

Preparation of Mon--dispersed MFI-type Zeolite Nanocrystals in Water/surfactant/oil Solution and Their Application to Synthesis of Olefins from Oxygen-containing Compounds

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ABSTRACT

Mono-dispersed ZSM-5 zeolite nanocrystals were successfully prepared in water/surfactant/oil solution under the hydrothermal conditions. It was found that the composition of the water/surfactant/oil solution affected strongly the size of nanocrystals. Moreover, the surfaces as well as bulk phase of the prepared nanocrystals with a diameter of approximately 50 nm were well-crystallized. Two kinds of MFI-type zeolites with different crystal sizes, 2.0 μm and 50 nm, were used as catalysts to synthesize olefins from acetone and methanol, in order to investigate the effect of crystal size on the catalytic activity. The decrease in the crystal size led to the increase in the catalytic activity and stability. Aromatic were, however, also produced, which was ascribed to the higher outer surface area of the nanocrystals. In order to overcome this problem, the acid sites on and near the outer surface of the nanocrystals were selectively deactivated using diphenyl silane (catalytic cracking of silane treatment, denoted as CCS treatment). The production of aromatics could be restricted by using the zeolite nanocrystals modified by CCS treatment, which exhibited the high olefin selectivity.

1. INTRODUCTION

Zeolites are crystalline aluminosilicates that possess strong activity, high surface area, high thermal stability, and a high adsorption capacity for hydrocarbons. Moreover, since each kind of zeolite has micropores of a specific diameter almost equal to the diameters of lighter hydrocarbons, zeolites exhibit a remarkable molecular sieving effect for these hydrocarbons. Hence, they have been widely used as shape-selective catalysts in various types of hydrocarbon processing, such as oil refining and olefin

synthesis from methanol.

Crystal sizes of zeolites prepared by conventional methods is, however, approximately 1–3 μm which is large as compared with the size of micropores exhibiting a molecular-sieving effect. When using zeolites as shape-selective catalysts, the diffusion rates of reactants, such as hydrocarbon molecules, within zeolite crystals are relatively low in comparison with the reaction rates. This resistance to mass transfer causes the limitation of the reaction rates, low selectivity of intermediates and coke deposition, leading to the short lifetime of the catalysts. In order to overcome these problems, it will be necessary to enhance the mass transfer rate of the reactants in the crystals; to this end, nanometer-sized zeolite crystals would be a promising solution. Zeolites, however, exhibit a low molecular sieving effect and/or non-shape-selective reaction, when the reaction of hydrocarbon proceeds over acid sites located on the outer surface of zeolite crystals. Moreover, the reaction of hydrocarbons over the acid sites located on the outer surface of the zeolite crystals causes coke deposition, leading to short lifetime for the catalysts. Therefore, a method is desired for selective deactivation of the acid sites located on the outer surface of the zeolite crystals to prevent these undesirable reactions.

Thus, the reduction in mass transfer resistance by the decrease in zeolite crystal size apparently has a trade-off relation to prevention of activity on the outer surface of zeolite crystals.

The zeolite nanocrystals have attracted the considerable attention of many researchers [1-4]. The syntheses of several types of zeolites with different nanometer sizes, such as silicalite-1, ZSM-5, A-type and Y-type, have been reported. Recently, micellar solutions or surfactant-containing solutions have been used for the preparation of A-type zeolite nanocrystals [5]. We have also successfully prepared MFI-type zeolite nanocrystals with and without Al in their frameworks, namely Silicalite-1 and ZSM-5 zeolites, respectively, by hydrothermal synthesis using surfactants [6-8]. Their crystals were mono-dispersed, and their sizes could be changed in the range from 40 to 150 nm [6-8].

On the other hand, the selective deactivation of acid sites on the outer surface is regarded as the prevention of non-selective activity. Niwa et al. [9, 10] have developed a method utilizing the chemical vapor deposition (CVD) technique with tetra-ethoxy-silane and/or tetra-methoxy-silane to form a silica (SiO_2) thin layer on the outer surface of zeolite crystals. We have proposed a method called the catalytic cracking of silane (CCS) method, in which SiO_2 units are formed selectively on the acid sites of the zeolite using organic silane compounds [11]. Moreover, in the CCS method, several types of silane compounds with methyl, ethoxy, and phenyl groups can be employed to deactivate the acid sites of zeolite catalyst [12]. Since the molecular diameter of the silane compounds depends on the types of organic groups bonding to Si atom, it is expected that the selective deactivation of the acid sites located near the outer

surface of the zeolite crystals can be achieved by the method using molecular sieving effect of zeolite against the silane compounds.

