Diesel Production from Waste Disposal using Catalytic Dissociation on Mn-zeolite Catalyst

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1. Theory

Catalytic dissociation reaction was studied for waste plastics. XRD and SEM analysis were performed to find crystal structure of prepared catalysts. GC-MAS analysis was also performed to find product distribution by kinds of catalysts.

2. Experiment

In this study, the making method of prepared catalysts are as follows; reactor with tefron have sodium silicate and sodiumaluminate mole ratio was 1:1 and chloroplatinic acid added 1wt% with respect to sodiumaluminate and also added sodiumhydroxide with two times of sodiumaluminate and last step water added 10 times of sodiumaluminate, and last step chloric acid added 1 wt% with respect to sodiumhydroxide. After then, stirred it over 1hr with over 500rpm at room temperature and reaction in the autoclave at 150℃ for 9hr. Dissociation catalyst has 3-dimension structure and involves alkali metal and water molecules and Si/Al ratio of it is above one. After previous process, it was centrifuged at 10,000rpm for 30 minutes and dried at 120℃ for 12hrs. and calcined at 500℃ for 3hrs.

Mn-zeolite, Pd-Zeolite, Ru-Zeolite, Zn-Zeolite, and Ir-Zeolite were prepared same method.

XRD(X-ray diffraction) analysis was performed to find structure of catalysts and SEM(Field Emission-SEM) analys was performed to find structure shape of ones.

3. Results & Discussions

3.1. XRD analysis

Lab. scale dissociation reactor was shown in Fig. 1. GC-MAS analysis was performed for product distribution. Dissociation reaction was took place with increasing temperature in the reactor and exhausted gas was condensed for GC-MAS analysis. As shown in Fig. 2. peaks of $Mn_2Al_4Si_5O_{18}$ and $Na_6MnAl_4Si_8O_{26}$ were found at 2θ = 8.65, 8.77, 3.40 and 2θ = 3.99, 3.56, 2.67 on the X-ray diffraction graph, respectively. Thus the structure of prepared Mn-zeolite catalyst consists of the combined crystal structure of $Mn_2Al_4Si_5O_{18}$ and $Na_6MnAl_4Si_8O_{26}$.

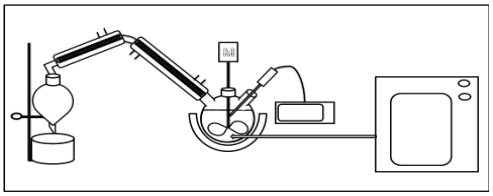

Fig. 1. Schematic diagram of reactor.

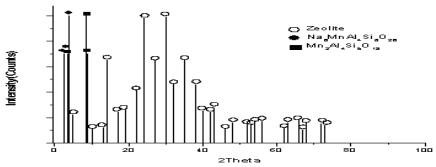

Fig. 2. XRD peaks of Mn-zeolite catalysts.

3.2. Dissociation reaction of waste plastics

3.2.1. The conversion of waste plastics according to temperature

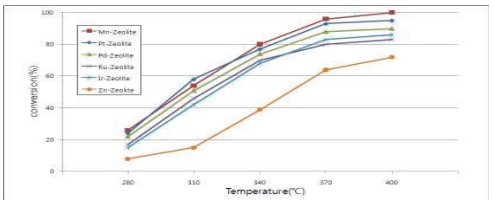

Fig. 3. PE dissociation conversion according to various catalysts.

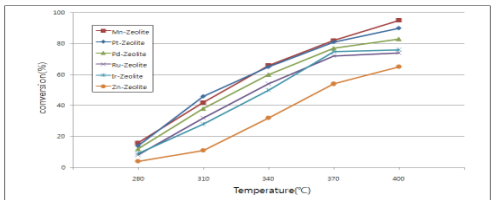

Fig. 4. PP dissociation conversion according to various catalysts.

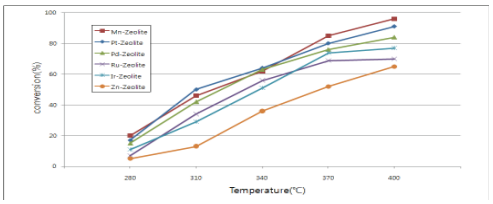

Fig. 5. ABS dissociation conversion according to various catalysts.

