

Development of Hydrotalcite-coated zeolite with Acid-Base Functionality for Glucose Conversion to 5-hydroxymethylfurfural

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Highlights

- Hydrotalcite layer was uniformly formed onto ZSM-5 by using proton type ZSM-5.
- Hydrotalcite coating provides basic sites onto ZSM-5
- Glucose and fructose can access Hydrotalcite-coated ZSM-5
- HMF yield achieved over 60 % from glucose.

1. Introduction

Acid-base catalysts are effective for aldol condensation, ketonization, and isomerization-dehydration to convert biomass-derived compounds into valuable materials [1]. Especially, isomerization and dehydration of glucose to 5-hydroxymethylfurfural (HMF) are key to achieving carbon neutrality, which is a promising material that can be platform for various chemical, including plastics, pharmaceuticals, fine chemicals, solvents, and biofuels. Glucose is isomerized to fructose at basic sites and then fructose is dehydrated to HMF at Brønsted acid sites. These reactions need catalyst such as Sn, Fe, or Cr-impregnated zeolite, $\text{SO}_4^{2-}/\text{TiO}_2$, $\text{SO}_4^{2-}/\text{ZrO}_2$, an amine-grafted zeolite, or amino-grafted mesoporous silica with sulfonic acid. These catalysts can promote isomerization and dehydration of glucose, achieving approximately 50% HMF yield from glucose [2]. On the other hand, strength of active sites affects these reactions [3], so it is important to control the strength of active sites for improving HMF yield. However, controlling the strength is not easy while maintaining other properties, as it requires changing metal or something. We have focused on a zeolite catalyst coated with hydrotalcite containing basic sites. This structure is a zeolite coated with hydrotalcite on its external surface. Additionally, zeolite and hydrotalcite are easy to control the strength of each active site. In this paper, we try to develop hydrotalcite-coated ZSM-5 catalyst and evaluate catalytic performance for glucose conversion to HMF.

2. Methods

At first, 2 g of commercial ZSM-5 (NHA-840) with Si/Al=20 and 100 mL of water are put into a beaker and ZSM-5 was homogenized in water by using ultrasound for 30 min named as solution A. The solution containing $\text{Mg}(\text{NO}_3)_2$ and $\text{Al}(\text{NO}_3)_3$ prepared with Mg/Al=3 was added dropwise to solution A at 60°C and then was stirring for 1 h. The solid collected was washed with distilled water and then sonicated with acetone for 30 min. The particle was dried at 120°C and then calcinated at 500°C for 5 h to obtain 1 wt% hydrotalcite-coated ZSM-5 catalyst ($\text{NH}_4\text{-ZSM-5@HT}$, H-ZSM-5@HT). Hydrotalcite (HT) was prepared using the above procedure without using ZSM-5. Pore properties of catalysts were evaluated by N_2 adsorption-desorption. The morphology of catalyst after hydrotalcite coating was observed by TEM. The amount of acidic and basic sites was estimated by $\text{NH}_3\text{-TPD}$ and $\text{CO}_2\text{-TPD}$.

Glucose conversion was performed using autoclave. At first, the following materials were put into the autoclave: glucose = 0.3 g, catalyst = 0.1 g, Water = 3.75 g, NaCl = 1.275 g, THF = 9.975 g. The mixture was stirring at 500 rpm and was increased up to 160°C and then maintained the temperature for 3 h. The

mixture obtained was analyzed by HPLC to calculate glucose, fructose, furfural, and HMF. The catalyst after the reaction was estimated by thermogravimetry to estimate the amount of component on the catalysts.

3. Results and discussion

Figure 1 shows TEM image of hydrotalcite-coated ZSM-5. ZSM-5 was coated with whisker-like and thin plate-like particles attributed to hydrotalcite layer after coating treatment. However, the thickness of coating layer was different when NH_4^+ - and H^+ -type ZSM-5 were used as a zeolite, implying that ammonium ion affected the interaction between zeolite and hydrotalcite and uneven hydrotalcite layer was formed on ZSM-5. Additionally, the morphology of hydrotalcite layer was similar before and after calcination at 500 °C for 5 h. These results indicate that uniform hydrotalcite layer was formed on H^+ -type ZSM-5 and the layer was coating on the surface of ZSM-5 even after calcination. N_2 adsorption-desorption measurement showed that nitrogen isotherm of H^+ -ZSM-5@HT was almost the same as that of ZSM-5, and BET specific surface area and pore volume were also the same.

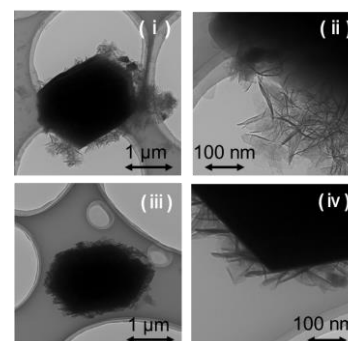


Figure 1. TEM image of ZSM-5@HT. (i), (ii): NH_4^+ -ZSM-5@HT, (iii), (iv): H^+ -ZSM-5@HT

Figure 2 shows CO_2 -TPD profile of hydrotalcite, ZSM-5, NH_4^+ -ZSM-5@HT, and H^+ -ZSM-5@HT. The amount of basic sites was calculated from total area except for the area of peak at 190 °C, which is physical adsorption. When hydrotalcite was coated on ZSM-5, the peak was shifted to high temperature due to the appearance of the peaks above 200 °C, which were attributed to basic sites from hydrotalcite-derived compound. Additionally, H^+ -ZSM-5@HT had more basic sites than NH_4^+ -ZSM-5@HT. On the other hand, when NH_3 -TPD was performed, the amounts of acid sites for HT, ZSM-5, NH_4^+ -ZSM-5@HT, and H^+ -ZSM-5@HT were 0.13, 0.57, 0.67, 0.52 mmol/g, suggesting that hydrotalcite coating almost no affects acid sites of ZSM-5. Thus, hydrotalcite-coated ZSM-5 with acid-base functionality was prepared successfully.

Figure 3 shows that H^+ -ZSM-5@HT produced higher HMF than other catalysts. Additionally, fructose was observed using HT coating ZSM-5, implying the coating promoted glucose isomerization to

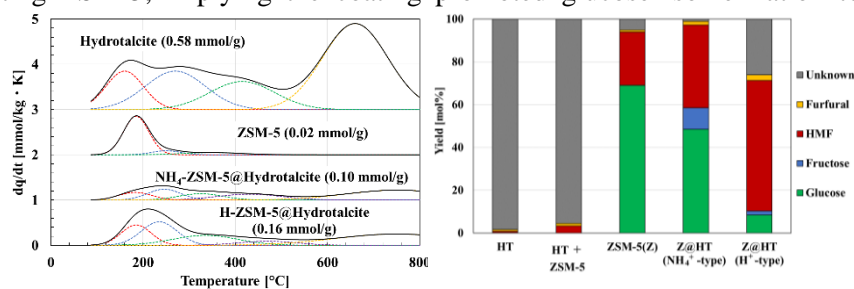


Figure 2. CO_2 -TPD profile of catalysts **Figure 3.** Glucose conversion to HMF

4. Conclusions

Hydrotalcite coating onto the surface of H^+ -type ZSM-5 provided basic sites on ZSM-5 while maintaining acid sites of ZSM-5. H^+ -ZSM-5@HT showed higher performance for glucose conversion to HMF.

References

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Keywords

Acid-base catalyst; Isomerization; Dehydration; 5-hydroxymethylfurfural