[Regular Paper]

Catalytic Properties of Amorphous Silica-alumina Prepared Using Dicarboxylic and Tricarboxylic Acids as Matrix in Catalytic Cracking of *n*-Dodecane

Atsushi ISHIHARA*, Hirotaka NEGURA, Kentarou INUI, Tadanori HASHIMOTO, and Hiroyuki NASU

Graduate School of Engineering, Mie University, 1577 Kurima Machiya-cho, Tsu 514-8507, JAPAN

(Received October 25, 2010)

Amorphous silica-aluminas were prepared by the sol-gel method using carboxylic acids, malic acid (MA), succinic acid and citric acid, and the reactivity for catalytic cracking was investigated. When the ratio of MA/TEOS (tetraethoxysilane) increased, surface area, pore volume and pore diameter increased and mesopores were formed. The maximum total conversions of *n*-dodecane were around 30% with the single amorphous silica-alumina. In contrast, the total conversion reached 91% with the single beta-zeolite. To investigate the reactivity of amorphous silica-alumina as a matrix, mixed catalysts consisting of zeolite, amorphous silica-alumina and binder (alumina sol) were prepared. The product distribution changed compared with the single zeolite or silica-alumina, and comparable activity to that of zeolite was obtained although the mixed catalysts included only 1/4 of zeolite. Mixed catalysts using amorphous silica-alumina with mesopores (MA122-5) exhibited higher ratio of multi-branched to single-branched products in the gasoline fraction (C5-C11) than single zeolite. The effect of the addition of 1-dodecene and 1-methylnaphthalene was also investigated.

KeywordsCatalytic cracking, Matrix, Amorphous silica-alumina, Sol-gel method, *n*-Dodecane, Beta zeolite catalyst**1. Introduction**

Silica-alumina together with zeolite form the major components of the catalyst in the FCC process^{1,2}. The active major component for catalytic cracking is zeolite, but the activity and product selectivity depend on the properties of both zeolite and the silica-alumina matrix^{3–5}. Heavy oils with higher boiling point such as vacuum gas oil (VGO) and atmospheric residue (AR) can be converted to more valuable petroleum products such as gasoline, kerosene, and gas oil using the catalytic cracking reaction. In the processing of these heavy oils, the diffusion rate affects the activity and selectivity of the catalysts. Silica-alumina has both acid sites and larger pore size than zeolite. Therefore, the presence of silica-alumina helps the diffusion of reactant molecules inside the catalyst particles since large molecules are cracked in advance to smaller molecules by a primary reaction. Silica-alumina also inhibits over-cracking and promotes isomerization which increases the octane number of the gasoline fraction. Further, the presence of silica-alumina inhibits attrition of the zeolite crystals and improves the stability of the hydrothermal condition even if zeolite suffers attrition and becomes amorphous in the regeneration tower⁵.

Therefore, silica-alumina and zeolite are the most important components in the FCC catalysts. The preparation of mesoporous materials such as silica-alumina, which has advantages for diffusion, and its application to catalytic cracking as a matrix will be more important in modern FCC processes. However, few studies have investigated catalytic cracking using silica-alumina with mesopore matrix compared with those using zeolite.

The control of hydrolysis and condensation in the sol-gel process is very important to obtain the desired porous materials such as catalyst supports with good reproducibility⁶. Organic ligands can be used to control this process and to form a metal complex^{7,8}. These ligands remain inside the gel formed and change the extent and rate of polymerization, but also change the size and diameter of pores formed⁹. Dicarboxylic and tricarboxylic acids are didentate and tridentate ligands and react with metal ions to form stable chelate complexes¹⁰. These ligands serve as not only templates for pore size and shape, but also as reagents for the dispersion of aluminum species and catalysts during the preparation of silica, alumina and silica-alumina by the sol-gel method. Recently, we reported that silica-alumina prepared by the sol-gel method using malic acid can serve as the matrix of catalytic cracking catalysts¹¹.

In this study, silica-alumina with larger mesopores than those of zeolite was synthesized using dicarboxylic

* To whom correspondence should be addressed.

* E-mail: ishihara@chem.mie-u.ac.jp

Table 1 Amounts of Reagents Used in the Preparation of Amorphous Silica-alumina Using Di- and Tri-carboxylic Acids

Sample name	Acid	Acid/TEOS [mol/mol]	Al ₂ O ₃ [wt%]/Al material
MA0.22-1	Malic acid	0.22	1/ASB
MA0.22-5	Malic acid	0.22	5/ASB
MA0.22-25	Malic acid	0.22	25/ASB
MA0.67-5	Malic acid	0.67	5/ASB
MA1.22-5	Malic acid	1.22	5/ASB
CA0.22-5	Citric acid	0.22	5/ASB
CA0.67-5	Citric acid	0.67	5/ASB
SA0.22-5	Succinic acid	0.22	5/ASB
SA0.67-5	Succinic acid	0.67	5/ASB
MA1.22-5/AlN	Malic acid	1.22	5/AlN
MA1.22-5/pH 9	Malic acid	1.22	5/ASB

MA: malic acid; CA: citric acid; SA: succinic acid; TEOS: tetraethyl orthosilicate; ASB: aluminum tri-*s*-butoxide; AlN: aluminum nitrate.

and tricarboxylic acids, which can be considered as a catalyst for hydrolysis of the precursor, template for the pores, and reagent for dispersion of Al species. The effects of the type of carboxylic acid on the physical and catalytic properties of silica-aluminas prepared were investigated using succinic acid, citric acid, and malic acid. The properties, reactivities for catalytic cracking, and suitability as matrix of the synthesized silica-alumina were investigated. The effects of the type of Al precursor in silica-alumina and the pH at the preparation of silica-alumina on the catalytic properties of silica-alumina were also evaluated. Beta-zeolite⁵⁾, which shows high activity for catalytic cracking but is less characterized than USY zeolite, was used. Further, the effects of the addition of 1-dodecene and 1-methylnaphthalene on the product selectivity and the activity in the cracking of *n*-dodecane were investigated.

