[Review Paper]

Selective Formation of Light Olefins by Catalytic Cracking of Naphtha Components over ZSM-5 Zeolite Catalysts

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Catalytic cracking of C6-8 hydrocarbons as model naphtha components was evaluated over H-ZSM-5 catalysts with various Si/Al ratios at 723–923 K to selectively form light olefins. The highest ethylene + propylene yield was 59.7 C-% with a propylene/ethylene ratio of *ca.* 0.72 at 99.6 % conversion in the cracking of *n*-heptane over H-ZSM-5 (Si/Al = 31) at 923 K. The selectivities and activation energies indicated that monomolecular cracking was predominant at temperatures higher than 923 K. Next, cracking of various C6-8 hydrocarbons on H-ZSM-5 at high temperatures in the presence of another hydrocarbon was also investigated. Coexistent 1-hexene did not affect the cracking rate of *n*-heptane, cyclohexane, or methylcyclohexane, also indicating that monomolecular cracking was predominant at temperatures as high as 923 K. In contrast, coexistent cyclohexane and methylcyclohexane considerably affected the cracking rate of *n*-heptane because of their slow diffusion in the pores of H-ZSM-5. Moreover, catalysts with activity equal or higher than that of H-ZSM-5 and steaming stability higher than that of H-ZSM-5 were examined. The 194 %Cu-ZSM-5 and 95 %Ag-ZSM-5 zeolites exhibited high steaming stabilities and higher cracking activities than H-ZSM-5 and P/H-ZSM-5. In particular, 194 %Cu-ZSM-5 exhibited an ultra-high steaming stability under conditions such as 1023 K and 10 h presumably because Cu²⁺ and Cu⁺ cations in the 194 %Cu-ZSM-5 are not reduced to Cu⁰ at a high temperature of 1023 K in the presence of O₂.

Keywords

Catalytic cracking, Naphtha, Light olefin, ZSM-5, Steaming stability

1. Introduction

Light olefins, such as ethylene, propylene, and butene, are important raw materials for the industrial manufacture of various polymers and petrochemicals. Ethylene is the major product of the naphtha thermal cracking process, whereas propylene is a byproduct of this process¹⁾. The petrochemical industry is currently facing a major shortage of propylene as a result of the increasing demand for propylene derivatives (*e.g.*, polypropylene). However, the naphtha thermal cracking process cannot meet the demand for propylene since the selectivity for specific olefins is difficult to control (propylene/ethylene weight ratio is 0.5–0.6). Moreover, this process is usually operated at high temperatures (> 1073 K), and so requires a large amount of energy²⁾. Therefore, the naphtha catalytic cracking process is currently under investigation as an alternative to naphtha thermal cracking, because of its superior ability to obtain a propylene/ethylene weight ratio higher than 0.6 at lower reaction temperature. Most research into model

compounds of naphtha have used *n*-paraffins because naphtha is a mixture of hydrocarbons and the main components are C5-8 *n*-paraffins. Zeolite is a typical catalyst used for naphtha cracking^{3)–23)}. Specifically, ZSM-5 zeolite is one of the most efficient catalysts for the naphtha catalytic cracking process at high temperatures (873–923 K)^{13)–23)}. The reaction mechanism of *n*-paraffin cracking has been extensively investigated^{3)–24)}, but has not been completely clarified. Understanding of the activity and selectivity of catalysts for naphtha cracking requires not only kinetic studies but also consideration of the reaction mechanism.

Coke formation is considerable during naphtha cracking over zeolite catalyst, resulting in coverage of the catalytic surfaces and blocking of the micropores, resulting in deactivation of the catalyst. Therefore, regeneration of H-ZSM-5 by calcination in air is necessary. However, a small amount of steam is generated during the regeneration, because coke contains a small amount of hydrogen²⁵⁾. Permanent deactivation of the catalyst can occur related to dealumination from the zeolitic framework in a hydrothermal atmosphere. Therefore, a much higher stability against steaming conditions than that of H-ZSM-5 is required for improved catalysts for naphtha cracking.

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This article reviews the reaction mechanism of catalytic cracking of C6-8 hydrocarbons as a model reaction of naphtha catalytic cracking over H-ZSM-5 zeolites with various Si/Al ratios at 723-923 K, and discusses the stability against steaming conditions of H-ZSM-5 and modified ZSM-5.

2. Cracking of Hydrocarbons over H-ZSM-5 Zeolite at High Temperature

H-ZSM-5 catalysts (Si/Al = 31, 34, 51, 106, and 200) were synthesized by a hydrothermal procedure followed by conventional ion exchange in 1 M (1 mol L⁻¹) HCl solution²⁶. Hydrocarbon cracking was performed at 723-923 K^{15,22}. The contribution of thermal cracking was not negligible at 773 K or higher temperatures. Therefore, the rate constant of catalytic cracking was subtracted from the contribution of thermal cracking^{15,17,21~23}.

