Iron Oxide-Based Catalyst for Catalytic Cracking of Heavy Oil

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Additional information is available at the end of the chapter

Abstract

This chapter describes an iron oxide catalyst containing Zr and Al for production of light hydrocarbons by catalytic cracking of petroleum residual oil in a steam atmosphere. The catalyst was hematite structure and useful for decomposition and desulfurization of residual oil. After lattice oxygen of iron oxide reacted with heavy oil fraction of residual oil, oxygen species generated from steam were supplied to iron oxide lattice and reacts with heavy oil fraction, producing light hydrocarbons and carbon dioxide. When the oxygen species were generated from steam, hydrogen species were simultaneously generated from steam. The hydrogen species were transferred to light hydrocarbons, hydrogen sulfide, and residue deposited on the catalyst. Supplies of the hydrogen species to light hydrocarbons suppressed alkene generation. Generation of hydrogen sulfide indicated decomposition of sulfur compounds of residual oil. The sulfur concentration of product oil decreased compared to the concentration of residual oil. Some oxygen species could be transferred to sulfur dioxide. Accordingly, hydrogenation and oxidation by the hydrogen and oxygen species derived from steam provided the decomposition and desulfurization of residual oil with the iron oxide-based catalyst in a steam atmosphere.

Keywords: iron oxide catalyst, atmospheric residue, steam catalytic cracking

1. Introduction

Petroleum refineries require production of transportation fuels by decomposition of petroleum residual oil. The residual oil has low H/C ratio, high viscosity, and impurities, such as sulfur, vanadium, and nickel. Hence, decomposition of the residual oil is not easy.

The conventional process to convert heavy oil, such as petroleum residual oil, to light hydrocarbons was coking, visbreaking, residue fluidized catalytic cracking (RFCC), and hydrocracking

[1, 2]. Heavy oil was decomposed with Ni-Mo or Co-Mo catalysts to produce light hydro-carbons with less coke under high hydrogen pressure in the hydrocracking process. The hydrocracking is a useful technique to produce light hydrocarbons, which has high H/C ratio, although hydrogen is expensive.

Steam can be an alternative hydrogen source for conversion of heavy oil to light hydrocarbons with catalysts. This technique requires the following catalyst properties: (i) a high ability to decompose heavy oil, (ii) stable activity under high steam temperature, and (iii) resistance to deposition of coke, sulfur, and metals. Iron oxide is not expensive and can be a candidate the catalyst to decompose heavy oil in a steam atmosphere.

This chapter describes an iron oxide-based catalyst for decomposition of heavy oil to produce light hydrocarbons. Properties of the catalyst and catalyst activity to decompose residual oil and desulfurization in a steam atmosphere are discussed.

2. Properties of iron oxide catalyst

Several studies reported the catalytic cracking of heavy oil with iron oxide catalysts. Fumoto et al. developed the ZrO_2-supporting α-Fe_2O_3 catalysts for oxidative cracking of petroleum residual oil under high steam temperature [3]. Hosseinpour et al. reported catalytic cracking of petroleum residual oil using silica-supported α-Fe_2O_3 nanoparticles under super critical water [4]. Nguye-Huy and Shin studied steam catalytic cracking of petroleum residual oil using ZrO_2-impregnated macro-mesoporous red mud, which consisted of α-Fe_2O_3 and TiO_2 [5]. Phase diagram of ferrite showed that Fe_2O_3 is alloyed with Al_2O_3 homogeneously [6]. Hence, Fumoto et al. modified the ZrO_2-supporting α-Fe_2O_3 catalysts by addition of Al to enhance the catalyst durability [7, 8]. We described the properties of the α-Fe_2O_3 catalysts containing Zr and Al in this section.

2.1. Preparation of α-Fe_2O_3 catalyst containing Zr and Al

The α-Fe_2O_3 catalyst containing Zr and Al was prepared by a coprecipitation method using aque-ous solution of $FeCl_3\cdot6H_2O$ (Special grade, Wako Pure Chemical Industries, Ltd., 146 mol/m^3), $AlCl_3\cdot6H_2O$ (Special grade, Wako Pure Chemical Industries, Ltd., 19 mol/m^3), and $ZrOCl_2\cdot8H_2O$ (Special grade, Wako Pure Chemical Industries, Ltd., 9 mol/m^3) with aqueous ammonia [9, 10]. The catalyst was pelletized without binder, crushed, and sieved to obtain particles of 300–850 μm after the treatment at 873 K for 1 h in a stem atmosphere. The atomic ratio of Fe, Zr, and Al in the catalyst was 1:0.06:0.13.

