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Transfer-hydrocracking of vacuum residue

I. Nakamura *, K. Fujimoto

Department of Applied Chemistry, Faculty of Engineering, The University of Tokyo, 7-3-1, Hongo, Bunkyo-ku, Tokyo 113, Japan

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Abstract

Hydrocracking of Arabian Heavy vacuum residue conducted in the presence of metal supported active carbon catalyst gave large amount of distillates (70%) with small hydrogen consumption. Especially, the Yallourn coal derived active carbon catalyst showed high cracking activity. The yield of asphaltene in the product oil was very low, whereas the coke yield was relatively high. In the metal-free active carbon system, the coke yield and the content of olefins, sulfur compounds and asphaltene in the product oil were higher than those of the metal-supported active carbon system. These results suggest that asphaltene in feed oil was adsorbed on the metal supported active carbon catalyst and was decomposed or dehydrogenated on it to form coke and hydrogen atoms. The hydrogen atoms formed migrated on the carbon surface to reach the metal site and transferred to free radicals, olefins or organo sulfur compounds.

Keywords: Carbon catalysts; Hydrocracking

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1. Introduction

The development of advanced technologies for upgrading heavy oils to high quality distillates has been attracting much attention as the key technology for promoting the new utilization of petroleum residue, oil sand bitumen, shale oil and coal liquid. Among the technologies, solid catalyzed hydrocracking processes are believed to be a promising technology, because of its high product quality [1]. However, the technology has several problems to be solved, such as low conversion level, low LHSV, high operation pressure and large hydrogen consumption.

The present authors have studied hydrogen transfer from naphtene hydrocarbons to organo sulfur compounds [2], olefins [3] or free radicals [4] via metal supported active carbon catalyst. In the present study, a new type of hydrocracking of heavy oil with metal supported active carbon catalyst is discussed. For further improvement, a new type of coal-derived disposable catalyst for the transfer hydrocracking has been developed.

2. Experimental

Catalyst were prepared by impregnating home made active carbons and a commercially available active carbon (Takeda HGS-616 made from wood) with aqueous solutions of ferric nitrate and other water soluble metal salts. The catalyst precursor was dried in air at 120°C, calcined in flowing nitrogen at 450°C for 3 h and activated by reduction in flowing hydrogen at 450°C for 3 h and then sulfided with a H_2–H_2S mixed gas

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* Corresponding author.

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(4/1 molar ratio) at 400°C for 1 h. Home made active carbons were prepared by treating brown coals with carbon dioxide. Coals were heated in flowing carbon dioxide at the heating rate 400°C/h to 600°C, held at 600°C for 1 h and heated at 600–900°C for 1 or 2 h.

Heavy oils were cracked using an autoclave with inner volume of 150 ml and with apparatus to make hydrogen gas flow [4]. Reaction conditions were as follows: feed oil, 40 g; catalyst, 0.4–4.0 g; process time, 30–60 min; and out let gas flow rate, 120 ml/min.

Dehydrogenation of methylcyclohexane (MCH) was conducted at 500°C using a pulse reaction apparatus in flowing nitrogen.

Gaseous products were analyzed by using gas chromatographs. Liquid products were distilled to naphtha (IBP-171°C), kerosene (172–232°C), gas oil (233–343°C), vacuum gas oil (344–525°C) and vacuum residue (525°C$^+$) fractions. The amounts of maltene, asphaltene and coke were determined as pentane soluble (PS), toluene soluble–pentane insoluble (PI–TS) and toluene insoluble (TI), respectively. Maltene was analyzed by silica–alumina column chromatograph for saturates (SA), monoaromatics (MA), diaromatics (DA), triaromatics and polyaromatics and polar compounds (PP).

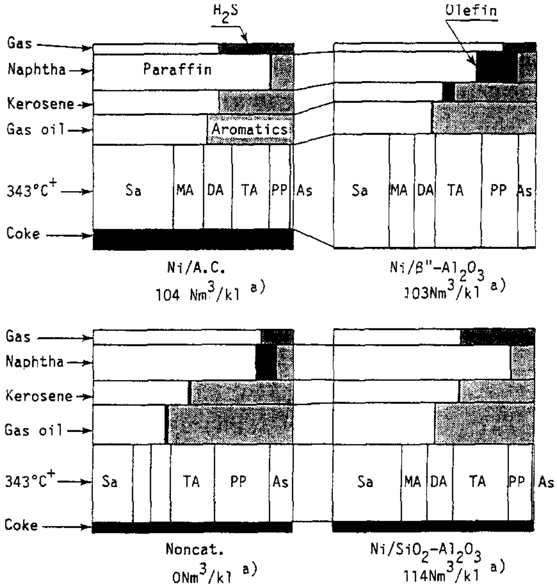
3. Results and discussion

3.1. Characteristics of transfer-hydrocracking of heavy oil

3.1.1. Product pattern of carbon catalyzed transfer-hydrocracking

The results of Kuwait atmospheric residue (KW-AR) cracking with various supported Ni catalysts and without a catalyst are given in Fig. 1. Carrier materials such as commercially available active carbon, β''-Al_2O_3 which is a typical basic support and SiO_2–Al_2O_3, which is a typical acidic support, were employed.

