[Regular Paper]

Role of Nanoporous Al₂O₃ as Matrix for Catalytic Cracking

Koji SAKASHITA*, Isao NISHIMURA, Mami YOSHINO, Toshiyuki KIMURA, and Sachio ASAOKA

School of Environmental Engineering, The University of Kitakyushu, 1-1 Hibikino, Wakamatsu-ku, Kitakyushu 808-0135, JAPAN

(Received January 25, 2010)

Nanoporous (*np*; 5–50 nm in pore diameter) Al₂O₃ was investigated as a matrix for a fluid catalytic cracking (FCC) catalyst as either a binder or a catalytic site using model compounds as feedstock to achieve not only high activity, but also less coking. The binder characteristics of *np* Al₂O₃ matrix were expected to increase the mechanical strength and hydrothermal resistance of the catalyst, because *np* Al₂O₃ from unimodal and non-aggregated boehmite sols has better mechanical strength than *np* Al₂O₃ from aggregated boehmite gels and can protect the zeolite component from hydrothermal degradation during catalyst regeneration more than *np* SiO₂. Application of *np* Al₂O₃ with controlled crystallite and pore sizes as an active matrix for catalytic cracking resulted in less coking, which indicated that *np* Al₂O₃ has an important role as a pre-cracking agent. A *np* Al₂O₃ matrix with a pore size diameter of *ca.* 11–15 nm was found to be optimum for a catalytic cracking catalyst.

Keywords

Fluid catalytic cracking, USY zeolite, Alumina matrix, Nanoporous alumina

1. Introduction

Catalytic cracking, known as fluid catalytic cracking (FCC) is a very important process in modern oil refinery industries that produce gasoline, jet fuel and diesel from vacuum residue, atmospheric bottoms and/or mixtures of these. Demand has been shifting to lighter fuels such as gasoline; therefore, it is easily expected that the ratio of vacuum residue in the feedstock for FCC is increasing. The active sites in the zeolite catalyst are damaged by coking of the residue when vacuum residue-rich feedstock is treated by FCC, in which the coke is produced predominantly from carbon residue. Therefore, a catalyst regenerator is installed in the FCC process in order to regenerate the catalyst activity by high temperature combustion of the coke accumulated on the surface of the catalyst. The catalyst is circulated between the FCC reactor and catalyst regenerator and is exposed to severe hydrothermal conditions during regeneration; therefore, such a catalyst is required to have not only high activity with less coking, but also a high mechanical strength and hydrothermal resistance. Such catalyst characteristics are also required in consideration of global crude oil supplies, which have recently continued to become heavier, so that the asphaltene and carbon residue contents in the feedstock are increased.

Research on FCC catalysts in the 1980s and earlier

was focused on the role of active sites in the zeolite crystal lattice¹⁾. Recently, discussion on the role of active sites has been given over to the role of extra-lattice or non-framework aluminum atoms. Several investigators have proposed reaction pathways in which non-framework alumina provides an initiation site for cracking^{2),3)}.

Modern industrial catalysts applied for FCC are typically 5–40% zeolite dispersed in a matrix support such as silica, alumina, a mixture of silica and alumina, and clay. At present, the ultrastable Y-type (USY) zeolite is mainly employed due to its higher hydrothermal resistance by dealumination. On the other hand, more attention has been given to the contribution of the matrix to the activity of FCC catalysts and on poisoning mechanisms by metals such as vanadium and nickel^{4)–17)}.

The pore size is also considered to be an important parameter that affects the catalytic performance of FCC catalysts^{18)–22)}. Most pre-cracking of large molecules occurs on the surface of mesopores and cracking of large molecules containing metals requires a larger surface area of macropores¹⁸⁾. In 2003, Engelhard Corp. commercialized a new catalyst named Flex-Tec, which was based on a distributed matrix structure (DSM)^{19),21)}. The key concept in DSM technology is the unique pore structure, which enhances the diffusion of feedstock molecules and provides highly selective pre-cracking sites²⁰⁾.

The purpose of this study is to clarify the role of nanoporous (*np*; 5–50 nm pore diameter) Al₂O₃ as a

* To whom correspondence should be addressed.

* E-mail: kindfuel@yahoo.co.jp

Table 1 Pore Structure Properties of *np* Al₂O₃ and *np* SiO₂

<i>np</i> Al ₂ O ₃ as sole	Median pore diameter [nm]	Pore volume [mL/g]	Surface area [m ² /g]
A	9.0	0.42	219
B	11.7	0.47	207
C	14.5	0.45	168
D	18.0	0.45	144
E	31.9	0.46	109
F	40.9	0.45	91
<i>np</i> SiO ₂	9.4	0.34	182

The symbol representations used in Table 1 are used here.

