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Studies on Catalytic Hydrotreating of Recycled Solvents from Coal Liquefaction Process (Part 2) Investigation of Kinetics, Catalyst Deactivation and Prediction of Catalyst Life

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The following items have been reported based on the results of a series of catalytic hydrotreating tests of feed solvents obtained from a coal liquefaction process using Ni-Mo/alumina catalyst: (1) the kinetics of the hydrogenation of the recycled solvents obtained from a 1 t/day PDU liquefaction process using Wandoan and Illinois No. 6 (River King) coals; (2) their reactivities on hydrogenation; (3) the catalyst deactivation during a 3,000 h test run using recycled solvent derived from Wandoan coal and a proposal of simple mathematical model and its application to the long run test data; (4) the prediction of catalyst life from hydrotreating tests of the recycled solvents prepared from Wandoan and Illinois No. 6 coals by maintaining constant hydrogenation rates.

1. Introduction

One of significant matters required of coal liquefaction processes is to produce solvents containing high donatable hydrogen by hydrogenation of middle distillates of the coal derived oils, and to recycle them to a liquefaction stage as hydrogen donor solvents¹⁾.

In this paper, the results of a series of the hydrotreating tests, using a commercially available Ni-Mo/alumina catalyst, are reported, as listed below:

- (1) The kinetics of the hydrogenation of recycled solvents obtained from a 1 t/day Process Development Unit (PDU) liquefaction process using Wandoan and Illinois No. 6 (River King) coals.
- (2) The reactivity of recycled solvent on hydrogenation.
- (3) The deactivation of catalyst during a 3,000 h test run of the recycled solvent obtained from Wandoan coal, and the proposal of simple mathematical models for deactivation of catalyst and the application of the model to the results of the long run test data.
- (4) The prediction of catalyst life (temperature-

time relation) during hydrotreating of recycled solvents derived from Wandoan and Illinois No. 6 coals.

2. Experimental

2.1. Feed Solvents

Three kinds of middle distillates (feed solvents A, B and C) derived from a 1 t/day PDU coal liquefaction process were used as feedstocks for hydrotreating. For our experiments, Wandoan and Illinois No. 6 coals were used. The operation modes of the process are shown in **Table 1**. The properties and distributions of hydrocarbon compounds of these solvents are given in **Table 2** and **Fig. 1**, respectively. The differences in properties and chemical compositions, especially in aromaticity (*fa*), between feed solvents A and B are attributed to the differences between the operation modes. The difference in the content of 350°C⁺ fraction is due to the difference in the cut points of hydrotreated products (200°C for feed solvent A and 220°C for feed solvent B).

The liquefaction process of these two coals were operated under the same conditions, and the differences in the physical properties and chemical compositions between feed solvents B and C are

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Table 1 Operation Model of 1 t/day PDU

Feed solvent	A	B	C
Source Δfa^a	Wandoan coal <0.03	Wandoan coal ~0.1	Illinois No. 6 coal ~0.1
Recycled type of 350°C+ fraction	Partial	Extinction (NEDOL mode)	Extinction (NEDOL mode)

a) Degree of hydrogenation at which the hydrotreating was conducted.

Table 2 Properties of Feed Solvents

Feed solvent	A	B	C
Specific gravity, d25/4°C	1.0104	0.9616	1.0288
Ultimate analysis [wt%]			
Carbon	89.23	88.98	88.41
Hydrogen	8.26	10.21	8.65
Oxygen	2.2	0.4	1.8
Total nitrogen	0.41	0.22	0.61
Basic nitrogen	0.31	0.12	0.35
Sulfur	0.07	0.16	0.12
Average molecular weight ^{a)}	181	229	202
<i>n</i> -Paraffins [wt%]	9.0	14.13	3.0
Aromaticity (<i>fa</i>) ^{b)}	0.68	0.48	0.60
350°C+ content [wt%]	17	31	35

a) Obtained from FI-Mass spectrum.

b) Obtained from ¹³C-NMR spectrum.

Fig. 1 Composition of Hydrocarbons of Feed Solvents

Table 3 Reaction Conditions of Hydrotreating Tests

Temperature	[°C]	320 to 400
Hydrogen pressure	[kg/cm ² -G]	50 to 100
LHSV	[h ⁻¹]	1.0 to 3.0
Hydrogen to liquid ratio	[NL/l]	1,000

probably attributed to the inherent differences between the coal types. High gravity, aromaticity (*fa*)¹⁾, and concentration of nitrogen and oxygen are characteristics of feed solvent C. Feed solvent C also has a higher concentration of fluorenes, and four-ring type of condensed aromatic compounds. On the other hands, a higher content of *n*-paraffins is characteristic of solvents A and B. Thus, coal type and the operation mode of the liquefaction process affect the properties of the recycled solvents.

