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Production of Gasoline Fuel from Alga-derived Botryococcene by Hydrogenolysis over Ceria-supported Ruthenium Catalyst

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Abstract

Hydrogenolysis of hydrogenated botryococcene (Hy-Bot) was conducted with various supported Ru catalysts, Ir/SiO_2 and Pt/SiO_2-Al_2O_3. Ru/CeO_2 with very high dispersion showed the highest yield (70%) of gasoline range (C5-C12) alkanes at 513 K. The main gasoline range products were dimethylalkanes. This yield value is comparable or higher than the literature values of gasoline yield from botryococcene which were obtained at much higher temperature. Ir/SiO_2 also showed high fuel yield, but the activity was much lower than Ru catalysts. The reaction over Pt/SiO_2-Al_2O_3 slowed down before total conversion of Hy-Bot. Ru/CeO_2 was stable in hydrogenolysis of Hy-Bot without loss of activity and selectivity during reuses. Carbon balance was low in hydrogenolysis of Hy-Bot over all catalysts when the main products were heavy hydrocarbons, while in hydrogenolysis of squalane the carbon balance was kept near 100%. ^{1}H NMR of product mixture and TG analyses of product mixture and recovered catalyst showed that formations of aromatic compounds, polymeric products and coke were negligible in the carbon balance. In model reaction using the substrate compounds with substructure of Hy-Bot, only 2,5-dimethylhexane which has C6 chain with two $C_{primary}$-$C_{tertiary}$ bonds produced cyclic product, 1,4-dimethylcyclohexane, which has higher boiling point than substrate. This dehydrocyclization made the products distribution in hydrogenolysis of Hy-Bot more complex.

Keywords

Algal biomass; Hydrogenolysis; Ruthenium; Biogasoline; Branched alkanes

Introduction

Today, the importance of biofuel produced from biomass is increasing to overcome depletion of petroleum resources and global warming [1-5]. Currently biofuel is produced from edible biomass resource such as vegetable oil and sugars [6,7]. In addition, biofuel contains oxygen atoms and therefore it is not fully compatible with petroleum-based fuel. Recently much effort has been paid to development of hydrocarbon-type biodiesel and biojet fuels including those produced from non-edible biomass such as lignocellulose [8-13]. However, production of hydrocarbon-type biogasoline is difficult because of the high oxygen content of lignocellulose and straight carbon chain of polysaccharides [14-24]. On the other hand, algal biomass is highly promising resource because of their high biomass productivity and no competition of algal cultivation with food production [25-29]. Among components of algal biomass such as triglyceride, polysaccharide and amino acid, hydrocarbons without hetero atom, which are produced by some algae species, attract attention because of the similarity to petroleum [30,31]. Representative hydrocarbons from algae are squalene (2,6,10,14,18,22-hexaen-2,6,10,15,19,23-hexamethyltetracosane) from *Aurantiochytrium mangrovei* [32] and botryococcene (polymethylated triterpenes C_nH_{2n-10} (n = 30 – 37)) from *Botryococcus braunii* [33,34]. In contrast to heterotrophic *A. mangrovei*, autotrophic *B. braunii* produces botryococcene essentially from CO_2, water and sunlight, and therefore botryococcene is more attractive resource than squalene. Catalytic gasification of oil-extracted residue of *B. braunii* have also been performed [35,36]. Algal hydrocarbons including botryococcene are basically classified into heavy oil fraction, and so they need to be lightened by cleaving some C-C bonds before use as transportation fuels such as gasoline. One of the most typical methods of C-C bond cleavage of heavy hydrocarbons is use of metal-acid bifunctional catalysts such as Pt/zeolite and Pt/SiO_2-Al_2O_3 [37-41]. Monofunctional metal catalysts have been also tested for C-C bond cleavage via hydrogenolysis, and the most typical catalyst of this type is Ir/SiO_2 [42-44]. Recently, we have discovered that highly dispersed Ru/CeO_2 catalyst is effective in regioselective hydrogenolysis of squalane (2,6,10,15,19,23-hexamethyltetracosane) which is the total hydrogenation product of squalene [45,46]. The C-C bonds between secondary carbon atoms were regioselectively cleaved without significant isomerization of carbon chain over Ru/CeO_2. This Ru/CeO_2-catalyzed reaction produced branched hydrocarbons from squalane, and good yield of fraction suitable to jet fuel (~C15, very low freezing point) was obtained. Ru/SiO_2 catalyst also showed good C-C hydrogenolysis activity; however, the regioselectivity was lower. Ru catalysts showed hydrogenolysis activity at much lower temperature (~513 K) than Ir/SiO_2 (typically 593 K)[47,48]. After our discovery of Ru/CeO_2-catalyzed hydrogenolysis of squalane, Kun Zhang et al. applied Ru/CeO_2 catalysts with different preparation procedure to production of bio-jet fuel from squalane and C30-C33 botryococcene [49]. Considering the more number of branches in botryococcene than squalene, gasoline is also an attractive target of botryococcene hydrogenolysis because multi-branched hydrocarbons have high octane number and stability. However, reports on the production of gasoline from botryococcene are very limited even with conventional acid-based catalysts, and the reaction temperature is very high: gasoline range (C1-C11) hydrocarbons were obtained in a 67 wt% yield with cobalt–molybdenum catalysts at the temperatures between 673 and 713 K [37]; aromatics-rich gasoline-range hydrocarbons (C5-b.p. 494 K) were produced with conventional FCC catalyst at 773 K [50]. The purpose of this work is the production of gasoline-range branched hydrocarbons via C-C hydrogenolysis from botryococcene at relatively low temperature. We used various Ru catalysts including Ru/CeO_2 and Ru/SiO_2, Ir/SiO_2, and Pt/SiO_2-Al_2O_3 at 513 K. Ru/CeO_2 showed higher gasoline yield than other tested catalysts. We also found that botryococcene hydrogenolysis over monofunctional catalysts has a unique side reaction (cyclization) that does not occur in squalane and *n*-alkane hydrogenolysis over the same catalyst.

