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論文内容要旨

【Introduction】 FeZSM-5, MFI-type zeolite which has Fe³⁺ and Al³⁺ ions in its framework position, shows great catalytic performances as solid acid catalysts on the reactions as typified by dimethyl ether-to-olefins or methanol-to-olefins reaction (DTO, MTO)¹⁾. In addition, extra-framework Fe species in zeolite has catalytic activities on redox reactions such as selective catalytic reduction of NO_x and hydroxylation of benzene so that FeZSM-5 is also utilized as a precursor for the preparation of MFI zeolite with extra-framework Fe species^{2,3,4)}. On the other hand, control of microstructures in zeolites, such as particle size and/or the control of spatial distribution of Al in framework, have been attracted for the purpose of the improvement in catalytic or separative performances^{5,6)}. These approaches should also enhance the catalytic performance of FeZSM-5. However, nano-particulate FeZSM-5 in wide composition ranges and/or FeZSM-5 with controlled spatial distribution of heteroatoms has not been synthesized so far.

Therefore, we set 1) the preparation of nano-particulate FeZSM-5 in wide composition ranges and 2) control of spatial distribution of Fe and Al in nano-particulate FeZSM-5 as goals of this study. To achieve these goals, we first synthesized nano-particulate FeSilicalite-1 which has Fe³⁺ as a heteroatom in zeolitic framework (Chapter 2). Secondly, we synthesized FeZSM-5 nanoparticles in controlled amounts of Fe and Al, based on the synthesis method in Chapter 2 (Chapter 3). In the next chapter (Chapter 4), we synthesized FeSilicalite-1 and FeZSM-5 nanoparticles from Fe and Al precursors prepared by mechanochemical treatment to change the spatial distributions of Fe and/or Al from conventional FeZSM-5. The synthesized zeolites were tested over DTO reaction to elucidate the effects of particle sizes, acidic properties, or spatial distributions of heteroatoms on catalytic activities.

【Chapter 2 : Size control of FeSilicalite-1 particles and the effect of these sizes on catalytic performance】

Size-controlled FeSilicalite-1 was synthesized by a hydrothermal method. The aqueous solutions of Fe(NO₃)₃, tetrapropyl ammonium hydroxide (TPAOH), HCl, Si(OC₂H₅)₄ were mixed (molar compositions, Si : 0.02 Fe : 0.5 TPAOH : 30 H₂O : 0 ~ 0.1 HCl). After stirred

Table 1 Synthesis conditions of F1 ~ F4.

Sample	HCl/Si	Preheating time (h)
F1	0	0
F2	0	24
F3	0.1	0
F4	0.1	24

for 48 h, the solution was preheated at 70 °C for 0 ~ 24 h and then heated at 160 °C for 48 h. The product was centrifugally washed with ion exchanged water, and then dried at 60 °C. Organic template was removed by calcination at 540 °C for 12 h in air. The resulting powder was ion exchanged by NH₄Cl aq. and calcined again to form Brønsted acid site. Synthesis conditions of FeSilicalite-1 (F1 ~ F4) were shown in Table 1. DTO reaction was carried out in fixed-bed reactor at atmospheric pressure. Only dimethyl ether (DME) was fed over the catalyst at 450 °C with 5.8 g·h/mol-DME in W/F.

XRD patterns of F1 ~ F4 showed that all samples had crystal structure of MFI-type zeolite. SEM images of samples (Fig. 1) showed that increase in preheating time or adding HCl resulted in the reduction of particle size. The resulting FeSilicalite-1 had almost the same Si/Fe molar ratio as that in precursor solution. NH₃-TPD measurement confirmed the presence of weaker Brønsted acid site in FeSilicalite-1 than that in ZSM-5. Catalytic properties of F1 (particle size: 600 nm) and F4 (particle size: 50 nm) on DTO reaction were compared. F4 showed longer catalyst lifetime than F1 (Fig. 2). Additionally, the coke amount of F4 after one or four hours on stream were less than those of F1. Therefore, the reduction of the particle size of FeSilicalite-1 enhanced the catalytic performance on DTO reaction by suppressing the formation of coke.