Fig. 1 Pore Distribution of *np* Al₂O₃ from Unimodal Sol

matrix for USY zeolite as a FCC catalyst. In addition to the role of the *np* Al₂O₃ matrix as a binder providing mechanical strength and protecting the zeolite component, and its pre-cracking activity and resistance to coking degradation were investigated. The *np* Al₂O₃ matrices discussed in this paper were prepared using unimodal sols of *np* boehmite. The fundamental part of this study is also concerned with techniques to provide resolvability to high-silica zeolites such as USY. Reasonability is induced by a concerted effect between the *np* Al₂O₃ and the high-silica zeolite, of which the *np* surfaces are controlled during catalyst preparation^{23)~28)}.

2. Materials and Experimental

2.1. Nanoporous Al₂O₃ for Pore-controlled Matrix

Dry powders of non-aggregated unimodal boehmite sols were prepared by hydrothermal aging under weakly acidic conditions with acetic acid at 180°C and were applied as a precursor for *np* Al₂O₃ of γ -alumina with unimodal pore diameters ranging from approximately 9 to 40 nm²⁹⁾. The dry powders of unimodal boehmite sols, which were still non-aggregated after drying at 180°C and returnable to sol dispersion were converted

Fig. 2 Rotary Kiln for Steaming Treatment to Model FCC Regeneration

to *np* Al₂O₃ by calcination at 550°C for 3 h.

The pore size distribution was measured with a mercury porosimeter (Amco Pascal 240). The pore structure properties of *np* Al₂O₃ used as a γ -alumina matrix for catalysts are shown in **Table 1** and **Fig. 1**. Compared with the *np* Al₂O₃ from unimodal sols in the mechanical strength, *np* Al₂O₃ from unimodal boehmite gels by pH swing precipitation as aggregated under weakly basic conditions at 95°C were used³⁰⁾. In addition, *np* Al₂O₃ prepared from as-aggregated non-unimodal boehmite gel was also used as another gel-derived type reference with higher mechanical strength.

np Al₂O₃ matrices were prepared by cylindrical extrusion (1.0 mm diameter, *ca.* 2-3 mm length) without the zeolite component and calcining at 550°C for 3 h. The side crushing strength of these *np* Al₂O₃ samples was measured using a digital force tester (Akzo No SCS-024). The force value of one cylindrical pellet was measured and divided by the diameter and length and the average of 50 pellets was used.

To compare with *np* Al₂O₃, *np* silica gel (AEROSIL® 200, Japan Aerosil Co.) was used as a precursor for *np* SiO₂ as a sol-derived type matrix. The average spherical primary particle size was *ca.* 12 nm. The pore structure properties of *np* SiO₂ are shown in **Table 1**.

2.2. Zeolite Component

USY zeolites with SiO₂ to Al₂O₃ ratios of 6-30 were prepared by a combination of hydrothermal treatment and Al-leaching in acid solution. Hydrothermal treatment was performed using the rotary kiln unit shown in **Fig. 2**. USY6 (SiO₂/Al₂O₃ = 6 mol/mol), USY12 (SiO₂/Al₂O₃ = 12 mol/mol) and USY30 (SiO₂/Al₂O₃ = 30 mol/mol) were prepared from HY, which was pro-

duced from NH₄Y derived from NaY (JGC Catalysts and Chemicals Ltd.). USY6, USY12 and USY30 were obtained by treating HY in a *ca.* 2 wt% steam effluent with a programmed rate of 3.3°C/min to holding temperatures of 625, 675 and 725°C, for 0.5 h, respectively, and washing with 0.2 M (1 M = 1 mol·dm⁻³) HCl solution at room temperature. Typically, a USY zeolite with a SiO₂ to Al₂O₃ ratio of 12 and manufactured by JGC Catalysts and Chemicals Ltd. was used as USY12 instead of the lab-made sample. The USY zeolite, which was dealuminated and stabilized, had typical zeolitic pore sizes of *ca.* 1 nm and mesopores of approximately 2-5 nm in diameter.

2. 3. Catalyst Preparation and Treatment

The catalyst was composed of 20 wt% USY zeolite with an 80 wt% matrix of *np* oxides, such as Al₂O₃. The six different *np* Al₂O₃ and *np* SiO₂ of sole matrix materials are shown in Table 1.

The catalysts were prepared by powder (zeolite and the matrix precursor) blending, wetness-control conditioning with de-ionized water, kneading, extrusion molding, air-drying for one night and drying at 120°C for 3 h, calcining at 550°C for 3 h and sizing. A laboratory kneader was used for wet conditioning and kneading. A muffle furnace was typically used for calcining.

