

Kinetic analysis of xylose hydrogenation over carbon-supported copper catalyst at relatively low hydrogen pressures

Hiroyasu Fujitsuka*, Taku Hiraoka, Motoaki Kawase

Department of Chemical Engineering, Kyoto University, Kyoto Daigaku Katsura, Nishikyo-ku, Kyoto, 615-8510
JAPAN

*Corresponding author: fujitsuka@cheme.kyoto-u.ac.jp

Highlights

- Xylose hydrogenation into xylitol was performed at relatively low hydrogen pressure.
- Xylitol production rate could be expressed as Langmuir type equation for xylose concentration
- Xylitol production rate was apparently proportional to hydrogen pressure at low hydrogen pressure.

1. Introduction

Xylitol is one of the most valuable biomass-derived chemicals. In general, xylitol is produced by hydrogenation of xylose which is a monomer of hemicellulose. The hydrogenation of xylose is usually carried out in aqueous phase and in the presence of noble metal catalysts loaded on metal-oxide support. To realize the selective production of xylitol, highly pressurized hydrogen atmosphere (> 4 MPa) is required to suppress the undesired reactions on the active sites of catalyst support[1]. Therefore, the decrease in hydrogen pressure in this reaction system is one of the challenges for conventional use.

We recently developed carbon-supported copper catalyst prepared from ion-exchange resin (Cu@C) for selective hydrogenation of xylose into xylitol at relatively low hydrogen pressure[2]. To improve the catalyst activity and develop the efficient reaction system, the understanding of the reaction kinetic is indispensable. Thus, in this study, the xylose hydrogenation over Cu@C catalyst was conducted at several xylose concentration and H₂ pressure, and the xylitol production rate was formulated.

2. Methods

Cu@C catalyst was synthesized by using weakly-acidic cation-exchange resin and copper nitrate as carbon and copper sources, as previously reported[2, 3]. 5 g of ion-exchange resin was dispersed in 100 mL of 0.2 mol/L copper nitrate aqueous solution at room temperature and then the pH value of the solution was adjusted to 8.8 by adding ammonia aqueous solution to ionize the resin. After 24 h of ion-exchange, the copper-loaded resin was collected by a filtration. Cu@C catalyst was finally obtained by carbonizing the copper-loaded resin at 500 °C for 30 min in a nitrogen stream. The catalyst was ground and sieved to particle size smaller than 53 μm, which was followed by reduction of copper particles in a 50% hydrogen in nitrogen stream at 350 °C for 30 min before characterization and reaction. The prepared Cu@C has 66 wt% of Cu loading measured by a thermogravimetric analyzer and 18.9 nm of Cu particle size measured by a X-ray powder diffraction.

The hydrogenation of xylose was performed using a Teflon-lined 97 mL stainless-steel batch reactor. 30 mL of xylose aqueous solution and 0.26 g of Cu@C catalyst were put into the reactor and the atmosphere in the reactor was replaced to pressurized hydrogen. The initial concentration of xylose aqueous solution was 33–467 mol/m³ and initial pressure of hydrogen was 0.6–1.1 MPa. The reaction was conducted at 130 °C for 3 h. Throughout the reaction period, the pressure inside the reactor was monitored by a pressure gauge. The whole gas and liquid in the reactor after the reaction were collected and analyzed by a gas chromatography and a high-performance liquid chromatography, respectively.

3. Results and discussion

Figure 1 shows the xylitol production rate at different xylose concentrations (Fig. 1(a)) and initial hydrogen pressures (Fig. 1(b)). The selectivity in xylitol was above 81 C-mol% for all experiments,