Experimental section

Catalyst preparation

Ru/support (Ru: 5 wt%) catalysts were prepared by impregnating various supports with $Ru(NO)(NO_3)_{3-x}(OH)_x$ in diluted nitric acid (Sigma Aldrich, Ru: 1.5 wt%) [45,46]. Used supports were as follows: SiO_2 (Fuji Silysia, G-6), CeO_2 (Daiichi Kigenso, HS), Al_2O_3 (Nippon Aerosil Co., Ltd., AEROXIDE Alu C), MgO (UBE, B-500), TiO_2 (Nippon Aerosil Co., Ltd., AEROXIDE P25), and ZrO_2 (Daiichi Kigenso, RC-100P). Ru/C (Ru: 5 wt%) was purchased from Wako Pure Chemical Industries. Ir/SiO_2 (Ir: 5 wt%) catalyst was prepared by impregnating SiO_2 with H_2IrCl_6 aq (Furuya Metals Co., Ltd.). Pt/SiO_2-Al_2O_3 (Pt: 1 wt%) catalyst was prepared by impregnating SiO_2-Al_2O_3 (JGC Catalysts and Chemicals Co., Ltd., JRC-SAL-2; Al_2O_3=13.75 wt%) with $Pt(NH_3)_2(NO_2)_2$ (Tanaka Kikinzoku Kogyo) dissolved in water. After evaporating the solvent, all prepared catalysts were dried at 383 K for 12 h, and Ru catalysts were pretreated in the N_2 flow at 573 K for 1 h. Ir/SiO_2 was calcined at 773 K for 3 h after drying. Pt/SiO_2-Al_2O_3 was calcined at 773 K for 4 h after drying and reduced in the H_2 flow at 673 K for 1 h.

Preparation of botryococcene

The BOT-22 strain [51,52] of *Botryococcus braunii* was cultured with *Botryococcus* seed culture system developed by University of Tsukuba (Algae Biomass and Energy System R&D Center and M. M. Watanabe laboratory) [53]. The oil fraction was extracted from air-dried *B. braunii* cells by soaking them into *n*-hexane, and then *n*-hexane was evaporated under reduced pressure. The crude oil was purified using a silica gel column chromatography with *n*-hexane eluent. The GC chart of purified hydrocarbon is shown in Figure S1a, of which main component is botryococcene $C_{34}H_{58}$ [52,54]. The purified botryococcene was hydrogenated over Pd/C (Wako) for 24 h at 353 K with 5.5 MPa hydrogen (at 353 K) in *n*-hexane solvent, and then *n*-hexane solvent was removed by a rotary evaporator to obtain fully hydrogenated botryococcene (Hy-Bot). The GC chart of Hy-Bot is shown in Figure S1b.

Activity tests

Activity tests were performed in a 190 ml stainless steel autoclave with a copper gasket. The pretreated catalyst was put into a reactor with Hy-Bot and a glass-coated magnetic spinner together. After sealing, the reactor was purged with hydrogen three times and filled with 3.5 MPa hydrogen. Then, the reactor was heated to 513 K. The heating took about 1 h, and the pressure became 6 MPa. Temperature was monitored using a thermocouple inserted in the reactor. Stirring rate was fixed at 600 rpm. After an appropriate time, the reactor was quickly cooled down to room temperature by water bath. Gas and liquid phases of the reaction mixture were transferred to a 10 L aluminum gas bag and a glass vial, respectively. Mesitylene (Wako, > 97 %, 20 mL) was used as washing solvent in the collection of the liquid phase. Very small amount of the liquid phase was separately collected and diluted with *n*-hexane before addition of mesitylene in order to analyze the products whose GC peak overlaps with that of mesitylene. The standard reaction conditions were as follows: 50 mg supported metal catalyst, 0.6 g Hy-Bot, 513 K reaction temperature, 6 MPa hydrogen pressure at 513 K, and 2 h reaction time. The products were analyzed with GC (Shimadzu GC-2014) equipped with flame ionization detector (FID). The Rtx®-1 PONA column (Restek) was used for separation. To the gas phase collected to the gas bag, 80 μL of dichloromethane was added as internal standard. 200 μL of gas sample was injected into GC. To the liquid phase, 40 mg of *n*-hexacosane (Sigma Aldrich, >99 %) was added as internal standard. 1.0 μL of liquid sample was injected into GC. The qualitative analysis of products was performed with GC-MS (Shimadzu ultra-2020) by EI and CI modes [45]. For reactions of other substrates, the substrate was commercially available and used as received. The conversion, selectivity, carbon balance, yield, and unquantifiable products were calculated with the formulas shown below. If carbon balance is over 100%, unquantifiable products are defined as 0%.

Conversion

$$(\%)=\left(\frac{\text{Amount of substrate input [mol-C]} - \text{Amount of unreacted substrate [mol-C]}}{\text{Amount of substrate input [mol-C]}}\right)\times 100$$

Selectivity

$$(\%)=\left(\frac{\text{Amount of each product [mol-C]}}{\text{Amount of substrate input [mol-C]} - \text{Amount of unreacted substrate [mol-C]}}\right)\times 100$$

Carbon balance

$$(\%)=\left(\frac{\text{Amount of unreacted substrate [mol-C]} + \sum \text{Amount of products [mol-C]}}{\text{Amount of substrate input [mol-C]}}\right)\times 100$$

$$\text{Yield (\%)=Conversion (-)} \times \text{Selectivity (-)} \times 100$$

$$\text{Yield of Unquantifiable products(\%)}=\left(1-\frac{\sum \text{Amount of products [mol-C]}}{\text{Amount of substrate input [mol-C] - Amount of unreacted substrate [mol-C]}}\right)\times 100$$

$$\text{Selectivity of Unquantifiable products(\%)}=\left(\frac{\text{Yield of Unquantifiable products [\%]}}{\text{Conversion [\%]}}\right)\times 100$$

For the reactions of squalane and model substrates, conversion and selectivity were calculated by the following formulas because the loss of carbon balance was negligible.