Therefore, nano-sized MFI-type zeolites without any acid sites on their outer surface can be expected to exhibit high activity, molecular sieving effect and long lifetime.

The main objective of this study was to develop a nano-sized MFI-type zeolite catalyst without any activity on its outer surface. Firstly, mono-dispersed ZSM-5 zeolite nanocrystals were prepared by our proposed method with water/surfactant/oil solution. Secondly, the possibility of the selective deactivation of acid sites on the outer surfaces of ZSM-5 zeolite crystals by the CCS method with different silane compounds was examined. Finally, the prepared zeolite catalysts were applied to the reactions of acetone and methanol, to verify the advantage of the prepared zeolites.

2. EXPERIMENTAL

2.1. Preparation of mono-dispersed ZSM-5 nanocrystals

Mono-dispersed ZSM-5 nanocrystals were prepared via hydrothermal synthesis in water- surfactant- oil solution [7]. First, tetraethylortho- silicate (abbreviated to TEOS) and aluminium isopropoxide were dissolved in water with tetra-propyl-ammonium-hydroxide (TPAOH) and sodium chloride. The water solution thus obtained was added to a surfactant-organic solvent solution, and the mixture was magnetically stirred at 50 degree C for 1 h. Polyoxyethylene (15) oleylether (O-15) and cyclohexane (C₆H₁₂) were employed as a surfactant and organic solvent, respectively. The mixture was then placed in a Teflon-sealed stainless bottle, heated to 373–413 K, and held at the desired temperature for 50 h with stirring to produce MFI-type zeolite nanocrystals. The prepared zeolites were centrifuged, washed thoroughly with distilled water, followed by the calcination in air stream at 773 K to remove the surfactant and the template.

On the other hand, MFI type zeolite was hydrothermally synthesized from Na₂SiO₂, Al₂(SO₄)₃, and NaCl, and TPA-Br as a template at 473 K for 48 h, followed by calcination at 773 K in an air stream.

Sodium ions in the zeolite framework were exchanged with NH₄⁺ by a conventional ion exchange technique with 10% NH₄NO₃ aqueous solution, then heated to 773 K to yield H-ZSM-5 zeolite with a Si/Al molar ratio of 50. The zeolite samples thus obtained were calcined at 723 K, pelletized without any binders, crashed and sieved to yield the samples of 28 to 48 mesh in size, and were used in the further experiments.

2.2. Selective deactivation of acid Sites of zeolite by the CCS method

The CCS treatment was carried out in a fixed bed reactor loaded with 0.5 g of

zeolites under an atmospheric pressure. First, powdery ZSM-5 zeolites were calcined at 823 K in an air stream, and were cooled to 373 K in a nitrogen stream. Next, N₂ was passed through a bubble column with a liquid silane compound, and was introduced to the reactor. Zeolites were exposed to silane compound vapor at 373 K in a N₂ stream, and the feed of the silane compound was then stopped to remove the physically adsorbed silane compounds on zeolites. Then, the zeolite samples were heated to 823 K in a N₂ stream at a heating rate of 5 K min⁻¹ to decompose silane compounds adsorbed on acid sites, followed by formation of silicon-containing coke. Finally, N₂ gas flowing around zeolites was switched to air stream, and the temperature of the reactor was held at 823 K in an air stream for 60 min, where the silicon-containing coke was oxidized, leaving a SiO₂ unit on each acid site. Thus, the acid sites, where the silane compounds are adsorbed, are deactivated by formed SiO₂ units. The sequence of the procedure described above was repeated three times. In this study, four kinds of silane compounds were employed; di-ethoxy-methyl silane (DEM-silane), di-phenyl silane (DP-silane), di-phenyl-methyl silane (DPM-silane), and tri-phenyl silane (TP-silane). The order of the molecular sizes of the silane compounds as well as the pore size of ZSM-5 zeolite are as follows; TP-silane > DPM-silane ≈ DP-silane ≈ pore diameter of ZSM-5 > DEM-silane.

