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Production of aromatics from heavier *n*-paraffins on hybrid cracking-reforming catalyst

Toshiyuki Kimura, Narihito Hata, Koji Sakashita, Sachio Asaoka*

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

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ABSTRACT

Selective production of aromatics from the heavier *n*-paraffins was studied on nano-structured (*ns*) catalysts consisting of *ns* alumina and MFI-type H-galloaluminosilicate (H-GaAlMFI) zeolite. Performance of the hybrid H-GaAlMFI zeolite catalyst with *ns* Al_2O_3 was improved considerably from those of the zeolite sole catalyst and USY or H-ZSM-5 catalyst. It was observed that in the *n*-$C_{16}H_{34}$ conversion, the product selectivity for aromatics (including intermediate olefins and byproducts) and the degradation rate depended on either the ratios of Ga/(Ga + Al) and Si/(Ga + Al) in the zeolite component or on the co-existence of *ns* Al_2O_3. It was found that aromatics could be produced selectively by controlling the reaction time. In regards to the catalytic active sites, the *ns* species at the zeolite surface layer and the surface distributions were confirmed by X-ray photoelectron spectroscopy with the Ar-etching method. It was determined that non-framework Ga species existed as Ga oxides after calcining. It was also revealed that the *ns* alumina had an important role in forming the *ns* species of non-framework Ga by extracting it from the zeolite framework and stabilizing it as an *ns* oxide at the zeolite particle surface which opened into the nano-space.

1. Introduction

Recently, demand for aromatics, especially *p*-xylene, as raw materials for the petrochemical industry has been increasing. Increased production of some heavier waxy diesel fractions has been accomplished by hydroconversion in oil refineries and by the gas-to-liquid (GTL) process in natural gas refineries. Generally, Pt/Al_2O_3 is used to produce aromatics from heavy naphtha by catalytic reforming. The demand of propylene as a raw material for the petrochemical industry is also increasing. Since propylene, and inevitably ethylene, is produced by thermal cracking of naphtha, the propylene/ethylene mixture can only be produced at a ratio of ca. 1:2. Thus, naphtha is used in a variety of fuels and petrochemical products. Therefore, without the use of naphtha feedstock, propylene and aromatics must be produced by a new process.

Catalysts that have been developed for aromatization can generally be grouped into the amorphous and/or the zeolitic type. Some hybrid catalysts that are a mixture of the amorphous and the zeolitic types have been developed. Previously, in the aromatization from propane and light naphtha over H-ZSM-5 (MFI-type) zeolite, it was confirmed that the catalyst had a high activity for light olefin oligomerization and aromatization due to its high proton acidity and shape selectivity [1–6]. The performance of the ZSM-5 catalyst in the aromatization of light olefins was improved by ion-exchange with Ga^{3+}, Zn^{2+}, Cu^{2+}, and Ag^{+} achieved by the impregnation of metal oxides like Ga_2O_3, ZnO, and Ag_2O to adjust the acid strength [7–9]. MFI-type H-galloaluminosilicate (H-GaAlMFI) zeolite catalyst has a higher performance than Ga/H-ZSM-5 catalyst in the aromatization from propane. Extra framework Ga oxides, which can be generated from the H-GaAlMFI zeolite by pretreating, are very highly dispersed and are effective for paraffin aromatization due to their dehydrogenation function [10–15].

In our recent research on zeolite catalysts, we intentionally focused on composites containing unimodal nanoporous nanostructured (defined as 5–50 nm, and hereafter referred to as *ns*) oxides with pore sizes ranging from about 5 nm to several tens of nanometers [16]. This research has provided new advances in catalysis, including hydrodesulfurization [17,18], hydrocracking [19,20], and catalytic cracking [21,22]. In developing catalytic cracking catalysts, we studied the efficiency of *ns* alumina matrices with different properties. We found some improvement with catalysts containing *ns* alumina matrices with optimum pore diameters. The activity was dependent on the pore size of the matrix because pre-cracking proceeded independently of the zeolite component, and there was a reverse relationship between the activity and the rate of degradation by coking, both of which were analyzed as a function of the pore diameter of the matrix. The *ns* alumina made from unimodal sols had characteristics of a catalytic cracking catalyst matrix, as the mechanical strength was stronger than those of

* Corresponding author.
E-mail address: asaoka@kitakyu-u.ac.jp (S. Asaoka).

