[Regular Paper]

Conversion of Light Naphtha into Aromatic Hydrocarbons (Part 3) Effects of Pre-sulfiding of ZnH-ZSM-5 on Catalytic Performance and Stability of Zinc

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The effects of steaming and hydrogen reduction of ZnH-ZSM-5, concerning catalytic activity in aromatization of *n*-hexane were examined to evaluate the stability of ZnH-ZSM-5 in commercial operating conditions, in comparison with H-ZSM-5. Steaming at high temperature resulted in greater drop in the yield of aromatics over H-ZSM-5 than that over ZnH-ZSM-5. Hydrogen reduction had little effect on the yield of aromatics over H-ZSM-5, while a remarkable drop in the yield of aromatics was observed over ZnH-ZSM-5. It was found that zinc oxide in ZnH-ZSM-5 was reduced with hydrogen to give metallic zinc, which was then vaporized from the catalyst. This vaporization led to an irreversible decline in the activity for aromatization. Pre-sulfiding of ZnH-ZSM-5 was found to be effective in preventing the vaporization of zinc, by conducting thermogravimetric measurement of vaporized zinc from the catalyst. ZnH-ZSM-5 was pre-sulfided, using thiophene, dimethylsulfide, and disulfidecarbonate, as sulfiding agents, which reduced not only the vaporization of zinc, but also the cracking activity to yield light gases, such as CH₄ and C₂H₆.

1. Introduction

The conversion of lower alkanes(C₂-C₆) to aromatic hydrocarbons has attracted much attention, since lower alkanes are abundant in petroleum fractions and aromatics are a substantial raw material in the petrochemical industry^{1)~4)}. With respect to ZSM-5 type zeolite catalysts for the upgrading of lower alkanes, attention was focused on modification of such by loading with zinc, gallium, and platinum, to improve the activity and the selectivity to aromatics^{5)~17)}. Moreover, extensive studies on the mechanism^{18)~23)} and kinetics^{24)~26)} of aromatization over these catalysts showed that loading with metal species, such as zinc or gallium, greatly enhanced the rate of the dehydrogenation of alkanes and the conversion of alkene intermediates, thus formed, to aromatics.

There is a major problem, the vaporization of zinc from zinc-containing H-ZSM-5, which occurs in reducing conditions, despite its high activity in aromatization. Yates²⁷⁾ reported that zinc-containing zeolite was reduced with hydrogen to give metallic zinc, which was then vaporized from the zeolite. Consequently, it

was found that the loss of zinc lead to an irreversible decline in the catalytic activity and life of the catalyst in the aromatization. Only a few studies were conducted to solve this problem. For instance, Mobil researchers^{28)~30)} proposed the incorporation of copper, gallium or palladium to zinc-containing H-ZSM-5, to prevent the vaporization of zinc by reducing the vapor pressure. The incorporation of these metal species may also enhance the production of light gases(C₁-C₂), however, attributed to the promotion of activity for hydrogenation of the catalysts.

Long term operations, including reaction-regeneration cycles, should be considered from industrial point of view. The stability of the catalyst in environment of steam produced in the course of regeneration is, thus, also important factor in performance of the catalyst. In view to the commercial application of the catalyst, the authors developed a method of improving the stability of ZnH-ZSM-5 without increase in the yield of light gases.

The objectives of the present work are: (i) to examine the activity and the stability of ZnH-ZSM-5 in environment of steam and hydrogen at high temperature, (ii) to stabilize ZnH-ZSM-5 by pre-sulfiding to prolong the life of catalyst in aromatization of *n*-hexane.