2.3. Characterization of zeolite

The morphology and crystallinity of the zeolites were investigated using a field-emission scanning electron microscope (FE-SEM; JEOL JSM-6500F), an X-ray diffractometer (XRD; JEOL JDX-8020) and Laser Raman spectrophotometer using the 532 nm line of an Hg laser (JASCO NRS-1000). The pore structure was evaluated by a N₂ adsorption and desorption method (BEL Japan Belsorp mini).

2.4. Location of SiO₂ unit formation on zeolite

In order to identify the chemical bonds of the silane compound adsorbed on the zeolites, we measured the infrared absorption spectra (IR) of the samples with an FT-IR apparatus (Perkin Elmer; IR spectrometer Paragon 1000) equipped with an *in situ* IR cell [11, 14]. For the case of the zeolite sample on which DEM-silane was adsorbed at 423 K under reduced pressure, *in situ* FT-IR measurements were carried out at temperatures ranging from 423 K to 823 K under the evacuation conditions.

To clarify the locations of the deactivated acid sites of ZSM-5 zeolite by the CCS method, changes in the number of acid sites and adsorption capacity prior to and after CCS treatment were examined. NH₃-TPD profiles prior to and after the CCS treatment were measured by the ac-TPD method [13]. The adsorption isotherms of benzene and carbon dioxide onto the zeolite samples were measured at 303 K with an automatic adsorption apparatus (BEL JAPAN, INC., BELSORP18 PLUS). Furthermore, the change in intracrystalline diffusivity of benzene within the zeolite samples due to SiO₂

unit formation was measured by a conventional volumetric method in temperatures ranging from 573 to 773 K [15].

2.5. Olefin synthesis from oxygen-containing compounds over ZSM-5 zeolite

Recently, because a large amount of acetone is obtained as a by-product in the cumene process for producing phenol, olefin synthesis from acetone over solid acid catalysts has been reported, in which olefins such as ethylene and propylene are obtained by cracking of iso-butane produced from aldol-condensation products of acetone [16]. In these olefin syntheses, selective production of lighter olefins is due to the molecular sieving effect of zeolite. Therefore, the reaction of acetone to olefins was selected as a model reaction. In order to verify the usefulness of the zeolite samples prepared in this work, the reaction of methanol to olefins was also conducted.

The olefin synthesis was performed using a fixed bed-type reactor under a N₂ stream at atmospheric pressure. ZSM-5 zeolites prior to and after the CCS treatment were employed as catalysts. The reaction temperature was 723 K, W/F was 0.5-1.0 kg-cat/(kg-reactant/h). The reaction products were analyzed using online gas chromatography (Shimadzu Co. Ltd., GC-14A) with a porapak-Q column.

3. RESULTS AND DISCUSSION

3.1. Characterization of mono-dispersed ZSM-5 nanocrystals

Figure 1(a) and 1(b) shows the FE-SEM photographs of ZSM-5 zeolites prepared by a conventional hydrothermal synthesis and by the method proposed by us, respectively. The zeolite prepared by the conventional method was macro-crystals, and their size was about 1 μm. On the other hand, that by the proposed method was mono-dispersed nano-crystals of 50 nm in size.

Figure 2 shows the N₂ adsorption isotherms of the ZSM-5 zeolites prepared by the conventional method and the proposed method. The steep increase in the amount of adsorbed N₂ in the region of low relative pressure (P/P_0), followed by the flat curve, corresponded to the filling of micro-pores. This result indicated that the nanocrystals contained considerable volume of micro-pores volume in their framework and were well crystallized.

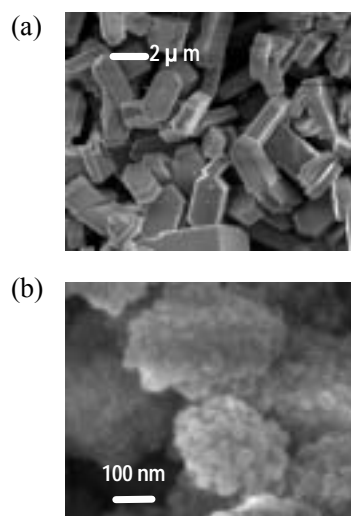


Fig. 1 FE-SEM photographs of ZSM-5 zeolites. (a) synthesis by conventional method, (b) synthesis by proposed method.