2.2. Structure of α-Fe_2O_3 catalyst containing Zr and Al

The morphology of the α-Fe_2O_3 catalyst containing Zr and Al was analyzed by scanning elec-tron microscope (SEM, JSM-6010LA, JEOL Ltd.). **Figure 1** showed a SEM image of α-Fe_2O_3 catalyst containing Zr and Al prepared by a coprecipitation method. The catalyst was com-posed of randomly shaped particles.

The crystalline construction of the catalyst was analyzed by X-ray diffraction (XRD, M03XHF22, Mac Science Co. Ltd.). **Figure 2** showed the XRD patterns of the catalyst and regent iron (III) oxide (α-Fe_2O_3, first grade, Wako Pure Chemical Industries, Ltd.) [9]. The patterns of the catalyst corresponded to that of α-Fe_2O_3. Absence of peaks corresponding to ZrO_2 and Al_2O_3 indicates high dispersion of Al and Zr in the α-Fe_2O_3 matrix [7]. The peaks of the catalyst are broader compared to the reagent iron oxide, indicating that the domain size of the α-Fe_2O_3 lattice was small. The catalyst containing Zr and Al showed smaller domain size than the ZrO_2-supporting α-Fe_2O_3 catalyst without Al, and the small domain size positively affected the catalyst durability [7, 8].

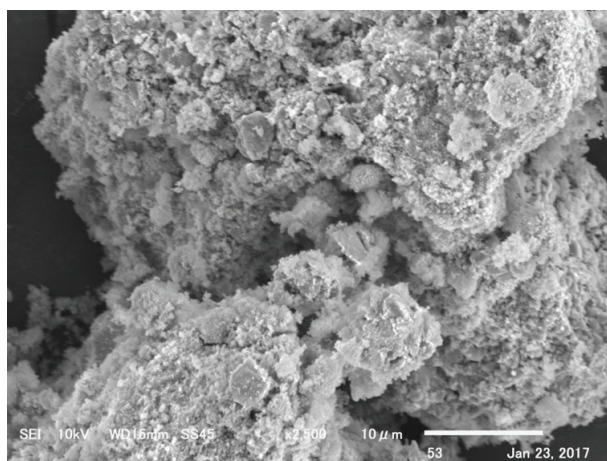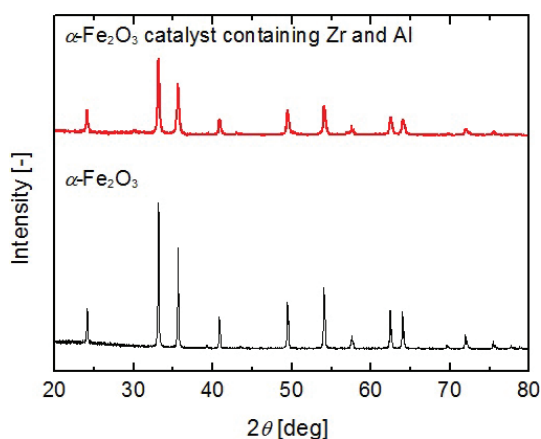**Figure 1.** SEM image of α-Fe_2O_3 catalyst containing Zr and Al.

Figure 2. XRD patterns of α-Fe_2O_3 catalyst containing Zr and Al and regent α-Fe_2O_3 (reproduced from elsewhere [9]).

3. Activity of α-Fe$_2$O$_3$ catalyst containing Zr and Al for decomposition of heavy oil

The α-Fe$_2$O$_3$ catalyst containing Zr and Al was used for catalytic cracking of atmospheric residual oil (AR) derived from Middle East crude [9]. **Table 1** showed the properties of AR [11]. Composition of light oil (boiling point <623 K), vacuum gas oil (VGO, boiling point 623–773 K), and vacuum residue (VR, boiling point >773 K) was determined by the gas chromatographic distillation (HP6890, Agilent Technologies) with a wide-bore capillary column according to ASTM D 2887. AR has high viscosity, low H/C ratio, and high content of high-boiling-point components. This section describes the activity of the catalyst to decompose AR in a steam atmosphere.

