Conversion of Light Naphtha to Aromatic Hydrocarbons (Part 5)
Evaluation of Catalytic Performance of Pt/KL for the Aromatization of Hexane in Pilot-scale Reactors

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Catalytic conversion of light naphtha to aromatics over platinum supported on zeolite L (Pt/KL) was studied using pilot scale units of an externally heated tubular reactor and an adiabatic reactor under operating conditions close to those used for commercial reactors, and simulated using data from laboratory experiments.

Product distributions and temperature profiles in the catalyst bed of the adiabatic reactor and the externally heated tubular reactor agreed fairly well with the simulated values. The simulated performances of the adiabatic reactor and the externally heated tubular reactor were compared, suggesting that the externally heated tubular reactor is more advantageous than the adiabatic reactor, since the operating temperature at the catalyst bed can be lowered, resulting in a slower reaction rate of hydrocracking and a consequent increase in the benzene yield.

1. Introduction

The aromatization process of light naphtha using Pt-, Zn-, or Ga-ZSM-5 has been extensively studied. We previously conducted kinetic studies on the aromatization of light naphtha over Zn- and Ga-ZSM-5. Pt/KL zeolite is significantly selective for the aromatization of n-hexane at 460°C, and much research into the aromatization of n-hexane to produce benzene has used Pt/KL because of its high activity and selectivity for benzene. Pt/BaKL shows improved selective conversion of aromatization of light naphtha and the industrial application of the catalyst has been investigated. Extensive characterizations of Pt/KL and investigations of the reaction mechanism have been performed to explain the high selectivity to aromatics. The high activity and selectivity of Pt/KL are generally accepted to result from its unique channels, non-acidity, and the appropriate interaction of platinum particles with zeolite.

Development and application of new industrial catalysts requires evaluation of the performance of the catalyst using a larger scale unit under operating conditions close to those for commercial reactors. The optimum operating conditions for reforming of naphtha over conventional bifunctional catalyst were investigated using a small laboratory scale isothermal reactor (2 ml catalyst volume) and mini-adiabatic reactor (100 ml catalyst volume). Reaction conditions must be close to those of commercial operations to evaluate the effects of linear mass velocity on the apparent catalyst activity, selectivity, and life. Linear mass velocity has a strong effect on the catalytic activity and the life of the conventional bifunctional catalyst in the reforming of naphtha using isothermal and adiabatic reactors.

Our previous study proposed a kinetic model for the aromatization of n-hexane over Pt/KL catalyst and determined the kinetic parameters for the reaction based on experimental aromatization of C6 hydrocarbons using a small bench-scale reactor. The aromatization of light naphtha over Pt/KL is highly endothermic, so the heat supply may be an important factor in commercial operations. The operating conditions must also be optimized, based on the characteristics of the catalyst.

In the present study, the aromatization of light naphtha over Pt/KL was studied using pilot scale units of an externally heated tubular reactor and an adiabatic reactor under operating conditions close to those used for commercial reactors. The kinetic parameters derived based on data from the bench-scale experiments were compared to the data from the pilot units. Furthermore, simulation and experimental investigation of the performance of the adiabatic reactor and externally heated tubular reactor were evaluated to select the best reactor type for the optimum use of Pt/KL catalyst.

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2. Experimental

2.1. Catalyst Preparation

The KL zeolite was obtained from Tosoh Co. (TSZ-500). Platinum was loaded on the zeolite by the impregnation method, using an aqueous solution of Pt(NH₃)₄Cl₂. The content of platinum metal in the catalysts was 1.0 wt%. The catalysts were dried in air at 80°C for 3 h, and then calcinated in air at 300°C for 1 h. The catalyst was shaped into spheres with a diameter of 2.0 mm.

