Catalytic property of hydrogen boride sheets

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Abstract: Recently, we have revealed that the hydrogen boride sheets (HB sheets) can be formed by the complete ion-exchange between Mg cations and protons. In this work, we have examined the catalytic property of the HB sheets for the ethanol conversion. The HB sheets show the catalytic activity for the ethanol dehydration reaction to form ethylene with a high selectivity as much as 91.6 %. The conversion and the selectivity were found to keep constant at 12 hours. HB sheets are thus found to be a solid acid catalyst.

Keywords: Two dimensional materials, Boron, Solid acid catalyst.

1. Introduction

Two-dimensional (2D) materials are promising for applications in a wide range of fields because of their unique properties. As a new member of 2D sheet, hydrogen boride (HB) sheets were predicted by theory, where intriguing electronic and mechanical properties were expected as well as hydrogen storage capacity [1]. Recently, we have revealed that the HB sheets can be formed by the complete ion-exchange between Mg cations and protons [2]. HB sheets hold protons and releases hydrogen molecules in a wide temperature range from 150 °C to 1200 °C. So, HB sheets can be expected to be useful material for a solid fuel and/or a solid acid catalyst. In this work, we examined catalytic activity for ethanol reforming reaction.

2. Experimental

Ion-exchange was conducted by adding MgB_2 powder to acetonitrile in the presence of an ion-exchange resin; this entire process was conducted under nitrogen at room temperature and ambient pressure with stirring. After 3 days, black precipitates were removed by filtration, and the filtrate was dried in an oil bath at 343 K under reduced pressure. Characterization of the HB sheets was carried out with a scanning electron microscope (SEM), X-ray photoelectron spectroscopy (XPS), thermal desorption spectroscopy (TDS), and so on.

To evaluate the catalyst property, we have selected the ethanol reforming reaction as a test reaction. In the reactor, a gaseous ethanol was introduced into HB sheets with an argon carrier gas under the atmospheric pressure at the fixed bed flow reactor. The product gas was analyzed thermal conductivity detector gas chromatography (TCD-GC) at downstream of the reactor.

3. Results and discussion

HB sheets were obtained as the ion-exchange reaction product at an average reproducible yield of 42.3%. The SEM image of HB sheets is shown in Fig. 1, where wrinkles and folds are identified, indicating that HB sheets are flexible and having a two-dimensional character. Fig. 2 and Fig. 3 show the XPS core level peaks of B1s and Mg2p for HB sheets and those of the starting material of MgB_2, respectively. It is found that Mg is no more detected from HB sheets. The peak at ~188 eV observed from the HB sheets indicate that boron is negatively charged as in the case of MgB_2. From the desorption amount of hydrogen by TDS measurement and the weight change before and after TDS, the amount of hydrogen contained in the

HB sheets was determined, as to be the ratio of boron to hydrogen was 1: 1. Those characterized results are the same with our previously reported results [2].

As the conversion products of ethanol by HB at 200 °C to 300 °C, methane, ethane, ethylene and a trace amount of acetaldehyde were detected together with the main product of ethylene ($C_2H_5OH \rightarrow C_2H_4 + H_2O$). Fig. 4 shows the conversion of ethanol at various W/F (weight of the catalyst divided by flow rate of C_2H_5OH) between 200 °C and 300 °C. The conversion was calculated using the amount of hydrocarbon in the product. It was found that the conversion depends on W/F and temperature, larger W/F and higher temperature shows higher conversion. At the condition of 300°C and W/F = 24.6, the conversion leached to about 90%. On the other hand, the product selectivity does not depend on W/F. This indicates that hydrocarbons other than ethylene were generated not by the kinetic reasons. Fig. 5 and Fig. 6 show that the conversion of ethanol and selectivity of products do not change by time. That is, the conversion was stable at around 40% for 12 hours, and the selectivity of ethylene was also stable at around 90% for long time. This indicates that the product gas is generated by the catalytic reaction on HB rather than by the reaction of HB itself. That is, HB sheets have a catalytic activity for the dehydration reaction of ethanol with high durability. These results indicate that the HB sheets have a catalytic activity as a solid acid catalyst.

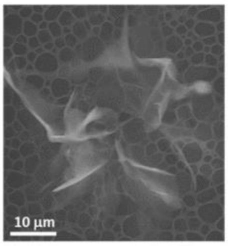

Figure 1. SEM result

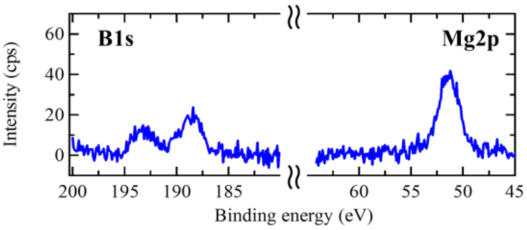

Figure 2. XPS result of MgB_2

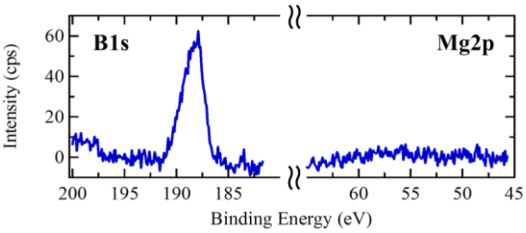

Figure 3. XPS result of HB sheets

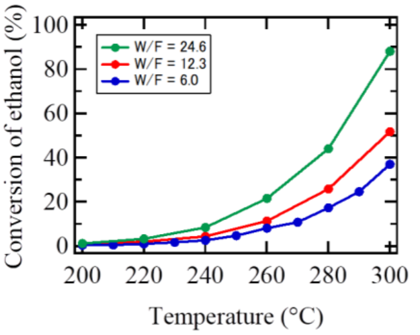

Figure 4. The conversion of ethanol

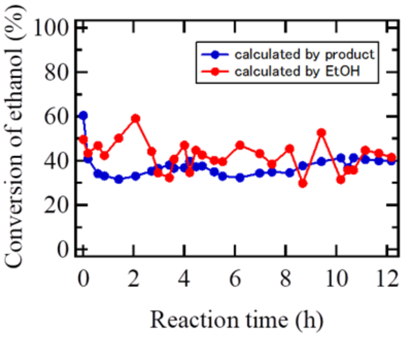

Figure 5. Time dependence of conversion

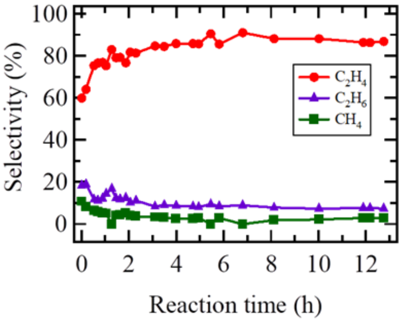

Figure 6. Selectivity of products

4. Conclusions

It was found that the HB sheets have catalytic activity for the dehydration reaction of ethanol, and it became clear that the HB sheets work as a solid acid catalyst.

References

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