A laboratory rotary kiln equipped with a steaming system (Fig. 2) was used for steaming treatment at 800°C for 3 h using 10% H₂O in N₂ to model FCC regeneration.

The dealuminated USY (SiO₂/Al₂O₃ = 45 mol/mol) was produced from USY12 (SiO₂/Al₂O₃ = 12 mol/mol) zeolite by the regeneration-simulated steaming and followed acid washing with 0.2 M HCl solution at room temperature.

2. 4. Reaction Test and Catalyst Evaluation

A continuous microreactor with a fixed bed (catalyst volume: 0.3 mL) was used both as a micro activity test (MAT) unit for one-pass activity and a flow type unit to measure the activity change for 90 min of time-on-stream.

Conversion during the initial 30 min on-stream was used as a simple indication of the catalytic activity. Coking is well-known as the only cause for catalytic degradation during such a short time-on-stream and can be confirmed by burning regeneration with diluted air; therefore, it was assumed that the rate of degradation by coking could be obtained from the change in activity over the time-on-stream.

In order to select appropriate reaction conditions to determine the differences in catalytic performance among catalysts with different compositions, reaction activities were examined for the reaction conditions summarized in Table 2. The liquid hourly space velocity (LHSV) was changed by flow rate control with a constant catalyst volume and partial pressure of reac-

Table 2 Experimental Conditions for the Reaction Test

Items		Evaluated condition	Selected condition
Reaction temperature	[°C]	450-500	450-500
Partial pressure of reactant	[kPa]	6.3-25	6.3
Liquid hourly space velocity	[h ⁻¹]	4-12	4
Zeolite content in catalyst	[wt%]	20-40	20
Reactant		<i>n</i> -C ₁₆ H ₃₄	<i>n</i> -C ₁₆ H ₃₄

tant. As a result, the following reaction conditions were selected: the reaction temperature was 450 to 500°C, the partial pressure of *n*-C₁₆H₃₄ was *ca.* 6.3 kPa, the LHSV was 4 h⁻¹, and the zeolite content of the catalyst was 20 wt%. *n*-Hexadecane (*n*-C₁₆H₃₄) was used as a model compound for the FCC feedstock, because (1) it is rather difficult to crack³¹⁾, and (2) it is the heaviest normal paraffin that is in a liquid phase at room temperature and can therefore be easily fed without the need for a feedstock vessel heating device.

The bulk density of the USY/*np* SiO₂ catalyst is smaller than that of the USY/*np* Al₂O₃ catalyst; therefore, the contact time of the USY/*np* SiO₂ catalyst was adjusted to that of the USY/*np* Al₂O₃ catalyst on the basis of the zeolite component.

The effectiveness of *np* Al₂O₃ as a matrix to protect the active sites of zeolite was confirmed by steam treatment and compared with dealumination. Steaming with 10% H₂O in nitrogen gas (420 mL gas/min/g catalyst) at 750°C for 3 h was assumed to be sufficient for simulated regeneration of the catalyst.

The catalysts were evaluated with respect to the optimum pore diameters of the *np* Al₂O₃ matrix for activity by measuring dependency on the reaction temperature, SiO₂ to Al₂O₃ ratio of the USY zeolite, and the carbon number of the feedstocks *n*-octane (*n*-C₈H₁₈), *n*-dodecane (*n*-C₁₂H₂₆), *n*-C₁₆H₃₄ and squalane (*i*-C₃₀H₆₂).

i-C₃₀H₆₂ was also used as a model component that typifies vacuum gas oil to determine the optimum pore size of the *np* Al₂O₃ matrix with respect to both the initial activity and the degradation rate by coking. To test the catalytic reaction performance, isothermal reaction conversions (*X*%) on three different residence times (1/LHSV) of the reactant liquid, 0.005, 0.01 and 0.02 h, were measured on a basis of 1/LHSV to establish the reaction kinetics. The reaction temperature was kept at 450°C and each reaction rate could be linearly related to a first-order model for reactant concentration, $\ln[100/(100 - X)] = k/\text{LHSV}$, which is shown in Table 3. The first-order rate constants (*k*) of three terms of time-on-stream (θ) for 0-0.5 h ($\theta = 0.25$ h), 0.5-1.0 h ($\theta = 0.75$ h) and 1.0-1.5 h ($\theta = 1.25$ h) were obtained experimentally. The three rate constants had an approximately linear relation based on the first-order degradation, $\ln k = -a\theta + \ln k_0$, where *a* is the slope and *k*₀ is the initial value of *k*. The initial rate constant *k*₀ at 0 h can be regarded as rep-