2.2. Apparatus for Adiabatic Reactor

The flow sheet of a pilot unit with an adiabatic reactor is shown in Fig. 1. The unit consisted of equipment for feed supply, preheating, adiabatic reaction, product separation, and product analysis. Light naphtha was fed from a feed storage tank (F-1) through a naphtha charge pump (P-1) and mixed with hydrogen gas. The mixed feed was passed through preheaters (H-1, H-2) and heated up to the desired temperature. The preheated feed mixture was introduced downward into the adiabatic reactor (R-1). The effluent from the reactor was partly withdrawn through a needle valve and analyzed by an on-line gas chromatograph. The mainstream of the reactor effluent was cooled by a condenser (C-1) and flushed to a separator (D-1). The flow rate of separated gases, which contained hydrogen and light hydrocarbons, was measured by a gasmeter, and samples of the gases were periodically analyzed by an off-line gas chromatograph. The liquid hydrocarbons were sent to a product storage tank. The line from the outlet of the reactor to the gas chromatograph was maintained hot (about 250°C) by a sieve heater to prevent condensation of hydrocarbons.

Figure 2 illustrates the detailed construction of the adiabatic reactor assembly. The reactor consisted of two major tube assemblies. The outer tube assembly...
was 1000 mm long and 114.3 mm O.D. (thickness 8.6 mm) made of type 316 s.s. material. The inner tube assembly was 725 mm long and 60.5 mm O.D. (thickness 2.8), and made of type 304 s.s. material. Pt/KL catalyst (1.1 kg) was charged into the inner tube assembly. The height of the catalyst bed was 560 mm. Inert ceramic balls (3 mm in diameter) were placed on the top of the catalyst bed to improve the gas flow distribution. The inner tube assembly was inserted into the outer tube assembly and joined with the outer tube assembly with a flange. The distance between the inner and outer tubes was about 18 mm. The preheated feed gases flowed into both inner and outer tube assemblies. The space between the inner and outer tubes was filled with feed gases, which might function as heat resistance. Heat transfer in the radial directions could, therefore, be reduced. Furthermore, the outer tube assembly was heated by four electric heater blocks (H-3). The temperature profile along the longitudinal axis of the outer tube skin was controlled to as close to that of the catalyst bed as possible. Therefore, heat flux in radial directions would be minimized and high adiabaticity would be achieved. Movable thermocouples were installed both in the center of the inner tube assembly and in the wall of the outer tube assembly. Fixed thermocouples were also installed on the outside wall of the outer tube assembly at an appropriate distance. These thermocouples allowed monitoring of the temperature profiles both radially and axially, and thus evaluation of the adiabaticity of the system. Prior to the reaction, Pt/KL was reduced in-situ at 540°C in flowing hydrogen at a GHSV (gas hourly space velocity) of 1600 h⁻¹ (about 2.5 Nm³/h) at atmospheric pressure for 24 h. The light naphtha feed contained 26.2 wt% of isohexane, 57.8 wt% of n-hexane, and 16.0 wt% of methylcyclopentane, unless otherwise indicated. The feed rate of the light naphtha was regulated to meet the specified WHSV (weight hourly space velocity) and ranged from 9.9 to 19.8 kg/h. The flow rate of hydrogen gas was also controlled by a flow controller (FC) to meet the desired hydrogen-hydrocarbon molar ratio (H₂/HC ratio). H₂/HC ratios ranged from 0.25 to 3 mol/mol in the experiments.

2.3. Apparatus for Externally Heated Tubular Reactor

The flow sheet of a pilot unit with an externally heated tubular reactor is shown in Fig. 3. The unit was similar to that for the adiabatic reactor unit except for the preheater and the reactor. Light naphtha was fed from a feed storage tank (F-1) through a naphtha charge pump (P-1) and mixed with hydrogen gas. The mixed feed was passed through a preheater (H-1) and heated up to a desired temperature. The feed mixture was passed through a preheater (H-1) and heated up to a desired temperature. The preheaters (material, type 304 s.s.) were filled with stainless packing (material, type 304 s.s.) to promote heat transfer, and were placed into a fluidized sand bath heater. The feed mixture was introduced to the tubular reactor (R-1). The reactor was placed into a fluidized sand bath heater (H-2). The separation of the reactor effluent was performed in the same manner as for the adiabatic reactor unit.

