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Catalytic Cracking of Soybean Oil Using Zeolite-containing Microporous and Mesoporous Mixed Catalysts with Curie Point Pyrolyzer

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Zeolite-containing catalysts with hierarchical structures were prepared by combining microporous zeolites (beta and Y zeolite) with mesoporous matrices (silicas and silica-aluminas with large mesopores) prepared by the gel skeletal reinforcement method and a binder. Morphology of the prepared catalysts was characterized by X-ray diffraction, nitrogen adsorption-desorption, ammonia adsorption-desorption, and thermogravimetric-differential thermal analysis. Catalytic cracking of soybean oil was performed with these mixed catalysts to observe the effect of the pore size on the catalytic activity and the selectivity of products using the convenient Curie point pyrolyzer. Zeolite-containing mixed catalysts exhibited great improvements in all aspects such as maximum increase of 31 % conversion, about 10 % higher gasoline yields, and maximum decrease of 36 % coke formation in comparison with single zeolite, indicating that the presence of the matrices greatly influenced the catalytic cracking. The yields of gasoline, single branched and multi-branched hydrocarbons increased with higher conversion, indicating that increased conversion was necessary to obtain higher yields of products. In comparison of product yields at the same conversion, Y zeolite-containing catalysts exhibited the higher yields than beta (β) zeolite-containing catalysts, indicating that the larger micropore diameter of Y zeolite in the catalysts induced the increase in the gasoline fraction and promoted the isomerization to produce the bulkier products. The conversion of soybean oil increased with increasing the pore diameter for β series catalysts and the conversions were maximum for MAT(200S)- β and MAT(200SA)- β with relatively larger mesopores, indicating that the diffusion of reactants and products affected the catalytic performance. In contrast to this phenomenon, MAT(OS)-Y and MAT(OSA)-Y with relatively smaller mesopores exhibited the maximum conversions for Y series catalysts.

Keywords

Gel skeletal reinforcement, Pore diameter, Curie point pyrolyzer, Catalytic cracking, Soybean oil

1. Introduction

Vegetable oil biomass is one of the renewable resources with potential for the production of clean fuels because it is convenient and ready to use as a feedstock without requiring pretreatment prior to the main process reaction. Various production technologies using such raw materials have been investigated based on reactions such as transesterification^{1)~3)}, hydrotreating process^{4)~6)}, thermal cracking⁷⁾, catalytic cracking^{8)~12)}, depending on the demand for the final product. Transesterification is the most common technique, but requires more processes to purify the organic liquid products, which include not only fatty acid methyl esters but also glycerol and carboxylic acids. In addition,

thermal cracking of the triglycerides resulted in excess fatty acids instead of normal hydrocarbons⁷⁾. Therefore, alternative processes have been proposed, of which catalytic cracking is one of the most promising technologies because of the applicability to various compounds.

Most catalysts for fluid catalytic cracking (FCC) are zeolites^{8)~12)} with high selectivity for the gasoline fraction. Catalytic cracking of hydrocarbons with high boiling point or high molecular weight suffers limitations in diffusion due to the bulky structure of the raw materials compared to the morphology of microporous catalysts^{13)~17)}. Vegetable oils include triglycerides which are likely to exhibit difficulty and limitations in diffusion into the active microporous sites of the zeolite catalyst. However, catalysts consisting of zeolites and mesoporous matrices for the catalytic cracking of vegetable oils into the gasoline fraction have not been investigated extensively. Four types of zeolites (Ultrastable Y (HY), Beta (BEA), micro-crystalline ZSM-5 (MZ) and nano-crystalline ZSM-5 (NZ)) were used in the cat-

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alytic cracking of jatropha oil in a fixed bed reactor, and found high yield of gasoline fraction with NZ catalyst due to its moderate acidity and stacking order of mesoporosity¹¹. HZSM-5/alumina with 35 wt% alumina catalyst gave higher gasoline yield and lower deactivation rate compared to microporous HZSM-5¹⁸. Mesoporous catalysts with AIMCM-41 (Si/Al=18) were the most active resulting in gasoline selectivity of 36 %¹⁹. Therefore, micro-mesoporous composite is expected to improve the diffusion of large molecules such as vegetable oils and to enhance the catalytic activity.

To prepare mesoporous matrices, we have modified the conventional sol-gel technique^{20)~27)} and developed the gel skeletal reinforcement (GSR) technique^{28)~31)}. Mesoporous matrices were mixed with zeolites and binder to form hierarchical structure. The pore diameter and pore volume of silica of the mesoporous matrix after calcination at 600 °C could be controlled to maximums of 30 nm and 3.1 cm³/g by the amount of tetraethylorthosilicate (TEOS) solution for reinforcement, indicating that the silica consisted mainly of mesopores²⁸. In this study, GSR mesoporous matrices prepared with different pore sizes were combined with β zeolite or Y zeolite, and alumina binder. Catalytic cracking of soybean oil was performed to investigate the effects of pore size on the activity and product selectivity of these catalysts using the Curie point pyrolyzer (CPP) method, which allows very convenient and simple investigation of catalytic cracking^{31)~35)}.