indicating that the hydrogenation of xylose into xylitol was selectively proceeded. In general, the xylose hydrogenation reaction was described as the reaction between the adsorbed xylose molecule and the dissociatively adsorbed hydrogen atoms on the catalyst surface[4]. The xylitol production rate increased with the xylose concentration while the increment became smaller at the xylose concentrations above 200 mol/m³. This tendency suggests that the adsorption of xylose onto copper surface was saturated at high xylose concentration, which is consistent with literature[4]. In contrast, the xylitol production rate monotonically increased with hydrogen pressure, while the reaction rate reported in literature was almost constant against H₂ pressure[4]. This difference could be because of the difference in H₂ pressure. In this study, the reaction was conducted at relatively low H₂ pressure and the adsorption of hydrogen on the copper surface was not saturated in this reaction conditions. Additionally, the pressure inside the reactor was almost constant throughout the reaction period. This indicates that the concentration of hydrogen in the reaction solution could be regarded as constant. From these findings, the reaction rate of xylose hydrogenation on Cu@C was assumed as following equation:

$$r_m = \frac{k_m K_A C_A}{1 + K_A C_A} p_{H_2} \quad (1)$$

where k_m , K_A , C_A , and p_{H_2} respectively represent apparent reaction rate constant, adsorption-desorption equilibrium constant of xylose, xylose concentration, and hydrogen partial pressure.

From Equation 1, the average reaction rate is equal to the reaction rate at the logarithmic mean of the xylose concentration. Finally, the values of kinetic parameters, k_m and K_A , were determined as 9.3×10^{-4} mol/(kg·MPa·s) and 5.6×10^{-3} m³/mol, respectively.

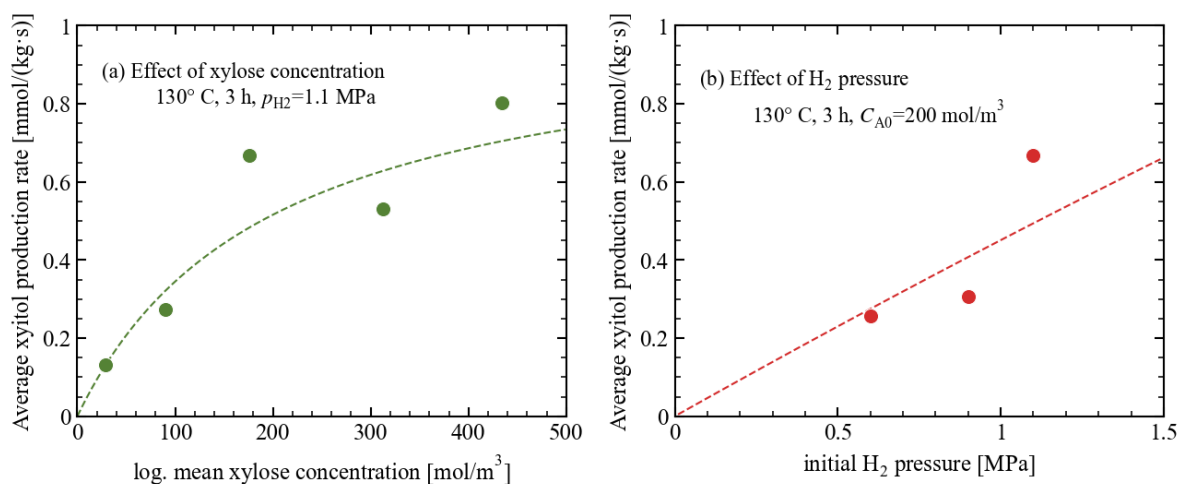


Figure 1. Xylitol production rate over Cu@C at different (a) xylose concentration and (b) H₂ pressure. (Dashed line was calculated reaction rate by using the obtained kinetic parameters)

4. Conclusions

To understand the reaction kinetics of xylose hydrogenation into xylitol at relatively low hydrogen pressure, the xylose hydrogenation reaction over Cu@C was performed at various xylose concentration and H₂ partial pressure. The dependency of reaction rate on xylose concentration was well explained by Langmuir type adsorption while the reaction rate was apparently proportional to hydrogen pressure because of the low hydrogen pressure. Finally, the kinetic parameters were successfully determined.

References

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Keywords

Xylitol, Copper catalyst, Kinetic analysis, Hydrogenation