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# Upgrading of Coal Liquid on Pentasil Type Ga-Silicate

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Although coal liquid showed negligible reactivity on the pentasil type Ga-silicate because of the presence of inhibitors, it significantly increased in reactivity by washing with polar organic solvents and afforded BTX in a 60% yield.

Recently, coal liquefaction process has gathered renewed interest because of the prospective exhaustion of crude oil resources. Since coal liquid contains various oxygen or nitrogen compounds, effective processes for the conversion of coal liquid into marketable products such as transportation fuels and chemical feedstocks have been sought.1) During the course of our work on the catalysis of microporous crystals,2) we have examined the reactivity of coal liquid on an H-Ga-silicate, and will propose here a new upgrading method by which naphtha fractions of a coal liquid is converted into aromatic compounds.

The coal liquid, concerned in the present work, was kindly provided by NEDO and was produced on a 1 t/d process servo-unit for NEDOL process3) by liquefaction of a Wandan coal at 450 °C and 170 kg/cm$^2$ for 60 min. Two naphtha fractions of the coal liquid were used; one was the light naphtha (LN: boiling range; 40-200 °C) and the other was the hydrogenated naphtha

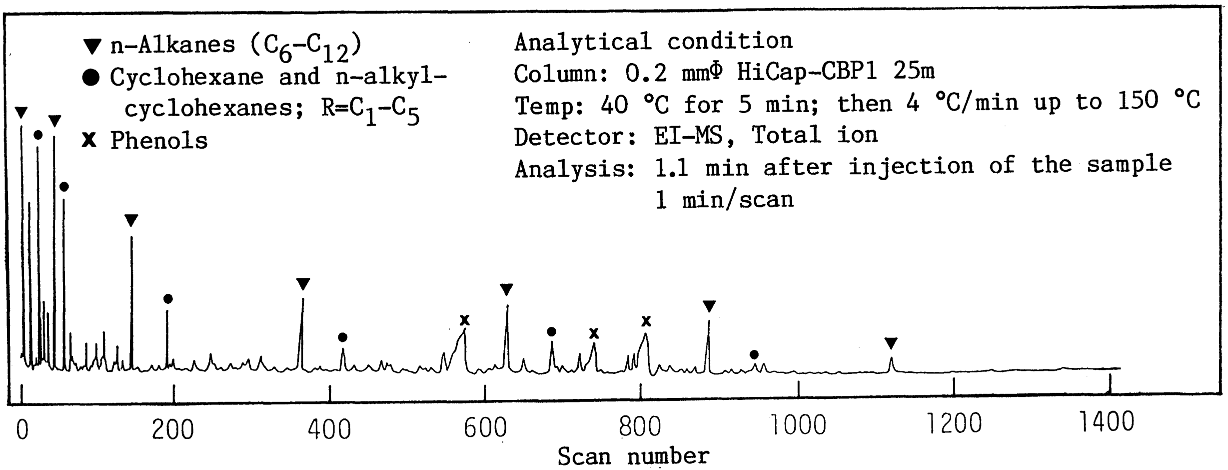

Fig. 1. Gas-chromatograph of the light naphtha.

(HN), the low boiling point fraction removed from hydrogenated vacuum distillate before recycling to the reactor as a hydrogenation solvent.

A pentasil-type Ga-silicate (Si/Ga = 20) was prepared according to the rapid crystallization method$^{4)}$ developed in this laboratory. The reactions were carried out in a flow reactor made from quartz tubing, 6.1 mm, i.d. The catalyst was tabletted, pulverized, sieved into 10-20 mesh, set in the reactor, and then pre-calcined in situ at 500 °C for 30 min in a flow of nitrogen. The feed material was introduced to the preheating zone of the reactor with a micro tube pump. The typical reaction conditions were as follows: LHSV, 1.8 $h^{-1}$; flow rate of entrainer (nitrogen), 1.2 l/h. The reaction temperature was gradually raised from 300 °C to 600 °C. The identification of components of the coal liquid and the products was carried out by using a Shimadzu QP1000EX GCMS with a Hicap-CBP1 column.