Haag *et al.* proposed that cracking of *n*-hexane and of 3-methylpentane proceeds through two simultaneous pathways, bimolecular cracking and monomolecular cracking^{3,4}. Bimolecular cracking is the classical chain process involving hydride transfer between a paraffin molecule and an adsorbed carbenium ion. Formation of a new carbenium ion is followed by skeletal isomerization prior to β -scission to avoid the formation of primary carbenium ions. Monomolecular cracking involves direct protonation of a paraffin to form a high energy transition state that may resemble a penta-coordinated carbonium ion, which is subsequently cracked or dehydrogenated. Bimolecular cracking predominates at low temperature and high olefin concentration, *i.e.* high conversion. Monomolecular cracking is favored by the opposite conditions.

bimolecular cracking:

where RH = original paraffin, R₁⁺ = smaller carbenium ion.

monomolecular cracking:

[$n = 0 \sim (m-1)$, $x + y = m - n$]

Monomolecular cracking only forms hydrogen, methane and ethane as primary products, excluding the effects of thermal cracking.

Haag *et al.* reported an activation energy of 126 kJ mol⁻¹ for the monomolecular cracking of *n*-hexane over H-ZSM-5 (Si/Al = 35) at 723-813 K and 153 kJ mol⁻¹ for the bimolecular cracking of *n*-hexane at 513-573 K⁴. Babitz *et al.* reported that the activation energy for the monomolecular cracking of *n*-hexane over H-ZSM-5

Table 1 k_c and E_a for the Catalytic Cracking of C6-8 Hydrocarbons

Reactant	k_c [mol g _{cat} ⁻¹ h ⁻¹]			E_a [kJ mol ⁻¹]
	723 K	823 K	923 K	
<i>n</i> -Hexane	0.0726	0.570	2.35	97
<i>n</i> -Heptane	0.177	0.719	2.60	74
<i>n</i> -Octane	0.275	1.06	3.28	69
3-Methylpentane	0.0453	0.409	2.07	106
2-Methylhexane	-	-	3.72	-
Methylcyclopentane	0.368	1.98	6.29	79
Cyclohexane	0.0959	0.704	2.78	94
Methylcyclohexane	0.132	0.881	2.37	81

(Si/Al = 25) at 753-813 K was 149 kJ mol⁻¹⁶. Narbeshuber *et al.* found the activation energy for the monomolecular cracking of *n*-hexane over H-ZSM-5 (Si/Al = 35) at 723-823 K was 105 kJ mol⁻¹ and that the activation energy decreased longer hydrocarbon chain length⁷. Nakasaka *et al.* reported that the activation energy for cracking of *n*-heptane over H-ZSM-5 (Si/Al = 320) at 823-923 K was 128 kJ mol⁻¹, and that at 748-823 K was 93 kJ mol⁻¹²⁰. Therefore, monomolecular cracking absolutely predominated in the cracking of *n*-hexane at 923 K. The reactivity of *n*-paraffins increased with higher carbon number.

Table 1 shows the rate constants and apparent activation energies for the catalytic cracking of C6-8 hydrocarbons²². The rate constants increased with higher carbon number at 923 K as observed at low temperatures⁷. However, the difference in the rate constants due to carbon number at 923 K was small compared to that at 723 K, probably because monomolecular cracking was predominant at high temperatures whereas both monomolecular and bimolecular cracking proceeded simultaneously at low temperatures.

The rate constants for the catalytic cracking of 2-methylhexane and methylcyclopentane containing a tertiary carbon were higher than those of *n*-heptane and cyclohexane without the tertiary carbon. The transition state in the monomolecular cracking of 2-methylhexane and methylcyclohexane is not so bulky compared with that in the bimolecular cracking of 2-methylhexane and methylcyclopentane, so no restricted transition state selectivity occurs in contrast to the cracking of 3-methylpentane on H-ZSM-5 at 811 K⁵. On the other hand, the rate constant for catalytic cracking of 3-methylpentane with a tertiary carbon was lower than that of *n*-hexane at low temperatures, because bimolecular cracking of 3-methylpentane via a bulky transition state is more restricted than that of *n*-hexane in narrow reaction spaces⁵. However, the effect on the rate constant at 923 K was much smaller than that at 723 K, because monomolecular cracking was predominant at high temperatures. The rate constants for the catalytic cracking of cyclohexane and methylcyclohexane were lower than that of methylcyclopentane, probably because of their

Table 2 Selectivity (C-%) at *ca.* 38 % Conversion for the Cracking of C6-8 Hydrocarbons at 923 K

Product	Reactant						
	<i>n</i> -Hexane	<i>n</i> -Heptane	<i>n</i> -Octane	2-Methylhexane	Methylcyclopentane	Cyclohexane	Methylcyclohexane
Ethylene	16.1	18.2	18.0	13.4	9.7	15.8	11.4
Propylene	37.1	31.9	33.1	40.3	61.5	44.3	33.3
Butenes	16.2	18.6	17.6	22.0	12.5	10.0	19.1
Benzene	0.5	0.5	0.4	0.2	1.7	8.3	7.3
Toluene	0.4	0.4	0.4	0.2	1.3	5.9	12.3
Xylene	0.1	0.1	0.1	0.0	0.6	2.5	3.1
Methane	3.6	2.5	2.3	5.2	0.9	0.9	2.8
Ethane	9.5	6.6	4.9	4.0	0.2	0.5	0.5
Propane	10.1	8.6	6.6	4.0	0.6	1.9	1.1
Butanes	4.1	7.4	7.0	6.6	0.3	0.4	0.4
C5+	2.4	5.2	9.6	3.9	10.6	9.3	8.7

slow diffusion rates.

