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Research article

Regioselective hydrogenolysis of alga-derived squalane over silica-supported ruthenium-vanadium catalyst

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ABSTRACT

Addition effect of 2nd metal to Ru catalysts in hydrogenolysis of squalane was investigated. Addition of V gave lower methane selectivity and higher C14-C16 selectivity and the effect was the most remarkable over SiO_2 support. However, addition of V decreased the catalyst activity and increased the deposited amount of carbonaceous species. From hydrogenolysis of *n*-hexadecane, addition of V suppressed the formation of methane via terminal C−C bond dissociation, but the formation via fragmentation was not suppressed. Ru and V valences in Ru-VO_x/SiO_2 (V/Ru = 0.25) after reduction were 0 and +III, respectively. The size of Ru particles was about 4 nm from XRD even in changing V/Ru ratio. H_2 chemisorption showed that V covered the Ru particles and reduced the size of Ru ensemble. In reuse test, it was difficult to retain the catalyst performance for hydrogenolysis of squalane even with various treatments of the recovered catalyst such as washing with *n*-hexane, heating in N_2 flow or calcination in air. From XAS analysis, the contact of Ru particles with air caused the aggregation of Ru metal especially when calcined in air.

1. Introduction

Alkanes are a highly valuable and important class of compounds that are industrially manufactured as fuels and chemicals. At present, most alkanes are obtained by petroleum refining [1]. On the other hand, the production of alkanes from edible biomass, for example vegetable oils [2–5] and sugars [6–10], has been investigated to replace the petroleum-based alkanes recently [11,12]. However, the raw biomass has high oxygen content, and total hydrodeoxygenation consuming large amount of H_2 is required to produce alkanes [13–17]. In addition, the competition of food production is a serious problem. The use of inedible biomass as a source of biofuel has been intensively investigated such as non-edible jatropha-oil [18–22], lignin [23,24], hemicellulose [25,26], and lignocellulose [27–32]. Algal biomass is also an attractive resource because of the high production rate and the different production area from staple food [33–35]. Recently, some researches have been carried out about hydrodeoxygenation of algal biomass such as triglyceride [36–41]. On the other hand, some microalgae species produce hydrocarbon-type biomass which is hardly obtained from plants. Typical hydrocarbons from microalgae are botryococcene (polymethylated triterpenes C_nH_{2n-10} (n = 30–37)) from *Botryococcus braunii* and squalene (2,6,10,14,18,22-hexaen-2,6,10,15,19,23-hexamethyltetracosane) from *Aurantiochytrium mangrovei* [42–44]. The catalytic gasification of oil-extracted residue of *Botryococcus braunii* has also been performed [45,46]. These hydrocarbon molecules are too large to use as transportation fuel like gasoline, jet fuel, and diesel fuel, and therefore cleavage of some C−C bonds is necessary. One of conventional methods of cleaving C−C bonds of hydrocarbons is the use of metal-acid bifunctional catalysts such as Pt/zeolite and Pt/SiO_2-Al_2O_3 [47–53]. This method involves isomerization and it is effective to refine the petroleum-based straight-chain hydrocarbons. In contrast, the alga-based hydrocarbons such as botryococcene or squalene are multi-branched ones, and therefore the skeletal isomerization unnecessarily makes the product mixture complicated. Ru is known to be active in hydrogenolysis of alkanes [47,54]. Recently, our group discovered Ru/CeO_2 catalyst with highly dispersed Ru for regioselective hydrogenolysis of squalane (2,6,10,15,19,23-hexamethyltetracosane), which is easily obtained by hydrogenation of squalene [55], without skeletal isomerization and aromatization [56]. The $C_{secondary}$−$C_{secondary}$ bonds with low steric hindrance in squalane are preferably cleaved, and the production of C4, C5, C9, C10, C14–16, C20, C21, C25, and C26 branched alkanes is more preferential than that of other alkanes (Fig. 1) [57]. In particular, the C14-C16 alkanes can be used as components of diesel or jet fuels. The Ru/CeO_2 catalysts with lower dispersion of Ru and Ru catalysts on other supports show lower regioselectivity. As comparison, we conducted the hydrogenolysis of

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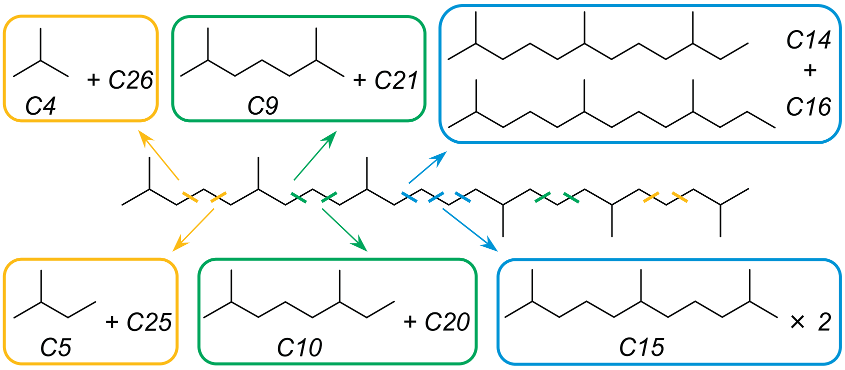
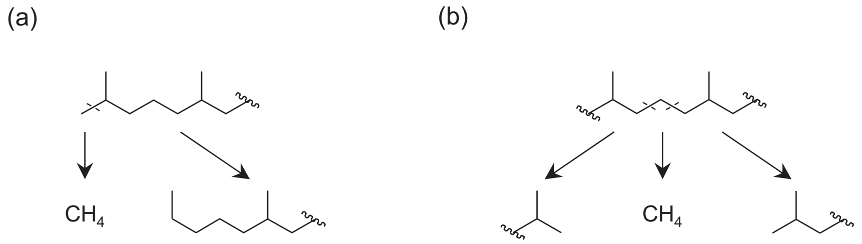


Fig. 1. Proposed $C_{secondary}$—$C_{secondary}$ dissociation in hydrogenolysis of squalane [56].