The both naphtha fractions were composed of $C_4$-$C_{12}$ hydrocarbons, phenols, and traces of amines. Normal paraffins were the dominant components in LN (Fig. 1), while n-alkylcyclohexanes were predominant in HN. Besides these compounds, more than 140 components including dialkylcycloalkanes, octahydroindenes and aromatics were detected and identified.

These compositions of the naphtha fractions promoted us to explore the conversion of the coal liquid on H-Ga-silicate because we had already found that the H-Ga-silicate exhibited quite high activities for aromatization of light paraffins or cycloalkanes.$^{5,6)}$ To our surprise, both naphtha fractions showed negligible reactivity on Ga-silicate. By examining the reactivity of the model compounds (n-octane for LN and cyclohexane or methylcyclohexane for HN) in the presence of phenols or amines, we concluded that the reasons for the low reactivity of the coal liquid are three fold: a) adsorption of the basic compounds on the acid sites of the catalyst; b) inhibitory effect of phenols;$^{7)}$ c) rapid deactivation of the catalyst due to the deposition of coke precursors formed during storage of coal liquid.$^{8)}$

Figure 2 shows the results of the conversion of HN before and after the washing with aqueous acid and base solutions. These treatments removed the inhibitors from the naphtha, significantly increasing the reactivity of the remaining hydrocarbons and the yield of

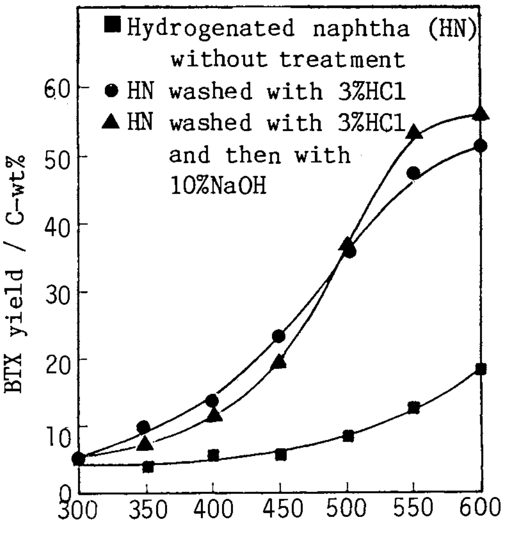

Fig. 2. Effects of washing with aqueous acid and base solutions on the upgrading of hydrogenated naphtha on Ga-silicate.

BTX. The light naphtha gave the similar results and the yield of BTX reached to 41% at 500 °C. From the practical point of view, however, such a process must treat huge amounts of waste water, which will cause other problems. Moreover, when the naphtha fractions after washing with acid and then base solutions were preserved for a few weeks, insoluble organic matter (sludge) was deposited. To overcome these disadvantages, we explored the extraction with aqueous methanol which can be easily separated from the extract by distillation. The partitions of phenols and hydrocarbons of LN between the hydrocarbon layer and the aqueous methanol layer with various methanol concentrations are shown in Fig. 3. As shown in Fig. 3, solvents with methanol content of 50-80 vol% are favorably used for extraction of polar compounds preventing the transfer of hydrocarbons into the aqueous methanol layer. Therefore, the naphtha fraction was washed with the solvent of the composition in this range.9) A result of upgrading on Ga-silicate is given in Table 1; BTX yield as high as 57% was attained at 500 °C. Besides methanol, many polar solvents were also effective. Among these solvents, sulfolane ($C_4H_8SO_2$) showed the best result as judged from the partition of phenols and color (orange) and reactivity (see Table 1) of the washed oil layer. However, recovery of phenols and sulfolane from the extract remains for further study.