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unimodal gels while maintaining minimal change of pore volume to the change of pore size. The *ns* alumina protected the zeolite component from hydrothermal degradation during catalyst regeneration. It was considered that this alumina matrix was effective in a variety of reactions, including aromatization at high temperature.

Selective production of aromatics from the heavier *n*-paraffins was studied on the hybrid catalysts consisting of *ns* alumina and MFI-type H-galloaluminosilicate (H-GaAlMFI) zeolite. In this study, the cooperation between the *ns* alumina and the H-GaAlMFI zeolite in the catalysis on aromatization was the main focus.

2. Experimental

2.1. Catalyst preparation

The H-GaAlMFI zeolites were synthesized using sodium silicate, aluminum sulfate 14–18 hydrate [$Al_2(SO_4)_3{\cdot}14$–$18H_2O$], gallium nitrate *n* hydrate [$Ga(NO_3)_2{\cdot}nH_2O$], tetrapropylammonium bromide [TPABr], sodium chloride, sulfuric acid, and deionized water. The reagents were mixed sequentially. The mixture was aged overnight at room temperature. The zeolite was synthesized by heating at 150 °C for 24 h. The synthesized zeolite was washed with H_2O until the pH reached 7, then dried overnight at room temperature, followed by drying at 120 °C for 3 h and calcining in air at 500–650 °C (typically 550 °C) for 3 h. The as-synthesized zeolite powders were converted into H zeolites by the conventional ion exchange method with an aqueous solution of NH_4NO_3.

Zeolites with various Ga/(Ga + Al) and Si/(Ga + Al) ratios were synthesized. Ga/(Ga + Al) ratios were 0, 0.15, 0.3, and 0.6, and Si/(Ga + Al) ratios were 15, 30, and 60. A typical H-GaAlMFI zeolite had Ga/(Ga + Al) and Si/(Ga + Al) ratios of 0.3 and 15, respectively, and a crystalline size of ca. 45 nm.

A moderate mature kind of dry unimodal boehmite sol powder was prepared by the hydrothermal aging method. This powder can be converted to a type of *ns* Al_2O_3 matrix material with a unimodal pore diameter of 14 nm by calcination, as reported [21,22].

ns Al_2O_3-H-GaAlMFI zeolite catalysts were synthesized by wet mixing followed by calcination. The two component catalysts were made from *ns* Al_2O_3 and H-GaAlMFI zeolite (dry weight ratio: 7:3). Two of these zeolite and boehmite powders were mixed with water to form a thick paste and this paste was mechanically kneaded. After kneading, the catalysts were extruded into pellets, then dried overnight at room temperature, followed by heating at 120 °C for 3 h. Finally, they were calcined at 550 °C for 3 h.

2.2. Reaction tests and catalyst evaluation

The catalytic performances of the catalysts were evaluated by using *n*-hexadecane (*n*-$C_{16}H_{34}$) as a feedstock [21]. This compound was selected as a model for the heavier *n*-paraffins that are contained in some heavier waxy diesel fractions.

A continuous-flow reactor with a down flow-type fixed bed catalyst (volume: 0.5 mL) was used for the reaction tests. Reaction conditions were: temperature: 550 °C; liquid hourly space velocity, LHSV: 2.0–80 h^{-1}(contact time, 1/LHSV: 0.0125–0.50 h); pressure: 0.1 MPa under nitrogen pressure; molar ratio of *n*-$C_{16}H_{34}$:N_2 = 1:15.

