Electronic Supplementary Information

"Novel crystalline organic-inorganic hybrid silicate material composed of the alternate stacking of semi-layered zeolite and microporous organic layer"

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- **Materials and methods**
- **Solid state MAS NMR spectra of KCS-5**

X-ray crystallographic data in CIF format is supplied as a separate data.

Materials and methods

1. Materials

Phenyltriethoxysilane (PTES; Tokyo Chemical Industry, Japan) and fumed alumina Al_2O_3-C (Nippon Aerosil, Japan) were used as silicon and aluminum sources, respectively. η-Alumina originating from the aluminum source was involved in the product as an impurity. Sodium hydroxide (Wako Pure Chemical, Japan) was also used in the synthesis of KCS-5.

2. Synthesis

PTES was hydrolyzed in an aqueous solution of sodium hydroxide at r.t. typically for 4 days. Subsequently, fumed alumina powder was added to this hydrolyzed mixture. The obtained mother mixture having the molar composition of 1.0 PTES : 0.2 Al_2O_3 : 1.0 NaOH : 5.0 H_2O was hydrothermally treated at 373 K for 7 days under static conditions. The obtained product was filtrated, washed with deionized water, and dried at r.t. overnight.

3. Characterization

Accurate powder X-ray diffractograms, usable for crystal structure analysis, were recorded on a Bruker ADVANCE D8 diffractometer with the Debye-Scherrer geometry and a position sensitive 1-D detector (VÅNTEC-1), using Cu Kα1 radiation (λ = 1.540593 Å) provided by a Ge(111) primary monochromator. A powder sample was packed into a borosilicate glass capillary tube with an inner diameter of 0.5 mm.

Solid-state magic-angle-spinning (MAS) NMR measurements were conducted using a Bruker AVANCEIII 400WB spectrometer (9.4 T magnet). A 4 mm HX VT-MAS probe was employed. The ^{1}H–^{29}Si dipolar-decoupled (DD) MAS NMR spectra were recorded at the spinning frequency of 6 kHz with a π/4 pulse length of 1.88 μs and a cycle delay time of 100 s. The {^{1}H}→^{29}Si cross-polarization (CP)/MAS NMR spectra were measured with a contact time of 4 ms and a cycle delay time of 5 s. The ^{27}Al direct-excitation (DE) MAS NMR spectra were measured at the spinning frequency of 14 kHz with a single pulse sequence a cycle delay time of 4 s. The {^{1}H}→^{13}C CP/MAS NMR spectra were measured at the spinning frequency of 10 kHz with a contact time of 3 ms and a cycle delay time of 5 s. SPINAL-64 decoupling of ^{1}H ($\nu 1 \approx$ 100 kHz) was applied during acquisition for DDMAS or CP/MAS experiment. Chemical shifts for each nucleus are reported in relative to glycine for ^{13}C, 1M $AlCl_3$ aqueous solution for ^{27}Al and hexamethylcyclotrisiloxane for ^{29}Si.

Thermogravimetric analysis was carried out on a Shimadzu ThermoPlus TG8120. A sample was heated from r.t. to 1073 K at a rate of 5 K·min^{-1} in dry air flow at 50 mL·min^{-1}.

Nitrogen gas adsorption isotherm at 77 K was collected on a BEL Japan BELSORP-mini, and benzene adsorption isotherm at 298 K was collected on a BEL Japan BELSORP-max. A powdery sample was preliminarily dehydrated at 473 K under vacuum for 3 h.

4. Structure analysis

Indexing analysis of PXRD data was carried out by the program Conograph [s1], estimating lattice constants and probable space group. For the structure analysis of KCS-5, the combination use of low-resolution PXRD data and solid-state NMR spectra was attempted. First, virtual molecules (e.g. SiO_4, AlO_4, $O_3Si–C_6H_4–SiO_3$ etc.) were assumed on the basis of local structures elucidated by NMR analysis. Subsequently, a crystal structure model built through the arrangement of virtual molecules was solved by the direct-space method with the parallel tempering algorithm using the program FOX [s2]. The initial structure model was refined by the Rietveld method using the program RIETAN-FP [s3]. In order to estimate partial structures, e.g. a position of alkali cations or adsorbed water molecules, and chemical bonding, electron density distribution (EDD) maps were calculated by the maximum entropy method (MEM). The MEM calculation was carried out by means of the program Dysnomia [s4]. Obtained structural models and EDD maps were visualized by using the program VESTA3 [s5].

