration/Diels-Alder products was carried out in the same steel tubular flow reactor as the one used for the hydrogenation of diacetone alcohol. 1.0 g 5wt.% Pd/C was used as catalyst. Before reaction, the catalyst was *in-situ* reduced with hydrogen flow (at a rate of 120 mL min<sup>-1</sup>) at 523 K for 2 h. After the reactor was cooled down to 443 K and stabilized at that temperature for 0.5 h, the liquid dehydration/Diels-Alder products (obtained over the Nafion resin under the optimum conditions) were pumped into the reactor (at a rate of 0.04 mL min<sup>-1</sup>), along with hydrogen flow (at a rate of 120 mL min<sup>-1</sup>). After passing a gas-liquid separator, the liquid phase product was drained from the separator and analyzed by an Agilent 7890A GC equipped with a HP-5 capillary column.

## 1.2.4 Synthesis of jet fuel range cycloalkanes by the one-pot reaction of diacetone alcohol and hydrogen

To fulfil the need of real application, we tried the one-pot process for the direct synthesis of jet fuel range cycloalkanes with diacetone alcohol and hydrogen. Firstly, a mixture of diacetone alcohol (20.0 g), 5wt.% Ru/C (1.0 g) and Nafion resin (2.0 g) was stirred at 333 K in H<sub>2</sub> atmosphere (4 MPa) for 3 h. After being purged with argon, the mixture was heated to 443 K and stirred at that temperature for 6 h. Finally, the hydrogen was introduced into the reactor (4 MPa). The mixture was stirred at 443 K for 3 h. From the analysis result of the GC-MS (see Figure S5), 2-methyl-pentane was identified as the major product from the one-pot process. The carbon yields of  $C_{12}$  and  $C_{10}$  cycloalkanes were very low. This is because tertiary alcohol is very easy to be dehydrated. Under the co-catalysis of 5wt.% Ru/C and Nafion resin, the major product in the first stage is 4-methyl-2-pentanol (from the dehydration/hydrogenation of diacetone alcohol) instead of 2-methyl-2,4-pentanediol (see Figure S6 for the GC-MS analysis result of the first stage product). In the second and third stage, the 4-methyl-2pentanol which was generated in the first stage will be further dehydrated and hydrogenated to 2-methyl-pentane. That is the reason why 2-methyl-pentane was identified as the major product from the one-pot process.

To avoid the unexpected dehydration reaction during the first stage, we also tried the one-pot process by another method. Firstly, we conducted the hydrogenation of diacetone alcohol (20.0 g) under the catalysis of the 5wt.% Ru/C (1.0 g). The hydrogenation reaction was carried out at 333 K in H<sub>2</sub> atmosphere (4 MPa) for 3 h.

After the hydrogenation stage, we opened the batch reactor and added Nafion resin (2.0 g) into the reaction system. The reaction was carried out at 443 K in Ar atmosphere for 6 h. Subsequently, the hydrogen was introduced into the reactor. The reaction was conducted at 443 K in hydrogen atmosphere (4 MPa) for 12 h. According to the analysis of the final product, 4.6% carbon yield of 2-methyl-pentane, 1.3% carbon yield of octane and 60.7% carbon yield of  $C_{10}$ - $C_{14}$  cycloalkanes ( $C_{10}$  cycloalkane yield: 12.2%;  $C_{12}$  cycloalkane yield: 44.3%;  $C_{14}$  cycloalkane yield: 4.2%) were obtained by such a one-pot process, indicating it is possible to directly synthesize  $C_8$ - $C_{14}$  cycloalkanes with diacetone alcohol and hydrogen.

#### 1.3. Microcalorimetric measurement of NH<sub>3</sub> adsorption

The microcalorimetric measurements of ammonia adsorption for the investigated acidic resins used in the hydrolysis reaction were performed at 353 K using a BT2.15 heat-flux calorimeter (France, Seteram) connected to a gas-handling and a volumetric system employing MKS Baratron Capacitance Manometers for precision pressure measurement ( $\pm 0.5 \times 10^{-4}$  Torr). Before each measurement, ammonia (purity > 99.9%) was purified by successive freeze-pump-thaw cycles. The specific mass of sample with similar amount of acid sites was evacuated in a quartz cell at 353 K overnight under high vacuum to remove the physically adsorbed substance. The differential heat was measured as a function of acid site coverage by repeatedly introducing small dosage of ammonia onto the samples until the equilibrium pressure reached about 5-6 torr. Then the system was evacuated overnight to remove the physically adsorbed ammonia, and a second adsorption was performed. The amount of irreversible adsorbed ammonia was

determined by the difference between the isotherms of the first and second adsorption cycles.





Figure S1. GC-MS chromatogram of the organic phase products from the dehydration/Diels-Alder reaction of 2-methyl-2,4-pentanediol over

Nafion resin. Reaction conditions: 443 K, 6 h; 4.5 g 2-methyl-2,4-pentanediol, 0.45 g catalyst.



**Figure S2**. GC-MS chromatogram of the aqueous phase products from the dehydration/Diels-Alder reaction of 2-methyl-2,4-pentanediol over Nafion resin. Reaction conditions: 443 K, 6 h; 4.5 g 2-methyl-2,4-pentanediol, 0.45 g catalyst.



**Figure S3.** Adsorption heat versus  $NH_3$  coverage at 353 K on Nafion ( $\blacksquare$ ), Amberlyst-45 ( $\blacktriangle$ ) and Amberlite IRC 76CRF ( $\blacktriangledown$ ) resins.



