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Facile Fabrication of ZSM-5 Zeolite Catalyst with High Durability to Coke Formation during Catalytic Cracking of Paraffins

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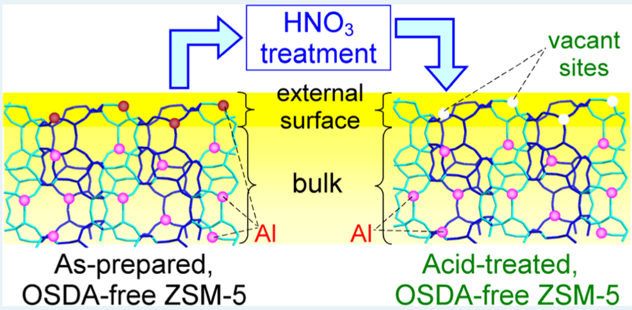
S *Supporting Information*

ABSTRACT: Post-synthetic HNO_3 treatment of ZSM-5 zeolite synthesized in the absence of organic structure-directing agent removes framework Al selectively from the external surface, producing a unique ZSM-5 zeolite catalyst that has very few acid sites on its external surfaces. The resulting external acid sites can be readily deactivated at the early stage of the reaction, giving a potentially long-life catalyst as a result of a high durability to coke formation during the cracking of hexane or other paraffin molecules.



KEYWORDS: *ZSM-5 zeolite catalyst, structure-directing agent, acid treatment, dealumination, external surface, durability to coke formation*

Zeolites, crystalline microporous aluminosilicates, are widely utilized as catalysts for petrochemical processes and adsorbents for gas separation processes because of the molecular sieve effect caused by their uniform micropores with sizes in the range 0.5−0.9 nm. ZSM-5 zeolite (**MFI** topology[1]) has been most widely used as an industrial catalyst for various petrochemical processes because of its high catalytic activity and shape-selectivity.

Since the synthesis of ZSM-5 by Mobil was first reported in 1972,[2] this highly siliceous pentasil zeolite has been intensively investigated. ZSM-5 is generally synthesized by a hydrothermal method using tetrapropylammonium (TPA^+) cations as an organic structure-directing agent (OSDA) in an alkaline medium.[2] ZSM-5 with Si/Al molar ratios ranging from about 8 to infinity (silicalite-1) have been obtained. Numerous efforts have been made to enhance the catalytic properties of ZSM-5 by optimizing the synthesis conditions (including the alkalinity, the temperature, and the types and amounts of additives and OSDA). Ultrathin ZSM-5 consisting of single-unit-cell nanosheets have recently been synthesized using the diquaternary ammonium surfactant, $CH_3(CH_2)_{21}{-}N^+(CH_3)_2{-}(CH_2)_6{-}N^+(CH_3)_2{-}(CH_2)_5CH_3$.[3]

Synthesis of individual zeolite crystals using an OSDA-free system is a promising alternative since it does not require an OSDA, and consequently, it circumvents the calcination step. Starting with the study by Grose and Flanigen,[4] there have been many investigations of crystallization of ZSM-5 from OSDA-free synthesis mixtures without[5−21] or with[22−27] seed crystals. OSDA-free synthesis of ZSM-5 is well-known and is used in both scientific and industrial applications; however, crystallization of pure and highly crystalline ZSM-5 in OSDA-free conditions is possible *only* in a limited range of Si/Al (10−40) and Na/Si (0.06−0.33) input molar ratios.[17,18] Furthermore, ZSM-5 crystals obtained by OSDA-free synthesis have high framework Al contents (Si/Al = 10−20). This causes rapid deactivation when they are used as catalysts, probably because of coke deposition on the ZSM-5 particle surfaces.[28]

