[Regular Paper]

Nanoporous Al₂O₃ Designed as Protective Matrix for Zeolite in Catalytic Cracking

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

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

(Received February 5, 2010)

The resistance to coking and metal deposition from heavier crude feedstocks is important to a fluid catalytic cracking (FCC) catalyst. The catalytic cracking of *n*-hexadecane (*n*-C₁₆H₃₄) as a model compound was studied on the ultrastable Y zeolite (USY) catalysts with nanoporous (*np*, 5–50 nm pore diameter) Al₂O₃. A combination of two *np* Al₂O₃ types with well controlled pore size (7 nm or 35 nm) was employed as binder and matrix. The catalyst made with the matrix from the combination of the two pore sizes, with an average pore size of around 14 nm, exhibited higher cracking activity and lower rate of degradation by coking, similar to the catalyst with the single matrix pore size of 14 nm. A USY zeolite catalyst fabricated with only the small pore size *np* Al₂O₃ exhibited better resistance to hydrothermal regeneration under model conditions than a catalyst with the large pore size *np* Al₂O₃. A catalyst partly containing small pore size *np* Al₂O₃ exhibited better resistance to hydrothermal regeneration after intentional deposition of vanadium than a catalyst made of the small pore size *np* SiO₂. Therefore, the small pore size *np* Al₂O₃ has functions to protect the zeolite component and its activity, against both of high temperature steam and vanadium species, by binding on the zeolite surface and trapping the vanadium which easily moves over *np* SiO₂ during regeneration. Furthermore, it was clarified that the large pore size *np* Al₂O₃ in the mixed matrix can also act as a trapping site for Ni deposition to reduce coking with hydrogen generation on the deposited Ni and protection of the zeolite component activity.

Keywords

USY zeolite, Nanoporous alumina, Fluid catalytic cracking, Coke degradation, Metal resistance

1. Introduction

Global crude supplies have continued to become heavier recently and the ratio of vacuum residue in the feedstock for fluid catalytic cracking (FCC) has increased^{1),2)}. When a vacuum residue-rich feedstock is treated by FCC, the asphaltene and metals in the residue cause coke formation and metal deposition from the residue, which damage the zeolite. Consequently, the active sites of the FCC zeolite catalyst are damaged and degraded. Simultaneous heat and steam generated by the combustion of coke during catalyst regeneration also attack the zeolite. An improved FCC catalyst for heavier feedstocks is expected to have higher resistance against the degradation caused by the deposited coke and metals^{3)–9)}.

Modern industrial catalysts applied for FCC are typically composed of 5–30 wt% zeolites dispersed in an oxide matrix such as silica. Ultrastable Y zeolite (USY) was developed as the high-silica zeolite component of the FCC catalyst with higher hydrothermal resistance

by dealumination^{10)–13)}. At present, the USY is mainly used to achieve higher resistance against high temperature steam during the catalyst regeneration process. The role of the matrix has also been studied with respect to reaction zones for pre-cracking and demetallation^{14)–17)}.

We have studied for USY-nanoporous (*np*, 5–50 nm pore diameter) Al₂O₃ catalysts to have a concerted effect between the high-silica surface of the USY and the fractal surface of *np* Al₂O₃ nanopores, which are controlled during catalyst preparation^{18)–23)}. We have found that the smaller pore size *np* Al₂O₃ FCC catalyst matrix protects the zeolite component from hydrothermal degradation during regeneration better than an *np* SiO₂ matrix. It is clarified that the nanopores of *np* Al₂O₃ with controlled pore sizes as an FCC matrix have an important role as a pre-cracking zone for less coking²⁴⁾. It was also concluded that the optimum *np* Al₂O₃ for an FCC catalyst matrix has a pore size diameter of *ca.* 15 nm. Therefore, the USY/*np* Al₂O₃ matrix catalyst is a potential candidate as an improved next generation FCC catalyst.

Much attention has been given to the contribution of the FCC catalyst matrix on the activity and mechanism of

* To whom correspondence should be addressed.

