Catalytic Hydrodealkylation of SRC (Solvent Refined Coal) Fractions

Toru IDA, Takashi KIKUKAWA, Kenji MATSUBAYASHI,
Mikio MIYAKE, and Masakatsu NOMURA*

Department of Applied Chemistry, Faculty of Engineering, Osaka University,
2-1, Yamadaoka, Suita, Osaka 565

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Hydrodealkylation (HDA) reactions of SRC fractions and the related aromatic hydrocarbons were examined over three types of catalysts, i.e., La-Y (La-exchanged Y-zeolite), NiMoCo (NiMoCo/SiO₂-Al₂O₃), and Cr (Cr₂O₃/MgO/Al₂O₃) catalysts. The NiMoCo catalyst showed the best results for HDA of hexane-soluble fraction (HS) of SRC, giving the highest yield of naphthalene (12 wt%) with a low yield of coke (9.9 wt%). The strong acidity of La-Y caused coke formation of both the HS fraction of SRC and 9-methylanthracene; and it also caused transalkylation of 2,6-dimethylnaphthalene and the formation of naphthalene (58 wt%). In view of the lesser formation of coke attained by suppressing the retrogressive reactions of the reactive fragments generated during HDA, hydrogenation activity seems to be very important for HDA catalysts of excellent performance.

1. Introduction

There are a number of coal liquefaction processes whose aims are to achieve economical production of liquid fuels from coal^{1,2)}. On the basis of coal structures proposed³⁾ hitherto, coal-derived liquids, such as SRC (Solvent Refined Coal), can not only be a potential source of liquid fuels but also a potential source of aromatic chemicals.

Since it is not possible to separate any specific compound efficiently from a complex or multi-component mixture such as SRC, hydrodealkylation (HDA) reaction should be one of the most promising process as to break down the complexity of such a mixture and to recover aromatic chemicals selectively. In practice, HDA of alkylbenzenes to produce benzene⁴⁾ has been carried out at reaction temperatures as high as 500—650°C, where coke formation is a serious problem⁵⁾. Therefore, it becomes very important to develop catalysts possessing high activity for HDA, high selectivity for aromatics, and high power for suppressing coke formation.

In this paper, hexane-soluble (HS) and benzene-soluble (BS) fractions of SRC were hydrodealkylated using three types of catalysts, and the results obtained were discussed by referring to and based on the results of HDA of the aromatic model compounds over these catalysts.

2. Experimental

2.1 Sample Preparation

SRC was prepared from Akabira coal (Japanese bituminous coal) using a 3t/d pilot plant built by Sumitomo Coal Mining Co., Ltd. Substances with boiling points lower than the boiling point of naphthalene were removed from SRC by distillation before use.

A 10 g of SRC was extracted in refluxed benzene (300 ml) for 3 hr, and the resulting benzene-extract was separated from the solid benzene-insolubles by filtration. The extract was concentrated to about 20 ml, then it was poured into 1,000 ml of hexane to precipitate out hexane-insolubles (HI-BS). Hexane-soluble (HS) was obtained by evaporating the hexane from the filtrate. Elemental analyses of HS, HI-BS, and benzene-soluble (BS) thus obtained are listed in Table 1.

2-Methylnaphthalene (2-MN), 2-ethylnaphthalene (2-EN) and 2,6-dimethylnaphthalene (DMN) were

Table 1 Elemental analyses of SRC fractions

Fraction	Content in SRC (wt%)	Elemental analyses(wt%)			
		C	H	N	S+O(diff.)
HS ^{a)}	34	89.6	7.3	1.0	2.1
HI-BS ^{b)}	13	84.1	6.4	2.0	7.5
BS ^{c)}	47	87.9	6.8	1.3	4.0

a): Hexane-soluble fraction.

b): Hexane-insoluble and benzene-soluble fraction.

c): Benzene-soluble fraction, before separating into HS and HI-BS.

* To whom correspondence should be addressed.

purchased and used without further purification. 9-Methylantracene (MA) was prepared from 9-anthrone according to the procedures described in the literature⁶⁾.