Table 3 Results of Reaction Rate Evaluation

First-order reaction rate equation of $A \rightarrow B$:	$-dC_A/dt = kC_A$
The integral for time $t = 0-t$:	$-\ln(C_A/C_{A0}) = kt$
Confirmed relation between LHSV and X :	$\ln[100/(100-X)] = k/\text{LHSV}$
Degradation of the reaction activity, k :	$\ln k = -a\theta + \ln k_0$

where

$t = 1/\text{LHSV}$: residence time [h],

k : first-order rate constant [h^{-1}],

LHSV: liquid hourly space velocity [L/h],

C_{A0} and C_A : molar concentrations of component A at $t = 0$ and $t = t$,

X : conversion of component A [%],

a : degradation rate [$1/\text{h}^2$],

θ : time-on-stream [h], k_0 is the initial reaction activity, and the rate constant at $\theta = 0$.

representative of the intrinsic activity without degradation by coking. The degradation rate a can be regarded as representative of degradation by coking, because coking is the predominant cause of activity degradation during one-pass conversion by catalytic cracking.

Gas chromatography mass spectrometry (GC-MS; Shimadzu QP5050) was used for identification of the reaction products and gas chromatography (Shimadzu GC14B/GC8A) was used for quantitative analysis of the reaction products.

The crystallinity of the zeolite component was measured by X-ray diffraction analysis using the intensity change of the (533) peak, $2\theta = 23.6^\circ$. Line broadening reflects the decrease of crystal size or dealumination effect on the peak height; therefore, the intensity was corrected by peak width.

3. Results and Discussion

3.1. Nanopore Size Control of Al_2O_3 Matrix for Catalytic Cracking Catalyst

Physical properties such as the pore volume (PV) and mechanical strength of the $\text{np Al}_2\text{O}_3$ matrix are first discussed with respect to the preparation methods. There are two methods to prepare unimodal $\text{np Al}_2\text{O}_3$; one is to use as-aggregated unimodal gels and the other is to use non-aggregated unimodal sols, as described in 2.1. It is well known that unimodal boehmite gels can be applied for the precise control of np oxides as catalyst carriers²⁹. However, the gel method has been assumed to be unfavorable for FCC catalyst, because the PV increases with pore size and as a result, the mechanical strength decreases.

It is well known that the crushing strength represents the material strength to some extent, including the attrition resistance³². To simplify this fundamental investigation, the side crushing strength of cylindrically extruded $\text{np Al}_2\text{O}_3$ samples was used to determine the effect of the matrix pore structure on the mechanical strength of the FCC catalyst. Figures 3 and 4 show the PVs and the mechanical strengths of each $\text{np Al}_2\text{O}_3$, respectively, in relation to the median pore diameter (MPD). The np boehmite in the sol state has the ad-

Circle: $\text{np Al}_2\text{O}_3$ from unimodal sol, Triangle: $\text{np Al}_2\text{O}_3$ from unimodal gel, Square: $\text{np Al}_2\text{O}_3$ from non-unimodal gel.

Fig. 3 Effect of Precursor on Relationship between Pore Volume (PV) and Median Pore Diameter (MPD) for $\text{np Al}_2\text{O}_3$

Circle: $\text{np Al}_2\text{O}_3$ from unimodal sol (this work), Triangle: $\text{np Al}_2\text{O}_3$ from unimodal gel, Square: $\text{np Al}_2\text{O}_3$ from non-unimodal gel.

Fig. 4 Effect of Precursor on Relationship between Mechanical Strength and MPD for $\text{np Al}_2\text{O}_3$

vantage of pore size control without a large change of the PV. The $\text{np Al}_2\text{O}_3$ prepared from the unimodal sol was stronger in mechanical strength than the equivalent pore-sized $\text{np Al}_2\text{O}_3$ prepared from the unimodal gels.

Circle: USY/*np* Al₂O₃, Triangle: USY/*np* SiO₂.

Fig. 5 Effect of *np* Oxide Matrix Species on the Relationship between *n*-C₁₆H₃₄ Conversion and Reaction Temperature

Although the PV of *np* Al₂O₃ prepared from the unimodal gels increased with the MPD, the PV of the *np* Al₂O₃ prepared from the unimodal sols remained low and almost constant, but sufficiently porous. These relations were reflected in the mechanical strength. Therefore, the unimodal sols were selected as precursors for the *np* Al₂O₃ to investigate the pore structure of the FCC catalyst matrix.

