Enhanced Conversion and Selectivity from Bio-ethanol to Aromatics over Modified HZSM-5 Zeolite Catalysts

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Abstract

The technology is developing amazingly. Fossil fuel will be depleted in 50 years. Therefore, scientists are working on renewable energy. Biomass is the most promising renewable energy source. In addition to using it to generate energy directly, many experts try to convert it to more valuable compounds like aromatics.

We synthesized HZSM-5 with different Si/Al ratio by hydrothermal method and find the lower Si/Al leads higher selectivity of aromatics. We also conducted the experiments under different conditions such as temperature, WHSV, water amount of reactant [1] and metal loading to propose how these parameters influence the reaction pathway. Lastly, we try to use real bio-ethanol as reactant and simulate the system as factory.

Keywords: ZSM-5, Bio-ethanol, Aromatics.

1. Introduction

Ethanol is one of the most important and promising renewable energy available today from an environmental and economic point of view. It can be produced from renewable sources such as agricultural and forestry residues, crops and other forms of biomass. Instead of using it as energy source, people try convert it into compounds to enhance its value.

Martin Chang [2] reported that little water in the reactant has assist in ethanol conversion to hydrocarbons by ZSM-5 zeolite. Hence, we can direct use ethanol broth as reactant and lower temperature to vaporize it to get the ethanol steam. In addition to energy saving process, we can reach the goal of zero foot print because hydrocarbons come from the plants. Moreover, the most valuable compounds in hydrocarbons is aromatics because of its high diversity and demand in market. We call this reaction ethanol broth to aromatics abbreviated as EBTA.

2. Experimental

We synthesized HZSM-5 with different Si/Al ratio by hydrothermal method. First, we want to find the optimum Si/Al for ethanol broth to aromatics reaction in lab-scale reactor like right one in Fig.1. Next, We conducted the experiments under different conditions such as temperature, WHSV, and water amount of reactant to propose how these parameters influence the reaction pathway. Lastly, we try to load different amounts of Gallium and Zinc on the HZSM-5 to see whether it can enhance the selectivity of aromatics [3] and increase the lifetime of the catalysts. X-ray Diffraction (XRD), Specific Surface Area and Pore Size Distribution Analyzer, Fourier-transform Infrared Spectroscopy (FTIR) and Thermogravimetric Analysis (TGA) are used to test the characterization of ZSM-5 to help describe the selectivity difference of all different parameter.

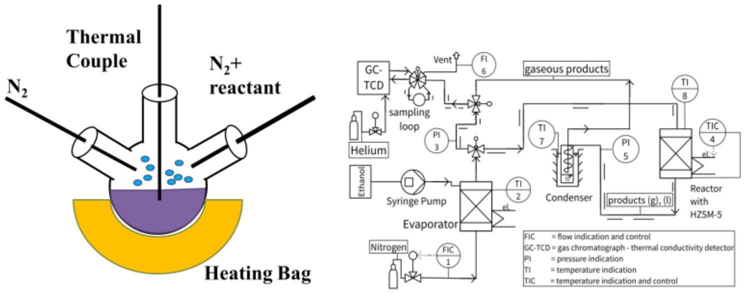

Figure 1. The schematic diagram simulation of factory system (left); The schematic diagram of lab-scale experimental setup(right).

3. Results and discussion

In different Si/Al experiment, we found conversion maintained stable in different Si/Al ratio and all of them were above 90%. Moreover, lower Si/Al ratio H-ZSM5 lead to higher selectivity of aromatics. Also, we got lower ethylene in gas product and higher aromatics in liquid product. Then, we found higher temperature leads to higher selectivity of aromatics. However, in 450°C, selectivity decreases a little. That's because cracking rate of aromatics gradually surpass the ethylene oligomerization rate. Next, we observed lower WHSV meaning longer contact time leads to higher selectivity of aromatics. On the other side, Higher WHSV meaning shorter contact time leads to more gas product like ethylene. Then, we concluded higher ethanol feed concentration leads to higher selectivity of aromatics. That's because water may occupy the active site making ethylene hard to react on that. However, selectivity in 40 wt% is a little higher because the adsorption of water reaches the saturation point. Hence, we predict lower than 40 wt% may have higher selectivity.

Last, from loading metal H-ZSM5 test, Gallium and Zinc promote the oligomerization in the reaction pathway because of the new active site on the surface. After all parameter tests, we successfully used real bio-ethanol as reactant to do EBTA under optimum reaction condition. Finally, we can get up to 30% (mole) selectivity of aromatics.

4. Conclusions

After parameter tests, we concluded the optimum reaction condition for ethanol broth to aromatics is on temperature equal to 400 ℃, WHSV equal to 1.81 hr^{-1} and feed concentration equal to 72 wt%. Moreover, Gallium and Zinc modified H-ZSM5 exactly help increase the aromatics selectivity for EBTA. In application part, we successfully simulated the factory system with real bio-ethanol as reactant and get the good selectivity of aromatics compared with lab-scale result.

References

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