2. 2. Catalyst and Reaction Conditions

The hydrotreating tests were performed using fixed-bed reactors²⁾. The catalyst was a commercial by available Ni-Mo/alumina extrudate, 1/16 inch in diameter. The conditions for the determination of the reaction kinetics and the catalyst reactivities are given in Table 3. Long run tests (ca. 3,000 h) using feed solvent A were performed to study changes in catalyst activities, such as temperature dependency of catalyst deactivation during hydrotreating. The conditions of the long run tests were: temperatures, 334,

350, 380°C; hydrogen pressure, 100 kg/cm²-G; LHSV, 1.0 h⁻¹; hydrogen to liquid ratio in volume, 1,000 NL/L.

3. Results and Discussion

3.1. Kinetics of Hydrogenation

Solvents consist of various types of compounds and, therefore, the determination of hydrotreating rate equations, solely using recycled solvent data, is more difficult than using model compound data. To obtain the apparent overall reaction rate equation in feed, the kinetics were investigated using a method which assumes that the concentration of the reactant is equal to an initial value of one. This method is typically used in kinetic studies of hydrodesulfurization (HDS) of petroleum fractions³⁾.

During hydrotreating, various reactions, such as the hydrogenation of aromatic-rings and the removal of hetero-atom, occur in parallel. This work focused on the hydrogenation of aromatic-rings. Since solvents are mixtures of various aromatic compounds, characterizations of individual reactions for each compound are not possible. The hydrogenation reaction rate, therefore, was represented by the rate of decrease in *fa* values.

3.1.1. Order of Reaction

Catalyst activity became nearly constant after 400 h, and the data obtained during this period were used to calculate the reaction order. The reaction order of the hydrogenation was calculated using the experimental data, which were obtained as LHSV changed from 1.0 to 3.0 h⁻¹. The first order plots of hydrogenation for feed solvents A and C are shown in Fig. 2. Since the plots are linear, hydrogenation is a first order reaction.

Fig. 2 First-order Reaction Plots on Hydrogenation

Fig. 3 Effect of Hydrogen Pressure on Hydrogenation

Fig. 4 Temperature Dependencies on Hydrogenation

3.1.2. Effect of Hydrogen Pressure

The effect of hydrogen pressure on the reaction rate constants was investigated. Figure 3 shows the results for feed solvents A and C. From these results, the effect of hydrogen pressure was found to be represented by Eq. (1):

$$k \propto P_{H_2}^n \quad (1)$$

where, P_{H_2} : hydrogen pressure (kg/cm²-G)

The exponent for feed solvent C was greater than that for A.

3.1.3. Temperature Dependency

Dependency on reaction temperature of the rate constants was investigated. Arrhenius' plots are shown in Fig. 4. The apparent activation energies [kcal/mol], were as follows:

Feed solvent A: 17 (during 320-360°C)

Feed solvent C: 15 (during 300-360°C)

The apparent activation energies for hydrogenation are different for temperatures below and above 360°C. For temperatures above 360°C, dehydrogenation occurring competitively with hydrogenation is substantial, accounting for the lower apparent activation energies. The difference of these activation energies is probably due to the difference in hydrocarbon composition of solvents shown in Fig. 1.

3.1.4. Equation for Overall Reaction Rate

The equation for apparent overall reaction rate for hydrogenation is represented by Eq. (2):

$$df/d(\text{LHSV}) = -r = A \cdot \exp(-E/RT) \cdot (P_{\text{H}_2}/100)^n \cdot f \quad (2)$$

3.2. Comparison of Reactivities

To study the reactivities of hydrogenation of recycled solvents, several hundred hours of hydrotreating, for quantitative interpretation from the catalyst activities and their changes, is required. The reactivities of the three feed solvents (A, B and C) were investigated. The changes in the hydrogenation rate constant, normalized at the conditions of 340°C and 100 kg/cm²-G of hydrogen pressure, as a function of time-on-stream, are shown in Fig. 5.

