Demethoxylation of Guaiacol Derivatives over Platinum Catalysts without External Hydrogen

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Abstract: Guaiacols are representative lignin-derived chemicals, and hydrodeoxygenation of guaiacol is a promising method to produce useful compounds. However, simple hydrogenation product, 2-methoxycyclohexanol, is co-produced[1]. In this study, we explored catalysts which convert 2-methoxycyclohexanone, a partial dehydrogenated product of 2-methoxycyclohexanol, to phenol, cyclohexanone and cyclohexanol by demethoxylation without external hydrogen. We tested this reaction with noble metal catalysts and various supports, and found that Pt/C exhibited the best performance. Reaction conditions were optimized with Pt/C and the yield of target products reached 44.4 % (water solvent, 493 K, 24 h). Reaction route was determined by reactions of possible intermediates.

Keywords: Biomass, Demethoxylation, Platinum

1. Introduction

Lignocellulosic biomass is promising alternative to petroleum. One of its main components, lignin, possesses aromatic rings and can be source of cyclic chemicals. Guaiacols (2-methoxyphenols) are representative lignin-derived chemicals, and hydrodeoxygenation of guaiacol has attracted much attention as a method to produce more useful chemicals. However, some amount of simple hydrogenation product, 2-methoxycyclohexanol, is co-produced[1]. 2-Methoxycyclohexanol has low reactivity and low demand now. In this study, we explored catalysts which convert 2-methoxycyclohexanone, a partial dehydrogenated product of 2-methoxycyclohexanol, to feedstocks of polymer (phenol, cyclohexanone and cyclohexanol) by demethoxylation without external hydrogen.

2. Experimental

The commercial active-carbon-supported platinum (Pt/C) was mainly used. Commercial catalysts of other noble metals (Rh/C, Pd/C, Ru/C) were also used. Pt catalysts on various supports were prepared by impregnation method using aqueous $Pt(NH_3)_4(NO_3)_2$ (for SiO_2 and TiO_2 supports) or H_2PtCl_6 (Al_2O_3, CeO_2, ZrO_2, MgO). After impregnation, catalysts were dried at 383 K overnight and calcined at 773 K for 3 h. All catalysts were reduced with H_2 at 493 K for 0.5 h just before reaction. Activity test was performed in a 190-ml stainless steel autoclave. Reduced catalyst (0.1 g; without exposure to air), 2-methoxycyclohexanone (5 mmol), water (20 ml) and stirrer tip were put into the autoclave under nitrogen atmosphere. Autoclave was filled with argon (1 MPa) and heated to the reaction temperature (493 K; 30 min for heating). Conversion and selectivity were calculated on carbon basis. Phenol, cyclohexanone and cyclohexanol were regarded as “target products”.

3. Results and discussion

We explored the best catalyst by testing various metals and supports in this reaction. Figure 1 shows the result of activity tests over typical noble metal catalysts. From 0 h data (only heating to 493 K), Pt/C catalyst had higher activity than other noble metal catalysts. Selectivity of target products was higher when Pt/C and Rh/C were used. Pd/C facilitated dehydrogenation of cyclohexane ring to guaiacol and Ru/C promoted hydrolysis to 2-hydroxycyclohexanone. For 24 h reaction, Pt/C gave the highest selectivity of target products. Over Ru/C, the amount of produced hydrogen was largest, probably because of aqueous phase reforming of methanol produced by hydrolysis. We explored the effect of supports. We compared the performance of Pt catalysts with seven 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. As all, Pt/C seems to be the best catalyst for this reaction.

We optimized the reaction conditions for Pt/C catalyst. For reaction temperature, we tested the range of 463 ~ 513 K. Simple hydrogenation product (2-methoxycyclohexanol) was the main product below 483 K, and total deoxygenation (to cyclohexane and benzene) proceeded over 513 K. The highest yield of target products was obtained at 493 K. For the effect of solvents, water, ethanol, *n*-dodecane, toluene, mesitylene were tested, and only water solvent gave high conversion and high selectivity of target products. CO was produced when the other solvents were used. CO is known to be adsorbed on Pt, decreasing its activity. Water may have helped CO to convert to CO_2 via water gas shift reforming. The best yield of target products (44.4 %) was obtained over Pt/C at 493 K for 24 h using water solvent.