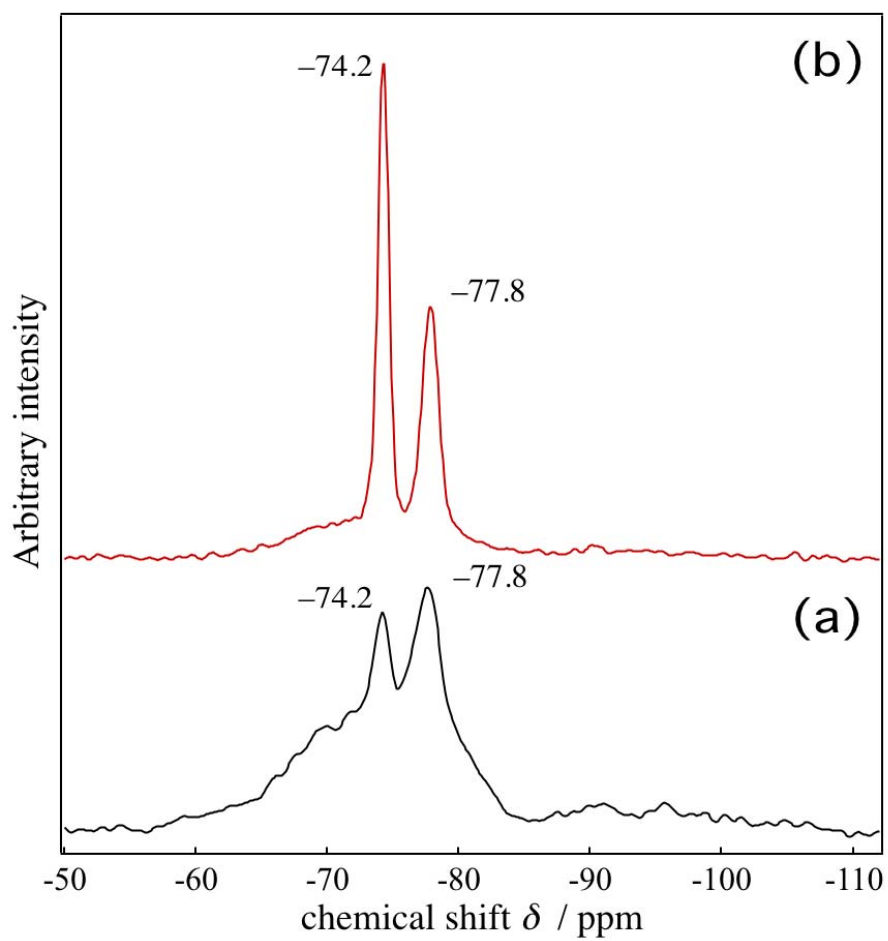[s1] R. Oishi-Tomiyasu, *J. Appl. Cryst.*, **47** 2055–2059 (2014).