The level of hydrogen consumption was the same for the catalyzed reactions (100 Nm^3/kl oil), which was 1/4–1/3 of that for a conventional hydrocracking. The yield of gas products was in the order SiO_2–Al_2O_3 > non-catalyzed > A.C. > β''-Al_2O_3. In the Ni/A.C. catalyzed reaction, the yield of gaseous hydrocarbons were lower than that of non-catalyzed or Ni/SiO_2–



a) H_2 consumption

Sa; Saturates,
MA; Monoaromatics,
DA; Diaromatics,
TA; Triaromatics,
PP; Polyaromatics and polar compounds,
As; Asphaltene,

AR-KW 40 g,
Catalyst 8g,
Reaction temp. 435 °C,
Hydrogen pres. 7.5 MPa,
Process time 60 min.

Fig. 1. Product patterns of KW-AR cracking.

Al_2O_3 catalyzed reaction, whereas the conversions of KW-AR were similar for these reactions. The olefin content in the distilled oil was β''-Al_2O_3 > non-catalyzed > SiO_2–Al_2O_3 $\geqslant$ A.C. $\geqslant$ 0, although the yield of naphtha, kerosene and gas oil in distilled oil were similar in these systems: naphtha 35–39%, kerosene 21–25%, gas oil 39–42%, respectively. The asphaltene yield was non-catalyzed $\geqslant$ β''-Al_2O_3» A.C. $\geqslant$ SiO_2–Al_2O_3 $\geqslant$ 0, although the coke yield was A.C. > non-catalyzed $\geqslant$ SiO_2–Al_2O_3» β''-Al_2O_3 $\geqslant$ 0. The amount of asphaltene in the β''-Al_2O_3 system was similar to that of KW-AR fed.

The characteristics of the Ni/A.C. catalyzed reaction are summarized as follows: (1) The yield of gaseous hydrocarbon was lower than that of the non-catalyzed or the Ni/SiO_2–Al_2O_3 catalyzed reaction, whereas the conversions of KW-AR were similar for these reactions, (2) the content of olefins in the distillates was very low, although the hydrogen consumption for Ni/A.C. system and Ni/β''-Al_2O_3 system was in the same level, (3) the coke yield was highest in these systems but the yield of asphaltene was almost zero.

These results suggest that the asphaltene in the residual oil was adsorbed or decomposed on the catalyst surface then converted to coke in the case of the carbon-catalyzed reaction. At the same time olefins were hydrogenated to paraffins.

3.1.2. *Effects of supported metals on active carbon*

In Table 1 are shown the results of KW-AR cracking at 455°C over a variety of metal sulfide catalysts supported on a commercially available active carbon. Conversion level was promoted from 67% to 80% or higher by adding active carbon catalysts whether it carried metals or not. The increase in the conversion level should be attributed to the carbon surface, since, free radicals on the active carbon surface should initiate cracking reaction.

The level of hydrogen consumption increased markedly from −34 and −38 m^3/kl oil for the non-catalyzed system and the metal-free active carbon system to about 60 m^3/kl oil by adding Ni or Mo on active carbon.

Although the level of desulfurization was very low in the non-catalyzed system, the reac-

Table 1
Effects of metal on active carbon

Catalyst	Non-cat.	A.C.	Nil wt.-% A.C.	Mol wt.-% A.C.	Fel wt.-% A.C.	Fel 0 wt.-% A.C.
Conversion (%)	67.3	87.3	79.3	85.6	88.0	83.9
H_2 consumption (Nm^3/kl)	−34	−38	67	53	−24	73
S removal (%)	15.2	22.6	60.0	62.4	29.7	64.1
Product Distribution (wt.-%)						
Gas	7.3	9.0	7.8	5.2	8.2	5.1
Naphta	20.8	26.8	19.8	18.7	21.0	22.8
Kerosene	10.9	10.5	10.2	24.1	17.3	19.0
Gasoil	22.2	20.0	27.2	19.5	19.8	29.2
343°C$^+$	32.2	12.6	20.1	14.8	11.8	16.4
Coke	6.6	21.1	14.9	17.7	21.9	7.5
Composition of Naphtha Fraction (vol.-%)						
Paraffin	72	83	90	88	76	92
Olefin	10	9	0	2	7	1
Aromatics	18	8	10	10	17	7

Reaction conditions: KW-AR 40 g, Catalyst 12 g, 455°C, 7.0 MPa, 30 min.

tions catalyzed by Ni/A.C. or Mo/A.C. gave much higher desulfurization level, which can be attributed to the hydrodesulfurization activity of these metals.