3.1. Decomposition of AR

Catalytic cracking of AR was conducted using a downflow-type fixed-bed reactor loaded with 1.5 g of catalyst at 748 K under atmospheric pressure [9, 12]. A 10 wt% solution of AR with toluene was fed to the reactor at flow rate (F) of 1.1 g/h using a syringe pump. AR was diluted with toluene to reduce the viscosity of AR, and the catalyst was confirmed to be

	AR
Composition [wt%]	
Light oil	7
VGO	49
VR	44
Density [g/cm³]	0.944
Elemental analysis [wt%]	
C	85.7
H	11.6
N	0.16
S	2.48
H/C [mol/mol]	1.63
Conradson carbon residue [wt%]	5.8
Metals [ppm]	
V	10
Ni	4
Fe	10

Reproduced from elsewhere [11].

Table 1. Properties of AR.

almost inactive to toluene. Total flow rate of mixture of steam and nitrogen was adjusted to 80 cm³(STP)/min. After 2 h of operation, the pump of AR solution was stopped, and the reactor was cooled. The gas products were separated through an ice trap and analyzed by gas chromatography (GC-12A and GC-14A, Shimadzu Corp.) with thermal conductivity and flame ionization detectors equipped with Porapak-Q and Unibeads 3S columns, respectively. The boiling point distribution was determined by the gas chromatographic distillation. The residue deposited on the catalyst was analyzed by elemental analysis (EA1110, Finningan Mat).

Figure 3 showed the composition of AR and product yield of the AR cracking at flow rate ratio of steam to AR solution (F_S/F) of 0.42 g/g [9]. The high-boiling-point components, such as VGO and VR, decreased, producing light oil, CO_2, organic gas (C_1–C_4), and residue. Generation of CO_2 indicated that the heavy oil fraction was oxidatively cracked.

Figure 4 showed the XRD patterns of the used catalysts after the catalytic cracking of AR with and without steam [9]. The patterns of reagent iron (III) oxide (α-Fe_2O_3) and iron (II, III) oxide (Fe_3O_4, Strem Chemicals, Inc.) were shown for comparison. The patterns of both used catalysts consisted of α-Fe_2O_3 and Fe_3O_4. The peaks of Fe_3O_4 mainly appeared in the patterns of the used catalyst without steam. These results indicated that part of lattice oxygen of α-Fe_2O_3 reacted with heavy oil fractions to produce light hydrocarbons and CO_2 at first [12]. Then, oxygen species generated from steam were incorporated into the iron oxide lattice and reacted with heavy oil fractions. Hence, the α-Fe_2O_3 structure was partially maintained after the reaction with steam. Consequently, the heavy oil fractions were oxidatively cracked using oxygen species derived from steam.

When dodecylbenzene was used as a model compound of heavy oil, a small amount of oxygen containing compounds, such as phenol, acetophenone, undecanone, and hydroxybiphenyl, was produced in the catalytic cracking of dodecylbenzene [9]. Kondoh et al. reported that the catalytic cracking of heavy oil with heavy oxygenated water ($H_2^{18}O$) produced CO_2 containing
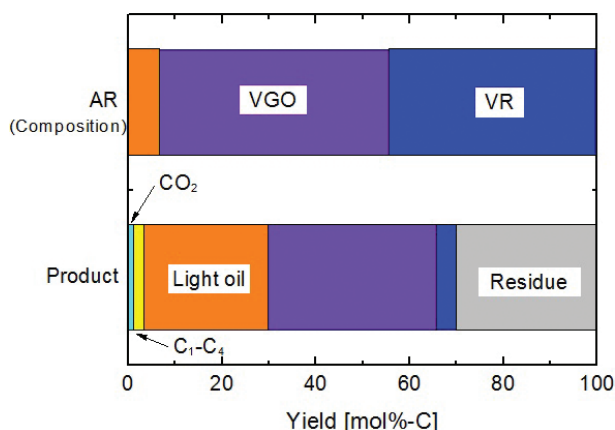

Figure 3. Product yield of catalytic cracking of AR with steam (F_S/F = 0.42) and composition of AR (reproduced from elsewhere [9]).
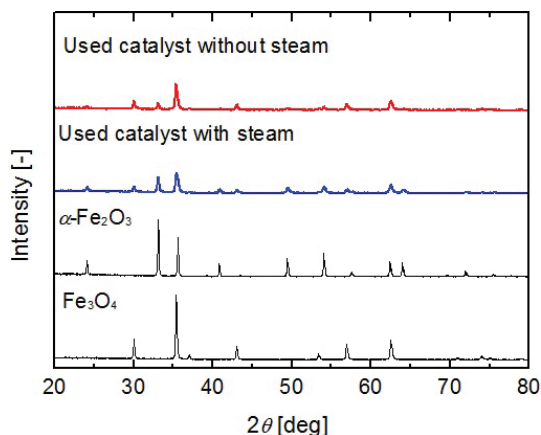
Figure 4. XRD patterns of used catalysts for catalytic cracking of AR with and without steam (F_S/F = 0, 0.42), regent α-Fe$_2$O$_3$, and reagent Fe$_3$O$_4$ (reproduced from elsewhere [9]).

heavy oxygen (CO^{18}O) [13]. Accordingly, most of oxygen species were supplied to form CO$_2$, and a small amount of oxygen species was supplied to oxygen –containing compounds.

