Synthesis of Gallosilicate Type Molecular Sieve with CDO Topology and Application to Solid Acid Catalyst

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The gallosilicate type CDS-1 zeolite ([Ga]CDS-1) with CDO topology is prepared from the precursor of gallium-containing layered material ([Ga]PLS-1) by calcination via dehydrative condensation, and the corresponding [Ga]PLS-1 can be successfully synthesized from the mixture of protonated kanemite (H-kanemite), Ga₂O₃, tetramethyl-ammonium hydroxide (TMAOH) as structure-directing agent (SDA), NaOH and H₂O. These materials have been characterized by powder XRD, TG-DTA, FE-SEM, nitrogen adsorption and solid state NMR, and their solid acid properties were evaluated by NH₃-TPD analysis after protonation. The obtained proton type [Ga]CDS-1 zeolite can be applied for catalytic cracking reactions (1-hexene and ethylbenzene) and methanol-to-olefin (MTO) reaction as a novel solid acid catalyst.

1. Introduction
Zeolite is a member of the tectosilicate family of minerals possessing a uniformed three-dimensional pore system and has been widely applied in many fields such as adsorbents, ion-exchangers and catalysts. Particularly, vast efforts on serving as a versatile solid catalyst in petroleum chemistry have been paid attention by many researchers. Among the explored zeolite catalysts, the gallium-containing zeolites substituting of Si⁴⁺ by trivalent Ga³⁺ into their framework, causing a Brønsted acid site, have been rendered a promising candidate.

Indeed, the aromatization of liquefied petroleum gas (LPG) alkanes into aromatics (mainly benzene, toluene and xylene) is well known process, and the researches on not only the practical catalysis but also the synthesis for isomorphous materials bearing different topology have been attractive task for the gallium incorporated zeolite.

The CDS-1 zeolite with CDO topology has been reported by Ikeda et al. in 2004 as a siliceous microporous material, which possesses a two-dimensional 8-membered ring (8 MR) pore system (4.7 × 3.1 Å and 4.2 × 2.5 Å, 1 Å = 1 × 10⁻¹₀ m). They have claimed that the CDS-1 zeolite was prepared from the layered silicate precursor denoted as PLS-1 by calcination via topotactic dehydrative condensation and that the hydrothermal synthesis including an organic additive in the starting gel successfully provided the corresponding PLS-1 crystalline. Recently, they have also developed the synthetic strategy utilizing protonated kanemite as a silica source, resulting in a facile access for preparing PLS-1 and its isomorphous analogues. The characteristic synthetic feature of the CDS-1 zeolite forming via layered zeolite precursor gives us an opportunity for extended researches such as MCM-22 and PREFER. However, a variety of the CDS-1 zeolite with respect to chemical components of its framework has not been satisfied yet. Our group has reported the synthesis of the boron-containing CDS-1 zeolite and Al-CDS-1 zeolite has introduced by Sano et al.

Here we wish to report the synthesis and characterization of the gallosilicate type CDS-1 zeolite ([Ga]CDS-1) and its zeolitic layered precursor [Ga]PLS-1, and also applied for the solid acid catalysis such as cracking and MTO reactions.

2. Experimental
2.1. Characterizations
Powder X-ray diffraction (XRD) was measured by a Shimadzu XRD-6000 diffractometer with Kα radiation (λ = 1.5418 Å). Elemental analyses were performed using an inductive coupled plasma (ICP) spectrophotometer (JOVIN YBON ULTIMA 2, HORIBA, Japan) after destructions of the samples by potassium carbon-
ate. Nitrogen adsorption isotherm measurements were carried out on a Belsorp 28SA apparatus (Bel, Japan). Solid-state 1H and 29Si magic angle spinning (MAS) NMR spectra, 13C and 29Si cross polarization (CP) MAS NMR were recorded at ambient temperature by using 4 mm diameter zirconia rotor with a spinning rate of 6 kHz (ECA-500 NMR spectrometer, JEOL). Thermal gravimetric (TGA) and differential thermal (DTA) analyses were carried out by using a Shimadzu DTG-50 analyzer at a ramping rate of 10 K/min under an air stream. The crystal size and morphology were measured by field emission scanning electron microscopy (FE-SEM) (S-4800; Hitachi High-Technologies Corp., Japan). Ammonia temperature programmed desorption (NH3-TPD) experiments were conducted on a TPD-66 apparatus (Bel, Japan): the sample was evacuated at 400 °C for 1 h, and ammonia was adsorbed at 100 °C followed by further evacuation for 1 h. Then, the sample was heated from 100 to 710 °C at the rate of 10 °C/min in a helium stream.

