



Review Article

Inorganic modification of layered silicates toward functional inorganic-inorganic hybrids

Thipwipa Sirinakorn (Tip)^a, Kamonnart Imwiset (Jaa)^a, Sareeya Bureekaew^b, Makoto Ogawa^{b,*}^a School of Molecular Science and Engineering, Vidyasirimedhi Institute of Science and Technology (VISTEC), 555 Moo 1 Payupnai, Wangchan, Rayong 21210, Thailand^b School of Energy Science and Engineering, Vidyasirimedhi Institute of Science and Technology (VISTEC), 555 Moo 1 Payupnai, Wangchan, Rayong 21210, Thailand

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Dedicated to the official retirement of Professors Eduardo Ruiz-Hitzky and Christian Detellier

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ABSTRACT

After careful investigation on the formation/preparation, the structures and the reactivity of a class of layered alkali silicates (kanemite, makatite, octosilicate, magadiite and so on) in 1960–80', the applications of the layered silicic acids and the alkaline metal silicates have extensively been investigated. The applications of these layered silicates range from the ion exchanger, adsorbent, catalyst and catalysts' support, bio-related one and so on. For the construction of functional nanomaterials, host-guest reaction has been applied to optimize materials performances as well as to find new functions. The functionalization of layered silicates with various organic functional groups has been investigated extensively and summarized in several review papers. In this review article, the functionalization of the layered alkali silicates and the silicic acids derived from with inorganic species will be summarized in order to highlight the present status of the materials chemistry on layered alkali silicates and their hybrids with inorganic species toward the practical application.

1. Introduction

Layered alkali silicates (including kanemite, octosilicate, makatite, magadiite and kenyaite) are a class of hydrated layered silicates composed of silicic acid layer (with different layer thickness) and the charge compensating (neutralizing) interlayer alkaline cations. Fig. 1 shows examples of the layered alkali silicates with some characteristic features. The preparation, characterization and application of the layered alkali silicates has been summarized in the following review articles (Schwieger and Lagaly, 2004; Ruiz-Hitzky et al., 2011; Selvam et al., 2014; Homhuan et al., 2017b). Some of the layered alkali silicates such as magadiite and kenyaite are found in nature (Eugster, 1967). However, if compared with bentonite (Bergaya et al., 2006), the available amount is limited and not enough for the industrial application. Not only for the practical application, but also for the fundamental understanding on the formation (crystallization from liquids), their preparation in the laboratory have been done so far (Iler, 1964; Wolf and Schwieger, 1979; Beneke and Lagaly, 1983; Fletcher and Bibby, 1987; Kosuge and Tsunashima, 1995; Iwasaki et al., 2006; Wang et al., 2006; Ma et al., 2013). Thanks to the successful syntheses of the layered alkali silicates in the laboratory, the crystal structures were carefully characterized using several instruments such as X-ray diffraction (Brindley, 1969; Borbely et al., 1991; Apperley et al., 1995; Almond et al., 1997; Vortmann et al., 1997; Borowski et al., 2007) and NMR (Schwieger

et al., 1985). The reactivity of the layered alkali silicates, especially for the formation of layered silicic acids by the acidic treatment, has been investigated using the layered silicates synthesized in the laboratory (Lagaly et al., 1975a, 1975b; Lagaly, 1979; Rojo et al., 1988; Schwieger and Lagaly, 2004).

Due to the structural characteristics (nanosheet nature with the reactivity of the surface silanol groups), the functionalization of the layered alkali silicates by intercalating guest species has been reported extensively. Cation exchange with various metallic, organic and organometallic cations has been reported for the functionalization of the layered silicates (Kim et al., 1997). Among reported functions of host-guest systems, photofunctional intercalation compounds of layered silicates have been prepared by intercalating functional dye cations (Ogawa et al., 2001a, 2001b; Ogawa, 2002, 2004; Okada et al., 2017). The ion exchanged layered silicates have also been used as precursor or scaffold for constructing porous pillared layered silicates (Sprung et al., 1990; Landis et al., 1991; Dailey and Pinnavaia, 1992b; Kim et al., 2012a). Transformation of layered silicates to three dimensional porous materials has been reported so far. The conversion of layered silicates to zeolites by solid-state reactions as well as hydrothermal treatment (Shimizu et al., 1996; Pal-Borbely et al., 1998) has been done extensively. Preparation of mesoporous silicas from kanemite through the ion exchange with cationic surfactant is another well-known approach for the functionalization of a layered alkali silicate (Yanagisawa et al.,

* Corresponding author.