Scheme 1. The two routes of production of methane: (a) dissociation of $C_{tertiary}$—$C_{primary}$ bonds, (b) fragmentation.

squalane over Pt/H-USY which is a metal-acid bifunctional catalyst [56]. The reaction over Pt/H-USY gave a more complex mixture of products, and the number of GC peaks over Pt/H-USY was much more (> 200 kinds of molecules) than that over Ru catalysts. Another and even more important character of C—C hydrogenolysis catalysts is the suppression of the formation of gaseous products, especially methane, because methane has lower value than other alkanes and the production of methane consumes large amount of H_2. Methane can be produced from squalane via two routes: dissociation of $C_{tertiary}$—$C_{primary}$ bonds and fragmentation (fast overhydrogenolysis before desorption of reacted molecules; Scheme 1) [49–51]. The Ru/CeO_2 catalyst with highly dispersed Ru metal species has low activity in the both routes to methane formation in comparison with other Ru catalysts, leading to very low methane selectivity [57]. Hydrogenolysis of hydrogenated botryococcene over Ru/CeO_2 catalyst was also reported [58,59]. Since botryococcene has more methyl branches than squalane/squalene, the $C_{secondary}$—$C_{secondary}$ bonds in hydrogenated botryococcene are more sterically hindered than those in squalane. The distribution of products in hydrogenolysis of hydrogenated botryococcene was much more complex than that in hydrogenolysis of squalane.

The high selectivity of Ru/CeO_2 catalyst can be due to the small Ru particle size and/or the electronic effect by CeO_2 support. While controlling the particle size and choosing appropriate support are frequently effective in improving the performance of noble metal catalysts, addition of 2nd metal can also improve the performance [60–62]. In particular, the uses of reducible metal oxides such as V, Mo, W, and Re as a 2nd metal have been reported to be effective in various noble-metal-catalyzed reduction reactions with H_2 [60–65]. Typically, the added 2nd metal makes direct bond with the surface of noble metal particles, affecting the catalytic behavior by changing the ensemble size, changing the electronic state of the noble metal, or providing the added metal species as activating site of substrate. Ru—V catalysts have been already reported for *n*-alkane hydrogenolysis in gas-phase reactions as catalysts with relatively good selectivity in dissociation of internal bonds: [66–70] Ru—V catalyst cleaves the $C_{secondary}$—$C_{secondary}$ bond of *n*-butane to ethane or methane, the latter of which is the over-hydrogenolysis product. However, the reactivity patterns between $C_{tertiary}$—$C_{secondary}$ and $C_{tertiary}$—$C_{primary}$ bonds which are present in squalane and hydrogenated botryococcene have not been investigated. In addition, we have reported that selectivity of Ru-catalyzed C—C hydrogenolysis is different between liquid- and gas-phase reactions, especially for fragmentation [57]. In this work, we investigated the effect of 2nd metal on Ru catalysts in hydrogenolysis of squalane. We found that addition of V increased the selectivity to products by $C_{secondary}$—$C_{secondary}$ bond dissociation and decreased the selectivity to methane.

2. Experimental section

2.1. Catalyst preparation

Ru/support catalysts (Ru: 5 wt%) 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%). Used supports were as follows: SiO_2 (Fuji Silysia Chemical Ltd., G-6), CeO_2 (Daiichi Kigenso Kagaku Kogyo Co., Ltd., HS), Al_2O_3 (Nippon Aerosil Co., Ltd., AEROXIDE Alu C), MgO (Ube Industries Ltd., 500A), TiO_2 (Nippon Aerosil Co., Ltd., AEROXIDE P25), and ZrO_2 (Daiichi Kigenso Kagaku Kogyo Co., Ltd., RC-100P). Ru-MO_x/support (Ru: 5 wt%; M = V, Re, Mn, Mo, Ni, W) catalysts were prepared by co-impregnation method with $Ru(NO)(NO_3)_{3-x}(OH)_x$ in diluted nitric acid and various metal precursor. Used metal precursors were as follows: NH_4VO_3 (Wako Pure Chemicals Industries, Ltd.), NH_4ReO_4 (Mitsuwa Chemicals Co., Ltd.), $Mn(NO_3)_2{\cdot}6H_2O$ (Soekawa Chemical Co., Ltd.), $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (Wako Pure Chemicals Industries, Ltd.), $Ni(NO_3)_2{\cdot}6H_2O$ (Wako Pure Chemicals Industries, Ltd.), and $(NH_4)_6H_2W_{12}O_{40}{\cdot}H_2O$ (Wako Pure Chemicals Industries, Ltd.). After evaporating the solvent, all the prepared catalysts were dried at 383 K for 12 h, and heated in the N_2 flow at 573 K for 1 h as pretreatment.

2.2. Activity tests

Activity tests were performed in a 190 ml stainless steel autoclave with copper gasket. The pretreated catalyst was put into a reactor with squalane (Wako Pure Chemicals Industries, Ltd., > 95%) or *n*-hexadecane (Wako Pure Chemicals Industries, Ltd., > 97%) and a glass-coated magnetic spinner together. After sealing, the reactor was purged