Catalytic cracking of heavy oil over TiO$_2$-ZrO$_2$ 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 naphthalene ring opening with cracking, oxidation, or hydrodenylation. 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 CeO$_2$-ure catalyst to decompose heavy oil and to produce lighter fuels. The catalyst after decomposition of oil sand bitumen will be introduced.

Experimental
Catalyst Synthesis: TiO$_2$-ZrO$_2$ 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 NH$_3$-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 /m$^2$ g$^{-1}$, F: feedstock flow rate /g h$^{-1}$) was maintained at 80-92 m$^3$ h$^{-1}$. F$_{H2O}$/F$_{feed}$ (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 NH$_3$-TPD apparatus.

Results and Discussion
Figure 1 shows the carbon yield after the catalytic cracking of AR under superheated steam over the TiO$_2$-ZrO$_2$ catalyst. 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 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).

NH$_3$-TPD profile of TiO$_2$-ZrO$_2$ catalyst was shown in Figure 2, in which the profiles of FeOx catalyst, TiO$_2$ and H-BEA zeolite were also shown for comparison. It was found that the TiO$_2$-ZrO$_2$ catalyst exhibited a comparable acidity to the H-BEA zeolite. Accordingly, the high yields of lighter fuels in TiO$_2$-ZrO$_2$ catalyst 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 TiO$_2$-ZrO$_2$ 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.

Acknowledgement
This work was supported by the Industrial Technology Research Grant Program, from Japan Petroleum Energy Center (JPEC) in Japan.

References