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Steam has good potential as a hydrogen source for upgrading of heavy oil. Catalytic cracking of petroleum residual oil with steam was examined using iron oxide-based catalysts containing zirconium and aluminum. After the lattice oxygen of iron oxide reacted with the heavy fractions, oxygen species were supplied to the iron oxide lattice from steam and reacted with heavy oil to produce light oil, residue, and carbon dioxide. Hydrogen species were also generated from steam and supplied to form light oil, preventing alkene generation. Sulfur compounds in the residual oil were reacted with the hydrogen species to form hydrogen sulfide. The compositions of iron, zirconium, and aluminum were not homogeneous in the catalyst. No coke was deposited in regions where the main component was iron oxide. Oxidative cracking of heavy fractions effectively occurred around such regions. Iron oxide-based catalyst containing zirconium and aluminum showed durable activity for the cracking of residual oil under a steam atmosphere.

Keywords
Heavy oil, Iron oxide catalyst, Steam catalytic cracking, Oxidative cracking, Hydrogenation

1. Introduction

Heavy oil, such as petroleum residual oil, requires upgrading for use in the production of transportation fuels in the petroleum industry. Heavy oil has low hydrogen to carbon (H/C) ratio and high viscosity, and contains impurities such as sulfur and metals. Various conventional upgrading processes including coking, visbreaking, hydrotreating, hydrocracking, residue fluid catalytic cracking (RFCC), and deasphalting have been developed. Hydrogen addition is useful to convert heavy oil to light fractions with high H/C ratio and low sulfur content, resulting in lower coke yield, but hydrogen is expensive.

Water has good potential as a hydrogen source for the upgrading of heavy oil. Upgrading of heavy oil with water requires the following catalyst properties: high activity to decompose heavy oil, stable activity under severe hydrothermal or steam conditions, and resistance to deposition of coke, sulfur, and metals. Upgrading of heavy oil with water has been reported using various catalysts, such as nickel potassium, cerium oxide, titania–zirconia, and iron oxide. Iron oxide is inexpensive and is a candidate catalyst for industrial upgrading of heavy oil with water.

We previously developed a zirconia-supporting iron oxide catalyst to decompose petroleum residual oil under a steam atmosphere. The physical durability of the catalyst was enhanced by addition of aluminum to iron oxide. Upgrading of oil sand bitumen was investigated with iron oxide-based catalysts using sub-and super-critical water. Catalytic cracking of petroleum residual oil can be achieved with silica-supported iron oxide catalysts in supercritical water. Steam catalytic cracking of petroleum residual oil is possible using zirconia-impregnated macro-mesoporous red mud, which contains iron oxide and alumina. This review examines catalytic cracking of heavy oil using iron oxide-based catalysts containing zirconium and aluminum under a steam atmosphere.

2. Catalytic Cracking of Heavy Oil with Steam

2.1. Oxidative Cracking of Heavy Oil

Catalytic cracking of atmospheric residual oil (AR) with steam was conducted at 748 K under atmospheric pressure using a fixed-bed reactor. Figure 1 shows the schematic experimental apparatus. A complex metal oxide catalyst was prepared by a coprecipitation method using a water solution of iron chloride, aluminum chloride, and zirconium oxychloride. The catalyst was treated at 873 K for 1 h under a steam atmosphere and sieved to obtain particles of 300-850 μm. The molar composition of the catalyst was Zr/Fe = 0.063, Al/Fe = 0.13, abbreviated as Zr-Al-FeOx. The obtained cata-
lyst was loaded ($W = 1.5 \times 10^{-3}$ kg) into the fixed-bed reactor. The feedstock was AR derived from Middle East crude and its properties are shown in Table 1. To reduce its viscosity, AR was diluted with toluene and a 10 wt% solution of AR ($F = 1.1 \times 10^{-3}$ kg/h) was fed to the reactor using a syringe pump. A preliminary experiment confirmed toluene was inert in this catalyst reaction. A mixture of steam ($F_s = 0.33 \times 10^{-3}$ kg/h) and nitrogen was passed through the reactor with a total flow rate adjusted to 80 cm$^3$(STP)/min. Liquid and gas products were separated with an ice trap and analyzed by gas chromatography (HP6890 and HP6890N, Agilent Technologies; GC-12A and GC-14A, Shimadzu Corp.). After 2 h of operation, the feedstock pump was stopped and the reactor was cooled to room temperature.