Johnson and Mooi³³⁾ confirmed that the pore size is nearly equivalent to the boehmite crystallite size and the values are almost equal to each other. However, there was only approximate consistency between the porosimeter data of pore (void of particle) size and electron microscopy observations on particle size, although the crystallite shapes of the unimodal boehmite sols were like thick oblong cards with similar aspect ratios. Therefore, the unimodal pore size shown in Table 1 and Fig. 1 was used as the physical characteristic of the *np* Al₂O₃ matrix used in this work.

3.2. Cracking Activities of *np* Al₂O₃ and *np* SiO₂ Matrix Catalysts

The difference in the cracking activity of *np* Al₂O₃ and *np* SiO₂ matrix catalysts is shown for *n*-C₁₆H₃₄ conversion in Fig. 5. The conversions appeared to be linear in the temperature range from 450 to 500°C, probably due to a balance between exponential increase and an upper conversion limit of 100%. The results indicate that the USY catalyst with *np* Al₂O₃ matrix has higher conversion than that with the *np* SiO₂ matrix. Therefore, the *np* Al₂O₃ matrix is more capable of improving the cracking activity of the catalyst than the *np* SiO₂ matrix. The *np* SiO₂ matrix rarely has a pre-cracking ability without some modification^{22),34)}, so that the cracking reaction on the USY/*np* SiO₂ catalyst is considered to proceed at the zeolite component. Therefore, it is supposed that the difference in conversion between USY/*np* SiO₂ and USY/*np* Al₂O₃ reflects pre-cracking at the *np* Al₂O₃ matrix.

Circle: USY/*np* Al₂O₃, Triangle: steamed (USY/*np* Al₂O₃), Square: dealuminated (USY/*np* Al₂O₃).

Fig. 6 Effect of Steaming and Dealumination on *n*-C₁₆H₃₄ Conversion over USY/*np* Al₂O₃ Catalysts

The product selectivities for various test runs of *n*-C₁₆H₃₄ on various catalysts were very similar, because the same USY zeolite was used. The typical pattern of cracked products is as follows: C₁ = 0 C%, C₂ = 0 C%, C₃ = 12 C%, C₄ = 28 C%, C₅ = 25 C%, C₆ = 19 C%, C₇ = 8 C%, C₈ = 3 C%, C₉ = 2 C%, C₁₀ = 1 C% and C₁₀₊ = 2 C%. This pattern is very similar to the result for *n*-C₁₆H₃₄ cracking on a Y zeolite catalyst reported by Nace³⁵⁾, compared to that on an amorphous SiO₂-Al₂O₃ catalyst. Therefore, the product selectivity of the FCC catalyst was not discussed in this study.

3.3. *np* Al₂O₃ as Anti-steaming Matrix

Three catalysts, USY/*np* Al₂O₃, steamed USY/*np* Al₂O₃ and dealuminated USY/*np* Al₂O₃, were compared to clarify the role of *np* Al₂O₃ as an anti-steaming matrix. USY12 (SiO₂/Al₂O₃ = 12 mol/mol) was used as the standard USY zeolite for USY/*np* Al₂O₃. Steamed USY/*np* Al₂O₃ was obtained by steaming under simulated regeneration conditions. Dealuminated USY/*np* Al₂O₃ was made from a dealuminated USY (SiO₂/Al₂O₃ = 45 mol/mol) obtained as a compulsorily degraded one without *np* Al₂O₃ as a model USY zeolite component unprotected during regeneration.

The catalytic performance of the three catalysts under selected conditions is shown in Fig. 6. The steamed (USY/*np* Al₂O₃) catalyst maintained activity equivalent to the USY/*np* Al₂O₃ catalyst and higher than the (dealuminated USY)/*np* Al₂O₃ catalyst in the reaction temperature range from 450 to 500°C, which suggests that no dealumination occurs on the steamed (USY/*np* Al₂O₃) catalyst and/or the *np* Al₂O₃ matrix stabilizes the catalyst during regeneration. X-ray diffraction observations also confirmed that there was little change between the steamed USY/*np* Al₂O₃ catalyst and the original USY/*np* Al₂O₃ catalyst, with a crystallinity of 98 and 100%, respectively, although the de-

Circle: 450°C, Triangle: 475°C, Square: 500°C,

Fig. 7 Effect of Reaction Temperature on Relationship between n -C₁₆H₃₄ Conversion and Pore Size (MPD) of np Al₂O₃ Matrix

aluminated USY had clearly lower crystallinity at 83%. It is considered that the moderately nanosize np Al₂O₃ matrix is stable against steaming and acts as a neutralizer against steaming of the zeolite due to its basicity.

