Development of gasoline synthesizing catalyst from light gas

1. Contents of empirical research

In aromatization of light hydrocarbon of carbon No. 5 or below, much research is being carried out using primarily zeolite catalyst. In this reaction, the carbon No. of the aromatic compound produced depends mainly on the reaction temperature regardless of the carbon No. of the raw material. For this reason, in using aromatic compound as gasoline base material, some type of treatment is required since the production of a substantial volume of benzene cannot be avoided. The R&D covered in this report was aimed at obtaining aromatics of lower benzene content from the same raw material by combining trans-alkyl formation with aromatics. A schematic diagram of the research is presented in Figure 1.

With respect to aromatization, an attempt was made to revise the method of catalytic adjustment and to control solid acidity for the purpose of developing aromatic catalyst of higher activity. Reaction and regeneration processing was instigated repeatedly on a trial basis over a long time period under diverse conditions, and optimum reaction conditions and regeneration conditions were investigated. With respect to transalkyl formation, trans-alkyl reaction activity was evaluated under various conditions using MFI zeolite, which was discovered in studies heretofore to be stable, undergoing the least change in activity. Activity was tested while changing reaction temperature, reaction pressure, raw material flow volume, gas/oil ratio, etc., and the impacts of these various conditions were reconfirmed. A detailed investigation was made especially of reaction temperature, which is believed to have a major impact on catalytic life. Evaluation tests of catalytic activity were carried out over a long time period and catalytic life was investigated.

![Figure 1: Schematic diagram of R&D](image-url)
2. Empirical research results and analysis thereof
2.1 Revision of aromatization catalyst

Thus far, in aromatization with propane raw material, the aromatic selectivity when H-Ga silicate is used in the catalyst has shown a high value of 67% or more, but because the raw material conversion rate is low, aromatic yield has not reached the target value of 65%. When H-A1 silicate was used, the aromatic yield was low because although raw material conversion rate was high, aromatic selectivity was low. It was found that the causes of differences in aromatization activity, arising from differences in these skeletal metal types, are related to solid acid strength and acid volume.

Accordingly, the catalyst adjustment method was revised and an attempt was made to control solid acidity and to combine advantages in an effort to improve aromatization activity still further. The gross weight of all the metal incorporated was held constant, and an improved catalyst was fabricated by incorporating these two metal types in various percentages. Shown in Figure 2 is a comparison of the results of a propane conversion reaction instigated with the normal-pressure, circulation-type reactor using these catalysts, and results in the case of H-Ga silicate and H-A1 silicate. As the figure shows, when the improved catalyst is used, both propane conversion rate and aromatic selectivity grow larger and the aromatic yield can be greatly improved. It was also found that the aromatic yield is largest when Ga among the skeletal metals is 25%.

![Figure 2](image)

**Figure 2** Results of propane conversion reaction with improved catalysts

- □: Propane conversion rate
- □: Aromatic yield
- △: Aromatic selectivity

To study these results, the acidity of the improved catalyst of highest activity was measured by the -TPD method. The results are shown in a comparison of H-Ga silicate and H-A1 silicate, presented in Figure 3. As the figure shows, acid volume and acid strength show roughly intermediate values for H-Ga silicate and H-A1, but it was learned that by improving the catalysts adjustment method, the characteristic acidity of both these metals could be suitably combined.

As suggested heretofore, the characteristic acidity of metallosilicate metal can be controlled by improving the catalyst adjustment method, and it was in this way that a highly active catalyst for propane aromatization could be fabricated.
2.2 Examination of reaction conditions on propane aromatization

2.2.1 Impact of reaction pressure on propane aromatization

In order to investigate the impact of reaction pressure on the propane aromatization reaction by improved catalyst presented above, propane aromatization reaction and regeneration process were tested repeatedly using a regenerative type reactor.

The dependency on reaction pressure of propane conversion rate, aromatic selectivity and aromatic yield in the early period of the reaction (one-hour circulation time) is shown in Figure 4. As the figure indicates, propane conversion rate was high when the reaction pressure was high. This is ascribed to the fact that as the reaction pressure grows higher, linear speed diminishes so that the residence time over the catalyst grows long. Aromatic selectivity was high when reaction pressure was low. It was also found that when the reaction pressure becomes high, selectivity of cracking byproducts becomes high and aromatic selectivity turns low. The higher the reaction pressure, the higher the selectivity of naphthalene and its derivatives.

It was thus found that by raising the reaction pressure, aromatic yield drops because the level of decline in aromatic selectivity is greater than the level of rise in propane conversion rate.
Figure 4  Dependency on reaction pressure of propane conversion rate and aromatic selectivity

- : Propane conversion rate  - : Aromatic yield  - : Aromatic selectivity

Temporal changes in propane conversion rate and in aromatic yield when propane conversion reaction and catalyst regeneration have been instigated repeatedly in four cycles are shown in Figure 5 and in Figure 6, respectively.