【Chapter 3 : Synthesis of FeZSM-5 nanoparticles of different compositions and their catalytic properties】

A series of FeSilicalite-1, ZSM-5, and FeZSM-5 nanoparticles were prepared by hydrothermal synthesis method from a solution with the molar ratio of Si : 0 ~ 0.02 Fe : 0 ~ 0.02 Al : 0.5 TPAOH : 30 H₂O : 0.1 ~ 0.2 HCl : 0 ~ 0.06 NaCl, based on the synthesis method in Chapter 2.

From XRD measurement, all products were determined as MFI structure. The particle sizes of the products were 50 ~ 100 nm, which were evaluated by their SEM images. Elemental analysis confirmed that the Si/Fe and Si/Al molar ratio in products were almost the same as those in precursor solutions. UV-vis spectra and

²⁷Al MAS NMR spectra of FeZSM-5 showed that most of Fe and Al were introduced into framework position. FTIR spectra of

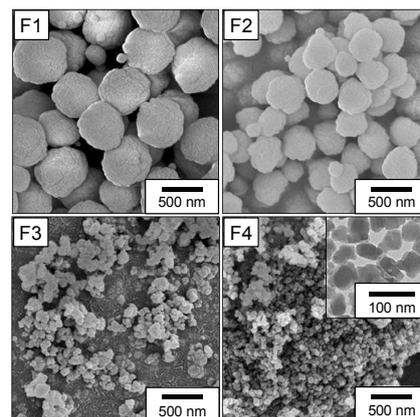


Fig. 1 SEM images of F1 ~ F4. (F4 inset : TEM image)

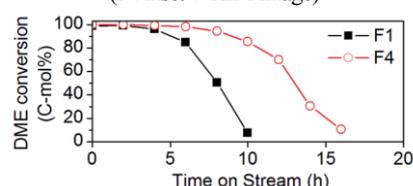


Fig. 2 Change in the conversion of DME with time on stream on F1 and F4.

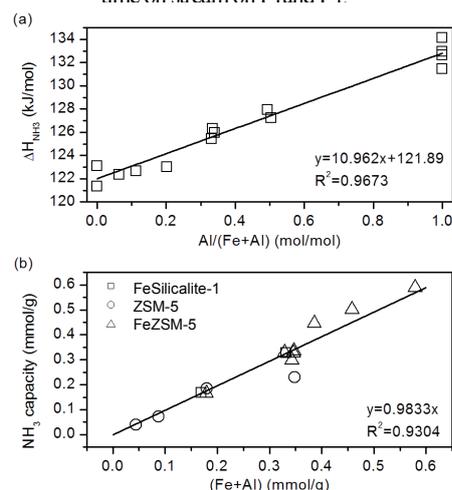


Fig. 3 Relationship between chemical compositions of zeolite nanoparticle and (a) average acid strength (b) acid site density.

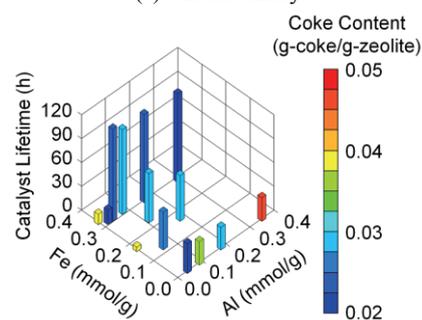


Fig. 4 Relationship between chemical compositions, catalyst lifetime, and coke content.