The product distribution was rather similar for each reaction system, among which the Ni/A.C. or Mo/A.C. catalyzed reaction gave lower gas yield and coke yield. It is also worth while to note that the product was rather rich in middle distillate (38–48 wt.-%), in spite of the high conversion level and that little olefinic products were formed. It suggests that the dehydrogenation and the decomposition of heavy fraction to coke and distillates proceeded, which was followed by the hydrogenation of distillates.

Although 1 wt.-% of supported iron was not effective as the additive, 10 wt.-% of iron gave the highest hydrogen consumption and the highest desulfurization and the lowest coke yield. It means that the hydrogenation activity of the catalyst is quite high.

3.1.3. *Effects of hydrogen pressure*

The effects of hydrogen pressure on the Ni/A.C. catalyzed reaction of KW-AR are shown in Fig. 2. With increasing hydrogen pressure, the hydrogen consumption increased linearly and the conversion of residual oil decreased slightly. Also, the degree of desulfurization increased and coke yield decreased with the increase in hydrogen pressure up to 3.0 MPa, but they were almost constant over 3.0 MPa. Since the degrees of desulfurization and the suppression of the coke formation are considered a measure of the hydrogenation of product oil, it is reasonable that the hydrogenation of product oil reached the same level in the case of 3.8 and 7.5 MPa of hydrogen pressure. The fact that hydrogenation of product oil was at the same level for reaction at hydrogen pressure of 3.8 and 7.5 MPa, while the hydrogen consumption at 3.8 MPa was much lower than that at 7.5 MPa, suggests that gaseous hydrogen was mainly consumed in the hydrogenation of products at 7.5 MPa. On the other hand, when the hydrogen pressure was moderate such as 3.8 MPa, the dehydrogenation of asphaltene to coke was enhanced and the hydrogen atom on the catalyst, which was formed from asphaltene coking, reacted with sulfur compounds or oil without desorbing to gas phase.

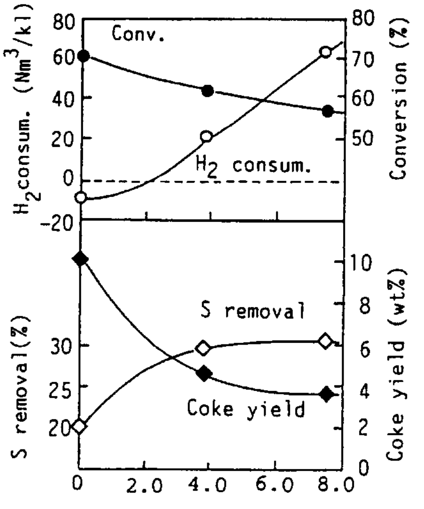


Fig. 2. Effects of hydrogen pressure. Feed: KW-AR, Catalyst; Ni 1 wt.-%/A.C. 20 wt.-%, 435°C, 60 min.

3.1.4. *Reaction model of hydrogen-transfer cracking*

The reaction model of the present system is demonstrated as in Fig. 3. In the system, cracking reaction initiated thermally or catalytically in the liquid phase to produce hydrocarbon radicals. The hydrocarbon radicals are decomposed into olefins and smaller radicals. On the other hand, the asphaltene which usually contains

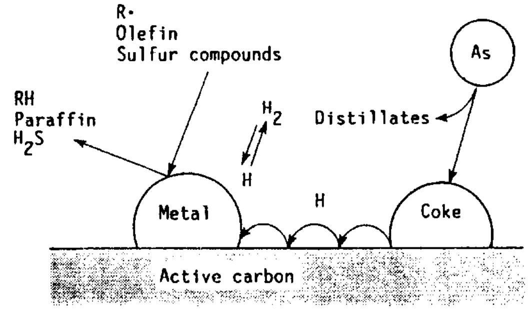


Fig. 3. Reaction model of hydrogen transfer cracking.

Table 2
Properties of activated [a] Morwell coal

Activation temp. (°C)	650	750	800	850
Surface area (m^2/g) (1)	523	667	940	1130
Pore volume (cm^3/g)	0.03	0.13	0.22	0.37
MCH [b] conv. (%) (2)	5.3	38.0	42.2	58.2
$\{(2)/(1)\} \times 10^2$	1.01	5.70	4.49	5.15

[a] In CO_2, 1 h.
[b] Methylcyclohexane.