Figure 4 illustrates the schematic diagram of the externally heated tubular reactors. Two different size
of tubes were used to examine the effects of tube diameter on the reactor performance. Reactor A was 2.4 m long and 43 mm I.D. (thickness, 2.8 mm), and the material was type 304 s.s. Reactor A had four sampling connections located every 300 mm along the catalyst bed and was equipped with an internal thermowell (3 mm O.D.) to monitor axially the central bulk temperature of the catalyst bed. The feed was introduced to the catalyst bed from the bottom of the reactor and flowed upward. The bottom of the reactor (150 mm in length) was filled with inert ceramic balls (3 mm in diameter) to promote heat transfer and also to improve the distribution of the fluid. Pt/KL catalyst (1.74 kg) was charged on the ceramic balls. The length of catalyst bed was 1.5 m. The upper 750 mm part of the reactor was also filled with inert ceramic balls to prevent the catalyst from moving out from the reactor. Reactor B was about 5.14 m in straight length and 28 mm I.D. (thickness, 3 mm). Reactor B had a curved construction to fit the size of the reactor heater (H-2). The reactor had four sampling nozzles and was equipped with an internal thermowell (3 mm O.D.). Pt/KL catalyst (1.6 kg) was charged into the reactor. The length of the catalyst bed was about 3.1 m. The reactor inlet and outlet portions were filled with inert ceramic balls (3 mm in diameter) to promote heat transfer, to improve the distribution of the fluid, and/or to prevent the movement of the catalyst out of the reactor.

Prior to the reaction, Pt/KL was reduced in-situ at 540°C in flowing hydrogen at a GHSV of 1000 h⁻¹ (about 2.2 Nm³/h for Reactor A and 2.0 Nm³/h for Reactor B) at atmospheric pressure for 24 h. During the reducing operation, the temperature of the hydrogen stream and the catalyst bed were maintained at 540°C by controlling the temperature of the sand baths H-1 and H-2. At the end of the reducing operation, the temperature of H-1 and H-2 were lowered gradually to the reaction temperature, and the hydrogen flow rate was adjusted.

Light naphtha feed, the same as in the case of the adiabatic reactions, was then introduced to the preheater to be vaporized and fed to the reactor, and the reaction was started. Reactor effluents were cooled by a condenser (C-1) and flushed into a separator (D-1). A small amount of the reactor effluent was directly withdrawn from each sampling nozzle installed on the reactor tube by opening needle valves and sent to an on-line gas chromatograph through stainless tubing (6 mm O.D.) which was maintained at ca. 250°C by a sieve heater to prevent condensation of hydrocarbons. The flow rate of gases from D-1, which contained hydrogen and light hydrocarbons, was measured by a gasmeter. The gases were periodically analyzed by an off-line gas chromatograph. The liquid hydrocarbons were sent to a product storage tank.

Conversion, selectivity, and yield of each product are defined as: Conversion (wt%) = [1 – (C₆ weight in products/C₆ weight fed to reactor)] × 100; Selectivity (wt%) = [(each hydrocarbons weight in products)/(C₆ weight fed to reactor – C₆ weight in products)] × 100; Yield (wt%) = (each product weight in products/C₆ weight fed to reactor) × 100.

3. Kinetic Modeling

3.1. Kinetic Model for Aromatization of Light Naphtha

The general kinetics of the aromatization of light naphtha (C₆ hydrocarbons) over Pt/KL catalyst were previously modelled based on the results of isothermal reactions using a bench-scale apparatus. Reactor simulations in this study used the same kinetic parameters.