The α-Fe$_2$O$_3$ catalyst containing Zr showed the higher activity than the α-Fe$_2$O$_3$ catalyst without Zr because ZrO$_2$ in the catalyst promotes the generation of oxygen species from steam [3]. Addition of Al to the catalyst enhanced the durability of the catalyst. The activity of the ZrO$_2$-supporting α-Fe$_2$O$_3$ catalyst without Al decreased after the sequence of reaction and regeneration because of phase change of iron oxide and subsequent peeling of ZrO$_2$ [7].

3.2. Effect of steam on product of AR cracking

To examine the effect of steam flow rate on product yield of AR cracking, catalytic cracking of AR was conducted at various steam flow rates (F_S/F = 0–3.0), and the product yield was shown in **Figure 5** [9]. The yields of light oil, VGO, VR, and residue little changed, suggesting that steam concentration hardly affected the decomposition of heavy oil. The heavy oil fractions reacted with oxygen species incorporated from steam to the iron oxide lattice after the lattice oxygen of α-Fe$_2$O$_3$ reacted with heavy oil fractions. The CO$_2$ yield increased with increase in the flow rate ratio of steam to AR solution due to increase in oxygen species derived from steam.

When oxygen species were generated from steam and reacted with heavy oil, hydrogen species were simultaneously generated from steam [9]. Consumed amount of steam was calculated from the CO$_2$ yield in the catalytic cracking of AR at flow rate ratio of steam to AR solution (F_S/F) of 3.0 g/g and shown in **Figure 6**. If half of the sulfur compounds in AR were converted to H$_2$S by the reaction of hydrogen species and sulfur compounds, approximately 14% of hydrogen species were supplied to form H$_2$S. Approximately 19% of hydrogen species
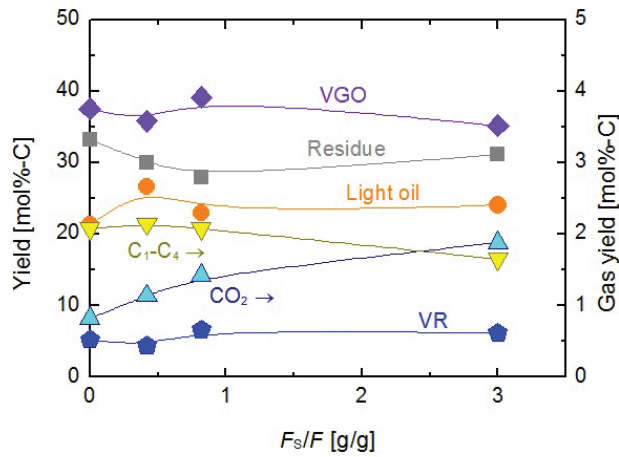
Figure 5. Product yield of catalytic cracking of AR with and without steam ($F_S/F = 0$–3.0) (reproduced from elsewhere [9]).
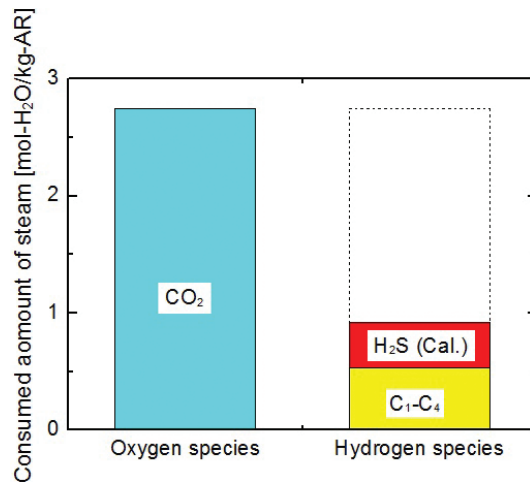

Figure 6. Consumed amount of steam for catalytic cracking of AR with steam ($F_S/F = 3.0$).

were supplied to form C_1–C_4 hydrocarbons if two moles of hydrogen species were supplied to 1 mole of C_1–C_4 hydrocarbons. Hence, the remaining hydrogen species (approximately 67%) might be supplied to liquid hydrocarbons and residue.

