[Regular Paper]

Competitive Reaction in Hydrodenitrogenation and Hydrodeoxygenation of Coal-derived Naphtha

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Hydrodenitrogenation (HDN) and hydrodeoxygenation (HDO) of coal-derived naphtha and its model compounds were examined by using a catalyst nickel-molybdenum supported on alumina. There are three types of nitrogen compounds in coal-derived naphtha. They are pyridine, pyrrole, and aniline. Aniline type nitrogen compounds in the coal-derived naphtha are more resistant to HDN than pyridine type compounds, though aniline is more reactive than pyridine when the reaction is carried out individually or singly. It is concluded that inconsistent results observed can be interpreted in terms of the competitive adsorption of the reactants onto the catalyst surface, as well as in terms of the reactivities of the reactants. Nitrogen compounds also restricted the HDO of phenolic compounds.

1. Introduction

The naphtha fraction derived from coal is expected to be one of the most suitable blending stocks for motor gasoline because of its high contents of cyclic hydrocarbons. Hydrogenated coal naphtha has been found to be preferable for reforming to the corresponding petroleum fraction in our preliminary study. Since the contents of nitrogen and oxygen are high in the coal naphtha, the amounts of these elements must be reduced to acceptable levels to meet the specification of nitrogen content less than 1 N ppm for the consecutive reforming step. While removing sulfur is the main objective in hydrotreating of petroleum naphtha, removing nitrogen and oxygen is essential for coal naphtha. It is widely recognized that the removal of nitrogen- and oxygen-containing compounds requires severer conditions than the removal of sulfur-containing compounds^{1)~9)}. The properties of coal naphtha will affect HDN and HDO performances. However, most of the studies on HDN and HDO have been developed with a single model compound system; and neither practical feed stocks nor mixtures of model compounds have been satisfactorily examined compared with single model compounds^{3)~9)}. In this work three kinds of coal naphtha have been investigated; naphthas derived

from Wandoan and Illinois #6 sub-bituminous coal with 1 t/d Process Support Unit (PSU) of NEDOL process in Japan and the naphtha derived from Yallourn brown coal with 50 t/d Brown Coal Liquefaction (BCL) process in Australia. The aim of this study is to clarify the HDN and HDO performances of practical feed stocks and to compare the model reactions of several representative nitrogen- and oxygen-containing compounds which are found in coal-derived naphthas.

2. Experimental

2.1. Coal-derived Naphtha and Model Compounds

Three types of coal-derived naphthas, Wandoan, Illinois #6 and Yallourn coal-derived naphthas were used for reaction. Chemicals for HDN and HDO model reactions were obtained from commercial sources, their purity was more than 99%, and they were used without further purification. All the nitrogen- and/or oxygen-containing model compounds were added to toluene. Carbon disulfide was also added to the toluene solvent to maintain catalyst activity.

2.2. Reaction Apparatus and Procedure

Experiments were conducted at 300°C under the pressure of 3.0 MPa, the hydrogen to oil ratio of 700 Nm³/kl in a fixed-bed, down flow conventional plug flow reactor as shown schematically in **Fig.**

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Fig. 1 Schematic Diagram of the Reaction System

1. The liquid hourly space velocity (LHSV) was varied to observe any changes in HDN and HDO performances. The catalyst employed was S424, 3.2% nickel, 13.2% molybdenum supported on alumina. This type of catalyst has proved to be more favorable than cobalt-molybdenum supported on alumina for HDN because of the high hydrogenation activity of nickel molybdenum catalyst^{10,11}. Prior to use the catalyst was presulfided with straight run petroleum gas oil (LGO), 1.6% sulfur content, and under 5.0 MPa at 350°C for 14 h. Then the coal derived naphtha or a model compound was fed for 70 h to stabilize catalyst activity. The feed was mixed with hydrogen at the inlet of the reactor and heated up to the reaction temperature prior to contacting with the catalyst. For each run, the standard conditions; 300°C, 3.0 MPa, hydrogen to oil ratio of

700 N m³/kl, and LHSV of 2.0, were used before and after the run to guarantee that the catalyst had not deactivated during the run.

