**[Regular Paper]**

# Catalytic Cracking of Heavy Oil with Iron Oxide-based Catalysts Using Hydrogen and Oxygen Species from Steam

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This study investigated the transfer of oxygen and hydrogen species from steam to product during the catalytic cracking of heavy oil with iron oxide catalysts containing zirconia and alumina. Light oil and carbon dioxide were produced in the catalytic oxidative cracking of petroleum residual oil in the presence of steam. The alkene/alkane ratio of light aliphatic hydrocarbons decreased and carbon dioxide yield increased with higher flow rate ratio of steam to feedstock. The steam catalytic cracking of dodecylbenzene as a model compound of heavy oil showed lower alkene/alkane ratio and generation of a small amount of oxygen-containing compounds. The oxygen species derived from steam reacted with heavy oil and were transferred to carbon dioxide and a small amount of oxygen-containing compounds, producing hydrogen species from the steam. The hydrogen species were transferred to light hydrocarbons, thus suppressing alkene generation. The alkene/alkane ratio decreased with higher supporting zirconia content in the catalyst because zirconia promotes hydrogen generation from steam.

## 1. Introduction

Upgrading of heavy oil is an important process in the petroleum industry to produce light oil for transportation fuels. The conventional processes of treating heavy oil, such as petroleum residual oil, include thermal cracking, residue fluidized catalytic cracking (RFCC), and hydrocracking[1]. Gas, liquid, and coke are produced by the thermal cracking of heavy oil in a coking process. Large amounts of light oil are generated at high temperature with long residence time, but the coke yield increases. The process requires hydrogenation of light oil to stabilize the product through the addition of hydrogen to the double bonds of the components. Hydrocracking is useful for producing stabilized light oil with low coke yield, but the use of hydrogen gas is expensive.

The use of water as a hydrogen source has good potential for upgrading heavy oil. Several studies have reported the use of steam and supercritical water[2]~[7]. Supercritical water can dilute the heavy oil, although the process requires high pressure and high tempera-ture[2],[3]. Aquaconversion is a catalytic steam conversion process to upgrade heavy oil into transportable oil, in which hydrogen is transferred from steam to hydrocarbons[4]. Catalytic cracking of heavy oil was achieved with iron oxide-based catalyst using steam[5]~[7]. Oxidative decomposition of heavy oil occurred over the iron oxide-based catalysts containing zirconia and alumina to produce light oil. After the lattice oxygen of iron oxide reacted with the heavy oil, the oxygen species derived from steam were incorporated into the iron oxide lattice and reacted with the heavy oil. Zirconia promoted the generation of oxygen species from steam, and alumina suppressed the phase change of iron oxide. Generation of oxygen species from steam occurs simultaneously with generation of hydrogen species. One previous study briefly reported that hydrogen species could be incorporated into light oil[7].

The present study further investigated the transfer of hydrogen species from steam to product using a model compound and petroleum residual oil, and examined the effect of the flow rate ratio of steam to feedstock, as well as the effect of the zirconia content of the catalyst on hydrogen transfer.

## 2. Experimental

### 2. 1. Catalyst

Iron oxide-based catalysts containing zirconia and alumina were prepared by a coprecipitation method using aqueous solution of $FeCl_3 \cdot 6H_2O$ (130-160 mol/$m^3$), $AlCl_3 \cdot 6H_2O$ (17-21 mol/$m^3$), and $ZrOCl_2 \cdot 8H_2O$ (0-17 mol/$m^3$). The catalysts were treated at 873 K for 1 h in a steam atmosphere, pelletized without binder, crushed, and sieved to obtain particles of 300-850 μm. The contents of Fe, Zr, and Al were analyzed using inductively coupled plasma (ICP). The $ZrO_2$ content of the catalysts was 0, 4.7, 8.6, and 18 wt%, and the Al/Fe molar ratio was 0.14. The structure of the catalysts was analyzed by X-ray diffraction (XRD, M03XHF22, Mac Science Co., Ltd., Japan).

