Development of active catalyst for direct conversion of biomass cellulose to C_3 and C_4 hydrocarbons at low temperature

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Abstract: Direct catalytic conversion of cellulose to C_3 and C_4 hydrocarbons at low temperature (443 K) in the presence of Pt/zeolite catalysts and water was investigated. Activity tests revealed that Pt supported on H^+-form ultra stable Y type (H-USY) zeolite catalyst (Pt/H-USY) enabled direct conversion of cellulose into C_3 and C_4 hydrocarbons without hydrogen and other expensive reagents. This production trend is attributable to the bifunctional catalysis of supported Pt and acid site in H-USY zeolite. Results revealed that the pre-treatment of catalyst was important to improve C_3 and C_4 olefin selectively. Air-oxidized Pt/H-USY catalyst showed higher C_3 and C_4 olefin selectivity than the catalyst reduced with hydrogen.
Keywords: Cellulose, C_3 and C_4 olefin, Hydrothermal reaction

1. Introduction

Renewable resources are attracting to contribute sustainable society. In particular, biomass cellulose offers numerous benefits as a ubiquitous feedstock. Recently, although C_3 and C_4 hydrocarbons are important raw materials used in petrochemistry, there is concerned about the shortage of these hydrocarbons supply in the future due to the stop of naphtha cracker (main light olefin production process). Therefore, development of new C_3 and C_4 hydrocarbons production process is anticipated. We focused on direct catalytic reaction of cellulose to C_3 and C_4 hydrocarbons. Recent reports described that a one-pot direct catalytic conversion of cellulose to C_3 and C_4 hydrocarbons over Pt/zeolite catalysts at 443 K under hydrothermal conditions without external hydrogen.1-3) The activity and selectivity in the reaction were affected by the zeolite structure and the Pt supported state. In the present work, to improve the olefin selectivity, effect of the pretreatment of catalyst on C_3 and C_4 olefin selectivity was investigated.2)

2. Experimental

Pt/H-USY catalyst was prepared using an ion exchange method. 1wt% Pt was supported on H-USY(14) (Tosoh Corp.) zeolite. The number in parenthesis representing the SiO_2/Al_2O_3 ratio. Catalyst was calcined at 803 K for 8 h. Catalyst was pretreated in a fix-bed continuous-flow glass reactor with 10% H_2 flow or air flow (100 ml/min) at 773 K for 1 h. Before the reaction, cellulose powder (MP Biomedicals) was pretreated using a ball mill (Pulverisette 6 classic line; Fritsch GmbH) to reduce its crystallinity.

Catalytic activity tests were performed in a batch-wise autoclave (30 ml, SUS316) with the following reaction conditions: 20 ml water, 0.25 g (8330 C-μmol) ball-milled cellulose, 0.25 g catalyst, 443 K temperature, 600 rpm stirring rate, 1-24 h reaction time. Catalytic reactions were conducted under Ar atmosphere. The reaction starting time was recorded when the reaction temperature reached the preset temperature. After the reaction, the reactor was cooled with water for 30 min. Gaseous products were collected and analyzed using GC-FID. Liquiform products were analyzed using TOC and HPLC.

3. Results and discussion

To improve C_3 and C_4 olefin selectivity, the effect of catalyst pretreatment on the catalytic activity and selectivity were investigated. Figure 1 shows C_3 and C_4 hydrocarbon selectivities over the air-oxidized and H_2-reduced Pt/H-USY zeolite catalysts. From Figure 1, air-oxidized Pt/H-USY catalyst showed higher olefin selectivity than that over the H_2-reduced Pt/H-USY catalyst. On the other hand, cellulose conversion and gaseous product amounts were almost identical in both pretreatment conditions. Results indicated that the oxidation pretreatment improved C_3 and C_4 olefin selectivities.

