

Accounts of Materials & Surface Research

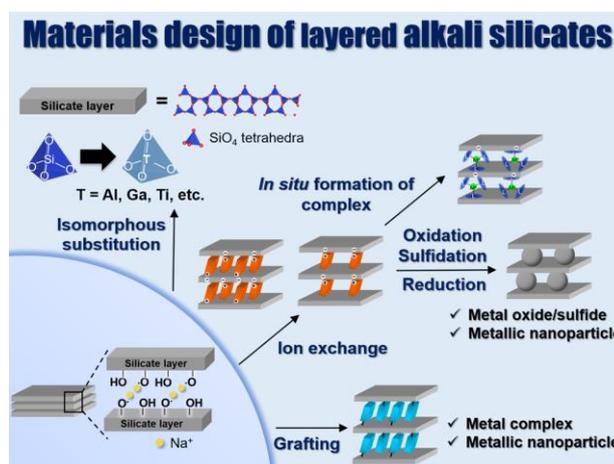
Materials design of layered alkali silicates; functionalization with inorganic species

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Layered alkali silicates, which are composed of alternately stacked SiO_4 sheets and exchangeable interlayer alkaline cations, have been investigated for fundamental science and practical applications. The silanol groups (SiOH/SiO^-) on the layer surface have been used to react for cation exchange and grafting to design various nanostructures. Their structures can also be converted to zeolite frameworks by interlayer condensation. Here, the preparation, reactivity for ion exchange, grafting, and isomorphous substitution of layered alkali silicates are summarized with the emphasis on the fixation of heteroelements in/on the silicates.



Keyword: Layered alkali silicate, Ion exchange, Grafting, Isomorphous substitution, Conversion to zeolite

Masashi Morita received his B.S. (2011) and M.S. (2013) from Waseda University under the supervision of Professor Makoto Ogawa. From 2013 to 2021, he worked as a researcher at Panasonic corporation, and was promoted to senior researcher (2017–) and worked as a project leader (2018–). In 2021, he received his Ph.D. degree from Nagoya University under the supervision of Professor Ryotaro Matsuda. After receiving his Ph.D. degree, he moved to the Division of Applied Chemistry, Institute of Engineering at Tokyo University of Agriculture and Technology as an assistant professor. His current research interests are design and synthesis of inorganic–organic hybrid materials focusing on 2D materials and metal complexes for adsorbents and catalysts.



Makoto Ogawa was educated in the Department of Applied Chemistry, Waseda University, supervised by Professor Chuzo Kato. After postdoctoral research at RIKEN, he joined Waseda University and worked on inorganic materials chemistry. In 2015, he moved to Thailand as an opening professor of the School of Energy Science and Engineering, Vidyasirimedhi Institute of Science and Technology (VISTEC), which opened in 2015 in Rayong, Thailand and continues his research activity in materials chemistry.



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1. General introduction

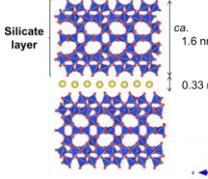
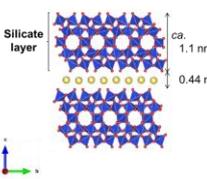
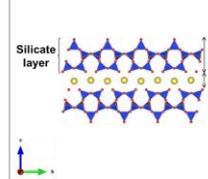
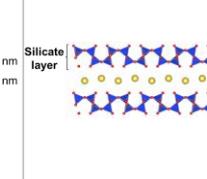
Layered materials have been investigated extensively for a variety of applications including environment, energy, electronics/optics, plastics, and life sciences using their characteristics as ultrathin layer (nanosheet) associating with the large surface area, chemical reactivity, thermal/chemical stabilities.¹⁾ Layered alkali silicates are class of layered materials composed of alternately stacked silicate layer and exchangeable interlayer cations,^{2,3)} and their application in the environment, energy and life science related fields has been reported.⁴⁻⁸⁾ Layered alkali silicates are advantageous over smectites, which are known naturally occurring layered silicates used in many industrial applications⁹⁾ from the following viewpoints; i) high cation exchange capacity, ii) the silanol groups on the layer surface for grafting and other host–guest reactions, iii) well-defined particle morphology,

iv) high crystallinity, v) facile syntheses in laboratory and so on. Herein, the function and the application of the layered alkali silicates and their intercalates/hybrids will be summarized with the emphasis on the functionalization with inorganic species.