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

Table 1 Pore Structure Properties of *np* Oxides for an FCC Catalyst Matrix

Matrices	Median pore diameter [nm]	Pore volume [mL/g]	Surface area [m ² /g]
<i>np</i> Al ₂ O ₃ A	7	0.42	220
<i>np</i> Al ₂ O ₃ B	15	0.45	170
<i>np</i> Al ₂ O ₃ C	35	0.45	90
<i>np</i> SiO ₂	9	0.34	182

Table 2 Composition of Sol-mixed *np* Al₂O₃ for Matrices

Sol-mixed <i>np</i> Al ₂ O ₃	<i>np</i> Al ₂ O ₃ A median pore diameter 7 nm	<i>np</i> Al ₂ O ₃ C median pore diameter 35 nm	Median pore diameter [nm]
S	2/3	1/3	9
M	1/2	1/2	14
L	1/3	2/3	16

poisoning by metals such as vanadium and nickel^{25)~31)}. The active sites in the zeolite are attacked by vanadium consecutively after its deposition on the matrix^{3),5),6)}. The deposited nickel causes dehydrogenation and coke production from carbon residue^{2),3),5)}. As the role of the matrix with respect to metal deposition becomes more important, both of the smaller and larger *np* Al₂O₃ matrices are expected to act as a metal trap.

In this paper, a combination of three functions of the FCC catalyst matrix was examined; (1) hydrothermal resistance, (2) metal trapping and (3) pre-cracking. A mixture of smaller pore size *np* Al₂O₃ matrix, which is capable of hydrothermal resistance and metal trapping, and the larger pore size *np* Al₂O₃ matrix, which is capable of metal trapping, was expected to result in an optimum *np* Al₂O₃ as pre-cracking zone for the FCC catalyst matrix. The resistance of the USY/*np* Al₂O₃ matrix catalyst against deactivation by coking and metal deposition during the regeneration recycle was also examined by simulated procedures.

2. Materials and Experimental

2.1. Nanoporous Oxides for Pore-controlled Matrix

Dry non-aggregated powders of unimodal boehmite sols were prepared by hydrothermal aging under weakly acidic conditions with acetic acid at 180°C. The powders were applied as a precursor for *np* γ -Al₂O₃ matrix, based on the previous work³²⁾. The nanopores of the *np* Al₂O₃ matrix controlled by precipitating and aging to non-aggregated sols have an advantage in that only the pore size is changed, while the pore volume, which affects the strength of the catalyst, is not changed²⁴⁾. Three kinds (less, moderate and well grown-up) of dry unimodal boehmite sol powders, which remained non-aggregated after drying at 200°C for 2 h and were returnable to a sol dispersion, were obtained by changing aging hours of 10, 20 and 40. The powders were converted to three types of *np* Al₂O₃ matrix materials with

unimodal pore diameters of 7, 14 and 35 nm by calcination at 550°C for 3 h. The calcined *np* Al₂O₃ could not be redispersed to the sol. The pore structure properties of the prepared *np* Al₂O₃ are shown in **Table 1**.

The pore size distributions were measured using a nitrogen gas sorption analyzer (Thermoquest Sorptomatic 1990) to accurately examine the nanoporosity more for sol-mixed *np* Al₂O₃ rather than use mercury porosimetry. The samples were pretreated at 200°C for 2 h under vacuum. The isothermal adsorption curve at P/P_0 less than 0.5, where there is no difference between the adsorption and desorption curves was analyzed using the Barrett-Joyner-Halenda (BJH) method.

Johnson and Mooi reported that the pore size of boehmite is equivalent to the crystallite size and the values were almost equal to each other³³⁾. However, there was only approximate consistency between the porosimeter data of pore size (void of particle) 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 which effect change of porosity. Therefore, the pore size and structure shown in **Table 1**, **Table 2** and **Fig. 1** were used as the physical characteristics of the *np* oxide matrices in this work.

Silica gel produced by (AEROSIL® 200, Japan Aerosil Co.) was used as a precursor for *np* SiO₂ matrix to be compared with *np* Al₂O₃ matrix. The average spherical primary particle size was *ca.* 12 nm. The pore structure properties of the *np* SiO₂ are also shown in **Table 1**.

2.2. Catalyst Preparation

Catalysts for evaluation were prepared by a combination of 20 wt% USY zeolite and 80 wt% *np* oxide matrix (Al₂O₃ or SiO₂). The USY zeolite that had a SiO₂ to Al₂O₃ ratio of 12 was combined with the one or two dry boehmite powders of different *np* Al₂O₃ precursors. The catalysts were prepared by powder (zeolite and boehmite) blending, wetness-controlled conditioning with de-ionized water, kneading, extrusion molding,

air-drying for 12 h 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, described in a previous paper²⁴), was used for steaming treatment using 10% H₂O in N₂ at 800°C to simulated FCC regeneration. Vanadium and nickel depositions on the catalyst were simulated by impregnation of vanadyl sulfate and nickel nitrate, respectively. The simulated vanadium deposited catalysts were prepared by the incipient wetness method for the shaped and calcined catalyst. Wet-impregnated catalysts were dried at room temperature overnight and at 120°C for 3 h. The dried samples were then calcined again in air at 450°C for 3 h before evaluation. The simulated nickel deposit catalysts were prepared by individual impregnation of each catalyst component by kneading the individual boehmite or zeolite powder with a nickel solution. The individually metal-loaded powders were dried at 120°C for 3 h followed by H₂ reduction at 370°C for 15 h and then used as raw materials for catalyst preparation. The Ni-loaded catalysts were reduced with H₂ at 450°C for 3 h before evaluation.