2. Experimental

2.1. Catalyst Preparation

Mesoporous silicas and silica-aluminas were prepared using tetraethylorthosilicate (TEOS, Nacalai Tesque, Inc.), aluminum tri-*s*-butoxide (ASB, Tokyo Chemical Industry Co., Ltd.), and 35 wt% hydrochloric acid (HCl, Nacalai Tesque, Inc.) diluted to 0.10 wt%, 28 wt% ammonia solution (NH₃ aq., Nacalai Tesque, Inc.) diluted to 2.5 wt%, ion-exchange water (prepared by Auto still WA200, Yamato Scientific Co., Ltd.), 2-butanol (Nacalai Tesque, Inc.) and 2-propanol (Nacalai Tesque, Inc.) as starting materials. The acid-base catalyzed sol-gel process including gel skeletal reinforcement (GSR) was used in this silica and silica-alumina preparation, as described in detail elsewhere³¹. The HCl solution was added dropwise into a stirring TEOS/2-propanol solution at room temperature and stirred for 30 min. After the pH of the solution was adjusted to 5 by adding aqueous NH₃ solution, gelation was performed at 50 °C and maintained for 5 h. Then, the gel was crushed roughly and immersed in deionized water at 50 °C for 24 h. After that, the gel was crushed to pieces of less than 5 mm size and solvent exchange with 2-propanol was performed to remove the remain-

ing water. The washed gel was kept in reinforcing solution (80 % TEOS with 20 % 2-propanol) at 50 °C for 48 h with different amounts of TEOS³¹; 100 % (same amount) and 200 % (double amount) of TEOS in reinforcing solution to TEOS as SiO₂ precursor. Then, the reinforcing solution was removed and the gel was washed again with 2-propanol. After storing the obtained gel at 70 °C for 72 h, the silica gel (named S) was calcined at 600 °C for 3 h. Afterwards, aluminum species were introduced into the prepared silicas (100S and 200S) by impregnation of aluminum tri-*s*-butoxide (ASB) and 2-butanol solution to form 5 wt% Al₂O₃ in silica-alumina (SA). Next, the silica-aluminas (100SA and 200SA) were heated at 600 °C for 3 h. Finally, 58 wt% of synthesized silicas and silica-aluminas were mixed with 16 wt% of alumina binder (Cataloid AP-1, JGC Catalysts and Chemicals Ltd.) and β zeolite (HSZ-940HOA; SiO₂/Al₂O₃ 37 mol/mol, Tosoh Corp.) or Y zeolite (JRC-HY5.5; SiO₂/Al₂O₃ 5.5 mol/mol, reference catalyst of Catalysis Society of Japan, Tosoh Corp.) by adding 2-propanol to obtain the required viscosity. The mixtures were then extruded and calcined at 600 °C for 3 h. The catalysts were named as MAT(type of silica or silica-alumina)-(type of zeolite)³¹, for example, MAT(OS)- β or MAT(OSA)- β .

2.2. Characterization of Prepared Catalysts

2.2.1. X-ray Diffraction Measurement

X-ray diffraction (XRD) patterns of the samples were obtained with an Ultima IV (Rigaku Corp.) using nickel-filtered Cu-K α X-ray source radiation ($\lambda = 1.5405$ nm). Each catalyst sample was ground, set up on the fixed glass holder inside the chamber and analyzed at 40 kV and 100 mA of applied voltage under the following conditions: scan mode CONTINUOUS, slit (SS) 1° (DS) 1° (RS) 0.3 mm, present time 1 s, scan speed 2°/min, measurement range $2\theta = 10$ –70°.

2.2.2. N₂ Adsorption and Desorption Measurement

N₂ adsorption of a calcined sample was performed using a BELSORP-mini-I (BEL Japan Inc.). First, the sample was degassed under 10⁻² kPa at 350 °C for 3 h before N₂ adsorption measurement by BELPREP II (BEL Japan Inc.). The Brunauer-Emmett-Teller (BET) method was chosen to calculate the total surface area, pore volume, and pore size distribution, and the Barrett-Joyner-Halenda (BJH) method was used *via* BEL Master program (BEL Japan Inc.) to estimate the characteristics of the mesopores.

2.2.3. NH₃ Adsorption and Desorption

To determine the number of acid sites, the amount of NH₃ adsorbed was measured by the pulse method using a gas chromatography-thermal conductivity detector (GC-TCD, under the following conditions; INJ/DET 170 °C; COL 140 °C; ATTN 16; current 100 mA; column flow 50 cm³/min GC-8A, Shimadzu Corp.). Sample 0.04 g was packed into a fixed-bed reactor, heated to

600 °C at 10 °C/min under a He stream of 30 mL/min, and held for 3 h. The reactor was cooled to 100 °C and NH₃ pulses of 1.0 mL were introduced using a six-way valve until the amount of NH₃ detected became constant. Before the desorption measurement, N₂ gas was used to flush the unnecessary NH₃ out of the system for 30 min. Then, the amount of NH₃ desorbed was measured by heating the NH₃ adsorbed sample from 100 to 650 °C at 10 °C/min.

2. 2. 4. Thermogravimetric-differential Thermal Analysis (TG-DTA)

TG-DTA was used to observe the amount of coke deposition on solid catalyst which occurred during catalytic cracking. The coke amount was estimated using Eq. (1) from the total weight loss of sample in the period of the exothermic peak (500-600 °C). The TG-DTA instrumentation consisted of differential thermogravimetric analysis (DTG-60AH, Shimadzu Corp., Japan), equipped with a flow controller (FC-60A, Shimadzu Corp., Japan) and a thermal analysis workstation (TA-60WS, Shimadzu Corp., Japan). Before measurement, without the sample, an empty aluminum sample set (cup with separated lid) was placed on the automatic sample tray to determine the blank sample under O₂ stream of 100 mL/min with heating rate of 10 °C/min to 25 °C. After the blank test, the catalyst sample was added into the same aluminum sample set using the same conditions and heated until the temperature reached 600 °C.

$$\text{Coke amount (\%)} = \frac{\text{Weight loss 500-600 } ^\circ\text{C (mg)}}{W_{\text{SBO}} \text{ (mg)} \times \text{carbon amount (\% in soybean oil)}} \times 100 \quad (1)$$

where W_{SBO} is the amount of soybean oil used in soybean oil cracking.