To confirm the reaction route, we conducted reactions of possible intermediates for short reaction time and with a small amount of Pt/C catalyst. The results are shown in Table 1. Target products are supposed to be produced through two routes (Figure 2). One route is dehydrogenation and hydrogenolysis. In this route, guaiacol is produced as an intermediate. The other route is hydrolysis, hydrogenation/dehydrogenation and hydrogenolysis. 2-Hydroxycyclohexanone, catechol and 1,2-cyclohexanediol are thought as intermediates in this route.

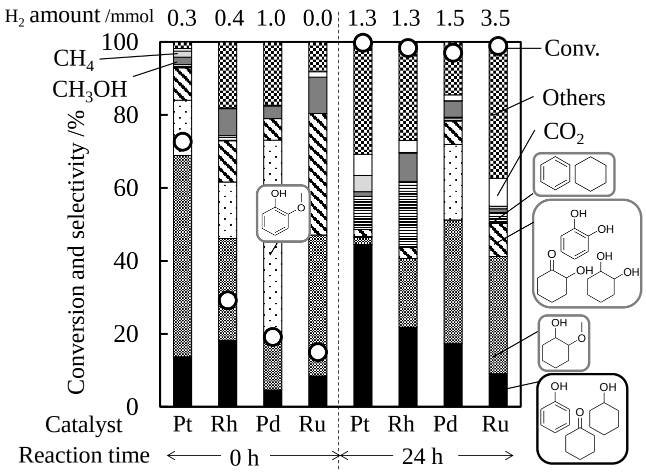
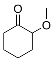
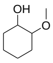
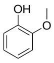
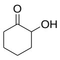
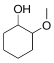
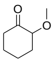
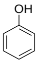
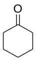
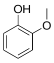
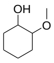
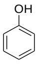
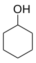
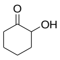
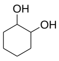
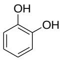
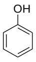
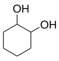
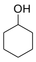
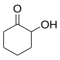
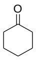
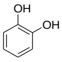
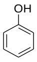
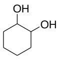
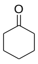


Figure 1. 2-Methoxycyclohexanone conversion over commercial noble metal catalysts. Conditions: 2-methoxycyclohexanone 5 mmol, water 20 mL, M/C 0.1 g, Ar 1 MPa, 493 K, 0 or 24 h.

Table 1 Reaction of intermediates in 2-methoxycyclohexanone conversion.

Substrate	Gas condition	Yield of main products /%					
	Ar		4.0		2.8		1.8
	Ar		8.7		0.8		0.7
	H_2+Ar		5.0		2.3		1.5
	Ar		29.3		18.4		5.3
	H_2+Ar		8.3		2.5		2.1
	H_2+Ar		11.7		8.2		3.3

Conditions : substrate 5 mmol, water 20 mL, Pt/C 0.02 g, Ar 1 MPa or H_2 0.1 MPa+ Ar 0.9 MPa, 493 K, 0 h.

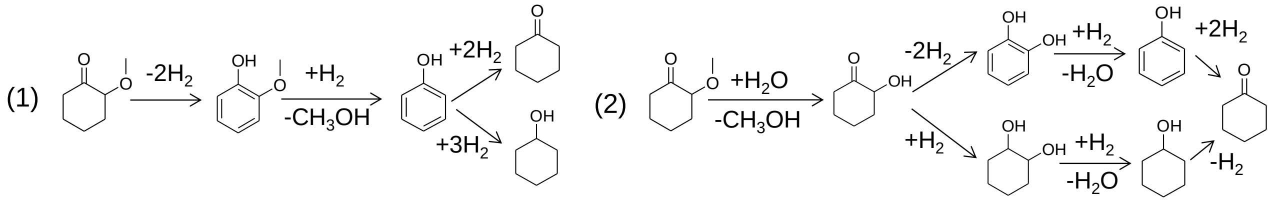


Figure 2. Supposed reaction routes to target products

4. Conclusions

Demethoxylation of 2-methoxycyclohexanone proceeded without external hydrogen over Pt/C. The yield of phenol and the hydrogenated derivatives reached 44.4% at 493 K in water solvent. Production of target products seems to proceed through two routes; (1) simple dehydrogenation + hydrogenolysis (demethoxylation), or (2) hydrolysis + hydrogenation/dehydrogenation + hydrogenolysis (deoxygenation).

References

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