No appreciable changes were found in the

reactivities between feed solvents A and B, but the reactivity of C was lower than those of A and B. The hydrogenation rate constants at 400 h were 0.24 and 0.14 for feed solvents A and C, respectively. The difference in reactivity between these two solvents may be ascribed to the differences in their physical properties and chemical compositions. A higher amount of 350°C+ fraction and fluorenes, which can be difficult to hydrogenate, was observed in the feed solvent derived from Illinois No. 6 coal.

Hydrogen input is very important for hydrotreating of recycled solvents in coal liquefaction processes. A significant relation exists between the degree of hydrogenation and the presence of donatable hydrogens from recycled solvents in the hydrotreating step of the processes. One of the important purposes of hydrotreating is to provide donatable hydrogen to solvents. Thus, the change in the amount of donatable hydrogens during the hydrotreating of solvents was investigated. The amount of donatable hydrogens (D_H) in feed solvents and hydrotreated oils was obtained by ¹H-NMR method as follows¹⁾:

$$D_H = H_D \cdot H_T \quad (3)$$

where, $H_D = (h_\alpha/x) + (h_n/y)$

h_α : the ratio of protons of α -methylenes to the total amount of protons from the ¹H-NMR spectrum (δ 2.3-3.0 ppm in ¹H-chemical shift)

h_n : the ratio of protons of β -methylenes to total proton of protons (δ 1.6-2.0 ppm in ¹H-chemical shift)

H_T : total hydrogen content (wt%)

$x = y = 2$

Fig. 5 Comparison of Reactivities of Solvents A, B and C on Hydrogenation

Fig. 6 Changes in Donatable Hydrogen Contents as a Function of Degree of Hydrogenation

Shown in Fig. 6 are changes in the amount of donatable hydrogens as a function of the degree of hydrogenation (Δfa). Δfa , obtained by ^{13}C -NMR, denotes the change in fa between the feed solvent and hydrotreated oil. The greater the value of Δfa shows, the greater the hydrogenation of solvents proceeds. The amount of donatable hydrogens from feed solvents A and B shows increase proportional with the first increase in Δfa . For both solvents, however, the increase became gradual above a Δfa of approximately 0.15. For feed solvent C, the proportional increase changes to a more gradual one above Δfa of approximately 0.08. The different profiles between solvents A/B and C are attributed to the difference in hydrocarbon composition of solvents, shown in Fig. 1. The profiles of the change in the amount of donatable hydrogens during hydrotreating of solvents correspond to the changes in their chemical composition. During hydrotreating, the amount of donatable hydrogens increases with the increase in amount of hydroaromatic compounds¹⁾. The amount of donatable hydrogens assigned to hydroaromatic compounds, however, becomes saturated with the increase in chemical hydrogen consumption, suggesting an increase in the amount of naphthenes¹⁾.

When hydrotreating of recycled solvents is considered from the aspect of contents of donatable hydrogens, a hydrotreating operation keeping Δfa at appropriate values to preserve are evidently required as is investigated above. The values of the Δfa in the standard operating conditions of 1 t/day PDU are between 0.03 and 0.1.

3. 3. Catalyst Deactivation in Hydrotreating of Recycled Solvents

3. 3. 1. Long Run Test Results

For the design and operation of reactors in hydrotreating processes, it is important to collect long run test experimental and kinetic data of catalyst deactivation during hydrotreating. In consideration thereof the long run test for feed solvent A was continuously conducted for ca. 3,000 h.

The change in aromaticity fa given in Fig. 7 indicates the gradual degradation of catalyst

Fig. 7 Change in Aromaticity and Rate Constant on Hydrogenation in the Long Run Test

activity during hydrogenation with time-on-stream, in each temperature range. After the long run test, the used catalyst was divided into five parts, and three of these parts were analyzed for the amount of deposited carbon and their physical properties. The analyzed results of the used and fresh catalysts are shown in Table 4. The amount of the deposited carbon was ca. 12 to 18 wt%, based on the fresh catalyst weight. The pore volume of catalyst decreased with carbon deposition. In addition, the surface area of the used catalyst was ca. 30 to 40% less than that of the fresh catalyst. Since no element other than carbon was detected by ultimate analysis, the catalyst deactivation must have been caused by the changes in the pore structures of catalysts with the deposition of carbonaceous materials on the surface of the catalyst.