3. 4. Dependency of Catalytic Activity on Pore Size of the np Al₂O₃ Matrix

3. 4. 1. Optimum Matrix Pore Size with Respect to Reaction Temperature

Four USY catalysts with np Al₂O₃ matrices with different pore sizes (9.0, 11.7, 14.5 and 18.0 nm) were examined with regard to cracking activity in the temperature range from 450 to 500°C, and the results are shown in Fig. 7. The dependency of cracking conversion on the pore diameter of the np Al₂O₃ matrix showed an optimum pore size of *ca.* 13 nm. The optimum pore size shifted slightly from 12 to 14 nm as the reaction temperature increased from 450 to 500°C. It is considered that the optimum pore size must provide free access for a heavier reactant to the matrix pore surface and pre-crack. The optimum pore size becomes slightly smaller as the mobility of the reactant increases at higher temperatures.

3. 4. 2. Optimum Matrix Pore Size with Respect to the SiO₂ to Al₂O₃ Ratios of the Zeolite

The dependency of the cracking activities at 475°C on the pore sizes of the np Al₂O₃ matrices ranged from 9.0 to 18.0 nm were compared for three USY/ np Al₂O₃ catalysts using USY6, USY12 and USY30 zeolite components. Figure 8 shows that the dependency of cracking activity on the pore sizes of the np Al₂O₃ matrices are very similar among the three USY catalysts, although there is some difference resulting from activity due to the zeolite component. The optimum matrix pore sizes for the three catalysts are between 11.7 and 14.5 nm and decrease slightly with increase of the zeolite SiO₂/Al₂O₃ ratio. This suggests that the

Circle: USY6 (SiO₂/Al₂O₃ = 6), Triangle: USY12 (SiO₂/Al₂O₃ = 12), Square: USY30 (SiO₂/Al₂O₃ = 30).

Fig. 8 Effect of SiO₂/Al₂O₃ Ratio of Zeolite on Relationship between n -C₁₆H₃₄ Conversion and Pore Size (MPD) of np Al₂O₃ Matrix

Circle: n -octane, Triangle: n -dodecane, Square: n -hexadecane.

Fig. 9 Effect of Feedstock Reactant on Relationship between n -Paraffin Conversion and Pore Size (MPD) of np Al₂O₃ Matrix

activity is mainly dependent on the pore size of the matrix and pre-cracking proceeds independently from the zeolite component.

3. 4. 3. Optimum Matrix Pore Size with Respect to the Carbon Number of n -Paraffin Feedstock

Conversion of n -C₈H₁₈ and n -C₁₂H₂₆, as smaller normal paraffins than n -C₁₆H₃₄, was tested over USY/ np Al₂O₃ catalysts with pore diameters ranging from 9.0 to 18.0 nm at 450°C and the results are shown in Fig. 9. The optimum matrix pore size was almost constant at *ca.* 13 nm for feedstock n -paraffin carbon numbers of 16 to 8. The matrix pore size that is preferable for a lighter reactant to freely access the matrix pore surface and be pre-cracked becomes only slightly smaller, because the mobility resulting from the carbon chain

Feedstock: squalane $i\text{-C}_{30}\text{H}_{62}$, isothermal at 450°C .

Fig. 10 Dependency of Activity and Degradation by Coking on Pore Size (MPD) of np Al_2O_3 Matrix for Catalyst Cracking

Fig. 11 Relationship between Activity and Degradation by Coking

length of the n -paraffin reactant has little influence, and the optimum pore size becomes slightly larger as the reactant reactivity increases³¹⁾.

3. 5. Relationship between Initial Activity and Degradation by Coking with Respect to the Al_2O_3 Matrix Pore Size

$i\text{-C}_{30}\text{H}_{62}$ was used as the heaviest model feedstock reactant and the reaction temperature was kept at 450°C . The rate constant k_0 and a for the first-order degradation model are plotted in **Figs. 10** and **11** as "Activity" and "Rate of Degradation by Coking."

Figure 10 shows the relation between both the activity and the rate of degradation by coking as a function of the MPD of the matrix. Both relationships show opposite trends to each other. The activity has a maximum in the MPD range from 11 to 15 nm and the rate of degradation has a minimum for the same pore size. The opposite trends of both features are shown in **Fig. 11** and it is that USY/np Al_2O_3 catalysts with higher activity and stronger resistance to degradation by coking. Both the activity and degradation of the cata-

Fig. 12 Dependence of Optimum Pore Size (MPD) on Carbon Number of Feedstock Reactant

lyst are dependent on the pore size of the matrix; therefore, coke deposition on the zeolite can be suppressed by pre-cracking in the matrix surrounding the zeolite. It means that the improvement of activity by pre-cracking on the np Al_2O_3 matrix is accompanied with suppression coking by removal of long chain hydrocarbons as coke precursors before arrival at the zeolite. The matrix acts as a firewall against coking to protect the zeolite, which has more active sites. Pre-cracking reduces coking of the reactants by the formation of conjugated unsaturated and poly-aromatics.