2. 2. Materials

The precursor of Na-kanemite, δ-Na2O·2SiO2 (PURIFEED®), was gifted from Tokuyama Siltech Co., Ltd., Japan. Other reagents are commercially available and used without any purification.

2. 3. Preparation of H-kanemite

An acidified form of Na-kanemite was prepared as follows. A 1.0 g of δ-Na2O·2SiO2 powder was stirred in distilled water (100 mL) for 3 h at room temperature. The resulting Na-kanemite was separated by filtration, and washed with deionized water and ethanol. The obtained white powder was dried in air overnight. A solution of aqueous 1.0 N HCl (7.5 mL) was added to the Na-kanemite (0.50 g) at room temperature. Resulting mixture was stirred for 2 h at the same temperature. After the filtration and wash with distilled water, the white powder of H-kanemite (H2Si2O5) was obtained and used without any purification.

2. 4. Synthesis of [Ga]PLS-1

The mixture of Ga2O3, TMAOH, NaOH in H2O was stirred vigorously for 10 min at ambient temperature, and then H-kanemite was added to the mixture. The optimized gel composition is as follows: 1.0 SiO2 : x Ga2O3 : 0.10 NaOH : 0.15 TMA+ : 5.0 H2O. After stirring for 30 min, the resulting gel was transferred into a Teflon-line autoclave and stood at 170 °C for 3 days. The product was filtered and washed with distilled water thoroughly, and dried at 50 °C overnight to yield [Ga]PLS-1. Description of [T]PLS-1(X) in this text represents the incorporated tetrahedral atom (T) and the molar ratio (X) of Si/T in the starting gel, respectively.

2. 5. Preparation of Na[Ga]CDS-1 Zeolite

The obtained [Ga]PLS-1 (0.5 g) was added into a 1.0 M HCl aqueous solution (10 mL), and stirred for an hour at room temperature. After filtration and wash with distilled water, the resulting white powder was dried at 50 °C. The sodium type Na[Ga]CDS-1 was obtained by calcination at 550 °C for 6 h (heating rate = 0.5 °C/min) under air flow.

2. 6. Ion-exchange to [H]GaCDS-1 Zeolite

The proton type [Ga]CDS-1 zeolite was prepared by ion-exchange treatment. The mixture containing the Na[Ga]CDS-1 zeolite and NH4NO3 in distilled water (weight ratio was 1.0 : 1.0 : 50) was stirred at 80 °C for 8 h, and the resulting powder was filtrated and dried. This procedure was repeated twice, and the obtained white powder was calcined at 550 °C for 6 h to afford a proton-type H[Ga]CDS-1. Description of M[T]CDS-1 (X) in this text represents the cation atom (M), the incorporated tetrahedral atom (T) and the molar ratio (X) of Si/T in the starting gel.

2. 7. Catalytic Cracking Reaction

Cracking reactions were taken place by pulse experiments as follows; the H[Ga]CDS-1 zeolite (20 mg, 18-32 mesh) was installed onto a glass wool fixed in a quartz tube (diameter 3.4 mm, length 100 mm) connecting with gas chromatography (Shimadzu GC-14A, capillary column: Ultra-1, 30 m × 0.53 mm). Reactions were performed by adding a 0.4 µL of substrate (1-hexene and ethylbenzene) at 300 °C under nitrogen flow (40 mL/min), and the catalytic activity was evaluated by their conversions.

2. 8. MTO Reaction

The reaction was carried out using a 7 mm quartz tubular down flow reactor. The zeolite (0.1 g, 18-32 meshes) was placed between two layers of quartz wool, and nitrogen was used as a carrier gas. The reaction temperature was at 400 °C, and feed of MeOH was 0.5 h⁻¹ (WHSV). The conversion of MeOH and product distributions (ethene; C2H4, propene; C3H6, others) were estimated by on-line gas chromatographs (Shimadzu GC-14B and GC-18B) equipping with FID detector using fused silica capillary columns (DB-1 and CP-Al2O3/KCl).