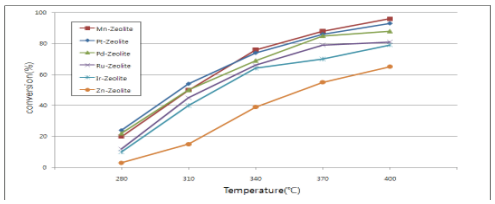

Fig. 6. Mixed PE, PP, and ABS conversion according to various catalysts.

Dissociation conversion showed in Fig. 3. ~ Fig. 5. according to temperature with respect to PE, PP, and ABS. Noble metal supported zeolite catalysts had a little high conversion at low temperature(280℃ and 310℃). Especially Pt-zeolite catalyst had the highest conversion among noble metal supported zeolite catalyst. However, Mn-zeolite catalyst had the highest conversion at higy temperaqture above 340℃. Fig. 6. represented the conversion of combined plastics (PE:PP:ABS=1:1:1) according to temperature. As you can see from this figure, Pt-zeolite and Pd-zeolite had a little higher conversion at low temperature(280℃ and 310℃), however it was not of important result because the conversion was very low about 20%. When it comes to starting main reaction over 340℃, Mn-zeolite catalyst had the highest conversion, on the other hand Zn-zeolite catalyst as a transition metal one had lower conversion with respect to Mn-zeolite one relatively.

Dissociation conversions of waste plastics were above 75 percentages over 340℃.

3.2.2. Product distribution

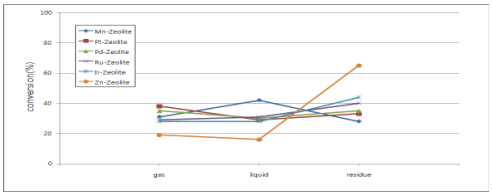

Fig. 7. Product distribution of PE at 340℃ according to various catalysts.

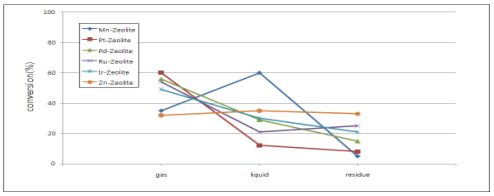

Fig. 8. Product distribution of PE at 400℃ according to various catalysts.

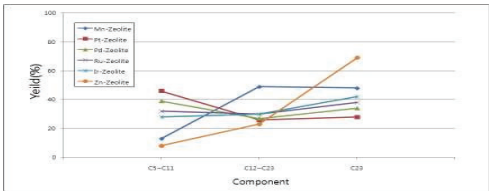

Fig. 9. Liquid product distribution of PE according to various catalysts at 340℃

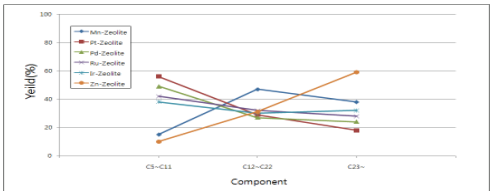

Fig. 10. Liquid product distribution of PE according to various catalysts at 400℃

Dissociation product and residue of gas and liquid phase for PE dissociation were shown in Fig. 7. and Fig. 8., respectively. At the temperature of 340℃, Almost product was residue and there was small amount of gas and liquid phase materials. However, there were a lot of products of gas and liquid phases and on the other hand, the amount of residue decreased drastically. Especially, noble metal based zeolite catalysts had a lot of gas phase product since their good cracking performance. In the case of Zn-zeolite catalyst, there are a lot of residue due to it's low activity. However, Mn-zeolite catalyst as a same transition metal one had a lot of liquid product, thus it had a high yield of diesel rather than light oil.

Fig. 9. and Fig. 10. represented liquid product distribution of waste polyethylene according to temperature. Pt-zeolite catalyst as well as noble metal base ones had high yield of C_5~C_{11} as petroleum. However, Mn-zeolite catalyst had high yield of C_{12}~C_{22} as diesel oil. While, Zn-zeolite catalyst had high yield of over C_{23} as heavy oil thus it can not be adapted as a diesel production catalyst.

Fig. 11.과 Fig. 12. showed liquis product distribution by using GC-MAS analysis of PE dissociation over Mn-zeolite catalyst. It represented that there was a lot of diesel oil components according to increasing temperature and there was maximum yield of diesel product such as C_{12}~C_{22} components at 340℃.