Filled circle (A): *np* Al₂O₃ of peak 7 nm. Filled diamond (C): *np* Al₂O₃ of peak 35 nm. Unfilled circle (S): sol-mixed *np* Al₂O₃ of (2/3 A + 1/3 C). Unfilled triangle (M): sol-mixed *np* Al₂O₃ of (1/2 A + 1/2 C). Unfilled square (L): sol-mixed *np* Al₂O₃ of (1/3 A + 2/3 C).

Fig. 1 Pore Size Distribution of Two Different Unimodal *np* Al₂O₃ and Mixtures by Sol Mixing

2. 3. Reaction Test and Catalyst Evaluation

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

The pore distributions of the sol-mixed *np* Al₂O₃ samples were examined with respect to pore distribution adjustment by sol-mixing of small and large pore size *np* Al₂O₃ to combine the functions of each. Catalysts consisting of pore-adjusted matrices were then examined for activity and coking degradation using *n*-hexadecane (*n*-C₁₆H₃₄) as a model FCC feedstock compound. Light gas oil and vacuum gas oil with a boiling point range between that of kerosene (232–288°C) and up to 566°C are generally preferred as feedstock for FCC units. *n*-C₁₆H₃₄ was chosen, because it can be easily supplied without the need for any heating device for feedstock vessel; the boiling point of *n*-C₁₆H₃₄ is 287°C and it is the heaviest *n*-paraffin in the liquid phase at room temperature and is also difficult to crack³⁴). The effectiveness of sol-mixed *np* Al₂O₃ as a matrix to protect the active sites of zeolite, compared with non-mixed *np* Al₂O₃ as a matrix, was confirmed by steaming treatment. The role of the *np* Al₂O₃ as a matrix compared with *np* SiO₂ was also confirmed with respect to the improvement and protection of the activity at the pre-cracking zone, in addition to protection of the zeolite against vanadium after deposition. The catalysts were also evaluated with respect to the site of nickel deposition.

n-Hexadecane (*n*-C₁₆H₃₄) was used as a model feedstock to test the catalytic reaction performance of the catalysts under isothermal (475°C) reaction conditions.

Isothermal reaction conversions (*X*%) for three different residence times (1/liquid hourly space velocity, 1/LHSV) of the reactant liquid at 0.005, 0.01 and 0.02 h were measured to establish the reaction kinetics (Table 3). Each reaction rate could be linearly related to the first-order model for reactant concentration:

$$\ln[100/(100 - X)] = k/\text{LHSV} \quad (1)$$

The first-order rate constants (*k* [1/h]) of three terms of time-on-stream (*θ*) for 0–0.5 h (*θ* = 0.25 h), 0.5–1.0 h (*θ* = 0.75 h) and 1.0–1.5 h (*θ* = 1.25 h) were obtained from the experimental results. The three rate con-

Table 3 Reaction Rate Evaluation

First-order reaction rate equation of A → B:	$-dC_A/dt = kC_A$
The integral for time $t = 0$ – t :	$\ln(C_{A0}/C_A) = kt$
Confirmed relation between LHSV and <i>X</i> :	$\ln[100/(100 - X)] = k/\text{LHSV} \quad (1)$
Degradation of the reaction activity, <i>k</i> :	$\ln k = -a\theta + \ln k_0 \quad (2)$

where $t = 1/\text{LHSV}$: residence time [h], *k*: first-order rate constant [1/h], LHSV: liquid hourly space velocity [1/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/h], *θ*: time-on-stream [h], and *k*₀: initial reaction activity rate constant at *θ* = 0.

a) Matrix from sol with uniform size. b) Mixing of sols with different size (this work). c) Mixing of gels with different sizes.

Fig. 2 Schematic Illustration Showing the Difference between Sol Mixing and Gel Mixing

stants had an approximately linear relation based on the first-order degradation:

$$\ln k = -a\theta + \ln k_0 \quad (2)$$

The initial rate constants k_0 [1/h], the rate constant at $\theta = 0$ [h], can be regarded as the intrinsic activity prior to degradation by coking. The rate of degradation a [1/h] can be regarded as representative of degradation by coking, because coking is the predominant cause of activity degradation during a one-pass conversion of catalytic cracking.