2. 3. Catalytic Cracking Reaction

Catalytic cracking was carried out using a Curie point pyrolyzer (CPP, JCI-22S, Japan Analytical Industry Co., Ltd.) under the following conditions: soybean oil (SBO) 0.20 mg (without any pretreatment, H: 10.95 %; C: 76.64 %; N: 0.30 %; single component: linoleic acid 55 %, oleic acid 22 %, palmitic acid 11 %, stearic acid 4 %, linolenic acid 8 %, Wako Pure Chemical Industries, Ltd.), prepared catalyst 1.50 mg (particle size 45-75 µm), at 500 °C, for 5 s. Sample preparation was done by wrapping soybean oil together with catalyst using a ferromagnetic alloy (Pyrofoil, F500, Japan Analytical Industry Co., Ltd.). The prepared sample was then set up in the CPP injector tool. This CPP was operated similarly to a fixed-bed type pyrolyzer at 500 °C in the absence of oxygen with the replacement of 0.45 MPa He stream instead. After pyrolysis for 5 s, all products were introduced directly into the gas chromatograph, GC-FID (Shimadzu GC-2010, column BP-1) and analyzed by referring to JIS K 2536-2. Details appear elsewhere¹⁴⁾. The measurement conditions were as follows: injection temperature 250 °C, detector temperature 320 °C, ATTN 1, injection

pressure 158 kPa, column flow 1.56 mL/min, line speed 27.64 cm/s, total flow 320 mL/min, split ratio 200, column BP-1, column length 60 m, column diameter 0.25 mm, film thickness 0.5 µm, column initial temperature 0 °C, 16 min, heating rate 2 °C/min, and final temperature 228 °C. The conversion of soybean oil was estimated by comparison between the total area of products and toluene standard as described below:

$$\text{Conversion of SBO} = \frac{A_{\text{SBO}}}{W_{\text{SBO}} C_{\text{SBO}}} \times \frac{W_{\text{Toluene}} C_{\text{Toluene}}}{A_{\text{Toluene}}} \times 100 \quad (2)$$

where the absolute determination method by peak areas derived from carbons in hydrogen-flame ionization detector (FID) of GC was used. Conversion of SBO is defined as the ratio of the amount of carbon detected by GC against the amount of carbon in SBO introduced in the CPP experiment. A_{SBO} represents total peak area of products in soybean oil cracking measured by GC, A_{Toluene} the peak area of the toluene standard measured by GC, C_{SBO} the weight ratio of carbon in the soybean oil determined by elemental analysis, C_{Toluene} the weight ratio of carbon in toluene injected, W_{SBO} the amount of soybean oil used in soybean oil cracking, and W_{Toluene} the amount of toluene injected.

3. Results and Discussion

3. 1. Characterization of Hierarchical Zeolite-containing Silicas and Silica-aluminas

β and Y zeolite-containing silicas and silica-aluminas were prepared by the sol-gel process including gel skeletal reinforcement and impregnation. **Figure 1** shows the XRD patterns of the mixed catalysts. Peaks of β zeolite and Y zeolite crystals and broad peaks of amorphous silica and silica-alumina were observed in the mixed catalysts, indicating that both crystals of β zeolite and Y zeolite were maintained in all amorphous matrices.

Tables 1 to 3 show results from the N₂ adsorption measurements. The pore sizes of silicas increased with increasing the reinforcing agent (80 % TEOS/PrOH), indicating that the pore sizes of mesoporous silicas can be controlled by the amount of reinforcing agent. Using 200 wt% of TEOS for the gel skeletal reinforcement, the pore volume (PV) and pore diameter (PD) measured by the BJH method increased to about 3.36 cm³/g and 37.9 nm, respectively. After impregnation with alumina, the pore sizes of silica-aluminas decreased slightly (maximum with $PV=2.36$ cm³/g and $PD=24.5$ nm) compared to the original silicas. β and Y zeolites had very low surface areas (SA), pore volumes and pore diameters measured by the BJH method (β zeolite; $SA=24$ m²/g, $PV=0.07$ cm³/g and $PD=3.3$ nm, Y zeolite; $SA=35$ m²/g, $PV=0.16$ cm³/g and $PD=3.3$ nm) and larger differences were observed for these values compared to the BET method³¹⁾ (β zeolite; $SA=613$ m²/g, $PV=0.32$ cm³/g and $PD=2.1$ nm, Y zeolite; $SA=724$ m²/g,

Fig. 1 XRD Patterns of a) Y Zeolite-containing Catalysts; b) β Zeolite-containing Catalysts

Table 1 Surface Areas, Pore Volumes, and Pore Diameters from N_2 Adsorption Analysis of Matrix Silicas and Silica-aluminas

Matrix	BET			BJH		
	Surface area, <i>SA</i> [m ² /g]	Pore volume, <i>PV</i> [cm ³ /g]	Pore diameter, <i>PD</i> [nm]	Surface area, <i>SA</i> [m ² /g]	Pore volume, <i>PV</i> [cm ³ /g]	Pore diameter, <i>PD</i> [nm]
OS	749	1.91	10.2	776	1.85	10.6
100S	651	2.76	17	587	2.71	24.5
200S	670	3.44	20.5	569	3.36	37.9
OSA	613	1.1	7.2	638	1.06	9.2
100SA	608	1.6	10.6	469	1.5	18.5
200SA	614	3.07	20	301	2.36	24.5

Table 2 Surface Areas, Pore Volumes, and Pore Diameters from N_2 Adsorption Analysis³¹⁾ and NH_3 Adsorption-desorption Measurement of β Zeolite-containing Catalysts

Catalyst	BET			BJH			Amount of NH_3 adsorbed [10 ⁻⁴ mol/g]
	Surface area, <i>SA</i> [m ² /g]	Pore volume, <i>PV</i> [cm ³ /g]	Pore diameter, <i>PD</i> [nm]	Surface area, <i>SA</i> [m ² /g]	Pore volume, <i>PV</i> [cm ³ /g]	Pore diameter, <i>PD</i> [nm]	
β zeolite	613	0.32	2.1	24	0.07	3.3	5.9 (4.1) ^{a)}
MAT(0S)- β	561	1	7.2	418	0.9	10.6	3.6 (2.7) ^{a)}
MAT(100S)- β	529	1.54	11.7	385	1.45	18.5	3.5 (2.4) ^{a)}
MAT(200S)- β	537	1.68	12.5	357	1.6	18.5 (37.9) ^{b)}	3.3 (2.5) ^{a)}
MAT(0SA)- β	549	0.79	5.7	430	0.7	4.8	4.0 (2.7) ^{a)}
MAT(100SA)- β	539	1.13	8.4	337	1.01	6.2 (12.1) ^{c)}	3.6 (2.3) ^{a)}
MAT(200SA)- β	548	1.89	13.8	381	1.79	28.3	4.0 (2.6) ^{a)}

a) Amounts of NH_3 desorbed are given in the parentheses.

b) Larger mesopore size distribution with a peak at 37.9 nm appeared in MAT(200S)- β compared with that of MAT(100S)- β .

c) Larger mesopore size distribution with a peak at 12.1 nm appeared in MAT(100SA)- β compared with that of MAT(0SA)- β .