3.2. Reactor Model

The two-dimensional model was applied for the simulation of the externally heated tubular reactor. The model consisted of the mass balance for each component, rate equations, heat balance for the process fluid, and a set of boundary and initial conditions for reactor operation. The assumptions of the model are summarized as follows:

(a) Velocity was assumed to be the same at each point in the radial direction.
(b) Mass and thermal axial dispersion effects were neglected.
(c) Concentration and temperature profiles between the catalyst pellets and the gas phase were considered negligible.
(d) Physical properties of the reactant stream were assumed to be constant and average values were used.
(e) Reactor skin temperature was assumed to be the same as that of the bulk temperature of the sand bath.

Mathematical equations for the model are shown below.
Mass balance

\[ \frac{\partial x_i}{\partial z} + D_r \left( \frac{\partial^2 x_i}{\partial r^2} + \frac{1}{r} \frac{\partial x_i}{\partial r} \right) + \frac{M_{avi}(-r_i)}{G} = 0 \]  

(1)

Heat Balance

\[ \frac{\partial t}{\partial z} + k_e \left( \frac{\partial^2 t}{\partial r^2} + \frac{1}{r} \frac{\partial t}{\partial r} \right) + \frac{\Sigma(-\Delta H_i)(-r_i)}{Gc_p} = 0 \]  

(2)

Boundary conditions

\[ r = 0 \quad \frac{\partial t}{\partial r} = 0, \quad \frac{\partial x_i}{\partial r} = 0 \]  

(3)

\[ z = 0 \quad r = T_0, \quad x_j = x_{j0} \]  

(4)

\[ r = R \quad \frac{\partial x_j}{\partial r} = 0, \quad -k_e \frac{\partial t}{\partial r} = h_w(t-t_w) \]  

(5)

For the simulation of the adiabatic reactor, \( h_w \) was set to be zero in Eq. (5).

4. Results and Discussion

4.1. Adiabatic Reactor

Commercial catalytic reforming for the production of high octane gasoline or aromatics from naphtha feedstock normally employs adiabatic reactors. The reforming of naphtha involves various reactions, including isomerization of paraffins, dehydrogenation of naphthenes, dehydrocyclization of paraffins to aromatics, and hydrocracking. The dehydrocyclization of paraffins to aromatics is highly endothermic, so the reforming of naphtha is overall an endothermic reaction. Therefore, the heat of reaction must be supplied by inter-stage heaters (typically 3 to 4 stages) for a high yield of aromatics. Thus, commercial reforming units require multi-bed adiabatic reactors with inter-stage heaters.

Table 1 lists the experimental conditions for adiabatic reactions. The total WHSV was determined, assuming that a commercial unit consists of 6 multi-bed adiabatic reactors. WHSV of 9 h\(^{-1}\) corresponded to one of the six multi-bed adiabatic reactors because the total WHSV was assumed to be 1.5 h\(^{-1}\).

The adiabaticity of the system was evaluated by calculating the reactor outlet temperature in terms of the enthalpy balance between the inlet and outlet of the reactor. The difference between the observed and calculated reactor outlet temperatures of each run was within 3\( ^\circ \)C. Therefore, the overall adiabaticity of the system was satisfactory.

4.1.1. Effects of Operating Pressure and H\(_2\)/HC Ratio on Adiabatic Reactor Performance

Figure 5 and Table 2 show the results of adiabatic reactions (Runs A1, A2, A3, and A4), indicating the effects of operating pressure and hydrogen-to-hydrocarbon ratio (H\(_2\)/HC ratio) on the reactor performance. The inlet temperatures of the reactor were around 475\( ^\circ \)C. Pressure at the reactor inlet and H\(_2\)/HC ratio ranged from 0.79 to 0.44 MPa and 2 to 0.5 mol/mol, respectively. As shown in the temperature profiles (Fig. 5), temperature decreased along the longitudinal axis in the catalyst bed due to the endothermic heat of reaction. The fall in temperature was significant at the inlet of the reactor and seemed to terminate near the outlet of the reactor. Moreover, higher falls in temperature were observed as the operating pressure was lowered.