2. Preparation and characterization of layered alkali silicates

Layered alkali silicates with varied layer thicknesses are available as summarized in Table 1. Kenyaite and magadiite were found at Lake Magadi, Kenya in 1967.²⁾ Layered alkali silicates are commonly synthesized by hydrothermal reactions in the laboratory.¹⁰⁻¹⁴⁾ Layered silicates with thicker silicate layer forms when silicon: alkali metal ion ratio increased. Silicon source (silica gel, fumed silica, alkoxy silane, etc.) was reported to affect the particle morphology of the resulting layered silicates.⁸⁾ Kanemite is synthesized from Na₂Si₂O₅, which is prepared by the solid-

Table 1. Typical example of layered alkali silicates and their structures.

	Kenyaite Na ₁₆ [Si ₁₆₀ O ₃₂₀ (OH) ₁₆]-64H ₂ O	Magadiite Na ₂ [Si ₁₄ O ₂₈ (OH) ₂]-8H ₂ O	Octosilicate Na ₈ [Si ₃₂ O ₆₄ (OH) ₈]-32H ₂ O	Kanemite NaH[Si ₂ O ₅]-3H ₂ O
Structure*				
Ideal cation exchange capacity (meq/g)	1.4	2.0	2.8	4.7
Reference	(12)	(11)	(14)	(16)

state reaction at 700 °C, by the reaction with H₂O.^{15,16)}

The structures and the reactivity of the layered alkali silicates have been investigated systematically.^{3,4)} The structures of layered silicates have been discussed in the analogy to those of zeolite, and the uses of layered silicates as zeolite precursors have been reported.^{5,17)} Some zeolites (framework types: NSI, CDO, RRO etc.) are obtained only by topotactic condensation of the layered silicates.¹⁸⁾ In order to extend the materials' variation, the preparation of novel layered alkali silicates has been examined. As an example, layered silicates named as Hiroshima University Silicates (HUSs) series are synthesized by hydrothermal reactions by Sano, Ikeda and their co-workers.^{19,20)} In HUS-1, tetramethylammonium (TMA) ions used as a structure-directing agent are located in the interlayer space (Figure 1).¹⁹⁾ The chemical composition of HUS-1 is Si₁₀O₂₄H₆ · 2(TMA) and its framework topology is similar to sodalite cage zeolites. As compared with other layered silicates (Table 1), the interlayer distance is very short (about 0.15 nm) as each layer is stacked by

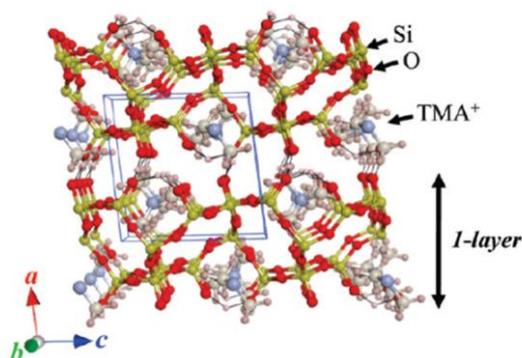


Figure 1. Structural model of HUS-1 viewed along [010] direction. Reprinted with permission from ref (19). Copyright (2011) American Chemical Society.

hydrogen bonding between the terminal silanol group of the silicate layer. HUS-3, its crystal structure has not been solved,²⁰⁾ was converted into a CDO-type zeolite by calcination, indicating that the structure of HUS-3 has partially similar to that of the CDO-type zeolite.