$PV = 0.41$ cm³/g and $PD = 2.3$ nm), indicating that these zeolites consisted mainly of micropores. In contrast, the mixed catalysts had mesoporous structure based on the BJH method (BJH method; $SA = 337$ – 430 m²/g for β zeolite-containing samples, $SA = 349$ – 497 m²/g for Y zeolite-containing samples, BET method; $SA = 529$ – 561 m²/g for β system, $SA = 523$ – 602 m²/g for Y system), indicating that mesoporous matrices prepared by the GSR method were maintained in the catalysts^{14)–17),25)–31)}. The mixed catalysts exhibited very similar pore size

distributions compared to the original matrices as shown in **Fig. 2**. Moreover, larger pore sizes and larger pore volumes (**Tables 2 and 3**) were observed with increasing the reinforcing reagent for MAT(OS, 100S or 200S) and MAT(OSA, 100SA or 200SA) catalysts. For the β system, the BJH pore sizes of MAT(OS, 100S or 200S) ranged from 10.6 to 37.9 nm and those of MAT(OSA, 100SA or 200SA) ranged from 4.8 to 28.3 nm. For the Y system, the BJH pore size of MAT(OS, 100S or 200S) was 10.6 to 37.9 nm and MAT

Table 3 Surface Areas, Pore Volumes, and Pore Diameters from N₂ Adsorption Analysis³¹⁾ and NH₃ Adsorption-desorption Measurement of Y Zeolite-containing Catalysts

Catalyst	BET			BJH			Amount of NH ₃ adsorbed [10 ⁻⁴ mol/g]
	Surface area, SA [m ² /g]	Pore volume, PV [cm ³ /g]	Pore diameter, PD [nm]	Surface area, SA [m ² /g]	Pore volume, PV [cm ³ /g]	Pore diameter, PD [nm]	
Y zeolite	724	0.41	2.3	35	0.16	3.3	9.2 (7.8) ^{a)}
MAT(0S)-Y	602	1.21	8.1	497	1.15	10.6	5.3 (3.2) ^{a)}
MAT(100S)-Y	572	1.85	13	429	1.76	24.5	4.6 (3.2) ^{a)}
MAT(200S)-Y	523	1.72	13.1	374	1.65	18.5 (37.9) ^{b)}	4.6 (3.0) ^{a)}
MAT(0SA)-Y	564	0.85	6	440	0.77	5.4	4.5 (3.7) ^{a)}
MAT(100SA)-Y	560	1.17	8.3	349	1.04	6.2 (14.1) ^{c)}	4.5 (3.3) ^{a)}
MAT(200SA)-Y	561	1.94	13.8	395	1.85	28.3	3.8 (3.0) ^{a)}

a) Amounts of NH₃ desorbed are given in the parentheses.

b) Larger mesopore size distribution with a peak at 37.9 nm appeared in MAT(200S)-Y compared with that of MAT(100S)-Y.

c) Larger mesopore size distribution with a peak at 14.1 nm appeared in MAT(100SA)-Y compared with that of MAT(0SA)-Y.

Fig. 2 BJH-plot of Prepared β Zeolite Catalysts with a) Mesoporous Silica; b) Mesoporous Silica-aluminas, and Y Zeolite Catalysts with c) Mesoporous Silica; d) Mesoporous Silica-aluminas

(0SA, 100SA or 200SA) was 5.4 to 28.3 nm.

Tables 2 and 3 show the NH₃ adsorption and desorption measurements. The amounts of NH₃ adsorbed and desorbed on the β and Y zeolite-containing catalysts were lower than those of the original single zeolites, because mixed catalysts contained only 26 wt% of zeolite. Y zeolite series catalysts adsorbed slightly larger amounts of NH₃ than the β zeolite series catalysts because original single Y zeolite has lower SiO₂/Al₂O₃ ratio, resulting in more acid sites. Moreover, the amounts of NH₃ desorbed from the Y zeolite series and β zeolite series were lower than the amounts of NH₃ adsorbed, probably because the N₂ gas continuously flowed through the system for 30 min to remove weakly

adsorbed NH₃, which may not be important for catalysis, out of the system before NH₃ desorption. Some NH₃ might have remained inside the catalyst structure due to the presence of very strong acid sites which are not important for the catalyst activity, because of rapid deactivation of these acid sites.