2.2 Catalyst Preparation

The catalysts used for HDA are:
a) Cr catalyst (12 wt% Cr₂O₃, 3 wt% MgO, bulk Al₂O₃, Nikki Chemical Co., Ltd.),
b) La-Y catalyst (85% of Na⁺ ion in Y-zeolite was exchanged with La³⁺)⁷⁾,
c) NiMoCo catalyst (10 wt% Ni, 3 wt% Mo, 1 wt% Co, bulk SiO₂/Al₂O₃; prepared by impregnation followed by reduction at 400°C for 6 hr under flowing hydrogen).

The catalysts were dried at 100°C for 2 hr under vacuum, and crushed to sizes smaller than 100 mesh before use.

2.3 Hydrodealkylation (HDA) Procedures

The HDA reaction was carried out using a 50 ml autoclave (Hastelloy-X). A substrate (1 g of a model compound or 2 g of an SRC fraction) was charged into the autoclave together with a catalyst (10 wt% of the substrate). HDA, using benzene as the solvent, was also carried out, where 1 g of a model compound, 4 g of benzene, and a catalyst (10 wt% of substrate) were charged into the autoclave. The system was flushed and purged several times with hydrogen and pressurized up to 2.0 MPa at ambient temperature. The reaction system was then heated up to 550°C at the rate of 5–7°C/min and kept at 550°C for 2 hr. After the reaction, the system was cooled to room temperature using an electric fan.

The gaseous products were collected in a gas bag and analyzed by GC (TCD). The liquid products obtained from HDA of the model compounds were collected in the form of acetone solution which was analyzed by GC (TCD). After HDA of the SRC fraction, the autoclave was kept at 40°C under vacuum to distill off the low-boiling point materials (LBP). The liquid and solid products remaining in the autoclave were then rinsed with benzene and separated into benzene-solubles (BS) and benzene-insolubles (Coke). The compositions of LBP and BS were analyzed with GC (FID) using cumene as an internal standard.

2.4 ¹H NMR Spectroscopy

Proton NMR spectra were recorded at a 400 MHz JEOL JNM-GXS 400 for 10 wt% chloroform-d₁ solutions of HS and HI-BS fractions containing TMS as an internal standard.

3. Results

3.1 HDA of Model Compounds

Table 2 shows the results of HDA of 2-MN and

Table 2 Results of HDA Reactions^{a)} of 2-MN^{b)} and 2-EN^{b)}

Run No.	1	2	3	4
Subst.	2-MN ^{b)}	2-MN ^{b)}	2-MN ^{b)}	2-EN ^{b)}
Cat./Solv.	—/—	Cr/—	Cr/Benzene	Cr/Benzene
Conv.	88	90	91	95
Products (wt%) ^{c)}				
Gas				
C ₁	11	11	13	7
C ₂	8	9	2	5
C ₃	2	5	1	1
Benzene	1	2	Solvent	Solvent
Toluene	1	2	1	1
Xylene	1	2	—	—
N ^{b)}	66	61	59	54
MN ^{b)}	12	10	9	2
EN ^{b)}	—	—	—	5

a): Reaction conditions : Substrate/Cat./Solvent=1/0.1/(4) g/g(/g), H₂(init.)=2.0 MPa, reaction temp.=550 °C, and reaction time=2 hr.
b): N : naphthalene, MN : methylnaphthalene and EN : ethylnaphthalene.
c): Yields are based on the amount of input substrate.

2-EN with and without benzene as the solvent over the Cr catalyst. No significant difference was observed between the HDA reactions of 2-MN with and without the solvent (Run 2, 3) in view of both conversion (about 90 wt%) and yield of naphthalene (N) (59~61 wt%). However, in the run with the solvent (Run 3) a substantial amount of biphenyl (about 20 wt% vs. substrate) was obtained due to the coupling reaction of the solvent. Both 2-MN (Run 3) and 2-EN (Run 4) seem to have similar reactivities toward HDA, though the naphthalene yield from 2-EN was slightly lower (54 wt%) than that from 2-MN (59 wt%).

