Recovery of Lighter Fuels from Petroleum Residual Oil by Oxidative Cracking with Steam over Zr–Al–FeO$_x$ Catalyst

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Zirconia-including iron catalyst with high durability was successfully prepared which had high activity for recovering lighter fuels from petroleum residual oil in a steam atmosphere. Zirconia dispersed highly in iron catalyst supplied enough amount of active oxygen species from steam into iron oxide lattice. Lattice oxygen in iron oxide reacted with heavy oil. Thus, oxidative cracking of heavy oil with steam was accelerated over iron catalyst with highly dispersed zirconia without any lack of lattice oxygen of iron oxide.

It is strongly desired to produce lighter fuels such as gasoline, kerosene, and gas-oil, even though the half of the primitive petroleum deposits have already been consumed. There are huge amounts of heavy oils such as atmospheric and vacuum distilled residual oils, which are generated as by-products in petroleum refinery process. Therefore, several methods, which are thermal cracking,[1,2] catalytic cracking[3,4] and hydrocracking[5–7] have been recognized as promising methods to recover useful lighter fuels from heavy oils. In all of these methods, a carbonaceous residue is, however, formed both in reactors and on catalysts, leading to serious problems, such as the plugging of reactors and rapid catalyst deactivation. Therefore, it has been reported that the formation of carbonaceous residues is reduced at high hydrogen pressures.[7] Hydrogen is, however, the finite resource, since this is produced from the petroleum deposits remaining as half of their primitive amount.

We have attempted to utilize the catalytic cracking of heavy oil with steam as an alternative hydrogen source. In our previous paper, we have shown that both atmospheric distilled residual oil and vacuum distilled one can be decomposed over zirconia-supporting iron oxide catalysts (denoted as Zr/FeO$_x$) in a steam atmosphere.[8,9] Steam is decomposed on zirconia and iron oxide, yielding active hydrogen and oxygen species. Hence, oxidative decomposition of heavy oil and hydrogenation of produced lighter hydrocarbons occur simultaneously without any carbonaceous residue.[8] The catalyst was, however, deactivated with the number of the sequence of reaction and regeneration. This is attributed to phase change of the iron oxide, followed by the collapse of pore structure of the catalyst. To reduce this collapse, alumina was added to the iron oxide lattice with little reduction of activity.[9] This catalyst is denoted hereafter as Zr/Al–FeO$_x$.

In order to prevent the catalyst deactivation, the essential cause, namely phase change of iron oxide, must be reduced. Oxidative cracking of heavy oil is the reaction between heavy oil and lattice oxygen of iron oxide, followed by addition of steam-derived hydrogen to produced lighter hydrocarbons. When the supplying rate of steam-derived active oxygen to iron oxide lattice is lower than the consumption rate of lattice oxygen due to the oxidative reaction, the structure of iron oxide changes from hematite to magnetite, namely phase change. Therefore, the enhancement in the decomposition rate of steam is considered to be a possible method to prevent the phase change of iron oxide. As compared with a conventional impregnation method for supporting zirconia on FeO$_x$ and Al–FeO$_x$ employed in previous works (preparation of Zr/FeO$_x$ and Zr/Al–FeO$_x$ catalysts),[8,9] a co-precipitation method with their corresponding solutions would achieve high dispersion of zirconia in catalysts. Therefore, in this study, firstly, the iron oxide catalyst was prepared by a co-precipitation method to improve the decomposition rate of steam. Secondly, the oxidative cracking of heavy oil by use of this prepared catalyst was conducted, to examine experimentally the activity and the durability of this catalyst.

Complex metal oxide of Fe, Al, and Zr was prepared by a co-precipitation method using water solutions containing iron(III) chloride ($150\,\mathrm{mol\,m^{-3}}$), aluminum sulfate ($6.2\,\mathrm{mol\,m^{-3}}$), and zirconium oxychloride ($9.1\,\mathrm{mol\,m^{-3}}$), followed by steam treatment at 873 K for 1 h. The catalyst thus obtained is denoted hereafter as Zr–Al–FeO$_x$. The amounts of ZrO_2 and Al_2O_3 in the Zr–Al–FeO$_x$ catalyst are 8.4 and 4.8 wt %, respectively. These catalysts were pelletized without any binders, crushed and sieved to yield particles of 300–850 µm in diameter, and were used in the further experiments. The structures of the catalysts were analyzed using an X-ray diffractometer (XRD; JDX-8020, JEOL).

Oxidative cracking of heavy oil with steam over the catalysts was conducted by use of a fixed-bed reactor loaded with the catalysts of about 1.0×10^{-3} kg under the conditions of reaction temperature of 773 K and one atmospheric pressure.[9] The 10% benzene solution of a residual oil of atmospheric distillation from a petroleum process (denoted as AR) was used as feedstock in order to reduce the viscosity of AR. The catalysts were confirmed to be inactive for benzene in advance.[8,9] Time factor W/F was 1.2 h, where F is the flow rate of the feedstock and W is the amount of the catalyst. This value corresponds to that from 12 of another time factor W/F_R, where F_R is the flow rate of AR without benzene. A mixture of steam and nitrogen was introduced into the reactor as a carrier gas, where flow rates of steam and nitrogen were $4.3 \times 10^{-3}\,\mathrm{m^3\,h^{-1}}$ and $3.0 \times 10^{-4}\,\mathrm{m^3\,h^{-1}}$, respectively. The liquid products were collected using an ice trap and their compositions were analyzed by a liquid chromatograph (CTO-10A; Shimadzu Co., Ltd.). The analysis of gaseous products was quantitatively performed using gas chromatographs with thermal conductivity and flame ionization detectors (GS20B; Shimadzu Co., Ltd.) with activated carbon and Porapak Q columns, respectively.