### 2. 2. Feedstock

We used atmospheric residual oil (AR) derived from Middle-East crude. Dodecylbenzene was used as the model compound of heavy oil. The C, H, N, and S contents in AR were 85.7, 11.6, 0.16, and 2.48 wt%, respectively. AR was diluted with toluene to reduce its viscosity and dodecylbenzene was dissolved in benzene. Benzene and toluene were confirmed to be little decomposed by the catalysts below 773 K in a steam atmosphere. A 10 wt% solution of AR and 9.8 wt% solution of dodecylbenzene were used as feedstocks in the following experiment.

### 2. 3. Catalytic Cracking

Catalytic cracking of dodecylbenzene and AR was performed using a down-flow type fixed-bed reactor at 748 K under atmospheric pressure. The iron oxide-based catalysts ($W = 1.5 \times 10^{-3}$ kg) were loaded into the reactor. The feedstock ($F = 1.1 \times 10^{-3}$ kg/h) and steam ($F_S = 0\text{-}3.3 \times 10^{-3}$ kg/h) were fed to the reactor by syringe pumps. Nitrogen was added to adjust the total flow rate of steam and nitrogen to 80 $cm^3$(STP)/min. Liquid and gas products were collected in an ice trap and a sampling bag, respectively. After 2 h of operation, the feedstock pump was stopped and the reactor was cooled to room temperature. The experimental apparatus was described previously[6].

Gas products were quantitatively 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 hydrocarbons deposited on the catalysts were measured by elemental analysis (EA1110, Finningan Mat) to determine the amount of residue on the catalyst. The liquid samples produced from AR cracking containing toluene solvent were analyzed by gas chromatographic distillation (HP6890, Agilent Technologies) with a wide-bore capillary column. The boiling range distribution was calculated after omitting the peak of toluene. The liquid products were defined as gasoline + kerosene (boiling point
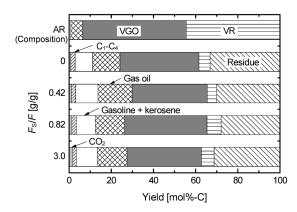


Fig. 1 Product Yield from the Reaction of AR with a Catalyst Containing 8.6 wt% $ZrO_2$

< 523 K), gas oil (523-623 K), vacuum gas oil (VGO, 623-773 K), and vacuum residue (VR, > 773 K). The liquid samples produced from the reaction of dodecylbenzene and AR 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.

## 3. Results and Discussion

### 3. 1. Effect of Flow Rate Ratio of Steam to Feedstock on Product Distributions of AR Cracking

**Figure 1** illustrates the product yield for the catalytic cracking of AR at flow rate ratios of steam to feedstock from 0 to 3.0 g/g. The composition of AR is shown for comparison. The product yields of VGO and VR decreased, and gas, gasoline, kerosene, gas oil, and residue were generated. The amount of light oil, such as gasoline, kerosene, and gas oil, was almost the same at different steam flow rates. Similar findings were observed in a previous study[6]. Heavy oil was decomposed on the catalyst and steam concentration hardly affected the decomposition of heavy oil.

The gas product contained carbon dioxide, methane, ethane, ethene, propane, propene, butane, and butene (**Fig. 2**). The amount of carbon dioxide increased with the flow rate ratio of steam to feedstock. The previous study reported that oxygen species derived from steam were supplied to iron oxide lattice after the lattice oxygen of iron oxide reacted with heavy oil, and the oxygen species reacted with heavy oil to form carbon dioxide[6,7]. The XRD patterns illustrates that both used catalysts consisted of hematite and magnetite, whereas the fresh catalyst was hematite (**Fig. 3**). However, the XRD patterns of the two used catalysts were different. The highest peak of catalyst used without steam was at 35°. On the other hand, peaks at 33° and 35° were high in the pattern of the catalyst used
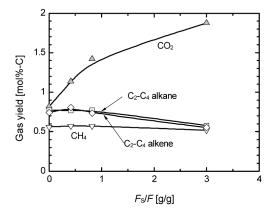
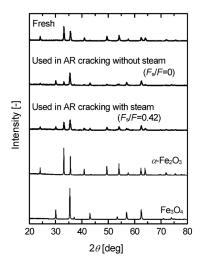Fig. 2 Gas Yield from the Reaction of AR with a Catalyst Containing 8.6 wt% $ZrO_2$