Gas chromatography-mass spectrometry (Shimadzu QP5050) was used for identification of 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. Pore Size Control by Sol Mixing of Two *np* Al_2O_3 Matrices

The USY zeolite of FCC catalysts, which normally has non-zeolitic pores as mesopores of *ca.* 2–5 nm in diameter, is a nanoporous (*np*) oxide^{10–13}. The matrix of the FCC catalyst, which surrounds the zeolite, is also an *np* oxide such as SiO_2 , Al_2O_3 or $\text{SiO}_2\text{--Al}_2\text{O}_3$ with pore sizes from 5 to over 40 nm. *np* Al_2O_3 less than 10 nm in diameter acts as a binder for zeolite particles^{19,24}. A matrix of *np* Al_2O_3 with pore sizes between 9 and 40 nm acts as a pre-cracking zone²⁴.

The method for mixing different unimodal sols as *np* Al_2O_3 precursors was applied for preparation of bimodal USY/*np* Al_2O_3 catalysts. Two sols for *np* Al_2O_3 with different unimodal sizes of small (*ca.* 7 nm) and large (*ca.* 35 nm) nanopores were provided by control of the crystal growth rate³². This confirmed that *np* Al_2O_3 with bimodal-like pore size could be prepared by mixing two different unimodal sols. The bimodal-like pore size can be considered as having one large size distribution peak accompanied by a smaller sized peak, and the large peak becomes intermediate sizes of two unimodal sizes. Pore size distributions for five different *np* Al_2O_3 are shown in **Fig. 1**. Pore structure properties of unimodal *np* Al_2O_3 A and C, and composition of sol-mixed *np* Al_2O_3 S, M and L are shown in **Tables 1** and **2**, respectively. In the case of mixing of different unimodal sols, the pore size distribution becomes unimodal, as shown in **Fig. 1**, because the small and large nanoparticle sols are mixed. However, in the case of mixing different unimodal gels as aggregated to form pores, the pore size distribution becomes bimodal, as pore formation is completed before mixing. This difference between sol mixing and gel mixing is illustrated in **Fig. 2**.

3.2. Catalytic Activity and Degradation by Coking on Sol-mixed *np* Al_2O_3 Matrix Catalyst

The obtained rate constant k_0 , and a for the first-order degradation model are plotted in **Fig. 3** as “Activity” and “Rate of Degradation by Coking” according to the matrix pore size. Both relations show opposite trends to each other. The activity has the highest peak at a pore size of *ca.* 14 nm (1.0 of small-to-large *np* Al_2O_3 ratio) and the rate of degradation was lowest at the same pore size (small-to-large *np* Al_2O_3 ratio). This opposite trend was also reported in a previous paper²⁴ and it confirms that USY/*np* Al_2O_3 catalysts with higher activ-

Feedstock: *n*-C₁₆H₃₄. Isothermal at 475°C. Circle: sol-mixed *np* Al₂O₃ matrix in Table 2. Triangle: single *np* Al₂O₃ matrix in Table 1. Unfilled marks with solid line: activity. Filled marks with dotted line: Rate of Degradation by Coking. Activity: initial rate constant of the first-order rate equation. Rate of Degradation by Coking: slope of the first-order degradation (refer to Table 3).

Fig. 3 Activity and Degradation by Coking on a Catalyst of Mixed Matrix Prepared by Sol Mixing

ity have stronger resistance against degradation by coking. Furthermore, both the activity and degradation of the catalyst are dependent on the pore size of matrix, which means that coking can be suppressed by pre-cracking at the mixed matrix surrounding of zeolite by design of the matrix pore size. The mixed matrix also acts as an anti-coking guard for protecting zeolite, which has more active sites susceptible to coking. The pre-cracking of *n*-C₁₆H₃₄ reduces the coking capability of the reactants that easily form conjugated unsaturated hydrocarbons and poly-aromatics.

3.3. Resistance of Catalyst to High Temperature Steam

Seven catalysts composed of 20 wt% USY zeolite and 80 wt% matrix were examined with respect to resistance against high temperature steam by using analysis of the zeolite component by X-ray diffraction. The catalyst matrices were three (S-1, M-1 and L-1) sol-mixed *np* Al₂O₃, S, M and L in Table 2, three (A-1, B-1 and C-1) single *np* Al₂O₃, A, B or C in Table 1, and *np* SiO₂ (R-1). The catalysts were treated by steaming at a partial pressure of 10 kPa at 800°C for 3 h to simulate regeneration of the catalyst.

