

ノート

低 H₂O/SiO₂ 比における純シリカ CHA 型ゼオライトの合成

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Pure-silica CHA-type zeolites synthesized using low H₂O/SiO₂ ratios

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Abstract

Highly crystalline pure-SiO₂ zeolites with CHA-type framework were prepared from three different silica sources of an alkoxide (tetraethyl orthosilicate), colloidal silica (AS-40) and fumed silica (Cab-O-Sil M5) in fluoride media. Single-phase CHA-type zeolites were successfully obtained with H₂O/SiO₂ molar ratios in the range of 1.2 – 1.3 in the final gel.

Research note

Introduction

Aluminosilicate zeolites with chabazite (CHA)-type framework topology are known to have three-dimensional pore systems with ellipsoidal cages that are accessible *via* eight-membered windows with dimensions of 0.38×0.38 nm [1]. Both a high-silica CHA-type aluminosilicate (SSZ-13) and a silicoaluminophosphate (SAPO-34) have attracted significant attention as potential catalysts for the selective catalytic reduction of NO_x [2] and the methanol-to-olefin conversion [3], respectively. We have also reported the possible hydrogen isotope (H₂ and D₂) separation of Na-CHA prepared by the interzeolite conversion method [4]. In addition, pure-silica zeolites are highly important because their adsorption and diffusion properties are complementary to those of the aluminosilicate zeolites [5]. As an example, while the hydrogen storage capacity of the pure-SiO₂ CHA zeolite is insufficient for mobile applications (2.86 mass%) [6], this material shows an intrinsic property in propylene/propane separation [7, 8].

The pure-silica CHA zeolite is typically synthesized using the fluoride anion as a mineralizer, along with tetraethyl orthosilicate [9] or colloidal silica as silica sources [10, 11]. A single crystalline CHA phase has been found to appear over a very narrow range of water content (that is, a narrow range of H₂O/SiO₂ ratios) between 3.0 and 5.3 [9, 10]. Either lower or higher H₂O content produce a mixture of CHA and STT-type zeolites [10, 12], and so careful control over the synthesis conditions is required to obtain the desired product.

The present paper describes the preparation of pure-SiO₂ CHA zeolites from an alkoxide, colloidal silica and fumed silica. Although the preparation conditions were not fully optimized, highly crystalline pure-SiO₂ CHAs were obtained regardless of the silica source. Pure-SiO₂ CHA zeolites could be synthesized under the preparation conditions with low H₂O/SiO₂ molar ratios of approximately 1.2 – 1.3.

In this work, pure-SiO₂ CHAs were synthesized according to the procedure described by Díaz-Cabañas et al., with slight modifications [9]. Specifically, three different silica sources were used: tetraethyl orthosilicate (TEOS, Fujifilm Wako Pure Chemical Co.), colloidal silica (AS-40, Sigma-Aldrich) and fumed silica (Cab-O-Sil M5, Cabot Corporation, USA). *N,N,N*-trimethyladamantan-1-ammonium hydroxide (TMAdaOH, Sachem Japan GK) was employed as the structure directing agent (SDA), dissolved in Millipore water in a Teflon® beaker. The silica source was then added slowly with vigorous stirring, and was continued stirring for approximately 12 h at room temperature while the mixture was covered with a polyethylene film. The molar composition in the resulting solution was 1.00 SiO₂ : 0.41 TMAdaOH : 31.3 H₂O. The solution was subsequently heated to 70 °C in a water bath with continuous stirring for approximately 7 h to evaporate the solvent. The resulting sticky gel was further dried in an oven at 70 °C for 20 h. The light yellow-to-white solid obtained was finely ground in an agate mortar. This material is referred to herein as the green precursor. Following, 1 g of the green precursor was loaded into a Teflon® vessel together with 0.148 mL (0.136 g based on a density of 0.922 g/cm³) of HF solution (46.0 – 48.0 %, assumed to be 47.0 %; Fujifilm Wako Pure Chemical Co.), and mixed manually with a stir rod to produce a homogeneous dispersion. The molar composition of SiO₂, HF and H₂O in this final gel mixture are provided in Table 1, where the amount of H₂O containing in green-precursors will be shown below have been taking into account. The Teflon® vessel was set in a stainless steel autoclave reactor and heated at 160 °C for 48 h in an oven under static. After cooling to room temperature, Millipore water was added

Table 1 The final gel compositions used for the synthesis of the pure-SiO₂ CHA zeolites and the SiO₂ and H₂O content in the respective green precursors.