Table 2 shows the selectivity (C-%) at a conversion of *ca.* 38 % for the cracking of C6-8 hydrocarbons at 923 K²²⁾. The selectivities for light olefins showed little difference between the C6-8 paraffins. The selectivity for propylene was very high for methylcyclopentane, because methylcyclopentane is stoichiometrically decomposed into two molecules of propylene. The selectivity for aromatics [benzene, toluene, and xylene (BTX)] was very high for cycloparaffins, especially for cyclohexane and methylcyclohexane. Therefore, the direct dehydrogenation reaction to the corresponding BTX, such as cyclohexane to benzene and methylcyclohexane to toluene, occurs in addition to the cracking reaction^{11),12),19)}. In fact, the selectivity for benzene was high for cyclohexane, and that for toluene was high for methylcyclohexane.

The relationships between selectivities expressed as C-% at a conversion of *ca.* 50 % and reaction temperatures for *n*-heptane cracking over H-ZSM-5 (Si/Al = 31) are shown in **Fig. 1**¹⁵⁾. Selectivities for ethylene and propylene increased at higher reaction temperature, whereas the propylene/ethylene ratio decreased from 3 at 723 K to 1.4 at 923 K. The selectivities for propane and butanes decreased with higher reaction temperature. The selectivities for methane and ethane increased, whereas those for butenes and BTX did not change noticeably with higher reaction temperatures. The change in selectivity with reaction temperature may be mainly caused by greater dominance of monomolecular cracking over bimolecular cracking at higher reaction temperature. The selectivities for methane, ethane, and light olefins increase, and the selectivities for propane and butanes decrease at a higher ratio.

The relationships between the selectivity expressed as C-% and conversion for *n*-heptane cracking over H-ZSM-5 (Si/Al = 31) at 923 K are shown in **Fig. 2**¹⁵⁾. The selectivities for propylene and butenes decreased with higher conversion. Only a small amount of BTX formed at low conversion, whereas the selectivity for BTX increased with higher conversion.

Fig. 1 Relationships between Selectivities at a Conversion of *ca.* 50 % and Reaction Temperatures for *n*-Heptane Cracking over H-ZSM-5 (Si/Al = 31) (TOS = 15 min)

Hydride transfer from olefins to carbenium intermediate species occurs on acid catalysts at high conversion levels to form paraffins and hydrogen-deficient species. Such hydrogen-deficient species, *e.g.* allyl-carbenium ion, would be further transformed into

Fig. 2 Selectivities for *n*-Heptane Cracking over H-ZSM-5 (Si/Al = 31) (reaction temp. = 923 K, TOS = 15 min)

BTX⁹⁾. The results shown in Fig. 2 indicate that BTX is secondary reaction product and forms mainly from propylene and butenes. Therefore, the formation of BTX reduces the olefin yields. On the other hand, little ethylene is consumed by the secondary reaction, because of the low reactivity of ethylene.

The ethylene + propylene selectivity increased, whereas the propylene/ethylene ratio decreased with higher reaction temperature. Therefore, high temperatures are required to obtain high ethylene + propylene yield. The highest ethylene + propylene yield obtained in this study was 59.7 C-% (propylene/ethylene ratio of *ca.* 0.72) at 99.6 % conversion over H-ZSM-5 (Si/Al = 31) at 923 K. This propylene/ethylene ratio is 1.4 times higher than that obtained from conventional thermal cracking (*ca.* 0.5)²⁾.

The yields of hydrogen, methane and ethane are almost proportional to the conversion up to 55 % conversion¹⁵⁾. Therefore, the selectivities for methane and ethane remain constant up to 55 % conversion. Most of the hydrogen, methane and ethane forms the primary

Fig. 3 Relationships between Sum of Selectivities for Hydrogen, Methane, or Ethane and Reaction Temperatures for *n*-Heptane Cracking over H-ZSM-5(51) (TOS = 15 min) (*n*-heptane conversion = 29-55 %)

products and little is formed or consumed by secondary reactions up to 55 % conversion. Consequently, that the ratio of monomolecular cracking to bimolecular cracking may not decrease at higher *n*-heptane conversion, *i.e.* olefin pressure, at the low initial pressure of *n*-heptane.

