

Catalytic cracking of heavy oil over TiO₂-ZrO₂ catalyst under a superheated steam

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Introduction

From the perspective of diversification of energy resources, it has been required that a technological development to convert unused fossil resources into useful fuels. In this study, catalytic cracking of atmospheric residue (AR) into lighter fuels such as gas oil or VGO was carried out under superheated steam atmosphere. Upgrading mechanisms are C-C bonds cleavage and naphthene ring opening with cracking, oxidation, or hydrogenolysis. Acidic C-C bond cleavage reaction is well-known as a FCC process, whereas coke formation on the catalyst is one of the serious problems, and a short reaction time followed by immediate regeneration process is indispensable. We have developed CeO₂-ZrO₂-Al₂O₃-FeOx catalyst (abbreviated as FeOx catalyst) for conversion of heavy oil into lighter fuel under superheated steam condition. In this catalytic cracking system, the lattice oxygen in FeOx is main active sites to decompose heavy oil [1]. Although the catalyst showed a high upgrading ability, the catalyst was gradually deactivated due to carbon deposition on the catalyst. In contrast, we have found that Titania-zirconia mixed oxide (TiO₂-ZrO₂) exhibits an acidic cracking activity for heavy oil cracking under superheated steam atmosphere. In this study, the effect of catalyst composition on the yield of the lighter fuel, catalyst activity and stability was examined.

Experimental

Catalyst Synthesis: TiO₂-ZrO₂ was prepared with each metallic alkoxide by sol-gel method. The gel thus obtained was calcinated at 773 K for 2 h. The crystallinity and acidity of the catalyst were analyzed by X-ray diffractometer and NH₃-TPD apparatus, respectively.

Catalytic conversion: AR diluted with toluene at 10 wt% was used as a feedstock. The catalysts were confirmed in advance to be inactive to toluene. The catalytic reaction under a superheated steam atmosphere was carried out in a fixed-bed type reactor. Because heavy oil decomposition proceeds on the catalyst surface, S/F (S : catalyst surface area filled the reactor /m² g⁻¹, F : feedstock flow rate /g h⁻¹) was maintained at 80-92 m² h g⁻¹. F_{H_2O}/F (F_{H_2O} : water flow rate /g h⁻¹, F : feedstock flow rate /g h⁻¹) was 2.0. Reaction temperature was 743 K. The gaseous and liquid products were analyzed by gas chromatography, and high-performance liquid chromatography, respectively. The amount of coke deposited on the catalyst after reaction was measured by a elemental analyzer and NH₃-TPD apparatus.

Results and Discussion

Figure 1 shows the carbon yield after the catalytic cracking of AR under superheated steam over the TiO₂-ZrO₂ catalysts. The number in parenthesis indicates the molar ratio of each component in the mixed oxide catalyst. The yield of lighter component (Gasoline and Kerosene, Gas oil, and VGO) depended on the composition of catalyst and reached to

approximately 65 mol%-C in Ti(50)Zr(50) catalyst. Moreover, the amount of coke on the Ti(50)Zr(50) catalyst was 15 mol%-C, which was lower than that on the FeOx catalyst (25 mol%-C).

NH₃-TPD profile of TiO₂-ZrO₂ catalyst was shown in Figure 2, in which the profiles of FeOx catalyst, TiO₂ and H-BEA zeolite were also shown for comparison. It was found that the TiO₂-ZrO₂ catalyst exhibited a comparable acidity to the H-BEA zeolite. Accordingly, the high yields of lighter fuels in TiO₂-ZrO₂ catalysts resulted from the strong acidity. From the view point of the yields of lighter fuel and coke, the Ti(50)Zr(50) was decided to be an appropriate catalyst.

In our presentation, durability of the catalyst as well as an application of the catalyst to decomposition of oil sand bitumen will be introduced.

Conclusions

The production of lighter oil by catalytic cracking of heavy oil with TiO₂-ZrO₂ catalyst in a superheated steam was investigated. Ti(50)Zr(50) is a promising catalyst to decompose the heavy oil and to produce lighter fuels.

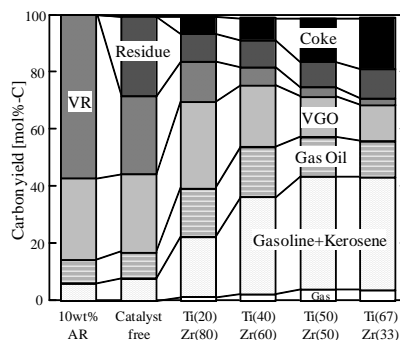


Figure 1. Total carbon yield after the reaction of 10wt% AR over TiO₂-ZrO₂ catalysts under the superheated steam condition. Reaction condition is $T = 743$ K and normal pressures. VR and VGO represent vacuum residue and vacuum gas oil.

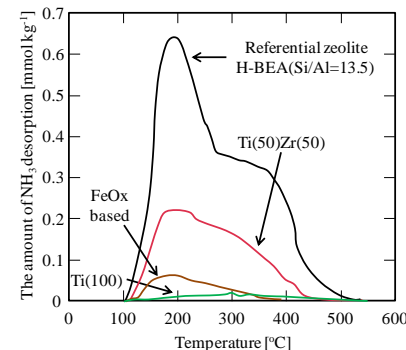


Figure 2. NH₃-TPD profiles of H-BEA, TiO₂, FeOx based and TiO₂-ZrO₂ (Ti : Zr = 50 : 50) catalysts before the reaction. FeOx based states CeO₂-ZrO₂-Al₂O₃-FeOx catalyst.

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References

1. S. Funai *et al*, *Journal of the Japan Institute of Energy*, **89**, 231-236, (2010)