When $n\text{-C}_{16}\text{H}_{34}$ was used as the test feedstock instead of $i\text{-C}_{30}\text{H}_{62}$ to elucidate the kinetics and the relationships between the matrix MPD, activity and the degradation rate by coking, similar trends to those shown in **Figs. 10** and **11** were obtained. Therefore, $n\text{-C}_{16}\text{H}_{34}$ is also a suitable model feedstock for the evaluation of FCC catalysts in the laboratory because n -paraffins are more easily changed to coke than isoparaffins which alkyl branches work as steric hindrance against formation of polycyclic aromatics.

The optimum pore size of the np Al_2O_3 matrix can be related to the carbon number of the reactants for catalytic cracking, as shown in **Fig. 12**. The relationship suggests that the optimum pore size for the np Al_2O_3 matrix increases only slightly from 14.5 nm when the feedstock is changed to a heavier reactant species. Therefore, it was concluded that the optimum pore size diameter of np Al_2O_3 for a FCC catalyst matrix to have sufficient activity over a wider range of carbon number is ca. 15 nm.

4. Conclusion

The np Al_2O_3 matrix is capable of improving the reaction activity and coke degradation of the USY/np Al_2O_3 catalyst for catalytic cracking. The USY/np Al_2O_3 catalyst exhibits good performance for the cracking of heavier hydrocarbons. It was concluded that the optimum

pore size diameter of *np* Al₂O₃ as a FCC catalyst matrix is *ca.* 15 nm. In addition, it was clarified that *np* Al₂O₃ prepared from unimodal and non-aggregated boehmite sols has improved characteristics as a FCC catalyst matrix, in that the mechanical strength is higher than that of *np* Al₂O₃ from unimodal and aggregated boehmite gels because the PV remains constant even with change in the pore size. The resistance to the steam is also improved because the *np* Al₂O₃ matrix acts as a protector for zeolite against steaming.

Acknowledgment

The authors would like to acknowledge financial support from CREST of the Japan Science and Technology Agency (JST) and assistance from S. Nang, S. Murayama, Y. Hayakawa and S. Sudo.