Figures 1 a~d show the results of HDA of 2,6-DMN at 550°C for 2 hr. Without catalyst, 74 wt% of 2,6-DMN was converted, yielding naphthalene in 40 wt% (Fig. 1 a). The Cr catalyst (Fig. 1 b) mainly increased the yields of cracking products (gas and alkylbenzenes) to 26 wt% compared to 20 wt% (Fig. 1 a) without catalyst. The La-Y catalyst drastically increased the conversion of 2,6-DMN (97 wt%), and the yield of cracking products increased (41 wt%; Fig. 1 c). As a result, it was observed that the yields of naphthalene were similar among these reactions and were in the range of 40~43 wt%.

The NiMoCo catalyst gave the highest conversion of 2,6-DMN (99 wt%) among the catalysts used; however, it mainly yielded cracking products (73 wt%), resulting in the lowest yield of naphthalene (22 wt%) as shown in Fig. 1 d.

Figure 2 shows the effect of reaction time on HDA of 2,6-DMN using the three catalysts. HDA of 2,6-DMN seems to proceed stepwise to produce MN and naphthalene. Among the catalysts used, the La-Y catalyst gave both the highest conversion

Fig. 1 Results of HDA of 2,6-Dimethylnaphthalene at 550°C for 2 hr (Substrate/Cat.=1/0.1 g/g, initial H_2 =2.0 MPa)

Fig. 2 Effect of Reaction Time on HDA of 2,6-Dimethylnaphthalene at 550°C (Substrate/Cat.=1/0.1 g/g, initial H_2 =2.0 MPa)

(100 wt%) and yield of naphthalene (58 wt%) when the reaction time was 3 hr. However, trimethylnaphthalene (TMN) was produced by transalkylation of DMN at an early stage of the reaction (less than 1 hr; Fig. 2) or at low reaction temperatures (Fig. 3). In addition to TMN, isomers of MN and DMN were observed in the HDA products over the La-Y catalyst, while these products were not observed over the Cr catalyst or over the NiMoCo catalyst. The production of TMN and isomers of MN and DMN probably resulted from the strong acidity of the La-Y catalyst. A high conversion (97 wt%; Fig. 2) was also obtained by using the NiMoCo catalyst, but the yield of naphthalene was less than 30 wt%.

Figures 4a~d show the results of HDA of 9-methylantracene (MA) over the three types of

Fig. 3 Effect of Temperature on HDA of 2,6-Dimethylnaphthalene over La-Y catalyst at 550°C for 2 hr (Substrate/Cat.=1/0.1 g/g, initial H_2 =2.0 MPa)

catalysts. HDA without catalyst (Fig. 4a) revealed that 99 wt% of the methyl group of 9-MA was thermally demethylated. The Cr catalyst promoted the decomposition of anthracene (AN) and increased MN, naphthalene (N), and gas yields (Fig. 4b). When the La-Y catalyst was used (Fig. 4c), conversion was unexpectedly low (94 wt%). A substantial amount of coke (17 wt%) was formed over this catalyst. This formation of coke resulted from both transalkylation and isomerization reactions that took place during the HDA of 2,6-DMN (Fig. 2c). The NiMoCo catalyst showed a 98 wt% conversion, however, it promoted the subsequent hydrocracking of AN, giving high yield (50 wt%) of cracking products such as gas and alkylbenzenes (Fig. 4d).

Yields of hydroaromatics by HDA of 9-MA were very small and they were included in 'Others' in Figs. 4a~d; for example, yields of 9,10-dihydro- and 1,2,3,4-tetrahydroanthracenes were less than

Fig. 4 Results of HDA of 9-Methylantracene at 550° for 2 hr (Substrate/Cat.=1/0.1 g/g, initial H_2 =2.0 MPa)

Fig. 5 Gas chromatograms of
a) HS fraction of SRC and
b) HDA Products from HS fraction of SRC at 550°C for 2 hr (Substrate/NiMoCo Cat.= 2/0.2 g/g, initial H_2 =2.0 MPa)

1/10 of the yield of naphthalene. The hydroaromatics would be dehydrogenated reversely or decomposed under the HDA conditions prevailed.