Figures 3 and 4 show X-ray diffraction patterns and Raman spectra of the obtained samples, respectively. The X-ray diffraction patterns of the samples showed peaks corresponding to pentasil-type zeolite. The peaks of Raman spectrum in the range of 300 – 650 cm^{-1} are indicative of the type of silicon-oxygen rings existing in the structure of zeolite [17, 18]. The spectrum of the nano-crystal showed peaks around 380 cm^{-1} , 430 cm^{-1} and 470 cm^{-1} , which corresponded to the five-, six- and four-member rings, respectively. These peaks were in good agreement with those of the macro-crystals of ZSM-5 zeolite prepared in water. In the structure of the MFI-type zeolite, continuous chains of five-member rings are connected by the four- and six-member rings. These results indicated that the surfaces of the nanocrystals were also well-crystallized without amorphous SiO_2 as well as the bulks of the crystals.

From these results, ZSM-5 zeolite prepared by the method proposed by us was confirmed to be mono-dispersed nano-crystals, which was well-crystallized both in their bulks and on their surfaces.

NH_3 -TPD spectra indicated that both nano-crystals and macro-crystals of ZSM-5 zeolites possessed almost the same acid amount from the desorption spectra of NH_3 above 573 K.

3.2. Adsorption behavior of silane compounds and control of the acid site location on ZSM-5 zeolite

In order to clarify the manner of adsorption of silane compounds on ZSM-5

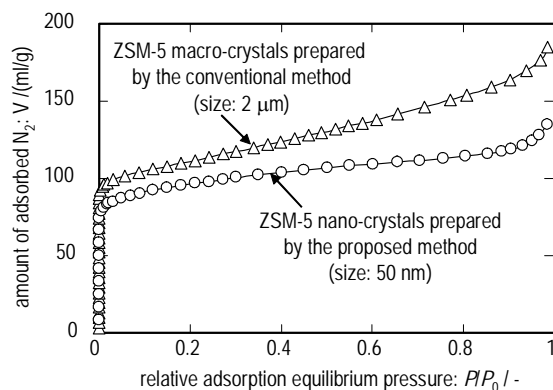


Fig.2 Adsorption isotherms of N_2 on ZSM-5 zeolites.

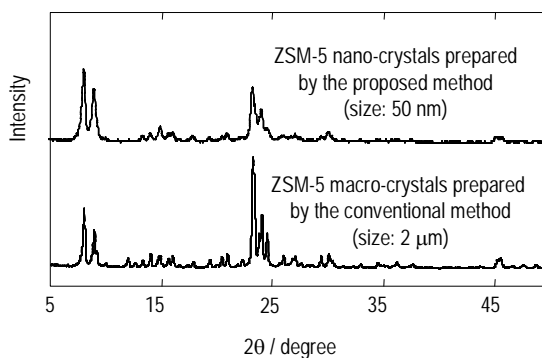


Fig.3 XRD patterns of ZSM-5 zeolites.

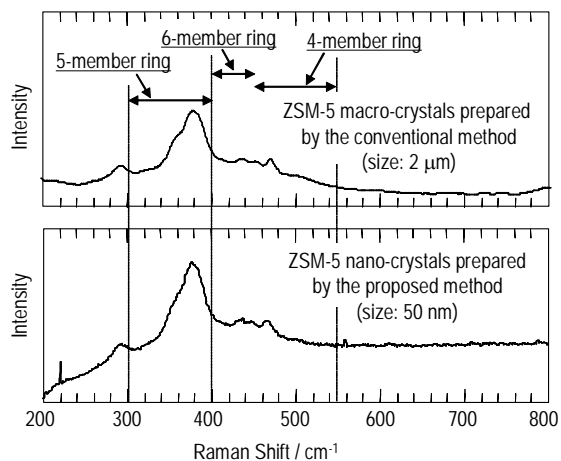


Fig.4 Raman spectra of ZSM-5 zeolites.

zeolite, FT-IR analysis was carried out through the following procedure: first, DEM-silane was adsorbed on the zeolite at 423 K. Next, the zeolite sample was evacuated at different temperatures and FT-IR spectra were recorded.