3.2. Catalytic Cracking of Soybean Oil Using Zeolite, Silica and Silica-alumina Mixed Catalysts

The evaluation of catalytic cracking of soybean oil by single β zeolite and β zeolite-containing silica and silica-alumina catalysts is shown in **Figs. 3a)** and **3b)** based on carbon number distribution and PONA distribution (selectivity for *n*-paraffins, *iso*-paraffins, *n*-olefins,

Fig. 3 a) Carbon Number Distribution of Products; b) Distribution of Paraffins, Olefins, Naphthenes, and Aromatics of Products from Catalytic Cracking Using β Series Catalysts

Table 4 Product Distribution and Parameters in the Gasoline Fraction for β Series Catalysts

Catalyst	Products distribution [wt%]			Conv. [%]	Coke [wt%]	Parameters in gasoline fraction			
	C1-C4	Gasoline (C5-C11)	C12-			O/P	<i>iso</i> -/ <i>n</i> -	m/s	RON ²²⁾
β zeolite	44	51	5	28	48 ^{a)}	0.42	4.28	0.12	95
MAT(0S)- β	35	57	8	25	36	1.03	3.72	0.32	96
MAT(100S)- β	34	60	6	36	12	0.88	4.20	0.34	96
MAT(200S)- β	34	58	8	42	13	0.92	4.09	0.29	96
MAT(0SA)- β	34	60	6	27	20	1.01	4.29	0.31	96
MAT(100SA)- β	31	61	8	36	13	1.03	4.08	0.36	95
MAT(200SA)- β	31	62	7	36	12	1.04	3.77	0.42	95

a) Calculated from different experiment.

iso-olefins, naphthenes and aromatics), respectively. Light fractions (C1 to C4) decreased from 44 % to minimum 31 % over the zeolite-containing mixed catalyst. Overcracking was inhibited by dispersion of acid sites on the catalysts and reduction of acid concentration with the matrices as shown in **Fig. 3a**). Such decrease in light fractions also occurs in the catalytic cracking of jatropha oil by zeolite ZSM-5 and ZSM + SiAl³⁶⁾, which resembled our present study in the presence of matrix. The gasoline fraction (C5 to C11) increased from 51 to 62 % maximum using zeolite-containing catalysts. Furthermore, the conversions of mixed catalysts tended to increase with increasing the amount of reinforcing agent as shown in **Table 4**. The conversion increased from 28 % for single zeolite to 42 % for MAT(200S)- β with silica matrices and to 36 % for MAT(200SA)- β with silica-alumina matrices. Therefore, the matrices improved the catalytic activity by providing larger reaction spaces and distributing the acid concentration of the catalyst.

In the PONA distribution (**Fig. 3b**), the selectivity for paraffins reached 52 % for single β zeolite, but reduced to around 34 % with mixed catalysts, indicating that the hydrogen transfer reaction was limited by greater distance between acid sites in the presence of matrices. Inhibition of hydrogen transfer led to more

olefins and aromatics, which is consistent with the previous results from catalytic cracking of *n*-paraffin¹⁷⁾.

Parameters of the gasoline fractions, olefin to paraffin ratio (O/P), branched products to normal products ratio (*iso*-/*n*- ratio), multi-branched products to single-branched products ratio (m/s) and research octane number (RON) are summarized in **Table 4**. The O/P and m/s ratios for β zeolite-containing catalysts were higher than those for single β zeolite. Gasoline selectivity increased from 51 % for single β zeolite to highest 62 % for mixed catalysts. As mentioned earlier, use of more reinforcing agents gave larger pore size of silica, which resulted in higher conversions and higher yields of multi-branched products. Therefore, feed oil could diffuse to the acid sites and release multi-branched products without further secondary cracking leading to the increase in lighter hydrocarbon products. Referring to other research with jatropha oil³⁷⁾, the performance of mesoporous catalysts also suggests that larger pores facilitate the transport of bigger triglycerides to the active sites. In the present study, however, the selectivity and the product distribution of silica and silica-alumina matrices showed only slight differences, probably because the alumina content was very low at 5 % in the silica-alumina matrices. In addition, the catalytic cracking activity would change because the mesoporous

structure in the matrix depended on the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio³⁸.

The amount of coke formation on a catalyst during cracking was determined by TG-DTA. **Figure 4** shows the TG-DTA profile of MAT(0SA)- β after the reaction. The total amount of sample (soybean oil and catalyst) was too small (~ 1.7 mg), so only slight weight loss was observed in the thermogravimetric curve. However, the differential thermal analysis (DTA) curve revealed exothermic increase in the range 500–600 °C, which is regarded as the region of coke combustion³⁹. Based on this exothermic region, the coke amount deposited during soybean oil catalytic cracking using single β zeolite was calculated as 48 % as shown in **Table 4**. On the other hand, the coke amount decreased to around 12 % with zeolite-containing mixed catalysts, possibly because the hydrogen transfer reaction was reduced in the present of matrices in the catalysts. In addition, greater pore sizes of catalysts also resulted in lower coke amount, probably because the larger pore size inhibited the hydrogen transfer reaction, which forms the aromatic coke precursor leading to coke formation.

The carbon number distribution and PONA distribution obtained in the catalytic cracking of soybean oil by single Y zeolite and Y zeolite-containing silica and silica-alumina catalysts are shown in **Figs. 5a** and **5b**), re-

spectively. Gas fractions (C1 to C4) decreased from 35 % to minimum 24 % over zeolite-containing mixed catalyst as shown in **Fig. 5a**), because overcracking was inhibited by dispersion of the acid sites of zeolite with the matrices. The gasoline fraction (C5 to C11) increased from 63 % for single zeolite to maximum 69 % for zeolite-containing catalyst. Moreover, the conversions increased from 21 % for single zeolite to the highest 52 % for mixed catalyst as shown in **Table 5**. However, the conversions of mixed catalysts tended to decrease with increasing reinforcing agents compared to MAT(0S)-Y and MAT(0SA)-Y. That is, conversion decreased in the order MAT(0S)-Y > MAT(100S)-Y > MAT(200S)-Y for silica matrices and MAT(0SA)-Y > MAT(100SA)-Y > MAT(200SA)-Y for silica-alumina matrices. These findings suggest that adsorption occurred more easily than diffusion with smaller pore size catalysts. Presumably the microporous zeolite structure induces adsorption of the aliphatic structures of cracked soybean oil inside the pores and allows further cracking^{31,35}. Matrices enhance the catalytic activity by providing bigger reaction spaces, dispersing the acid sites of the catalyst, prohibiting coke formation and liberating the products outside the catalyst^{14–17}. However, Y zeolite-containing catalysts have much lower activity than β zeolite-containing catalysts in the catalytic cracking of the aliphatic hydrocarbon *n*-dodecane¹⁷. In the present catalytic cracking of soybean oil, catalytic cracking of aliphatic hydrocarbons also occurs and Y zeolite-containing catalysts would have lower activity for cracking of aliphatic hydrocarbons than β zeolite-containing catalysts. Therefore, adsorption rather than diffusion may be important using Y zeolite-containing catalysts, because Y zeolite-containing catalysts need high concentrations of the reactant to obtain higher conversion. This mechanism can be explained using **Fig. 6** (graphical abstract) where the model structures of MAT(200S or 200SA)- β , MAT(0S or 0SA)- β , MAT(200S or 200SA)-Y, MAT(0S or 0SA)-Y are shown. The concentrations of reactants and products are appropriate to maintain high activity