Conversion

$$(\%)=\left(\frac{\sum \text{Amount of products [mol-C]}}{\text{Amount of unreacted substrate [mol-C]} + \sum \text{Amount of products [mol-C]}}\right)\times 100$$

$$\text{Selectivity (\%)}=\left(\frac{\text{Amount of each product [mol-C]}}{\sum \text{Amount of products [mol-C]}}\right)\times 100$$

Reuse experiment

Procedure of reuse experiment of Ru/CeO_2 or Pt/SiO_2-Al_2O_3 for hydrogenolysis of Hy-Bot is as follows. First, we conducted normal activity test with each catalyst. Next, we collected all the reaction mixture using mesitylene as washing solvent. The used catalyst was recovered by centrifugation, washed with *n*-hexane, and dried in air. The next run was conducted in the same scale, where small amount of fresh catalyst (about 10%) was added to compensate the loss in the recovery process.

Instruments

X-ray diffraction (XRD) patterns were recorded by a diffractometer (Rigaku UltimaIV). Cu Kα (λ = 0.154 nm, 45 kV, 40 mA) radiation was used as an X-ray source. Thermogravimetry-differential thermal analysis (TG-DTA) was carried out with a Rigaku Thermo Plus EVO-II under air atmosphere. Nuclear magnetic resonance (NMR) analysis was conducted with a BRUKER DPX-400 at room temperature.

Results and discussion

Conversion of botryococcene

Hydrogenolysis of hydrogenated botryococcene (Hy-Bot) was conducted with various catalysts such as Ru/CeO_2. Figure 1 is a typical chromatogram of liquid products produced by hydrogenolysis of Hy-Bot over Ru/CeO_2. The carbon number of each product was determined by GC-MS (CI mode) and it is also displayed in Figure 1. Products with wide carbon number range were detected, similarly to the cases of squalane hydrogenolysis over the same catalyst [45,46] and *Botryococcus braunii* liquid hydrogenolysis over similar Ru/CeO_2 catalyst [49]. The number of peaks was larger than the case of squalane hydrogenolysis, because of the more complex structure of botryococcene molecule than that of squalene. Nevertheless, the pattern is much simpler than that obtained from Pt-Re/SiO_2-Al_2O_3 catalyst in the literature [41]. The pattern is also simpler than that of literature study of *Botryococcus braunii* liquid over Ru/CeO_2 [49]. The difference is probably due to the purity of substrate: we use almost pure single $C_{34}H_{70}$ compound (Figure S1b), while the literature study [49] used mixture of C30-C33 compounds. While the structure determination of heavy products is difficult, the structure of lighter products in the gasoline range can be determined. The main C6 and C7 products were 2,3-dimethylbutane (RON: 103.5) [55] and 2,3-dimethylpentane (RON: 91.1) [55], respectively. Heavier main products would also have two or more branches. The multi-branched structure of gasoline-range products suggests the potential drop-in use for gasoline without further reforming. This is in contrast to the case of squalane hydrogenolysis where main ≤C8 products are monobranched ones with lower RON.

Figure 2 shows the results of hydrogenolysis of Hy-Bot with various supported Ru catalysts, Ir/SiO_2, and Pt/SiO_2-Al_2O_3. We also conducted hydrogenolysis of squalane with the same Ru catalysts and the results are shown in Figure 3 for comparison. Here, the products in the gas phase and the products whose GC signal overlaps with washing solvent were also analyzed and included. All the tested catalysts showed activity in hydrogenolysis of Hy-Bot as well as squalane. In comparison with hydrogenolysis of squalane, the effect of support on activity and selectivity of Ru-catalyzed hydrogenolysis was small for Hy-Bot: the activity difference of Ru catalysts between the highest (Ru/SiO_2; Conv. = 73.3% for 1 h) and lowest (Ru/MgO; Conv. = 55.9% for 2 h) was about two-fold for Hy-Bot (Figure 2), while Ru/TiO_2 showed about one order higher activity (Conv. = 52.7% for 2 h) than Ru/MgO (Conv. = 4.9% for 2 h) for squalane (Figure 3). Ru/CeO_2 showed very low selectivity to $C_{tertiary}$-C dissociation products such as gas (C1-C3) in hydrogenolysis of squalane, as reported in our previous paper, and the unique selectivity might be due to the high dispersion [45]; however the selectivity to gas was similar in hydrogenolysis of Hy-Bot among all the Ru catalysts. Another important point is the low carbon balance in hydrogenolysis of Hy-Bot over all catalysts, while in hydrogenolysis of squalane the carbon balance was kept near 100%. This point will be discussed later.

Considering the unique selectivity of Ru/CeO_2 in squalane hydrogenolysis and inert nature of SiO_2 support, we selected Ru/CeO_2 and Ru/SiO_2 as representatives of Ru catalysts in the following studies.

Figure 4 shows the time course of hydrogenolysis of Hy-Bot over Ru/CeO_2, Ru/SiO_2, Ir/SiO_2, and Pt/SiO_2-Al_2O_3. The product molecules became smaller at longer reaction times over Ru catalysts and Ir/SiO_2. The order of catalytic activity (conversion rate) was as follows: Ru/SiO_2 > Ru/CeO_2 >> Ir/SiO_2. In the case of Pt/SiO_2-Al_2O_3 (Figure 4d), after 12 h reaction time when Hy-Bot was almost converted, selectivity of all products did not increase or decrease, indicating that the reaction almost stopped. The carbon balance over Ru and Ir catalysts (Figure 4a-c) was increased at longer reaction time after the conversion reached 100%. In order to determine the cause of the loss of carbon balance, we analyzed the sample after reaction by several methods. First, ^1H NMR of the liquid phase after the reaction over Ru/CeO_2 was measured. No peak was detected in the range of >3 ppm, indicating that no olefinic or aromatic compounds were formed (Figure S2). TG analysis of the liquid phase of the reaction was conducted under inert atmosphere. The weight became zero at similar temperature at which the weight in TG of Hy-Bot became zero, indicating that there were no compounds with much larger molecular weight than Hy-Bot such as dimerization products. Further, TG-DTA analysis of recovered Ru/SiO_2 catalyst was conducted under air (Figure S3). The amount of weight loss by combustion was 0.4 mg/9 mg_{cat}, which corresponds to 0.3%-C yield from Hy-Bot. This value is much lower than the loss of carbon balance. Considering that the yields and selectivities were calculated by sum of quantifiable products, formations of many kinds of paraffin isomers could be the cause of the loss of carbon balance. At longer reaction time, the product molecules became small and the number of product isomers was limited, which can cause the recovery of carbon balance. Figure 5 shows the chromatograms in C21-C23 range at 6 h and 30 h reaction times over Ru/CeO_2. The chromatogram at 6 h reaction time had weak sway in addition to quantifiable peaks, and the sway disappear at 30 h.