	Final gel composition (molar ratio)				Content in green-precursor (TG)	
	SiO ₂	HF	H ₂ O	(TMAdaOH)*	SiO ₂ wt%	H ₂ O wt%
psCHA(alk)	1.00	0.49	1.26	(0.41)	38.8	7.6
psCHA(cs)	1.00	0.51	1.33	(0.41)	38.4	7.9
psCHA(fs)	1.00	0.50	1.24	(0.41)	38.4	7.1

* Value from the initial mixed solution (1.00 SiO₂ : 0.41 TMAdaOH : 31.3 H₂O).

to the paste-like product, which was then removed by filtration, washed and dried at 70 °C. Finally, the material was calcined at 600 °C for 1 h (at a ramp rate of 0.5 °C/min) under an air flow of approximately 100 cm³/min to remove the SDA. The resulting pure-SiO₂ CHA zeolites prepared from TEOS, colloidal silica and fumed silica are denoted herein as psCHA(alk), psCHA(cs) and psCHA(fs), respectively. The yields of these materials ranged from 75 to 80 % based on the SiO₂ amounts.

The X-ray diffraction (XRD; X'Part PRO MPD

PW3040, PANalytical, The Netherlands) patterns of the prepared CHAs are presented in Figure 1. A single crystalline CHA phase was observed in all cases, with no impurity phases (expected STT-type zeolite with the most intense 020 peak at $2\theta = 8.11^\circ$) [11-13]. The diffraction signals could be assigned to a trigonal crystal system (space group: $R\bar{3}m$ (#166)) and the optimized cell parameters were determined to be $a = 1.354(2)$, $c = 1.480(3)$ nm for the psCHA(alk), $a = 1.354(2)$, $c = 1.480(3)$ nm for the psCHA(cs), and $a = 1.352(1)$, $c = 1.489(3)$ nm for the psCHA(fs). These parameters were almost equivalent to one another.

Scanning electron microscopy (SEM; JSM-6701F, JEOL) images of the psCHA(alk), psCHA(cs) and psCHA(fs) are shown in Figure 2. The prepared CHAs exhibited the intergrowth of crystals, as seen in Figures 2(A) to (C). These crystals were evidently quasi-cubic and likely comprised parallelepiped single particles, as shown in Figures 2(D) to (F). It is worth noting that the plate-like particles found in previous research were not observed in this study [11]. The energy-dispersive spectroscopic (EDS; JED-2300, JEOL) analyses

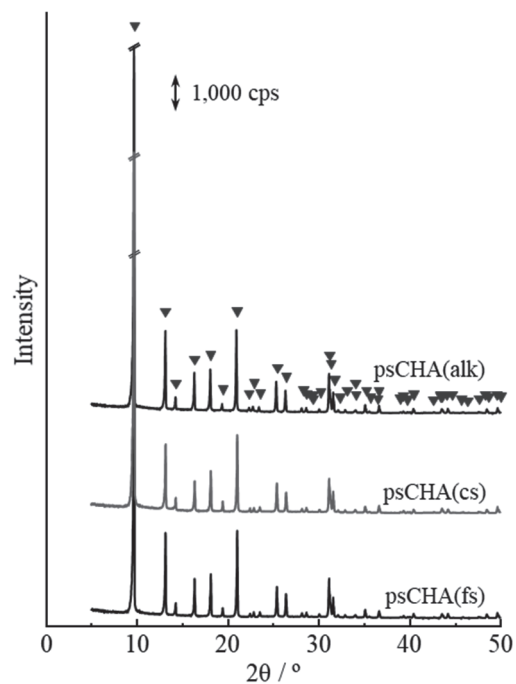


Fig. 1 The XRD patterns of pure-SiO₂ CHA zeolites. The triangles mark the main peaks that can be assigned to a CHA-type structure.