Advanced characterization and data analyses (powder X-ray diffraction data and 3D electron diffraction)^{11,12)} have been used to solve the crystal structures of magadiite and kenyaite.

3. Reactions of layered alkali silicates

3.1. Ion exchange

i) Inorganic cation²⁷⁾

The ion exchange selectivity of magadiite and octosilicate was reported by Wolf and Schwieger as the following order; H⁺ > Na⁺ > Li⁺ > K⁺.²¹⁾ Proton exchanged forms have been used extensively. Rojo *et al.* and Lagaly *et al.* investigated the intercalation of alkylamine and pyridine derivatives into protonated magadiite systematically.^{22,23)} Protonated layered silicates are useful as the intermediate for pillaring and grafting.²⁴⁻²⁶⁾

Muraishi reported the preparation of alkali metal cation (Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺) exchanged-magadiites and kenyaite^{28,29)} and their structures were investigated by XRD, thermal analyses, and FT-IR spectroscopy.^{30,31)} The cation exchange reactions of magadiite with metal ions (Mg²⁺, Ca²⁺, Al³⁺, Co²⁺, Cu²⁺, Zn²⁺, Fe³⁺, etc.) were quantitatively investigated by Muraishi and Hatsushika.³²⁻³⁴⁾ In addition to the cation exchange, formation of hydroxide on the surface may occur depend on the experimental condition and metal ions.

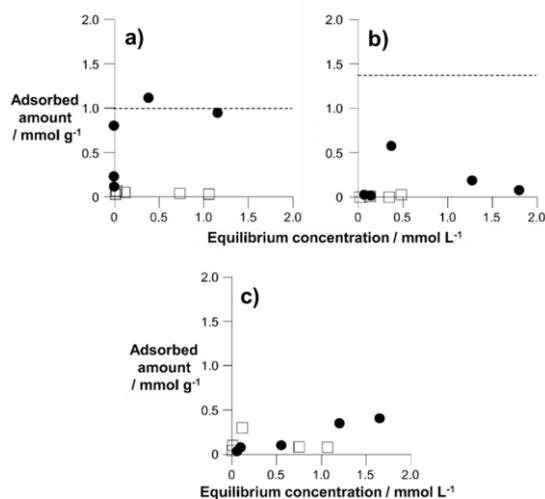


Figure 2. Adsorption isotherms of Zn²⁺ (●) and Cd²⁺ (□) on a) magadiite, b) octosilicate, and c) ion-exchange resin (IRC748, Organo) from a seawater-mimicking solution containing Zn²⁺ and Cd²⁺. The dotted lines denote the cation exchange capacities. Reprinted with permission from ref (38). Copyright (2011) John Wiley and Sons.

The adsorption isotherms of Eu³⁺, In³⁺ and Pb²⁺ on magadiite and octosilicate from water were reported to be H-type, indicating strong interactions between the silicate sheets of magadiite and the metal ions.³⁵⁻³⁷ Selective concentration of Zn²⁺ over Cd²⁺ onto magadiite from a seawater-mimicking solution was reported as shown in Figure 2.³⁸

ii) Complex ions

The ion exchange of complex cations has also been reported. Dailey and Pinnavaia investigated the intercalation of cobalt sepulchrate (sep) complex into the interlayer space of magadiite by the reaction of Na⁺-magadiite and Co(sep)Cl₃ at 100 °C.³⁹ However, a part of Co(sep) complex was decomposed to Co²⁺, resulted the presence of both Co²⁺ and Co(sep)³⁺ in the interlayer