Some amount of products might be present in the baseline sway. On the other hand, types of gasoline-range compounds are limited and all of them would be separately quantified. Therefore, the loss of carbon balance would mainly affect the yield of heavier products. We here focus on the gasoline yield.

The maximum yields of each fuel are summarized in Table 1. Because of the low carbon balance, the jet and diesel yields may be considerably underestimated. Ru/CeO_2 showed the highest gasoline yield of about 70%-C. This value is comparable or higher than the literature value of gasoline yield from botryococcene, even though the definition of "gasoline range" is different between reports; in this work "gasoline range" is C5-C12. In addition, the reaction temperature of this work is lower. The reason for the higher gasoline yield over Ru/CeO_2 than over Ru/SiO_2 may include that the lower activity of Ru/CeO_2 than Ru/SiO_2 in the excess hydrogenolysis of $C_{tertiary}$-C bonds which are abundant in Hy-Bot-derived products. Ir/SiO_2 also gave good gasoline yield; however the value was smaller than that over Ru/CeO_2, and in addition the activity of Ir/SiO_2 was much lower.

Catalyst stability

The reuse experiment was conducted to see the stability of the Ru/CeO_2 (Figure 6). The catalyst can be used 5 times without loss of activity and selectivity, similarly to the case of squalane hydrogenolysis [45]. The XRD patterns before and after reaction were essentially identical and did not have the peaks for Ru metal, which supports the stability of Ru/CeO_2 (Figure S4).

As shown in Figure 4d, the activity of Pt/SiO_2-Al_2O_3 was decreased during the reaction. To determine whether this deactivation was caused or not, we conducted the reuse experiment of Pt/SiO_2-Al_2O_3 (Figure S5). The recovered catalyst after simple washing with mesitylene and *n*-hexane showed comparable activity to fresh ones, showing that the deactivation during the reaction was partial. The causes of deactivation may include adsorption of mesitylene-soluble compounds on the active sites.

Model reactions

The large loss of carbon balance is a significant feature of hydrogenolysis of Hy-Bot, while there is no such loss in hydrogenolysis of squalane (Figure 3), *n*-hexadecane, and C6 alkanes [45,46]. We tested the reactivity of model substrates, namely 2,3-dimethylheptane, 3,3-dimethylheptane and 2,5-dimethylhexne, all of which are substructures of Hy-Bot and not substructures of squalane (Table 2). In the hydrogenolysis of 2,3-dimethylheptane and 3,3-dimethylheptane, all the main products were substructures of the substrate, similarly to the hydrogenolysis of squalane, *n*-hexadecane, and C6 alkanes. Small amount of isomerized products were also formed; however no products with higher boiling point than substrates were formed. On the other hand, hydrogenolysis of 2,5-dimethylhexane produced 1,4-dimethylcyclohexane by dehydrocyclization in addition to substructures of substrate. Such cycloalkanes has higher boiling point than acyclic substrate, while such dehydrocyclization did not occur in the case of squalane, *n*-hexadecane, and C6 alkanes [45,46]. The dehydrocyclization is the reaction of two terminal methyl groups of C6 chain. However, both 2,3-dimethylheptane and 3,3-dimethylheptane also have C6 chain with two terminal methyl groups. The difference in C6 chain between 2,5-dimethylhexane and dimethylheptanes is the reactivity of terminal C1-C2 and C5-C6 bonds to hydrogenolysis. In the case of 2,5-dimethylhexane, both terminal bonds are $C_{primary}$-$C_{tertiary}$ ones with low activity [46]. On the other hand, one terminal bond of C6 chain in dimethylheptanes is reactive $C_{primary}$-$C_{secondary}$ one. The dehydrocyclization seems to proceed only between methyl groups bonded to tertiary carbon. Hy-Bot indeed contains such structure (Figure 7). Ring-opening of dehydrocyclization products by hydrogenolysis produces isomers of substrates, and this dehydrocyclization-ring-opening will complicate the reaction mixture. In fact, small amount of 3-methylheptane, which is a ring-opening product of 1,4-dimethylcyclohexane, was detected (0.1%-C selectivity) in 2,5-dimethylhexane hydrogenolysis as shown in Table S1. Such increase in the kinds of products may contribute to the loss of carbon balance in Hy-Bot hydrogenolysis.

Conclusions

Good gasoline (C5-C12) yield (70%-C) was obtained from hydrogenated C34 botryococcene by hydrogenolysis over monofunctional Ru/CeO_2 catalyst at 513 K. The main components of gasoline products were dimethylalkanes which have good RON and stability. The gasoline yield was much higher than those obtained over Ru/SiO_2 and Pt/SiO_2-Al_2O_3 catalysts. Typical monofunctional Ir/SiO_2 catalyst also showed good gasoline yield; however the activity was much lower than Ru/CeO_2. The Ru/CeO_2 catalyst was stable and reusable. Large loss of carbon balance was observed for all tested catalysts when the main products were still large molecules, which may be due to the complex isomerization to many kinds of product isomers. One isomerization reaction is the dehydrocyclization of C6 chain with two terminal $C_{primary}$-$C_{tertiary}$ bonds and subsequent ring opening. This type of C6 chain is absent in squalane, and in squalane hydrogenolysis such large loss of carbon balance was not observed.