The crystallinity results based on fresh zeolite for the zeolite components are shown in Fig. 4. The crystallinity of the single *np* Al₂O₃ matrix (A-1) and two sol-mixed *np* Al₂O₃ matrices (S-1 and M-1) with pore sizes of 7, 9 and 14 nm, respectively, did not change. On the contrary, in the case of two single *np* Al₂O₃ matrices (B-1 and C-1) and *np* SiO₂ matrix (R-1), the pore sizes of which were 14, 35 and 9 nm, respectively, the crystallinity changed until the level reached by the bare zeolite, 84%. In the case of sol-mixed *np* Al₂O₃ matrix (L-1) with a pore size of 16 nm, the crystallinity

Circle: sol-mixed *np* Al₂O₃ matrix in Table 2. Triangle: single *np* Al₂O₃ matrix in Table 1. Square: *np* SiO₂ matrix. Dashed line drawn at 84%: sole zeolite without matrix.

Fig. 4 X-ray Diffraction Analysis for Crystallinity of Zeolite Component after Treatment with 10% Steam at 800°C for 3 h

did not decrease significantly.

The steamed USY/*np* Al₂O₃ catalysts composed of single *np* Al₂O₃ matrix (A-1) and two mixed *np* Al₂O₃ matrices (S-1 and M-1) maintained the same activity as before the steam treatment. The USY/*np* Al₂O₃ catalyst made of the steamed zeolite and single *np* Al₂O₃ matrix with a pore size of 7 nm had similar activity to that for the two single *np* Al₂O₃ matrices (B-1 and C-1) and *np* SiO₂ matrix (R-1). The catalysts containing *np* Al₂O₃ with a pore size of 7 nm showed both stable crystallinity and unchanged activity after the steam treatment, which indicates that the USY zeolite component is protected by the *np* Al₂O₃ matrix with 7 nm diameter pores. In the case of sol-mixed *np* Al₂O₃ matrix (L-1) with 16 nm diameter pores, the content of the smaller *np* Al₂O₃ is probably not enough to cover the zeolite surface for protection, because almost all of the small *np* Al₂O₃ may be contained in the void of the large *np* Al₂O₃.

We previously reported that *np* Al₂O₃ can be bound to USY zeolite surface Si-OH groups to generate new acid sites, based on NH₄-temperature programmed desorption (TPD)¹⁸⁾. Therefore, it is considered from hydrocracking activity in hydroisomerization²¹⁾ that it is difficult for Al species to leave the zeolite lattice to the surface Si-OH site, because the precursors of *np* Al₂O₃ are chemically combined with the zeolite surface. The surface non-framework Al that works as an active acid site of hydrolysis for framework dealumination during steaming is changed to a less active site by the combination. A schematic illustration is shown in Fig. 5 where the non-framework Al, which is known as a strongly acidic sites (shown as H⁺ in hydrated state during steaming), changes into moderately acid sites by binding with the precursor of the small *np* Al₂O₃.

Fig. 5 Surface Model of the Interface between *np* Al_2O_3 and USY Zeolite

3.4. Resistance of Catalyst to Vanadium Deposition

There have been many studies on the mechanism for catalyst poisoning by metals such as vanadium and nickel^{25)~31)}. The active sites in the zeolite are considered to be attacked by the mobile metals, especially vanadium^{3),5),6)}. Five vanadium-deposited catalysts were examined with respect to resistance against high temperature steam by X-ray diffraction analysis of the zeolite component. The catalysts selected were one (M-1) of sol-mixed *np* Al_2O_3 , three (A-1, B-1 and C-1) of single *np* Al_2O_3 , and the *np* SiO_2 . The phenomenon of vanadium deposition is similar to that of high temperature steam as shown in Fig. 5. It is shown in Fig. 6 that although the two (B-1 and C-1) single *np* Al_2O_3 matrices exhibit some resistance against vanadium deposition, the single *np* Al_2O_3 matrix (A-1) with *ca.* 7 nm diameter pores has the highest resistance. It is considered that the *np* Al_2O_3 acts as a binder, because the *np* Al_2O_3 matrix with 7 nm diameter pores can make many contacting points with the zeolite.