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2. Experimental

2.1. Preparation of Catalyst

ZSM-5 zeolite was synthesized by the method described in the patent³¹⁾. Zinc was introduced into NH₄ZSM-5 by impregnation or ion-exchange method. In the case of impregnation method, NH₄ZSM-5 was first soaked in an aqueous solution of zinc nitrate at reduced pressure, then dried at 110°C for 12 h and finally calcinated in air at 520°C for 3 h. In the case of ion exchange method, NH₄ZSM-5 was soaked in an aqueous solution of zinc nitrate at 80°C for 3 h. The ion-exchanged zeolite was separated by decantation, filtrated, washed several times with deionized water, dried at 110°C for 12 h and finally calcinated in air at 520°C for 3 h.

The catalysts thus obtained were pressed, crushed, and sieved in the range of 16-32 mesh. Characterizations of the catalysts were performed by X-ray diffraction (RU-200, Rigaku Corp.), high-resolution solid-state NMR (GSX-270, JEOL Ltd.), and Benzene-Filled Pore Method³²⁾. The content of zinc loaded into the catalysts was measured by atomic absorption analysis (AA-640-12, Shimadzu Corp.). The structure of zeolite was confirmed as that of ZSM-5 by these characterizations. Si/Al ratios and external surface areas were in the range of 50 to 60 and 10 to 13 m²/g, respectively.

2.2. Physicochemical Property Measurements

Acidity of the catalysts was evaluated by calorimeter (MPC-11, Tokyo Riko), measuring the differential heat of adsorption of ammonia. A sample (0.5 g, 16-32 mesh) was placed in a cell and evacuated in the condition of 10⁻⁴ Torr and 400°C for 1 h. The sample was, then, set in the calorimeter, into which ammonia gas was introduced. The differential heat of adsorption of ammonia and the amount of ammonia absorbed were then measured.

The infrared spectroscopy of adsorbed ammonia was obtained as follows: About 50 mg of crushed sample were shaped in a wafer with a diameter of 20 mm. This shaped sample was placed into an infrared cell. Ammonia was, then, introduced into the cell and kept there for 30 min. After that, the cell was evacuated at 3 × 10⁻³ Torr. The IR spectra measurement was conducted at room temperature, using FT/IR-3 Type (JASCO Corp.).

2.3. Procedures for Pre-sulfiding and Aromatization of *n*-Hexane

2.3.1. Pre-sulfiding of ZnH-ZSM-5

The apparatus used for the continuous flow experiments and pulse reactions was similar to that described previously^{24),25)}. ZnH-ZSM-5 catalysts were charged into a stainless tubular reactor (10 mm i.d.) or into a quartz micro reactor (4 mm i.d.). Both reactors were mounted on a vertical electric heater and were heated

up to 530°C in a flow of air and kept at this temperature for 1 h. After that, air was replaced by helium. Pre-sulfiding was achieved *in situ* by pulsation of various sulfide agents. The analysis for sulfur of the pre-sulfided catalyst was conducted to determine the content of sulfur loaded into the catalysts.

2.3.2. Aromatization of *n*-Hexane

In a continuous flow reaction, performance of the catalyst was evaluated, using the continuous flow reactor. *n*-Hexane was fed by micro-pump to meet the specific space velocity. Temperature and pressure, unless otherwise indicated, were 530°C and atmospheric pressure, respectively.

A pulse flow reaction was carried out using the quartz micro reactor. Hydrogen or helium was used as a carrier gas.

Analyses of the reaction products were performed by on-line FID-type and TCD-type gaschromatograph equipped with columns of OV-101 (0.25 mm i.d., 45 m) and Porapak Q (3.0 mm i.d., 3 m), respectively.

Conversion of *n*-hexane and yield of hydrocarbons were defined as follows: Conversion of *n*-hexane = [1 - (weight of *n*-hexane in products/weight of *n*-hexane fed to reactor)] × 100; yield of each hydrocarbon = (weight of each product/weight of *n*-hexane fed to reactor).