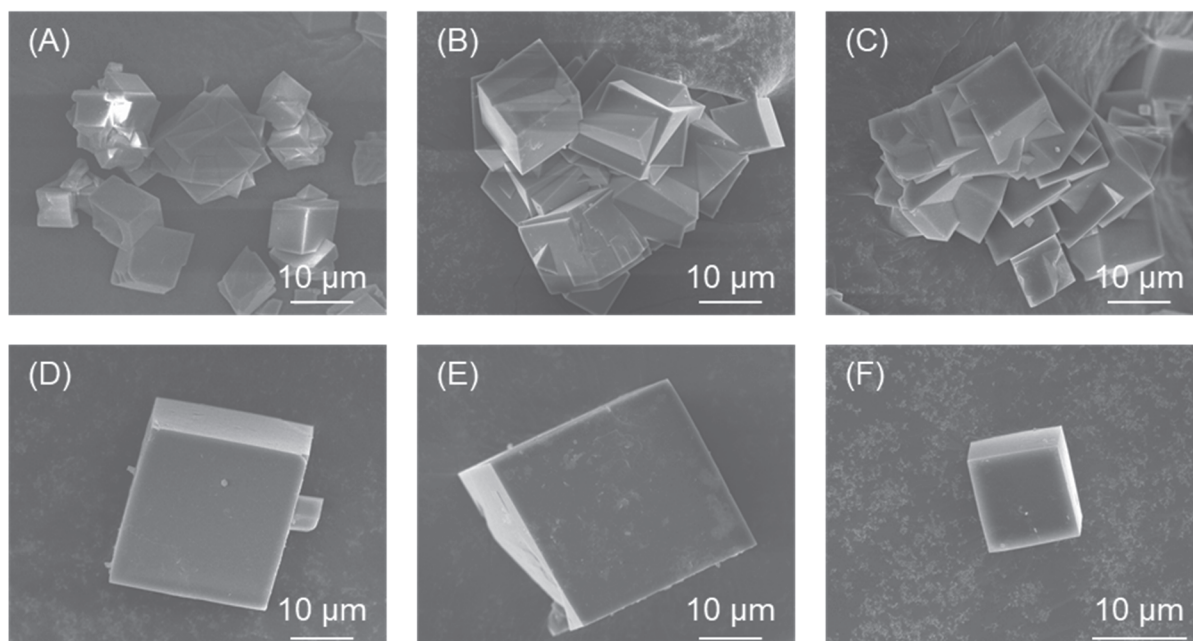


Fig. 2 SEM images of the pure-SiO₂ CHA zeolites. (A and D) psCHA(alk), (B and E) psCHA(cs) and (C and F) puCHA(fs).

demonstrated the absence of Na in these specimens (less than 0.1 wt%), even in the case of the psCHA(cs), although the colloidal silica (AS-40) contained a small amount of Na (SiO₂/Na₂O = 160 – 270 in catalog).

Figure 3 shows the N₂ sorption isotherms of the pure-SiO₂ CHA zeolites measured at 77 K (Autosorb-iQ, Quantachrome Instruments). Type I isotherm with steep increase (approximately 200 cm³/g-STP) of N₂ adsorption in the low relative pressure region was clearly seen. The apparent surface areas (*S*_{BET}) calculated by the Brunauer-Emmett-Teller (BET) method in the P/P₀ region of 0.005 – 0.05 were 783, 778 and 803 m²/g for the psCHA(alk), psCHA(cs) and psCHA(fs), respectively. The pore volumes (*V*_p) less than approximately 1.0 nm of pore diameter, which arisen from about 0.0122 (P/P₀) according to the Kelvin equation, were determined to be 0.283, 0.283 and 0.290 cm³/g for the psCHA(alk), psCHA(cs) and psCHA(fs), respectively. The

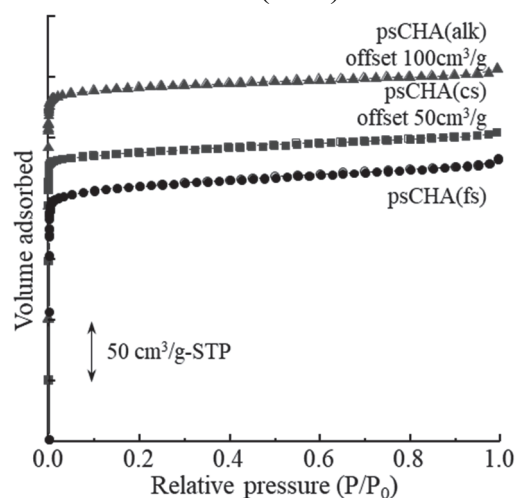


Fig. 3 N₂ sorption isotherm of the pure-SiO₂ CHA zeolites.