3.2 HDA of SRC Fractions

FD-MS measurements¹⁶⁾ suggested that both HS and HI-BS fractions of SRC are multi-component mixtures of hydrocarbons having molecular weight distributions up to m/z 500 (with HS) and 1,000 (with HI-BS).

However, Curie-point Pyrolysis-GC-MS (Py-GC-MS) analyses¹⁶⁾ revealed that 88 wt% of HS and 57 wt% of HI-BS fractions of SRC were devolatilized by pyrolysis, and they were very similar from the viewpoint of chemical constituents. The constituents were mainly alkylnaphthalenes along

with benzene, biphenyl, dibenzofuran, fluorene, phenanthrene, anthracene, and their alkyl homologues. Though the pyrograms of these fractions are very complicated by the presence of such alkylaromatics mentioned above, it seems possible to simplify the compositions of these fractions by HDA under selective reaction conditions to facilitate the production of individual aromatic chemicals from these fractions.

Figures 5 a and b show the gas chromatograms of HS and HDA products from HS, respectively. These figures demonstrate that HDA could give a simplified composition containing the aromatic compounds of above mentioned skeletons.

The results of HDA of HS from SRC over the

Table 3 Results of HDA Reactions^{a)} of SRC HS Fraction

Run No.	5	6	7	8	9	10
Substrate	HS	HS	HS	HS	BS	BS
Catalyst	—	Cr	La-Y	NiMoCo	—	NiMoCo
Products (wt%) ^{b)}						
Gas	23.9	27.0	22.1	25.9	27.4	27.4
LBP ^{c)}	11.3	5.5	7.7	5.1	10.3	10.4
Naphthalene	7.8	8.5	10.1	12.0	1.1	0.9
Naphthalene-R ^{c)}	6.6	8.1	10.5	6.5	4.0	16.5
Biphenyl	1.4	1.8	1.9	1.7	1.1	2.2
Biphenyl-R ^{c)}	1.3	1.6	1.5	1.3	0.9	2.3
Dibenzofuran	4.2	3.7	5.6	3.6	2.4	4.7
Fluorene	5.5	6.6	8.2	7.8	3.3	9.3
Phenanthrene +Anthracene	2.7	4.0	5.3	5.7	2.4	6.6
Others ^{d)}	24.3	14.5	8.4	15.8	— ^{d)}	— ^{d)}
Coke	16.2	14.1	18.7	9.9	28.5	26.9

a): Reaction conditions : SRC HS/Cat=2/0.2 (g/g), H₂ (init.)=2.0 MPa, reaction temp.=550 °C, and reaction time=2 hr.

b): Yields are based on the input substrate.

c): Gas : C₁—C₄, LBP : materials with low boiling point, -R : alkylated homologues, Others : materials with high boiling point.

d): Not calculated.

three catalysts are summarized in **Table 3**. Naphthalene, the target product of HDA of SRC fractions, was obtained with a yield of 7.8 wt% without catalyst (Run 5). A large quantity of coke formation (16.2 wt%) might have been caused by catalysis due to the wall effect of the autoclave⁸⁾. The NiMoCo catalyst showed the best result of HDA (Run 8) with a naphthalene yield of 12.0 wt% and with a low formation of coke (9.9 wt%). The La-Y catalyst gave a 10.1 wt% yield of naphthalene; however, a substantial amount of coke (18.7 wt%) was produced (Run 7). These results are different from the results of HDA reactions of 2,6-DMN and 9-MA, in which naphthalene yields over the La-Y catalyst were higher than over the NiMoCo catalyst.

The Cr catalyst showed relatively low activity for HDA, yielding 8.5 wt% of naphthalene and 14.1 wt% of coke. This result may be attributed to the MgO usually added to the the Cr catalyst to control its acidity⁹⁾.

HDA of BS was carried out with and without the NiMoCo catalyst, and the results obtained are listed in **Table 3**. When the NiMoCo catalyst was used (Run No. 10), yields of alkynaphthalenes reached 16.5%; however, the yield of naphthalene was less than 1%. A large amount of coke (over 26%) was produced from both HDA runs (No.9 and 10). The coke made it difficult to recover the products.