3. Results and Discussion

3.1. Comparison of Catalytic Properties between H-ZSM-5 and ZnH-ZSM-5

According to Yates²⁷⁾, zinc-containing zeolite was reduced with hydrogen to give metallic form at temperatures above 500°C and the metal was vaporized from the zeolite. In aromatization of hydrocarbons using ZSM-5 type catalysts, hydrogen atmosphere is unavoidable, since hydrogen is produced from the dehydrogenation of reactants. There is a problem, thus, of zinc oxide in ZnH-ZSM-5 being reduced with hydrogen to give metallic zinc which is then vaporized, since the aromatization is carried out at high temperatures, above 500°C. As a result, aromatization activity of ZnH-ZSM-5 is decreased. In addition, the process of aromatization of hydrocarbon are accompanied by generation of steam in the course of periodical regeneration by burning out deposited coke with oxygen. Some changes in the structure of zeolite framework, such as dealumination attributed to steaming, therefore, may take place³³⁾, which would lead to change in catalytic activity.

As a preliminary investigation, the effects of steaming and hydrogen reduction on catalytic properties of H-ZSM-5 and ZnH-ZSM-5 were investigated with the activity for aromatization of *n*-hexane and acidity.

Table 1 Effect of Steaming and H₂ Reduction of ZnH-ZSM-5 and H-ZSM-5

Catalyst	Treatment	Yield of aromatics [wt%]		Loss of aromatics ^{c)} [wt%]	<i>S_{p-xylene}</i> ^{d)} [wt%]
		Fresh	Treated		
H-ZSM-5	Steaming ^{a)}	40	16	60	38
ZnH-ZSM-5 ^{e)}	Steaming ^{a)}	55	41	25	26
H-ZSM-5	H ₂ reduction ^{b)}	40	38	5	23
ZnH-ZSM-5 ^{e)}	H ₂ reduction ^{b)}	55	43	22	23

Reaction temperature: 373°C, WHSV: 2 h⁻¹, Reactant: *n*-hexane.

a) at 630°C for 12 h with WHSV 2.5 h⁻¹.

b) at 630°C for 20 h with GHSV 3750 h⁻¹.

c) Calculated from the yield of aromatics; (Fresh - Treated)/Fresh × 100.

d) *S_{p-xylene}*; Selectivity to *p*-xylene.

e) Zn, 2 wt%.

3. 1. 1. Steaming and Hydrogen Reduction of Catalysts

Listed in Table 1 are the effects of steaming and hydrogen reduction of the catalysts on the catalytic performances of H-ZSM-5 and ZnH-ZSM-5 in the aromatization of *n*-hexane. Steaming was conducted *in situ* at 630°C for 12 h in flowing water with WHSV of 2.5 h⁻¹. The hydrogen reduction of the catalysts was also conducted *in situ* at 630°C for 20 h in flowing hydrogen with GHSV of 3750 h⁻¹.

The results shown in Table 1 are summarized below:

(1) Steaming decreased yield of aromatics over H-ZSM-5, more greater than that over ZnH-ZSM-5.

(2) In the case of steamed H-ZSM-5, the weight fraction of *p*-xylene in all the xylenes (*o*-, *m*-, *p*-) was 38%, which was higher than the thermodynamic equilibrium value of 23%. ZnH-ZSM-5 exhibited value of around the thermodynamic equilibrium value.

(3) Hydrogen reduction decreased yield of aromatics over ZnH-ZSM-5 greatly, by as much as 22%.

(4) The weight fraction of *p*-xylene in all the xylenes was that of the thermodynamic equilibrium value, both over H-ZSM-5 and ZnH-ZSM-5, and subjected to hydrogen reduction treatment.

In the case of steaming, the decrease in the yield of aromatics may be due to the change in the nature of the zeolite framework. Sano *et al.*³³⁾ investigated the effect of steaming on the stability of H-ZSM-5 type zeolite containing alkaline earth metals and reported that dealumination of the framework of the zeolite attributed to steaming was greatly inhibited by the addition of metals such as Ca, Mg, and Ba. The stability of the zeolite was, thus, improved. The minor drop in aromatics yield over steamed ZnH-ZSM-5, therefore, may be attributed to the stabilization of the zeolite framework by the introduction of zinc cation which may bond with aluminum atoms through some kind of interaction.