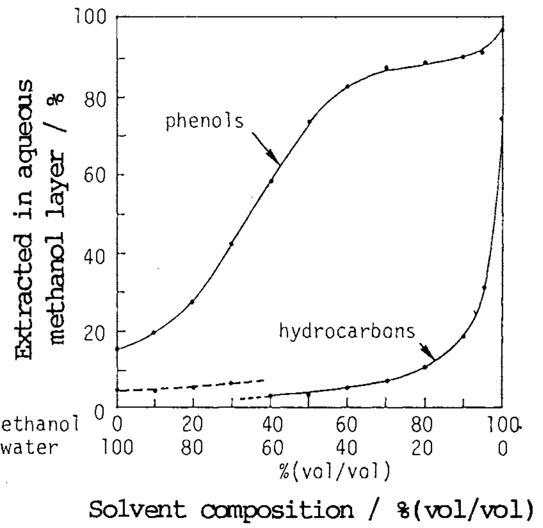

Fig. 3. Washing of light naphtha with equal volume of aqueous methanol.

Discontinuity in percent hydrocarbon extracted is due to the formation of a black middle layer at the range of lower methanol contents.

Although the present reaction afforded fairly large amounts of lower hydrocarbons, the amount of methane formed as an undesirable byproduct was quite small (ca. 4%). This result should be compared with the result reported by Pregermain who examined the pyrolysis of a coal liquid distillate having a similar boiling range as LN of the present study and reported that the yield of BTX was ca. 50%; however the process also afforded a large amount of methane (15-20%).1b)

In Table 1, the amounts of a large number of unreacted components such as dialkylcyclohexanes and alkylocatahydroindens are summed up and shown as "others". These remaining components are highly bulky, which indicates that aromatization of coal liquid proceeded in the pore system of Ga-silicate remaining the bulky components unreacted.

Table 1. Upgrading of naphtha fractions of coal liquid on Ga-silicate at 500 °C

| Product distribution (Cwt%) / Naphtha fraction / Treatment[a)] | Hydrogenated naphtha |  | Light naphtha |  |  |  |
|---|---|---|---|---|---|---|
|  | none | A | none | A | B | C |
| Methane | 0.42 | 1.68 | 0.26 | 4.55 | 3.93 | 3.88 |
| Ethane, ethylene | 3.23 | 4.02 | 1.84 | 8.93 | 7.53 | 5.11 |
| Propane, propylene | 8.64 | 8.00 | 5.09 | 11.92 | 10.07 | 9.83 |
| $C_4$ | 5.45 | 7.45 | 3.35 | 4.54 | 2.72 | 3.54 |
| $C_5$ | 1.58 | 0.89 | 7.52 | 0.11 | 0.04 | 0.23 |
| n-Alkanes($C_6$-$C_{12}$) | 7.20 | 3.59 | 20.78 | 0.49 | 0.03 | 0.05 |
| Cyclohexane | 13.17 | 5.98 | 5.93 | 0.38 | 0.17 | 0.13 |
| n-Alkylcyclohexanes | 21.12 | 8.14 | 9.49 | 0.46 | 0.26 | 0.28 |
| Others | 28.32 | 21.74 | 38.63 | 14.81 | 14.98 | 16.15 |
| Benzene | 1.78 | 11.01 | 1.49 | 14.91 | 17.25 | 19.58 |
| Toluene | 3.79 | 16.86 | 1.64 | 24.07 | 27.83 | 27.90 |
| Ethylbenzene | 0.57 | 1.02 | 0.50 | 0.87 | 0.82 | 0.90 |
| Xylenes | 2.35 | 6.75 | 1.72 | 11.36 | 10.86 | 10.31 |
| $C_9$ aromatics | 2.07 | 2.14 | 1.59 | 1.58 | 1.20 | 1.14 |
| Naphthalene | 0.07 | 0.36 | 0.10 | 0.53 | 1.06 | 0.53 |
| Methylnaphthalenes | 0.18 | 0.29 | 0.07 | 0.36 | 0.89 | 0.31 |
| Dimethylnaphthalenes | 0.06 | 0.08 | tr. | 0.13 | 0.36 | 0.13 |
| BTX | 8.49 | 35.64 | 5.35 | 51.21 | 56.76 | 58.69 |

a) Naphtha fraction was washed with: A, 3% HCl and then 10% NaOH; B, 80 vol% methanol - 20 vol% water; C, sulfolane.

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9) Sludge was also deposited when washed LN was allowed to stand for two weeks; however, the amount of the sludge was a quarter of that formed in LN after washed with aqueous acid and base solutions.

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