The relationship between the sum of selectivities for hydrogen, methane, and ethane, and reaction temperature for heptane cracking over H-ZSM-5 (Si/Al = 51) (*n*-heptane conversion = 29-55 %) is shown in Fig. 3. Hydrogen + methane + ethane selectivity (mol%) increased with higher reaction temperature, and the selectivity reached 65 % at 873 K and 923 K. Therefore, monomolecular cracking predominantly proceeded at 873 K and higher temperatures.

The relationship between the sum of selectivities for hydrogen, methane, and ethane, and *n*-heptane pressure for *n*-heptane cracking is shown in Fig. 4. The sum of selectivities for hydrogen, methane, and ethane decreased with higher heptane pressure at 773 K. The partial pressure of the produced olefin increases with higher heptane pressure so the contribution of bimolecular cracking is increased by greater carbenium ion concentration on the catalyst surface. On the other hand, the sum of selectivities for hydrogen, methane, and ethane remained almost unchanged even at high heptane pressure. Presumably monomolecular cracking predominantly proceeded even at high heptane pressure.

From these results, we conclude that high temperatures such as 873 K or 923 K, at which monomolecular cracking predominates, are desirable to increase the olefin yield.

3. Coexistence of other Hydrocarbons in Cracking on H-ZSM-5 Catalyst at High Temperatures

In order to understand the cracking chemistry of naphtha, both cracking of a single hydrocarbon and cracking of binary mixtures of hydrocarbons are important to study, because naphtha is a mixture of hydrocarbons. Moreover, understanding the effect of coexistence of other hydrocarbons in cracking on H-ZSM-5 is important to design the catalytic process for the cracking of naphtha.

First-order plots for the catalytic cracking of *n*-heptane and 1-hexene, and binary *n*-heptane/1-hexene mixtures at 923 K were obtained²²⁾. Proportional relationships were observed in the catalytic cracking of *n*-heptane coexisting with 1-hexene, and for the catalytic cracking of cyclohexane and methylcyclohexane coexisting with 1-hexene. These results indicate that the catalytic cracking of *n*-heptane, cyclohexane, and methylcyclohexane coexisting with 1-hexene obeys first-order kinetics. On the other hand, no proportional relationship was observed for the catalytic cracking of 1-hexene, because the conversion of 1-hexene was too high (> 93 %) to determine the rate constant. **Table 3** shows the rate constants for the catalytic cracking of

single and binary reactants at 923 K²²⁾. The rate constants (k_c) for the cracking of *n*-heptane, cyclohexane, and methylcyclohexane were almost the same in the presence and absence of 1-hexene. Therefore, coexisting 1-hexene does not affect the cracking rate of *n*-heptane, cyclohexane, or methylcyclohexane. These findings indicate that monomolecular cracking is predominant at 923 K. Cracking of *n*-hexane accelerates at 643 K with the coexistence of an olefin⁴⁾, because the cracking proceeds by bimolecular cracking, which predominates at such a low temperature. The reaction rate of a low reactivity reactant will accelerate in the presence of high reactivity reactant in bimolecular cracking.

If additivity in product yields can be established in binary cracking, the selectivity for each product in binary cracking can be calculated from the cracking yield of each product. Cracking of *n*-heptane and 1-hexene, and binary *n*-heptane/1-hexene was carried out under constant reaction conditions; constant temperature, W/F_{total} , and initial pressure of each reactant. The calculated selectivity agrees precisely with the selectivity obtained experimentally²²⁾. Therefore, cracking of *n*-heptane and 1-hexene proceeded almost independently.

First-order plots for the catalytic cracking of *n*-heptane, methylcyclohexane, and binary *n*-heptane/methylcyclohexane at 923 K were obtained²²⁾. Proportional relationships were observed in the catalytic cracking of *n*-heptane and methylcyclohexane and in the cracking of the binary mixture, and in the catalytic cracking of cyclohexane and *n*-heptane and in the cracking of the binary mixture. These results indicate that the catalytic cracking of *n*-heptane, cyclohexane, and methylcyclohexane in a binary mixture obeys first-order kinetics. **Table 4** shows the rate constants for catalytic cracking of single and binary reactants at 923 K²²⁾. The rate constants (k_c) for the cracking of cyclohexane and methylcyclohexane are almost the same in the presence and absence of *n*-heptane. Therefore, *n*-heptane does not affect the cracking rate of cyclohexane and methylcyclohexane. On the other hand, the rate constant (k_c) for the cracking of *n*-heptane was lower in the presence than in the absence of cyclohexane or methylcyclohexane. Therefore, cyclohexane and methylcyclohexane affect the cracking rate

Fig. 4 Relationships between Sum of Selectivities for Hydrogen, Methane, or Ethane and *n*-Heptane Pressure for *n*-Heptane Cracking over H-ZSM-5(51) (TOS = 15 min) (*n*-heptane conversion = 40 %)