To clarify the difference of selectivity, TEM and EXAFS measurements were conducted. From TEM images, no significant difference in average Pt particle size was observed. Figure 2 shows Pt L_3-edge EXAFS spectra after Fourier transformation for air-oxidized and H_2-reduced Pt/H-USY(14) catalysts. Only Pt-Pt bond was observed over H_2-reduced Pt/H-USY(14) catalyst. On the other hand, both Pt-O bond and Pt-Pt bond were observed for air-oxidized Pt/H-USY(14) catalyst.2) It was indicated the supported Pt was partially oxidized. Therefore, partially oxidized Pt species (PtO_x) might be effective for C_3 and C_4 olefin production.

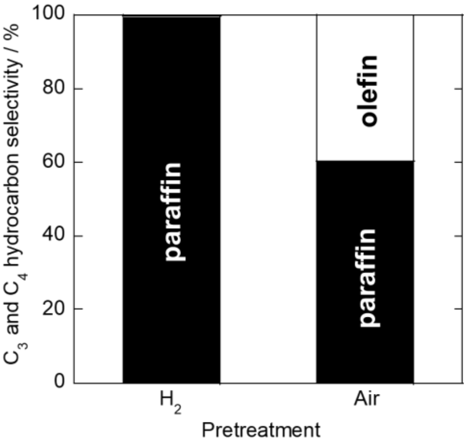

Figure 1. Effect of catalyst pretreatment on C_3 and C_4 hydrocarbons selectivity in the cellulose conversion over Pt/H-USY(14) catalyst at 443 K for 3 h.

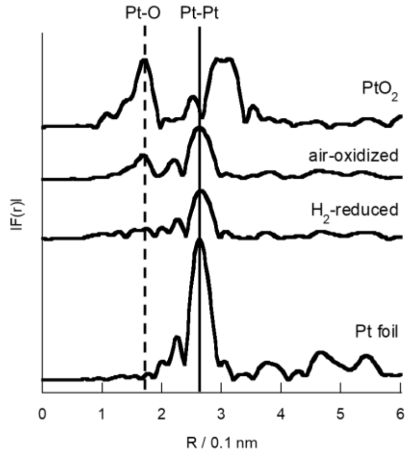

Figure 2. EXAFS spectra for Pt L_3-edge after Fourier transformation over Pt/H-USY(14) catalysts after pretreatment under H_2 or air flow at 773K for 1 h.2)

Next, we investigated the effect of reaction time on the olefin selectivity over air-oxidized Pt/H-USY(14) catalyst. Catalytic conversion of cellulose over Pt/H-USY(14) catalyst was conducted at 443 K for 1-24 h. Cellulose conversion and C_3 and C_4 hydrocarbon yield increased with increased reaction time. On the other hand, C_3 and C_4 olefin selectivities decreased gradually with increased reaction time up to 7 h, and then drastically decreased after further increase of reaction time. These results suggested that hydrogenation of olefin to paraffin proceeded with increased reaction time.

Then, to clarify the reaction intermediates, catalytic conversion of various substrates (cellobiose, glucose, fructose and xylose) were conducted over the Pt/H-USY(14) catalyst at 443 K for 3 h. In cases for cellobiose, glucose and fructose conversions, C_4 hydrocarbons were formed with high selectivity. In the case of xylose conversion, C_3 hydrocarbons were formed with high selectivity. These results indicate that C_6 sugars are reaction intermediates for C_4 hydrocarbon formations and C_5 sugars are reaction intermediates for C_3 hydrocarbon formations.

4. Conclusions

Air-oxidized Pt/H-USY catalyst showed higher olefin selectivity than that on H_2-reduced catalyst. Catalyst pretreatment condition influenced the oxidation state of the supported Pt and thereby changed olefin selectivity. C_3 and C_4 hydrocarbon yields increased with increased reaction time while C_3 and C_4 olefin selectivities decreased. C_6 sugars are reaction intermediates for C_4 hydrocarbons and C_5 sugars are reaction intermediates for C_3 hydrocarbons from cellulose over Pt/H-USY(14) catalyst.

References

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