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**Table 1** Properties of AR Derived from Middle East Crude

| AR                  | wt%     | [mol/mol] | wt%     | ppm   |
|---------------------|---------|-----------|---------|-------|
| Elemental analysis  |         |           |         |       |
| C                   | 85.7    |           |         |       |
| H                   | 11.6    | 1.62      | 0.011   |       |
| N                   | 0.16    |           |         |       |
| S                   | 2.48    |           |         |       |
| H/C                 |         | 5.8       |         |       |
| S/C                 |         |           |         |       |
| Conradson carbon residue | 5.8 |           |         |       |
| Metals              |         |           |         |       |
| V                   | 10      |           |         |       |
| Ni                  | 4       |           |         |       |
| Fe                  | 10      |           |         |       |

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**Figure 2** shows the product yield for the catalytic cracking of AR with and without steam using Zr-Al-FeO$_x$ catalyst for 2 h. The composition of AR is also shown for comparison. Liquid products were analyzed by gas chromatographic distillation according to ASTM D2887 and the liquid products were defined as light oil (boiling point < 623 K), vacuum gas oil (VGO, 623-773 K), and vacuum residue (VR, > 773 K). The carbon residue on the catalysts was measured by elemental analysis (EA1110, Finningan Mat). Heavy fractions, such as VR and VGO, were decomposed with the catalyst producing light oil, organic gas (C1-C4), carbon dioxide, and residue. To examine the reaction mechanism, fresh and used Zr-Al-FeO$_x$ catalysts were analyzed by X-ray diffraction (XRD, M03XHF22, Mac Science Co., Ltd., Japan) as shown in Fig. 3. The fresh catalyst showed the hematite ($\alpha$-Fe$_2$O$_3$) structure whereas the used catalysts consisted of hematite and magnetite (Fe$_3$O$_4$). Peaks at 33° and 35° were high in the pattern of the catalyst used with steam, whereas the highest peak of catalyst used without steam was at 35°. Therefore, the magnetite/hematite ratio of the catalysts used with steam was lower than in the catalyst without steam. The proposed reaction mechanism is shown in Fig. 4 as follows. First, lattice oxygen of iron oxide reacted with heavy fractions, producing light fractions and carbon dioxide. Next, oxygen species were generated from steam and supplied to the iron oxide lattice. Zirconia on the catalyst promoted the generation of oxygen species from steam. Addition of aluminum prevented phase change of the iron oxide lattice. Therefore, the hematite structure was partially maintained during the reaction with steam and the heavy fractions were oxidatively cracked producing light fractions and carbon dioxide. In the catalytic cracking of AR without steam, lattice
Oxygen of the iron oxide was supplied to form carbon dioxide, so the lattice oxygen was consumed during the reaction, resulting in the phase change from hematite to magnetite.

Oxygen species derived from steam were supplied to form carbon dioxide and oxygen-containing compounds. The oxygen content of the liquid product generated by the catalytic cracking of AR with steam was approximately 0.7 wt%\textsuperscript{13),} although the feedstock did not contain oxygen. Approximately 10 % of the oxygen species were incorporated into the product oil, and the remaining 90% were converted to carbon dioxide\textsuperscript{13).} Part of the carbon dioxide was derived from steam in the cracking of heavy oil with iron oxide-based catalyst as demonstrated using heavy oxygenated water\textsuperscript{20).} Generation of oxygen-containing compounds was confirmed by the catalytic cracking of a model compound\textsuperscript{14).} Small amounts of oxygen-containing compounds, such as phenol, acetophenone, undeca-none, and hydroxybiphenyl, were generated through the catalytic cracking of dodecylbenzene with steam using Zr-Al-FeO\textsubscript{x} catalyst. These results demonstrate the oxidative cracking of heavy fractions.