2. 3. Analysis

Gaseous products were measured by on-line gas flow meter and analyzed by on-line gas chromatography. Liquid products were measured using a load cell in order to calculate material balance, product yields and hydrogen consumption. The total nitrogen content in the liquid products was determined using a chemiluminescence analyzer (Mitsubishi Kasei, TN05). The amount of total oxygen was estimated by IR detection after converting the oxygenates to carbon monoxide in a combustion tube (Heraeus, CHN-O Rapid) under oxygen-free atmosphere. For identification and quantification of each molecule an external standard method, for carbon and oxygen a gas chromatography (HP5890II) equipped with an atomic emission detector (HP5921A), and for nitrogen a nitrogen-phosphorous detector were used, respectively.

3. Results

3. 1. HDN and HDO of Coal-derived Naphtha

3. 1. 1. Properties of Coal-derived Naphtha

The properties of coal naphtha derived from NEDOL process (in Japan) and BCL process (in Australia) are tabulated in Table 1. Concentrations of the representative nitrogen- and oxygen-containing compounds are tabulated in Table 2. The nitrogen-containing compounds primarily consists of three types, namely, pyridine/

Table 1 Properties of Coal-derived Naphtha

Liquefaction process		BCL		PSU	
Coal		Yallourn		Illinois #6	
Fraction		IBP-180°C		IBP-180°C	
				IBP-200°C	
				Wandoan	
				IBP-200°C	
Specific gravity		0.8041		0.7898	
Analysis				0.8256	
Oxygen [wt%]		3.2		2.1	
Nitrogen [wt%]		1,400		2,900	
Sulfur [wtppm]		1,600		1,950	
FIA [vol%]				1,600	
Paraffin & Naphthene		64.2		78.4	
Olefin		25.1		9.7	
Aromatics		10.7		11.9	
Distillation [°C]				21.1	
IBP		35		15	
5%		61		63	
10%		69		83	
20%		87		99	
30%		98		117	
40%		108		134	
50%		124		151	
60%		135		164	
70%		148		171	
80%		166		180	
90%		173		189	
95%		181		195	
EP		196		211	

Table 2 Nitrogen- and Oxygen-compounds in Coal-derived Naphtha

Coal-derived naphtha			Nitrogen compounds [N wtppm]					Oxygen compounds [O wt%]
Process	Coal	Fraction	Pyridine	Piperidine	Pyrrole	Pyrrolidine	Aniline	Phenol type
BCL	Yallourn	IBP-180°C	37	1	7	0	0	1.13
PSU	Illinois #6	IBP-180°C	11	0	50	0	33	1.16
PSU	Illinois #6	IBP-200°C	12	7	40	1	306	2.49
PSU	Wandoan	IBP-200°C	12	4	3	2	60	2.52

Table 3 Hydrodenitrogenation Conditions of Coal-derived Naphtha

Liquefaction process	BCL		PSU		
Coal	Yallourn		Illinois #6	Illinois #6	Wandoan
Fraction	IBP-180°C		IBP-180°C	IBP-200°C	IBP-200°C
LHSV [h ⁻¹]	1.1		0.9	0.5	0.7

Reaction conditions: 320°C, 30 kg/cm², 700 Nm³/kl (N<1 ppm).

Fig. 2 Effect of Fraction Range on HDN (changes in nitrogen compounds partial pressure of IBP-200°C and IBP-180°C fractions of Illinois #6 coal-derived naphtha versus spacetime)

piperidine, pyrrole/pyrrolidine and aniline. The oxygen compounds mainly consists of phenolic compounds.