In Run A1 (pressure 0.79 MPa), the outlet temperature was 414\( ^\circ \)C; the drop in temperature was 61\( ^\circ \)C.
The yield of benzene was 10.8 wt%. In Run A3 (pressure 0.44 MPa), the outlet temperature was 396°C; the total drop in temperature was 76°C. The yield of benzene was 12.3 wt%. These results show that aromatization proceeds favorably at lower pressure and the yield of benzene is increased due to the thermodynamic characteristics of the dehydrocyclization of paraffins. In Run A4 (pressure 0.79 MPa, H2/HC ratio 0.5 mol/mol), the outlet temperature was 391°C and the drop in temperature was 85°C. The yield of benzene was 12.7 wt%, which was higher than that of any other run. This result also indicates that lower hydrogen partial pressure results in a higher yield of benzene.

4.1.2. Simulation of Adiabatic Reactor

Figure 6 and Table 3 compare the observed and simulated values of the temperature profile along the longitudinal axis of the catalyst bed and the product distribution for Runs A5, A6, and A7. The reaction conditions for Run A5 and Run A6 corresponded to the 1st and the 6th reactors of a six multi-bed adiabatic reactor system. The feedstock in Run A6 contained 50.5 wt% benzene, and 3 mol/mol (H2/HC ratio) was selected to match the conditions for a reactor in commercial operation. The temperature of the reactor inlet in Run A6 was set to be higher than that in A5, since a thermodynamic limitation exists in the production of benzene from the dehydrocyclization of paraffins. Run A7 was carried out to examine the effects of WHSV on the reactor performance in the adiabatic reaction.

In Run A5, the outlet temperature was 390°C; the drop in temperature was 73°C. The yield of benzene was 11.0 wt%. In Run A6, the outlet temperature was 425°C; the total drop in temperature was 66°C. The contents of benzene in the feedstock and products in Run A6 were 50.5 and 58.3 wt%, respectively. Therefore, the yield of benzene was 7.8 wt%. In Runs A5 and A6, the falls in temperature were significant at the inlet of the reactor. Moreover, the fall in temperature tended to terminate near the outlet of the catalyst bed. These trends in the temperature profiles were similar to those shown in Fig. 5. These results indicate that the yield of benzene was limited by the thermodynamic equilibrium in both Run A5 and Run A6, in accordance with the operating conditions at the outlet of the catalyst bed.

In Run A7, the temperature profile showed similar features to those in Run A5 and Run A6, although space velocity was twice as high as in Runs A5 and A6, indicating again that the yield of benzene for Run A7 was limited by the thermodynamic equilibrium under the operating conditions at the outlet of the catalyst bed. Based on the experimental results, the yield of benzene in the adiabatic reactor is determined by the thermodynamic limitation. Therefore, production of a higher amount of benzene requires multi-bed reactors and the necessary amount of heat must be supplied through the inter-stage heaters. Furthermore, the temperature in the downstream reactors should be increased to produce a higher amount of benzene, based on the thermodynamic and kinetic characteristics.

Figure 6 shows the observed and simulated temperatures profiles agreed fairly well. Moreover, the differences between the observed and simulated the prod-

![Temperature profile comparison](image-url)
uct distributions listed in Table 3 ranged from 0.1 to 2.8 wt%. The difference was less than 0.5 wt% for the benzene distribution. Therefore, the kinetic model and parameters used in this simulation are useful for plant design.

4.2. Externally Heated Tubular Reactor

Table 4 lists the experimental conditions for externally heated tubular reactors. The experiments were carried out using two reactors (Reactor A and Reactor B) to examine the effects of the size of the reactor tube and operating variables, such as temperature and H2/HC ratio, on the reactor performance. The flow rates of light naphtha for Reactor A and Reactor B were 7.0 and 3.2 kg/h, and the linear velocities were about 4800 and 5300 kg/(m²h), respectively.