2.2. Hydrogenation Using Hydrogen Species Derived from Steam

Hydrogen species were also generated from steam when the corresponding oxygen species were reacted with heavy fractions of AR on the Zr-Al-FeO\textsubscript{x} catalyst. Figure 5 shows the consumed amount of steam calculated from the yield of carbon dioxide. The yield of carbon dioxide increased with higher flow rate ratio of steam to feedstock because large amounts of oxygen species were generated at high steam flow rates, but the product distribution was almost the same at different steam flow rates (Fig. 2). The hydrogen species derived from steam might be consumed to form liquid hydrocarbons, organic gas, hydrogen sulfide, and residue. The amount of steam supplied to organic gas and hydrogen sulfide was calculated on the assumption that 2 moles of hydrogen species are supplied per 1 mole of organic gas and half of the sulfur compounds in AR react with hydrogen species to form hydrogen sulfide (Fig. 5). The remaining 40-67 % of hydrogen species are supplied to form liquid hydrocarbons and residue.

To examine the supplies of hydrogen species from steam to liquid hydrocarbons, the alkene/alkane ratio of C9-C20 aliphatic hydrocarbons was determined from the liquid products analyzed by gas chromatography as shown in Fig. 6\textsuperscript{14).} The alkene/alkane ratio of C9-C15 hydrocarbons decreased with higher flow rate ratio of steam to feedstock, indicating the transfer of hydrogen species from steam to liquid hydrocarbons. Generally,
alkene/alkane ratio increases as decomposition is promoted. Supercritical water conditions promote polyethylene pyrolysis, resulting in decrease in molecular weight and increase in 1-alkene/n-alkane ratio of light products with higher water density. The present study found the opposite trend that steam did not promote cracking of heavy fractions but rather hydrogenation of product oil. The steam flow rates did not affect the alkene/alkane ratio of C16 aliphatic hydrocarbons because of the lower amount of C16 alkene.

The hydrogen species derived from steam might also be supplied to form residue. Table 2 shows the H/C atomic ratios of residue determined by elemental analysis of used catalysts. The H/C ratios of residue generated in the reaction with steam were higher than that in the reaction without steam, suggesting that the hydrogen species were transferred to residue.

In the catalytic cracking of AR with Zr-Al-FeO x catalyst, the product distribution was almost same at various steam flow rates, although the alkene/alkane ratio of C9-C15 hydrocarbons was low at higher steam flow rate and H/C ratios of residue were high with steam catalytic cracking. Therefore, hydrogen transfer from steam rather than hydrogen generated by dehydrogenation of hydrocarbons to form hydrocarbons suppressed alkene generation.

3. Desulfurization of Heavy Oil with Steam

3.1. Effect of Steam on Desulfurization of Heavy Oil

The hydrogen and oxygen species derived from steam might also react with the sulfur compounds contained in heavy oil. Desulfurization of AR with the Zr-Al-FeO x catalyst with and without steam was examined at 748 K. Figure 7 shows the sulfur contents after AR cracking using the Zr-Al-FeO x catalyst. Concentrations of sulfur in liquid products, hydrogen sulfide and sulfur dioxide in gas products, and sulfur in residue were analyzed by oxidative microcoulometry according to JIS K 2541-2, gas detecting tubes (GASTEC Corp.), and elemental analysis (EA1110, Finningan Mat.), respectively. The sulfur concentrations in the product oil were 1.2-1.4 wt%, which is approximately half of that in the feedstock AR (2.48 wt%), and hydrogen sulfide was generated in the reaction with steam.

The yield of hydrogen sulfide increased with higher flow rate ratio of steam to feedstock, whereas little hydrogen sulfide was generated in the reaction without steam (Fig. 7). Figure 8 shows the relationship between the yields of hydrogen sulfide and carbon dioxide for the catalytic cracking of AR. The yield of hydrogen sulfide increased in proportion to that of carbon dioxide except in the reaction without steam. The results indicated that the hydrogen species derived from steam reacted with sulfur compounds in AR. The hydrogen species were supplied to form hydrogen sulfide and the oxygen species were supplied to form carbon dioxide in the oxidative cracking of the heavy fractions.