Acid leaching of Al from the zeolite framework is commonly used to post-synthetically alter the chemical composition of zeolite crystals.[29] A fully or partially dealuminated zeolite possessing intracrystalline site defects consisting of hydroxyl nests can be modified into a transition-metal-substituted zeolite catalyst by post-synthetic insertion techniques.[30−35] In addition, dealumination of ZSM-5 by $SiCl_4$ vapor realized selective removal of Al atoms from external surfaces and produced a solid acid catalyst with highly shape-selective catalysis.[36] When ZSM-5 with a high Al content is hydrothermally treated by a mineral acid (typically aqueous HCl solution), highly siliceous ZSM-5 can be obtained with its **MFI** structure intact;[15,30,37−42] however, dealumination of ZSM-5 is not as straightforward as might be thought. For instance, Kornatowski et al.[37,38] reported that the degree of dealumination of ZSM-5 increases with increasing acid treatment time for boiling 1.25 M HCl, whereas Kooyman et al.[42] reported that prolonged 1 M HCl treatment

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of ZSM-5, which is similar to the method employed by Kornatowski et al.,[37,38] does not greatly increase the degree of dealumination. Some researchers[30,40,42] consider that subtle differences in the synthesis conditions may play an important role in determining the degree of dealumination of the obtained ZSM-5, but this has yet to be unequivocally demonstrated.

This paper reports that dealumination by HNO_3 treatment of ZSM-5 zeolite crystallized under OSDA-free conditions yields a unique ZSM-5 zeolite catalyst that does not have acid sites on its external surfaces. The Supporting Information summarizes the methods used to prepare the ZSM-5 zeolite catalysts, their characterization, and the procedures of the three catalytic test reactions used.

Supporting Information Figure S1 shows X-ray diffraction (XRD) patterns of the as-synthesized product (parent OSDA-free ZSM-5) and acid-treated solids. A pure and highly crystalline ZSM-5 was obtained by OSDA-free synthesis in this study (see Figure S1a). Acid treatment of the obtained ZSM-5 by 0.1−6.0 M HNO_3 at 160 °C for 24 h in an autoclave clearly gives XRD peaks that correspond to the **MFI** phase (see Figure S1b−e). Figure 1 summarizes the degrees of dealumination produced by HNO_3 treatment of OSDA-free ZSM-5 and TPA^+-assisted ZSM-5. The Al contents of OSDA-free ZSM-5 decreased very little during HNO_3 treatment: the Si/Al molar ratio of the parent OSDA-free ZSM-5 was 15.4, mild acid treatment with 0.1 M HNO_3 slightly reduced the Al content (Si/Al = 16.1), and severe acid treatment using 6.0 M HNO_3 gave partially dealuminated ZSM-5 (denoted deAl(6.0)-ZSM-5; Si/Al = 19.8). In contrast, much more extensive dealumination occurred for ZSM-5 (Si/Al = 52.4) synthesized using TPAOH as an OSDA. A great decrease in the Al content (>80%) was observed for the severe acid treatment with 6.0 M HNO_3. We speculate that this difference in the dealumination behaviors of OSDA-free ZSM-5 and TPA^+-assisted ZSM-5 is due in part to the different Al distributions at the 12 inequivalent T sites in the **MFI** framework.[43−47] For TPA^+-assisted ZSM-5, Al sites will be located mainly at the intersections of the two types of 10-membered-ring (10-MR) channels because the positively charged nitrogen atoms of the OSDA will be located at these intersections, making the counter-anions ($[Si-O-Al]^-$) face the intersections. In contrast, for OSDA-free ZSM-5, there is no reason for the anionic Al sites ($[Si-O-Al]^-$) to face the intersections because the counter Na^+ cations can be located anywhere inside the pores. In this case, we speculate that Al atoms exist mainly at T sites that face either sinusoidal or straight channels, *not* intersections. Further investigations are required to definitively demonstrate this.

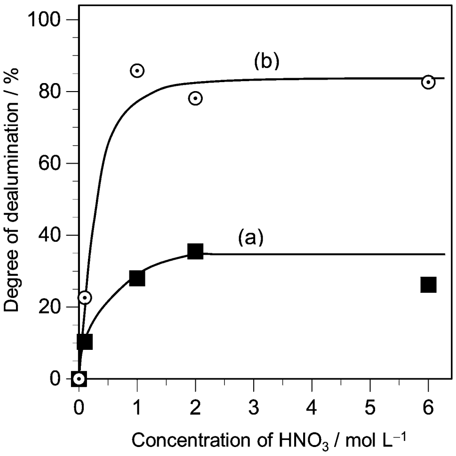

Figure 1. Effect of HNO_3 concentration for acid-treatment on the degrees of dealumination of (a) OSDA-free ZSM-5 (initial Si/Al = 15.4) and (b) TPA^+-assisted ZSM-5 (initial Si/Al = 52.4).