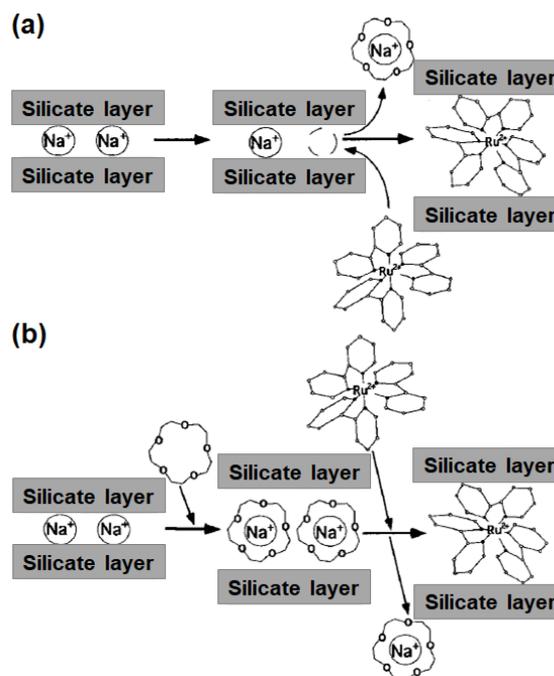


Figure 3. Schematic drawing of the crown ether (15-crown-5) assisted for ion exchange with [Ru(bpy)₃]²⁺. Reprinted with permission from ref (42). Copyright (1999) American Chemical Society.

space. Platinum tetraammine cation ([Pt(NH₃)₄]²⁺) and silver diamine cation ([Ag(NH₃)₂]⁺) were also intercalated into the interlayer space of magadiite and subsequent calcination to form the metallic Pt and Ag nanoparticles in the range of 5–12 and 3–5 nm, respectively.^{40,41} Tris(2,2'-bipyridine)ruthenium(II) cation ([Ru(bpy)₃]²⁺) exchanged magadiite was obtained by the aid of a crown ether (15-crown-5), which interacts with Na⁺ to promote the ion exchange reaction (Figure 3).⁴² [Ru(bpy)₃]²⁺ and a cationic cyanine dye were intercalated into the interlayer space using alkylammonium-exchanged magadiite as an intermediate.^{43,44}

The surface modification of layered silicates is one of the promising materials design to adsorb metal and complex ions.⁴⁵ For example, the layer surface modification of octosilicate with organosulfonic acid moiety

adsorbed $[\text{Ru}(\text{bpy})_3]^{2+}$ in the interlayer space.^{46,47} The amount of the immobilized organosulfonic-acid moiety is important for the intercalation capability and the mobility and the spatial distribution of $[\text{Ru}(\text{bpy})_3]^{2+}$ in the interlayer space.

3.2. Reaction of the intercalated metal ions

The functional design of layered silicates has been extended by the reaction of the intercalated cation in the interlayer space. The intercalated metal ions (Zn^{2+} , Ag^+ and $[\text{Cd}(\text{NH}_3)_4]^{2+}$) in magadiite have been converted to metal oxide, metallic and metal sulfide nanoparticles, respectively, (ZnO, Ag and CdS) by the oxidation, reduction and sulfidation.⁴⁸⁻⁵⁰ For example, Ag nanoparticles (average size: 24 nm) formed from Ag^+ -exchanged magadiite by the reduction using NaBH_4 .⁴⁹ This reduction method (no surface modification of layered silicates) led the aggregation of Ag nanoparticles on the external surface of magadiite. Preparation of metallic nanoparticles in the interlayer space of layered silicates will be introduced in Section 3.3.

In addition, *in-situ* formation of the complex has been reported by the reaction of the intercalated metal ions and organic ligands in the interlayer space. This concept was used to introduce the catalytic and adsorptive active sites, and also expect to exhibit unique properties. Wang *et al.* reported the formation of metal 8-hydroxyquinoline complexes in the interlayer space by the solid-solid reaction of Li^+ , Cu^{2+} and Al^{3+} -exchanged magadiite (Figure 4).⁵¹ The fluorescence of these compounds was different from those of their crystals, indicating the influence on the