The improvement of the stability of the zeolite attributed to the introduction of zinc cation is evidenced by

significant difference in content of *p*-xylene in all the xylenes obtained over steamed H-ZSM-5 and ZnH-ZSM-5. *p*-Xylene content in all the xylenes obtained over steamed H-ZSM-5 was significantly higher than that of the thermodynamic equilibrium value. This result suggests that amorphous alumina dealuminated from the zeolite framework may plug the pores of the zeolite and reduce the pore size. As a result, the diffusion of *o*- and *m*-xylenes, with relatively large molecular size, through zeolite pores may be limited. On the other hand, ZnH-ZSM-5 exhibited around the thermodynamic equilibrium value for *p*-xylene content because of the stabilization of the zeolite framework attributed to zinc cation.

In the case of hydrogen reduction, decrease in aromatics yield was more remarkable over ZnH-ZSM-5 than over H-ZSM-5. This may be attributed to zinc oxide in the zeolite being reduced with hydrogen to metallic zinc which was then vaporized from the catalyst. The activity for aromatization was, thus, greatly decreased.

3. 1. 2. Acidity of H-ZSM-5 and ZnH-ZSM-5

The acidic properties of H-ZSM-5 and ZnH-ZSM-5 were measured in terms of the differential heat of adsorption of ammonia and IR spectra of ammonia adsorbed on the catalysts. The results are shown in Figs. 1 and 2. As shown in Fig. 1, the amount of acid having the strength ranging from 90 to 120 kJ/mol was increased with an increase in zinc content. A similar trend of change in the acidity of zinc-exchanged ZSM-5 was reported by Mole *et al.*¹⁸⁾

As shown in Fig. 2, H-ZSM-5 was composed of both Brönsted acid sites(1450 cm⁻¹) and Lewis acid sites(1630 cm⁻¹). The IR spectra of ZnH-ZSM-5 showed an increase in absorbance of the band(1630 cm⁻¹) attributed to Lewis acid. These results indicate that Lewis acid, which has relatively strong acidity, was produced by loading H-ZSM-5 with zinc. Similar results were reported by Yakerson *et al.*³⁵⁾. They observed that the amount of Brönsted acid decreased with an increase in zinc content, while the

Fig. 1 Comparison of Acidic Property between H-ZSM-5 and ZnH-ZSM-5 by Calorimetry Method

Fig. 2 IR Spectra of Adsorbed Ammonia on H-ZSM-5 and ZnH-ZSM-5

amount of Lewis acid sites increased linearly.

Lewis acid formed attributed to zinc-loading seems to act as a promoter for aromatization. This behavior agrees with the hypothesis described by Scurrill³⁴⁾ who stated that zinc may promote hydride transfer by acting as a strong Lewis acid center and that hydride ions were abstracted by zinc cations rather than by carbenium ions.

After hydrogen reduction, as shown in Fig. 1, the

Fig. 3 Reductive Properties of Metal Oxides and Metal Sulfide

amount of acid with the strength of 90 to 120 kJ/mol decreased remarkably. In connection with the results shown in Table 1, it is suggested that the retention of zinc cation in ZnH-ZSM-5 was essential to maintain high aromatization activity and long catalyst life in the aromatization of *n*-hexane.

3. 2. Reductive Properties of Zinc Oxide, Cadmium Oxide, and Gallium Oxide

In aromatization of hydrocarbons over metal-containing ZSM-5 type catalyst, the catalyst activity may decline attributed to the reduction of metal compound by hydrogen produced. For instance, zinc oxide in ZnH-ZSM-5 is reduced with hydrogen to give metallic zinc. In the case where the reaction temperature is high enough, the metal may be vaporized from the catalyst attributed to its substantial vapor pressure. In case the metal compound were hardly reduced from the view point of thermodynamic equilibrium, however, the metal could exist stably in the catalyst. It can be assumed, therefore, that the catalyst activity could be maintained by affording the metal compound stability to effect of hydrogen. Reductive properties of zinc oxide and zinc sulfide were, thus, examined to evaluate the effect of pre-sulfiding of ZnH-ZSM-5 concerning the stability of the catalyst in the presence of hydrogen, compared with that of other metal oxides.