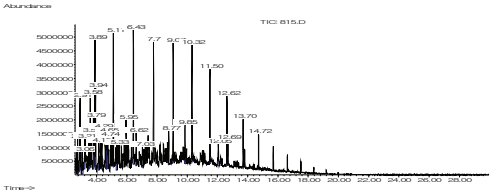

Fig. 11. GC-MAS peaks of product distribution for PE catalytic dissociation at 340℃

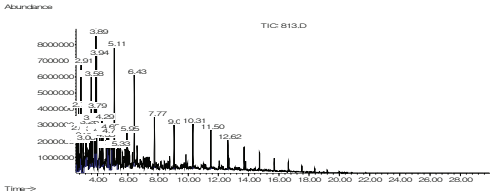

Fig. 12. GC-MAS peaks of product distribution for PE catalytic dissociation at 400℃

3.3. SEM analysis

These were SEM images of Zn-zeolite, Pt-zeolite, Pd-zeolite, and Mn-zeolite catalysts as showm in Fig. 13. ~ Fig. 16.

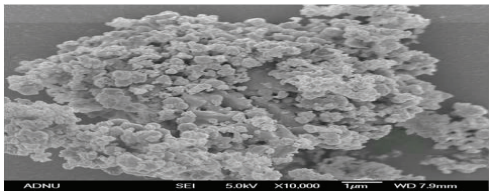

Fig. 13. SEM image of the Zn-Zeolite catalyst.

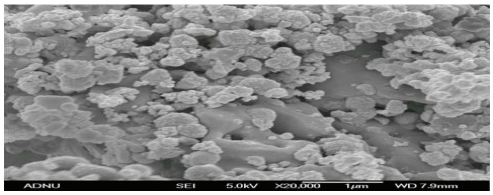

Fig. 14. SEM image of the Pt-Zeolite catalyst.

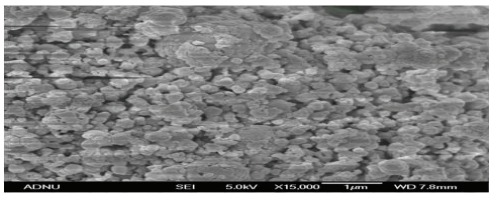

Fig. 15. SEM image of the Pd-Zeolite catalyst.

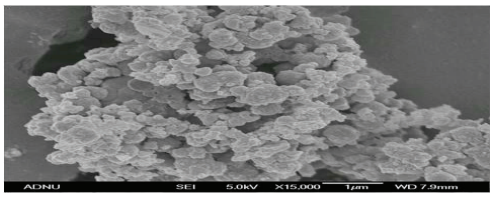

Fig. 16. SEM image of the Mn-Zeolite catalyst.

4. Conclusions

(1) Mn-zeolite catalyst had a highest yield of diesel oil such as C_{12}~C_{22} for waste plastic dissociation reaction.

(2) Dissociation efficiency and diesel yield were excellent when the structure of prepared Mn-zeolite catalyst consisted of the combined crystal structure of $Mn_2Al_4Si_5O_{18}$ and $Na_6MnAl_4Si_8O_{26}$.

(3) The dissociation conversion of PE, PP, and ABS above 340℃ over Mn-zeolite catalyst was above 75 percentages.

Acknowledgement

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Reference

1. H. J. Park, J. K. Jeon, S. H. Park, J. H. Yim, J. M. Sohn, and Y. K. Park "Research and Development Trends on Bio-oil Upgrading via Catalytic Vapor Cracking" J. Korean Ind. Eng. Chem., Vol. 20, No. 1, February 2009, 1-8
2. J. Adam, E. Antonakou, A. Lappas, M. Stocker, M. H. Nilsen, A. Bouzga, J. E. Hustad, and G. Øye, Micropor. Mesopor. Mater., 96, 93 (2006).
3. Y. C. Bak., J. H. Choi, and T. H. Cho "The Effects of Zeolite-Type Catalysts on the Pyrolysis Reaction of Raw Material Resin to Produce Fuel-Oil from Waste Vinyl" Korean Chemical Engineering Research, Vol.47, No.3, 303-309, 2009