In the case of the USY/*np* SiO_2 catalyst (R-1) the crystallinity of zeolite component after steaming is decreased to the level of the bare zeolite (58%). On the contrary, the crystallinity of the USY/*np* Al_2O_3 catalyst (M-1) remains stable against steaming and is no different before and after the vanadium deposition and steaming. The crystallinity change depends on the capture ability for vanadium on the matrix. When non-captured vanadium is present, the vanadium moves to the zeolite surface and degrades the crystallinity, which results in a decrease of activity. The crystallinity of the steamed two USY/*np* Al_2O_3 catalysts remained unchanged, which is shown in Fig. 6. It indicates that all vanadium is captured in the *np* Al_2O_3 matrix with 7 nm diameter pores and cannot approach the zeolite surface.

The activity and rate of degradation are shown in Fig. 7 and Table 4, comparing between before and after steaming for the USY/*np* Al_2O_3 catalysts (M-1 and M-2) and the USY/*np* SiO_2 catalysts (R-1 and R-2). The USY/*np* Al_2O_3 catalyst prepared from mixed and

Circle: sol-mixed *np* Al_2O_3 matrix in Table 2. Triangle: single *np* Al_2O_3 matrix in Table 1. Square: SiO_2 matrix. Dashed line drawn at 58%: sole zeolite without matrix.

Fig. 6 X-ray Diffraction Analysis for Crystallinity of the Zeolite Component in 5000 wtppm Vanadium Deposited Catalysts after Treatment with 10% Steam at 800°C for 3 h

Feedstock: *n*- $\text{C}_{16}\text{H}_{34}$. Isothermal at 475°C. Catalysts: steamed with 10% H_2O at 800°C for 3 h. M-1: sol-mixed *np* Al_2O_3 matrix of *ca.* 14 nm diameter pores before V deposition. M-2: *ibid.* after 5000 wtppm V deposition. R-1: *np* SiO_2 matrix with 7 nm diameter pores before V deposition. R-2: *ibid.* after 5000 wtppm V deposition. White: activity. Shaded: Rate of Degradation by Coking. Activity: initial rate constant of the first-order rate equation. Rate of Degradation by Coking: slope of the first-order degradation (refer to Table 3).

Fig. 7 Activity and Rate Degradation by Coking at Vanadium Deposition

optimized *np* Al₂O₃ (M-1) has higher activity than the USY/*np* SiO₂ catalyst (R-1) due to the improved cracking activity before V deposition. It is indicated in comparison of M-2 and R-2 that the crystallinity of the zeolite component does not change after steaming and V deposition; M-2 does not change from that of M-1. Vanadyl sulfate, which was used as the simulated compound of deposited vanadium during actual regeneration, has a low melting point and strong acidity so that it can move easily on neutral or acidic surfaces such as SiO₂ to zeolite. On the contrary the role of *np* Al₂O₃ is illustrated in Fig. 8 as a protective matrix against vanadium attack on the zeolite. Although vanadium deposited on *np* SiO₂ easily migrates on the *np* SiO₂ surface to zeolite after changing to acidic species, vanadyl sulfate during regeneration, vanadium deposited on *np* Al₂O₃ is strongly trapped with a stable chemical bond

due to the basicity of smaller *np* Al₂O₃ and cannot move to the zeolite surface.

Degradation by coking was reduced after vanadium deposition, more for M-2 than M-1, and for R-2 than R-1, as shown in Fig. 7. It was supposed that the deposited sulfate may act as a coking retardant by skeletal isomerization of normal olefins as a precursor of conjugated dienes.

3. 5. Resistance of Catalyst to Nickel Deposition

Nickel accelerates dehydrogenation and coking from carbon residue; therefore, an FCC catalyst will lose the catalytic activity by Ni deposition on the surface. It is clearly difficult to avoid Ni deposition on the FCC catalyst because the deposition occurs non-catalytically by thermal decomposition. However, it should be possible to assign the location of Ni deposition to less-active sites, due to its immobility on the surface. In order to determine such non-active sites for trapping Ni, the resistance to Ni deposition on the USY/*np* Al₂O₃ catalyst prepared from the sol-mixed and optimized *np* Al₂O₃ (M-1) was examined and compared with the non-deposited catalyst and three simulated Ni deposited catalysts listed in Table 5; M-3, Ni deposited on only large pore size *np* Al₂O₃; M-4, Ni deposited on both small and large pore size *np* Al₂O₃; M-5, Ni deposited

Table 4 Prepared Catalysts with Simulated Vanadium Deposition

Catalyst	Matrix	Simulated V deposition [wtppm]
M-1	Sol-mixed <i>np</i> Al ₂ O ₃ M	0
M-2		5000
R-1	<i>np</i> SiO ₂	0
R-2		5000

a): R-1 to R-2 (USY/*np* SiO₂). b): M-1 to M-2 (USY/*np* Al₂O₃).