Figure 5  Temporal change in propane conversion rate under each reaction pressure
These figures indicate that the speed of decline in propane conversion rate with the passage of time is large when the reaction pressure is low. This is ascribed to the fact that the series of successive reactions, namely dehydration, cyclization and aromatization, are more advanced the lower the reaction pressure is, and this in turn causes the generated volumes of condensed aromatic and of coke to become large. As a result, the order of aromatic yield reverses in part when the circulation time exceeds 10 hours. Figure 7 presents the results obtained for total aromatic yield produced in one cycle of 18 hours of circulation. The figure indicates that the total aromatic yield in one cycle maximizes at a reaction pressure of 0.1 ~ 1.0 kg/cm$^2$G.

2.2.2 Impact of GHSV and of raw material concentration on propane aromatization

In order to investigate the impact of propane concentration and GHSV on the aromatization reaction, propane conversion reactions were instigated under combined conditions of propane concentration at 10% or 20%, and GHSV at 1,000 h$^{-1}$ or 2,000 h$^{-1}$. The resulting temporal change in aromatic yield is depicted in Figure 8. As the figure shows, the lower the propane concentration and the lower the GHSV, the higher the propane conversion rate, aromatic selectivity and aromatic yield. At 10% propane concentration and GHSV of 1,000 h$^{-1}$, in particular, aromatic yield reached 75% or more early in the reaction, greatly surpassing the target value of 65% or more. It was learned that although aromatic yield declines gradually with
the passage of circulation time, the target value of 65% or more can be reached within one cycle at a full reaction time of 18 hours.

A comparison of speeds of deterioration revealed that deterioration speed increases, as GHSV grows higher. A comparison was also made with propane concentration at 10% and GHSV at 2000 h\(^{-1}\) and with propane concentration at 20% and GHSV at 1000 h\(^{-1}\). Although the volumes of propane were equivalent, deterioration progressed more rapidly at 10% propane concentration and GHSV of 2000 h\(^{-1}\), so that although aromatic yields exhibited roughly equal values early in the reaction, differences could be noted as the circulation time elapsed. This is ascribed to the impact of diffusion at the catalytic bed. Accordingly, more detailed studies are scheduled since this is expected to become a major problem during scale-up in the future.

Meanwhile, with respect to toluene selectivity in all aromatics, the target value of 40% could not be reached. In a comparison of product distributions, it was found that the selectivity of naphthalene and its derivatives lowers as a result of high concentration and high GHSV so that toluene selectivity in the all aromatics becomes high. It is believed that by incorporating these results, both target values can be reached simultaneously.

![Figure 8 Dependency of aromatic yield on propane concentration and GHSV](image)

2.2.3 Impact of reaction temperature on propane aromatization

Research thus far has revealed that toluene selectivity in total aromatics becomes large when the reaction temperature is lowered. Propane conversion reactions were thus instigated at 500°C and 520°C, temperatures lower than 540°C, where most reactions have been conducted thus far. Temporal changes in aromatic yield and in toluene selectivity in total aromatics are shown in Figure 9 and Figure 10, respectively. It was confirmed, as indicated in the figures, that toluene selectivity in total aromatics rises when reaction temperature is lowered. When the reaction temperature was reduced to 500°C, however, the target value of 40% for toluene selectivity in total aromatics could not be reached.

It was thus learned that at present, under optimum running conditions for reaching both target values simultaneously, aromatic yield is 63% and toluene selectivity in total aromatics is 37% at a reaction temperature of 500°C.
2.3 Regeneration conditions affecting propane aromatization

2.3.1 Regeneration conditions studied through exhaust gas analysis

In order to investigate conditions of regeneration, using a TPO device with MASS equipped into the detector, used catalyst was switched to an oxidizing atmosphere at fixed temperature, and the temporal change in CO$_2$ in the gas produced was investigated. The results are presented in Figure 11. It was discovered, as indicated in the figure, that almost no CO$_2$ could be detected after 4 hours at 580°C, and coke combustion and removal was close to total. At 540°C and at 560°C, on the other hand, CO$_2$ could be detected after 4 hours and coke combustion and removal did not take place completely within 4 to 5 hours. Consequently, it is believed that either raising the regeneration temperature or extending the regeneration time is more effective than the conventional regeneration conditions.

