Regioselective hydrogenolysis of alga-derived squalane over Ru-VO_x/SiO_2 catalyst

Yosuke Nakaji,[a] **Masazumi. Tamura,**[a] **Yoshinao. Nakagawa,**[a] **Keiichi. Tomishige**[a*]
[a]*Tohoku University, Sendai, 980-8579, Japan*
**K. Tomishige: 022-795-7215, tomi@erec.che.tohoku.ac.jp*

Abstract: We investigated the addition effect of 2nd metal to Ru catalysts in hydrogenolysis of squalane. Addition of V gave lower methane selectivity and higher C14-C16 selectivity and the effect was most remarkable for SiO_2 support, but activity decreased with increase of V amount. Especially, Ru-VO_x/SiO_2 (V/Ru=0.25) was the most effective catalyst in regioselective hydrogenolysis of squalane in terms of the balance of selectivity and activity. H_2 chemisorption experiment showed that V species covered half of surface Ru atoms in Ru-VO_x/SiO_2 (V/Ru=0.25). V species covered the Ru particles surface and reduced size of Ru ensemble, which may cause the selectivity change.

Keywords: Ruthenium, Hydrogenolysis, Algal biomass.

1. Introduction

Alkanes are a highly valuable and important class of compounds that are industrially manufactured as fuels and chemicals. Some microalgae species produce hydrocarbon-type biomass which is hardly obtained from plants. Typical hydrocarbons from microalgae is squalene (2,6,10,14,18,22-hexaen-2,6,10,15,19,23-hexamethyltetracosane) from *Aurantiochytrium mangrovei*. This hydrocarbon molecule is too large to use as transportation fuel and therefore cleavage of some C-C bonds is necessary. Recently, our group discovered highly dispersed Ru/CeO_2 catalyst for regioselective hydrogenolysis of squalane (2,6,10,15,19,23-hexamethyltetracosane), which is easily obtained by hydrogenation of squalene, without skeletal isomerization and aromatization.[1] 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 are more preferential than that of other alkanes. Another important character of C-C hydrogenolysis catalysts is the suppression of the formation of gaseous products, especially methane. The Ru/CeO_2 catalyst with highly dispersed Ru species has low activity to methane formation in comparison with other Ru catalysts, leading to very low methane selectivity. Hydrogenolysis of hydrogenated botryococcene, which is hydrocarbon derived from algal biomass, over Ru/CeO_2 catalyst was also reported.[2]

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. In this study, we investigated the effect of 2nd metal on Ru catalysts for squalane hydrogenolysis. 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

Ru-VO_x/SiO_2 (Ru: 5wt%, V/Ru=0-1) catalysts were prepared by co-impregnation method with $Ru(NO)(NO_3)_{3-x}(OH)_x$ in diluted nitric acid and NH_4VO_3*aq*. After evaporating the solvent, all the prepared catalysts were dried at 383 K for 12 h, and pretreated for 1 h in the N_2 flow at 573 K. Activity tests were performed in a 190 ml stainless steel autoclave with a copper gasket. Reaction conditions were as follows: catalyst (Ru: 5 wt%, V/Ru=0-1), 300 mg; squalane, 4.23 g (10 mmol); H_2, 6 MPa; 513 K; 2-39 h. The amount of H_2 chemisorption was measured in a high-vacuum system using a volumetric method in the vacuum line. Before adsorption measurements, the catalysts were reduced in H_2 at 573 K for 1 h. Selectivity was calculated based on carbon amount.

3. Results and discussion

The effect of V amount in Ru-VO_x/SiO_2 catalyst on the performance is shown in Figure 1. The order of activity was 0 (V/Ru)> 0.25 > 0.5 ≈ 1 from Figure 1(a). In view of selectivity, the order of methane selectivity was 0 (V/Ru)> 1 > 0.25 > 0.5 (Figure 1(b)) and C14-C16 selectivity was 0.5 ≈ 0.25 > 0.5 > 1 (Figure 1(c)). The methane selectivity was lower and the C14-C16 selectivity was higher over V/Ru = 0.25 or 0.5 catalysts than those over Ru/SiO_2 (V/Ru = 0) when compared at similar conversion level. From the balance of activity, and selectivity, we selected 0.25 as the best V/Ru ratio in Ru-VO_x/SiO_2 catalyst for hydrogenolysis of squalane.