In addition to the above-mentioned investigation about the dealumination behaviors of OSDA-free ZSM-5 and TPA^+-assisted ZSM-5, we tried to perform independent experiments to compare them starting from closer Si/Al ratios. As shown in Supporting Information Table S1, dealumination of TPA^+-assisted ZSM-5 was again more prominent than that of OSDA-free ZSM-5, suggesting that the resistance to dealumination by the OSDA-free ZSM-5 may be a general tendency. In addition to the speculation described above, another possible factor for the degree of dealumination could be the presence of defect sites, which tend to be formed when high-silica zeolite is synthesized using OSDA.[48]

The ^{27}Al magic-angle spinning nuclear magnetic resonance (MAS NMR) measurements indicate that both the parent OSDA-free ZSM-5 and acid-treated ZSM-5 consist of tetrahedrally coordinated Al corresponding to the framework Al within the **MFI** framework, although a few octahedrally coordinated Al species corresponding to extra-framework Al species formed after HNO_3 treatment (see Supporting Information Figure S2) are present. These results imply that the OSDA-free ZSM-5 prepared in this study has a high resistance to dealumination by acid treatment.

For the purpose of obtaining the information about the acid sites on the external and internal surfaces, we evaluated the catalytic properties of dealuminated ZSM-5 obtained by HNO_3 treatment of OSDA-free ZSM-5 by comparing the catalytic cracking reactions of two substrates (cumene and 1,3,5-triisopropylbenzene (TIPB)) using a pulse-type reactor (see Supporting Information Figure S3).[36] Catalytic cracking of TIPB should occur only at acid sites on the external surface of ZSM-5 catalyst because TIPB molecules are much larger than the pore diameters of the two types of interconnected 10-MR micropores (straight channel, 0.51 × 0.55 nm; sinusoidal channel, 0.53 × 0.56 nm)[1] within the **MFI** framework. In contrast, cumene molecules, which are much smaller than TIPB molecules, can penetrate the 10-MR micropores in the **MFI** framework. Catalytic cracking of cumene thus evaluates the acid sites on both the external and internal surfaces of ZSM-5 catalysts.

Figure 2 shows typical catalytic results for parent OSDA-free H^+-ZSM-5 (denoted H^+-ZSM-5_{OSDAF}) and dealuminated H^+-ZSM-5 obtained by acid treatment with 6.0 M HNO_3 (deAl(6.0)-ZSM-5). The parent H^+-ZSM-5_{OSDAF} has high activities for both TIPB and cumene cracking reactions (Figure 2A). In this case, the conversion of TIPB gradually decreased with each subsequent pulse, indicating that the external acid sites became poisoned, probably by propylene oligomers and dehydrogenated carbonaceous species formed there. In contrast, the deAl(6.0)-ZSM-5 converted almost no TIPB, despite having some intact acid sites, as confirmed by the high conversion (steadily over 90%) of cumene (Figure 2B). A slight cracking of TIPB at the first pulse (conversion of ~8%) may be due to the very small number of acid sites remaining on the external surface. No conversion of TIPB was observed after the first pulse, which means that the complete deactivation of the external acid site was readily accomplished by poisoning of the few residual acid sites on the external surfaces by a slight coke deposition during TIPB cracking at the first pulse. These results