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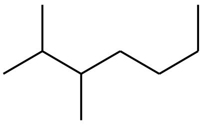
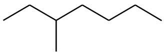
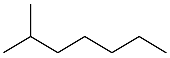
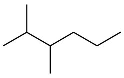
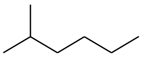
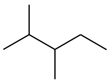
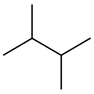
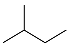
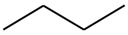
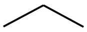
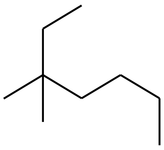
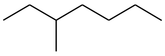
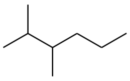
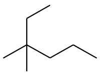
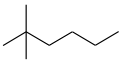
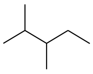
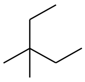
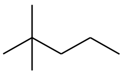
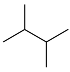
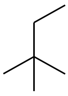
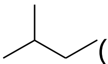
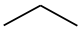
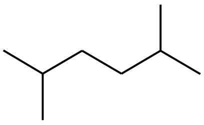
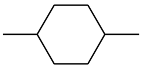
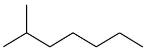
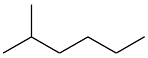
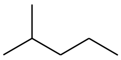
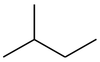
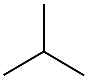
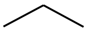
Table 1. The maximum yield of each fuel in the results of Figure 4

Catalyst	Yield [%-C] ($W_{cat}\cdot t$ [g·h])		
	Gasoline (C5-C12)	Jet[a] (C9-C18)	Diesel[a] (C10-C21)
Ru/CeO_2	70 (1.5)	52 (0.9)	50 (0.9)
Ru/SiO_2	39 (0.75)	29 (0.6)	30 (0.3)
Ir/SiO_2	56 (28.8)	64 (28.8)	63 (28.8)
Pt/SiO_2-Al_2O_3	4.1 (2.4)	4.5 (0.4)	4.7 (0.4)

[a] Might be significantly underestimated (see text).

Table 2. Hydrogenolysis of model substrates of Hy-Bot

Substrate	Conv. [%]	Product (Selectivity [%])
 2,3-dimethylheptane	18	 (3.6)  (1.3)  (31)  (22)  (0.9)  (0.5)  (13)  (1.7)  (1.3)  (7.3) C_2H_6 (6.9) CH_4 (6.2) Others [a] (4.3)
 3,3-dimethylheptane	19	 (0.6)  (0.9)  (46)  (15)  (1.2)  (12)  (2.2)  (0.7)  (3.1)  (0.5)  (1.7) C_2H_6 (3.4) CH_4 (11.3) Others [a] (1.4)
 2,5-dimethylhexane	23 [c]	 (0.6 [b])  (1.2)  (13)  (3.7)  (5.0)  (63)  (3.7) C_2H_6 (1.2) CH_4 (5.5) Others [a] (3.1)

Conditions: Ru/CeO_2, 50 mg; dimethylheptane, 0.51 g (4 mmol); H_2, 6 MPa; 513 K; 1 h. [a] Products with < 0.5% each selectivity. All of the products had lower boiling point (shorter retention time) than the substrate. [b] trans/cis = 5/1. [c] Ru/CeO_2, 300 mg; 2,5-dimethylhexane, 1.14 g (10 mmol); 2 h. More detailed lists of products are shown in Table S1.

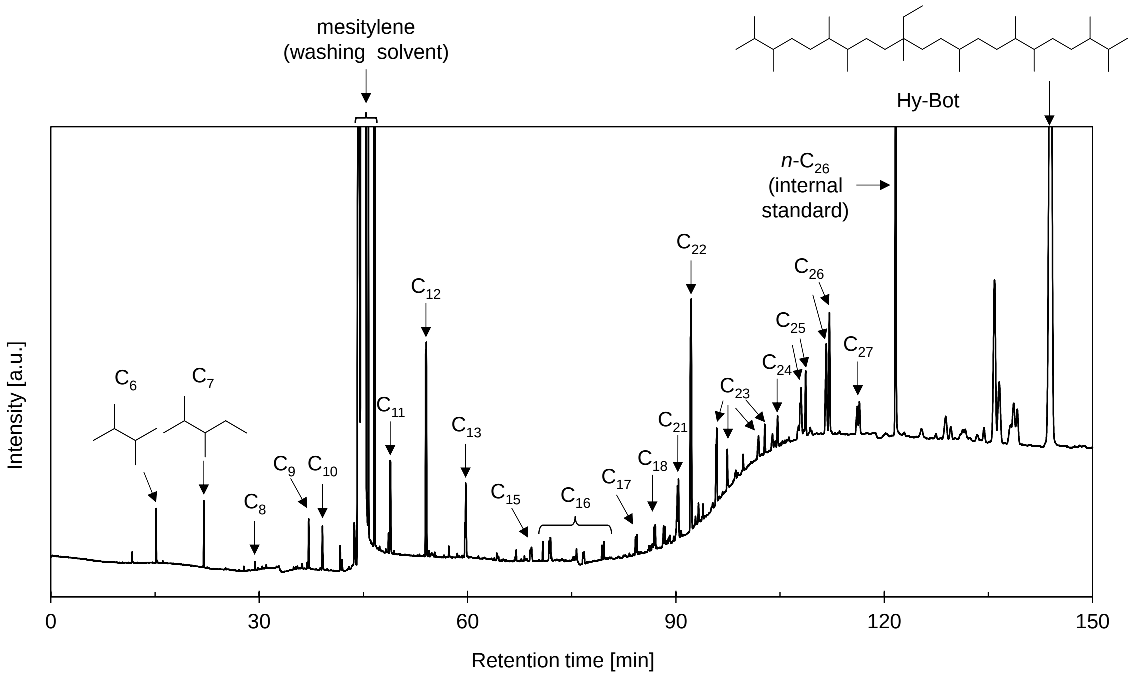


Figure 1. GC chart of liquid sample of hydrogenolysis of Hy-Bot over Ru/CeO$_2$. Conditions: Ru/CeO$_2$, 50 mg; Hy-Bot, 0.6 g; H$_2$, 6 MPa; 513 K; 6 h.

