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Synthesis of renewable high-density fuel with isophorone

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1,1,3-Trimethyl-5-(2,4,4-trimethylcyclohexyl)cyclohexane, a renewable high density fuel, was first produced in a high overall carbon yield (~70%) with isophorone which can be derived from hemicellulose. The synthetic route used this work contains three steps. In the first step, 3,3,5-trimethylcyclohexanone was synesized by the selective hydrogenation of isophorone. Among the investigated catalysts, the Pd/C exhibited the highest activity and selectivity. Over this catalyst, a high carbon yield (99.0%) of 3,3,5-trimethylcyclohexanone was achieved under mild conditions (298 K, 2 MPa H_2, 1 h). In the second step, 3,5,5-trimethyl-2-(3,3,5-trimethylcyclohexylidene)cyclohexanone was produced in a high carbon yield (76.4%) by the NaOH catalyzed self-aldol condensation of 3,3,5-trimethylcyclohexanone which was carried out in a round bottom flask attached to the Dean–Stark apparatus. In the third step, the 3,5,5-trimethyl-2-(3,3,5-trimethylcyclohexylidene) cyclohexanone was hydrodeoxygenated under solvent-free conditions. High carbon yield (93.4%) of 1,1,3-trimethyl-5-(2,4,4-trimethylcyclohexyl)cyclohexane was obtained over the Ni/SiO_2 catalyst. The 1,1,3-trimethyl-5-(2,4,4-trimethylcyclohexyl)cyclohexane as obtained has a density of 0.858 g mL^{-1} and a freezing point of 222.2 K. As a potential application, it can be blended into conventional fuels (such as RP-1, RG-1, etc.) for rocket propulsion.

With the increasing of social concern about the sustainable energy and environmental problems, the catalytic conversion of renewable biomass to high quality fuel[1–3] and useful chemicals[4–9] has drawn a lot of attention. Polycycloalkanes are a family of nontoxic propellants which are widely used for rockets and missile[10–13]. Due to their relatively higher densities (or volumetric heat values) than traditional refined fuels, polycycloalkanes can be used to increase the range and payload of aircrafts without increasing the volume of fuel tank. This character is especially useful for rocket to save more space (or weight) for electronic equipment, astronauts and other components.

Currently, the most used rocket fuels (such as RP-1, RG-1, etc.) are derived from the petroleum in few special oil fields[14]. In the long run, the exploration of new route for synthesis of high-density fuels with the renewable and CO_2 neutral biomass is highly expected. During the past years, several routes have been developed for the production of polycycloalkanes with terpenes[15–18]. Due to the limited resource of terpenes, it is still necessary to develop some new synthetic route for polycycloalkanes with cheaper and more available biomass[19–26]. Hemicellulose is one of the major components of agriculture and forest wastes (see supplementary Table S1 for the hemicellulose contents in various terrestrial biomasses). Isophorone is the trimerization product of acetone which is the by-product in the Acetone-Butanol-Ethanol fermentation of hemicellulose[27]. Based on the cyclic chemical structure of this compound, we think that it can be used as potential feedstock for the synthesis of high-density polycycloalkanes. To the best of our knowledge, there is no report about this.

In this work, 1,1,3-trimethyl-5-(2,4,4-trimethylcyclohexyl)cyclohexane (*i.e.* the compound **5** in Fig. 1), a C_{18} bicycloalkane with a density of 0.858 g mL^{-1} and a freezing point of 222.2 K, was first synthesized in an overall carbon yield of ~70% by the selective hydrogenation and the self-aldol condensation of isophorone, followed by the solvent-free hydrodeoxygenation (HDO) of the C_{18} condensation product. The synthetic route for this C_{18}