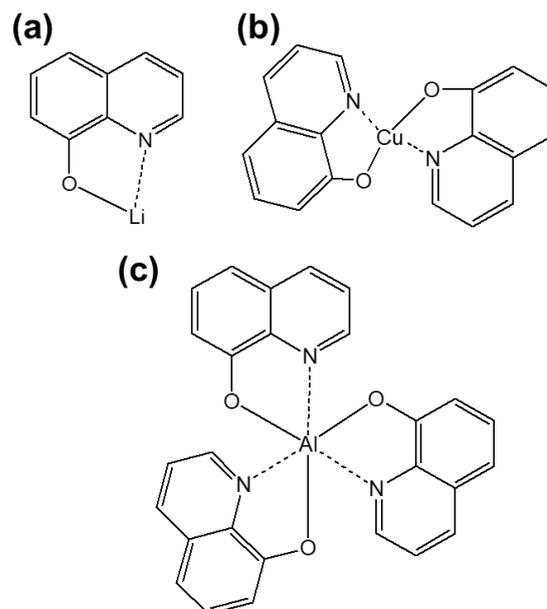


Figure 4. The molecular structures of (a) Li^+ , (b) Cu^{2+} and (c) Al^{3+} ion coordinated with 8-hydroxyquinoline.

complexes confined in a 2D nanospace. As a nanoscopically confined metal–organic framework (MOFs) or porous coordination polymer (PCP),⁵² formation of a coordination polymer in the interlayer space of layered silicates has also been reported.⁵³ The hybrid microporous material adsorbed methanol from a methanol/water vapor mixture.

3.3. Immobilization of metallic nanoparticles

The surface modification with silane coupling reagents is one of the promising strategies for the immobilization of metallic nanoparticles.^{54,55} The organic modification of the interlayer silanol groups with mercaptopropylsilyl group, urea and iminodiacetate functional groups has been reported for their strong interactions with noble metals. The adsorption of metal precursors (HAuCl_4 , AgNO_3 and K_2PdCl_4) on the organically modified octosilicate/magadiite and the *in-situ*

reduction by NaBH_4 have been reported for the immobilization of Au (Figure 5), Ag, and Pd nanoparticles/nanoplates.⁵⁶⁻⁵⁸ The Ag/Pd nanoplates showed higher catalytic activity for the hydrolysis of NH_3BH_3 and dehydrogenation of formic acid than spherical nanoparticles.^{57,58}

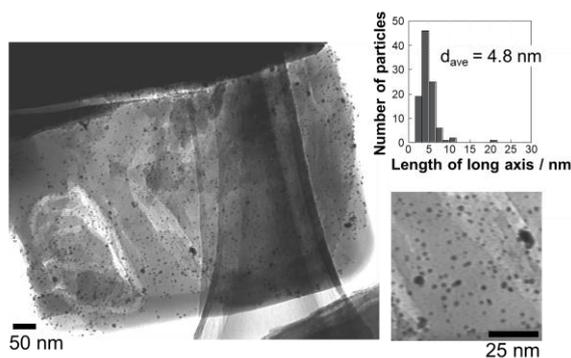


Figure 5. TEM images of Au nanoparticle in the interlayer space of octosilicate. Reprinted with permission from ref (56). Copyright (2007) American Chemical Society.

3.4. Grafting

Taking advantage of the reactivity of silanol groups on the layer surface, grafting has been reported extensively for the immobilization of organic functionalities on and in the interlayer space of the layered silicates.^{5,7} Along this line, active/unstable metal complexes have been immobilized in the interlayer space of layered silicates. Ti(IV) acetylacetonate was grafted in the interlayer space of a layered silicate, HUS-2 ($\text{Si}_{20}\text{O}_{40}(\text{OH})_4 \cdot 4[\text{C}_5\text{H}_{14}\text{NO}]$). The grafted Ti on the silicate existed as an isolated tetrahedrally coordinated species. The product exhibited higher photocatalytic activity than the representative titanosilicate, TS-1, and high selectivity for partial oxidation of cyclohexane.⁵⁹ Ide *et al.* reported a dimeric

aqua-Fe(III) complex stabilized on the silicate surface of protonated magadiite.⁶⁰ The location and the state of a dimeric aqua-Fe(III) species were confirmed by XANES/EXAFS spectra and density functional theory (DFT) calculations. The aqua-Fe(III) species-immobilized magadiite exhibited higher UV-shielding performance than TiO_2 rutile.