4.2.1. Characteristics of the Externally Heated Tubular Reactor

Figure 7 shows the changes in the product distribution of n-hexane and benzene along the axial length of the catalyst bed for Run T1 (Reactor A). The reactor performance was evaluated by analyzing the reaction products sampled at four different points and by monitoring the temperature of the center of the catalyst bed. The concentration of n-hexane and benzene at the wall of the reactor tube, and middle and center of the catalyst bed were simulated. The simulation showed that the conversion of n-hexane and the yield of benzene in the radial direction decreased with the distance from the wall of the reactor. Moreover, the experimental values of the concentration of n-hexane and benzene were close to the simulated values at the tube wall.

As the reaction proceeded, the temperature of the catalyst bed decreased along the axial catalyst bed due to the endothermic heat of reaction. The reaction rate of aromatization at the center of the catalyst bed may be slow due to the low temperature since the radial heat transfer in the catalyst bed was limited and thus adequate heat would not be supplied. On the other hand, at the wall side of the catalyst bed, the temperature was relatively high and thus the reaction rate would be fast.

Figure 8 (a), 8 (b) compare the observed and simulated values of the temperature profile and products distribution for Run T1 (Reactor A).
4.2.2. Effects of Tube Size on Reactor Performance

Figure 9 (a), 9 (b) compare the observed and simulated values of the temperature profile of the catalyst bed and product distribution in Reactor B (I.D. 28 mm), indicating the effects of the diameter of the reactor tube on the reactor performance. The temperature of the sand bath was maintained at 470°C. As shown in Fig. 9 (a), a significant fall in temperature was observed at the center of the catalyst bed. The temperature decreased by 50°C at 300 mm from the reactor inlet and then gradually increased by about 35°C at the reactor outlet. This temperature profile was similar to that in Run T1 shown in Fig. 8 (a).

The experimental results of Run T1 and Run T2 are summarized in Table 5 to analyze the difference in reactor performance between Reactor A and Reactor B. The product distribution for Reactor B at WHSV of 4 h⁻¹ was estimated from the yield profile shown in Fig. 9 (b). The yields of benzene at WHSV of 4 h⁻¹ for Reactor A and Reactor B were close, i.e., 36 and 38 wt%, respectively. Moreover, the yields of other components for Reactor A were nearly equal to those for Reactor B. The temperature of the sand bath in Run T1 (Reactor A) was 483°C, which was higher than 470°C in Run T2 (Reactor B). Moreover, the temperature at the center of the catalyst bed for Reactor A (Fig. 8 (a)) was lower than that for Reactor B (Fig. 9 (a)). This indicates that the reaction rate of the aromatization at the center of the catalyst bed of Reactor A was lower and that the catalyst was not effectively utilized, compared to Reactor B. Therefore, the operating temperature of Reactor A was required to be higher than that of Reactor B.

4.2.3. Simulation of Product Distribution

Table 6 compares the observed and simulated values of the product distribution for Runs T2, T3, and T4. The differences between the observed and the simulated values ranged from 0.1 to 2.3%. The difference was less than 0.3% for benzene. The kinetic parameters used in this simulation are useful for plant design.

