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Development of Layered Double Hydroxide-based Highly Functionalized Solid Catalysts for Utilization of Biomass Derived Saccharides

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Introduction

From the 19th century, the development of catalysis science and chemical industry, especially petrochemical industry, has enriched our lives by enabling mass production of energy and chemical products. Recently, catalytic conversion of biomass derived materials into value-added chemicals including furfural has been attracted much attention because biomass has potential to substitute for fossil resources as the only renewable carbon source. The main objectives of this dissertation are the development of highly functionalized solid catalysts and apply them to transformation of biomass derived saccharides. I basically focused on high functionality of layered double hydroxide (LDH), one of a layered solid base catalyst which has Brønsted base site. Some strategies to develop highly functionalized LDH-based catalysts, preparation methods, results of characterizations, activity for chemical reactions including biomass derived saccharides as well as outlook based on my research are summarized in this doctoral thesis.

Results and Discussion

The one-pot transformation of xylose, one of the main components of hemicellulose, into furfural or furfural derivatives by combined use of Brønsted base Mg-Al LDH and solid acid resin Amberlyst-15 was conducted and described in **Chapter 2**. The effective synthesis of (2-furanylmethylene)malononitrile (FMM), the Knoevenagel product of furfural with malononitrile, was progressed *via* three elemental reactions; (i) aldose-ketose isomerization of xylose into xylulose over LDH, (ii) dehydration of xylulose into furfural over Amberlyst-15 and (iii) the Knoevenagel condensation of furfural with malononitrile over LDH, with FMM yield of 21% in a one-pot manner. To facilitate the aldose-ketose isomerization, rate-determining step in the one-pot synthesis, I synthesized two types of bi-functional Lewis acid – Brønsted base catalyst, Cr/Mg-Al LDH and Ni^{2+}-modified Al_2O_3 catalyst, and found that the bi-functional acid-base sites effectively promote the aldose-ketose isomerization. In **Chapter 3**, study of the detailed local structure and the optimized surface structure on the bi-functional acid-base Cr/Mg-Al LDH was conducted. The results of various characterizations and investigation of catalytic activities revealed that (i) below 1 wt%, a part of a Lewis acidic Cr^{3+} oxide monomer is trapped by peripheral defect sites of Mg-Al hydroxide layer, and others are immobilized onto LDH surface, (ii) Lewis acidic Cr^{3+} oxide dimer or trimer is generated on the LDH surface with covering LDH surface up to 5 wt%, (iii) above 5 wt%, excess Cr^{3+} species form Mg-Cr and/or Mg-Al-Cr LDH-like composite. Above 0-15 wt%, the 5 wt%Cr/Mg-Al LDH surface that comprises LDH carrier and covering layer of Cr^{3+} oxide possesses the most effective interaction between Lewis acidic Cr^{3+} oxide and basic Mg-Al LDH surface to generate abundant bi-functional Lewis acid – Brønsted base sites, leading to the best catalytic activity with 59% yield of furfural and FMM. Description of **Chapter 4** is the development of immobilized fine-crystallized SiO_2@LDH catalyst for improvement of basicity on LDH. Various SiO_2@LDHs were prepared by co-precipitation method with coexistence of spherical SiO_2(40nm). They have smaller LDH crystallite compared with conventional LDHs and showed highly base catalysis for the Knoevenagel condensation. For instance, in the case of Mg-Al type LDH with Mg/Al ratio of 3, the reaction rate over optimized SiO_2@LDH was 2.2 times higher than that of conventional LDH. Based on the results of ^{29}Si CP-MAS NMR and STEM-EDS, I concluded that dispersion of starting points of LDH crystal growth on SiO_2 surface lead to generate fine crystalline LDH which exhibits highly base catalysis.

Conclusion

In conclusion, I discovered the preparation methods of the LDH-based highly functionalized solid catalysts such as Lewis acid – Brønsted base bifunctional catalysts and immobilized fine-crystallized LDH catalysts. I also demonstrated that the multifunctional solid catalytic system composed of bifunctional Lewis acid-Brønsted base LDH-based catalysts effectively catalyzed one-pot synthesis of pentoses to furfurals. These achievements described in this doctoral thesis give catalytic science new strategies to design the multi-functionalized supported catalysts and to increase the original function of the layered catalysts for the development of noble modern organic synthesis including biomass-derived saccharides transformations.

Keywords: Layered Double Hydroxide, Solid Surface, Heterogeneous Bi-functional Acid – Base Catalysis, Control of Crystalline, Biomass Transformation