Fig. 4 Alkene/alkane Ratio of Light Hydrocarbons Produced by the Reaction of AR with a Catalyst Containing 8.6 wt% $ZrO_2$



Fig. 3 X-ray Diffraction Patterns of Fresh and Used Catalysts Containing 8.6 wt% $ZrO_2$

with steam. Accordingly, the magnetite/hematite ratio of the catalysts used with steam was lower than that without steam. These results indicate that oxygen species derived from steam and part of the lattice oxygen of iron oxide were supplied to form carbon dioxide. The carbon dioxide yield increased because the amount of oxygen species increased with the flow rate ratio of steam to feedstock.

The reaction of heavy oil with oxygen species derived from steam produces hydrogen species from steam[7]. The hydrogen species might be supplied to form liquid hydrocarbons, gas hydrocarbons, hydrogen sulfide, and residue. Hydrogen sulfide was detected in the reaction with steam, but was hardly generated in the reaction without steam. If half of the sulfur compounds in AR reacted with the hydrogen species derived from steam to produce hydrogen sulfide, then the consumed hydrogen would be approximately 0.8 mol-H/kg-AR. The supply of hydrogen species from steam to gas hydrocarbons was estimated to be approximately
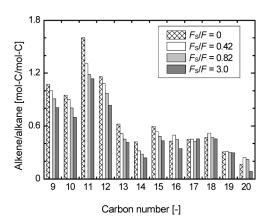
1.2 mol-H/kg-AR, assuming that 2 moles of hydrogen species were supplied per 1 mole of gas hydrocarbon. The total amount of hydrogen species generated from steam was estimated to be 3.3-5.5 mol-H/kg-AR based on the yield of carbon dioxide. Accordingly, 33-60 % of the hydrogen species were included in the gas product, and the remaining hydrogen species were added to liquid hydrocarbons and residue.

To investigate the addition of hydrogen species to liquid hydrocarbons, the alkene/alkane ratios of $C_9$-$C_{20}$ aliphatic hydrocarbons were calculated from the data of the GC-FID analysis (**Fig. 4**). The flow rate ratio of steam to feedstock was not correlated with the alkene/alkane ratio of $C_{16}+$ aliphatic hydrocarbons because the amount of $C_{16}+$ alkene was less. The alkene/alkane ratio of $C_9$-$C_{15}$ aliphatic hydrocarbons decreased with higher flow rate ratio of steam to feedstock. This trend is consistent with our previous findings[7]. However, the opposite trend was found in polyethylene pyrolysis under supercritical water conditions[8]. Molecular weight decreased and 1-alkene/$n$-alkane ratio of light products increased with higher water density because the supercritical water conditions promoted polyethylene pyrolysis due to dissolution of some hydrocarbons in supercritical water[8]. In contrast, the present study found that steam did not promote heavy oil cracking but rather hydrogenation of product oil.

Some residue was formed on the catalysts in the reaction of AR with and without steam (**Fig. 1**). The hydrogen to carbon (H/C) mole ratios of the residue determined by elemental analysis are listed in **Table 1**. The H/C ratio of residue generated in the reaction with steam was higher than that in the reaction without steam. The results of the decreased alkene/alkane ratio (**Fig. 4**) and the higher H/C ratio of residue generated with steam (**Table 1**) suggest that hydrogen species derived from steam were added to hydrocarbons rather than hydrogen generated by dehydrogenation of hydrocarbons. Accordingly, hydrogen transfer from steam

to product hydrocarbons suppressed alkene generation.