Metal oxides such as gallium oxide and cadmium oxide, as well as, zinc oxide exhibited activity for dehydrogenation and aromatization of alkanes²⁴⁾. Shown in Fig. 3 are the relation between temperature and equilibrium constant for the reduction of zinc oxide, cadmium oxide, gallium oxide, and zinc sulfide with hydrogen. Zinc oxide and cadmium oxide can be

Sample weight: 2 g, H₂ flow rate: 400 cm³/min, Heating rate: 400°C/h, ○: ZnO, □: ZnS.

Fig. 4 Weight Loss Curve for ZnO and ZnS in Hydrogen Reduction by TG Measurement

easily reduced to metals, taking the thermodynamic equilibrium into consideration. When the oxides of zinc and cadmium are reduced, the metals formed may be vaporized from the catalysts during aromatization, because aromatization is normally conducted at above 500°C, which is higher than melting points of zinc(419°C) and cadmium(312°C).

Despite the fact that gallium oxide has a significantly low metallic melting point, *i.e.* 30°C, gallium can exist stably during reaction because gallium oxide is little reduced, considering the thermodynamic equilibrium.

Zinc sulfide is more favorable compared to zinc oxide, because the equilibrium constant ($\log K$) for $\text{ZnS} + \text{H}_2 \rightarrow \text{Zn} + \text{H}_2\text{S}$ (-10) is smaller than that for $\text{ZnO} + \text{H}_2 \rightarrow \text{Zn} + \text{H}_2\text{O}$ (-5) at 500°C. Pre-sulfiding of ZnH-ZSM-5 might, therefore, be effective to retain zinc in the catalyst during reaction.

3. 3. Reduction of Zinc Oxide and Zinc Sulfide

The stability of zinc oxide (ZnO) and zinc sulfide (ZnS) in reducing atmosphere of hydrogen was investigated, using thermogravimetry (TG). Each sample(2 g) of ZnO or ZnS was reduced with hydrogen, at a flow rate of 400 cm³/h. Rate of heating was 400°C/h. The samples were weighed during reduction with hydrogen. Results are shown in Fig. 4. A decrease in the weight of ZnO was observed at temperature of approximately 420°C, which corresponds to the melting point of metallic zinc. Decrease in the weight of 600 mg was observed at 800°C. The sample of ZnO (2 g) contained 390 mg of oxygen before reduction with hydrogen. This result indicates that, as a result of reduction of ZnO with hydrogen, the vaporization of

Reaction conditions

Temperature: 592°C, GHSV(H₂): 10,000 h⁻¹,

Catalyst: 0.5 g ZnH-ZSM-5(Zn, 2.7 wt%),

Pre-sulfiding agent: Thiophene.

○: Pre-sulfided, □: Non pre-sulfided

Fig. 5 Weight Loss Curve for Pre-sulfided and Non Pre-sulfided ZnH-ZSM-5

zinc evidently occurred. On the other hand, in the case of ZnS, a decrease of the weight was observed at above approximately 570°C. As shown in Fig. 3, this is because ZnS is hardly reduced with hydrogen as compared to ZnO, taking the thermodynamic equilibrium into consideration. These experimental results would suggest that pre-sulfiding of ZnH-ZSM-5 could effectively inhibit the vaporization of zinc at high temperature.