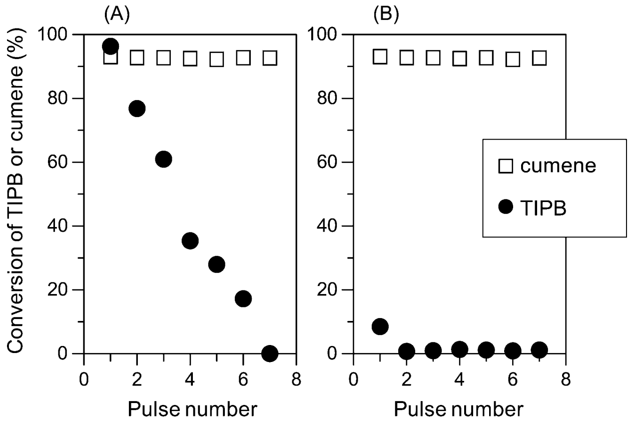

Figure 2. Catalytic results of the cracking of 1,3,5-triisopropylbenzene (TIPB) or cumene over (A) parent OSDA-free ZSM-5 and (B) deAl(6.0)-ZSM-5 by using a pulse-type reactor (see Supporting Information Figure S3). Reaction conditions: catalyst, 20 mg; temperature, 300 °C; flow rate of helium, 30 cm^3 (NTP) min^{-1}; dose amount of TIPB, 0.6 μL; dose amount of cumene, 0.8 μL.

strongly imply that framework Al species on the external surfaces of OSDA-free ZSM-5 are selectively removed by HNO_3 treatment, while the framework Al is retained on its internal surfaces. Even if very few acid sites remain on the external surface, they can be readily deactivated by poisoning at the early stage of the reaction, as mentioned above.

Table 1 lists the contents of the acid sites determined by temperature-programmed desorption of ammonia (NH_3-TPD) from the region of the so-called *h*-peak[49] in the profiles (see Supporting Information Figure S4). The contents of acid sites decreased on HNO_3 treatment, and the decrease in acid sites was consistent with that in Al contents. The parent H^+-ZSM-5_{OSDAF} typically had an acid strength similar to that reported by Katada et al. ($\Delta H = \sim 132$ kJ mol^{-1}),[49] and the acid strength of dealuminated ZSM-5 was preserved after partial dealumination by HNO_3 treatment. These results suggest that dealumination by HNO_3 treatment of OSDA-free ZSM-5 may cause selective dealumination of its external surface and that the acid strength that originates from the **MFI** framework is retained on the internal surfaces.

On the issue of external/internal and Brønsted/Lewis acid sites, significant information was obtained by means of IR spectroscopy using some appropriate probe molecules. IR spectra of parent H^+-ZSM-5_{OSDAF} and acid-treated ZSM-5 (deAl(6.0)-ZSM-5) are compared in Figure 3A. Two absorption bands are observed on both spectra at 3620 and 3746 cm^{-1}, which are assigned to Brønsted acidic OH and silanol groups, respectively. There was no considerable change in surface hydroxy groups observed before or after acid treatment. When CO molecules were adsorbed on both samples, IR spectra shown in Figure 3B were observed. As is clearly shown in Figure 3B(a) on the parent H^+-ZSM-5_{OSDAF} sample, the band at 2231 cm^{-1} is attributed to CO adsorbed on strong Lewis acid sites of zeolitic or silica–alumina species, whereas that at 2222 cm^{-1} is assignable to Lewis acid sites of alumina species.[50] During the adsorption experiments, the band at 2230 cm^{-1} first appeared at low introduction pressures, followed by that at 2222 cm^{-1}. It is clear that both bands, especially the former, decreased in intensity on deAl(6.0)-H^+-ZSM-5.

On the other hand, the band due to CO adsorbed on the acidic OH groups (2174 cm^{-1} in Figure 3B) was observed similarly in both spectra a and b. Since the 2174 cm^{-1} band appeared after CO on Lewis acid sites were saturated (Supporting Information Figure S5), the stronger intensity of this band is because of the larger amount of adsorbed CO on the acidic OH groups. After complete saturation of CO on the acid sites, the intensity of the 2174-cm^{-1} band becomes so strong that the 2222–2230 cm^{-1} bands are relatively negligible. Assuming that absorption coefficients of CO stretching bands appearing at similar frequencies are almost the same, the majority of acid sites can be regarded as Brønsted sites. Therefore, it is found that the acid treatment eliminates most minor existing Lewis acid sites.