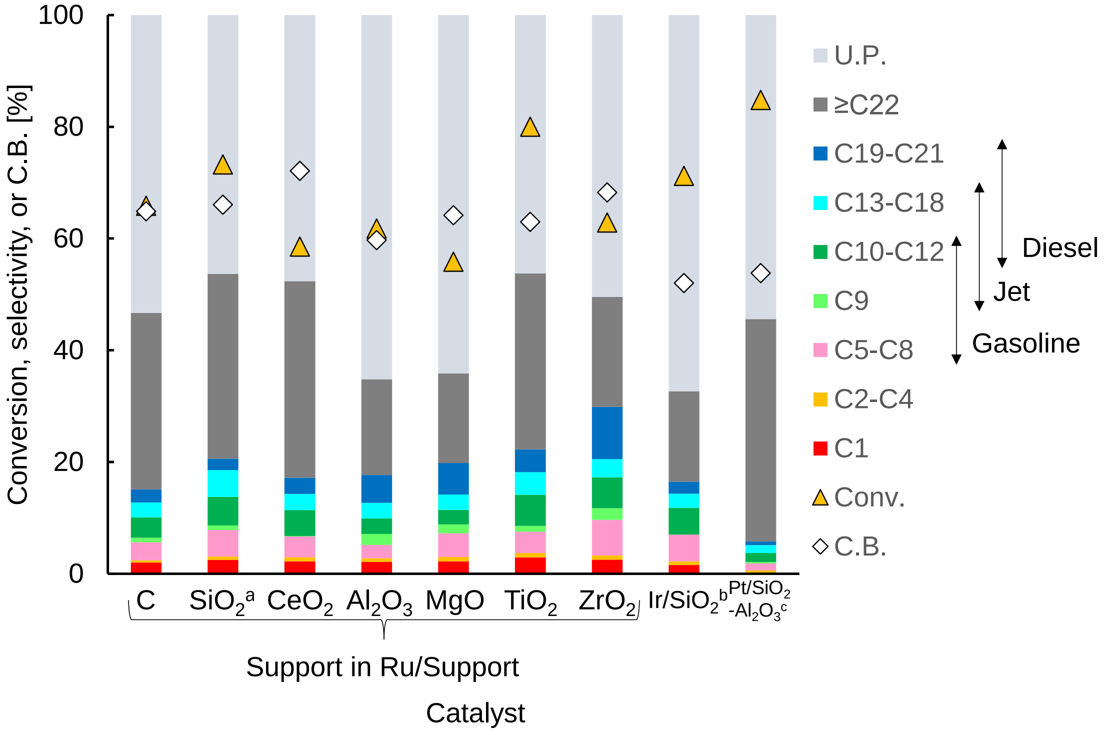


Figure 2. Hydrogenolysis of Hy-Bot over various catalysts. Conditions: catalyst 50 mg (^{b} 400 mg, ^{c} 100 mg); Hy-Bot, 0.6 g; H_2, 6 MPa; 513 K; 2 h (^{a} 1 h, ^{b} 12 h);. C.B.: Carbon balance, U.P,: Unquantifiable products.

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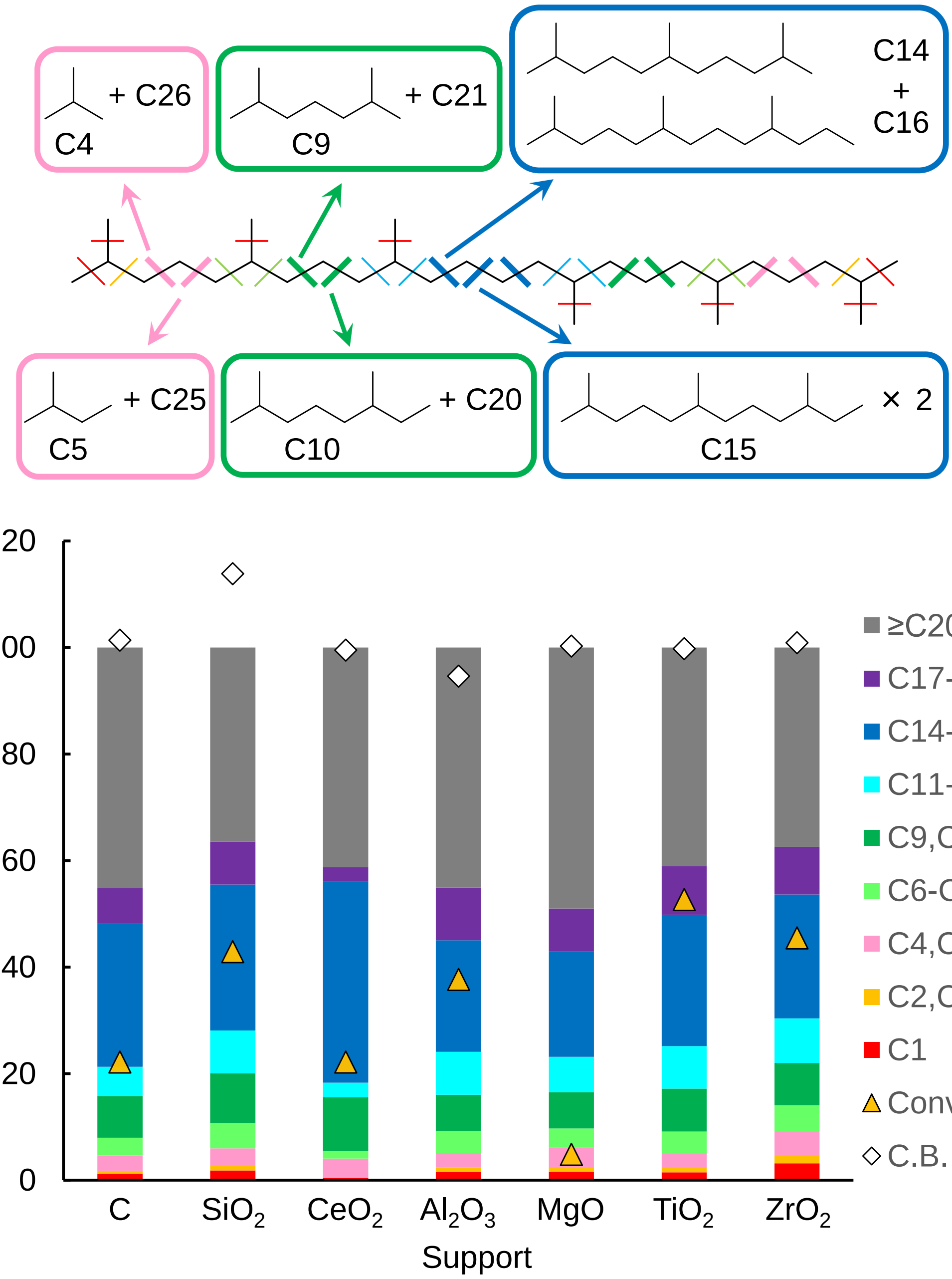