The effect of pre-sulfiding on the behavior of zinc in ZnH-ZSM-5 was investigated in atmosphere of hydrogen at 592°C. Samples(0.5 g) of non pre-sulfided and pre-sulfided catalysts using thiophene were weighed during reduction with hydrogen. The samples initially contained about 13.5 mg of zinc. The amount of zinc lost was calculated with the decrease in the weight of each sample, on the assumption that the decrease is due to the loss as ZnO. The results are shown in Fig. 5. In the case of non pre-sulfided ZnH-ZSM-5, the catalyst lost about 80% of initially loaded zinc after 25 h by reduction with hydrogen(weight loss of the sample was 13.5 mg, corresponding to *c.a.* 11 mg as Zn).

In the case of pre-sulfided ZnH-ZSM-5, a significant amount of improvement was achieved. Loss of zinc after 25 h was 10% of loaded zinc (weight loss of the sample was 1.9 mg, corresponding to *c.a.* 1.5 mg as Zn).

Yates²⁷⁾ reported that zeolite loaded with metal such as Cd, Zn, or Hg was reduced with hydrogen to give metallic form at temperatures above 500°C and the metals thus formed were vaporized and lost from the zeolite attributed to their substantial vapor pressure. The rate of loss of the metals did not vary over the

range of hydrogen pressures used in that study. Moreover, it was observed that the rate of loss of zinc was much smaller than that of cadmium, despite the higher vapor pressure of zinc, compared to that of cadmium. Fu *et al.*³⁶⁾ suggested that zinc oxide interacted with H-ZSM-5 and zinc cations were introduced into the channels of zeolite, which interacted with acid sites of the zeolite. Based on the results described above, zinc in ZnH-ZSM-5 may be considered to exist not only as ZnO but also as zinc cations. The nature of zinc in ZnH-ZSM-5 might affect the strength of the interaction between zinc and zeolite, which might lead to changes in the characteristics of ZnH-ZSM-5 such as reductive properties with hydrogen and vapor pressure of metallic zinc. Thus, as reported by Yates²⁷⁾, the rate of loss of metals may not fully correspond with the vapor pressure of the metals.

3.4. Conversion of *n*-Hexane over Non-sulfided and Sulfided ZnH-ZSM-5

In order to investigate the effects of pre-sulfiding of ZnH-ZSM-5, on catalytic performance, aromatization of *n*-hexane over pre-sulfided and over non pre-sulfided catalysts, were performed in carrier gas of hydrogen or helium, using a pulse reactor at 520°C. The results are shown in **Table 2**. In hydrogen, the yield of C₁-C₄ was higher than that in helium over non pre-sulfided ZnH-ZSM-5, since hydrocracking and hydrogenation of olefins intermediates seem to proceed more easily in the presence of hydrogen. By pre-sulfiding the catalyst with thiophene, a significant increase in the yield of aromatics was observed, whereas the yield of C₁-C₄

decreased. This result indicates that the pre-sulfiding of the catalyst is effective for decreasing the activity of zinc for hydrocracking and hydrogenation of olefins intermediate. From the measurement of acidic properties, in terms of the differential heat of adsorption of ammonia, it was found that the amount of strong acid of the catalyst is decreased slightly by pre-sulfiding. This result suggests that the pre-sulfiding might also inhibit the cracking activity of the catalyst attributed to the decrease in strong acid.

Aromatization of *n*-hexane over ZnH-ZSM-5 pre-sulfided with thiophene, dimethylsulfide, and disulfide-carbonate were conducted to examine the effect of pre-sulfiding agents on the catalytic performance of ZnH-ZSM-5 using a continuous flow tubular reactor. Listed in **Table 3** are the product distributions in aromatization of *n*-hexane over the catalysts pre-sulfided with various sulfiding agents, together with the results over non-sulfided ZnH-ZSM-5. The yield of light

Table 2 The Effects of Pre-sulfiding of ZnH-ZSM-5 on Products Distribution in Pulse Reactor

Carrier gas	Sulfide treatment	Yield of products [wt%]	
		C ₁ -C ₄	Aromatics
Helium	None	45.7	53.2
Hydrogen	None	82.9	17.1
Hydrogen	C ₄ H ₄ S, 10 μl	65.7	33.8

Catalyst: ZnH-ZSM-5 (Zn, 2.7 wt%), Weight: 0.3 g. Pre-sulfiding agent: Thiophene, Reactant: *n*-hexane, Pulse wide: 5 μl, Reaction temperature: 520°C.