Table 2 Hydrogen to Carbon Atomic Ratio of Residue Produced by AR Cracking with and without Steam Using Zr-Al-FeO x Catalyst for 2 h

| Fg/F [g/g] | H/C of residue [mol/mol] |
|-----------|-------------------------|
| 0         | 0.61                    |
| 0.42      | 0.68                    |
| 0.82      | 0.77                    |
| 3.0       | 0.74                    |

Adapted from ref. 14.)
Some lattice oxygen of iron oxide reacted with sulfur compounds and was supplied to form a small amount of sulfur dioxide in the catalytic cracking of AR without steam (Fig. 7). Such sulfur dioxide might also be generated by the reaction of the oxygen species derived from steam and sulfur compounds in the steam catalytic cracking of AR, but sulfur dioxide was not detected in the product gas because of the high solubility of sulfur dioxide in water.

The high solubility of sulfur dioxide and hydrogen sulfide in water and measurement error are the likely causes of the total sulfur yield of 76-79%. Some hydrogen sulfide was detected as nitrogen was injected into the water collected in the catalytic cracking of AR with steam. Therefore, much more of the oxygen and hydrogen species reacted with sulfur compounds and greater amounts of hydrogen sulfide and sulfur dioxide can be generated in the catalytic cracking of AR.

The sulfur to carbon (S/C) atomic ratios of the residue were 0.010-0.011, which were almost the same as that of AR (S/C = 0.011). The sulfur content in the residue and oil gradually decreased as the ratio of steam to feedstock increased from 0 to 1.0 g/g (Fig. 7). Sulfur compounds in AR were deposited on the catalyst and reacted with the larger amounts of the oxygen and hydrogen species under higher flow rate ratio of steam to feedstock, resulting in the formation of light sulfur compounds and hydrogen sulfide. The sulfur content in the oil increased as the ratio of steam to feedstock increased from 1.0 to 2.7 g/g because larger amounts of oxygen and hydrogen species promoted decomposition of the heavy sulfur compounds, resulting in higher content of light sulfur compounds in the oil.

3.2. Desulfurization of Thiophene Compounds

Various types of sulfur compounds including acyclic and cyclic compounds are contained in AR. Acyclic sulfur compounds, such as thiols and disulfides, and saturated cyclic sulfur compounds and aromatic compounds containing sulfur in six-membered rings are highly reactive and can be easily removed (23). On the other hand, cyclic sulfur compounds containing sulfur in five-membered aromatic rings, such as thiophene, are much less reactive and the ease of sulfur removal decreases with higher number of rings.

To examine the desulfurization of thiophene compounds, catalytic cracking of dibenzothiophene (DBT) with the Zr-Al-FeO$_x$ catalyst ($W_0$-3.0 × 10$^{-3}$ kg) was conducted at 748 K with steam ($F_S$ = 2.9 × 10$^{-3}$ kg/h) (15). Approximately 1 wt% solution of DBT dissolved in benzene was fed into the fixed-bed reactor ($F = 1.1$ × 10$^{-3}$ kg/h). Figure 9 shows the conversion of DBT calculated from the amount of unreacted DBT (15). DBT conversion increased with higher time factor, $W/F$, which is the ratio of catalyst weight to flow rate of feedstock. DBT cracking formed carbon dioxide, hydrogen sulfide, and small amounts of C1-C4 hydrocarbons (1.3-2.4 × 10$^{-5}$ mol/mol-DBT). The results suggested that the Zr-Al-FeO$_x$ catalyst was active to decompose not only acyclic compounds but also thiophene compounds with the oxygen and hydrogen species derived from steam.

4. Durability of Catalysts

4.1. Change in Catalytic Activity During Heavy Oil Cracking

The Zr-Al-FeO$_x$ catalyst is useful for upgrading of AR with steam. The hematite structure of iron oxide was partially reduced to magnetite and some residue was deposited on the catalyst. This phase change and residue deposition are key factors affecting the catalyst durability in the upgrading process. The catalyst durability was investigated using various iron oxide-based catalysts (9,10). Catalytic cracking of 10 wt% AR solu-
tion diluted with benzene was conducted using a fixed-bed reactor loaded with \( W = 1.0 \times 10^{-3} \) kg of the catalyst at 773 K for 2 h under a steam atmosphere. The time factor, \( W/F_R \), was 12-15 h, where \( F_R \) is the flow rate of AR without benzene. The catalysts were FeOx, Zr/FeOx, and Zr-Al-FeOx. FeOx was obtained from iron(III) hydroxide. Zirconia was supported on the FeOx by a conventional impregnation method, to obtain Zr/FeOx. Zr-Al-FeOx was prepared by the coprecipitation method. These catalysts were crushed, sieved, and treated with steam at 873 K for 1 h. The spent catalysts were regenerated by air calcination and used for AR cracking again.