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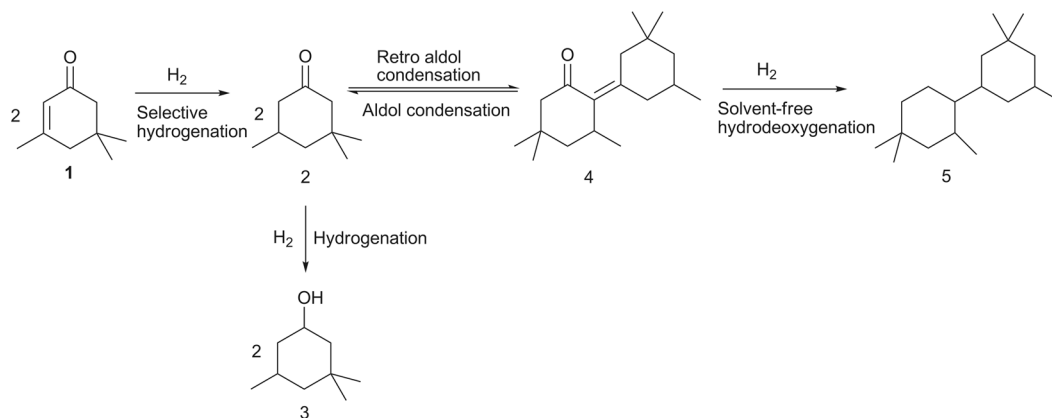
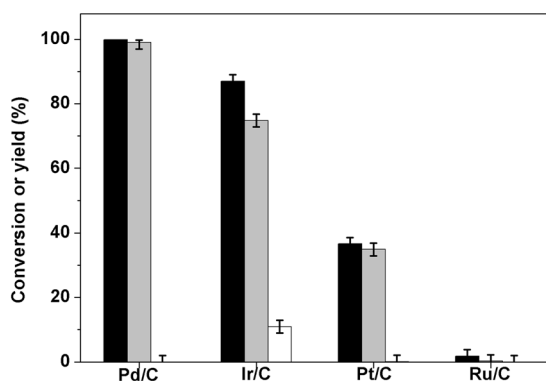**Figure 1.** Strategy for the synthesis of compound 2 with isophorone and hydrogen.

Figure 2. Isophorone conversions (black bars) and the carbon yields of compound 2 (gray bars), and compound 3 (white bars) over the different catalysts. Reaction conditions: 298 K, 1 h; 1.16 g (8.4 mmol) isophorone, 0.05 g catalyst, 2.0 MPa H_2.

bicycloalkane was illustrated in Fig. 1. As a potential application, the compound **5** obtained in this work can be blended into conventional high-density fuels for rocket propulsion.

Results and Discussion

Synthesis of 3,3,5-trimethylcyclohexanone.

3,3,5-Trimethylcyclohexanone (*i.e.* the compound **2** in Fig. 1) is a chemical which is widely used as a solvent for vinyl resins, laquers, varnishes, paints and other coatings[28, 29]. In the first part of this work, we investigated the selective hydrogenation of isophorone to compound **2** over a series of noble metal catalysts (see Fig. 2). From the analysis of GC and NMR spectra (see Supplementary Figs S1 and S2), compound **2** was identified as the major component in the hydrogenation products. This result can be rationalized because the hydrogenation of C=C bond in isophorone is very fast and thermodynamicly more favorable than the hydrogenation of C=O bond[30]. Among the investigated catalysts, the Pd/C catalyst has the highest activity and selectivity for the hydrogenation of isophorone to 3,3,5-trimethylcyclohexanone. Over this catalyst, high carbon yield of compound **2** (99.0%) was achieved after the reaction was carried out at 298 K for 1 h. According to literature[31, 32], this result can be explained because Pd is more active and selective than Ir, Pt, Ru for the hydrogenation of C=C bond in unsaturated carbonyl compounds. The higher activity Pd for the hydrogenation of C=C bond can be explained by the stronger H_2/metal interactions accompanied by a preferred formation of surface hydrogen atoms[33]. In the hydrogenation product over the Ir/C catalyst, small amount of 3,3,5-trimethylcyclohexanol (*i.e.* the compound **3** in Fig. 1) was also detected (see Supplementary Figs S1 and S3). This compound was produced from the simultaneous hydrogenation of C=C and C=O bonds in isophorone molecule (see Fig. 1).

Synthesis of 3,5,5-trimethyl-2-(3,3,5-trimethylcyclohexylidene)cyclohexanone.