Fig. 4 TG-DTA Curve of MAT(0S)- β Catalyst after Pyrolysis

Fig. 5 a) Carbon Number Distribution of Products; b) Distribution of Paraffins, Olefins, Naphthenes, and Aromatics of Products from Catalytic Cracking Using Y Series Catalysts

Table 5 Product Distribution and Parameters in the Gasoline Fraction for Y Series Catalysts

Catalyst	Products distribution [wt%]			Conv. [%]	Coke [wt%]	Parameters in gasoline fraction			
	C1-C4	Gasoline (C5-C11)	C12-			O/P	<i>iso/n-</i>	m/s	RON ²²⁾
Y zeolite	35	63	2	21	32 ^{a)}	0.36	4.79	0.20	90
MAT(OS)-Y	24	68	8	52	21	0.35	5.77	0.23	92
MAT(100S)-Y	24	68	8	36	13	0.38	5.30	0.23	91
MAT(200S)-Y	25	69	6	30	n/a	0.47	5.45	0.31	92
MAT(OSA)-Y	25	69	6	41	26	0.50	4.55	0.25	92
MAT(100SA)-Y	26	68	6	27	25	0.48	4.86	0.27	91
MAT(200SA)-Y	25	68	7	23	17	0.57	4.48	0.28	92

a) Calculated from different experiment.

Fig. 6 Adsorption and Diffusion Model of Reactants and Products in Catalytic Cracking Using Zeolite Surrounded by Mesoporous Materials

in MAT(200S or 200SA)- β , whereas the concentrations of reactants and products are very high and coke formation easily occurs in MAT(OS or OSA)- β . In contrast, the concentration of reactants is too low in MAT(200S or 200SA)-Y to maintain high activity, whereas the concentration of reactants is high enough and the concentration of products is low enough to maintain high activity in MAT(OS or OSA)-Y.

Figure 5b) reveals the PONA distribution for catalytic cracking using single Y zeolite with 54 % paraffins, 22 % olefins, 8 % naphthenes and 16 % aromatics. The amount of paraffins decreased to around 40 % with zeolite-containing mixed catalysts, consistent with the findings for β series catalysts, in which the hydrogen transfer reaction was inhibited by dispersion of acid sites in the presence of matrices. The product distribution and parameters of the gasoline fractions are shown in **Table 5**. O/P, *iso/n-* and m/s ratios were higher in catalytic cracking using mixed catalysts com-

pared to single zeolite. The gasoline selectivity also increased from 63 % with single Y zeolite to 69 % with mixed catalysts. In addition, the larger pore size of silica increased the amount of multi-branched products, which was consistent with the findings for β zeolite-containing catalysts, although the m/s ratio for MAT(200S)- β was slightly lower than that for MAT(100S)- β because of its higher activity. In this case, however, single branched yield of 10 % for MAT(200S)- β was higher than the 9 % for MAT(100S)- β , which may be related to the pore distribution of the catalysts. Furthermore, although the pore volume of MAT(200S)-Y was very close to that of MAT(100S)-Y, MAT(200S)-Y showed wider pore size distribution than MAT(100S)-Y, which may have led to the higher yield of multi-branched products for MAT(200S)-Y. Therefore, both pore volume and pore size distribution are important for the formation of branched products. The wider space in the matrices is likely to facilitate the transfer of bulkier

products inside the catalyst system^{14)~17),28)~35)}. The selectivity and the product distribution were not so different between silica and silica-alumina matrices, as previously mentioned in the β system. The amounts of coke formed in the catalytic cracking of soybean oil using Y series catalysts are also shown in **Table 5**. The amount of coke formed on single zeolite was 32 % whereas the amount of coke formed on zeolite-containing catalysts was around 13 %, consistent with the results for the β series catalysts. Therefore, the hydrogen transfer reaction decreased in the presence of matrices in the catalysts.

3.3. Comparison of Differences in the Catalytic Cracking of Soybean Oil between β and Y Series Catalysts

Differences in the catalytic cracking of soybean oil between β and Y series catalysts are compared in this section. β zeolite-containing mixed catalysts showed higher conversion with greater pore size, whereas Y zeolite-containing mixed catalysts showed lower conversion with higher pore size. As mentioned earlier, the zeolite structure can adsorb aliphatic hydrocarbon molecules easily into the inside of their pores and cracking occurs. Furthermore, the activity of β zeolite systems for the catalytic cracking of aliphatic *n*-dodecane is much higher than that of Y zeolite systems¹⁷⁾. Rapid coke formation may occur if the concentrations of reactants and products exceed the capacity of the catalyst. On the other hand, a catalyst with smaller mesopore size of the matrix has higher adsorption on the catalyst surface than a catalyst with larger mesopore size of the matrix. In contrast, the diffusion rates of reactants and products are higher for catalysts with large mesopores of the matrix than for those with small mesopores of matrix. Interpretation of the present results with such preliminary observation can elicit interesting facts. Conversion was 25 % for MAT(OS)- β and 52 % for MAT(OS)-Y, whereas coke yields were 36 % for MAT(OS)- β and 21 % for MAT(OS)-Y. The higher activity of β zeolite systems will increase the concentration of products in the pore orifices of zeolite, which may lead to confusion in the pore orifice as shown in **Fig. 6**, because products and reactants come together there specifically if smaller mesoporous matrices like OS and OSA were used.