Table 3 Products Distribution in *n*-Hexane Conversion over ZnH-ZSM-5 Pre-sulfided with Various Pre-sulfiding Agents

Sulfiding agent		None		20 μl C ₄ H ₄ S		16 μl CS ₂		26 μl (CH ₃) ₂ S	
Time on stream	[h]	5	18	7	19	3	23	10.5	22.5
Conversion	[wt%]	100	100	100	100	99.9	99.9	99.9	99.8
Product distribution [wt%]									
C ₁		11.5	11.1	7.7	8.5	6.7	7.2	7.4	7
C ₂ (C ₂ ⁼)		21.9(0.3)	17.2(0.5)	10.7(1.6)	11.8(1.6)	10.2(2.1)	10.2(2.0)	10.9(1.9)	10.5(2.0)
C ₃ (C ₃ ⁼)		10.7(0.7)	11.8(0.9)	19.0(1.3)	17.5(1.5)	24.7(1.5)	19.8(1.8)	22.8(1.3)	20.7(1.8)
C ₄ (C ₄ ⁼)		0	0.7	4.1	2.0	4.6	4.8	4.0	4.9
C ₅ ⁺		54.9	57.8	55.6	57.1	50.2	54.2	51.7	53.6
Total		100	100	100	100	100	100	100	100
Product in C ₅ ⁺ [wt%]									
C ₅ ⁺ non-aromatics		0	0	0.1	0.2	0.1	0.2	0.2	0.3
C ₆ aromatics		29.3	30.7	26.8	27.6	24.1	25.9	24.9	25.3
C ₇ aromatics		41.5	41.8	42.9	41.6	44.6	42.4	44.4	42.9
C ₈ aromatics		26.1	25.7	24.1	24.5	24.8	24.6	24.5	24.7
C ₉ aromatics		3.1	1.8	6.1	6.1	6.4	6.9	6.0	6.8
Total		100	100	100	100	100	100	100	100
Total aromatics yield ^{a)}		60.6	64.5	67.8	67.6	65.5	67.3	65.7	66.9

Catalyst: 1.85 g ZnH-ZSM-5 (Zn, 2.7 wt%).

Reaction condition: Temperature; 530°C, WHSV; 1.5 h⁻¹, Reactant; *n*-hexane.

a) Calculated on the supposition that 50% of LPG(C₃-C₄) could be aromatized.

Reaction conditions

Temperature: 530°C, WHSV: 1.5 h⁻¹,
 Catalyst: 1.85 g ZnH-ZSM-5 (Zn, 2.7 wt%),
 Pre-sulfiding agent: 40 μl Thiophene.
 Conversion of *n*-hexane: (△ ▲), Yield of C₁-C₂: (○ ●),
 LPG: (□ ■), Aromatics: (◇ ◆). Open keys are for ZnSH-ZSM-5 and closed for ZnH-ZSM-5.