FeZSM-5 indicated that both “Si(OH)Al” and “Si(OH)Fe” structures were existed. The average of acid strength and acid site density were evaluated by NH₃-TPD measurement. The enthalpy change by the desorption of ammonia from acid sites (ΔH_{NH_3})⁷ increased linearly as increasing Al/(Fe+Al) molar ratio in product (Fig. 3 (a)). In addition, desorption amounts of ammonia were coincident with total amounts of heteroatoms (Fig. 3 (b)). Therefore, it was confirmed that average of acid strength and acid site density were controlled by the amount of Fe and Al.

FeZSM-5 showed better catalyst lifetime and less coke amount after four hours on stream on DTO reaction than that of ZSM-5 or FeSilicalite-1 (Fig. 4). This result was probably because the coexistence of strong acid site and weak acid site resolve the problem of strong / weak acid site (proceeding of hydride transfer reaction ↔ lack of catalytic activity of cracking reaction of olefins or aromatics). Contrary to the case of FeZSM-5, the mixing of FeSilicalite-1 and ZSM-5 was not effective to enhance catalytic lifetime on DTO reaction, which means that the existence of Fe and Al in the same particle was important to improve the catalytic performance. The repeatability of FeSilicalite-1, ZSM-5, or FeZSM-5 catalyst on DTO reaction was tested by regenerating spent catalyst at 550 °C or 650 °C in dry air. The catalyst lifetime of FeZSM-5 in third round of test was much longer than that in the first test (107 h → 345 h). In addition, it was confirmed that FeZSM-5 after regeneration had strong acid site by Al and extra-framework Fe species. Considering that partial pressure of water vapor was fairly high in the catalyst bed during DTO reaction, the migration of framework Fe into extra-framework position might be caused by heated steam. Moreover, the enhancement of catalyst lifetime was probably due to the suppression of the deposition of coke by steam-reforming coke precursors into carbon oxides at extra-framework Fe sites which had catalytic activity on redox reaction.

【Chapter 4 : Synthesis of nano-particulate FeSilicalite-1 and FeZSM-5 from mechanochemically-treated precursors and their catalytic properties】

Mechanochemical treatment between α -Fe₂O₃ and SiO₂ was carried out in a planetary ball-milling system (Si/Fe molar ratio = 20, 600 rpm, treatment time: 0 ~ 96 h). From the XRD patterns, the disappearance of diffraction patterns of α -Fe₂O₃ was observed as an increase of treatment time. In addition, decrease of absorption band from $\lambda = 350$ nm to 600 nm, which is due to the existence of α -Fe₂O₃ phase, was also observed in their UV-vis spectra (Fig. 5). Therefore, the amorphization of α -Fe₂O₃ phase and the dispersion

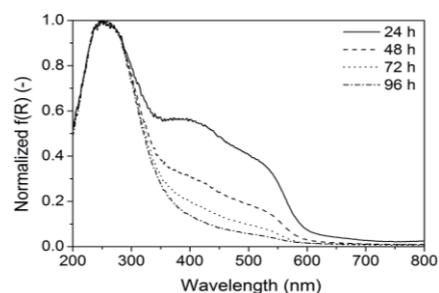


Fig. 5 UV-vis spectra of mechanochemically-treated Fe precursors.

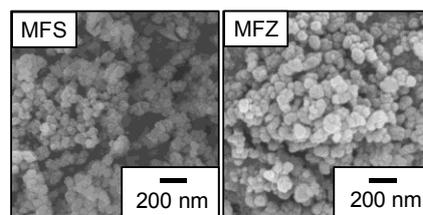


Fig. 6 SEM images of nano-particulate MFS and MFZ. (MFS: Fe 0.34 mmol/g, MFZ: Fe 0.33 mmol/g, Al 0.09 mmol/g)