4. Discussion

The features of the catalysts used in this work differed among themselves as follows: both the Cr and La-Y catalysts have Lewis acidity which would promote HDA by carbenium ion mechanism, while the NiMoCo catalyst exhibits high activity

in hydrogenation reaction that would promote HDA by radical mechanism. Such features of the catalysts are well demonstrated by the results of HDA of the model compounds. For example, the first order rate constants of HDA of 2,6-DMN were calculated from **Fig. 2** as 0.29, 1.16, and 2.30 hr⁻¹ over the Cr, La-Y, and NiMoCo catalysts, respectively, resulting in the conversions of 2,6-DMN (**Fig. 1**) of 73 wt% (Cr), 97 wt% (La-Y), and 99 wt% (NiMoCo).

The HDA of 2,6-DMN would be initiated by the addition of proton (H⁺) or hydrogen atom (H·) as follows^{10)~14)}:

The stronger acidity of the La-Y compared to that of the Cr would have resulted in the high activity of the La-Y in HDA of 2,6-DMN (**Fig. 1**). At an early stage of the reaction, the acidity of La-Y is assumed to cause the transalkylation of 2,6-DMN to generate TMN as follows^{10),15)}:

TMN could be hydrodealkylated at times of reaction longer than 2 hr (**Fig. 2**) or at temperatures higher than 550°C (**Fig. 3**). However,

the intermolecular reaction of Eq. (2) would be unfavorable to the substrate which has a larger aromatic system, such as for 9-MA or HS fraction of SRC. As for HDA reactions without catalyst, differences in HDA reactivities among 9-MA, 2-MN, and 2,6-DMN can easily be expected on the basis of their aromatic ring size^{12)~14)}. When 9-MA is hydrodealkylated over the NiMoCo catalyst, the dealkylated product, anthracene, seems to undergo further hydrogenation, resulting in high yields of gas and alkylbenzenes and a low yield of anthracene (2 wt%; **Fig. 4 d**).

Although the chemical composition of HS of SRC is very complex because of the maximum MW of about 500 measured by FD-MS analysis, Py-GC analysis revealed that 88% of HS were devolatilized by pyrolysis. The devolatilized materials were basically alkylaromatics¹⁶⁾, which were considered to be acceptors of H⁺ or of H· during the HDA reaction over the catalysts used in this work. However, the production of a large amount of coke produced by using the Cr catalyst or the La-Y catalyst suggests that it would not be appropriate to carry out HDA over acidic catalysts under the conditions employed in this work. Thus, the HDA catalyst should attain the activity for hydrogenation as high as that attained by the NiMoCo catalyst.

The HDA of HS did not show such a distinctive difference in the catalytic activity as was observed in the HDA of the model compounds. For example, the gas yields from HDA of 2,6-DMN (**Fig. 1**) and 9-MA (**Fig. 4**) increased in the order: without catalyst < Cr catalyst < La-Y catalyst < NiMoCo catalyst. The NiMoCo catalyst especially showed a high gas yield of over 45%, which would have resulted from the cracking of the hydrogenated aromatics. Such order of catalyst activities was not observed in the gas yields from HDA of HS, but it appeared in the yields of naphthalene and coke. Such observations suggest that the NiMoCo catalyst would promote the hydrogenation (stabilization) of the reactive fragments generated from HS.

As for the HDA reaction of BS fraction of SRC (**Table 3**), runs with the NiMoCo catalyst showed an alkyl naphthalene yield of 16.5%, whereas it also produced as large an amount of coke as that from HDA without the catalyst (26.9 and 28.5%, respectively). The Py-GC analysis revealed that 56.9 wt% of HI-BS was devolatilized by pyrolysis and the resulting volatile materials had structures similar to those from HS. However, a larger amount of pyrolysis residue (43 wt% from HI-BS and 12 wt% from HS), a wider range of distribution of molecular weight (up to 1,000 in HI-BS and