Higher yields in branched products were obtained with both β and Y series catalysts prepared with more reinforcing agent, as the pore size of the catalyst became larger. In general, high catalyst activity increases the ratio of *iso*-/*n*- products because isomerization easily occurs. Furthermore, the micropore size of Y zeolite is larger than that of β zeolite, so *iso*-/*n*- ratios are larger for Y zeolite series catalysts than for β zeolite series catalysts. This result is also related to the high hydrogen transfer rate of Y zeolite where single branched products can be rapidly eliminated from the catalyst

system. On the other hand, multi-branched products are also formed if the activity is high. Longer retention time of carbenium ions increases the possibility of the formation of multi-branched products. Therefore, slower hydrogen transfer would increase this possibility, as confirmed by the higher observed *m/s* ratios for β zeolite series catalysts than for Y zeolite series catalysts. However, some branched products are lost as multi-branched products increase^{28)~35)}, which also led to the decrease in *iso*-/*n*- ratio for β zeolite series catalysts.

The research octane number (RON) was higher for mixed catalysts compared to their single zeolites due to the larger amounts of olefins, aromatics and branched hydrocarbons in the products. Furthermore, the RON of β containing catalysts was around 96 compared to 92 for Y containing catalysts because of the higher O/P ratio of β containing catalysts.

The relationships between conversion and yields of gasoline, single-branched products and multi-branched products, are shown in **Fig. 7**. Gasoline yield increased with higher conversion for both β and Y zeolite systems in a linear relationship in **Fig. 7a**), indicating that high gasoline yield is possible by increased conversion using highly active catalyst. Comparing gasoline yields at the same conversion, the Y zeolite system exhibited higher gasoline yield than the β zeolite system, indicating that the gasoline selectivity depends on the type of zeolite and that the conversion greatly relies on the presence of matrices in the catalysts as shown in our previous studies^{17),28)~35)}. In addition, the gasoline yields of silica matrices and silica-alumina matrices lay on the same line, indicating that the effect of matrices on product distribution is very small. The relationships between single- and multi-branched yields and conversion were approximately linear with both zeolite catalysts as shown in **Figs. 7b**) and **7c**). This optimistic behavior was also found in the catalytic cracking of soybean oil in comparison with that of VGO³⁵⁾ and the catalytic cracking of VGO and AR³¹⁾. The same plots of yields *versus* conversions showed different slopes for SBO and VGO³⁵⁾ where yields of SBO were lower than those of VGO at the same conversion, resulting from significant coke and aromatics formation in the catalytic cracking of SBO.

The reaction profiles of the catalytic cracking using the same β series and Y series catalysts are compared between high molecular weight vacuum gas oil (VGO)³¹⁾ and soybean oil in **Tables 6** and **7**. Aromatics formation increased for soybean oil probably because of the high contents of double bonds and oxygen in the structures of oleic acid and linoleic acid, which were easily reacted and converted to aromatics. This may also explain the higher reactivity of soybean oil than of VGO. This type of reaction would be controlled by both adsorption and diffusion as shown in **Fig. 6**. Smaller pores are advantageous for adsorption (MAT(OS) and

Fig. 7 Effects of Conversion on Yields of a) Gasoline; b) Single-branched Products; c) Multi-branched Products from Catalytic Cracking Using β and Y Catalysts

Table 6 Effects of the Type of Feed on the Product Distribution and Catalytic Properties in Catalytic Cracking Using CPP (β zeolite and β zeolite-containing catalysts, soybean oil and ^aVGO).

Catalyst	Products distribution [wt%]			Conv. [%]	Parameters in gasoline fraction			
	C1-C4	Gasoline (C5-C11)	C12-		O/P	iso-/n-	m/s	RON ²²⁾
β zeolite	44	51	5	28	0.42	4.28	0.12	95
MAT(0SA)- β	34	60	6	27	1.01	4.29	0.31	96
MAT(100SA)- β	31	61	8	36	1.03	4.08	0.36	95
MAT(200SA)- β	31	62	7	36	1.04	3.77	0.42	95
^a β zeolite	47	51	2	29	0.18	4.14	0.11	90
^a MAT(0SA)- β	38	60	2	28	0.98	3.28	0.29	92
^a MAT(100SA)- β	41	58	1	46	0.74	3.79	0.26	92
^a MAT(200SA)- β	38	60	2	46	0.89	4.01	0.24	94

Table 7 Effects of the Type of Feed on the Product Distribution and Catalytic Properties in Catalytic Cracking Using CPP (Y zeolite and Y zeolite-containing catalysts, soybean oil and ^aVGO).

Catalyst	Products distribution [wt%]			Conv. [%]	Parameters in gasoline fraction			
	C1-C4	Gasoline (C5-C11)	C12-		O/P	iso-/n-	m/s	RON ²²⁾
Y zeolite	35	63	2	21	0.36	4.79	0.20	90
MAT(0SA)-Y	25	69	6	41	0.50	4.55	0.25	92
MAT(100SA)-Y	26	68	6	27	0.48	4.86	0.27	91
MAT(200SA)-Y	25	68	7	23	0.57	4.48	0.28	92
^a Y zeolite	36	62	2	24	0.12	7.33	0.12	87
^a MAT(0SA)-Y	28	71	2	27	0.45	6.33	0.26	90
^a MAT(100SA)-Y	27	72	1	26	0.46	5.89	0.25	90
^a MAT(200SA)-Y	25	73	2	43	0.43	6.71	0.27	90

