TOPICAL REVIEW

Geomaterials: their application to environmental remediation

Hirohisa Yamada¹, Kenji Tamura¹, Yujiro Watanabe², Nobuo Iyi¹ and Kazuya Morimoto³

¹ Environmental Remediation Materials Unit, National Institute for Materials Sciences, Namiki 1-1, Tsukuba 305-0044, Japan
² Advanced Materials Science Research and Development Center, Environmental Research Institute, Kanazawa Institute of Technology, Yatsukaho 3-1, Hakusan, Ishikawa 924-0838, Japan
³ Department of Functional Material Science, Graduate School of Science and Engineering, Ehime University, Bunkyo-cho 2-5, Matsuyama 790-8577, Japan
E-mail: YAMADA.Hirohisa@nims.go.jp

Received 31 July 2011
Accepted for publication 12 October 2011
Published 28 December 2011
Online at stacks.iop.org/STAM/12/064705

Abstract
Geomaterials are materials inspired by geological systems originating from the billion years long history of the Earth. This article reviews three important classes of geomaterials. The first one is smectites—layered silicates with a cation-exchange capacity. Smectites are useful for removing pollutants and as intercalation compounds, catalysts and polymer nanocomposites. The second class is layered double hydroxides (LDHs). They have an anion-exchange capacity and are used as catalysts, catalyst precursors, sorbents and scavengers for halogens. The third class of geomaterials is zeolites—microporous materials with a cation-exchange capacity which are used for removing harmful cations. Zeolite composites with LDHs can absorb ammonium and phosphate ions in rivers and lakes, whereas zeolite/apatite composites can immobilize the radioactive iodine. These geomaterials are essential for environmental remediation.

Keywords: apatite, geomaterial, LDH, remediation, smectite, zeolite

1. Introduction

On 11 March 2011, a 9.0-magnitude earthquake occurred off the east coast of Japan; it triggered a 10-m-high tsunami that swept away everything in its path. The Earth’s geological system is dichotomous: natural disasters such as earthquakes and tsunami represent its negative side, but it also has many positive aspects that originate from the 4.6 billion year history of the Earth. It has produced mild climates, beautiful landscapes, and many natural resources and minerals. Over 14,000 minerals have been identified in and on the Earth. Each mineral has a unique chemical composition and structure that may impart it with interesting properties and functions. One of the important functions of geological materials is environmental purification and remediation. In this review, we introduce three classes of geomaterials that have the potential to solve environmental problems. The first class is smectites—layered clay minerals possessing a cation-exchange capacity. The second class is layered double hydroxides exhibiting an anion-exchange capacity, and the third class is zeolites that have a nanoporous structure and a cation-exchange capacity. We describe their applications in various mineral-related industries, as well as their crystal structures and other properties relevant to nanotechnology.

2. Smectite

2.1. Basic properties

Smectite is one of the major components of clays and clay minerals [1–4]. Smectite has a layered structure that is similar to that of mica, a phyllosilicate mineral. Its atomic structure
is responsible for its plasticity and hardening and is the origin of its unusual properties for inorganic materials, such as the ability to react with organic compounds through intercalation, ion exchange, absorption and catalytic reactions. The various technological applications of smectite are closely related to its basic properties.

The smectite crystal structure consists of an octahedral sheet sandwiched between two opposing tetrahedral sheets (figure 1). The SiO$_4$ tetrahedron, in which Si$^{4+}$ is coordinated to four O$^{2-}$, is linked to adjacent tetrahedra by sharing three corners to form an infinite two-dimensional sheet with a hexagonal network structure. In the octahedral sheet, each octahedron (e.g. AlO$_6$ or MgO$_6$) is connected to neighboring octahedra by sharing edges. The edge-shared octahedra form a sheet of hexagonal or pseudo-hexagonal symmetry. The net charge of the smectite layer is negative owing to the isomorphous substitution of Si$^{4+}$ in the tetrahedral sheet with Al$^{3+}$ or that of Al$^{3+}$ in the octahedral sheet with Mg$^{2+}$. To neutralize the net negative charge, the exchangeable cations are present between two tetrahedral sheets facing each other.

2.2. Removal of metals using the cation exchange property of smectite

Vast amounts of metals are used in daily life and large quantities of harmful waste are produced in metallurgical processes. Acidic mine waste containing harmful metals (e.g. cadmium, copper, zinc, lead, mercury, etc) may occasionally contaminate the underground and natural streams. Therefore, it is necessary to clean up polluted rivers and lakes, and implement regulations for the disposal of metal-containing waste.

In the smectite structure, the cations in the interlayer space can easily be exchanged, and this high cation-exchange capacity can be used to absorb metals from wastewater [5–7]. Therefore, the interactions between smectite and various metals in solution have been investigated for evaluating environmental impact. The retention of metal ions in smectite can be controlled by factors such as the surface charge, surface area, pH, temperature, ionic concentration, ion strength and the amount of metals [8, 9].