Fig. 6 ¹H NMR Spectra of
a) HS and
b) HI-BS fractions of SRC

500 in HS by FD-MS analyses)¹⁶⁾, and higher contents of heteroatoms (**Table 1**) suggest that more complicated structures and many types of bonding are likely to exist in HI-BS than in HS. Proton NMR spectra of HS fraction (**Fig. 6 a**) and HI-BS fraction (**Fig. 6 b**) also support such differences in chemical structure between the two fractions, i.e., the peaks in the region of aliphatic protons (chemical shift of about 0.2~5.0 ppm) are broader in the spectrum of HI-BS and the degree of substitution, σ , calculated by Brown-Ladner's method¹⁷⁾, is higher for HI-BS (0.44) than for HS (0.29). Therefore, it is likely to assume that the cleavages of aryl-alkyl or aryl-ether bonds would proceed at lower temperatures than those of HS. Unless such radicals could be stabilized by hydrogenation at low temperatures, they would be stabilized by recombination leading to coke formation (**Table 3**). The HDA of such a heavy fraction as BS of SRC needs further optimization of reaction conditions, for example, application of higher H₂ pressures or use of solvent to utilize more hydrogen or to facilitate dispersion of the catalyst into the SRC/solvent mixture.

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要 旨

SRC (Solvent Refined Coal) から得た留分の接触水素化脱アルキル反応

井田 徹, 菊川隆司, 松林賢司, 三宅幹夫, 野村正勝

大阪大学工学部, 565 大阪府吹田市山田丘 2-1

本研究では, タイプの異なる 3 種の触媒を用いて, SRC (Solvent Refined Coal) のヘキサン可溶分 (HS), ベンゼン可溶分 (BS), およびモデル化合物としてアルキル置換芳香族化合物を選び, それらの水素化脱アルキル反応 (HDA) を行い, 生成物の分析からアルキル置換芳香族化合物の構造の違いと HDA に対する反応特性の関係および触媒活性の評価を行った。

使用した触媒は NiMoCo 触媒 (10 wt% Ni, 3 wt% Mo, 1 wt% Co, bulk $\text{SiO}_2/\text{Al}_2\text{O}_3$), La-Y 触媒 (Y-型ゼオライトの Na^+ イオンの 85% を La^{3+} で交換したもの) および Cr 触媒 (12 wt% Cr_2O_3 , 3 wt% MgO , bulk Al_2O_3) である。反応には 50 ml/ハステロイ-X 製オートクレーブを用い, 試料 (SRC 留分 2 g と触媒 0.2 g またはモデル化合物 1 g と触媒 0.1 g) を充填し, 初期水素圧 2.0 MPa, 反応温度 550 °C で 2 時間反応させた。また反応温度と時間を変化させた実験も行った。

2-メチルナフタレン (Table 2), 2-エチルナフタレン (Table 2), 2,6-ジメチルナフタレン (Fig. 1) および 9-メチルアントラセン (Fig. 4) の結果の比較から, アルキル置換芳香族化合物の HDA 特性はアルキル鎖の炭素数よりも, 縮合芳香環の大き

さやアルキル置換基の数に大きく依存する傾向が得られた。2,6-ジメチルナフタレンの HDA を 550 °C で反応時間を変化させて行ったところ, 触媒活性は NiMoCo, La-Y, および Cr 触媒の順で低下することがわかった。

La-Y 触媒はその強い Lewis 酸性のため, 2,6-ジメチルナフタレンの HDA (Fig. 2) では不均化反応生成物 (トリメチルナフタレンやメチルナフタレン) および異性化反応生成物であるジメチルナフタレンの異性体を生成し, また 9-メチルアントラセンの HDA では, アルキルベンゼン類やガスのような分解生成物が多く生成した。

SRC-HS の HDA をこれら NiMoCo, La-Y, および Cr 触媒を用いて行ったところ, ナフタレン収率 (それぞれ 12.0, 10.2 および 8.5 wt%) およびコーク生成量 (それぞれ 9.9, 18.7 および 14.1 wt%) の点から, NiMoCo 触媒が最も優れた結果を示した。

以上の結果から, 高温条件下で行われる HDA 用の触媒としては, 生成する活性フラグメントの安定化という観点から, 水素化能の高いことが非常に重要であると考えられる。

Keywords

Solvent refined coal, Model compound, Hydrodealkylation, Lanthanum zeolite Y, Chromium magnesia alumina, Nickel molybdenum cobalt