Table 3 k_c for the Catalytic Cracking of Single and Binary Reactants at 923 K

Combination	Component	k_c [mol g _{cat.} ⁻¹ h ⁻¹]	
		Single	Binary
<i>n</i> -Heptane/1-hexene	<i>n</i> -Heptane	2.60	2.61
	1-Hexene	-	-
Cyclohexane/1-hexene	Cyclohexane	2.78	2.85
	1-Hexene	-	-
Methylcyclohexane/1-hexene	Methylcyclohexane	2.37	2.46
	1-Hexene	-	-

of *n*-heptane. The reaction obeys first-order kinetics, indicating that coverage of the reactant on the active sites is very low. Therefore, retardation of *n*-heptane cracking by coexistent cyclohexane and methylcyclohexane is not caused by their adsorption on the active sites, but by their slow diffusion in the pores of H-ZSM-5, as observed in *n*-octane cracking on H-ZSM-5 at 673 K¹⁰. The apparent activation energies of cracking of cyclohexane and methylcyclohexane were small, probably because the rate determining step is diffusion in the pores (Table 1).

Catalytic cracking of *n*-heptane, cyclohexane, and methylcyclohexane, and binary *n*-heptane/cyclohexane and *n*-heptane/methylcyclohexane mixtures at 923 K at relatively low conversion (13–21 %) were performed. If two reactants crack individually in the cracking of a binary reactant, additivity in the selectivity will be established. Thus, the selectivity for the cracking of binary reactants was calculated from the yields for the cracking of *n*-heptane and cyclohexane or methylcyclohexane. The calculated selectivity agreed well with the selectivity obtained experimentally²². Therefore, the cracking of *n*-heptane and cyclohexane or methylcyclohexane proceeds independently.

4. Effect of Si/Al Ratio of H-ZSM-5

The effect of reaction temperature and acid site density on *n*-heptane cracking activity can be inferred from the activation energy as a function of Al content of H-ZSM-5 catalysts. The activation energies obtained from the Arrhenius plots over various Si/Al ratios are shown in Fig. 5¹⁵. The activation energy for the catalytic cracking of *n*-heptane tended to decrease with higher acid site density. Post *et al.* reported a similar phenomenon for *n*-hexane cracking over H-ZSM-5 with various Si/Al ratios, and concluded that the bimolecular cracking route is favored by the presence of two neighboring acid sites²⁴.

The selectivities (not C-% but mol%) at 923 K as a function of Si/Al ratio at conversion of *ca.* 70 % are shown in Table 5¹⁵. Since the selectivity is a function of the conversion, meaningful comparison of selectivities can only be made at similar conversions, which was achieved by adjusting the catalyst weight (*W*). All H-ZSM-5 zeolites exhibited almost the same selectivities, olefin/paraffin ratios (*O/P*), and ratio of *i*-butene/*n*-

butenes. These observations indicate that the acid site density little affects the selectivity at a relatively high conversion of 70 %.

On the other hand, CMR ratios, which Post *et al.* defined as a parameter of the ratio of monomolecular cracking to bimolecular cracking²⁴, increased significantly with higher Si/Al ratio, suggesting that the ratio of monomolecular cracking to bimolecular cracking may increase with higher Si/Al ratio. This consideration agrees with Post *et al.*²⁴. However, the CMR may not be a suitable parameter in our reaction conditions, because ethylene is produced by a secondary reaction at high reaction temperatures such as 923 K. Moreover, the observation that the acid site density little affects the selectivity suggests that the ratio of monomolecular cracking to bimolecular cracking may not greatly change with the Si/Al ratio, because the ratio must affect the selectivity. Brønsted acid strength is constant or slightly weakened with higher Al contents²⁷. Therefore, we consider that there is a distribution of acidity and the acid strength increases with higher acid site density of H-ZSM-5 based on the activation energy.

Fig. 5 Effect of Acid Site Density of H-ZSM-5 on the Apparent Activation Energy of *n*-Heptane Cracking

Table 4 k_c for the Catalytic Cracking of Single and Binary Reactants at 923 K

Combination	Component	k_c [mol g _{cat} ⁻¹ h ⁻¹]	
		Single	Binary
<i>n</i> -Heptane/cyclohexane	<i>n</i> -Heptane	2.60	2.35
	Cyclohexane	2.78	2.77
<i>n</i> -Heptane/methylcyclohexane	<i>n</i> -Heptane	2.60	2.10
	Methylcyclohexane	2.37	2.40

Table 5 Effect of Acid Site Density of H-ZSM-5 on Selectivities (mol%) for Cracking of *n*-Heptane at ca. 70 % Conversion (reaction temp. = 923 K, TOS = 15 min)