3. 1. 2. HDN and HDO of Coal-derived Naphtha

Table 3 tabulates the LHSV required for decreasing the nitrogen level less than 1 N ppm by keeping the other reaction conditions constant. Coal, liquefaction process, and fraction range affected the reaction conditions. Figure 2 shows the change in nitrogen contents of IBP-180°C and -200°C fractions of Illinois #6 of NEDOL process as a function of reciprocal LHSV (IBP stands for initial boiling point). Apparently, IBP-200°C fraction requires severer conditions to remove its nitrogen than IBP-180°C fraction because not only of the higher content of nitrogen in IBP-200°C fraction but also because of the higher content of aniline type nitrogen-containing compounds

which are the most resistant nitrogen-containing compounds in coal naphtha as will be described below. Figure 3 shows the changes in pyridine/piperidine, pyrrole and aniline contents of the IBP-180°C fraction. Piperidine in Fig. 3 is the hydrogenated intermediate found in HDN of pyridine. In the coal-derived naphtha, aniline is more resistant than pyridine or pyrrole to HDN. Furthermore the HDN curve of aniline in Fig. 3 has a point of reflection. As HDN of pyridine or pyrrole proceeded, HDN of aniline is accelerated. A similar performance was also observed in HDN of the IBP-200°C fraction. As shown in Table 2, the IBP-200°C fraction of Illinois #6 contains aniline about an order of magnitude larger than in the IBP-180°C fraction. And the content of all aniline-type compounds is proportional to the content of aniline. Consequently, the IBP-200°C fraction contains not only more nitrogen-containing compounds, but more resistant compounds to HDN than the IBP-180°C fraction.

Figure 4 shows the change as a function of reciprocal LHSV in the phenolic oxygen compounds, which are practically the entire oxygenates in coal naphtha derived from Illinois #6. The rate of hydrodeoxygenation (HDO) is faster in the IBP-180°C fraction than in the IBP-200°C fraction. In HDO of phenolic compounds, the initial rate of HDO is increased with increasing initial content of phenolic compounds. The inconsistent results in this case is resulted from the inhibition effects of nitrogen compounds as will be described below.

3. 2. HDN and HDO of Model Compounds

3. 2. 1. Properties of the Feeds of Model Reaction

Pyridine, pyrrole and aniline as typical nitrogen-containing compounds were added to the toluene solvent and made to react individually or singly (referred to as a single nitrogen-containing

Fig. 3 Changes in Partial Pressure of Pyridine/Piperidine, Pyrrole, and Aniline in IBP-180°C Fraction of Illinois #6 Coal-derived Naphtha versus Spacetime

system or reaction). In the other case, all the compounds were added together and made to react simultaneously (referred to as three nitrogen-compound system). On the one hand, each nitrogen-containing model feed for single system was prepared to meet the requirement of 0.3 N wt% nitrogen content. On the other hand, the feed for three nitrogen-containing system, the total content was also 0.3 N wt%, 0.1 N wt% each. Phenol as a

Fig. 4 Effect of Fraction Range on HDO (changes in partial pressure of phenolic oxygen compounds of IBP-200°C and IBP-180°C fractions of Illinois #6 coal-derived naphtha versus spacetime)

typical oxygen-containing compounds were blended with the solvent in the amount of 2.0 O wt%. A model feed containing three nitrogen compounds, 0.1 N wt% each, and phenol, 2.0 O wt%, was also prepared to examine the interaction between nitrogen- and oxygen-containing compounds. All the model feeds contained 0.2 S wt% carbon disulfide to maintain the catalytic activity.

3. 2. 2. HDN of Model Nitrogen Compounds

Figure 5 (A) and (B) show the results of HDN of representative nitrogen-containing compounds, which are contained in the coal-derived naphtha. In (A) are shown the results of HDN reaction of nitrogen-containing compounds of pyridine, pyrrole and aniline carried out individually at the same initial nitrogen content and under the same reaction conditions. In contrast, in (B) are the results of HDN reaction of a pyridine, pyrrole, and aniline mixture in which the reaction was performed simultaneously as coal-derived naphtha. In the case of the single reaction, the removal of pyridine (pyridine and piperidine) was the most resistant among the three nitrogen compounds as indicated in Fig. 5 (A). This is an inconsistent result with the result of HDN of coal-derived naphtha. However, the result of the simultaneous reaction of the three nitrogen compounds in the same phase shown in Fig. 5 (B) represents a similar performance as that of the coal-derived naphtha as shown in Fig. 3.