2.3. Smectite intercalation compounds

Intercalation here refers to the incorporation of organic molecules and organic and inorganic cations between the layers of clay minerals. Smectite intercalation compounds are produced by several processes, including the displacement of water molecules in the interlayer space by polar organic molecules, the formation of interlayer cation–neutral organic ligands complexes, and the exchange of interlayer cations with various organic cations [10–13]. Cationic dyes and complexes are functional optical materials exhibiting nonlinear optical effects, photochemical hole burning, fluorescence and photoisomerization [14–23]. Other important smectite intercalation compounds are clay polymer nanocomposites, which are discussed in section 2.5.

2.4. Catalytic properties of smectites

Smectite clay minerals are used as catalysts and catalyst supports because they have relatively high surface areas and abundant surface acid sites [24, 25]. Smectites containing transition metal ions can be tailored for specific catalytic applications [26]. For example, synthetic Ni-substituted saponite clay is an efficient catalyst for the selective dimerization of ethane [27]. The catalytic behavior of hectorite-like smectites containing Ni in the lattice has been investigated for the decomposition of 2-propanol [28]. Iron-containing smectites have been widely used in catalytic degradation [29–31], catalytic reduction [32, 33], organic synthesis [34, 35] and other processes.

Pillared clays can provide a large surface area and pore volume after the cation exchange of polynuclear hydroxyl-cation species between layers followed by calcination [36]. Pillared clays have also been used for preparing heterogeneous metal complex—clay hybrid catalysts [37, 38]. Pillared clays with ceramic pillars of nanometer size in the interlayer space have micro- and mesoporous structures similar to those of zeolites. They are also nanohybrid materials with a high thermal resistance owing to the silicate nanolayers.

The photodegradation of the organic dyes, rhodamine B (Rhb), rhodamine 6G and a stilbazolium derivative, is significantly enhanced in an aqueous suspension of Mg-substituted smectite [39]. The hybridization of organic dyes with approximately 1-nm-thick exfoliated smectite has been reported to accelerate photodegradation. Moreover, smectites containing iron degrade the cationic organic dyes, RhB and malachite green, by employing H$_2$O$_2$ as an oxidant under visible light; however, they are inactive to anionic dyes [40]. It has been concluded that the photocatalytic originates from the iron species in the smectites, and that the adsorption of the dyes on the negatively charged smectite is essential for the photoreaction to occur.
Figure 2. Dispersion conditions of a layered silicate in a nanocomposite: (a) well-stacked intercalated layered silicate with polymer chains, (b) partially exfoliated layered silicate-polymer nanocomposite and (c) completely exfoliated layered silicate-polymer nanocomposite.

2.5. Polymer-clay nanocomposites

Novel functional composite materials have been studied in recent years with the aim of developing new engineering technologies. To improve various material properties such as strength, stiffness, corrosion resistance, surface finish, weight and fatigue, two or more substances are combined at microscopic and macroscopic scales. Of particular interest are recently developed nanocomposites that consist of a polymer and a layered silicate, as they often exhibit remarkably improved mechanical and other properties as compared with those of pure polymers or conventional micro- and macro-composites. These nanocomposites are organic–inorganic hybrid materials, where the inorganic filler has at least one dimension of the nanometer size. The filler is typically a clay mineral that belongs to a family of layered silicates (such as montmorillonite). The nanoscale dispersion of the clay within the polymer matrices leads to tremendous interfacial contacts between the organic and clay phases. This results in an interfacial material with a completely different morphology and superior properties to those of the bulk polymer. The following subsections describe specific types of nanocomposites that have been prepared from layered silicates.

2.5.1. Morphology. Layered silicate-polymer nanocomposites are generally classified according to their levels of intercalation and exfoliation (figure 2). At one end of this classification scheme are well-ordered and stacked multilayers [41, 42]. These consist of polymer chains intercalated between the host layers. At the other end are exfoliated silicate layers in a continuous polymer matrix. Some exfoliated layered silicate-polymer nanocomposites have already been used in practical applications because of their acceptable rigidity, strength and barrier properties while having a much lower silicate content than that in conventional composites filled with other minerals [43, 44]. Three main methods have been used for the preparation of these nanocomposites, namely, solvent intercalation, in-situ polymerization and melt blending. However, melt processing has attracted the most interest [44–46] because it is generally considered more economical and flexible for formulation, and it involves compounding and fabrication facilities commonly used in industry. For most purposes, complete exfoliation of the silicate platelets, i.e. separation of the platelets from one another and their individual dispersion in the polymer matrix, is the desired goal of the formation process. During exfoliation, the layered silicate not only becomes much smaller but also the shape changes simultaneously from rigid platelets to thin, flexible nanolayers. The shape of a layered silicate platelet is usually expressed by its aspect ratio (lateral length to thickness ratio, figure 3). Large aspect ratios of the dispersed silicate platelets are an important factor in achieving excellent performance from layered silicate-polymer nanocomposites.