Si/Al ^{a)}	31	34	51	106	200
C ₂ H ₄	32.5	33.0	34.0	32.3	31.9
C ₃ H ₆	28.7	26.3	29.9	29.3	28.3
<i>n</i> -C ₄ H ₈	6.0	5.2	5.8	6.0	6.2
<i>i</i> -C ₄ H ₈	3.2	2.8	3.2	3.3	3.4
BTX	1.5	2.5	1.0	1.0	0.7
CH ₄	6.4	8.4	5.9	6.4	7.6
C ₂ H ₆	8.2	9.2	7.1	8.4	9.0
C ₃ H ₈	8.2	7.9	7.8	7.7	7.1
<i>n</i> -C ₄ H ₁₀	3.5	3.1	3.5	3.6	3.6
<i>i</i> -C ₄ H ₁₀	0.4	0.4	0.3	0.3	0.2
C ₅ +	1.5	1.4	1.5	1.7	2.1
CMR ^{b)}	118	131	158	174	202
<i>O/P</i> ^{c)}	3.47	3.28	3.90	3.54	3.50
<i>i</i> -C ₄ H ₈ / <i>n</i> -C ₄ H ₈	0.54	0.55	0.55	0.55	0.55

a) Determined by ICP measurement.

b) (C₁ + ΣC₂)/*i*-C₄ (as described²⁴⁾).

c) C_{*n*}H_{2*n*}/C_{*n*}H_{2*n*+2} (*n* = 2-4).

5. Steaming Stability of H-ZSM-5, Ag-ZSM-5 and Cu-ZSM-5

Phosphorus impregnation is known to be effective for improving the steaming stability of H-ZSM-5²⁸⁾. However, phosphorus-impregnated H-ZSM-5 (P/H-ZSM-5) exhibits lower activity for catalytic cracking than H-ZSM-5, because the Brønsted acidity of P/H-ZSM-5 is lower than that of H-ZSM-5. Sano *et al.* reported that protons catalyze the dealumination of H-ZSM-5²⁹⁾. Therefore, a catalyst with lower Brønsted acidity may exhibit higher steaming stability, but lower activity for catalytic cracking. Catalyst regeneration is carried out in the presence of O₂; whereas cracking over H-ZSM-5 at high temperatures takes place in a reductive atmosphere, due to the formation of a considerable amount of H₂. Therefore, catalysts with low Brønsted acidity in an oxidative atmosphere and high Brønsted acidity in a reductive atmosphere are likely to have both high steaming stability and high catalytic activity. We considered that Ag-ZSM-5 and Cu-ZSM-5 with redox properties were candidate catalysts for the naphtha catalytic cracking process at high temperatures.

Exchange rates of Ag⁺ and Cu²⁺ were determined to be 95 % and 194 % by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) measurements, respectively. Such high exchange rate of 194 % for Cu²⁺ indicates that [Cu(OH)]⁺ cations occupy almost all of the cation exchange sites¹⁷⁾.

The temperature-programmed desorption of ammonia (NH₃-TPD) spectra for H-ZSM-5, 95 %Ag-ZSM-5, and 194 %Cu-ZSM-5 were obtained²³⁾. H-ZSM-5 exhibited two desorption peaks at low (477 K) and high (660 K) temperatures. The high temperature peak was assigned to the desorption peak of ammonia, which was adsorbed on the Brønsted acid sites, whereas the low

temperature peak was assigned to ammonia weakly held or physically adsorbed on the zeolite^{30),31)}. In contrast, the desorption peak of ammonia at 660 K was scarcely observed in the case of 95 %Ag-ZSM-5 and 194 %Cu-ZSM-5, but desorption peaks were observed at 756 K for 95 %Ag-ZSM-5 and at 847 K for the 194 %Cu-ZSM-5. We will discuss the nature of these peaks later.

The Fourier transform infrared (FTIR) spectra of pyridine adsorbed on H-ZSM-5, 95 %Ag-ZSM-5, and 194 %Cu-ZSM-5 were obtained²³⁾. The band at 1545 cm⁻¹ was assigned to pyridinium ions formed by proton transfer from Brønsted acid sites, and the band at 1455 cm⁻¹ was identical to pyridine adsorbed on Lewis acid sites. Clearly oxidized 95 %Ag-ZSM-5 and oxidized 194 %Cu-ZSM-5 had few Brønsted acid sites and considerable amounts of Lewis acid sites. The NH₃-TPD desorption peaks at 756 K for 95 %Ag-ZSM-5 and at 847 K for the 194 %Cu-ZSM-5 may be attributed to these Lewis acid sites. On the other hand, the amounts of Brønsted acid sites on reduced 95 %Ag-ZSM-5 and reduced 194 %Cu-ZSM-5 are similar to those on H-ZSM-5. These findings indicate that these catalysts have low Brønsted acidity in an oxidative atmosphere and high Brønsted acidity in a reductive atmosphere.