Figure 3. Hydrogenolysis of squalane over various Ru catalysts. Conditions: Ru/Support, 50 mg; squalane, 4.23 g (10 mmol); H_2, 6 MPa; 513 K; 3 h. C.B.: Carbon balance.

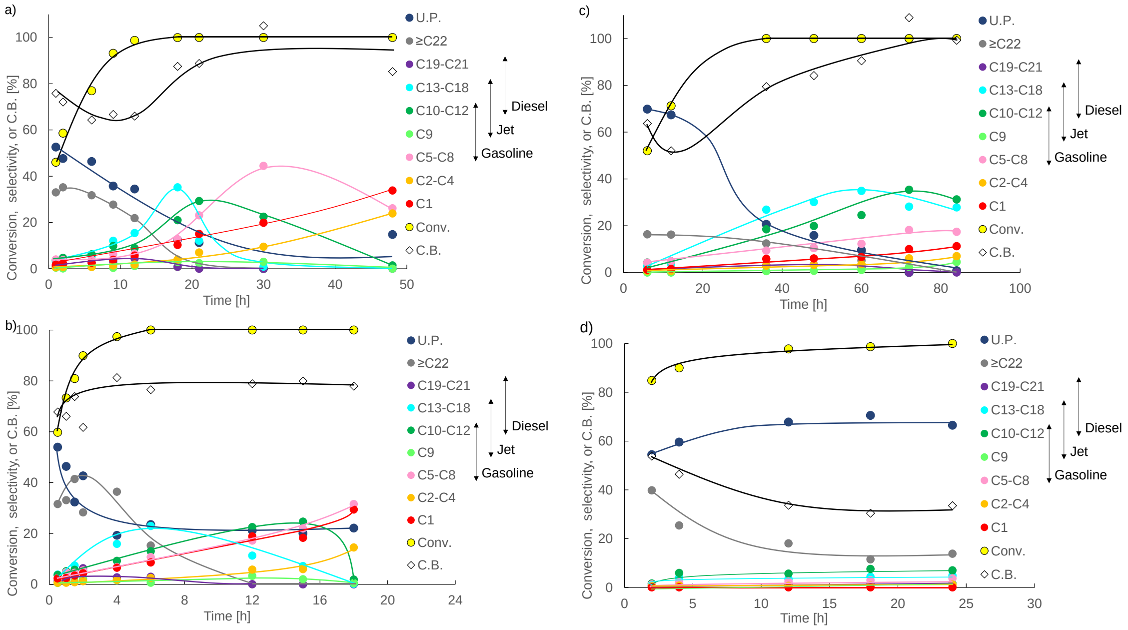


Figure 4. Time course of hydrogenolysis of Hy-Bot over a) Ru/CeO_2, b) Ru/SiO_2, c) Ir/SiO_2, d) Pt/SiO_2-Al_2O_3. Conditions: Catalyst, (a,b) 50 mg, (c) 400 mg, (d) 100 mg; Hy-Bot, 0.6 g; H_2, 6 MPa; 513 K. C.B.: Carbon balance, U.P.: Unquantifiable products.

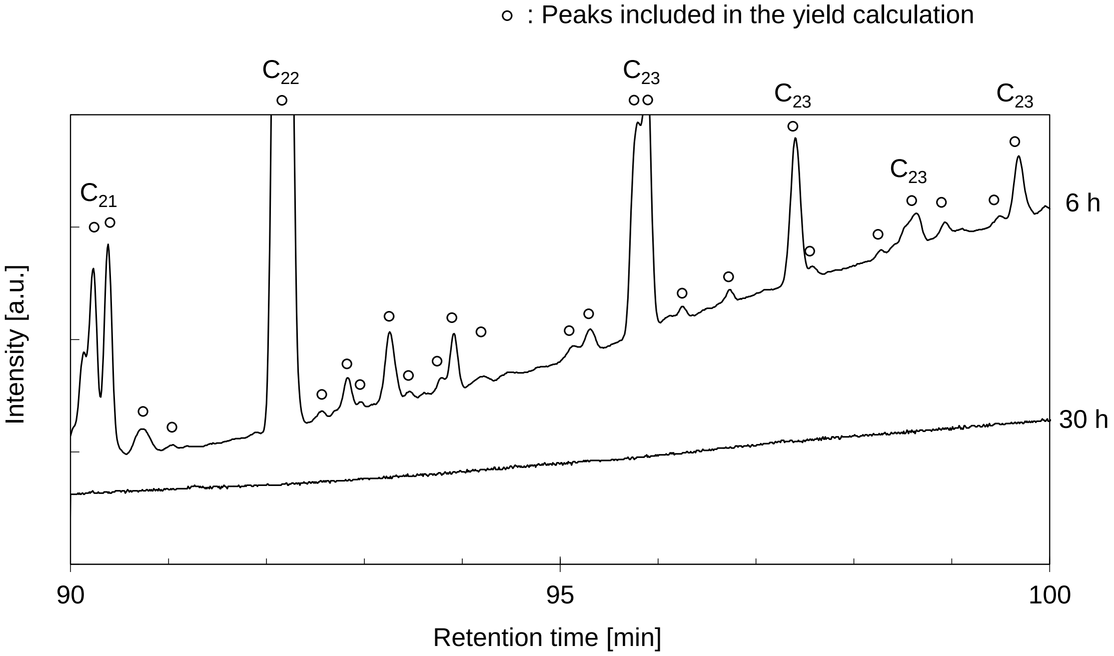


Figure 5. GC charts in C21-C23 region of liquid samples of hydrogenolysis of Hy-Bot over Ru/CeO_2. Conditions: Ru/CeO_2, 50 mg; Hy-Bot, 0.6 g; 6 or 30 h; H_2, 6 MPa; 513 K; 6 h or 30 h. Full scale charts are shown in Figure 1 (6 h) and Figure S6 (30 h).