Using the reactivity of silanol groups on a variety of nanostructured layered silicates, various metal complexes and molecular species may densely be immobilized/stabilized on silicate surfaces.

3.5. Doping of heteroelements into the silicate layer

The introduction of heteroelements into silica/silicate framework by the isomorphous substitution of Si is important for the development of catalyst and adsorbent. The doping of heteroelements (Al^{3+} , Ti^{4+} and Co^{2+}) into the silicate layer (kanemite and magadiite) during the crystallization of the layered silicates has been reported.⁶¹⁻⁶⁶ The Al-containing magadiites (6.4–12.7 sites/ nm^2) had a higher density of surface hydroxyl groups (silanol/aluminols) than magadiite (Al-free, 4.7 sites/ nm^2).⁶⁶ The Al-containing magadiites adsorbed Pb^{2+} and methylene blue efficiently from single/binary-component solutions.

Ti-containing octosilicates and magadiites were successfully prepared by the hydrothermal reactions using TiCl_4 as the Ti source in the starting mixture of magadiite and octosilicate.⁶⁷ Spectroscopic studies (UV-vis absorption and XAFS spectra) suggested that the incorporated Ti was tetrahedrally coordinated with oxygen by

substituting Si in the silicate sheets. The capacity of the framework incorporation of Ti without structural alteration was Si/Ti = 50 and 100 for magadiite and octosilicate, respectively (Figure 6). In the case of the Ti-containing octosilicate (Si/Ti = 50), Ti existed as a tetrahedrally coordinated species together with octahedrally coordinated species. In addition, as the Si/Ti ratio increased (Si/Ti = 10 and 20 for magadiite and octosilicate), the products were not crystalline phases as shown by their XRD patterns. The capacity of the incorporation of Ti into the silicate framework by the isomorphous substitution of Si is higher for the silicates with thicker silicate layers (magadiite > octosilicate, Table 1).

The applications of the layered silicates doped with heteroelements as the precursor of porous materials are worth investigating further. Novel materials' design by the functionalization through the ion exchange and grafting will be done.

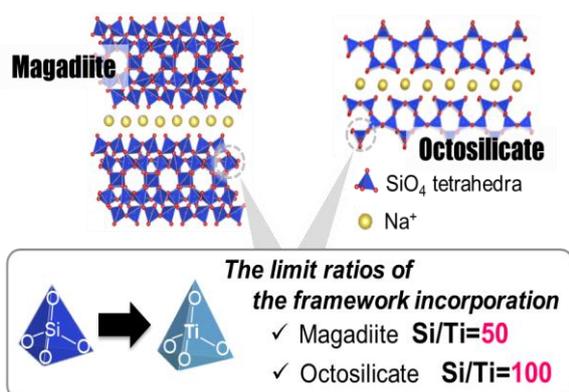


Figure 6. Schematic drawing of isomorphous substitution of Si with Ti in the silicate layers. Reprinted with permission from ref (67). Copyright (2022) American Chemical Society.

4. Conclusion and future perspective

The preparation, the reactivity for ion exchange, the grafting, and the isomorphous substitution of layered alkali silicates were summarized to show the present status of the chemistry, the function and the application of their intercalates/hybrids. Using the reactivity of silanol groups on the surface of layered silicates, a wide variety of metal ions, metal complexes, metal oxide/sulfide compounds, and metallic nanoparticles have been immobilized. The isomorphous substitution of Si^{4+} in the frameworks of layered silicates with other metal cations, such as Al^{3+} and Ti^{4+} , has been used to obtain novel functional layered silicates.

The functionalization of the interlayer space, external surface and silicate framework of layered silicates with inorganic elements has been reported and the conversion of the heteroelements doped layered silicates into porous structures such as zeolites, mesoporous silicas, and pillared layered structures is worth investigating further.

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