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 synthesized 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 H2, 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/SiO2 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 fuel1–3 and useful chemicals4–9 has drawn a lot of attention. Polycycloalkanes are a family of nontoxic propellants which are widely used for rockets and missile10–13. 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 fields14. In the long run, the exploration of new route for synthesis of high-density fuels with the renewable and CO2 neutral biomass is highly expected. During the past years, several routes have been developed for the production of polycycloalkanes with terpenes15–18. Due to the limited resource of terpenes, it is still necessary to develop some new synthetic route for polycycloalkanes with cheaper and more available biomass19–26. 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 hemicellulose27. 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 C18 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 C18 condensation product. The synthetic route for this C18...
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. 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 thermodynamically more favorable than the hydrogenation of C=O bond. 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, 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 H₂/metal interactions accompanied by a preferred formation of surface hydrogen atoms. 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 C₂ 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.
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 of 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 pKₐ 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 SiO₂ supported non-noble metal catalysts (see Fig. 5). Among the investigated catalysts, the Ni/SiO₂ and Co/SiO₂ catalysts exhibited evidently higher HDO activity than those of the Cu/SiO₂ and Fe/SiO₂ catalysts. Over the Ni/SiO₂ and Co/SiO₂ 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 C₉-C₁₇ 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, these C₉-C₁₇ 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) and other lignocellulose derived dicycloalkanes (such as dicyclohexane and dicyclopentane which has been reported in recent literature (see Supplementary Table S3),
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/SiO₂ catalyst under the investigated conditions. As we can see from Fig. 7, the Ni/SiO₂ 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/SiO₂ catalyst decreased, while the carbon yield of C₉-C₁₇ cycloalkanes slightly increased. According to the characterization of fresh and used Ni/SiO₂ 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-tri methyl-2-(3,3,5-trimethylcyclohexylidene)-cyclohexane was synthesized by the self-aldol condensation of...
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/SiO₂ 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/SiO₂, Co/SiO₂, Cu/SiO₂ and Fe/SiO₂ 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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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

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