3. 3. 2. Applying the Model of Catalyst Deactivation

As described above, deactivation of catalyst during hydrotreating of recycled solvents is primarily caused by deposition of carbonaceous materials. The behavior of carbon deposition on the catalyst, therefore is a dominant factor governing the deactivation and life of the catalyst. Deactivation catalyst caused by carbon deposition on the catalyst during the upgrading processes of coal derived oil

Table 4 Changes of Catalyst Properties and Deposited Carbon

	Fresh catalyst	Used catalyst		
		Inlet	Middle	Outlet
Physical properties				
Surface area [m ² /g]	269	155	166	183
Pore volume [ml/g]	0.53	0.21	0.24	0.29
Deposited carbon [wt% on fresh catalyst]	—	17.6	14.4	12.5

by HDN and/or HDS have been reported in several studies^{4)~7)}. However, a model of catalyst deactivation for hydrotreating of coal-derived oils has not been proposed to date, because sufficient quantitative elucidation on the relation between the change in feed oils and the rate of carbon deposition may still be lacking. In this work, catalyst deactivation during hydrogenation was studied in accordance with a method proposed by Krishnaswamy *et al.*⁸⁾. Assuming that fixed-bed reactors employed in the hydrotreating were operated with an isothermal plug flow, catalyst deactivation could be analyzed based on a model of concentration-independent deactivation. In accordance with the model, the degree of catalyst deactivation (ψ) is defined by Eq. (4):

$$\psi = k_t/k_0 \quad (4)$$

where, k_0 : reaction rate constant at the start-of-run, $t = 0$

k_t : reaction rate constant at t in time-on-stream.

The reaction rate constant of hydrogenation at t of a given value of LHSV is represented by Eq. (5):

$$k_t = k_0\psi = \ln(f_0/f)\text{LHSV} \quad (5)$$

$$k_0 = A_d \cdot \exp(-E_d/RT_0) \quad (6)$$

For a first order, concentration-independent decay, the change in catalyst deactivation with time is given by Eq. (7):

$$-(d\psi/dt) = k_d \cdot \psi \quad (7)$$

where, k_d is the deactivation rate constant, which indicates an Arrhenius' temperature dependence, as described below.

$$k_d = A_d \cdot \exp(-E_d/RT) \quad (8)$$

Substitution of Eq. (8) into Eq. (7) and integration give:

$$\psi = \exp\{-A_d \cdot \exp(-E_d/RT) \cdot t\} \quad (9)$$

where, A_d : frequency factor for catalyst deactivation

E_d : activation energy for catalyst deactivation.

With the substitution of Eq. (9) into Eq. (4), the reaction rate constant for a case where catalyst deactivation at t is as follows;

$$k_t = k_0 \cdot \exp\{-A_d \cdot \exp(-E_d/RT) \cdot t\} \quad (10)$$

The reaction rate constant, when catalyst deactivation is considered in each temperature range as shown in Fig. 7, is represented by Eqs. (11), (12) and (13)

For $t = t_0 - t_1$ and $T = T_1$,

$$k_t^{\text{sim}} = k_0 \cdot \exp\{-A_d \cdot \exp(-E_d/RT_1) \cdot t\} \quad (11)$$

For $t = t_1 - t_2$ and $T = T_2$,

$$k_t^{\text{sim}} = k_{t_1}^{\text{sim}, T_1} \cdot \exp[-E/R \cdot (T_2^{-1} - T_1^{-1})] \cdot \exp\{-A_d \cdot \exp(-E_d/RT_2) \cdot (t - t_1)\} \quad (12)$$

For $t = t_2 - t_3$ and $T = T_3$,

$$k_t^{\text{sim}} = k_{t_2}^{\text{sim}, T_2} \cdot \exp[-E/R \cdot (T_3^{-1} - T_2^{-1})] \cdot \exp\{-A_d \cdot \exp(-E_d/RT_3) \cdot (t - t_2)\} \quad (13)$$

A_d and E_d , the kinetic parameters of catalyst deactivation on hydrogenation, was optimally estimated by the least squares method, using Eqs. (11), (12), and (13). Their values were obtained, using a reaction rate constant from the long run test data obtained by computer simulation based on the following objective function:

$$\text{Min } \Sigma (k_t^{\text{sim}} - k_t^{\text{exp}})^2 \quad (14)$$

where, k_t^{sim} : reaction rate constant at t obtained from Eqs. (11), (12), and (13)

k_t^{exp} : reaction rate constant obtained from the long run test data

A_d and E_d : 2.4×10^4 and [kcal/mol], respectively.