**Figure S4**. GC-MS chromatogram of the liquid products from the hydrogenation of the dehydration/Diels-Alder products over the 5wt.% Pd/C catalyst. Reaction conditions: 443 K, 0.1 MPa H<sub>2</sub>; 1.0 g 5wt.% Pd/C catalyst, hydrogen flow rate: 120 mL min<sup>-1</sup>, the flow rate of liquid feedstock: 0.04 mL min<sup>-1</sup>.



Figure S5. GC-MS chromatogram of the final products from the one-pot process of diacetone alcohol and hydrogen under the co-catalysis of the

5wt.%Ru/C and Nafion resin.



**Figure S6**. GC-MS chromatogram of the first stage products from the one-pot process of diacetone alcohol and hydrogen under the co-catalysis of the 5wt.%Ru/C and Nafion resin.

**Table S1.** Conversions of feedstocks and the carbon yields of  $C_{10}$  or  $C_{12}$  cycloalkenes from the Diels-Alder reaction of conjugated dienes in the absences of catalyst. Reaction conditions: 443 K, 6 h; 2.0 g 2-methyl-1,3-pentadiene or 4-methyl-1,3pentadiene.

Feedstock	Conversion (%)	Carbon yield (%)	
		C <sub>10</sub> cycloalkane	C <sub>12</sub> cycloalkane
Isoprene	73.5	71.1	0
2,3-Dimethyl-1,3-butadiene	39.6	0	27.3

**Table S2.** Carbon ratio of the  $C_{12}$  hydrocarbons to the  $C_{10}$  and  $C_{14}$  hydrocarbons ( $C_{12}$  /( $C_{10} + C_{14}$ )) in the dehydration/Diels-Alder products and the contribution of  $C_6$  route vs.  $C_4$  and  $C_8$  routes ( $C_6/(C_4 + C_8)$ ) to the hydrocarbon products. Reaction conditions: 443 K, 6 h; 4.5 g 2-methyl-2,4-pentanediol and 0.45 g catalyst.

Entry	Catalyst	$C_{12}/(C_{10}+C_{14})^a$	$C_6/(C_4 + C_8)^b$
1	Nafion	2.6	3.9
2	Amberlyst-45	1.9	3.1
3	Amberlite IRC 76CRF		6.0
4 <sup><i>c</i></sup>	$H_2SO_4$	3.7	4.1
5 <sup>c</sup>	H <sub>3</sub> PO <sub>4</sub>	6.3	4.7
6 <sup>c</sup>	Acetic acid		6.8

*a*:  $C_{12}/(C_{10} + C_{14}) = (Carbon in the C_{12} hydrocarbons)/(Carbon in the C_{10} and C_{14} hydrocarbons);$ *b* $: <math>C_{6}/(C_{4} + C_{8}) = 2 \times [(Carbon in the C_{6} and C_{12} hydrocarbons) + 0.6 \times (carbon in C_{10} hydrocarbons) + 3 \times (carbon in C_{14} hydrocarbons)/7]/{3 \times [(Carbon in C_{4} and C_{8} hydrocarbons) + 0.4 \times (carbon in C_{10} hydrocarbons) + 4 \times (carbon in C_{14} hydrocarbons)/7]}.$ *c*: 0.45 mL acid solution was used in the test. The concentrations of the H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub> and acetic acid solutions were controlled as 4 N.

**Table S3.** Carbon ratio of the  $C_{12}$  hydrocarbons to the  $C_{10}$  and  $C_{14}$  hydrocarbons ( $C_{12}$  /( $C_{10} + C_{14}$ )) in the dehydration/Diels-Alder products over Nafion resin and the contribution of  $C_6$  route vs.  $C_4$  and  $C_8$  routes ( $C_6/(C_4 + C_8)$ ) to the hydrocarbon products.

Entry	Reaction	Catalyst	Reactio	$C_{12}/(C_{10} + C_{14})^a$	$C_{6}/(C_{4}+C_{8})^{b}$
	temperatur	dosage (g)	n time		
	e (K)		(h)		
1	333	0.45	6	34.6	47.3
2	353	0.45	6	10.3	14.3
3	383	0.45	6	9.4	8.9
4	413	0.45	6	3.6	4.5
5	443	0.45	6	2.6	3.9
6	473	0.45	6	2.0	3.2
7	443	0.045	6	3.3	4.3
8	443	0.225	6	3.6	4.8
9	443	0.90	6	2.5	3.7
10	443	0.45	0.5	5.3	6.0
11	443	0.45	1	4.2	5.1
12	443	0.45	3	3.3	4.7
13	443	0.45	12	1.9	3.0
14	443	0.45	24	2.6	3.8

*a*:  $C_{12}/(C_{10} + C_{14}) = (Carbon in the C_{12} hydrocarbons)/(Carbon in the C_{10} and C_{14} hydrocarbons);$ *b* $: <math>C_6/(C_4 + C_8) = 2 \times [(Carbon in the C_6 and C_{12} hydrocarbons) + 0.6 \times (carbon in C_{10} hydrocarbons) + 3 \times (carbon in C_{14} hydrocarbons)/7]/{3 \times [(Carbon in C_4 and C_8 hydrocarbons) + 0.4 \times (carbon in C_{10} hydrocarbons) + 4 \times (carbon in C_{14} hydrocarbons)/7]}.$ 

### References

F. Chen, N. Li, W. Wang, A. Wang, Y. Cong, X. Wang and T. Zhang, *Chem. Commun.*, 2015, **51**, 11876-11879.