3. 2. 3. HDO of Model Oxygen Compounds

Phenol is the most abundant oxygen-containing compound in coal-derived naphtha. Therefore

Fig. 5 Changes in Partial Pressure of Pyridine/Piperidine, Pyrrole, and Aniline in Individual Reaction (A) and Simultaneous Reaction (B) versus Spacetime in Model Reaction

hydrodeoxygenation (HDO) of model reaction was examined by using phenol. The contents and compositions of nitrogen-containing compounds are the same as the model feed of simultaneous reaction of the three nitrogen compounds. **Figure 6** represents the HDO performance of phenol for the cases of including and not including nitrogen-containing compounds. HDO of phenol is strongly inhibited by the nitrogen-containing compounds. This performance is similar to that of coal-derived naphtha.

4. Discussion

4. 1. HDN Performance of Coal-derived Naphtha

Typical nitrogen-containing compounds in coal-derived naphtha are pyridine, pyrrole, and aniline and their alkyl derivatives. Though aniline and pyrrole are more reactive than pyridine

Fig. 6 Inhibition Effects of Nitrogen Compounds on HDO of Phenol (changes in phenol partial pressure in nitrogen compounds included and excluded case in model reaction)

Scheme 1 Competitive Reaction in HDN

in the single reactions; aniline was the least reactive in simultaneous reactions such as HDN of coal-derived naphtha and mixtures of nitrogen compounds. It is generally recognized that a Langmuir-Hinshellwood type kinetic expression is employed to represent the HDN reaction. For instance, as shown in **Scheme 1**, aniline is as reactive as pyrrole if the reaction is examined individually.

On the one hand, the rate of HDN was expressed as follows, assuming that hydrogen was adsorbed on different sites from the sites on which nitrogen-containing compounds was adsorbed.

$$-\frac{dP_{\text{pyr}}}{dt} = \frac{K_{\text{pyr}}P_{\text{pyr}}}{1 + K_{\text{pyr}}P_{\text{pyr}} + K_{\text{AM}}P_{\text{AM}}} P_{\text{H}_2}k_{\text{pyr}}$$

$$-\frac{dP_{\text{ani}}}{dt} = \frac{K_{\text{ani}}P_{\text{ani}}}{1 + K_{\text{ani}}P_{\text{ani}} + K_{\text{AM}}P_{\text{AM}}} P_{\text{H}_2}k_{\text{ani}}$$

P_{pyr} , P_{ani} , P_{AM} , and P_{H_2} donate partial pressures of

pyrrole, aniline, ammonia, and hydrogen, respectively. K_{pyr} , K_{ani} , and K_{AM} are the corresponding adsorption equilibrium constants. k_{pyr} and k_{ani} are HDN rate constants of pyrrole and aniline. On the other hand, the rate of HDN is expressed as follows when pyrrole and aniline are existing in the same phase in which aniline is more resistant to HDN than pyrrole.

$$-\frac{dP_{\text{pyr}}}{dt} = \frac{K_{\text{pyr}}P_{\text{pyr}}}{1 + K_{\text{pyr}}P_{\text{pyr}} + K_{\text{ani}}P_{\text{ani}} + K_{\text{AM}}P_{\text{AM}}} P_{\text{H}_2}k_{\text{pyr}}$$

$$-\frac{dP_{\text{ani}}}{dt} = \frac{K_{\text{ani}}P_{\text{ani}}}{1 + K_{\text{pyr}}P_{\text{pyr}} + K_{\text{ani}}P_{\text{ani}} + K_{\text{AM}}P_{\text{AM}}} P_{\text{H}_2}k_{\text{ani}}$$