psCHA(fs) exhibited the largest S_{BET} and V_p . It is important to note, however, these values do not reflect a realistic accessible pore structure in ultramicropores [14]. These are probably valuable as an identification information concerning crystallinity. For comparison, S_{BET} and V_p values for pure-SiO₂ CHA zeolites have been reported in the range of 679 – 850 m²/g and on the order of 0.30 cm³/g, respectively [13, 15]. Our results therefore indicate that the psCHA(alk), psCHA(cs) and psCHA(fs) compared favorably with other pure-SiO₂ CHA zeolites reported. The results described above thus confirm the successful synthesis of pure-SiO₂ CHA-type zeolites. Significant differences were not found between these materials, indicating that the product was unaffected by the silica source employed during synthesis. However, prior work has shown that the hydrophobicity of the product was changed when switching between TEOS and AS-40 [10]. The clear type I isotherms in Figure 3 suggests that these zeolites could have significant H₂ and D₂ sorption abilities [4], and the psCHA(fs) was found to adsorb 6.05 and 6.77 mmol/g H₂ and D₂ at 95 kPa and 77 K, respectively. Such large H₂ and D₂ sorption capacity suggests that pure-SiO₂ CHAs are not well suited for effective hydrogen isotope separation [4], however, we intend to further investigate D₂/H₂ separation in the future.

Pure-SiO₂ CHA zeolites have been commonly prepared from TEOS or colloidal silica as the silica sources [9-11]. In this study, we also performed the synthesis using fumed silica. The thermogravimetric analysis (TG; Rigaku, ThermoPlus2) curves of the green precursor for the psCHA(fs) in air (up to 800 °C) and N₂ (up to 600 °C) are shown in Figure 4. Both curves are similar and three distinctive weight losses are apparent at about below 110, about 110 – 300 and above 300 °C. The weight loss below 110 °C (approximately 7.1 wt%) was attributed to the

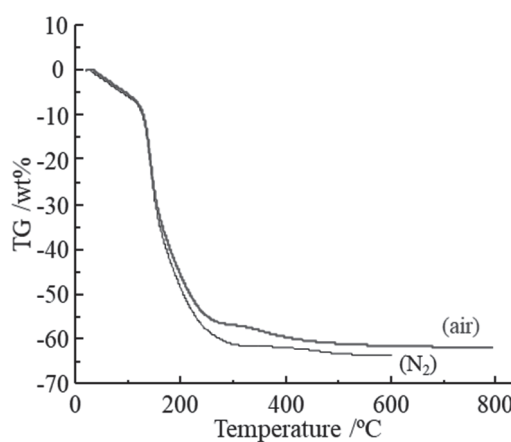


Fig. 4 TG curves for the green precursor for psCHA(fs) acquired under air and N₂ (100 cm³/min) with a heating rate of 2 °C/min.

desorption of H₂O, while the steep change between 110 and 300 °C was ascribed to the combustion (under air) or desorption (under N₂) of the SDA. Above 300 °C, the condensation of silanol groups in addition to the combustion or desorption of residual SDA-related materials gave gradual weight loss. The final weight (38.4 wt%) at 800 °C under air corresponded to the mass of SiO₂ in the specimen. The weight loss between about 110 and 800 °C was 54.5 wt%, which was in good agreement with the initial content (55.4 wt%) of SDA based on the molar ratio of 1.00 SiO₂ : 0.41 TMAOH. Taking the amounts of H₂O and SiO₂ in the green precursor into consideration, the composition of SiO₂, HF and H₂O in the final gel after adding the HF solution could be calculated to be 1.00 : 0.50 : 1.24, respectively. Similarly, the final gel compositions for the psCHA(alk) and psCHA(cs) were calculated based on the TG data and are given in Table 1. The H₂O/SiO₂ molar ratios in the final gels were determined to be 1.26, 1.33 and 1.24 for the psCHA(alk), psCHA(cs) and psCHA(fs), respectively.

The water content in the final gel is a crucial for the formation of pure-SiO₂ CHA zeolites. Specifically, higher H₂O concentrations (H₂O/SiO₂ =5.8) [13] lead to the formation of STT-type zeolite (SSZ-23) as a minor impurity. Furthermore, Miyamoto et al. reported that not only a higher water content (6.0 < H₂O/SiO₂) but also a lower water content (H₂O/SiO₂ <3.0) resulted in the formation of the STT-type zeolite [10]. Although a direct comparison with prior work is difficult, our results demonstrate the potential formation of pure-SiO₂ CHA zeolites at lower water content below 3.0 (H₂O/SiO₂).

In conclusion, pure-SiO₂ CHA-type zeolites were successfully synthesized from an alkoxide, colloidal silica and fumed silica. No significant differences were identified in the resulting materials when varying the silica source, based on analyses by XRD, SEM and N₂ sorption. In all cases, highly crystalline and single phase zeolites were obtained. Based on TG analyses of the green precursors, the H₂O/SiO₂ molar ratios in the final gel were found to be in the range of 1.2 – 1.3, which are lower than previously reported values.

Acknowledgements

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