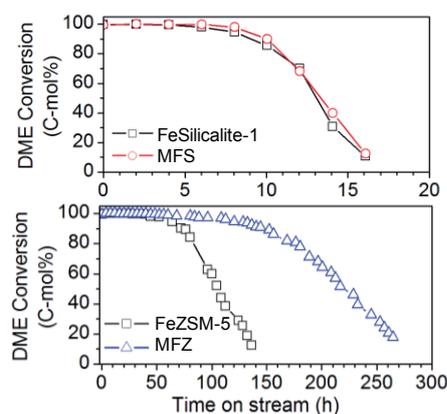


Fig. 7 Change in the conversion of DME with time on stream on MFS and MFZ.

of Fe atoms in SiO₂ matrix were caused by mechanochemical treatment. Mechanochemical FeSilicalite-1 (MFS) were synthesized by hydrothermal method using the products of mechanochemical treatments as Fe precursors. The synthesis procedure was as follows: First, Fe precursor, SiO₂, NaCl, TPAOH, HCl, and H₂O were mixed in a Teflon-made vessel (molar compositions, 1Si: 0.02 Fe: 0 ~ 0.3 HCl: 0 ~ 0.5 NaCl: 0.5 TPAOH: 15 ~ 45 H₂O). This mixture was stirred at room temperature for 0.25 ~ 168 h, and then heated at 160 °C for 3 ~ 120 h. Preheating treatment at 50 ~ 110 °C was also carried out in some cases before heating at 160 °C. As a result, nano-particulate MFS (average size: 80 nm, left image in Fig. 6) was obtained in optimized synthesis condition by increasing the concentration of semi-ordered polymeric (ferri) silicate which is directly transformed into zeolite nuclei. In addition, mechanochemical FeZSM-5 (MFZ) nanoparticle was also synthesized from mechanochemically-treated Fe precursor and Al precursor (Fig. 6, right). Elemental analysis of MFZ indicated that both of Al content and Fe content were controllable though a small amount of Al was included in MFS due to the contamination of Al in Fe precursor. NH₃-TPD measurement of nano-particulate MFS and MFZ showed that both the enthalpy change by desorption of ammonia and the desorption amount of ammonia were similar to those of FeZSM-5 synthesized via conventional route in Chapter 3. Catalytic properties of nano-particulate MFS and MFZ were also compared with nano-particulate FeSilicalite-1 and FeZSM-5 in Chapter 3. FeSilicalite-1 in Chapter 3 and MFS showed almost the same catalytic performance. On the other hand, catalyst lifetime of MFZ was more than twice as long as that of FeZSM-5 in Chapter 3 (Fig. 7). The enhancement in catalytic performance was presumably due to the improvement of the homogeneity of the spatial distribution of Fe and Al by changing synthesis method.

【Summary】 In this study nano-particulate FeZSM-5 in wide composition ranges was successfully synthesized by hydrothermal method, based on the synthesis of nano-particulate FeSilicalite-1. In addition, FeZSM-5 nanoparticle was also synthesized from Fe and Al precursors obtained by mechanochemical treatment between SiO₂ and metal oxide. The acidic properties (acid strength and acid site density) of resulting zeolites were controlled by their chemical compositions. The comparison of catalytic properties of zeolites on DTO reaction clarified that the coexistence of Fe and Al enhanced the catalyst stability. The existence of extra-framework Fe species in FeZSM-5 also enhanced catalyst lifetime on DTO reaction probably due to steam reforming of coke precursors. In addition, the homogeneity of the spatial distribution of Fe and Al presumed to affect the catalytic performances on DTO reaction.

【Reference】 1) K.-Y. Lee *et al.*, *Ind. Eng. Chem. Res.*, **53**, 10072 (2014). 2) X. Feng and W.K. Hall, *J. Catal.*, **166**, 368 (1997). 3) D. Meloni *et al.*, *J. Catal.*, **214**, 169 (2003). 4) G. Berlier *et al.*, *J. Catal.*, **208**, 64 (2002). 5) S. Mintova *et al.*, *Chem. Soc. Rev.*, **44**, 7207 (2015). 6) P. Sazama *et al.*, *J. Catal.*, **254**, 180 (2008). 7) M. Niwa *et al.*, *J. Phys. Chem.*, **99**, 8812 (1995).