2. Experimental

2.1. Catalyst Preparation

The reagents for the preparation of gel were tetraethyl orthosilicate (TEOS, Nacalai Tesque, Inc.), aluminum tri-*s*-butoxide (ASB, Tokyo Chemical Industry Co., Ltd.), aluminum nitrate nonahydrate (AlN, Nacalai Tesque, Inc.), ion-exchange water (prepared with Auto still AW 200, Yamato Co., Ltd.), ammonia solution (Nacalai Tesque, Inc.), anhydrous ethyl alcohol (refluxed and distilled using Mg, GR, Nacalai Tesque, Inc.), malic acid (MA, HOOCCH₂CH(OH)COOH, Nacalai Tesque, Inc.), succinic acid (SA, HOOCCH₂CH₂COOH, Nacalai Tesque, Inc.) and citric acid (CA, HOOCCH₂C(OH)(COOH)CH₂COOH, Nacalai Tesque, Inc.). The gel was prepared as follows: a mixture of ethyl alcohol and TEOS was stirred at 25°C for 30 min and aqueous solution of organic carboxylic acid was added dropwise over 20 min. A mixture of ASB and ethyl alcohol was then added dropwise at 25°C over 20 min. After the mixture was stirred at 25°C for 1 h, gelation was performed at 60°C. After the stirrer

stopped and gelation was complete, aging was performed at 60°C for 24 h. The prepared gel was calcined at 600°C for 3 h (heating rate 2.4°C/min) in a stream of air dried through silica-gel. During calcination, acid and solvent were removed.

Sample names include the acid abbreviation (MA, SA or CA), acid/TEOS mol ratio (0.22, 0.67 or 1.22), and Al₂O₃ content (0, 5 or 25 wt%). All sample names of silica-alumina, molar ratio of each reagent, alumina content, and Al raw materials are summarized in **Table 1**. In the case of a mixed catalyst of zeolite and amorphous silica-alumina (see below), the name begins with MAT and the silica-alumina is given in parentheses.

The mixed catalyst of zeolite and silica-alumina includes 56 wt% of silica-alumina, 25 wt% of zeolite (beta-zeolite, SiO₂/Al₂O₃ (mol/mol) 37, Na₂O 0.1 wt%, crystal size 0.05 μm, mean particle size 5 μm, cation type H⁺, HSZ-940HOA, Tosoh Corp.) and 19 wt% of alumina sol as a binder (Cataloid AP-1, JGC Catalysts and Chemicals Ltd.). Silica-alumina was the sol-gel prepared amorphous silica-alumina MA1.22-5, MA1.22-5/AlN and MA1.22-5/pH 9. Zeolite, silica-alumina and binder were mixed and water was added until the mixture became as soft as clay with kneading. The material obtained was adjusted to a cylindrical shape pellet through a press machine with 0.5 mm hole (Miki Seisakusho Co., Ltd.). The pellet was calcined at 600°C for 3 h (heating rate 3.0°C/min) in a stream of air dried through silica-gel. The pellet was used in cracking of *n*-dodecane as prepared.

2.2. Characterization of Catalysts

X-ray diffraction patterns of the samples were obtained using a Rigaku RAD-C diffractometer using nickel-filtered CuKα X-ray source radiation ($\lambda = 1.5405 \text{ \AA}$, $1 \text{ \AA} = 10^{-10} \text{ m}$) operated at 40 kV and 100 mA 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 $2\theta = 10\text{--}70^\circ$. Fourier transform infrared spectroscopy (FT-IR) spectra of gel samples before calcination were mea-

Fig. 1 Reaction Apparatus for Catalytic Cracking

sured with the KBr method on a FT/IR-550 spectrophotometer (JASCO Corp.). N_2 adsorption of a calcined sample was measured using a BELSORP mini II (BEL Japan Inc.). Total surface area, pore volume, and pore distribution were calculated by the BET methods. To estimate values for mesopores, the BJH method was used. The sample was degassed under 10^{-2} kPa at 350 $^\circ\text{C}$ for 3 h before N_2 adsorption measurement. NH_3 adsorption was measured by the pulse method using gas chromatograph-thermal conductivity detector (GC-TCD) to determine the amount of acid sites and the dispersion of Al (one mol of NH_3 adsorbed to one mol of Al added is defined as dispersion of 100%). 0.1 g of a calcined sample was packed into a fixed bed reactor, heated to 400 $^\circ\text{C}$ at a heating rate of 10 $^\circ\text{C}/\text{min}$ under 30 mL/min N_2 stream and held for 3 h. After that, the reactor was cooled to 100 $^\circ\text{C}$ and 1.5 cm^3 NH_3 pulses were introduced using a six-way valve until the amount of NH_3 detected became constant.

2. 3. Catalytic Cracking Reaction

The reaction apparatus is shown in Fig. 1. The conversion of n -dodecane and the selectivity of products were investigated. The typical procedure was as follows: 1 g of catalyst was packed into a fixed-bed reactor (stainless tube, length 30 cm, inner diameter 8 mm, outer diameter 10 mm). The glass wool and quartz sand were packed at the upper and lower sides of the catalyst. The reactor was heated to 500 $^\circ\text{C}$ at a heating rate of 10 $^\circ\text{C}/\text{min}$ under 30 mL/min of N_2 stream. After stopping the N_2 stream, n -dodecane was introduced at 1.1 mL/min for 80 s. After that, 30 mL/min of N_2 was introduced again at 500 $^\circ\text{C}$ for 20 min. Liquid products were collected in a cold trap at -10°C (for silica-alumina single use) or -50°C (for zeolite single use or a mixed catalyst with zeolite). Gas products were collected into the tedlar bag with N_2 . The liquid and gas products were analyzed by GC hydrogen flame ionization detector (FID) (Shimadzu GC-2014). Measurement conditions were as follows: Injection temp. 250 $^\circ\text{C}$, Detector temp. 320 $^\circ\text{C}$, ATTN 1, Injection press. 158 kPa, Column flow 1.56 mL/min, Line speed 27.64 cm/s, Total flow 320 mL/min, Split ratio 200,

Fig. 2 XRD Pattern of Amorphous Silica-alumina Prepared with Dicarboxylic Acids

Column BP-1, Column length 60 m, Column diameter 0.25 mm, Film thickness 0.5 μm , Column initial temp. 0 $^\circ\text{C}$ 16 min, Heating rate 2 $^\circ\text{C}/\text{min}$, Final temp. 228 $^\circ\text{C}$, Liquid sample 0.2 μL , Gas sample 0.5 mL. All products could be determined by reference to JIS K 2536-2 and the analyses of standard gasoline supplied from the Japan Petroleum Institute and the standard hydrocarbon gases supplied from GL Sciences Inc. Most product molecules were smaller than n -dodecane.

3. Results and Discussion

3. 1. Characterization of Amorphous Silica-alumina Prepared Using Malic Acid, Succinic Acid or Citric Acid

Figure 2 shows the X-ray diffraction (XRD) patterns of silica-alumina MA0.22-1, MA0.22-5, MA0.22-25, MA0.67-5, SA0.22-5 and SA0.67-5 prepared using MA and SA. No peak was observed and the silica-alumina prepared by this method was confirmed as amorphous. Other silica-alumina using different amounts of MA or CA was also confirmed as amorphous.