The first-order rate constants for the cracking of cumene over the catalysts are shown in **Table 6**²³⁾. The activities of reduced 194 %Cu-ZSM-5 and reduced 95 %Ag-ZSM-5 were much higher than those of oxidized 194 %Cu-ZSM-5 and oxidized 95 %Ag-ZSM-5. These findings indicate that the Brønsted acid sites were generated by reduction of copper cations and silver cations. Moreover, the activities of reduced 194 %Cu-ZSM-5 and reduced 95 %Ag-ZSM-5 were higher than that of H-ZSM-5. Catalytic activity for cracking or

isomerization of hydrocarbons in the presence of H_2 is enhanced by the addition of a metal capable of H_2 dissociation to acidic zeolites^{32),33)}. Hattori *et al.* proposed that such enhancement is due to the generation of molecular hydrogen-originated protonic acid sites³³⁾. The higher activity of Cu-ZSM-5 and Ag-ZSM-5 than that of H-ZSM-5 may be caused by the reduction of Cu^{2+} and Ag^+ , resulting in the formation of Brønsted acid sites, Cu metals, and Ag metals with H_2 dissociation ability at 923 K. On the other hand, the activities of oxidized Cu-ZSM-5, oxidized Ag-ZSM-5, and P/H-ZSM-5 were lower than that of H-ZSM-5, because the modifications decreased the Brønsted acidity of the H-ZSM-5. Moreover, the activities of the oxidized Cu-ZSM-5 and oxidized Ag-ZSM-5 decreased with higher exchange rate. These findings are consistent with the NH_3 -TPD spectra. The order of cumene cracking activities was H-ZSM-5 > P/H-ZSM-5 > oxidized 95 %Ag-ZSM-5 > oxidized 194 %Cu-ZSM-5. These findings show that Cu-ZSM-5 and Ag-ZSM-5 have low Brønsted acidities in the presence of O_2 and high Brønsted acidities in a reductive atmosphere compared with H-ZSM-5.

In order to clarify the steaming stabilities, we carried out cracking of *n*-heptane over catalysts after steaming under more severe conditions (1023 K, 10.0 h). The steaming stabilities are shown in Table 7²³⁾. The order of retained percentage activity, which is a function of the steaming stability, was 194 %Cu-ZSM-5 > 95 %Ag-ZSM-5 > P/H-ZSM-5 > H-ZSM-5, which was the reverse order of the cumene cracking activities in the presence of O_2 . Cumene cracking activity is a function of the Brønsted acidity. Therefore, the steaming stability of a catalyst is strongly related to its

Brønsted acidity.

In order to examine the reduction temperatures of Cu^{2+} in Cu-ZSM-5 and Ag^+ in Ag-ZSM-5, we carried out H_2 -temperature-programmed reduction (H_2 -TPR) measurements. The H_2 -TPR spectra for 194 %Cu-ZSM-5 and 95 %Ag-ZSM-5 are shown in Fig. 6²³⁾. The low temperature peak of 194 %Cu-ZSM-5 was ascribed to Cu^{2+} reduction to Cu^+ and the high temperature peak to Cu^+ reduction to Cu^0 ³⁴⁾. Therefore, Cu^{2+} cations in Cu-ZSM-5 were reduced to copper metal at around 723 K. The low temperature peak of 95 %Ag-ZSM-5 was ascribed to the silver cationic clusters (Ag_n^+) formed by reaction between Ag^0 and Ag^+ , and the high temperature peak to Ag_n^+ reduction to silver metal^{35)~37)}. Therefore, some silver cations in ZSM-5 were reduced to silver metal at low temperatures at around 473 K, and all silver cations in Ag-ZSM-5 were reduced to silver metal at around 653 K. These findings indicate that the Ag^+ cations in Ag-ZSM-5 are readily reduced to metal, compared with the Cu^{2+} cations in Cu-ZSM-5. The amounts of H_2 consumption for each peak in the H_2 -TPR spectra were calculated from the peak areas and theoretical values were calculated from the cation exchange rate²³⁾. H_2 consumptions at low and high temperatures were almost the same and their sum was nearly equal to the theoretical value for 194 %Cu-

Fig. 6 H_2 -TPR Spectra for 194 %Cu-ZSM-5 and 95 %Ag-ZSM-5

Table 6 First-order Rate Constants for Cracking of Cumene

Catalysts	First-order rate constant ^{a)} [mol g _{cat} ⁻¹ h ⁻¹]
H-ZSM-5	1.16
194 %Cu-ZSM-5(O_2)	0.11
194 %Cu-ZSM-5(H_2)	1.44
95 %Ag-ZSM-5(O_2)	0.16
95 %Ag-ZSM-5(H_2)	1.89
P/H-ZSM-5	0.79

a) Data at 15 min on stream.

Table 7 Steaming Stabilities of Catalysts (steaming conditions: 1023 K, 10.0 h, H_2O/N_2 or $H_2O/O_2 = 1/1.83$)

Catalysts	k_c ^{a)} [mol g _{cat} ⁻¹ h ⁻¹]		Percent activity retained ^{b)} [%]
	Fresh	Steamed	
H-ZSM-5	1.78	0.30 [N_2]	17
P/H-ZSM-5	1.51	0.59 [N_2]	39
95 %Ag-ZSM-5	2.07	1.22 [O_2]	59
194 %Cu-ZSM-5	2.27	2.36 [O_2]	104

a) Data at 15 min on stream.

b) (Percent activity retained) = (k_c for steamed catalyst)/(k_c for fresh catalyst) $\times$ 100 %.