The results are summarized in Fig. 5. Peaks at wave number ranges of 1400–1500,

2100-2300, and 2900-3000 cm^{-1} correspond to Si-CH₃, Si-H, and Si-OC₂H₅, respectively. These peaks appear after the zeolite is exposed to DEM-silane vapor. The intensity of these peaks decrease with the increase in evacuation temperature, and they can be hardly noticed, when the temperature reaches at 773 K. Peaks around 3200-3400 and 3550-3700 cm^{-1} represent associating Si-OH, and non-hydrogen bonding OH groups, respectively. The former peak disappears and the latter peak increases in height by the adsorption of DEM-silane. As DEM-silane has three kinds of reactive groups (-H, -CH₃, and -OC₂H₅) for silane coupling, three kinds of the adsorption species of DEM-silane were considered, as shown by [I], [II] and [III] in Fig. 6. The FT-IR spectra of Fig.5 indicate that the adsorption species have Si-CH₃, Si-H, and Si-OC₂H₅ groups, and the formation of these species generates non-hydrogen bonding OH groups. The [I] form in Fig. 6 can most reasonably explain these results.

During heating the zeolite sample with adsorbed DEM-silane, the color of the zeolite sample changed from white to black, as the chemisorbed silane compounds were decomposed, leaving coke with Si atoms bonded to the zeolite framework by a siloxane bond. The coked sample was calcined at 823 K in an air stream, leaving a white zeolite sample with an SiO₂ unit on each active site of it. The IR-spectra of this sample might be represented by the spectra marked by “calcined at 823 K in air” in Fig. 5. The coverage of active sites by SiO₂ units can be increased by repeating this sequence. This procedure described above is named the catalytic cracking of silane

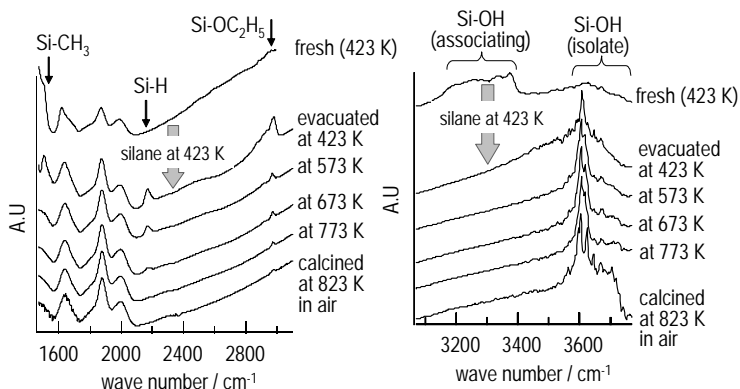


Fig. 5 FT-IR spectra of ZSM-5 zeolite pre-adsorbed with di-ethoxy-methyl silane.

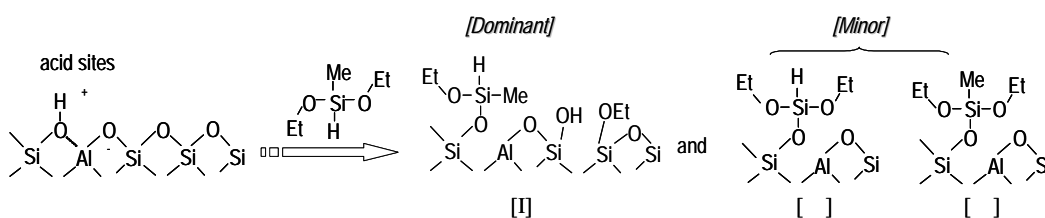


Fig.6 Adsorbed species of di-ethoxy-methyl silane on ZSM-5 zeolite.

(CCS) method.

This method can be applied to control the location of deactivate acid sites by varying the types of organic groups bonding to Si atom in silane compounds, the molecular sizes of which are different. Therefore, we employed four kinds of silane compounds with different molecular sizes; di-ethoxy-methyl silane (DEM-silane), di-phenyl silane (DP-silane), di-phenyl-methyl silane (DPM-silane), and tri-phenyl silane (TP-silane). The order of the molecular sizes of the silane compounds are TP-silane > DPM-silane \approx DP-silane \approx pore diameter of ZSM-5 > DEM-silane.