Figure 3 shows the IR spectra of silica-alumina gels (SA0.67-5, MA0.67-5), alumina gel (MA- Al_2O_3 , MA/Al = 026, and silica gel (MA0.22- SiO_2). In the spectrum of SA0.67-5, two peaks at 1727 and 1691 cm^{-1} were assigned to C=O stretching vibrations for carbonyl groups of succinic acid. Further, two peaks at 1421 and 1311 cm^{-1} were due to a coupling of a O-H bending vibration and a C-O stretching vibration for a face formed in a dimer of succinic acid¹²⁾. Therefore, most succinic acid did not form a chelate compound but remained as an original acid in the gel prepared after hydrolysis. Any interaction of TEOS with SA was not stable in the presence of water. It is likely that the

Fig. 3 FT-IR Spectra of Silica-alumina Gels Prepared Using Dicarboxylic Acid (before calcination)

chelate complex decomposed and the polymerization of TEOS proceeded rapidly. Therefore, the pore volume and the surface area of silica-alumina prepared using SA were lower than those for silica-alumina using MA and CA, and the pore structure did not develop, as described below in detail. However, there was a slight broad peak at 1637 cm^{-1} which may be assigned to the C=O stretching vibration of a carboxylate complex of Al with SA. As shown below, the conversion of *n*-dodecane and the amount of NH_3 adsorbed for silica-alumina using SA were higher than those for silica-alumina using MA and CA, indicating that a chelate complex of Al with SA may have contributed to the dispersion of active acid sites for cracking.

In the FT-IR spectrum of silica-alumina gel for MA0.67-5 prepared using MA, no peak was observed at 1700 cm^{-1} assigned to a dimer of MA. However, a peak at 1733 cm^{-1} might be due to the weakened interaction of a dimer of MA in the presence of silica-alumina gel. Two peaks at 1637 cm^{-1} and 1398 cm^{-1} were assigned to C=O stretching vibration of carboxylate complexes of Al with MA, suggesting that carboxylate complexes were maintained even after hydrolysis. These peaks for MA0.67-5 were larger than those for SA0.67-5. Further, when the heights of these peaks were compared with those at 1080 cm^{-1} and 1190 cm^{-1} assigned to Si-O bonds, both the carbonyl peak and the carboxylate peaks increased with higher amount of MA added, suggesting that not only Al carboxylate complex but also Si carboxylate complex might be formed. The formation of carboxylate complexes would retard the growing of silica skeleton by polycondensation at low temperature, which formed the larger surface area and pore volume as a result. Mesopores developed with the amount of MA at 0.67 and MA/TEOS ratio more than 0.67, which may be related to maintaining a carboxylate skeleton with Si during the preparation of silica-alumina gel.

An alumina gel (MA- Al_2O_3) prepared using ASB and MA showed two large broad absorptions at 1637 and

1398 cm^{-1} assigned to an Al carboxylate complex. Similar peaks were also observed for MA0.67-5, but a carbonyl peak derived from free MA was not observed. A silica gel (MA0.22- SiO_2) prepared using TEOS and MA showed an absorption at 1735 cm^{-1} assigned to a carbonyl group of MA, and two peaks at 1637 and 1398 cm^{-1} assigned to a carboxylate complex, indicating that a Si carboxylate complex also remained in the gel. When the amount of Al_2O_3 added to the silica gel (MA0.22- SiO_2) increased, the absorption at 1735 cm^{-1} was shifted to lower wave number and disappeared for the silica-alumina gel MA0.22-25. Instead of the carbonyl peak of MA, absorptions of carboxylate increased with higher Al_2O_3 and only absorptions at 1654 and 1396 cm^{-1} remained, indicating that most absorptions derived from carboxylate complexes were due to Al complexes. In addition to these absorptions, broad absorptions from about 1080 to 1200 cm^{-1} derived from Si-O bonds were observed for SA0.67-5, MA0.67-5, MA0.22- SiO_2 , although not for MA- Al_2O_3 . When citric acid was used, two absorptions assigned to carboxylate complexes were also observed at 1654 and 1376 cm^{-1} .

3. 2. Surface Area and Pore Structure

The results of N_2 adsorption measurements are shown in Table 2. Initially, pore structures of amorphous silica-alumina MA0.22-5, MA0.67-5 and MA1.22-5 were compared to examine the effect of the added amount of MA on the pore structures. The patterns of the adsorption isotherm for MA0.67-5 and MA1.22-5 exhibited overlap of I type (microporous texture) and IV type (mesoporous texture) whereas that for MA0.22-5 was almost I type. The BET surface area for MA0.67-5 was the highest at $958\text{ m}^2/\text{g}$. The pore volume and average pore diameter increased with higher amount of MA added and for MA1.22-5 reached $1.07\text{ cm}^3/\text{g}$ and 5.1 nm , respectively. When the pore size distribution was estimated by the BJH method using a desorption branch of the adsorption isotherm, MA0.67-5 and MA1.22-5 exhibited peaks at 3.7 and 5.4 nm pore diameter, respectively, whereas MA0.22-5 did not show any definite peak. Since pores with diameter more than 3.3 nm were estimated in the BJH plot, the surface area and pore volume calculated by the BJH method can be considered as derived from mesopores. Therefore, the difference between values for the surface area or pore volume of the BET and BJH methods can be considered as approximate values for the surface area and pore volume derived from micropores. From this point of view, MA0.22-5 contained mainly micropores, MA1.22-5 contained mainly mesopores, and MA0.67-5 had both micropores and mesopores.

The effect of the amount of Al added on the pore structures of MA0.22-1, MA0.22-5 and MA0.22-25 was investigated. As expected, the BET surface area

Table 2 Specific Surface Area, Pore Volume, and Average Pore Diameter of Synthesized Silica-alumina

Catalyst	BET			BJH		
	Surface area [m ² ·g ⁻¹]	Pore diameter [nm]	Pore volume [cm ³ ·g ⁻¹]	Surface area [m ² ·g ⁻¹]	Pore diameter [nm]	Pore volume [cm ³ ·g ⁻¹]
MA0.22-1	803	2.2	0.43	50	3.3	0.05
MA0.22-5	677	2.0	0.34	16	3.3	0.09
MA0.22-25	310	4.1	0.31	166	3.7	0.22
MA0.67-5	958	2.9	0.70	357	3.7	0.33
MA1.22-5	844	5.1	1.07	695	5.4	0.93
CA0.22-5	759	2.4	0.45	96	3.3	0.09
CA0.67-5	909	4.2	0.94	661	3.7	0.74
SA0.22-5	433	2.1	0.23	28	3.3	0.03
SA0.67-5	572	2.9	0.41	104	3.3	0.16

MA: malic acid; CA: citric acid; SA: succinic acid.

and pore volume decreased with increasing Al₂O₃ content. In the BJH plot, only MA0.22-25 showed a definite peak at 3.7 nm and about a half of the surface area was derived from mesopores. MA0.22-1 and MA0.22-5 had very few mesopores and most of the surface area was derived from micropores. Therefore, the formation of mesopores in MA0.22-25 was based on the presence of the larger amount of Al₂O₃.