2.3.2 Impact of regeneration temperature on propane aromatization

In light of the above results, propane conversion reaction and catalyst regeneration were tested repeatedly at a regeneration temperature of 580°C. No change could be noted, however, in a gradual decline of initial activity after regeneration.
2.3.3 Impact of regeneration time period on propane aromatization

Next, propane conversion reaction and catalyst regeneration were tested repeatedly at a regeneration temperature of 540°C and an 8-hour regeneration time period. Since the duration of one cycle was 24 hours, the reaction time was 14 hours. The resulting temporal change in propane conversion rate is presented in Figure 12. As the figure indicates, the drop in initial activity after regeneration could be held down to 0.5% or less. It can be inferred, therefore, that not only lengthening the regeneration time period but shortening the reaction time also has an effect.

![Graph showing temporal change in aromatic yield in propane conversion reactions of different regeneration time periods.]

Figure 12 Temporal change in aromatic yield in propane conversion reactions of different regeneration time periods

- ○: 4 hour regeneration (18 hour reaction)
- □: 8 hour regeneration (14 hour reaction)

2.4 Impact of reaction temperature on transalkyl formation

In regard to transalkyl formation, tests conducted thus far have revealed that MFI-type zeolite undergoes the least change in activity, and is stable. A more detailed investigation of reaction conditions was conducted, therefore, using MFI-type zeolite. One potential cause of catalytic deterioration in this reaction is coke deposition. Reaction temperature was investigated, since it is believed to have the greatest impact on coke deposition.

Taking a mixture of benzene and 1,2,4-trimethyl benzene (mol ratio 1:2) as the raw material at a reaction pressure of 30 kg/cm², an H₂/oil ratio of 200 NL/L and LHSV at 1.0 h⁻¹, a transalkyl reaction was instigated at a reaction temperature ranging from 350 to 400°C, using a regenerative reactor. The resulting temporal changes in benzene conversion rate, in 1, 2, 4-trimethyl benzene conversion rate, in toluene yield, and in xylene yield are shown in Figures 13 to 16. As the figures show, benzene conversion rate and 1, 2, 4-trimethyl benzene conversion rate climbed sharply with an increase in reaction temperature, and toluene and xylene yields also increased. Consequently, at the reaction temperature of 400°C, the toluene + xylene yield reached 65C-wt%. It was found that a reaction temperature of about 370°C is sufficient for reaching a benzene conversion rate of 40%, the target value.
The yields of heavy compound of tetra methylbenzene or above and of C1 ~ C4 light hydrocarbons, the products of another side reaction, are presented in Figure 17 and Figure 18, respectively. Figure 17 shows that the yield of C1 ~ C4 low-grade hydrocarbon climbed sharply when the reaction temperature was increased beyond 375°C up to 400°C. As a result, the fluid yield dropped. Figure 18 shows that the yield of heavy compound of tetra methylbenzene or above also increased sharply. With respect to high-boiling-point compound of pentamethylbenzene or above, although almost no change was detected up to a reaction temperature of 375°C, production of such heavy compounds could be detected after raising the reaction temperature to 400°C.

These heavy compounds could be related to catalytic deterioration due to coke deposition. Also, when C1 ~ C4 light hydrocarbons are increased, fluid yield drops. It is apparent, therefore, that a reaction temperature of 400°C or less is ideal for lengthening catalytic life and for improving fluid yield.
2.5 Evaluation of the life of transalkyl catalyst

Based on the above findings, catalytic life in a transalkyl reaction was evaluated at a reaction temperature of 380°C. The results are given in Figure 19. The figure shows that catalytic activity does not change even after 800 hours or more of circulation time; the benzene conversion rate can be kept at 50 to 60%, and the toluene + xylene yield can be kept at 50 C-wt%. No signs of deterioration are noted at this stage, and it is conjectured that activity can be maintained for an even longer period.

Figure 17  Temporal change in C1-C4 hydrocarbon yield at each reaction temperature

Figure 18  Temporal change in heavy aromatic yield of tetra methyl benzene or above at each reaction temperature

Figure 19  Temporal change in benzene conversion rate and in toluene and xylene yields during tests of transalkyl reaction life

Reaction temperature: 380°C, Reaction pressure: 30 kg/cm²G, LHSV: 1.0 h⁻¹, Gas/oil ratio 200 N1/1
3. Results of empirical research

From the results of the R&D conducted this year, the following points have been clarified.

(1) By combining metal types of different solid acidity, a metallosilicate catalyst having the intermediate acidity of both metal species could be fabricated. In conducting a propane conversion reaction, using this improved catalyst, propane conversion rate and aromatic selectivity were dramatically improved, as was the aromatic yield. It was learned that aromatic yield is highest when Ga among the skeletal metals is 25%.