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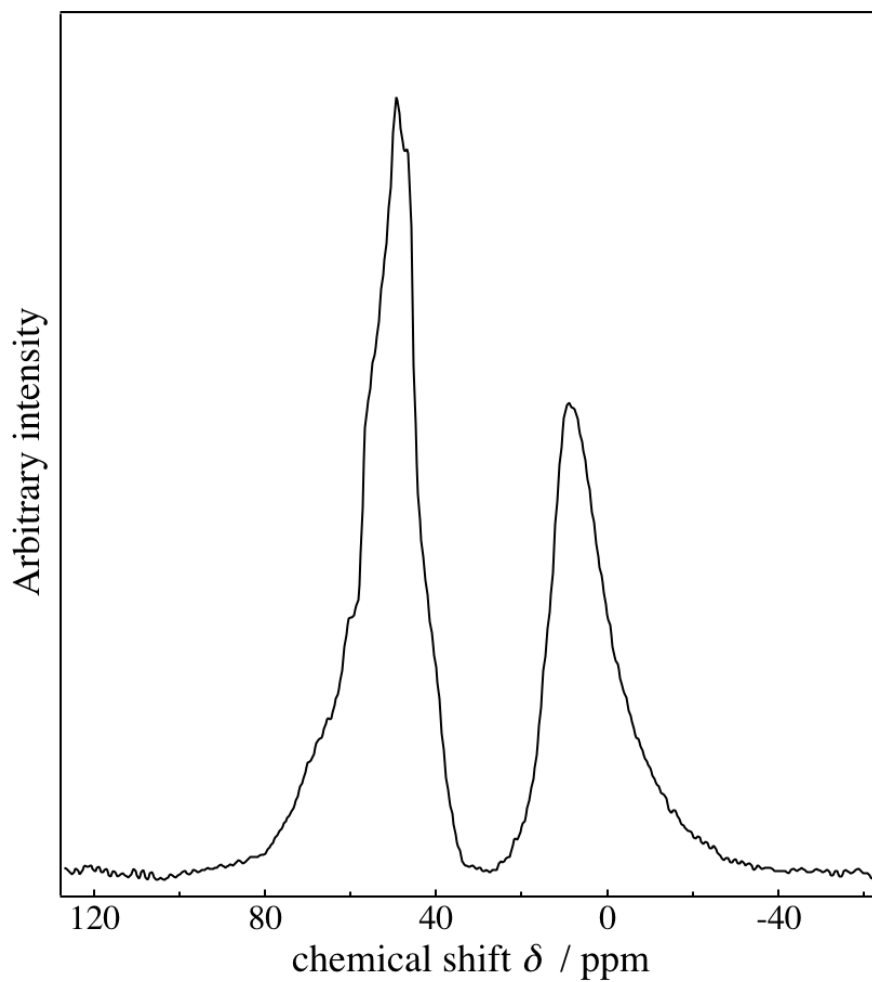
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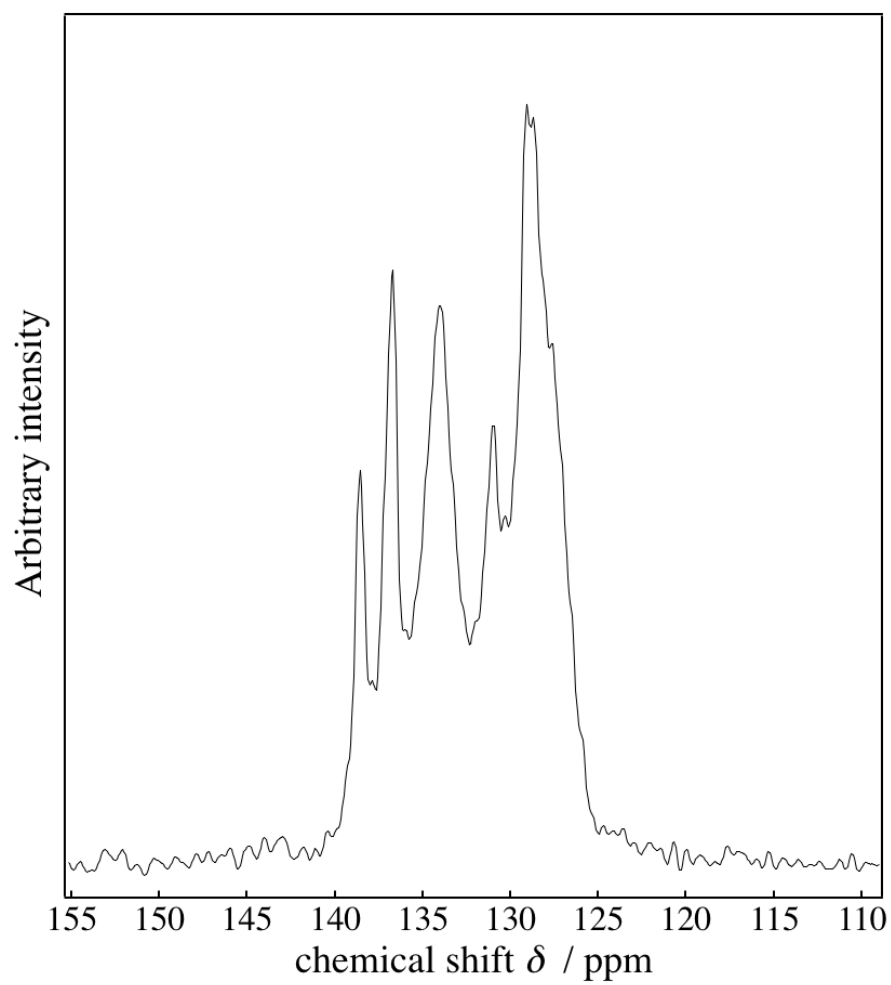
Solid state MAS NMR spectra

Fig.S1 ^{29}Si MAS NMR spectra of KCS-5 (a) DDMAS and (b) CP/MAS.

Fig.S2 ^{27}Al dfs MAS NMR spectrum of KCS-5.

The resonance peak around 9 ppm is assigned to η-alumina originating from the aluminum source involved as an impurity.

Fig.S3 ^{13}C CP/MAS NMR spectrum of KCS-5.