Each reaction rate could be linearly related to the first-order model for reactant concentration:

$$\ln\left[\frac{100}{100-X}\right] = \frac{k}{\mathrm{LHSV}} \quad (X:\ \text{Conversion})$$

The first-order rate constants (k [1/h]) of five terms of time-on-stream (θ) for 0–1 h (θ = 0.5 h), 1–2 h (θ = 1.5 h), 2–3 h (θ = 2.5 h), 3–4 h (θ = 3.5 h) and 4–5 h (θ = 4.5 h) were obtained from the experimental results. The five rate constants had an approximately linear relation based on the first-order degradation:

$$\ln k = -\mathbf{a}\theta + \ln k_0$$

The initial rate constants k_0 [1/h], the rate constant at θ = 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.

Table 1
Comparison of catalytic performance of H-GaAlMFI and *ns* Al_2O_3/H-GaAlMFI catalysts at short contact time (0.025 h).

Catalysts	H-GaAlMFI	*ns* Al_2O_3/H-GaAlMFI
Conversion (%)	83.4	91.7
Degradation rate by coking (h^{-1})	0.15	0.06
Paraffin selectivity (carbon-mol%)	23.2	22.0
Olefin selectivity (carbon-mol%)	67.2	66.7
Aromatics selectivity (carbon-mol%)	9.6	11.3

The comparison was based on the same zeolite volume.

2.3. Catalyst characterization

Elemental compositions of the H-GaAlMFI zeolite surface layer were measured by X-ray photoelectron spectroscopy (XPS) with Ar-etching. XPS was performed with a KRATOS spectrometer equipped with a mono Al source operating at 450 W. The spectra were acquired at room temperature and narrow scans with rather high 40 eV pass energy for the samples. The spectrometer energy scale was calibrated with Ag 3d5/2. The binding energies and atomic concentrations of the catalysts were calculated by the XPS results using the total integrated peak areas of the Al 2p, Si 2p, Ga 2p, O 1s, and C 1s regions.

3. Results and discussion

3.1. Catalytic performance on ns Al_2O_3/H-GaAlMFI catalyst

Aromatization of *n*-hexadecane was investigated over the H-GaAlMFI zeolite catalysts shaped with *ns* Al_2O_3 (*ns* Al_2O_3/H-GaAlMFI catalyst), and compared with the H-GaAlMFI zeolite sole catalyst. The results at short contact time, where the comparison was based on the same zeolite volume, are shown in Table 1.

As shown in Table 1, *ns* Al_2O_3/H-GaAlMFI catalyst had higher catalytic performance than H-GaAlMFI zeolite sole catalyst, as illustrated by its higher activity, stability and aromatic yield. Because the same zeolite was used in both catalysts, this performance is considered to be due to the *ns* Al_2O_3 component. Since there was a possibility that the acid sites with mild strength were derived from alumina, not the interface, it was confirmed by a reaction test that *ns* Al_2O_3 itself did not hold meaningful activities. Therefore, in the composite of *ns* Al_2O_3 and H-GaAlMFI zeolite, the acid sites were generated at the boundary face between the Si–OH of the zeolite and the Al–OH of *ns* Al_2O_3. As the active sites opened into the nanospace, they became more highly active toward larger molecules. The generated acid sites were not involved in coking because the acids were mild. Additionally, the milder *ns* Al_2O_3 at the strong acid sites on the zeolite surface suppressed hydrogen transfer. Therefore, the degradation rate by coking decreased to less than half that without *ns* Al_2O_3. Thus, it was confirmed that zeolite catalysts shaped with *ns* Al_2O_3 were effective for the aromatization from *n*-hexadecane.

The concerted effects of various zeolite species, H-GaAlMFI zeolite, H-AlMFI (H-ZSM-5) zeolite and USY zeolite with *ns* Al_2O_3 were