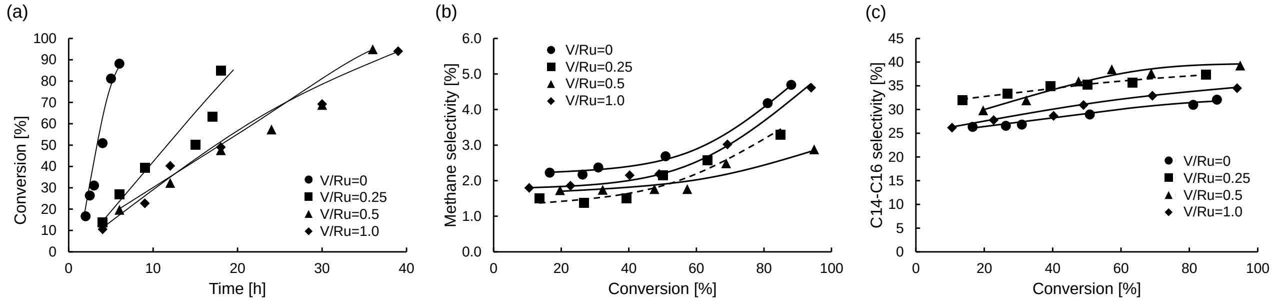

Figure 1. Results of squalane hydrogenolysis over Ru-VO_x/SiO_2 catalysts with various V amounts. (a) Squalane conversion vs reaction time, (b) Relation between methane selectivity and squalane conversion, (c) Relation between C14-C16 selectivity and squalane conversion. Conditions: catalyst (Ru: 5 wt%), 300 mg; squalane, 4.23 g (10 mmol); H_2, 6 MPa; 513 K; 2-39 h.

The amount of H_2 chemisorption was measured to count the number of active surface metal atoms (Table 1). While the H_2 chemisorption on Ru/SiO_2 well accorded with the Ru particle size (dispersion (H/Ru = 0.19)), the H_2 chemisorption amount was decreased with increase of V amount. In Ru-VO_x/SiO_2 (V/Ru = 0.25), about half of surface Ru was calculated to be covered by V species, and in Ru-VO_x/SiO_2 (V/Ru = 1) catalyst the coverage became 90%. The loss of activity of Ru-VO_x/SiO_2 was due to limited Ru active site for hydrogenolysis of squalane by V species. Above the results, blocking by V species changes the selectivity patterns due to reducing the ensemble size of Ru metal surface.

Table 1. Summary of H_2 chemisorption on Ru-VO_x/SiO_2 (Ru: 5.0×10^{-4} mol/g)

V/Ru	Amount of H_2 chemisorption [$\times 10^{-6}$ mol/g]	Dispersion [a] [-]	V surface coverage [b] [%]
0 (Ru/SiO_2)	46.6	0.19	0
0.25	21.0	0.08	54
0.5	6.9	0.03	85
1	4.5	0.02	90

[a] Dispersion = 2 × (Amount of H_2 chemisorption) / (Ru amount in catalyst)

[b] V surface coverage = {(Amount of H_2 chemisorption on Ru/SiO_2) × 2 – (Amount of H_2 chemisorption on Ru-VO_x/SiO_2) × 2} / {(Amount of H_2 chemisorption on Ru/SiO_2) × 2} × 100 [%]

4. Conclusions

Addition of V to Ru/SiO_2 catalyst prepared by co-impregnation and heating under N_2 improved the regioselectivity in squalane hydrogenolysis, although the activity was decreased. Ru-VO_x/SiO_2 (V/Ru=0.25) gave lower methane selectivity and higher C14-C16 selectivity than Ru/SiO_2. The loss of activity of Ru-VO_x/SiO_2 was caused by V species covering Ru surface and limiting the Ru active sites for hydrogenolysis of squalane. On the other hand, the V blocking changed the selectivity patterns probably via reducing the ensemble size of Ru metal.

References

1. S. Oya, D. Kanno, H. Watanabe, M. Tamura, Y. Nakagawa, K. Tomishige, *ChemSusChem* 8 (2015) 2472-2475.
2. Y. Nakaji, S. Oya, H. Watanabe, M. M. Watanabe, Y. Nakagawa, M. Tamura, K. Tomishige, *ChemCatChem* 9 (2017) 2701-2708.
3. Y. Nakagawa, S. Oya, D. Kanno, Y. Nakaji, M. Tamura, K. Tomishige, *ChemSusChem* 10 (2017) 189-198.