ZSM-5. Therefore, all copper cations in Cu-ZSM-5 were Cu^{2+} in the form of $[\text{Cu}(\text{OH})]^+$ after the pretreatment followed by oxidation, Cu^{2+} was reduced to Cu^+ at around 540 K, and finally Cu^+ was reduced to Cu^0 by H_2 at around 723 K as shown below:

where ZO^- denotes the zeolite framework. If reoxidation of Cu^0 is ideal, Cu^0 is oxidized to $[\text{Cu}(\text{OH})]^+$ by O_2 as follows:

H_2 consumption for reduction of silver cations at low temperature was lower than that at high temperature and their sum was lower than the theoretical value for 95 %Ag-ZSM-5. This indicates that some silver cations were thermally reduced by the oxidation treatment at 923 K. The H_2 consumption at high temperature was approximately half of the theoretical value. Therefore, Ag_2^+ was formed at around 473 K, and finally Ag_2^+ was reduced to silver metal by H_2 at around 653 K as shown below:

If reoxidation of Ag_2^0 is ideal, Ag_2^0 is oxidized to 2Ag^+ by O_2 as follows:

We conclude that Cu^{2+} and Cu^+ cations in 194 %Cu-ZSM-5 are not reduced to Cu^0 at a high temperature of 1023 K in the presence of O_2 and, therefore, 194 %Cu-ZSM-5 exhibits ultra-high steaming stability in the presence of O_2 . The Brønsted acidity of 95 %Ag-ZSM-5 is extremely low, almost equal to that of 194 %Cu-ZSM-5. However, thermal reduction of Ag^+ occurs during steaming even in the presence of O_2 at a high temperature of 1023 K and, therefore, the steaming stability of 95 %Ag-ZSM-5 in the presence of O_2 is much lower than that of 194 %Cu-ZSM-5.

6. Conclusion

This study reviewed the reaction mechanism of the catalytic cracking of C6-8 hydrocarbons as naphtha components over H-ZSM-5 catalysts at high temperature to selectively form light olefins, and methods for enhancing the steaming stability of H-ZSM-5. High temperature such as 873 to 923 K at which monomolecular cracking progressed predominantly is desirable to obtain high ethylene and propylene yields. There may be a distribution of acidity and the acid strength may

increase with higher acid site density of H-ZSM-5. 194 %Cu-ZSM-5 exhibits an ultra-high steaming stability and higher cracking activity than H-ZSM-5, P/H-ZSM-5 and Ag-ZSM-5, as Cu^{2+} and Cu^+ cations in the 194 %Cu-ZSM-5 are not reduced to Cu^0 at a high temperature of 1023 K in the presence of O_2 .

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要 旨

ZSM-5系ゼオライト触媒上でのナフサ成分の接触分解による低級オレフィンの選択的合成

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ナフサから低級オレフィンを選択的に得るために, 723 ~ 923 K で種々の Si/Al 比の H-ZSM-5 系ゼオライト触媒上で, ナフサ成分である C6 ~ 8 炭化水素の接触分解を行った。最初に, 923 K, H-ZSM-5 (Si/Al = 31) 上で *n*-ヘプタンの接触分解を行ったところ, 転化率 99.6 % で 59.7 C-% の高いエチレン+プロピレン収率 (プロピレン/エチレン比 = 約 0.72) が得られた。そして, 生成物分布と活性化エネルギーから, 923 K 以上の高温では単分子反応機構が支配的であることを明らかにした。次に, 2成分系炭化水素の接触分解を行った。その結果, 1-ヘキセンの共存は, *n*-ヘプタン, シクロヘキサン, またはメチルシクロヘキサンの分解速度に影響を与えないことから, 923 K 以上の高温では単分子反応機構が支配的であることが支持され

た。一方, シクロヘキサンやメチルシクロヘキサンの共存は, *n*-ヘプタンの分解速度にかなりの影響を与えることから, H-ZSM-5 細孔内でそれらの拡散速度が遅いことが示唆された。さらに, H-ZSM-5 と同等もしくはそれ以上の触媒活性と H-ZSM-5 よりも高い耐スチーム性を有する触媒の開発について検討したところ, 194 % Cu-ZSM-5 や 95 % Ag-ZSM-5 が H-ZSM-5 や P/H-ZSM-5 に比べて耐スチーム性が高いことが明らかとなった。特に, 194 % Cu-ZSM-5 は, 1023 K, 10 h のスチーム条件で極めて高い耐スチーム性を示した。この理由は, 194 % Cu-ZSM-5 中の Cu²⁺ および Cu⁺ が, 1023 K, 酸素共存下において Cu⁰ に還元されないためである。