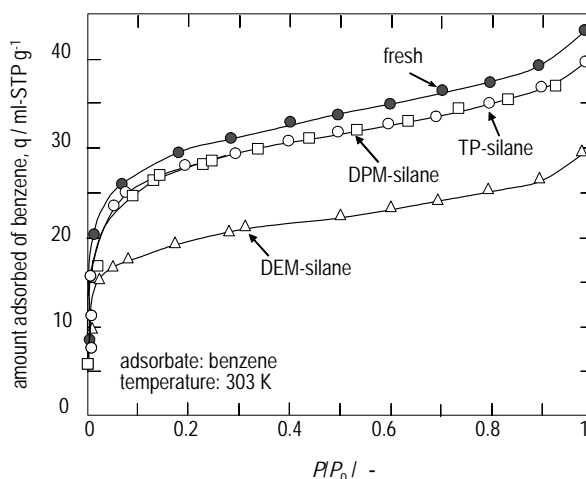


Fig.7 adsorption isotherms of benzene onto ZSM-5 zeolite treated by the CCS method.

Figure 7 shows the adsorption isotherms of benzene onto ZSM-5 zeolites by treating the CCS method with several silane compounds. It is difficult for benzene to pass through pore positions with SiO₂ units formed. Therefore, the amount adsorbed of benzene onto ZSM-5 zeolite treated by DEM-silane was markedly lower than that of fresh one, indicating that acid sites in pores were deactivated. On the other hand, there is a little decrease in the adsorption capacities of benzene onto ZSM-5 zeolites treated by DPM- and TP-silanes, suggesting that only acid sites located on and near the outer surface of zeolite crystals were selectively deactivated.

In order to confirm the location of acid sites deactivated by the CCS method with different silane compounds, the intracrystalline and effective diffusivities of benzene were measured for the ZSM-5 zeolites treated by DEM- and TP-silanes, as shown in Fig.

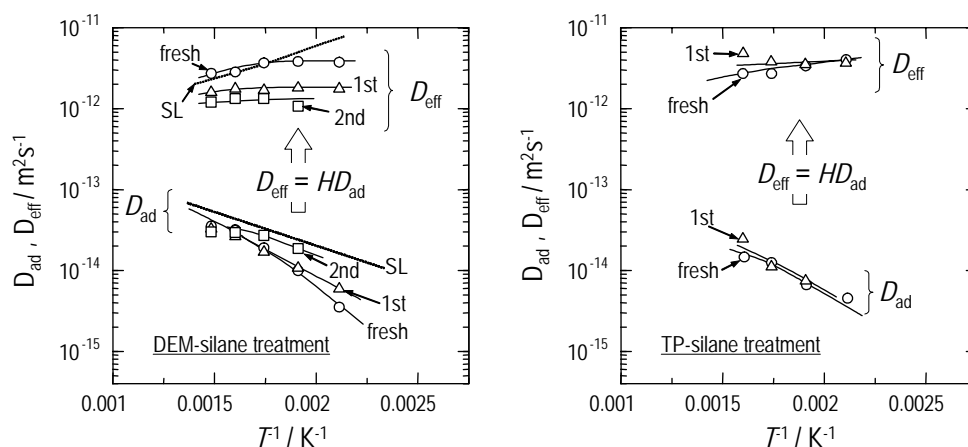


Fig. 8 Intracrystalline and effective diffusivities of ZSM-5 zeolite treated by DEM- and TP-silanes.

8. The intracrystalline diffusivity represents the mobility of each diffusate molecule, and increases as decrease in active acid sites [15]. The effective diffusivity is expressed by multiplying the intracrystalline diffusivity by the partition factor. Formation of SiO_2 units causes the decrease in the pore space where diffusate molecules can access, leading to the decrease in the partition factor. Therefore, the formation of SiO_2 units in pores leads to the decrease in the effective diffusivity. The results for ZSM-5 zeolite treated by DEM-silane supports this phenomenon. On the other hand, there are little changes in both diffusivities for the ZSM-5 zeolite treated by TP-silane, indicating that acid sites on the outer surface were selectively deactivated by SiO_2 unit formation.

3.3. Olefin synthesis from acetone using ZSM-5

In the reaction of acetone, olefins (ethylene, propylene, and iso-butene) and aromatics were produced from acetone over ZSM-5 zeolite catalysts. Iso-butene was first produced from aldol-condensation products of acetone, followed by production of propylene and ethylene by cracking of iso-butene over acid sites. Thus, the reaction of acetone is one of reaction in series, and olefins are intermediate species.