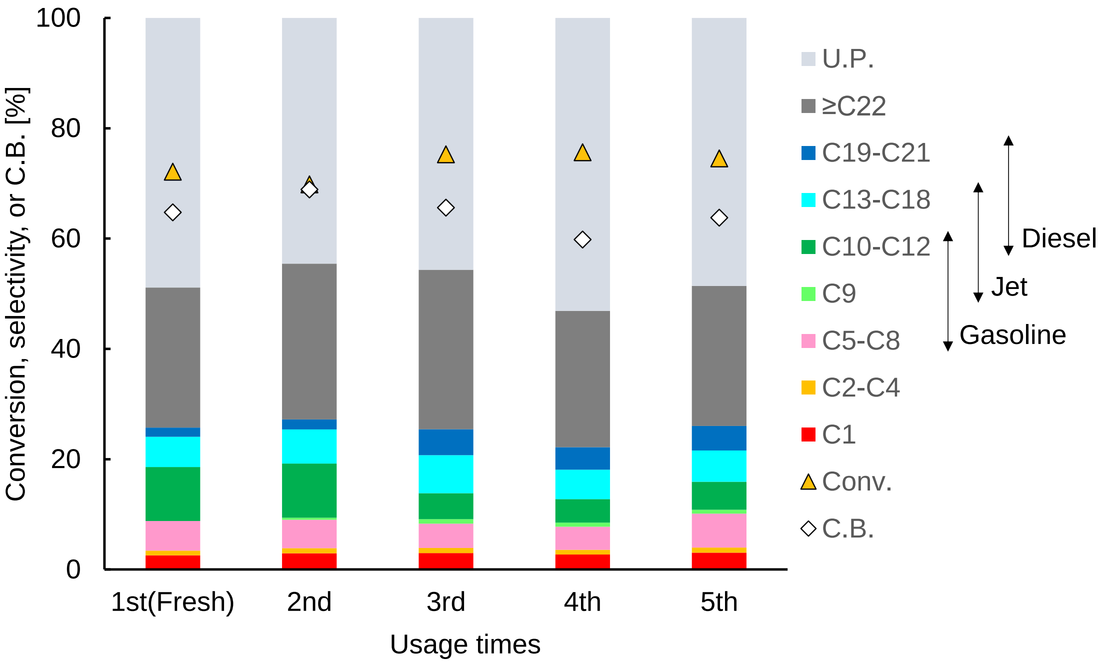


Figure 6. Reuse of Ru/CeO_2 in hydrogenolysis of Hy-Bot. Conditions: Ru/CeO_2, 100 mg; Hy-Bot, 0.6 g; H_2, 6 MPa; 513 K; 2 h. C.B.: Carbon balance, U.P.: Unquantifiable products

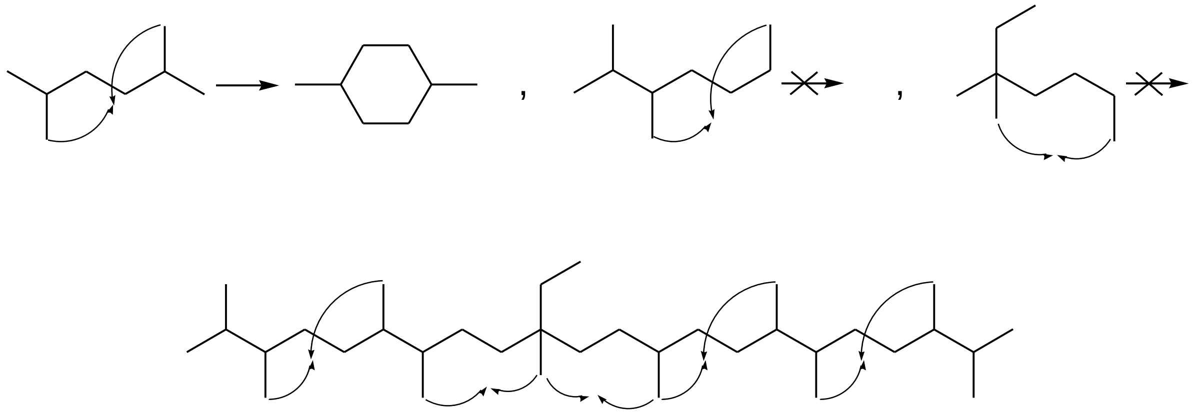
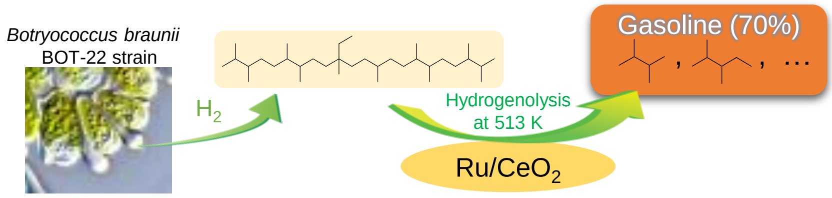


Figure 7. Possible dehydrocyclization sites



Crack the C-C bond: Ceria-supported ruthenium are highly active in C-C hydrogenolysis of hydrogenated botryococcene to gasoline-range fuel (C5-C12) at relatively low temperature (513 K). The main components of gasoline products were dimethylalkanes which have good RON and stability.