In the second part of this work, we explored the self-aldol condensation of compound **2** under the catalysis of NaOH. From the analysis of GC-MS (Supplementary Figs S4 and S5), 3,5,5-trimethyl-2-(3,3,5-trimethyl-cyclohexylidene) cyclohexanone (*i.e.* compound **4** in Fig. 1) was identified as the major product from this reaction. No C_{27} oxygenates from the trimerization of compound **2** was detected in the product, which can be explained by the conjugate chemical structure of compound **4**. The compound **4** as obtained exists as a liquid at room temperature (see Supplementary Fig. S6). Therefore, it can be directly used for the HDO process without using any solvent.
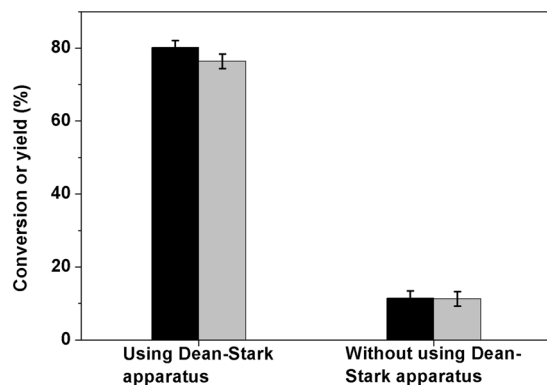
Figure 3. Conversion of compound 2 (black bars) and the carbon yield of compound 4 (gray bars) under the catalysis of NaOH. Reaction conditions: 443 K, 72 h; 20.0 g (0.143 mol) compound 2, 50 mmol NaOH and 20 mL *p*-xylene.
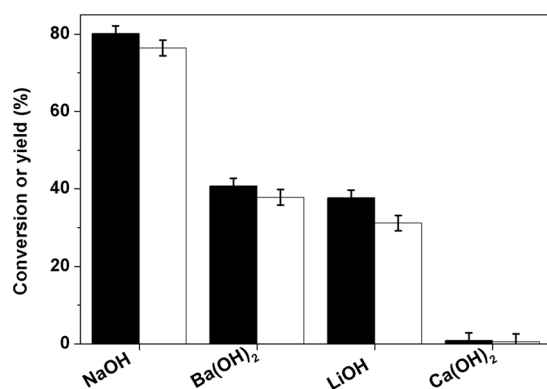

Figure 4. Conversion of compound 2 (black bars), the carbon yields of compound 4 (gray bars) over base catalysts. Reaction conditions: 443 K, 72 h; 20.0 g (0.143 mol) compound **2**, 50 mmol alkali hydroxide (or 25 mmol alkaline earth metal hydroxide) and 20 mL *p*-xylene.

From the Fig. 3, it was noticed that the utilization of Dean-Stark apparatus is beneficial for the generation of compound **4** from the self-aldol condensation of compound **2**. This result can be comprehended from the point view of reaction equilibrium. As we know, the aldol condensation is a reversible reaction. Therefore, the removal of water from the reaction system is favorable for the generation of compound **4** and the restraining of retro-aldol condensation reaction.

Subsequently, we also compared the activity of series of base catalysts for the self-aldol condensation of compound **2** (see Fig. 4). Among them, NaOH exhibited the highest activity. Over this catalyst, high carbon yield of compound **4** (76.4%) was achieved after the reaction was carried out at 443 K for 72 h. The activity of base catalysts decrease in the order of $NaOH > Ba(OH)_2 > LiOH > Ca(OH)_2$ which is basically consistent with the base strength (see pK_b values in Supplementary Table S6) sequence of these catalysts.