## 3. 2. Product Distributions of Model Compound Cracking

AR cracking produced aliphatic and aromatic hydrocarbons. To investigate the addition of hydrogen from steam to aromatic hydrocarbons, catalytic cracking of dodecylbenzene with or without steam was examined as a model compound of heavy oil. **Figures 5** and **6** show the product yield and total ion chromatogram of GC-MS analysis of products detected before dodecylbenzene. The side chain of dodecylbenzene was cleaved, producing $C_1$-$C_{11}$ aliphatics (alkane and alkene) and light aromatics (alkylbenzene, alkenylbenzene, and other aromatics, such as acenaphthene). Some carbon dioxide, oxygen-containing compounds, heavy aromatics (detected after dodecylbenzene), and residue were also produced. **Table 2** shows the conversion of dodecylbenzene calculated as (1 – (moles of unreacted dodecylbenzene)/(moles of dodecylbenzene in feedstock)). The conversion was almost same under both conditions.

The peak of ethylbenzene (10.0 min in **Fig. 6**) was larger in the reaction with steam than without steam. To investigate the addition of hydrogen species to aromatic and aliphatic hydrocarbons, the area ratio of alkene-containing compounds to alkane-containing compounds was calculated from the data of GC-MS analysis. **Figure 7** shows the area ratio of alkene/alkane of $C_8$-$C_{11}$ aliphatics and that of alkenylbenzene/

alkylbenzene of aromatics with $C_2$-$C_7$ side chains. The ratio of aliphatics and aromatics was lower in the reaction with steam than without steam. Therefore, hydrogen species were transferred from steam to aliphatic hydrocarbons and the side chain of aromatic hydrocarbons.

Catalytic cracking of dodecylbenzene with steam produced oxygen-containing compounds, such as phenol (13.2 min in **Fig. 6 (a)**), acetophenone (15.9 min), undecanone (23.0 min), and hydroxybiphenyl (28.7 min), whereas only a small peak of phenol was detected in
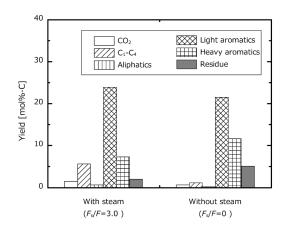


Fig. 5 Product Yield from the Reaction of Dodecylbenzene with a Catalyst Containing 8.6 wt% $ZrO_2$

Table 1 Hydrogen to Carbon Mole Ratio of Residue Produced by Cracking AR with a Catalyst Containing 8.6 wt% $ZrO_2$

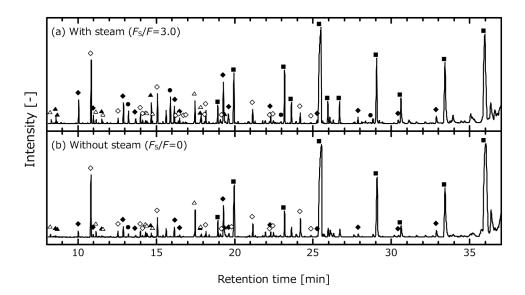| $F_S/F$ | [g/g] | 0 | 0.42 | 0.82 | 3.0 |
|---|---|---|---|---|---|
| H/C of residue | [mol/mol] | 0.61 | 0.68 | 0.77 | 0.74 |



Fig. 6 Total Ion Chromatograms of GC-MS Analysis of Product from the Reaction of Dodecylbenzene with a Catalyst Containing 8.6 wt% $ZrO_2$ (▲: alkane, △: alkene, ◆: alkylbenzene, ◇: alkenylbenzene, ●: oxygen-containing compounds, ■: other aromatic compounds)

the reaction without steam. The amount of these oxygen-containing compounds was less than 0.1 %. Oxygen-containing compounds indicate that hydrocarbons react with oxygen species derived from steam. The previous study reported that oil produced by catalytic cracking of AR with steam contained a small amount of oxygen[7]. Accordingly, small amounts of oxygen species were transferred from steam to these oxygen-containing compounds and remaining oxygen species formed carbon dioxide.