(2) Using a regenerative reactor, the impact of pressure on aromatization reaction was investigated. In a comparison of activity early in the reaction, propane conversion rate grew high together with a rise in reaction pressure, but aromatic selectivity dropped low. Since the level of decline in aromatic selectivity was greater than the level of gain in propane conversion rate, it was found that the aromatic yield grows higher at the side of lower pressure. However, because the rate of decline in activity is faster at the low-pressure side, when the circulation time is extended, the order reverses. Taking a circulation time of 18 hours in one cycle as standard, the total aromatic yield in one cycle maximizes at a reaction pressure of 0.1 ~ 1.0 kg/cm$^2$ G.

(3) Using a regenerative reactor, the impact of propane concentration and of GHSV on aromatization reaction was investigated. It was found that as GHSV becomes lower, at low propane concentration, the aromatic yield grows high. As a result, it was determined that an aromatic yield of 65% or more, the target value throughout almost the entire circulation period, can be reached by having propane concentration at 10% and GHSV at 1,000 h$^{-1}$. It was also discovered that, with equal volumes of propane supply, the speed of deterioration is greater in circulation at high GHSV (low concentration).

(4) Using a regenerative reactor, the impact of reaction temperature on aromatization reaction was investigated. It was found that the selectivity of toluene in all aromatics rises together with a decline in reaction temperature.

(5) Using a TPO unit, the conditions of regeneration were examined by investigating temporal changes in the composition of exhaust gas during coke combustion. At 580°C, almost no CO$_2$ was detected after 4 hours and coke combustion and removal were almost complete. At 540 and 560°C, on the other hand, CO$_2$ was detected after 4 hours, and within 4 to 5 hours, coke combustion and removal was not complete. It was thus learned that either raising the regeneration temperature or extending the regeneration time is more effective than the conventional regeneration conditions.

(6) Using a regenerative reactor, the impact of reaction temperature on aromatization reaction—regeneration, induced repeatedly, was investigated. Even when the regeneration temperature was elevated to 580°C, the drop in initial activity after regeneration could not be curtailed.

(7) Using a regenerative reactor, the impact of regeneration time period on aromatization reaction—regeneration, induced repeatedly, was investigated. By extending the regeneration time period from 4 hours, the conventional duration, to 8 hours, the drop in initial activity after regeneration could be held down to 0.5% or below. However, the time period of one cycle was fixed at 24 hours, and since the reaction time period was reduced from 18 to 14 hours, the effect of this change might also be manifested.
(8) Using MFI-type zeolite, the impact of reaction temperature on transalkyl reaction was investigated. It was found that a reaction temperature of about 370°C is sufficient for reaching a benzene conversion rate of 40%, the target value. When the reaction temperature is elevated to 400°C, the yield of C1-C4 low-grade hydrocarbon climbs dramatically and fluid yield drops. At 400°C, the yield of tetra methylbenzene, a heavy aromatic, also increases.

(9) In an evaluation of the catalytic life of transalkyl catalyst at 380°C reaction temperature, using the aforesaid MFI-type zeolite, no change in activity was noted over 800 hours of circulation time. Benzene conversion rate could be kept at 50 to 60% and the toluene + xylene yield was held at 50 C-wt%.

4. Summary
In the development of aromatization catalyst for light hydrocarbons, an aromatic yield early in the reaction of 75% or more was obtained, far surpassing the target value of 65% or more, by improving the catalyst fabrication method and by investigating reaction conditions. Although the aromatic yield slowly declined with the passage of circulation time, the target yield of 65% more was reached within one cycle, that is a total reaction time of 18 hours. It also became apparent that toluene selectivity in all aromatics could reach 40 % or more by lowering the reaction temperature and by raising propane concentration and GHSV. At present, under optimum conditions for reaching both target values simultaneously, aromatic yield is 63% and toluene selectivity in all aromatics is 37%.

With respect to aromatic–trans alkyl formation, optimum reaction conditions were investigated, using MFI-type zeolite, which was found to be stable and to exhibit the least change in activity in research conducted up to last year. Of these conditions, reaction temperature, in particular, was investigated in detail. It was found that a reaction temperature of about 370°C is sufficient for reaching a benzene conversion rate of 40% or more, the target figure. When the reaction temperature is elevated to 400°C, although the toluene+xylene yield reaches 60C-wt% or more, the yield of C1–C4 low-grade hydrocarbon grows large and fluid yield drops. At 400°C, the yield of tetra methyl-benzene, a heavy aromatic, also increases. Based on these findings, catalytic life in transalkyl formation reaction was evaluated at a reaction temperature of 380°C. It was discovered that catalytic activity does not change even after 800 hours or more of circulation time. The benzene conversion rate can be kept at 50 to 60%, and the toluene + xylene yield can be kept at 50 C-wt%.

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