The comparison of the test data (triangle marks) with the simulation data (solid lines) are shown in Fig. 7, indicating good agreement. Thus, the model of catalyst deactivation on the hydrogenation of recycled solvents was found to be applicable to a first-order reaction. The influence of hydrogen pressure and the hydrogen to liquid ratio on the catalyst deactivation was not included, however, since the test was performed while these two conditions were held constant. The applicability of the present model of catalyst deactivation, therefore, is limited to the conditions of 100 kg/cm²-G of hydrogen pressure and 1,000 Nl/l of hydrogen to liquid ratio.

3. 4. Prediction of Catalyst Life in Hydrotreating of Recycled Solvents

Generally, the operating method, which maintains the conversion of hydrogen at a given level by a rise in reactor temperature, corresponds to the degree of catalyst deactivation with time-on-stream and has been adopted for commercial reactors in the HDS of petroleum light fractions. Catalysts are usually exchanged or regenerated when the maximum temperature for the reactors is reached.

For hydrotreating of recycled solvents on a commercial scale, a similar operating method, as described above, can be adopted.

Using A_d , E_d , and the reaction temperature required to attain the intended degree of hydrogenation by Eq. (10), temperature-time curves can be simulated. In this work, the influence of the degree of hydrogenation and of the characteristics of feed solvents on catalyst life were investigated.

3. 4. 1. Influence of the Intended Degree of Hydrogenation

A temperature-time relation was estimated, based on the model using the parameters of catalyst deactivation during hydrotreating of solvent A from Wandoan coal. Shown in Fig. 8, the simulated temperature-time curves as the Δfa between the feed solvents and hydrotreated oils is set at 0.05, 0.1 and 0.15, respectively. The figure serves to indicate that the Δfa needed to keep in the operation had an appreciable influence on the catalyst life. Abrupt changes of the curve above 360°C were not due to catalyst deactivation, but could be attributed to the temperature effect of dehydrogenation occurring competitively with hydrogenation.

3. 4. 2. Influence of Characteristics of Feed Solvents

The influence of the characteristics of feed solvents on catalyst life is attributable to properties of coal and to the operating modes of the coal liquefaction process, including hydrotreating. The reaction rate constants at 400 h in time-on-stream (k_0) of feed solvents A, B and C used in the simulation were 0.25, 0.25 and 0.14, respectively. It was assumed that the values of the rate parameters for catalyst deactivation, A_d and E_d , for feed solvents B and C were equal to those of feed solvent A.

Shown in Fig. 9 are simulated temperature-time curves during hydrotreating for each feed solvent,

Fig. 8 Prediction of Temperature-time Curve (dependency on degree of hydrogenation, Δfa)

Fig. 9 Prediction of Temperature-time Curve (dependency on characteristics of feed solvent)

when Δfa is set at 0.05. Despite the same coal properties and similar hydrogenation reactivities, the catalyst life with feed solvents A and B appreciably different. This difference can be attributed to the unlike fa of the feed solvents and to the varying operating mode of the 1 t/day PDU, as shown in Table 1. For feed solvents A and C, an appreciable difference in catalyst life was found. The difference in hydrogenation reactivity was due to the variances in the characteristics of the coal.

From this study, it was found that the catalyst life during hydrotreating fluctuated widely by differing operating mode of the coal liquefaction process, including hydrotreating; the characteristics of employed solvents; the intended degree of hydrogenation; and the reactivity of hydrogenation.

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要 旨

石炭液化プロセスからの循環溶剤の接触水素化処理に関する研究 (第 2 報) 動力学的検討, 触媒の活性劣化の検討および寿命予測

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石炭液化油からの循環溶剤の接触水素化処理に関して一連の研究を行ってきたが, 本報では, Ni-Mo/アルミナ系触媒を用いて次の項目について検討した。(1) ワンドアン炭およびイリノイ No.6 (リバーキング) 炭を原料炭とする 1 t/日 PDU の液化プロセスから得られた循環溶剤の水素化反応の動力学的検討, (2) これら溶剤の水素化反応性に関する検討, (3) ワン

ドアン炭液化油からの循環溶剤の 3,000 時間にわたる水素化処理試験における触媒の性能変化, 特に活性劣化について。触媒の活性劣化のシミュレーションに対する数学的モデルの適用および水素化処理の長期運転試験のデータに対する適用, (4) 循環溶剤の水素化度を一定に保持しての水素化反応における触媒寿命の予測。

Keywords

Coal liquid, Hydrogenation, Catalyst deactivation, Catalyst life, Kinetics, Hydrocarbon