### 3.3. Effect of Zirconia Content on Product Distribution of AR Cracking

Zirconia catalyzes the formation of oxygen and hydrogen species from steam[9]. The effect of zirconia content in the catalysts on hydrogen transfer from steam to product was investigated. **Figure 8** shows the product yield for the catalytic cracking of AR with steam using catalysts containing 0 to 18 wt% zirconia. The yield of light oil, such as gasoline, kerosene, and gas oil, increased with higher zirconia content, except for the catalyst containing 18 wt% zirconia. Similar trends were previously reported. Oxidative cracking of heavy oil with iron oxide catalyst was promoted because of the activity of zirconia to generate oxygen species.

The yield of residue increased with higher zirconia content, and the H/C ratios of residue generated with the

catalysts containing 4.7 wt% and 8.6 wt% of zirconia were obviously larger than those obtained using the catalyst without zirconia (**Table 3**). The increase in residue was due to the deposition of residue on the zirconia. Higher zirconia content promoted generation of light hydrocarbons, causing larger amounts of residue production. However, hydrogen transfer from steam to residue might increase when using catalysts containing zirconia because zirconia promotes the generation of hydrogen species.

The structure of the catalyst containing no zirconia changed from hematite to magnetite after the reaction (**Fig. 9**), whereas the hematite structure of the catalyst containing zirconia was partially maintained (**Fig. 3**). Structural durability of the catalyst containing no zirconia was low because of the absence of Zr in the complex metal oxide of Fe, Zr, and Al. The lattice oxygen of iron oxide reacted with heavy oil, causing the phase change from hematite to magnetite, and the addition of oxygen species from steam to the iron oxide lattice was insufficient because the amount of oxygen species was low due to the absence of zirconia. The yield of carbon dioxide for the reaction with the catalyst containing no zirconia was 3.6 mol%-C, which was larger than that of other catalysts ($CO_2$ : 1.4-1.9 mol%-C) because large amounts of lattice oxygen were used to form carbon dioxide. On the other hand, the structure of the complex metal oxide of Fe, Zr, and Al (catalyst containing zirconia) hardly changed. Therefore, the oxygen forming carbon dioxide was derived from steam and the amount of carbon dioxide increased with higher zirconia content.

Larger amounts of hydrogen species might be gener-

Table 2  Conversion of Catalytic Cracking of Dodecylbenzene

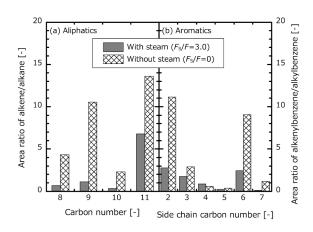| | With steam [$F_S/F = 3.0$] | Without steam [$F_S/F = 0$] |
|---|---|---|
| Conversion [mol-C/mol-C] | 0.40 | 0.39 |



Fig. 7  Area Ratio of Alkene/alkane of GC-MS Analysis of Product from the Reaction of Dodecylbenzene with a Catalyst Containing 8.6 wt% $ZrO_2$
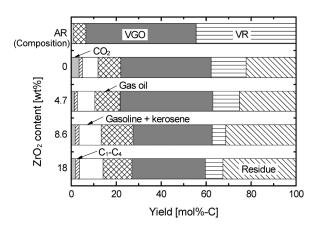


Fig. 8  Product Yield from the Reaction of AR with a Flow Rate Ratio of Steam to Feedstock of 3.0 g/g

Table 3  Hydrogen to Carbon Mole Ratio of Residue Produced by Cracking AR with a Flow Rate Ratio of Steam to Feedstock of 3.0 g/g

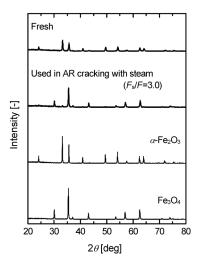| $ZrO_2$ | [wt%] | 0 | 4.7 | 8.6 | 18 |
|---|---|---|---|---|---|
| H/C of residue | [mol/mol] | 0.60 | 0.75 | 0.74 | 0.64 |