Fig. 8 Schematic Illustration of the Difference of Vanadium Deposition on USY/*np* SiO₂ and USY/*np* Al₂O₃

Table 5 Prepared Catalysts with Simulated and Controlled Nickel Deposition

Catalyst	Simulated nickel deposition (wtppm/each component) ^{a)}			
	USY zeolite	7 nm Al ₂ O ₃ A	35 nm Al ₂ O ₃ C	Catalyst total
M-1	0	0	0	0
M-3	0	0	6300	2500
M-4	0	3100	3100	2500
M-5	2500	2500	2500	2500

a) Simulated Ni deposited component was prepared by individual impregnation of each component followed by H₂ reduction at 370°C for 15 h. The simulated Ni deposited catalyst was prepared by mixing the Ni deposited components followed by typical catalyst preparation.

Feedstock: $n\text{-C}_{16}\text{H}_{34}$. Isothermal at 475°C . Catalysts: steamed with 10% H_2O at 800°C for 3 h. M-1: sol-mixed Al_2O_3 matrix with *ca.* 14 nm diameter pores before V deposition. M-3: 2500 wtppm (based on total catalyst) Ni deposited on only large pore size $\text{np Al}_2\text{O}_3$. M-4: Ni deposited on both small and large $\text{np Al}_2\text{O}_3$. M-5: Ni deposited on all of the catalyst. White: activity. Shaded: Rate of Degradation by Coking. Activity: initial rate constant of the first-order rate equation. Rate of Degradation by Coking: slope of the first-order degradation (refer to Table 3).

Fig. 9 Activity and Rate of Degradation by Coking for Various Catalysts after Nickel Deposition

on all of the catalyst. The amount of Ni deposited was totally 2500 wtppm of each catalyst. The weight ratio of Ni to V is usually 0.5 in the feedstock for an industrial FCC plant, and the catalyst is replaced when vanadium deposition reaches *ca.* 5000 wtppm of the catalyst due to degradation. The results for activity and rate of degradation by coking after the same amount of Ni deposition are shown in Fig. 9. The degradation order is $\text{M-4} > \text{M-3} > \text{M-5} > \text{M-1}$, and that for activity is $\text{M-3} > \text{M-1} = \text{M-4} > \text{M-5}$; the activity before and after Ni deposition are almost the same.

The catalyst without Ni has the lowest rate of degradation by coking, which indicates that the deposited Ni accelerates coke formation. It is also confirmed that the active sites of the zeolite are protected from nickel species by the $\text{np Al}_2\text{O}_3$ matrices.

The degradation order of $\text{M-4} > \text{M-3} > \text{M-5} > \text{M-1}$ corresponds to the Ni concentration at the *ca.* 7 nm pore size $\text{np Al}_2\text{O}_3$ matrix and is inverse to that at the *ca.* 35 nm pore size $\text{np Al}_2\text{O}_3$ matrix, and the Ni-loaded catalyst on the zeolite (M-5) has the lowest activity. The results indicate that *ca.* 35 nm pore size $\text{np Al}_2\text{O}_3$ matrix can satisfactorily trap the nickel species as less active type sites in order to prevent Ni deposition as Ni high dispersion on the small pore size $\text{np Al}_2\text{O}_3$ matrix such as the *ca.* 7 nm pores of M-4, which produce coke precursors that can easily move onto the active sites of zeolite to change into coke and degrade the catalyst. Therefore, an FCC catalyst with an $\text{np Al}_2\text{O}_3$ matrix can be carefully designed against Ni deposition by controlling the pore structure. In the design the nickel should

Nickel: deposited and trapped as rather large particles. Vanadium: stabilized and trapped to protect zeolitic active sites.

Fig. 10 Schematic Illustration of the Role of Sol-mixed $\text{np Al}_2\text{O}_3$ Matrix to Control Vanadium and Nickel Deposition

be trapped and less dispersed by forming large particles on a large pores size $\text{np Al}_2\text{O}_3$ matrix such as M-3.

Ni deposition occurs simultaneously with V deposition at larger pores, due to the large molecular size of the metal compounds of the feedstock in an industrial FCC plant; therefore, the design concept obtained from this simplified investigation will be surely effective. The role of the sol-mixed $\text{np Al}_2\text{O}_3$ matrix for controlling V and Ni deposition is illustrated in Fig. 10. Ni is trapped as less active type sites at the larger pore size $\text{np Al}_2\text{O}_3$ surface and V is more strongly trapped as stable type sites at higher surface areas with smaller pore size.