**Figure 10** shows the reaction rate constant during the repeated sequence of catalytic cracking of AR and regeneration of the catalyst\(^{9,10}\). Heavy oil cracking followed second-order kinetics\(^{24}\) and the reaction rate constant, \( k_{C_{30}^+} \), was calculated by Eq. (1) using the weight fraction of carbon number above 30, \( f_{C_{30}^+} \). The weight fraction of AR and product oil were measured by gel permeation chromatography using a liquid chromatograph (CTO-10A, Shimadzu Corp.).

\[
\frac{df_{C_{30}^+}}{d(W/F_R)} = -k_{C_{30}^+}f_{C_{30}^+}^2
\]  

The activity of the zirconia-supporting catalysts (Zr/FeOx, Zr-Al-FeOx) for cracking of the heavy fraction was higher than that of FeOx, because zirconia promoted the generation of oxygen and hydrogen species from steam\(^{8}\). The hematite structures of FeOx and Zr/FeOx catalysts were transformed to magnetite during the reaction due to consumption of the lattice oxygen of iron oxide. Therefore, these catalysts were regenerated by air calcination to oxidize magnetite to hematite and the sequence of reaction and regeneration was repeated. The reaction rate constant of Zr/FeOx decreased to that of FeOx, whereas FeOx showed almost no change. Deactivation of the Zr/FeOx catalyst was due to the phase change in the hematite and magnetite and subsequent peeling of zirconia\(^{9}\). To enhance the durability of the catalyst by preventing such phase change, aluminum was added to iron oxide. The hematite structure of Zr-Al-FeOx was partially maintained (Fig. 3) and so catalytic activity was maintained after AR cracking was repeated twice without regeneration of the catalyst (Fig. 10).

Catalytic cracking of AR with Zr-Al-FeOx catalyst was conducted for 2-6 h\(^{21}\). A 50 % solution of AR with toluene was used and the liquid was analyzed by gas chromatographic distillation (7890B GC, Agilent Technologies) according to ASTM D2887. The VR conversion, \( X_{VR} \), was calculated by Eq. (2) using the VR yield, \( f_{VR} \), residue yield, \( f_{residue} \), and composition of VR in AR, \( f_{VR,0} \).

\[
X_{VR} = \left(1 - \frac{f_{VR} + f_{residue}}{f_{VR,0}}\right) \times 100
\]  

**Table 3** shows VR conversion, residue yield, and H/C atomic ratio of residue after AR cracking for 2-6 h\(^{21}\). The VR conversion showed negligible change and carbon dioxide (0.34-0.57 mol\%-C) was generated after 2-6 h of AR cracking. The results indicated durable catalytic activity for oxidative cracking of heavy fractions with the Zr-Al-FeOx catalyst. The residue yield decreased with longer reaction time and the highest H/C atomic ratio of residue was observed after 2 h. The residue consisted of both coke and heavy hydrocarbons, and the residue obtained after 2 h included relatively large amounts of heavy hydrocarbons. The heavy

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**Table 3** Vacuum Residue Conversion, Residue Yield, and H/C Atomic Ratio of Residue Produced by Catalytic Cracking of AR for 2-6 h\(^{21}\).

| Reaction time [h] | \( X_{VR} \) [mol\%-C] | Residue yield [mol\%-C] | H/C of residue [mol/mol] |
|------------------|------------------------|------------------------|------------------------|
| 2                | 45.9                   | 14.1                   | 0.52                   |
| 4                | 52.5                   | 9.7                    | 0.43                   |
| 6                | 49.4                   | 7.3                    | 0.43                   |

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hydrocarbons deposited on the catalyst were decomposed slowly to light fractions. Consequently, residue yield and H/C ratio decreased after 4 h. Heavy hydrocarbons were deposited on the catalyst in the initial reaction stage but a complex metal oxide catalyst of iron, cerium, zirconium, and aluminum was durable after 6 h in supercritical water with less than 10% coke\(^{17}\). In the present study, less than 10% coke may be achieved and so the catalyst was durable for AR cracking under a steam atmosphere.