3. Results and Discussions

3. 1. Synthesis and Characterization of Layered Zeolitic [Ga]PLS-1

In order to obtain the layered precursor of [Ga]PLS-1 from the gel containing H-kanemite, Ga2O3, NaOH, TMAOH and H2O, we have screened the appropriate gel compositions according to our recent procedure and have optimized the molar ratios and reaction conditions for synthesizing [Ga]PLS-1 crystal as follows; 1.0 Si : x Ga : 5x NaOH : 0.2 TMAOH : 5.0 H2O, 170 °C for 3 days. According to the optimized gel compositions and reaction conditions for synthesizing of [Ga]PLS-1, we then examined the preparation of PLS-1 bearing different Si/Ga ratios, the powder XRD charts of the obtained...
samples are given in Fig. 1. At the highest Si/Ga ratio of 5.0, the clear and monotonous dense phase corresponding to SOD topology was observed (Fig. 1(a)), and the intensity of its diffraction peaks were decreased with accompanying PLS-1 phase at the ratio of 10 (Fig. 1(b)). Only single diffraction patterns corresponding to PLS-1 phase appeared over 25 in the Si/Ga ratio (Fig. 1(c) to (f)). Thus, it is found that the installed amount of Ga$^{3+}$ in the layered precursor of [Ga]PLS-1 can be tunable over 25 in the Si/Ga ratios.

Figure 2 shows the FE-SEM images of the obtained [Ga]PLS-1(50 and 100) samples. They show the aggregates of thin-plate morphologies, those are similar to that of the reported siliceous PLS-1\(^{12,23}\).

The elemental analysis by inductively coupled plasma (ICP) revealed the good correlation with the installed amount of Ga in the initial gel; Si/Ga = 21 (25), 40 (50), 89 (100) and 168 (200) (The values in parentheses are ratios of Si/Ga at the starting gel).

The solid-state \( ^1 \text{H} \) MAS and \( ^{13} \text{C} \) CP/MAS NMR spectra of [Ga]PLS-1(50) (sample in Fig. 1(d)) revealed that single and sharp peaks corresponding to the occluded TMA$^+$ molecule between layers were detected at 3.3 ppm for \( ^1 \text{H} \) and 57 ppm for \( ^{13} \text{C} \), respectively (figures not shown). The \( ^{29} \text{Si} \) CP/MAS NMR spectra of obtained [Ga]PLS-1 samples are shown in Fig. 3. Three broad peaks resulting from \( Q^3 \) and \( Q^4 \) silicon in the framework were obviously observed: two peaks at \(-99 \) ppm and \(-103 \) ppm were assignable as \( Q^3 \) silicon, and the broad peak at \(-112 \) ppm was \( Q^4 \) silicon. Former two \( Q^3 \) peaks are attributed to the HOSi(OSi)$_3$ and the tetrahedrally coordinated silicon which is substituted by more than one Ga$^{3+}$ (HOSi(OSi)$_3$–(OGa)$_n$, \( n = 1 \) to 3). These \( Q^4 \) peaks can be often found in the metal substituted layered silicate PLS-1 analogues\(^{25}\).
3.2. Na[Ga]CDS-1 Zeolite

Due to the characteristic feature for preparing CDS-1 zeolite vide supra, the calcination conditions severely affect the essential properties for a microporous material such as surface area, pore size distribution, pore volume and hydrophobicity, that is, inappropriate treatment often causes a collapse of the framework and/or a stacking fault between interlayers. Thus, we have examined the influence of the calcined temperature using a [Ga]PLS-1(50) sample to discriminate the suitable conditions and have found to be determined the calcination conditions as follows; 550 °C for 6 h, heating rate: 0.5 °C/min, air flow rate: 100 mL/min.

Figure 4 shows the powder XRD charts of Na[Ga]CDS-1 zeolites prepared from the corresponding [Ga]PLS-1 (Fig. 1(c) to (f)) precursors under the optimized calcination conditions. All of diffraction peaks were broaden due to their small particle sizes; however, good agreement with that of siliceous CDS-1 zeolite without any other impurities.

FE-SEM images of the obtained Na[Ga]CDS-1 zeolites given in Fig. 5 also show the thin-plate like morphologies as similar to those of [Ga]PLS-1 (Fig. 2), suggesting that the topotactic conversion from the zeolitic layered precursor of [Ga]PLS-1 to zeolite (Na[Ga]CDS-1) smoothly occurs during the calcination.