Supplies of hydrogen species from steam to liquid hydrocarbons and residue resulted in decrease in alkene generation and increase in H/C of residue [9]. **Figure 7** showed the alkene/alkane ratio of aliphatic hydrocarbons and H/C ratio of residue produced by the catalytic cracking of AR with and without steam. The aliphatic hydrocarbons in the liquid
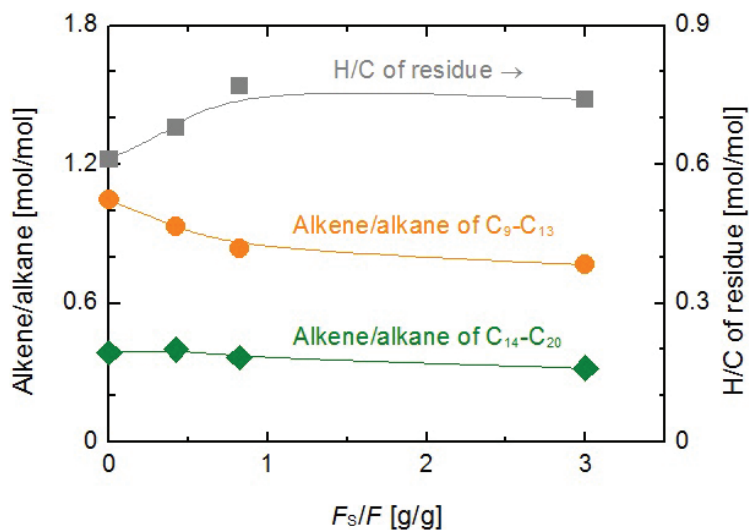
Figure 7. Alkene/alkane ratio of aliphatic hydrocarbons and H/C ratio of residue produced by the catalytic cracking of AR with and without steam (F_s/F = 0–3.0) (reproduced from elsewhere [9]).

product were analyzed by gas chromatography with a flame ionization detector (GC-FID, 6890N, Agilent Technologies) and mass spectrometry (GC-MS, HP6890-HP5973, Agilent Technologies) with capillary columns. The alkene/alkane ratio of light hydrocarbons (C_9–C_{13}) decreased with increase in flow rate ratio of steam to AR solution, suggesting that hydrogen transfer from steam to light hydrocarbons suppressed alkene generation. The H/C ratio of residue produced by the AR cracking with steam was higher than that produced by the AR cracking without steam. Some hydrogen species supplied from steam to the residue and others supplied to light hydrocarbons.

4. Activity of α-Fe$_2$O$_3$ catalyst containing Zr and Al for desulfurization of heavy oil

The petroleum residual oil including AR contains sulfur. Hydrodesulfurization is the useful method to remove sulfur from petroleum, producing high-quality oil. The residual oil contains acyclic sulfur compounds, such as thiols and disulfides, and cyclic compounds including thiophene ring. The decomposition of the cyclic sulfur compounds was harder than acyclic compounds [14].

The catalytic cracking of heavy oil with steam using the α-Fe$_2$O$_3$ catalyst containing Zr and Al produced the hydrogen species during the reaction of heavy oil with the oxygen species derived from steam [9]. Some hydrogen species were supplied to hydrocarbons and residue. The remaining hydrogen species might react with sulfur compounds in AR and be supplied to form H$_2$S [10]. Hence, desulfurization of AR with the catalyst in a steam atmosphere was examined in this section.

4.1. Desulfurization of AR

Catalytic cracking of AR with the α-Fe_2O_3 catalyst containing Zr and Al was conducted in a steam atmosphere ($F_S/F = 2.7$) [10]. The reaction conditions were the same as decomposition of AR at 3.1. Produced amounts of H_2S and SO_2 were measured by gas detecting tube (GASTEC Corp.). Sulfur content in liquid products was determined by oxidative microcoulometry according to JIS K 2541-2. Sulfur contents deposited on the catalyst were measured by elemental analysis (EA1110, Finningan Mat.)