MAT(0SA) series) and larger pores for diffusion (MAT(200S) and MAT(200SA) series). Large molecules are cracked to produce more reactive smaller molecules which may be converted to aromatics and cokes more rapidly. Reactive molecules are thought to be difficult to eliminate from smaller pores, which would lead to rapid deactivation. The catalytic cracking of VGO showed higher conversion with larger pore diameter of both β series and Y series catalysts, indicating that large pores promoted the rapid elimination of products to inhibit rapid deactivation. Catalytic cracking of soybean oil for the β series was consistent with that of VGO and showed higher conversion with greater

pore diameter. However, more reactive SBO cracking exhibited contrasting behavior with Y series catalysts, indicating that not only diffusion but also adsorption was promoted for these catalysts. The strong reactivity for the β series accelerated the rapid deactivation whereas the weak reactivity for the Y series eliminated the reactive products effectively resulting in increased activity. In our previous study, the Y series showed much lower activity for the catalytic cracking of aliphatic *n*-dodecane than the β series¹⁷⁾. In catalytic cracking of soybean oil, larger amounts of aliphatic hydrocarbons may be produced at the initial stage of the reaction. At this stage, the reaction rate of the Y series was lower

Fig. 8 Effects of Pore Diameter on Yields of a) Gasoline; b) Single-branched Products; c) Multi-branched Products from Catalytic Cracking Using β and Y Catalysts

than that of the β series, which may promote the effective elimination of products with low concentration (MAT(OS or OSA)-Y in Fig. 6). In contrast, the more reactive β series will not eliminate the reactive aliphatic products with high concentration from the catalyst system (MAT(OS or OSA)- β in Fig. 6). Consequently, different substrates reacted with different zeolite catalyst types revealing dissimilar phenomena in the catalytic cracking activity.

The correlation between catalyst pore diameter and the yields of gasoline, single-branched products and multi-branched products, is illustrated in Fig. 8. Catalysts with the appropriate size of mesopores were effectively prepared using the gel skeletal reinforcement method by varying the amount of reinforcing agents. Use of more reinforcing agents resulted in larger pore diameter. Higher pore diameter for β zeolite catalyst systems achieved improvement of all product yields, confirming the effect of pore size in the catalytic cracking reaction. However, contradictory results were obtained for Y zeolite catalyst systems. The cracking activity and the behavior of coke formation varied with use of different types of zeolite in the cracking reaction as shown in Fig. 6, and can be explained by the reactivity of zeolite for aliphatic hydrocarbons, the pore size of mesoporous matrices, and the concentrations of reactants and products. β zeolite systems had higher activity for aliphatic hydrocarbon cracking than Y zeolite systems, and thus produce larger amounts of products which lead to the higher concentrations of products around zeolite particles. Therefore, larger mesopores would be necessary to avoid the significant formation of coke on β zeolite systems. In contrast, relatively narrow pores would be preferred to adsorb the larger amount of reactants on Y zeolite systems.

4. Conclusions

Novel types of silicas and silica-aluminas with large mesopores were prepared using the gel skeletal reinforcement method developed from the conventional

sol-gel method. The amount of reinforcing agents successfully controlled the pore sizes of the mesoporous materials. The effects of the pore size of catalysts and the type of zeolites on catalytic cracking of soybean oil using the Curie point pyrolyzer (CPP) method were investigated. Zeolite-containing mixed catalysts exhibited tremendous improvement in all aspects of the conversion, the product yields and the amount of coke, compared to single zeolites, indicating that the presence of the matrices greatly influenced the catalytic cracking. The differences in catalytic activity between matrix silicas and silica-aluminas were very small and the use of silica-aluminas slightly decreased the ratio of branched hydrocarbons for both β and Y zeolite systems. Higher conversion was needed to expand the yields of gasoline and branched products. Furthermore, Y zeolite-containing catalysts exhibited the higher yields of gasoline than β zeolite-containing catalysts at the same conversion. Greater pore diameter of zeolite-containing catalysts seemed to promote isomerization forming bulkier branched products. However, the catalytic activity and coke formation properties depended on the type of zeolite contained in the catalyst systems. The catalytic activity and the coke formation properties of β zeolite systems were higher than those of Y zeolite systems, leading to different phenomena in the change in the conversion and the product yields with enlargement of pore size diameter in the β and Y zeolite systems.

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要 旨

**キュリー・ポイント・パイロライザー法を用いたゼオライト含有マイクロ孔とメソ孔の
混合触媒による大豆油の接触分解反応**

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階層構造を持つゼオライト含有触媒を、ゲル骨格補強法により作製したメソ孔を持つマトリックス（大きなメソ孔を持つシリカおよびシリカ-アルミナ）、マイクロ孔を持つゼオライト（ β および Y）およびバインダーを用いて作製した。作製した触媒を X 線回折法、窒素吸脱着測定、アンモニア吸脱着測定と熱重量、示差熱分析で調べた。簡便なキュリー・ポイント・パイロライザー法を用いて触媒活性と生成物の選択性に対する細孔サイズの効果を研究するために、混合触媒を用いて大豆油の接触分解を行った。ゼオライトを含む混合触媒は、ゼオライト単独と比較して、転化率が最大で 31 %、ガソリン収率が 10 % 上昇し、さらにコーク生成が最大 36 % 減少するなど明らかに触媒としての特性の向上が見られ、マトリックスの存在が接触分

解に大きく影響した。ガソリン収率と単分枝、多分枝炭化水素の収率は転化率が向上するほど増加し、転化率の向上が生成物の収率向上に不可欠であった。さらに、これらの生成物の収率を同じ転化率で比較したとき、Y ゼオライト含有触媒の方が β ゼオライト含有触媒より高い収率を示し、触媒中の Y ゼオライトのより大きなマイクロ孔がガソリン留分を増加させ、かさ高い生成物の生成へと導いた。大豆油の転化率は、 β ゼオライト含有触媒では、細孔サイズが大きくなるほど増加し、比較的大きな細孔を持つ MAT(200S)- β と MAT(200SA)- β に対し最大値を示し、反応物と生成物の拡散が触媒活性に影響を及ぼした。この現象とは対照的に、比較的小さなメソ孔を持つ MAT(0S)-Y と MAT(0SA)-Y は、Y シリーズ触媒で最大の転化率を示した。

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