The effect of the type of template on the pore structure was investigated. The surface area and pore volume increased with higher amounts of succinic acid and citric acid added. However, the surface area and pore volume were rather low using succinic acid compared with those using MA and CA. Rapid polycondensation and growth of silica-alumina particles probably occurred after hydrolysis since little carboxylate complex of succinic acid was present as shown by FT-IR. Comparison of SA0.22-5, SA0.67-5, CA0.22-5 and CA0.67-5 showed only CA0.67-5 exhibited a mesopore peak at 3.7 nm pore diameter in the BJH plot. The BET and BJH surface areas for CA0.67-5 were 909 and 661 m²/g, respectively, indicating that the larger part of the pore structure for CA0.67-5 was formed by mesopores. In contrast, most of the pore structures of SA0.22-5, SA0.67-5 or CA0.22-5 consisted of micropores.

The preparation of silica and silica-alumina using non-surfactant reagents such as carboxylic acids is one of the methods to prepare porous materials with large pore volume and surface area. Different methods for the preparation of silica using malic acid have been described. In one method¹⁰⁾, the mixture of TEOS and malic acid was hydrolyzed at higher temperature than room temperature. The complex of TEOS and malic acid was formed before hydrolysis. Malic acid controlled the rate of polycondensation and acted as a catalyst and a template. The pore diameter (PD) at the peak of mesopore size distribution decreased with increasing MA/TEOS ratio and PD values at 1.17 and 1.00 of MA/TEOS were about 4 nm. The former finding was not consistent with our results, whereas the lat-

ter was consistent. The pore volume reached the maximum 1.0 cm³/g at 0.67 or 0.83 of MA/TEOS. The difference probably originated in the timing of the addition of MA. Although not discussed, the micropores might have been formed at low MA/TEOS ratio. In the other report⁹⁾, a malic acid solution was mixed at room temperature after the hydrolysis of TEOS at 70°C. In this case, malic acid in partially polymerized silica gel acted as a template rather than a catalyst because further gelation was performed at room temperature for two months and the template was removed by Soxhlet extractor over three to four days. In this method, large surface area and pore volume similar to our prepared silica-alumina were obtained with smaller amounts of malic acid than used in the present study. However, the time required was much longer time. In our method, silica-alumina with similar pore volume and surface area can be prepared using a larger amount of acid within a much shorter time. Further, the hydrolysis of TEOS was performed first using aqueous solution of malic acid, the ASB solution was added at the same temperature, and the mixture was heated because the difference between the hydrolysis rates of ASB and TEOS had to be considered in our method. Although these previous methods were not consistent completely, the reaction occurring in the gelation might be similar and large surface area and pore volume were achieved for every sample. The presence of a template such as malic acid controls the rate of polycondensation of TEOS and ASB, and prevents the rapid growth of silica-alumina particles, resulting in the desirable large surface area and pore volume. As shown in the NH₃ adsorption experiment below, Al species for silica-alumina prepared in the present study were dispersed successfully. The presence of malic acid is also important in this process.

3. 3. Ammonia Adsorption and Dodecane Cracking Using Silica-alumina

Table 3 shows the amount of ammonia adsorbed and the dispersion of Al as a percentage of the ratio of the

Table 3 Amount of NH₃ Adsorption, Al Dispersion, and Conversion of *n*-Dodecane for Silica-alumina

Catalyst	NH ₃ adsorption [NH ₃ 10 ⁻⁴ mol·g ⁻¹]	Al dispersion [%]	Conversion of <i>n</i> -dodecane [%]
MA0.22-1	2.3	118	10
MA0.22-5	3.8	39	14
MA0.22-25	4.2	8.6	31
MA0.67-5	5.9	60	22
MA1.22-5	4.6	47	31
SA0.22-5	6.5	66	32
SA0.67-5	6.4	64	27
CA0.22-5	7.0	73	23
CA0.67-5	3.7	38	15

MA: malic acid; CA: citric acid; SA: succinic acid.

The conversion was calculated from the amount of dodecane which remained after the reaction.

amount of ammonia adsorbed (mol) to the content of Al (mol). Since the amount of NH₃ adsorbed was measured by a pulse method, in which several pulses of 1.5 cm³ NH₃ were introduced into the catalyst until saturation, the physical adsorption was considered negligible. Further, the desorption of NH₃ was not observed in this pulse experiment. Since the catalyst is exposed to an excess amount of NH₃ in a normal TPD experiment, the problem of physical adsorption of NH₃ may be more important. The amount of NH₃ adsorbed for MA0.22-1 was 2.3 (10⁻⁴ mol/g) and the dispersion of

Al was more than 100%, indicating that Al is adequately dispersed if the amount of Al was small enough. Although the amount of NH₃ adsorbed increased with higher content of Al₂O₃, the dispersion of Al significantly decreased. Although the amount of NH₃ adsorbed changed depending on the amount of carboxylic acid added, no definite tendency could be observed.

The catalytic cracking of *n*-dodecane was performed with a fixed-bed reactor as shown in Fig. 1 to estimate the properties of amorphous silica-alumina for this reaction. The conversion of dodecane for each catalyst was rather low but the conversion tended to be higher when the amount of NH₃ adsorbed was larger, indicating that acid sites worked effectively. When succinic acid was used, the amounts of NH₃ adsorbed were rather large and the conversions of dodecane were relatively higher. The amount of NH₃ adsorbed and the conversion of dodecane were larger for CA0.22-5 than for CA0.67-5. These results were consistent with the tendency for higher conversion with larger amounts of NH₃ adsorbed, indicating that the acid sites worked effectively in these catalysts.