The properties of the obtained samples were also elucidated by elemental analysis by ICP, and it revealed that the installed amount of Ga in CDS-1 zeolite exhibited good agreement with the content in its [Ga]PLS-1 precursor. This indicates that there was no severe leaching during the calcination treatment at high temperature. Nitrogen adsorption isotherms of all samples exhibiting the typical I-type curves also indicate the sufficient microporosity (Fig. 6).
Figure 7 presents the $^{29}$Si MAS NMR spectra of Na[Ga]CDS-1 samples. The broad peaks at around $Q^4$ silicon region (−110 ppm) were obviously observed, and the $Q^3$ silicon found at around −100 ppm in [Ga] PLS-1 samples were vanished in all samples, suggesting that dehydrative condensation at the interlayer smoothly occurs under appropriate calcination process.

3.3. H[Ga]CDS-1 Zeolite

In general, after the ion-exchange process in the group 13 atoms (such as B$^{3+}$, Al$^{3+}$ and Ga$^{3+}$) incorporated zeolites, the resulting proton-type zeolite can be applied for solid acid catalyst owning to its Brønsted acid site in the framework. We have also prepared the proton-type gallium-containing CDS-1 zeolite by protonation using aqueous NH$_4$NO$_3$ solution. Figure 8 shows the NH$_3$-TPD profiles of the obtained H[Ga] CDS-1 zeolites. Characteristic desorption peaks of NH$_3$ are observed at around 150, 300 and 480 °C, respectively. The first peak at low temperature ($l$-peak) is resulting from the physically adsorbed ammonia (van der Waals adsorption). The second peak ($h$-peak) at around 300 °C is ascribed to the chemisorbed NH$_3$ at the acid site of zeolite, and it is obvious that the peak intensity is decreased with the decreasing of the incorporated Ga amount. The observed $h$-peak temperature and the estimated acid amounts are listed in Table 1. These values and surface areas estimated from N$_2$ adsorption analysis are acceptable and reasonable for those of typical microporous materials. However, the third lower peak at the highest temperature (480 °C) indicates the existence of bulk gallium oxide (Ga$_2$O$_3$) caused by the calcination.

Table 1 Properties of Siliceous CDS-1 Zeolite, Na[Ga]CDS-1 and H[Ga]CDS-1 Zeolites

| Entry | Sample | Si/Ga ratio$^{a)}$ | N$_2$ adsorption S.A.$^{b)}$ [m$^2$ g$^{-1}$] | P.V.$^{c)}$ [mL g$^{-1}$] | Sample | Si/Ga ratio$^{a)}$ | N$_2$ adsorption S.A.$^{b)}$ [m$^2$ g$^{-1}$] | P.V.$^{c)}$ [mL g$^{-1}$] | NH$_3$-TPD h-peak$^{d)}$ [°C] | Acid amount$^{e)}$ [mmol g$^{-1}$] |
|-------|--------|------------------|-----------------|-----------------|-------|------------------|-----------------|-----------------|-----------------|-----------------|
| 1     | CDS-1  | -                | 283             | 0.12            |       |                  |                 |                 |                 |                 |
| 2     | Na[Ga]CDS-1(25) | 29              | 294             | 0.14            | H[Ga]CDS-1(25) | 31              | 234             | 0.13            | 293             | 0.193           |
| 3     | Na[Ga]CDS-1(50) | 43              | 270             | 0.17            | H[Ga]CDS-1(50) | 44              | 270             | 0.20            | 293             | 0.157           |
| 4     | Na[Ga]CDS-1(100) | 91              | 296             | 0.13            | H[Ga]CDS-1(100) | 93              | 270             | 0.22            | 294             | 0.077           |
| 5     | Na[Ga]CDS-1(200) | 173             | 255             | 0.13            | H[Ga]CDS-1(200) | 187             | 266             | 0.17            | 298             | 0.038           |

| Entry | Sample | Si/Ga ratio$^{a)}$ | N$_2$ adsorption S.A.$^{b)}$ [m$^2$ g$^{-1}$] | P.V.$^{c)}$ [mL g$^{-1}$] | Sample | Si/Ga ratio$^{a)}$ | N$_2$ adsorption S.A.$^{b)}$ [m$^2$ g$^{-1}$] | P.V.$^{c)}$ [mL g$^{-1}$] | NH$_3$-TPD h-peak$^{d)}$ [°C] | Acid amount$^{e)}$ [mmol g$^{-1}$] |
|-------|--------|------------------|-----------------|-----------------|-------|------------------|-----------------|-----------------|-----------------|-----------------|

a) Measured by ICP. b) Surface area. c) Pore volume. d) Temperature at the maximum intensity of the desorbed NH$_3$ peak. e) Estimated from NH$_3$-TPD chart.