Adsorption of collidine, which was found not to migrate into pores of **MFI** zeolites,[51] supports the removal of acid sites on the external surface of samples. The band at 1634 cm^{-1} in Figure 3C is assignable to collidine on Lewis acid sites;[51,52] however, a certain number of Brønsted acid sites could also exist on the basis of the reported fact that the collidine, which is protonated from the acidic OH groups of HY zeolite, shows bands at 1649 (weak) and 1637 (medium) cm^{-1}.[52] All these bands are absent on the deAl(6.0)-ZSM-5, indicating that the acid-treatment completely removes the IR-detectable acid sites on the external acid sites. Two bands at 1618 and 1574 cm^{-1} are assigned to collidine hydrogen-bonded to silanol groups.[51,52] A large band of the acidic OH groups (3620 cm^{-1} observed similarly in both spectra a and b in Supporting Information Figure S6) as well as a very slight negative peak or the negligible perturbation of the band of acidic OH groups in the subtracted spectrum c in Figure S6 infers the presence of acidic OH groups inside the micropores of zeolite samples, even after the acid treatment. Thus, it is concluded from spectral analysis that the acid treatment shown in the present study is an effective method to eliminate acid sites on the

Table 1. Chemical and Textural Properties of OSDA-free ZSM-5 and Dealuminated ZSM-5

sample[a]	concentration of HNO_3[b]/M	Si/Al molar ratio[c]	Al content[c] /mmol g^{-1}	amount of acid sites[d] /mmol g^{-1}	BET surface area[e] /m^2 g^{-1}	micropore volume[f] /cm^3 g^{-1}
parent ZSM-5	none	15.4	1.07	1.01	407	0.155
deAl(0.1)-ZSM-5	0.1	16.1	0.96	0.73	422	0.164
deAl(1.0)-ZSM-5	1.0	20.3	0.77	0.72	428	0.154
deAl(2.0)-ZSM-5	2.0	22.8	0.70	0.70	433	0.162
deAl(6.0)-ZSM-5	6.0	19.8	0.79	0.71	420	0.160

[a] A parent ZSM-5 was hydrothermally synthesized under OSDA-free conditions. [b] HNO_3 treatment was carried out in a 23 mL autoclave at 160 °C for 24 h. [c] The Si/Al molar ratio of ZSM-5 was determined by using ICP–AES. [d] The amounts of acid sites of ZSM-5 were determined from NH_3-TPD profiles. [e] BET surface area of ZSM-5 was determined from the nitrogen adsorption–desorption isotherm. [f] Micropore volume was estimated by using the *t*-plot method.