2.5.2. Mechanical properties of nanocomposites. In conventional polymer composites, micron-size fillers are added to polymers to enhance their mechanical properties. Such properties are related to the volume fraction, shape and size of the filler particles. Following the pioneering work of Toyota researchers on a nylon 6-clay nanocomposite in the early 1990s [43, 47, 48], well-exfoliated nanocomposites have been produced in various nylons [44, 49–51], polystyrene [52], certain polyimides [53], polypropylene [54–57], polylactide [58, 59] and epoxies [60–62]. These studies showed that the improvement in the mechanical performances of nanocomposites mainly originated from the nanosize dimensions of silicates (as this results in an extremely large aspect ratio) and from strong polymer–filler interactions that might affect the effectiveness of the load transfer between the silicate layers and polymer matrix.

Figure 4 shows the specific rigidities of three different nylon 66 (PA66) composites: nylon 66 containing a distearyl(dimethylammonium-modified synthetic expandable fluoromica (DSDMA-SEFM) (a), a talc-filled nylon 66 composite (b) and a glass-fiber-reinforced nylon 66 (so-called FRP) (c) [44]. The DSDMA-SEFM nanocomposite has high rigidity and is significantly lighter than conventional FRP [63]. Figure 5 shows transmission electron microscopy (TEM) images of nylon 6 composites containing DSDMA-SEFM (a) and DSDMA-modified synthetic smectite
2.5.3. Gas permeability. Gas permeability strongly depends on the diffusion of the gas through the polymer and can therefore be significantly affected by the nanomorphology as illustrated in figure 6. Various barrier models have been proposed to predict the permeability of composites containing dispersed platelets [64–68]. These models usually assume a random spatial arrangement of platelets oriented perpendicular to the permeation direction. At a high aspect ratio, which can be achieved in nanocomposites (such as these with an exfoliated silicate layer), a significant decrease in permeability has been predicted and observed in practice.

Figure 7 shows the time dependence of the steady-state permeability of neat nylon and nanocomposite films to methanol vapor at 40 °C, indicating a significantly enhanced barrier property in the nanocomposites. The nanocomposites were characterized by a larger decrease in permeability with increasing silicate content, which suggests that the path must follow a more convoluted path during its movement through the polymer [67, 69]. The permeability decreased with both the level of exfoliation and the amount of silicate layer loading, i.e. the corresponding nanocomposites exhibited enhanced barrier properties. These results can be attributed to the improved dispersion of the silicate nanolayers inside the nylon 6 matrix, which obstruct the path of methanol molecules.

Some previous barrier models [64–68] were based on longer diffusive paths along which a gas must travel due to the presence of a filler. According to these models, the reduction of permeability should depend on the quantity of filler, its aspect ratio, and the orientation of the platelets. The effect of the nanoplatelets on the free volume and the interfacial regions was also emphasized by positron annihilation lifetime spectroscopy (PALS) measurements [70]. The common feature in all the models is the dependence of the relative permeability on the volume fraction, aspect ratio, free volume and the fraction of interfacial regions, and all these predictions have been verified by experiments.

2.5.4. Flame resistance. The reduced flammability of polymer nanocomposites is not yet fully understood. Gilman et al demonstrated that the presence of exfoliated silicate significantly improves the fire retardancy of...
polymeric matrices such as polypropylene, polystyrene and polyamides [71–74]. According to their research, the associated mechanism should involve both physical and chemical processes. Several effects have been observed that may help explain this fire retardancy, the major ones being the barrier effect and catalytic effects for charring reactions.

During the thermal degradation of nanocomposites, the barrier effect of dispersed silicate layers may reduce the rate of mass loss by retarding the escape of volatile decomposition products outside the degrading material. The layered silicates also have a twofold catalytic effect on the thermal degradation of the organic constituents. Carbon–carbon bond scission is accelerated by the silicate layer when the temperature is increased in an inert atmosphere (thermal degradation), and this competes with the acceleration of carbon–hydrogen bond scission in the presence of oxygen (thermal oxidation). While thermal degradation often produces volatile materials, the multilayered carbonaceous-silicate structure may act as an excellent insulator and mass transport barrier, slowing the escape of the volatile products generated during decomposition.

The reduced flammability upon nanofiller addition is not evident in some of the more common fire performance tests (Underwriter Labs (UL) 94, ASTM flammability tests). In specific cases (e.g. the nylon 66 system) the silicate nanolayers can result in reduced flammability rating due to the melt viscosity increase preventing dripping as a mechanism of flame extinguishment (change UL94 rating from V-2 (vertical mounted) to HB (horizontal mounted)). In such cases, the addition of a small amount of flame retardant enabled the system to pass the fire performance test [44].