Figures 4 and 5 show the carbon number distribution and the distribution of paraffin, olefin, naphthene, and aromatics (PONA) in the products of catalytic cracking, respectively. The selectivity of products strongly reflects the nature of the acid sites. Using only an amorphous silica-alumina, a maximum of 124 types of

Fig. 4 Distribution of Carbon Number on Catalytic Cracking Using Amorphous Silica-alumina

Fig. 5 Distribution of Paraffins, Olefins, Naphthenes, and Aromatics on Catalytic Cracking Using Amorphous Silica-alumina

Table 4 Summary of Pore Structure of Silica-alumina and Mixed Catalysts

Catalyst	BET			BJH		
	Surface area [m ² ·g ⁻¹]	Pore diameter [nm]	Pore volume [cm ³ ·g ⁻¹]	Surface area [m ² ·g ⁻¹]	Pore diameter [nm]	Pore volume [cm ³ ·g ⁻¹]
Beta-zeolite	628	2.0	0.31	24	3.3	0.07
Silica-alumina						
MA1.22-5/AlN	944	4.3	1.02	695	4.8	0.82
MA1.22-5/pH 9	345	10.7	0.92	237	4.8	0.86
Mixed catalyst						
MAT (MA1.22-5)	691	4.3	0.74	448	4.8	0.58
MAT (MA1.22-5/AlN)	619	3.7	0.57	364	4.2	0.41
MAT (MA1.22-5/pH 9)	382	7.4	0.71	196	4.8	0.62

MA: malic acid; AlN: Al precursor Al(NO₃)₃ was used; pH 9: silica-alumina was prepared at pH 9; MAT represents the mixed catalyst.

a: adsorption/desorption isotherms, b, c: mesopore size distribution (BJH-plot).

Fig. 6 N₂ Adsorption Measurement of Silica-alumina and Mixed Catalysts

products were detected. As shown in Fig. 4A, the selectivity for C3 was higher for MA0.22-1 than for other catalysts. Comparison of MA0.22-1, MA0.22-5 and MA0.22-25 showed the selectivities of products with lower carbon numbers decreased with increasing content of Al₂O₃. Although the carbon numbers of products changed with increasing amount of acid added or changing the type of acid, the difference was not so large as that caused by changing the Al₂O₃ content, indicating that the characters of the acid sites are similar. As shown in Fig. 5A, the ratio of paraffin to olefin for MA0.22-1 was the smallest at about 2 : 3, whereas that for MA1.22-5 was the highest at about 3 : 2. The ratios for other catalysts were about 1 : 1. These findings suggested that the addition of large amounts of acid produced large pores which allowed easy hydrogen transfer in the pores. As shown in Figs. 4B and 5B, the profiles of the product yield are different from those of the product selectivity, since the yield reflects the amount of acid sites, which controls the effective conversion, rather than the character of the acid sites.

3.4. Characterization and Catalytic Cracking Properties for Mixed Catalysts of Zeolite and Silica-alumina, a Zeolite Single Catalyst and Silica-alumina Single Catalysts

XRD was performed of zeolite (beta), mixed catalyst of zeolite and silica-alumina, and silica-alumina. No XRD peaks were detected for silica-aluminas prepared, indicating these catalysts were amorphous. The mixed catalyst included 25% of zeolite and showed weakened signals for beta-zeolite, indicating that zeolite is dispersed in the mixed catalyst.

Table 4 and Fig. 6 show the results from N₂ adsorption measurement. The pore structure of beta-zeolite consisted of mainly micropores and the surface area for mesopores estimated in the BJH method was very small. To investigate the effects of the type of Al precursor in silica-alumina on the catalytic properties of silica-alumina, aluminum nitrate nonahydrate was used instead of ASB and MA1.22-5/AlN was prepared. Further, to investigate the effects of the pH during the preparation of silica-alumina, silica-alumina, MA1.22-5/pH 9, was prepared at pH=9. The effect of Al precursor was very small and the pore structure of MA1.22-5/AlN was almost same as that for MA1.22-5 in Table 2. In contrast, MA1.22-5/pH 9 showed mod-

Table 5 Product Distributions and Catalytic Properties of Cracking Reaction by Changing the Feed

Catalyst	Conversion	Product distribution [%]			Gasoline			
		C1-C4	gasoline	C12-	olefin/ paraffin	iso-/n-	multi/single branch	RON
	<i>n</i> -C12							
MAT (MA1.22-5)	79	55.4	44.4	0.1	0.69	3.1	0.16	86
MAT (MA1.22-5/AlN)	82	52.5	47.0	0.5	0.68	3.2	0.10	87
MAT (MA1.22-5/pH 9)	82	53.6	46.1	0.3	0.67	2.9	0.08	86
Zeolite	91	57.8	41.7	0.5	0.46	2.9	0.07	86
	<i>n</i> -C12 <i>n</i> -C'12							
MAT (MA1.22-5)	67 100	48.9	50.8	0.3	1.47	7.0	0.15	93
	<i>n</i> -C12 M-Naph							
MAT (MA1.22-5)	68 15	58.4	40.8	0.8	1.05	3.8	0.07	91

MA: malic acid; AlN: Al precursor $\text{Al}(\text{NO}_3)_3$ was used; pH 9: silica-alumina was prepared at pH 9; MAT represents the mixed catalyst. *n*-C12: *n*-dodecane; *n*-C'12: 1-dodecene; M-Naph: 1-methylnaphthalene.

erate surface area and very wide pores, indicating that silica particles, major parts of silica-alumina, cohered at higher pH. The BJH surface areas of MA1.22-5/AlN and MA1.22-5/pH 9 were 695 and 237 m^2/g , respectively, indicating that mesopores formed significant parts of pores for these silica-aluminas. The pore structures of the mixed catalysts MAT(MA1.22-5), MAT(MA1.22-5/AlN), and MAT(MA1.22-5/pH 9) directly reflected the original pore structures of the corresponding silica-aluminas and the pore size distributions were very similar to those of the original silica-aluminas, as shown in Fig. 6. That is, the peak location of the distribution for the mixed catalyst was almost same as that for the original silica-alumina whereas the peak height was lower because the ratio of the original silica-alumina in the mixed catalyst was only 56%. Although micropore distribution is not shown here, the pore peaks of beta-zeolite for mixed catalysts were also observed at the same positions as for the original beta-zeolite, but were smaller than the original peaks for the same reason.