<p>| Table 5 Product Distribution in the Aromatization of Light Naphtha for the Externally Heated Tubular Reactor |
|--------------------------------------------------|--------------------------------------------------|--------------------------------------------------|</p>
<table>
<thead>
<tr>
<th>Component</th>
<th>Reactor A (a)</th>
<th>WHSV = 4 h⁻¹</th>
<th>Reactor B (b)</th>
<th>WHSV = 4 h⁻¹</th>
<th>WHSV = 2 h⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1-C5</td>
<td>3.0</td>
<td>2.5</td>
<td>3.3</td>
<td>2.9</td>
<td>2.2</td>
</tr>
<tr>
<td>C5</td>
<td>2.4</td>
<td>2.0</td>
<td>2.6</td>
<td>2.4</td>
<td>1.7</td>
</tr>
<tr>
<td>i-C6</td>
<td>24.4</td>
<td>24.3</td>
<td>26.9</td>
<td>26.0</td>
<td>34.3</td>
</tr>
<tr>
<td>n-C6</td>
<td>11.1</td>
<td>10.5</td>
<td>13.5</td>
<td>13.7</td>
<td>22.4</td>
</tr>
<tr>
<td>MCP</td>
<td>2.5</td>
<td>3.8</td>
<td>2.7</td>
<td>4.2</td>
<td>2.8</td>
</tr>
<tr>
<td>Benzene</td>
<td>35.6</td>
<td>56.9</td>
<td>51.0</td>
<td>50.8</td>
<td>36.6</td>
</tr>
<tr>
<td>Total</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
</tr>
</tbody>
</table>

a) Yield of each component is estimated from the yield curve in Fig. 9. b) Run No.: T1. c) Run No.: T2.
4.3. Comparison of Reactor Performance between Adiabatic and Externally Heated Tubular Reactors

The product distributions were simulated to compare the reactor performance of the externally heated tubular reactor and the adiabatic reactor for the aromatization of light naphtha over Pt/KL. The results are summarized in Table 7. The simulated reactor tube for the externally heated tubular reactor (Runs ST-1 and ST-2) was 4 m long and 22.2 mm I.D. (thickness 2.5 mm). The external temperature of the tube was set at 500°C.

The aromatization of light naphtha is highly endothermic. Therefore, the heat of reaction must be supplied by heating the feed stream up to the reaction temperature for the adiabatic reactor. Accordingly, six multi-bed reactors with inter-stage heaters were assumed in the simulation for the adiabatic reactor (Runs SA-1, SA-2, and SA-3). The length of the catalyst bed and WHSV for each reactor were 670 mm and 9 h⁻¹, respectively. Each reactor inlet temperature was set to obtain nearly the same yield of benzene. Therefore, the inlet temperature of the downstream reactor was increased (Runs SA-1 and SA-2). Another simulation for adiabatic reactors was conducted with the inlet temperature of the reactor at 510°C (Run SA-3). Total WHSV was the same in all cases.

Runs ST-1 and SA-1 compare the reactor performance of an externally heated tubular reactor and an adiabatic reactor at the same H₂/HC ratio (5 mol/mol) and reactor inlet pressure (0.79 MPa). The inlet temperature of each adiabatic reactor was regulated to obtain almost the same conversion as in the case of an externally heated tubular reactor. The selectivity to hydrocracked products (C₁-C₅) in the externally heated tubular reactor was lower than that in the adiabatic reactor, which resulted in a higher selectivity for benzene.

In a commercial adiabatic reactor system, the effluent from each reactor is passed through inter-stage heaters and additional pressure drops caused by the heaters must be considered. On the other hand, an externally heated tubular reactor system has no inter-stage heaters. Therefore, the inlet pressure of the adiabatic reactor might be higher than that of the externally heated tubular reactor.

The adiabatic reactor favors higher H₂/HC ratio, because of the need for a heat supply. If the H₂/HC ratio is reduced to, e.g., 0.5 mol/mol, the conversion and the yield of benzene would fall due to the reduction in the heat supply. However, in the case of the externally heated tubular reactor, H₂/HC ratio would be lowered since the heat of reaction can be supplied externally. A decrease in H₂/HC ratio also causes a reduction in the inlet pressure of the externally heated tubular reactor due to a decrease in the pressure drop within the reactor.