Catalytic cracking of AR produced approximately 61 mol%-C of oil product, 4 mol%-C of gas product, and 35 mol%-C of residue. Sulfur concentration in the product oil decreased to 1.4 wt% compared to the 2.5 wt% of sulfur in AR, and H_2S was generated, indicating that sulfur compounds in AR were decomposed [10]. When desulfurization was conducted using dibenzothiophene as a model compound of a cyclic sulfur compound in AR, dibenzothiophene was decomposed producing CO_2, H_2S, hydrocarbons, and sulfur compounds [10]. Hence, acyclic and cyclic sulfur compounds might be decomposed with the catalyst in a steam atmosphere.

4.2. Effect of steam on desulfurization of AR

To examine the effect of steam on desulfurization of AR, catalytic cracking of AR was conducted at various steam flow rates ($F_S/F = 0$–2.7) [10]. **Figure 8** showed the sulfur yield of catalytic cracking of AR at flow rate ratio of steam to AR solution (F_S/F) of 0–2.7. The carbon yield of oil and residue was almost constant as shown in **Figure 5**. The catalytic cracking of AR without steam produced little H_2S, and the H_2S yield increased with increase in flow rate ratio of steam to AR solution. The CO_2 yield also increases with increase in the flow rate ratio of steam to AR solution. These results indicated that sulfur compounds reacted with some hydrogen species derived from steam to produce H_2S when oxygen species reacted with heavy oil.
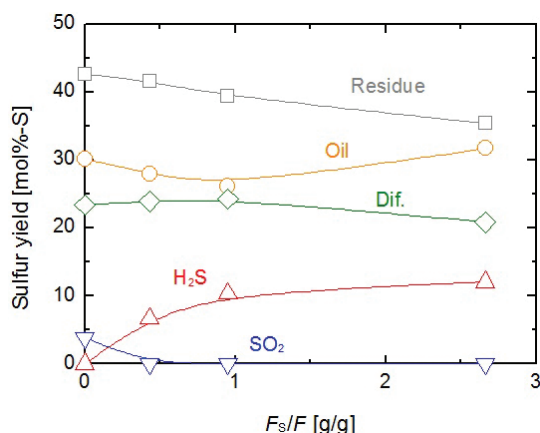

Figure 8. Sulfur yield of catalytic cracking of AR with and without steam ($F_S/F = 0$–2.7) (reproduced from elsewhere [10]).

The SO_2 was detected only in the reaction without steam. The lattice oxygen of iron oxide reacted with sulfur compounds, producing SO_2 in the catalytic cracking of AR without steam. The SO_2 has high solubility in water (1.4 mol/kg at 25°C [15]). Hence, no SO_2 might be detected in the catalytic cracking of AR with steam, even if oxygen species generated from steam reacted with sulfur compounds to form SO_2. Some H_2S produced in the reaction also could be dissolved in water. When nitrogen was injected into the water collected in this reaction, H_2S was detected [10]. The difference was approximately 23 mol%-S because of sulfur content, such as H_2S and SO_2, in water and measurement errors of sulfur concentration.

Sulfur content in residue decreased with increase in flow rate ratio of steam to AR solution. Larger amounts of hydrogen species were generated at higher ratio of steam to AR solution and reacted with heavy sulfur compounds deposited on the catalyst to produce light sulfur compounds and H_2S. Sulfur concentration in the oil decreased because sulfur compounds were decomposed to produce H_2S. Increase in sulfur concentration in the oil at $F_S/F = 2.7$ was resulted from production of light sulfur compounds by the reaction of heavy sulfur compounds with large amounts of oxygen and hydrogen species.

5. Conclusion

Decomposition and desulfurization of AR were examined using α-Fe_2O_3 catalyst containing Zr and Al in a steam atmosphere. The catalyst was prepared by coprecipitation method. Heavy oil fraction of AR was decomposed with the catalyst, producing CO_2, light hydrocarbons, and residue. The lattice oxygen of α-Fe_2O_3 reacted with heavy oil at first. Then, oxygen species generated from steam were supplied to the iron oxide lattice and react with heavy oil fraction, producing light hydrocarbons and CO_2. Hydrogen species generated from steam during the reaction of the oxygen species, and heavy oil fraction supplied to light hydrocarbons, H_2S, and residue. Supplies of the hydrogen species to light hydrocarbons suppressed alkene generation. Some hydrogen species reacted with sulfur compound of AR, producing H_2S. Some SO_2 could be generated by the reaction of sulfur compound and oxygen species derived from steam. Consequently, hydrogen species and oxygen species derived from steam reacted with heavy oil fraction and sulfur compound of AR with the α-Fe_2O_3 catalyst containing Zr and Al in a steam atmosphere to produce light hydrocarbons.

Acknowledgements

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