References

- 1) Chen, N. Y., Mitchell, T. O., Olson, D. H., Pelrine, B. P., *Ind. Eng. Chem., Prod. Res. Develop.*, **16**, (3), 247 (1977).
- 2) Fowler, R. W., Hu, R., *Prep. Pap. Am. Chem. Soc. Div. Petrol. Chem.*, **48**, 348 (2003).
- 3) Fowler, R. W., Hu, R., *Stud. Surf. Sci. Catal.*, **149**, 123 (2004).
- 4) Occelli, M. L., Psaras, D., Suib, S. L., Stencel, J. M., *Appl. Catal.*, **28**, 143 (1986).
- 5) Otterstedt, J.-E., Zhu, Y.-M., Sterte, J., *Appl. Catal.*, **38**, 143 (1988).
- 6) Altomare, C. A., Koermer, G. S., Martins, E., Schubert, P. F., Suib, S. L., Willis, W. S., *Appl. Catal.*, **45**, 291 (1988).
- 7) Humphries, Adrian, Wilcox, Jack, R., *Oil & Gas J.*, **87**, 45 (1989).
- 8) Abner, D. K., Brady, M. F., Humphries, A. P., Yanik, S. J., *Prep. Pap. Am. Chem. Soc. Div. Petrol. Chem.*, **34**, (4), 713 (1989).
- 9) Sajkowski, D. J., Roth, S. A., Iton, L. E., Meyers, B. L., Marshall, C. L., Fleisch, T. H., Delgass, W. N., *Appl. Catal.*, **51**, (1), 255 (1989).
- 10) Hayward, C.-M. T., Winkler, W. S., *Hydrocarbon Processing*, **69**, 55 (1990).
- 11) Cheng, W.-C., Juskelis, M. V., Suárez, W., *Appl. Catal. A: General*, **103**, 87 (1993).
- 12) Wormsbecher, R. F., Cheng, W.-C., Harding, R. H., *Prep. Pap. Am. Chem. Soc. Div. Petrol. Chem.*, **40**, 482 (1995).
- 13) Cao, Hui, Suib, Steven, L., *Appl. Spectro.*, **49**, 1454 (1995).
- 14) Haas, A., Nee, J. R. D., *Erdoel Erdgas Kohle/EKEP*, **112**, 312 (1996).
- 15) Xu, M., Liu, X., Madon, R. J., *J. Catal.*, **207**, (2), 237 (2002).
- 16) Chen, Q., Shen, B.-X., Ling, H., *J. East China Univ. Sci. Tech.*, **30**, (6), 623 (2004).
- 17) Chen, Q., Shen, B.-X., Tan, C.-G., *J. East China Univ. Sci. Tech.*, **31**, (4), 438 (2005).
- 18) Andersson, S.-I., Myrstad, T., *Stud. Surf. Sci. Catal.*, **134**, 227 (2001).
- 19) Stockwell, D. M., Liu, X., Nelson, P. J., Gegan, T. A., Keweshan, C. F., *Prep. Pap. Am. Chem. Soc. Div. Petrol. Chem.*, **48**, (3), 216 (2003).
- 20) Stockwell, D. M., Liu, X., Nagel, P., Nelson, P. J., Gegan, T. A., Keweshan, C. F., *Stud. Surf. Sci. Catal.*, **149**, 257 (2004).
- 21) Fu, J. C., Xu, M., *Prep. Pap. Am. Chem. Soc. Div. Petrol. Chem.*, **51**, (2), 588 (2006).
- 22) Holland, B. T., Subramani, V., Gangwal, S. K., *Ind. Eng. Chem. Res.*, **46**, (13), 4486 (2007).
- 23) Asaoka, S., Ito, K., Minohara, S., Ali, M. A., Bamufleh, H. S., *Prep. Pap. Am. Chem. Soc. Div. Petrol. Chem.*, **50**, 372 (2006).
- 24) Ali, M. A., Asaoka, S., *Petrol. Sci. Tech.*, **27**, 984 (2009).
- 25) Asaoka, S., Miyazaki, M., Minohara, S., Sakashita, K., *Stud. Surf. Sci. Catal.*, **172**, 613 (2007).
- 26) Sakashita, K., Ito, K., Asaoka, S., *Prep. Pap. Am. Chem. Soc. Div. Petrol. Chem.*, **53**, 372 (2008).
- 27) Ito, K., Jang, H., Sakashita, K., Asaoka, S., *Pure Appl. Chem.*, **80**, (11), 2273 (2008).
- 28) Sakashita, K., Yoshino, M., Nishimura, I., Hayakawa, Y., Asaoka, S., *Prep. Pap. Am. Chem. Soc. Div. Petrol. Chem.*, **54**, 38 (2009).
- 29) Sato Research Co., US Pat. US-A1-20030044348.
- 30) Chiyoda Corp., US Pat. 4562059; US Pat. 4555394.
- 31) Emmett, P. H. ed., "Catalysis," Vol. VI, (1958).
- 32) Knudsen, F. P., *J. Am. Ceram. Soc.*, **42**, 376 (1959).
- 33) Johnson, M., Mooi, J., *J. Catal.*, **10**, 342 (1968).
- 34) Grace W. R., US Pat. 6379536.
- 35) Nace, D. M., *Ind. Eng. Chem., Prod. Res. Dev.*, **8**, 31 (1969).

.....

要 旨

接触分解触媒マトリックスとしてのナノポーラスアルミナの役割

坂下 幸司, 西村 勲, 芳野 真実, 木村 俊之, 浅岡 佐知夫

北九州市立大学国際環境工学部, 808-0135 北九州市若松区ひびきの1番1号

流動接触分解 (FCC) プロセスの原料への残渣油の割合が増大していることに対応するために, 高活性でコークが出にくく, かつ機械的強度が強く耐水熱性を有する FCC 触媒に関して基礎的な研究を行った。結晶成長が制御されたゲル化していないペーマイトを原料とする均一なナノサイズの細孔径 (5~50 nm) を有するアルミナが, ゲル化している場合に比べて, その細孔の大きさが機械的強度を損なうことなく良好に制御されることを確認し, この研究に用いた。FCC 触媒のマトリックスとしてのこのナノポーラスなアルミナが, 再生工程での水熱的劣化を低減することにおいてナノポーラスなシリカよりも

優れることを確認した。また, このナノポーラスアルミナはコーキングを抑制する予備分解を起こさせるのに重要な役割を有すること, その能力に関して最適な細孔径で示されるサイズがあることを明らかにした。その最適径は, 炭素数の異なるモデル化合物を反応原料として用いることによって, 反応原料にはあまり依存しないことを確認した。したがって, FCC 触媒マトリックスとしての最適なナノポーラスなアルミナは, 実用的な条件において基本的には, 細孔直径として約 11~15 nm を示すものであると結論した。

.....