### 4.2. Characterization of Catalysts

To investigate the factors affecting on catalyst durability, such as consumption of lattice oxygen of iron oxide and coke deposition, the used catalyst was characterized using XRD (D2 PHASER, Bruker AXS) and transmission electron microscopy (TEM, EM-002B, TOPCON) equipped with energy-dispersive spectroscopy (EDS, Thermo Fisher Scientific).

Figure 11 shows the XRD patterns of the used catalysts after 2-6 h of AR cracking\(^ {21}\). The lattice oxygen of hematite was partially consumed and the used catalyst contained a mixture of hematite and magnetite. The structure did not change from 2 to 6 h because the oxygen species derived from steam were supplied to the iron oxide. The domain size of hematite showed negligible change after 6 h of AR cracking with steam using a catalyst with an adequate composition of iron, zirconium, and aluminum\(^ {12}\). In the present study, the structure of the Zr-Al-FeO\(_x\) catalyst was durable with a composition of Zr/Fe = 0.063 and Al/Fe = 0.13.

To examine the coke deposited on the catalyst, TEM/EDS analysis were conducted. Figure 12 shows the TEM images of used catalysts after 6 h\(^ {21}\). Coke deposition was observed around regions II and III, whereas almost no coke was deposited around region I. The EDS analysis around regions I, II, and III determined Zr/Fe, Al/Fe, and C/(Fe + Al + Zr) as shown in Fig. 13\(^ {21}\). The average atomic composition of the catalyst was Zr/Fe = 0.063 and Al/Fe = 0.13 calculated from the amounts of chemicals used for the catalyst preparation. The distribution of iron, aluminum, and zirconium in the catalyst was not homogeneous. Almost no coke was deposited around region I, where Zr/Fe and Al/Fe were lower than the average composition and the main component was iron oxide. The ratios of C/(Fe + Al +

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*Fig. 11 X-ray Diffraction Patterns of Fresh and Used Zr-Al-FeO\(_x\) Catalyst after 2-6 h of AR Cracking with Steam\(^ {21}\).* Reprinted with permission from ref. 21). Copyright (2018) American Chemical Society.

*Fig. 12 Transmission Electron Microscopy Images of Used Zr-Al-FeO\(_x\) Catalyst after 6 h of AR Cracking with Steam\(^ {21}\).* Reprinted with permission from ref. 21). Copyright (2018) American Chemical Society.
and hydrogen species and the hydrogen species were supplied to form hydrogen sulfide. Both acyclic sulfur compounds and thiophene compounds were decomposed with the Zr–Al–FeO catalyst. The catalyst was durable for 2-6 h of AR cracking. Addition of aluminum to iron oxide enhanced the catalyst durability and the structures of hematite and magnetite were maintained between 2-6 h of AR cracking because the oxygen species were effectively supplied to the iron oxide lattice. The composition of the catalyst was not homogeneous. Almost no coke was deposited on regions where iron oxide was the main component, whereas coke deposition increased in regions with higher Zr/Fe and Al/Fe. The oxidative decomposition of heavy oil effectively occurred around the regions with less zirconium and aluminum. Consequently, VR conversion was maintained after 6 h of AR cracking.

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要 旨
水蒸気を利用した酸化鉄系触媒による重質油のアップグレーディング

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水素源として水蒸気を用い、石油系残油の接觸分解を実施した。触媒はジルコニウムとアルミニウムを含む酸化鉄を用いた。まず、酸化鉄の格子酸素と重質成分が反応した後、水蒸気から生成した酸素種が酸化鉄格子へ組み込まれる。この酸素種が重質成分と反応し、軽質油や残査と二酸化炭素が生成する。水蒸気からは同時に水素種が生成し、軽質油に添加されてアルケンの生成が抑制される。残油中の硫黄化合物はこの水素種と反応し、硫化水素が生成した。触媒中の鉄、ジルコニウム、アルミニウムの組成は不均一であり、触媒中の酸化鉄が主成分である領域においてほとんどコーク付着が見られなかった。この領域では、重質成分の酸化分解が有効に起こったと考えられ、水蒸気雰囲気下での残油分解において、本触媒は安定な活性を示した。