In our previous paper, FT-IR measurement of pyridine species adsorbed on catalysts was performed and the absorptions of 1540 and 1450 cm^{-1} were assigned to the Brønsted acid site (B) and Lewis acid site (L), respectively¹¹⁾. Further, the ratios of B/L were estimated using the peak areas of B and L absorptions. In this study, the ratio of B/L for MA1.22-5 was 0.23. In general, the Brønsted acid site is considered to be directly related to the activity for catalytic cracking. The conversion of *n*-dodecane for MA1.22-5 was 31% (Table 3). The ratio of B/L and the conversion of dodecane for the single use of beta-zeolite were 0.61 and 91%, respectively, which were higher than those for MA1.22-5. The amount of NH_3 adsorbed on beta-zeolite was 7.3 ($10^{-4} \text{ mol} \cdot \text{g}^{-1}$)¹¹⁾ and much larger than that for MA1.22-5 ($4.6 \cdot 10^{-4} \text{ mol} \cdot \text{g}^{-1}$ in Table 3). These results show that the amount of Brønsted acid sites is closely related to the activity for catalytic cracking. The ratio of B/L for the mixed catalyst MAT(MA1.22-5)

was 0.27. The amount of NH_3 adsorbed for MAT(MA1.22-5) was 6.9 ($10^{-4} \text{ mol} \cdot \text{g}^{-1}$), which was remarkably high compared with that of single MA1.22-5¹¹⁾. Although MAT mixed catalysts contained only 25% of beta-zeolite, the conversions of dodecane were in the range 79-82%, which was very close to that of single zeolite, 91%, as shown in Table 5. These results show that zeolite was effectively dispersed and embedded into the silica-alumina in the mixed catalyst and that Brønsted acid sites on zeolite were actively involved in the cracking of dodecane¹³⁾.

Silica-alumina prepared by the combination of chitosan addition and hydrothermal treatment exhibited higher conversion of triisopropylbenzene (TIPB). In this case, the ratio of B/L for pyridine adsorption was 0.13, which was not so high, so the higher activity was attributed to the large pore diameter of 10 nm¹⁴⁾. In the same study, silica-alumina with the highest B/L ratio 0.23 exhibited comparatively higher conversion of TIPB although neither hydrothermal treatment nor chitosan were used for this catalyst and the pore diameter was smaller at 3.2 nm. These results showed that both the amount and nature of acid sites, and the size of pores were related to the catalytic activity.

The product selectivity and the catalytic activity can be changed by dealumination of USY zeolite with citric acid to change the nano pores and nature of the acid site¹⁵⁾. The linear relationship between the activity and the amount of Brønsted acid sites was not necessarily clear. However, if USY was treated with citric acid, the pore distribution was not changed but both the amount of Brønsted acid sites and the activity increased. FT-IR measurement of pyridine adsorption showed absorption for pyridinium ions on Brønsted acid sites did not decrease even with evacuation at 350°C whereas the absorption for pyridine species adsorbed on Lewis acid sites decreased with evacuation at 250°C. Therefore, the Brønsted acid sites may be closely related with the cracking activity.

Four catalysts, MAT(MA1.22-5), MAT(MA1.22-5/

P = paraffin, O = olefin, N = naphthene, A = aromatics, H⁺ = proton, H⁻ = hydride; When one compound has the same subscript number as another compound, they have the same carbon number.

Fig. 7 Reaction Pathways in Catalytic Cracking of *n*-Paraffin

AlN), MAT(MA1.22-5/pH 9) and beta-zeolite, are compared in **Table 5**. The conversions of *n*-dodecane were 79, 82, 82 and 91%, respectively, although the content of zeolite in each mixed catalyst was only 25%. Comparison of the distributions of products showed the selectivities of gasoline fractions for the mixed catalysts (44-47%) were larger than that for single zeolite (42%), indicating that overcracking of dodecane by zeolite was inhibited by the presence of matrix silica-aluminas. The ratios of olefin/paraffin (o/p), iso-/*n*-hydrocarbons (i/n), multi/single branched hydrocarbons (m/s) and RON in the gasoline fraction were compared between the MAT mixed catalysts and single zeolite. The three mixed catalysts exhibited higher ratios of o/p and m/s than the single zeolite, whereas the ratio of i/n and RON were almost the same. Although zeolite has the ability of hydrogen transfer, this decreased in the presence of silica-alumina. The introduction of the larger pores into the catalysts presumably brought about the increase in the m/s ratio. Among the mixed catalysts, MAT(MA1.22-5) revealed the highest m/s ratio, 0.16, which was more than twice that for single zeolite. In general, although higher olefin ratio brings about higher RON value, the following hydrodesulfurization unit for low sulfur gasoline may decrease both the olefin yield and the RON value. To overcome this situation, increase of the ratios of i/n and m/s is effective. The presence of both larger pores, which enables easy isomerization, and acid sites giving the higher activity in the matrix, are very important to obtain higher ratios of i/n and m/s. The m/s ratio is especially important if the RON value for the products with C6 and higher carbon number than C6 is considered. The yields of C6 and higher than C6 products are not so high and the m/s ratio does not directly contribute to the RON value in the catalytic cracking of dodecane. However, this ratio will

affect the RON value in the catalytic cracking of vacuum gas oil and atmospheric residue. The results show that the combination of a matrix with larger pores and appropriate strength of acid sites with zeolite would inhibit excessive cracking by zeolite and provide higher selectivity for the desired products while maintaining the high ability of zeolite for hydrogen transfer.

3.5. Effects of the Addition of Dodecene and 1-Methylnaphthalene on the Activity and Product Selectivity

Effects of the addition of dodecene and 1-methylnaphthalene on the activity and product selectivity were investigated as shown in **Table 5**. When dodecane : dodecene 1 : 1 solution was used for a feed, the conversion of dodecane decreased from 79 to 67% whereas that of dodecene was 100%. The selectivity for gasoline, the ratios of o/p and i/n, and RON value increased with the addition of dodecene, but the ratio of m/s remained almost constant. The result shows that the presence of olefin is important for the production of gasoline with high octane number. However, the hydrodesulfurization of VGO or AR, which precedes the catalytic cracking unit, would result in the hydrogenation of olefin. Therefore, the actual hydrotreated VGO or AR feed may include paraffins and aromatics. When the effect of the addition of 5% 1-methylnaphthalene (MN) was investigated, the conversion of dodecane also decreased and the conversion of MN was only 15%. The selectivity for gasoline decreased. Although the ratios of o/p and i/n, and RON value increased, the ratio of m/s decreased. These results show that adsorption of aromatics onto the acid sites of the catalyst may affect the activity and the selectivity negatively, resulting in decreased yield of gasoline, so the remaining amount of aromatics in hydrotreated VGO or AR may be quite important.