Figure 1 shows the typical product yield after the reaction of AR over Zr–Al–FeO$_x$ catalyst. The experimental results without catalyst and with the catalysts, Zr/FeO$_x$ and Zr/Al–FeO$_x$ are shown in the figure for comparison. The compositions of Zr of

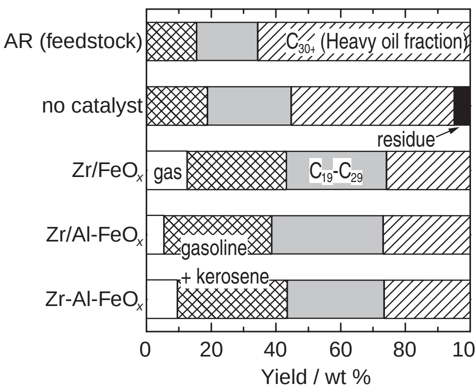

Figure 1. Product yield after reaction of AR with steam over Zr–Al–FeO$_x$, Zr/FeO$_x$, and Zr/Al–FeO$_x$ catalysts. Reaction time = 2 h.

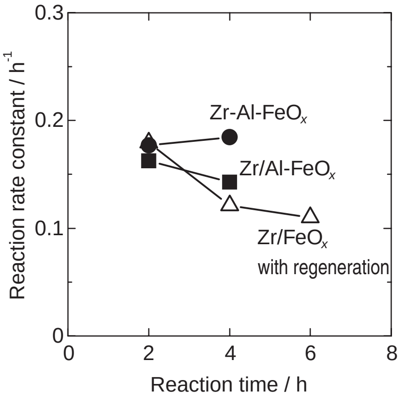

Figure 2. Change in the reaction rate constant over Zr–Al–FeO$_x$, Zr/FeO$_x$, and Zr/Al–FeO$_x$ catalysts.

these two catalysts are almost the same as that of Zr–Al–FeO$_x$. When the catalysts were used, the main products were gasoline and kerosene without any carbonaceous residue. Moreover, the dominant gaseous product was CO_2, as expected in view of the oxidative cracking of heavy oil over zirconia-supporting iron oxide catalysts.[8,9] This reaction is strongly related to the decomposition rate of steam over zirconia, which generates active oxygen species.[8] Hence, zirconia in the Zr–Al–FeO$_x$ catalyst has an activity for decomposing steam to generate active oxygen and hydrogen species, and is dispersed to the same degree as those of Zr/FeO$_x$ and Zr/Al–FeO$_x$, at least.

We have previously reported that the reaction rate of the decomposition of AR was expressed to be the second order with respect to heavy oil fraction.[9] To reveal the stability of the catalysts, the reaction rate constant was calculated from the yield of heavy oil fraction, and is shown in Figure 2. When the activity of ZrO_2 is insufficient, the phase change of iron oxide from hematite to magnetite easily proceeds due to consumption of lattice oxygen of FeO$_x$ in hematite, leading to catalyst deactivation.[9] Therefore, Zr/FeO$_x$ and Zr/Al–FeO$_x$ catalysts were gradually deactivated. On the other hand, Zr–Al–FeO$_x$ catalyst showed stable activity, suggesting that production of active species from steam was enhanced enough to suppress the consumption of lattice oxygen of FeO$_x$ during the oxidative cracking of AR.

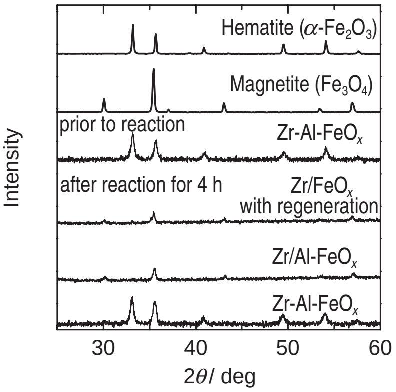

Figure 3. XRD patterns of Zr–Al–FeO$_x$, Zr/FeO$_x$, and Zr/Al–FeO$_x$ catalysts prior to and after reaction of AR for 4 h.

To clarify the consumption of lattice oxygen of FeO$_x$, the XRD patterns of the catalysts after the reaction of AR for 4 h were measured, as shown in Figure 3. The pattern of fresh Zr–Al–FeO$_x$ is also shown in the figure for comparison. Those of fresh Zr/FeO$_x$ and Zr/Al–FeO$_x$ were almost the same as that of Zr–Al–FeO$_x$, indicating that the structure of iron oxide among the fresh catalysts were that of hematite. The structures of iron oxide in Zr/FeO$_x$ and Zr/Al–FeO$_x$ changed from hematite to magnetite during the reaction due to the insufficient activity of zirconia.[8] On the other hand, Zr–Al–FeO$_x$ catalyst held hematite structure during reaction, as expected from Figure 2. The activity of the decomposition of steam is considered to be the surface of supported zirconia. Hence, zirconia of Zr–Al–FeO$_x$ catalyst would be dispersed highly than those of Zr/FeO$_x$ and Zr/Al–FeO$_x$. With this consideration, almost zirconia units contact with iron oxide lattice of hematite, and steam-derived active oxygen species can easily spill over from zirconia to neighboring positions where lattice oxygen of hematite is lacked due to the oxidative reaction. This mechanism would keep hematite structure, leading to stable activity of the Zr–Al–FeO$_x$ catalyst.

It was concluded that the Zr–Al–FeO$_x$ catalyst was active to produce lighter hydrocarbons from heavy oil, and that the catalyst was also durable, because the supported ZrO_2 was sufficiently active to generate active oxygen species and consumption of lattice oxygen of iron oxide was suppressed.

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