Synthesis of 1,1,3-trimethyl-5-(2,4,4-trimethylcyclohexyl)cyclohexane. Finally, we studied the solvent-free hydrodeoxygenation (HDO) of compound **4** over a series of SiO_2 supported non-noble metal catalysts (see Fig. 5). Among the investigated catalysts, the Ni/SiO_2 and Co/SiO_2 catalysts exhibited evidently higher HDO activity than those of the Cu/SiO_2 and Fe/SiO_2 catalysts. Over the Ni/SiO_2 and Co/SiO_2 catalysts, compound **4** was completed hydrodeoxygenated at 573 K, high carbon yield (93.4% and 91.8%) of 1,1,3-trimethyl-5-(2,4,4-trimethylcyclohexyl)cyclohexane (*i.e.* compound **5**) was achieved. Besides compound **5**, small amount of C_9-C_{17} alkanes (such as 1,1,3-trimethylcyclohexane and 1,1,3-trimethyl-5-(2,4-dimethylcyclohexyl)cyclohexane) were also identified in the HDO product (see Supplementary Figs S7–S10). According to literature[34, 35], these C_9-C_{17} cycloalkanes may be generated by the C-C cleavage reactions (such as retro-aldol condensation, hydrocracking, *etc.*) during the HDO process. The reaction pathways for the generation of different alkanes from the HDO process were proposed in Fig. 6. According to our measurement, the cycloalkane mixture as obtained has a density of 0.858 g mL^{-1} and a freezing point of 222.2 K. As a potential application, it can be blended into conventional high density fuels for rocket propulsion. Compared with the RP-1 fuel (which is widely used as the first-stage boosters or the propellant for many rockets[14]) and other lignocellulose derived dicycloalkanes (such as dicyclohexane[23] and dicyclopentane[19–21]) which has been reported in recent literature (see Supplementary Table S3),
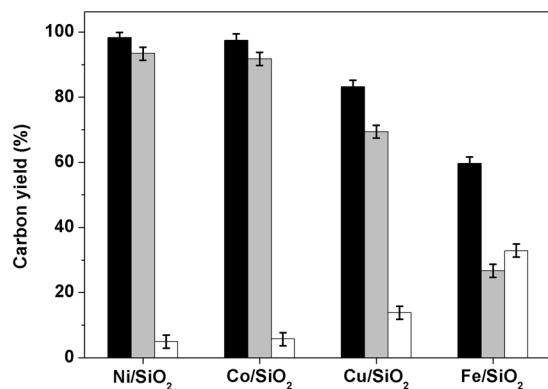
Figure 5. Carbon yields of compound 5 (gray bars), C_9-C_{17} cycloalkanes (white bars) and cycloalkanes (*i.e.* the sum of compound 5 and C_9-C_{17} cycloalkanes) (black bars), from the solvent-free HDO of compound 4 over the SiO_2 loaded non-noble metal catalysts. Reaction conditions: 573 K, 6 MPa H_2; 1.8 g catalyst, compound 4 flow rate: 0.04 mL min^{-1}, hydrogen flow rate: 120 mL min^{-1}.
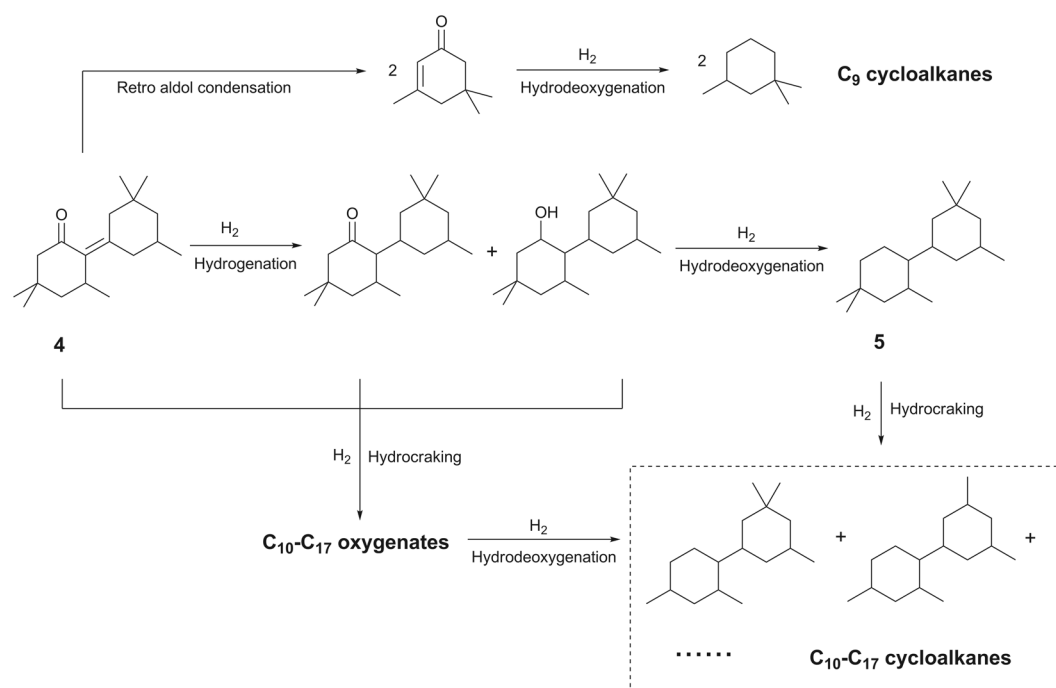

Figure 6. Reaction pathways for the production of different cycloalkanes from the solvent-free HDO of compound 4.

the compound **5** obtained in this work has higher density or lower freezing point, which is advantage in the real application.