HDN of nitrogen-containing compounds can be interpreted in terms of the competitive adsorption of each nitrogen-containing compound onto the catalyst surface. Nagai *et al.*⁹⁾ explained the reactivity of nitrogen compounds in terms of gas-phase basicity (GB); the adsorption equilibrium constant is proportional to GB's. Aue *et al.*¹²⁾ measured the gas-phase basicities of several nitrogen compounds and obtained order of GB as piperidine (221.5 kcal/mol) > pyridine (220.4) > aniline (207) > pyrrole (205). Myton *et al.*¹³⁾ calculated GB's from the heats of formation of 127 compounds containing carbon, hydrogen, nitrogen and oxygen. They also resulted in the same order as Aue *et al.* had determined. Therefore the reactivity of each nitrogen-containing compound could be explained by its GB; the greater is the GB value of a molecule, the stronger is its adsorption onto the catalyst surface. This is expressed by $K_{\text{ani}} > K_{\text{pyr}}$. As a consequence, the order of rate would be $r_{\text{ani}} > r_{\text{pyr}}$ because HDN rate is almost the same when HDN reaction is performed individually. The terms of r_{ani} and r_{pyr} stand for HDN rate of aniline and pyridine, respectively. In contrast to the single reactions, pyrrole is more reactive than aniline in simultaneous reactions. The value of $K_{\text{pyr}}k_{\text{pyr}}$ will then be larger than that of $K_{\text{ani}}k_{\text{ani}}$. The denominator of the equation for the reaction of pyrrole and aniline together is the same at any reaction time.

4.2. HDO Performance of Coal-derived Naphtha

As shown in Fig. 6, hydrodeoxygenation (HDO) of phenol is strongly inhibited by coexisting nitrogen-containing compounds. Though phenol is an acidic compound and such nitrogen-containing compounds as pyridine, pyrrole, and aniline are basic compounds, these two types of compounds react competitively¹⁴⁾. Myton *et al.* calculated the phenol GB value to be 149.6 kcal/mol, while GB's of pyridine, pyrrole, and aniline

were in the range of 199.4–209.8 kcal/mol; moreover, the adsorption equilibrium constant of phenol would be less than the constants of the nitrogen-containing compounds. Consequently, the HDO of phenol could also be explained by the Langmuir–Hinshellwood type competitive reaction.

5. Conclusions

Hydrodenitrogenation (HDN) and hydrodeoxygenation (HDO) of coal naphthas derived from NEDOL Process, Process Support Unit, in Japan, and those derived from BCL Process in Australia were examined in order to clarify the reactivities of nitrogen- and oxygen-containing compounds, and the results are compared with those of individual reactions. A Langmuir–Hinshellwood type competitive reaction is suggested for the reaction of HDN and HDO of practical feed stocks. Though aniline is the most reactive and the pyridine the least reactive among three representative nitrogen-containing compounds, pyridine, pyrrole, and aniline in the individual reactions, pyridine is denitrogenated in preference to aniline in both the simultaneous reaction and the coal naphtha reaction. It is clear that the accessibility of nitrogen-containing molecules to the catalyst surface, as well as their reactivities, gives a pronounced influence on the HDN and HDO performances in the reaction of practical feed stocks. Compounds that have relatively weak accessibility to the catalyst surface are easily inhibited from reaching the catalyst surface by other compounds in the feed stock.

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要 旨

石炭液化油ナフサ留分の水素化脱窒素, 脱酸素における反応物の相互阻害

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Ni-Mo/Al₂O₃ 系触媒にて石炭液化油ナフサ留分とそのモデル物質の水素化脱窒素と水素化脱酸素を調べた。石炭液化油については沸点範囲が変わったときに反応速度にどのように影響を及ぼすかを主に調べた。液化油中には含窒素化合物としてアニリン, ピロールおよびピリジン系の化合物, 含酸素化合物としてフェノール系の化合物が含まれる。アニリン, ピロール, ピリジンの脱窒素を個別に調べるとアニリンの反応が最も速い

が, 液化油のようにこれらの窒素化合物が共存している系では, 逆にアニリンの脱窒素が最も遅くなる。さらに, 窒素化合物とフェノール系の酸素化合物が共存した場合, 窒素化合物は脱酸素反応を阻害する。これらの現象は窒素化合物同士, または窒素化合物と酸素化合物の間での競争吸着メカニズムで説明できる。

Keywords

Naphtha, Nitrogen compound, Oxygen compound, Hydrodenitrogenation, Hydrodeoxygenation