Demethoxylation of 2-Methoxy-cyclohexanone over Noble Metal Catalysts without External Hydrogen

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Lignocellulosic biomass is promising alternative to petroleum. One of its main components, lignin, possesses aromatic rings and can be source of aromatic chemicals. Guaiacols are representative lignin-derived chemicals, and demethoxylation of guaiacol produces more useful chemicals. However, some amount of methoxy compounds with cyclohexane ring is co-produced in hydrodemethoxylation [1]. In this study, we explored catalysts which convert 2-methoxycyclohexanone, one of hydrogenated products of guaiacol, to demethoxylated products (phenol, cyclohexanone and cyclohexanol; Fig. 1).

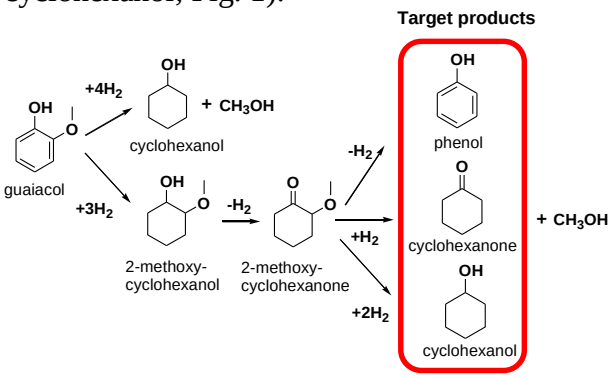

Fig. 1 Reaction pathway from guaiacol to target products.

Figure 2 shows the result of activity tests over various commercially available noble metal catalysts. Pt/C catalyst has the highest activity and selectivity to target demethoxylated products. Pd/C facilitated dehydrogenation of cyclohexane ring to guaiacol and Ru/C promoted demethylation to 1,2-cyclohexanediol and 2-hydroxycyclohexanone. Hydrogenation reaction with H_2 produced by dehydrogenation proceeded over all catalysts, especially over Rh/C, Pd/C and Ru/C. Regarding C1 products, methanol was formed over all catalysts, indicating that demethoxylation actually proceeded. However, over Pt/C, significant amount of CH_4 and CO_2 was also formed probably via reduction of methanol and aqueous phase reforming, respectively. The yield of target products was 35.4% over Pt/C.

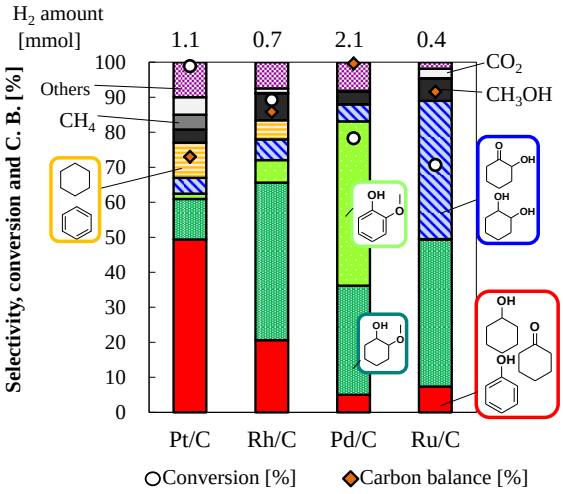

Fig. 2 Reaction over noble metal catalysts.
Reaction conditions: 2-Methoxycyclohexanone 5 mmol, water 20 mL, catalyst (5 wt% metal) 0.1 g, Ar 1 MPa, 493 K, 3 h

Next, we investigated the effect of reaction temperature. Reaction was conducted in the range of 463 ~ 513 K for 3 h and 24 h. For 3 h reaction, target products' yield increased with increasing the temperature until 503 K, and it decreased above 503 K. For 24 h reaction, however, high temperature caused extra deoxygenation of produced target products to cyclohexane and benzene. The yield of demethoxylation products was decreased. In this experiment, we got target products in 44.4 % yield under the conditions of 493 K and 24 h.

We investigated the effect of supports. We compared the performance of Pt catalysts with 7 supports (SiO_2, Al_2O_3, TiO_2, CeO_2, ZrO_2, MgO and activated carbon). Pt/C (activated carbon) had the highest activity and selectivity of target products.

In conclusion, demethoxylation of 2-methoxycyclohexanone proceeded without external hydrogen over Pt/C. The yield of phenol and the hydrogenated derivatives reached 44.4%.

REFERENCES

[1]M. Ishikawa, M. Tamura, Y. Nakagawa, K. Tomishige, Appl. Catal. B. Environ., 182 (2016) 193.