To fulfil the need of real application, we also studied the stability of the Ni/SiO$_2$ catalyst under the investigated conditions. As we can see from Fig. 7, the Ni/SiO$_2$ catalyst is stable in the first 19 h. With the further increase of reaction time from 19 h to 45 h, the carbon yields of compound **5** and cycloalkanes over the Ni/SiO$_2$ catalyst decreased, while the carbon yield of C_9-C_{17} cycloalkanes slightly increased. According to the characterization of fresh and used Ni/SiO$_2$ catalyst (see supplementary Table S4), this phenomenon can be explained by the aggregation of Ni particles during the HDO test.

Conclusions

Herein, we reported a new route for the synthesis of a renewable high density dicycloalkane, 1,1,3-trimethyl-5-(2,4,4-trimethylcyclohexyl)cyclohexane with isophorone. In the first step, isophorone was converted to 3,3,5-trimethylcyclohexanone by selective hydrogenation. Over the Pd/C catalyst, 99.0% carbon yield of 3,3,5-trimethylcyclohexanone was obtained under mild conditions. In the second step, 3,5,5-trimethyl-2-(3,3,5-trimethylcyclohexylidene)-cyclohexanone was synthesized by the self-aldol condensation of
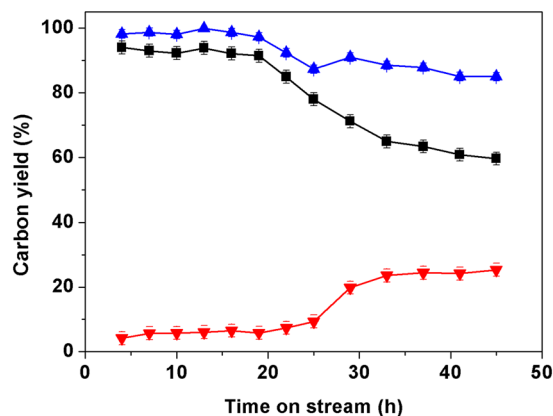
Figure 7. Carbon yields of compound 5 (■), C_9-C_{17} cycloalkanes (▼) and cycloalkanes (*i.e.* the sum of compound 5 and C_9-C_{17} cycloalkanes) (▲), from the solvent-free HDO of compound 4 over the Ni/SiO$_2$ catalyst as the function of reaction time. Reaction conditions: 573 K, 6.0 MPa H$_2$; 1.80 g Ni/SiO$_2$ catalyst, compound 4 flow rate: 0.04 mL min^{-1}, hydrogen flow rate: 120 mL min^{-1}.

3,3,5-trimethylcyclohexanone under the catalysis of NaOH. The utilization of Dean-Stark apparatus is favorable for this reaction. In the third step, the 3,5,5-trimethyl-2-(3,3,5-trimethylcyclohexylidene)cyclohexanone as further hydrodeoxygenated under solvent-free conditions. High carbon yields of 1,1,3-trimethyl-5-(2,4,4-trimethylcyclohexyl)cyclohexane (93.4%) was achieved over the Ni/SiO$_2$ catalyst at 573 K. The polycycloalkanes mixture as obtained has a density of 0.858 g mL^{-1} and a freezing point of 222.2 K. As a potential application, it can be blended into conventional cycloalkane fuels (such as RP-1) for rockets propulsion.

Methods

Preparation of catalysts. The Pd/C, Ir/C, Pt/C, Ru/C, LiOH, NaOH, Ca(OH)$_2$ and Ba(OH)$_2$ catalysts are commercial available. The Ni/SiO$_2$, Co/SiO$_2$, Cu/SiO$_2$ and Fe/SiO$_2$ catalysts used in the hydrodeoxygenation (HDO) process were prepared by the method described in supporting information.

Activity test. The hydrogenation of 3,3,5-trimethylcyclohexanone was conducted with a stainless steel batch reactor. The self-aldol condensation of 3,3,5-trimethylcyclohexanone was carried out in a flask which was attached to the Dean-Stark apparatus to remove the water generated during the reaction. The solvent-free HDO of 3,5,5-trimethyl-2-(3,3,5-trimethylcyclohexylidene)cyclohexanone was conducted at 573 K using a fixed-bed continuous flow reactor. The detail information for the activity tests was described in supporting information.

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Acknowledgements

Author Contributions

Zhang T. and Li N. designed the experiments. Wang W. and Liu Y. carried out the experiment with the help of Li G. Y. and Wang W. T.. Wang A. Q. and Wang X. D. analysed the data. All authors discussed the results, and wrote the the manuscript.

Additional Information

Supplementary information accompanies this paper at doi:10.1038/s41598-017-06556-7

Competing Interests: The authors declare that they have no competing interests.

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