Fig. 6 Effect of Pre-sulfiding of ZnH-ZSM-5 on the Products Distribution and Catalyst Activity

gases(C₁-C₂) over non pre-sulfided ZnH-ZSM-5 at 5 h of time on stream was 33.7 wt% and that of LPG(C₃-C₄) was 11.4 wt%. The tendency of the product distribution over pre-sulfided ZnH-ZSM-5 was different from that over non pre-sulfided ZnH-ZSM-5. For instance, over ZnH-ZSM-5 pre-sulfided with 20 μl thiophene, the yields of light gases and LPG at 7 h of time on stream were 20 wt% and 24.4 wt%, respectively. Thus, the pre-sulfiding of the catalysts led to a decrease in the yield of light gases(C₁-C₂) and an increase in the yield of LPG(C₃-C₄). This trend is similar to those in the other catalysts pre-sulfided with dimethylsulfide or disulfidecarbonate. On the other hand, with respect to the yield of liquid products (mainly aromatic hydrocarbons), pre-sulfided catalysts showed almost the same yield as non pre-sulfided catalyst. When LPG is recycled in commercial operation, the yield of aromatics will increase significantly because LPG components can be converted into aromatics. Assuming that 50% of recycled LPG were converted into aromatics, the total yield of aromatics over pre-sulfided ZnH-ZSM-5 would be higher by 5-7% than that over non pre-sulfided ZnH-ZSM-5. This assumption supports the idea that the pre-sulfiding of catalysts is favorable for increasing the yield of aromatics as well as for preventing the vaporization of zinc. The catalyst pre-sulfided with thiophene showed relatively higher yield of aromatics than that of other catalysts pre-sulfided with dimethylsulfide or disulfidecarbonate. Based on these results, it was concluded that thiophene is the most favorable agent for pre-sulfiding.

Shown in Fig. 6 are the effects of pre-sulfiding on the products distributions and the catalyst life in conversions of *n*-hexane over non pre-sulfided and pre-sul-

fided ZnH-ZSM-5, using a continuous flow reactor. Pre-sulfiding resulted also in a high yield of aromatics and a low yield of light gases(C₁-C₂).

4. Conclusion

To load H-ZSM-5 with zinc by ion-exchange or impregnation method was effective for stabilizing the zeolite structure in the presence of steam at high temperature, such as in the regeneration of catalyst. Furthermore, loading with zinc increased the amount of Lewis acid which might act as a promoter in aromatization.

Pre-sulfiding of ZnH-ZSM-5 proved to be a beneficial method for retaining zinc in the catalyst, since zinc sulfide (ZnS) thus formed was more stable than zinc oxide (ZnO) in a atmosphere of hydrogen. It was found, moreover, that the pre-sulfiding of ZnH-ZSM-5 decreases the yield of light gases without decreasing the yield of aromatics, attributed to the drop in hydrocracking and hydrogenation activity.

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要 旨

軽質ナフサからの芳香族炭化水素の製造（第3報） ZnH-ZSM-5 の触媒性能および安定性に及ぼす予備硫化処理の影響

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ZnH-ZSM-5 上での *n*-ヘキサンの芳香族化活性に及ぼすスチーム処理ならびに水素還元処理の影響を H-ZSM-5 と比較して検討した。高温条件下でスチーム処理を行うことにより, H-ZSM-5 は ZnH-ZSM-5 と比べて著しく芳香族化活性が低下した。一方, 水素還元処理は H-ZSM-5 には影響を及ぼさないが, ZnH-ZSM-5 の芳香族化活性を著しく低下させることが分かった。ZnH-ZSM-5 中の酸化亜鉛 (ZnO) は *n*-ヘキサン芳香族化の過程で生成した水素により還元されて 0 価の金属亜鉛と

なり, 熔融後, 触媒上から蒸発・飛散することが分かった。その結果, 芳香族化活性が低下したものと考えられる。

亜鉛の蒸発・飛散を抑制し芳香族化活性を維持するために, ZnH-ZSM-5 の予備硫化処理が有効であることを見出した。ZnH-ZSM-5 をチオフエン, ジメチルサルファイド, 二硫化炭素を用いて予備硫化処理することで, 亜鉛の飛散を抑制できるとともにメタン, エタン等の分解ガスの生成が抑えられ芳香族収率が増加することが分かった。

Keywords

Light naphtha, Aromatization, Pre-sulfiding, Catalyst stability, Catalyst pretreatment, Zinc silicate