3.4. Catalytic Reactions

We obtained the proton-type [Ga]CDS-1 zeolite, thus applied for catalytic reactions as a preliminary examination. The catalytic cracking reactions of 1-hexene and ethylbenzene were examined by utilizing H[Ga]CDS-1.
(50) sample (Table 1, entry 3), and the results were given in Fig. 9. It revealed that the catalytic activity obviously depended on the size of used molecules: the conversion of 1-hexene, smaller linear alkene, was at around 40 %; however, the catalyst is almost inert for cracking reaction of ethylbenzene, because the CDS-1 zeolite does not possess enough pore size (8 MR) to accept the sufficient diffusion of such larger molecule 26). Indeed we also examined the cracking of cumene, but the result is the same as that of ethylbenzene (figure not shown).

Methanol-to-olefin (MTO) reaction is one of the attractive catalytic reactions due to its higher selectivity for producing of propene than that of conventional cracking of naphtha 27–29). Many researches have been reported by using solid acid catalysts such as zeolite. Among them, zeolites possessing eight membered ring (8 MR) such as SAPO-34, SSZ-13 (CHA topology) and representative ZSM-5 zeolite have realized as a promising candidate for this reaction 17,30–34), thus it has been also reported the reaction over zeolite catalysts with 8 MR, so far35–39). The CDS-1 zeolite with CDO topology has a two-dimensional 8 MR pore system vide supra, therefore, it is interesting to evaluate its catalytic performance for MTO reaction. The results are given in Fig. 10. Conversion of methanol was found to be at around 30 % in all time-on-stream, but slightly declined with prolonged time. In product distribution, ethane (C2) and ethene (C2') are predominantly obtained in 31 to 43 % and 40 to 35 %, respectively. The selectivity of propene (C3') is around 10 % and a mixture n-butane (ca. 10 %), i-butane (5 %) and a trace amount of propane (C3, ~ 0.4 %) are detected as others. Compared with the reported H-SAPO-34 results29,37), the lower selectivity of C3' implies that CDS-1 zeolite has no sufficient space allowing cyclic cation species that are responsible for the selective production of propene based on the well-recognized hydrocarbon-pool mechanism 27–29,39–41).

4. Conclusion

The gallosilicate molecular sieve with CDO topology, [Ga]CDS-1 zeolite, is successfully prepared from the corresponding layered precursor [Ga]PLS-1 via dehydrative condensation. The amount of gallium atom (Si/Ga ratio) can be tunable from 25 to infinity, and the obtained zeolite exhibits reasonable microporosity. After ion-exchange to proton, the H[Ga]CDS-1 zeolite shows the solid acidity by NH3-TPD analysis, however, accompanying small amount of ammonia desorption corresponding to Ga2O3 during the calcination. The obtained H[Ga]CDS-1 zeolite shows the catalytic activity for cracking reaction of 1-hexene, and moderate in MTO reaction. The results of the cracking reactions reveal that H[Ga]CDS-1 zeolite acts as a molecular sieve. This is the first report on the gallium-containing CDS-1 zeolite and its catalytic performance. Further research is now undergoing in our laboratory.

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CDO 型トポロジーを有するガロシリケートモレキュラーシールの合成と固体触媒への応用

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プロトン化したカネマイト、構造安定剤として TMAOH、酸化ガリウムから調製したゲルから CDS-1 ゼオライトの前駆体である結晶性の PLS-1 を得た。層間のシラノールを焼成により脱水重組合させることで、対応するガリウム含有 CDS-1 ゼオライトを得た。次いで、Na[Ga]CDS-1 ゼオライトを硝酸アンモニウムにてプロトン化を行い、固体触媒としての性質をアンモニア TPD にて測定したところ、Ga が骨格に置換したことで生じるプレステッド酸点由来の脱着ピークを確認したが、少量のパルクの酸化ガリウム (Ga₂O₃) が副生していることも分かった。得られた H[Ga]CDS-1 は、ヘキセンに対しては高いクラッキング活性を示すが、エチルベンゼンに対して全く活性を示さなかったことから、外表面の酸化ガリウムの影響は無視できると考えられ、CDS-1 ゼオライト本来の触媒性能のみを示した結果と考えられる。さらに、MTO 反応の触媒として H[Ga]CDS-1 を用いたところ、これまでに報告されている 8 員環ゼオライト触媒と比べ、メタノールの転化率、プロパンの選択性ともに低い結果となった。