論文審査結果の要旨

本論文は、Fe および Al を結晶骨格中に含むゼオライトである FeZSM-5 粒子の広範な組成条件下でのナノサイズ化と、粒子内における Fe, および Al の空間的分布の制御法の確立を目的として遂行された。

第 1 章では、本研究の背景および目的について述べた。ゼオライトのナノ粒子化や、置換元素の三次元的分布の制御といった高度な構造制御は、近年触媒特性、分離特性等の向上のための手法として注目されている。これらのアプローチは、dimethyl ether to olefin (DTO) 反応をはじめとした触媒として注目される FeZSM-5 の性能向上にも有効であると考えられるが、FeZSM-5 のナノ粒子化や内部のヘテロ元素分布制御は困難なため、未だ達成されていない。本論文では、Fe のみを含むゼオライト (FeSilicalite-1) 合成法を基にした FeZSM-5 合成、そしてメカノケミカル処理により調製した Fe, Al 前駆体からの FeZSM-5 合成により、粒径制御法と元素分布制御法を確立することを目的とした。

第 2 章では、FeSilicalite-1 の粒子サイズ制御法の確立、および粒径と DTO 反応触媒性能の関係の解明を行った。その結果、前駆体溶液 pH の制御 (12 ~ 12.4)、および 70 °C での予熱処理により粒径約 50 nm のナノ粒子が得られることを見出した。また合成した粒径の異なる FeSilicalite-1 の触媒活性試験から、ナノ粒子化により反応中のコーク生成速度が減少し、触媒寿命が向上することが示された。

第 3 章では、第 2 章の方法を基に Fe, および Al 量の異なる FeZSM-5 ナノ粒子の合成を図った。その結果、(Si/Fe \geq 50, Si/Al \geq 50, Fe/Al \geq 1) の各条件にて粒径 100 nm 以下のナノ粒子を得ることに成功した。得られた FeZSM-5 は総金属量と Fe/Al 比によって酸密度と平均酸強度が制御可能であることが確認された。FeZSM-5 では FeSilicalite-1 や ZSM-5 と比較して DTO 反応における触媒寿命が向上し、一方 FeSilicalite-1 と ZSM-5 との物理混合試料では性能の向上が確認されなかったことから、Fe と Al が近く分布していることが触媒性能向上に寄与していることが示唆された。試料の再生を行ったところ再生後の FeZSM-5 はさらに優れた触媒安定性を示し、一部の骨格 Fe 種が酸化鉄クラスターや酸化鉄微粒子へと変化したことが原因であると推察された。

第 4 章では、メカノケミカル処理による Fe 前駆体、Al 前駆体の作製と、それらを用いた FeZSM-5 ナノ粒子の合成を行った。その結果、ゼオライト核前駆体の過飽和度が高くなるように最適化した合成条件において粒径約 80 nm の FeZSM-5 ナノ粒子を得ることに成功した。第 3 章の手法と第 4 章の手法により、組成のほぼ等しい FeSilicalite-1, および FeZSM-5 ナノ粒子を合成し触媒活性試験を行ったところ、FeSilicalite-1 では合成法による触媒性能の違いは確認されなかった。一方 FeZSM-5 ではメカノケミカル処理した Fe, Al 前駆体から合成した試料が第 3 章の手法で合成した FeZSM-5 の 2 倍以上の触媒寿命を示した。これは粒子内部の Fe, Al 分布が均一な FeZSM-5 が得られたためと推察された。

第 5 章では本論文を総括し、今後の展望を述べた。

以上より、本論文はこれまで困難であった FeZSM-5 のナノ粒子化を達成し、また異なる Fe, Al 前駆体を使用した FeZSM-5 中での Fe, Al 分布制御法の確立に関し、一定の成果を収めたと判断される。

よって、本論文は博士(工学)の学位論文として合格と認める。