Fig. 8 Reaction Pathway of Carbenium Ion in Catalytic Cracking of n -Paraffin

3. 6. Concerning Reaction Mechanisms

The proposed reaction pathway of catalytic cracking is illustrated in Fig. 7¹¹⁾. The n -paraffin molecule undergoes cracking to form paraffin and olefin molecules at the ratio 1 : 1. The olefin may undergo dehydrocyclization and eliminate H^+ and H^- to give an aromatic compound. The eliminated H^+ and H^- are supplied to another olefin in the system to form another paraffin. This route is called hydrogen transfer. If the initially formed paraffin is cracked again, another paraffin and another olefin are formed at 1 : 1. Cracking of the initially formed olefin forms two olefin molecules. If there is no hydrogen transfer, the formation of aromatic and olefin molecules will increase. However, a catalyst with high ability for hydrogen transfer increases the formation of paraffin molecules. Since the hydrogen transfer occurred appropriately the o/p ratio in the gasoline fraction was lower than 1 in our system. Isomerization may occur with each process of cracking, hydrogen transfer, dehydrogenation, and cyclization. Not only the amount and strength of acid sites but also the steric effect related to pore structure (size and shape) is very important for this isomerization. From this point of view, MAT(MA1.22-5) in our system exhibited higher ability for hydrogen transfer to form larger amounts of paraffin. Further, the presence of the larger pores and appropriate acid sites in MAT(MA1.22-5) promoted isomerization and increased the iso/n and multi/single ratios.

We have already reported that use of silica-alumina in the upper bed and zeolite in the lower bed in the same fixed-bed reactor (silica-alumina $\rightarrow$ zeolite system), the catalyst system exhibited higher activity and product selectivity was closest to those for mixed catalyst with zeolite, silica-alumina and binder alumina-sol¹¹⁾. Therefore, the primary reactions to produce olefin proceed on the silica-alumina and further reaction on zeolite, resulting in higher activity and selectivity. Figure 8 shows the reaction pathways of carbenium ion in the catalytic cracking of n -paraffin. In this reaction pathway, hydride abstraction initially forms a carbenium ion which undergoes cracking to form an olefin and a primary carbenium ion. Although the primary carbenium ion hardly undergoes cracking, isomerization or hydride transfer occur instead to produce secondary or tertiary carbenium ion, which undergoes fur-

Fig. 9 Structure and Reactivity of Mixed Catalyst (MAT catalyst) Using a Matrix of Amorphous Silica-alumina, Zeolite and Binder Alumina

ther cracking to give olefin and primary carbenium ion. Cracking and isomerization occur simultaneously through the reaction pathway. A model structure of a catalytic cracking catalyst proposed in our previous paper¹¹⁾ is illustrated in Fig. 9. A smaller amount of zeolite is embedded into the larger amount of matrix and acid sites on the matrix are considered to effectively crack saturated hydrocarbons into reactive olefins. The formed olefins were small, but may be adsorbed on acid sites of zeolite to effectively inhibit the rapid reaction of other reactive molecules such as aromatics and the formation of coke by polymerization. If the amount of zeolite is large or zeolite is located in the upper bed, excess amount of olefin will be formed, which may lead to the rapid deactivation of the catalyst system. If the appropriate amount of reactive molecules such as olefins are present in a feed, the cracking of saturated hydrocarbons is promoted¹³⁾. Therefore, primary cracking of n -dodecane on silica-alumina is likely to promote secondary cracking on zeolite and inhibit coke formation. The distance for transfer of hydrocarbons inside the catalyst may be longer if the pore size of the matrix is larger. Further, the presence of larger spaces in the larger pores facilitate the isomerization. Acid sites with the appropriate amount and strength on the matrix could also promote isomerization as well as inhibit overcracking of olefins and branched paraffins.

New acid sites were formed by embedding wet zeolite into alumina and silica-alumina and recrystallization of the zeolite component resulted in high hydrothermal stability and catalytic activity⁵⁾. This catalyst system exhibited higher activity than the physical mixture of zeolite and matrix components. In our previous experiment, the silica-alumina $\rightarrow$ zeolite and mixed catalyst systems exhibited very similar selectivities and properties for products. The activity of the latter was higher than that of the former, indicating that embedding of zeolite into silica-alumina increased the activity. Amorphous silica-alumina with mesopores had lower hydrothermal stability and the acid property was also weak¹⁶⁾. As shown before, however, simultaneous usage

of zeolite and amorphous silica-alumina maintained the crystallinity of zeolite and recrystallized zeolite, indicating that amorphous silica-alumina still has great potential for use in catalytic cracking⁵⁾. On the other hand, growing zeolite crystals with mesopores was tried using zeolite with micropores as a seed crystal or by assembling zeolite precursor^{17)~22)}. Surface-active agents such as tetraalkylammonium salts were used with the seed crystals to grow the zeolite structure and higher hydrothermal stability was obtained, compared with MCM-41 which had lower hydrothermal stability. However, insufficient information is available for catalytic cracking. For example, although direct catalytic cracking of heavy oil was sometimes performed, the differences between catalysts are difficult to identify. In many cases, only cracking of alkylbenzene was performed and cracking of saturated hydrocarbons, of which large amounts are included in heavy oil, has hardly been discussed. In our results, the cracking reactivity of saturated hydrocarbon on mesoporous catalysts including amorphous silica-alumina and zeolite can be investigated and described.

Recently, an example using amorphous silica and Y zeolite was reported²³⁾. In this case, cracking of 1,3,5-triisopropylbenzene was performed. Using amorphous silica-alumina in the upper bed to zeolite, the catalyst system showed higher activity, lower coke formation, and lower CO generation than a physical mixture of zeolite and silica-alumina or 100% zeolite. When only zeolite with strong acid sites was used, deactivation occurred because of coke formation. When using silica-alumina in the upper bed to zeolite, primary cracking occurred to produce propylene which reacted with the acid sites on zeolite and inhibited the direct reaction of aromatic compounds with the strong acid sites effectively.

In the present study, the formation of branched paraffin was especially noted. When the cracking of VGO and AR is considered, the gasoline produced will undergo further hydrodesulfurization. The olefins in the gasoline are expected to be hydrogenated at hydrodesulfurization and the RON value of the gasoline will decrease. To overcome this situation, the catalyst must be designed to increase the RON value by increasing branched paraffin formation. Although the desired formulation of gasoline is unknown, this must be an important factor in the development to increase the RON value by branched paraffin formation. The development of catalysts with selectivity for branched paraffins will also be very important to obtain the stability of diesel oil at lower temperature. The technology can be applied to hydrocracking of WAX produced in the GTL process.

