Production of Gasoline Fuel from Alga-Derived Botryococcene by Hydrogenolysis over Ru/CeO$_2$

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Today, the importance of biofuel produced from biomass is increasing to overcome depletion of petroleum resources and global warming. Biofuel is produced from edible biomass resource such as vegetable oil and sugars, but such biomass competes with food production. 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. Among some components of algal biomass, hydrocarbons attract attention because of the structural similarity to petroleum. Representative hydrocarbon from algae is botryococcene (Fig. 1a) from Botryococcus braunii. Algal hydrocarbons are basically classified into heavy oil fraction, and so they need to be lightened by cleaving some C-C bonds to be used for biofuel. In particular, botryococcene has many branches in structure, so gasoline-range (C5-C12) fuel is an attractive target because multi-branched hydrocarbons have high octane number. Recently, we have discovered that highly dispersed Ru particle on ceria (Ru/CeO$_2$) catalyst is effective in regioselective hydrogenolysis of squalane which is also one of hydrocarbons from algae [1,2]. In this study, we conducted hydrogenolysis of hydrogenated botryococcene (Hy-Bot; Fig. 1b) over Ru/CeO$_2$ catalyst to gasoline-range branched alkanes.

![Fig. 1 The structure of a) botryococcene and b) Hy-Bot](image)

Figure 2 shows the time course of hydrogenolysis of Hy-Bot over Ru/CeO$_2$. The product molecules became smaller at longer reaction times. The carbon balance was lower than 100% at short time. But it was increased at longer reaction time after the conversion reached 100%. At 30 h reaction time, Ru/CeO$_2$ showed the highest gasoline-range fuel yield of about 70%-C, and the main components were dimethylalkanes. This value is comparable to or higher than the literature value of gasoline yield from botryococcene. In addition, the reaction temperature of this study is lower (513 K).

In order to determine the structure of products, we analyzed the sample of the liquid phase after the hydrogenolysis of Hy-Bot over Ru/CeO$_2$ by $^1$H NMR. No peak was detected in the range of $>3$ ppm, indicating that no olefinic or aromatic compounds were formed, and the products were mainly paraffin.

Considering that the yield and selectivity were calculated by sum of quantifiable products, formations of many kinds of paraffin isomers would 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.

![Fig. 2 The time course of hydrogenolysis of Hy-Bot over Ru/CeO$_2$. Reaction conditions: Ru/CeO$_2$, 50 mg; Hy-Bot, 0.6 g; H$_2$, 6 MPa; 513 K. C.B.: Carbon balance, U.P.: Undetected products.](image)

REFERENCES