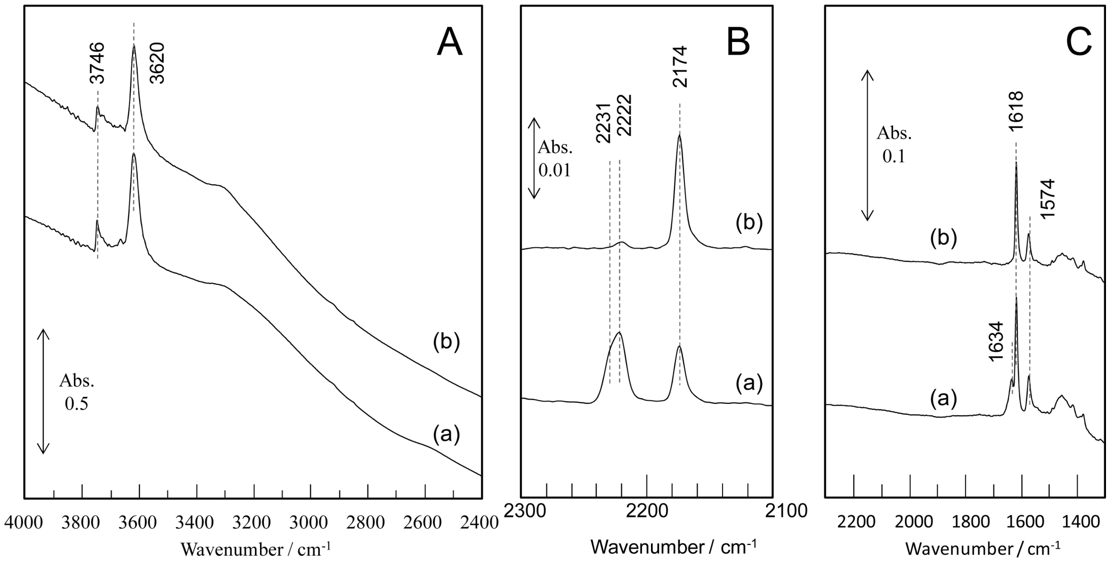

Figure 3. IR spectra of (A) background, (B) CO-adsorbed and (C) collidine-adsorbed (a) parent H^+-ZSM-5_{OSDAF} and (b) acid-treated ZSM-5 (deAl(6.0)-ZSM-5). CO (5 Pa) was introduced at 153 K, and spectra were measured without evacuation, whereas spectra in panel C were measured after evacuation of collidine (0.1 kPa) at 298 K. Spectra in panels B and C were obtained by subtraction of background spectra (panel A) from those measured after adsorption procedures.

external surface of ZSM-5 zeolite, which is consistent with the catalytic results.

The cracking of *n*-hexane is often examined as a model reaction for the FCC catalytic test[53,54] to simplify the complicated aspects of naphtha cracking catalyzed by zeolite as the FCC catalyst. In the catalytic test during *n*-hexane cracking at 650 °C (see Supporting Information Figure S7), the product distribution for acid-treated ZSM-5 (deAl(6.0)-ZSM-5; Si/Al = 22.6) was almost similar to that of parent H^+-ZSM-5_{OSDAF} (Si/Al = 16.4). Although parent ZSM-5 exhibited sufficient catalytic activity for hexane cracking, it was rapidly deactivated during the 275 min of reaction. This deactivation was probably caused by the large amount of coke (120 mg of coke/g of catalyst after 460 min of the reaction) formed on the catalyst. In contrast, acid-treated ZSM-5 maintained the initial catalytic activity after 455 min of hexane cracking and showed a high durability of coke formation (49.7 mg of coke/g of catalyst). Such a high durability of coke formation is probably caused by the absence of the acid sites on the external surface, indicating that acid-treated ZSM-5 is potentially applied as a long-life catalyst in the catalytic cracking processes.

All the ZSM-5 samples prepared in this study had typical type I isotherms and no hysteresis loops for relative pressures in the range 0.5−0.9, indicating that the HNO_3 treatment did not produce intracrystalline mesopores (see Supporting Information Figure S8). The BET surface area and micropore volume of ZSM-5 changed very little during the dealumination treatment (see Table 1), implying that the **MFI** framework of OSDA-free ZSM-5 has a high tolerance to HNO_3 treatment and that it was only partially dealuminated. Field-emission scanning electron microscopy (FE-SEM) observations (see Supporting Information Figure S9) reveal that the particle sizes of parent OSDA-free ZSM-5 were ∼0.5−1.0 μm and that their morphologies and sizes were changed little by the HNO_3 treatment.

In summary, dealumination by HNO_3 treatment of OSDA-free ZSM-5 produced a unique ZSM-5 catalyst that has almost no acid sites on its external surfaces, and the textural and morphological properties of the parent ZSM-5 are retained. The unique ZSM-5 catalyst could be potentially applied to catalytic cracking process, that is, naphtha cracking, because with this type of ZSM-5, it is possible to avoid the coke formation on their external acid sites. We have observed similar selective dealumination of the external surfaces of **TON** and **MSE**-type zeolites; the results will be reported elsewhere.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Further details of experimental section, reactor setup, powder XRD patterns, ^{27}Al MAS NMR spectra, TPD profiles, IR spectra, the results of hexane cracking, isotherms, and FE-SEM images. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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