Runs SA-2 and SA-3 and Run ST-2 compare the reactor performance at different reactor inlet pressures and H₂/HC ratios. The H₂/HC ratios of the adiabatic reactor (Runs SA-2 and SA-3) and the externally heated tubular reactor (Run ST-2) were 5 and 0.5 mol/mol, respectively. Table 7 shows the conversion and the selectivity to benzene in Run ST-2 were significantly improved, compared to Run ST-1, due to the reduction of H₂/HC ratio and the operating pressure. The conversion and the selectivity for benzene in Run ST-2 were higher than those in the adiabatic reactor (Runs SA-2) whereas the selectivity for hydrocracked products (C₁-C₅) was lower than that in the adiabatic reactor. In the simulation for Run SA-3, the inlet temperature...
ture of each adiabatic reactor was set at 510°C. The conversion was increased, but the selectivity for hydro-cracked products (C1-C5) was unfavorably increased in comparison with Run SA-2.

Figure 10 shows the simulation of the temperature profile of the catalyst bed and the yield of benzene and cracked products in the adiabatic Reactor (Run SA-3) and externally heated tubular reactor (Run ST-2). The externally heated tubular reactor had a lower temperature profile, compared to the adiabatic reactor. The lower reaction temperature may lead to a slower hydrocracking reaction and thus an increased yield of benzene.

The simulation indicates that an externally heated tubular reactor is more advantageous for the aromatization of light naphtha over Pt/KL compared to an adiabatic reactor.

5. Conclusion

The conversion of light naphtha to aromatics over platinum supported zeolite L (Pt/KL) was studied using an externally heated tubular reactor and an adiabatic reactor under operating conditions close to those used for commercial reactors. In the adiabatic reactor, the conversion and the yield of benzene were limited by the thermodynamic equilibrium of the reaction. The yield of benzene was increased by using a higher temperature at the reactor inlet and reducing the operating pressure. In the externally heated tubular reactor, a smaller diameter of the reactor tube favored the production of benzene, based on the radial heat transfer in the catalyst bed.

Using the kinetic parameters determined from the data of bench-scale experiments, the product distribution and the temperature at the catalyst bed of the pilot-scale adiabatic reactor and externally heated tubular reactor were successfully simulated. These kinetic parameters are useful for the design of reactors. The performances of the adiabatic reactor and the externally heated tubular reactor were compared by simulation, which suggested that the externally heated tubular reactor was more advantageous than the adiabatic reactor, since the operating temperature at the catalyst bed can be lowered, reducing the reaction rate of hydrocracking and increasing the benzene yield.

Nomenclatures

Cj: concentration of component j [kg-mol/m3]
Dr: effective diffusivity in the radial direction [m2/h]
ΔHi: heat of reaction for i-th reaction [kJ/kg-mol]
Mav: average molecular weight [—]
R: radius of reactor tube [m]
T0: temperature of fluid at reactor inlet [°C]
hw: heat transfer coefficient [kJ/(h m2 °C)]
ke: effective radial thermal conductivity [kJ/(h m °C)]
r: radial coordinate [m]
ri: rate of reaction for i-th reaction [kg-mol/(h m3)]
rj: rate of reaction for component j [kg-mol/(h m3)]
t: temperature [°C]
u: linear interstitial velocity [m/h]
xj: conversion of component j [—]
xj0: conversion of component j at reactor inlet [—]
z: axial coordinate [m]

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要旨
軽質ナフサからの芳香族製造（第5報）
パイロット装置によるPt/KL触媒のヘキサンの芳香族化反応性能評価
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Pt/KL触媒による軽質ナフサの芳香族化に使用する反応器型式の検討を行った。断熱反応器、外部加熱型チューブラー反応器を用いて、実装置条件下でn-ヘキサン主成分とする軽質ナフサの芳香族化反応試験を行い、実測値とシミュレーション結果を比較検討した。その結果、いずれの反応器においても生成物分布および触媒層の温度分布を良好にシミュレートすることができた。

Keywords
Light naphtha, Aromatization, Kinetics, Zeolite L, Reactor