Fig. 9 X-ray Diffraction Patterns of Fresh and Used Catalysts Containing 0 wt% $ZrO_2$
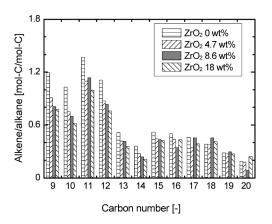


Fig. 10 Alkene/alkane Ratio of Light Hydrocarbons Produced by the Reaction of AR with a Flow Rate Ratio of Steam to Feedstock of 3.0 g/g

ated from steam with catalysts containing zirconia compared to those without zirconia. **Figure 10** shows the alkene/alkane ratio of $C_9$-$C_{20}$ aliphatic hydrocarbons generated by the reaction with steam using catalysts containing 0 to 18 wt% zirconia. The alkene/alkane ratio of $C_9$-$C_{15}$ aliphatic hydrocarbons decreased with higher zirconia content, with the exception of $C_{11}$ hydrocarbons. There was no correlation between zirconia content and the alkene/alkane ratio of $C_{16}+$ aliphatic hydrocarbons due to the low amount of $C_{16}+$ alkene. These results suggested that zirconia promoted hydrogen transfer from steam to product hydrocarbons, thus suppressing alkene generation. Heavy oil was oxidatively decomposed on the iron oxide by the reaction of heavy oil and oxygen species supplied from steam to the iron oxide lattice. Zirconia promoted generation of hydrogen species from steam and the hydrogen species were transferred to the decomposed hydrocarbons.

## 4. Conclusions

Catalytic cracking of AR and dodecylbenzene was conducted with steam using iron oxide-based catalysts containing zirconia and alumina. Heavy oil reacted with the oxygen species supplied from steam to the iron oxide lattice after the lattice oxygen reacted with heavy oil, producing light oil, gas hydrocarbons, carbon dioxide, and residue. The oxygen species were transferred from steam to carbon dioxide and a small amount of oxygen-containing compounds. The reaction of heavy hydrocarbons with the oxygen species produced the hydrogen species from steam. Approximately 33-60 % of hydrogen species were supplied to gas hydrocarbons and hydrogen sulfide, and the remaining hydrogen species were added to liquid hydrocarbons and residue in the reaction of AR. The alkene/alkane ratio of light aliphatic hydrocarbons produced by AR cracking decreased with higher flow rate ratio of steam to feedstock. Dodecylbenzene cracking with steam showed that hydrogen was transferred from steam to aliphatic hydrocarbons and the side chain of aromatic hydrocarbons. Furthermore, the alkene/alkane ratio decreased with higher zirconia content in the catalyst. Zirconia promotes the generation of hydrogen species, and hydrogen species were transferred from steam to product hydrocarbons, thus suppressing alkene generation.

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**要　　旨**

## 水蒸気由来水素種と酸素種を利用した酸化鉄系触媒による重質油の接触分解

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　ジルコニアとアルミナを含む酸化鉄系触媒による重質油の接触分解を水蒸気雰囲気下で行い，水蒸気由来水素種と酸素種の生成物への添加について検討した。常圧残油の接触分解により軽質油や二酸化炭素が生成し，原料に対する水蒸気の割合が増加すると軽質脂肪族炭化水素のアルケン／アルカン比が減少して二酸化炭素の収率が増加した。モデル物質としてドデシルベンゼンの分解を行った結果，常圧残油分解と同様にアルケン／アルカン比が減少する傾向がみられ，少量の含酸素化合物が生成した。これらの結果から，水蒸気由来酸素種は重質油と反応して二酸化炭素と少量の含酸素化合物へ組み込まれる。このとき水蒸気由来水素種が生成し，軽質炭化水素へ組み込まれてアルケンの生成が抑制される。また，ジルコニアは水蒸気からの水素種生成を促進するため，触媒のジルコニア含有量が増加するとアルケン／アルカン比が減少した。

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