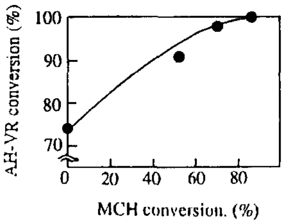


Fig. 4. Dehydrogenation activity vs. cracking activity.

polycyclic moieties, is adsorbed and cracked or dehydrogenated on the active carbon surface, probably because of the chemical affinity between the aromatic nuclei of asphaltene and the carbon surface and the dehydrogenating activity of active carbon surface, to form coke and hydrogen atoms. The hydrogen atoms on the carbon surface migrate on it to reach supported metal particles, where, they react with olefins, free radicals or sulfur compounds or they recombine to hydrogen molecules to be desorbed into gas phase. When the reaction is operated under pressurized hydrogen, hydrogen molecules are adsorbed on metal surface to dissociate to hydrogen atoms, whereby the desorption of hydrogen from the carrier surface is suppressed. This phenomenon is called spillover effect [5]. When the pressure of hydrogen in the gas phase is high, hydrogen in the gas phase comes into the metal surface to react with other materials resulting the hydrogen consumption. When the hydrogen pressure is low, the hydrogen on the solid surface should be desorbed to the gas phase by the reverse spillover [6]. Under particular reaction condition, neither absorption nor desorption of hydrogen would be observed as demonstrated in Fig. 2.

Table 3
Transfer hydrocracking of AH-VR with coal derived catalyst

Carrier	Non-cat	HP-C [a]	HGS-616 [b]	Morwell [a]	Yallourn [a]
Properties of carrier					
Surface area (m^2/g)	–	260	1280	1130	840
Pore volume (cm^3/g)	–	0.05	0.48	0.37	0.18
MCH [c] conversion (%)	–	0.4	56.3	58.2	70.7
VR conversion (wt.-%)	80.6	76.6	90.7	95.0	100
H_2 consum. (Nm^3/kl oil)	−19	140	114	77	32
S removal (wt.-%)	16.4	26.0	29.7	26.8	26.7
Product distribution (wt.-%)					
Gas	8.5	7.4	12.4	8.8	6.2
Naphtha	5.5	12.9	17.2	12.0	31.7
Kerosene	7.0	8.3	11.0	10.3	15.5
Gas oil 1	13.3	17.5	18.0	20.6	17.0
Vacuum gas oil	25.2	27.8	22.8	37.9	13.2
Vacuum residue	19.4	25.8	9.4	5.0	0.0
Coke	21.1	0.3	9.2	5.4	16.4

Reaction conditions: AH-VR 40 g, Fe 5 wt.-%/A.C. 4 g, 435°C, 7.0 MPa, 60 min.
[a] Activated in CO_2 for 1 h at 850°C,
[b] Commercially availableactive carbon,
[c] Methylcyclohexane.

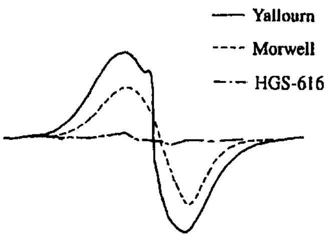


Fig. 5. ESR spectra of carbon carriers.

3.2. *New type of coal-derived disposable catalyst for transfer hydrocracking*

3.2.1. *Effect of activation temperature*

Morwell coal was activated in flowing carbon dioxide at several treatment temperature. Part of hydrogen, which is consumed for hydrogenation of olefin, hydrocarbon radical or sulfur compound, is supplied by dehydrogenation of asphaltene adsorbed on an active carbon in transfer hydrocracking of heavy oil. Therefore, the catalyst is required to have sufficient surface area and pore volume to adsorb asphaltene and activity for dehydrogenation of asphaltene. Surface area and pore volume of activated coal increased with increasing the treatment temperature as shown in Table 2. And it should be noted that dehydrogenation activity of MCH in pulse reaction increased drastically over 700°C.

3.2.2. *Transfer hydrocracking on various active carbon catalysts*

Table 3 shows the results of hydrocracking with various iron supported active carbon catalysts. VR conversion for Yallourn coal derived catalyst was the highest in all the carbon catalyst, while surface area and pore volume of Yallourn coal derived carrier were smaller than those of Morwell coal–char and commercially available active carbon. The order of VR conversion was corresponded to the order of MCH dehydrogenation conversion; Yallourn > Morwell > HGS-616 > HP-C.

The correlation between activity for heavy oil cracking and activity for dehydrogenation of MCH was shown more clearly in Fig. 4. Fig. 5 shows the ESR spectra of carbon carriers. It is clear that spin concentration in ESR measurement was in the order Yallourn > Morwell > HGS-616. The order of VR conversion also correspond with order of the spin concentration.

These results suggest that the conversion level should be attributed to the catalyst action of active carbon, since, the free radical on the carbon surface should initiate cracking reaction by hydrogen abstraction from hydrocarbon.

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