3. 6. Design Concept for the Pore Size of $\text{np Al}_2\text{O}_3$ Matrix

Finally, the design and composition of the size of the $\text{np Al}_2\text{O}_3$ matrix is discussed with respect to the activity and the rate of degradation by coking. The understanding of pore distribution in the catalyst with the sol-mixed $\text{np Al}_2\text{O}_3$ matrix for control of demetallation, pre-cracking, coking, and V/Ni deposition in an FCC catalyst is illustratively summarized in Fig. 11. The pre-cracking zone is from 6 to 18 nm, as indicated in Fig. 3, so that the coking zone is considered to be covered from 2 to 5 nm of zeolite surface mesopore. On the other hand, the demetallation zone for metal trapping is preferably the $\text{np Al}_2\text{O}_3$ surface with a pore size range larger than the pre-cracking zone in order to retard pre-cracking, and not to accelerate coking and zeolite degradation.

4. Conclusion

Catalytic cracking with coking were studied on catalysts consisting of USY zeolite with $\text{np Al}_2\text{O}_3$ employed as binder and matrix to develop a new FCC catalyst with good resistance to degradation by coke and metal deposition, which is suitable as crude feedstocks tend to become heavier.

The studied concept for the matrix is a combination of two $\text{np Al}_2\text{O}_3$ types with well controlled pore sizes. A catalyst with middle pore size of around 14 nm made

Checked pores: for Ni deposition and trapping as rather large particles. Gray pores: for V stabilized and trapping. Unfilled pores: protected zeolitic active sites.

Fig. 11 Summary of Pore Distribution of a Sol-mixed *np* Al₂O₃ Matrix for Controlling Demetallation, Pre-cracking, Coking, and V/Ni Deposition in an FCC Catalyst

from two different pore size *np* Al₂O₃ of 7 nm (small) and 35 nm (large) exhibited higher cracking activity and lower rate of degradation by coking, similar to that made of 14 nm (middle) pore size *np* Al₂O₃ matrix. Catalysts containing the small pore size *np* Al₂O₃ exhibit better resistance against hydrothermal regeneration after V deposition than that with small pore size *np* SiO₂. The small pore size *np* Al₂O₃ protects the zeolite component and its activity against both high temperature steam and V species by binding on the zeolite surface and trapping the highly mobile V during regeneration. The large pore size *np* Al₂O₃ in a sol-mixed matrix can function as a trapping site for Ni deposition to reduce coking and protect the zeolite component activity.

Acknowledgment

Financial support from CREST of the Japan Science and Technology Agency (JST) and assistance by S. Nang, S. Murayama, Y. Hayakawa and S. Sudo are greatly acknowledged.

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要 旨

接触分解触媒のゼオライト成分を保護するマトリックスとしてのナノポーラスアルミナ

坂下 幸司, 西村 勲, 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

原油の重質化に伴い流動接触分解（FCC）触媒に要求されるコーク生成および金属分堆積による劣化に対する耐性に関して、USY ゼオライトとナノポーラスなアルミナ複合触媒を用いて、モデル化合物ヘキサデカン（ $n\text{-C}_{16}\text{H}_{34}$ ）の接触分解反応性とコーキングを検討した。バインダーおよびマトリックスとしてナノ多孔性が制御されたアルミナを用いた。単独では小細孔（7 nm）と大細孔（35 nm）を有し、混合後は中細孔（約 14 nm）を示す2種類のナノポーラスアルミナを組み合わせた触媒は、単独で中細孔（約 14 nm）を有するナノポーラスアルミナを用いた触媒と同様に高い分解活性と低いコーク劣化を示した。USY ゼオライトと複合化後の高温スチーム模擬再生テストにおいて、小細孔ナノポーラスアルミナを含んだ触媒は中細孔あるいは大細孔ナノポーラスアルミナを単独で用いた触媒

や小細孔ナノポーラスシリカを単独で用いた触媒よりも耐性に優れた。また、小細孔ナノポーラスアルミナを含んだ触媒のもつ優れた耐性は模擬的なバナジウム堆積後でもほぼ維持された。この小細孔ナノポーラスアルミナの役割は、小さなナノポーラスアルミナがゼオライト表面と結合するとともにバナジウムをトラップすることによって、高温スチームとシリカの上では再生時に移動するバナジウムに対してゼオライトおよびその活性を保護していると考えられた。さらに、組み合わせる大細孔ナノポーラスアルミナがニッケルの堆積トラップサイトとなることによって、堆積ニッケル上での脱水素によるコーキングを抑えるとともにゼオライトの活性点を守る働きをすることが分かった。

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