E-mail address: makoto.ogawa@vistec.ac.th (M. Ogawa).

	Structure	CEC
Kenyaite $\text{Na}_2\text{Si}_{22}\text{O}_{45} \cdot 10\text{H}_2\text{O}$		1.36 meq/g
Magadiite $\text{Na}_2\text{Si}_{14}\text{O}_{29} \cdot 9\text{H}_2\text{O}$		2.0 meq/g (pH=10)
Octosilicate $\text{Na}_8[\text{Si}_{32}\text{O}_{64}(\text{OH})_8 \cdot 32\text{H}_2\text{O}]$		2.8 meq/g
Kanemite $\text{NaHSi}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$		4.7 meq/g

Fig. 1. The examples of layered alkali silicates and their characteristics.

1990a; Inagaki et al., 1993).

The host-guest reactions (or modifications) are required to achieve (or optimize) materials' performances for several applications. In addition, thanks to the reactivity of the silanol groups, which is located in the interlayer space, organic functional groups have been attached in the interlayer space covalently (grafting) through the condensation reactions of the silanol groups with chlorosilanes, alkoxy silanes and alcohols. Both the cation exchange reactions of interlayer alkali ions with organic cations, namely cationic surfactants, (Lagaly, 1986; Lagaly and Beneke, 1991; Ogawa and Iwata, 2010) and the grafting of the silanol groups on the silicate layer with silane coupling reagents (Ruiz-Hitzky and Rojo, 1980; Ruiz-Hitzky et al., 1985; Ogawa et al., 1998a, 1998b; Takahashi and Kuroda, 2011) have been utilized for further functionalization (Wang and Pinnavaia, 1998; Isoda et al., 2000; Fujita et al., 2003, 2005; Yukutake et al., 2009; Ide et al., 2012; Nakamura and Ogawa, 2012; Ide et al., 2013; Vieira and Pastore, 2014; Li et al., 2017; Mao et al., 2017) of the layered silicates. Thus, the host-guest reactions of the layered silicates have been investigated extensively using several cationic molecular species as guest or covalent modification with various organic and inorganic functionalities (Okada et al., 2012, 2015; Ogawa et al., 2014). Thanks to the exfoliation of silicate layer by the interaction with tetrabutylammonium hydroxide, which was originally developed for the exfoliation of layered titanates and niobates, (Keller et al., 1994; Sasaki et al., 1996; Osada and Sasaki, 2009; Ma and Sasaki, 2015), bulky and non-cationic species has been complexed to give layered host-guest materials by re-stacking from the exfoliated nanosheet (Chen et al., 2013).

In the present review article, the studies on the functionalization of layered alkali silicates with inorganic species (metallic ions and inorganic nanoparticles) will be summarized in order to highlight the present status and future possibilities of the host-guest reactions of

layered alkali silicates as a method to obtain functional inorganic-inorganic hybrids. The conversion of layered silicates to porous silica/silicates including zeolite and dense silica by the thermal or hydrothermal reactions will be also introduced as a way of functionalization of layered silicates.

2. Ion exchange for the collection of target ions from environments

2.1. Procedures of the preparation of hybrids from layered alkali silicates

Protons of the interlayer silanol groups are exchanged with alkali ions, the cation exchange capacity of the layered alkali silicates is strongly pH dependent (Lagaly, 1979). Protons compete with other cations at $\text{pH} < 7$, leading the transformation of the silicates to the silicic acids. The careful spectroscopic examination on the nature of the cation exchange sites has been done (Rojo et al., 1988; Schwieger and Lagaly, 2004). Taking this fact into consideration, cation exchange reactions of layered alkali silicates with various inorganic and organic cations have been reported. Intercalation of cation (ion exchange) into layered silicates is conducted by the following processes; the powder of silicate is mixed with an aqueous solution of guest and the mixture is allowed to react at room temperature (with mixing) for several hours (or days). Solid sample is separated by centrifugation or filtration, and is used for the structural and compositional characterization. Grafting of the interlayer silanol group is done through two procedures; one is the reaction with organosilicone compounds from dehydrated and solvated silicic acid (Ruiz-Hitzky and Rojo, 1980) and the other is from organoammonium-exchanged silicate (Okutomo et al., 1999).

For the characterization of the obtained inorganic-inorganic hybrids, X-ray powder diffraction (XRD), infrared (IR) and Raman

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