Olefin synthesis from acetone was carried out over ZSM-5 zeolite macro- and nano-crystals, and are shown in Figs. 9 and 10, respectively. In case of the ZSM-5 macro-crystals, there is a resistance to mass transfer within the crystals, leading to undesirable excessive reaction, namely coke formation. Therefore, rapid deactivation was observed. On the other hands, the ZSM-5 nano-crystals avoid the coke formation, resulting in long life-time.

As shown in Fig. 10, the selectivity of aromatics was, however, much high, since

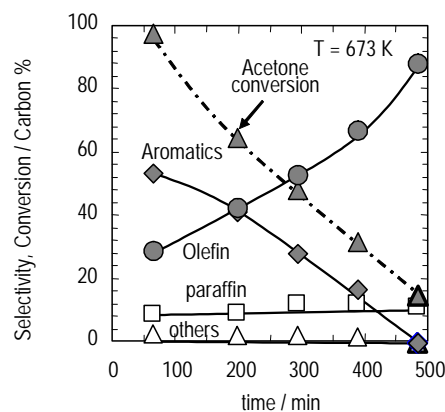


Fig. 9 Conversion and selectivity of acetone reaction on ZSM-5 zeolite macro-crystals.

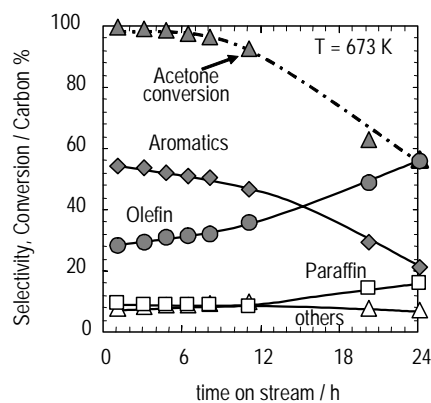


Fig. 10 Conversion and selectivity of acetone reaction on ZSM-5 zeolite nano-crystals.

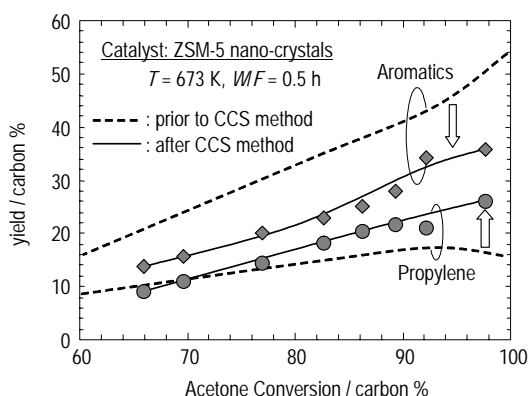


Fig.11 Relationship between acetone conversion and product yields of aromatics and propylene.

aromatics also are produced by the excessive reaction of the produced olefins over the acid sites located on and near the outer surface of the ZSM-5 crystals. In order to inhibit aromatic formation, the acid sites located on and near the outer surface were selectively deactivated by the CCS method. Figure 11 shows the relationship between acetone conversion and product yields of aromatics and propylene for the ZSM-5 zeolite nano-crystals prior to and after the CCS treatment with DPM-silane. As expected, the ZSM-5 zeolite treated by the CCS treatment exhibited high olefin selectivity as well as low aromatics selectivity as compared with the that prior to the CCS treatment. The olefins yield reached up to 60%, with the main product being propylene. The selective deactivation of the acid sites on and near the outer surface was effective in decreasing aromatic production and increasing olefin yield.

The similar results were also obtained for the methanol reaction.

4. CONCLUSIONS

Mono-dispersed ZSM-5 zeolite nanocrystals of 50 nm in size were successfully prepared using water/surfactant/oil solution. The prepared crystals were found to be well-crystallized on the surface as well as the bulk phase. In order to prevent the surface activity, acid sites on and near the surface area of the crystals were selectively deactivated by the catalytic cracking of silane (CCS) method with several kinds of silane compounds. Two kinds of ZSM-5 zeolites with different crystal sizes, 2.0 μm and 50 nm, were used as catalysts to synthesize olefins from acetone and methanol. The decrease in the crystal size led to the increase in the catalytic activity and stability. Aromatic were, however, also produced, which was ascribed to the higher outer surface area of the nanocrystals. The production of aromatics could be restricted by using the zeolite nanocrystals modified by the CCS treatment, which exhibited the high olefin selectivity.

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