4. Conclusions

Amorphous silica-aluminas were prepared using the sol-gel method with the addition of various amounts of dicarboxylic and tricarboxylic acids to control the pore structure. Although these silica-aluminas had much lower activities for dodecane cracking than beta-zeolite, acid sites could be introduced into the skeletal matrix using aluminum tri-*s*-butoxide (ASB) to catalyze the cracking. When mixed with zeolite and binder for use as matrix, pore distributions of silica-aluminas were maintained although the specific surface area and pore volume decreased. Moreover, the product distribution for the mixed catalyst changed compared with single zeolite or silica-alumina, and *n*-dodecane cracking activity comparable to that of zeolite was obtained. Aluminum trinitrate nonahydrate could be used instead of ASB and a very similar pore structure was obtained. Further, although silica-alumina was prepared at pH 9, the pore size distribution became much broader compared with those of silica-aluminas prepared at acid pH. The activities of the mixed catalysts using these silica-aluminas were almost the same, but the ratios of multi-branched products to single branched products decreased in the gasoline fraction. The pore structure and the acidity of synthesized silica-aluminas are important in cracking and isomerization using mixed catalysts.

Acknowledgment

This work was entrusted by the Japan Petroleum Energy Center under a subsidy of the Ministry of Economy, Trade and Industry.

References

- 1) Satou, S., Morimoto, Y., Takatsuka, T., Hashimoto, H., *J. Jpn. Petrol. Inst.*, **29**, (1), 60 (1986).
- 2) Rajagopalan, K., Habib Jr., E. T., *Hydrocarbon Process*, **9**, 43 (1992).
- 3) Falco, M., Morgado, E., Amadeo, N., Sedran, U., *Appl. Catal., A: General*, **315**, 29 (2006).
- 4) Andreu, P., *Catal. Lett.*, **22**, 135 (1993).
- 5) Kubicek, N., Vaudry, F., Chiche, B. H., Hudec, P., Di Renzo, F., Schulz, P., Fajula, F., *Appl. Catal. A: General*, **175**, 159 (1998).
- 6) Sakka, S., "Handbook of Sol-gel Science and Technology, Processing Characterization and Applications," Klumer Academic Publishers, (2005).
- 7) Wei, Y., Jin, D., Ding, T., Shih, W. H., Liu, X., Cheng, S. Z. D., Fu, Q., *Adv. Mater.*, **10**, 313 (1998).
- 8) Wei, Y., Xu, J., Dong, H., Dong, J. H., Qiu, K. Y., Jansen-Varnum, S. A., *Chem. Mater.*, **11**, 2023 (1999).
- 9) Pang, J. B., Qiu, K. Y., Wei, Y., *J. Non-Crystal. Sol.*, **283**, 101 (2001).
- 10a) Mizukami, F., Kobayashi, Y., Niwa, S., Toba, M., Shimizu, K., *J. Chem. Soc., Chem. Commun.*, 1540 (1988).
- 10b) Izutsu, H., Mizukami, F., Sashida, T., Maeda, K., Kiyozumi, Y., Akiyama, Y., *J. Non-Cryst. Sol.*, **212**, 40 (1997).
- 11) Ishihara, A., Negura, H., Hashimoto, T., Nasu, H., *Appl. Catal. A: General*, **388**, 68 (2010).

- 12) Nakanishi, K., Solomon, P. H., Furutani, N., "Infrared Absorption Spectroscopy," Nankodo, (1978).
- 13) Gates, B. C., Katzer, J. R., Schuit, G. C. A., "Chemistry of Catalytic Processes," Mc. Graw-Hill, (1979).
- 14) Falco, M., Retuert, J., Hidrobo, A., Covarrubias, C., Araya, P., Sedran, U., *Appl. Catal. A: General*, **366**, 269 (2009).
- 15) Xin-Mei, L., Zi-Feng, Y., *Catal. Today*, **68**, 145 (2001).
- 16) Corma, A., *Chem. Rev.*, **97**, 2373 (1997).
- 17) Liu, Y., Zhang, W., Pinnavaia, T. J., *J. Am. Chem. Soc.*, **122**, 8791 (2000).
- 18) Liu, Y., Zhang, W., Pinnavaia, T. J., *Angew. Chem., Int. Ed.*, **40**, (7), 1255 (2001).
- 19) Han, Y., Wu, S., Sun, Y., Li, D., Xiao, F., Liu, J., Zhang, X., *Chem. Mater.*, **14**, 1144 (2002).
- 20) Zhang, Z., Han, Y., Xiao, F., Qiu, S., Zhu, L., Wang, R., Yu, Y., Zhang, Z., Zou, B., Wang, Y., Sun, H., Zhao, D., Wei, Y., *J. Am. Chem. Soc.*, **123**, 5014 (2001).
- 21) Tang, Q., Bao, X., Song, T., Fan, Y., Shi, G., Shen, B., Liu, C., Gao, X., *J. Catal.*, **251**, 69 (2007).
- 22) Frunz, L., Prins, R., Pirngruber, G. D., *Microporous Mesoporous Mater.*, **88**, 152 (2006).
- 23) Hosseinpour, N., Mortazavi, Y., Bazyari, A., Khodadadia, A. A., *Fuel Process Technol.*, **90**, 171 (2009).

.....

要 旨

2価および3価カルボン酸を用いて調製したシリカ-アルミナの n-ドデカン接触分解におけるマトリックスとしての触媒特性

石原 篤, 根倉 広宇, 乾 健太郎, 橋本 忠範, 那須 弘行

三重大学大学院工学研究科, 514-8507 津市栗真町屋町1577

本研究では、リンゴ酸 (MA)、コハク酸、クエン酸を用いたゾル-ゲル法によって非晶質シリカ-アルミナを調製し、それらの接触分解特性が評価された。MA/TEOS (テトラエトキシシラン) 比を増加させると表面積、細孔容積、細孔径が増加し、メソ孔が形成された。非晶質シリカ-アルミナ単独では、ドデカンの接触分解における転化率の最大値は約30%であったのに対して、 β -ゼオライト単独では91%に達した。非晶質シリカ-アルミナのマトリックスとしての反応性を評価するために

ゼオライト、非晶質シリカ-アルミナおよびバインダーとしてのアルミナゾルからなる混合触媒を調製した。生成物分布はゼオライト単独やシリカ-アルミナ単独の場合と異なり、ゼオライトを1/4しか含まないがゼオライト単独に匹敵する活性が得られた。また、メソ孔を持つシリカ-アルミナ (MA1.22-5) を用いて調製した混合触媒では、ゼオライト単独と比べてガソリン留分 (C5~C11) 中の多分枝/単分枝比がゼオライト単独の場合より高かった。

.....