2.5.5. Nanocomposites using non-traditional layered silicates. Smectites, which are commonly used in polymer-based nanocomposites, are only one type of the many layered silicates. For example, micaceous clay minerals and mica minerals have a higher negative layer charge than smectites. Their interlayer K+ ions are believed to be non-exchangeable because they are strongly bound to the interlayer surfaces [75, 76]. For these reasons, micaceous clay minerals and mica minerals have not been used in nanocomposites. If their silicate layers could be exfoliated, the aspect ratio of the individual layers would greatly exceed that of smectites. Recently, new polymer nanocomposites of this type have been prepared using a conventional polymer process [77, 78]. These nanocomposites were based on a natural potassium sericite—a common type of mica with the composition (K0.77Na0.03)(Al1.67Fe0.18Mg0.10)(Si3.24Al0.76)O10(OH)2. Figure 8 shows TEM images of the initial (a) and organically modified (b) sericite/epoxy nanocomposites [77], revealing silicate nanolayers with extremely high aspect ratios—dozens to hundreds of times greater than those in conventional exfoliated clay-polymer nanocomposites. This property should be useful for applications. Other new composite systems may extend the field of high-performance materials beyond traditional applications to encompass unexpected new functionalities. It is important, not only from the viewpoint of materials development but also for environment, to elucidate the exfoliation behavior of non-expandable layered silicates and to apply them in nanotechnology.

3. Layered double hydroxides

3.1. Basic properties

Layered double hydroxides (LDHs) are anionic clays and a class of layered materials with the ideal formula $\left[M^{3+}_{n/2-x}M^{3+}_{x}(OH)_2\right]^+\left[A^{m-n}_{n/2}mH_2O\right]$, where $M^{2+}$ is a divalent metallic ion, $M^{3+}$ is a trivalent ion and $A^{m-}$ is an anion with a valence of $n$ [79–82] (figure 9). Their structure consists of positively charged brucite-like layers sharing edges with $M^{2+}(OH)_6$ and $M^{3+}(OH)_6$ octahedral. Partial $M^{2+}$ to $M^{3+}$ substitution imparts the layers with a positive charge, which is compensated by the exchangeable interlayer anions, which are usually hydrated. The anions in the interlayer have a valence of $n$ (e.g. Cl–, NO3–, CO3– and carboxylic acids); their substitution is possible and depends on the type of anion. Hydrotalcite is a typical LDH, which is why LDHs are also referred to as hydrotalcite-like compounds.

The interlayer anions in LDHs are exchangeable in the following order of preference: $\text{NO}_3^- < \text{Br}^- < \text{Cl}^- < \text{F}^- < \text{OH}^- < \text{SO}_4^{2-} < \text{CrO}_4^{2-} < \text{HAsO}_4^{2-} < \text{HPO}_4^{2-} < \text{CO}_3^{2-}$.
[83–85], indicating the strong affinity of carbonate anions. This order presumably depends on charge, charge density and hydrogen bonding. The selectivity for divalent anions is higher than that for monovalent anions. LDHs with nitrate and chloride anions in the interlayer space are the best precursors for exchange reactions. It is thus very important from a materials science perspective to eliminate the carbonate anions, as discussed in the next section. The interlayer anions can be exchanged for other inorganic or organic anions, thus imparting new functionalities to the LDH. LDHs have been used as catalysts and catalyst precursors, as sorbents and scavengers for halogens and weak acids [86, 87], and, more recently, for storing and delivering biologically active materials [88]. They might also be capable of removing phosphates from water [89–91].

3.2. Decarbonation of carbonate-type LDHs

Among the LDHs containing various anions, LDHs containing interlayer carbonate ions (CO$_3^{2-}$)LDHs) are most common in industry, and the well-crystalline CO$_3^{2-}$LDHs can be easily prepared. However, because of the high affinity of CO$_3^{2-}$ for LDHs, it is very difficult to deintercalate CO$_3^{2-}$ by anion exchange. Consequently, CO$_3^{2-}$ LDHs have not been used as the starting material for preparing LDH compounds containing other anions. Considering that most industrial LDHs contain carbones, conversion of CO$_3^{2-}$LDHs into anion-exchangeable LDHs is an important process in LDH chemistry.

3.2.1. Reconstruction method. The removal of carbonate ions from LDHs, i.e. decarbonation, has been conducted by the ‘reconstruction method’, in which a CO$_3^{2-}$LDH is calcined at 500–600 °C [82]. Because the LDH structure changes at these temperatures, decarbonation proceeds not via anion exchange. The original LDH structure can be restored by incorporating certain anions via the reaction of the calcined product with an aqueous solution containing the anions [82, 92, 93]. This method is convenient and therefore was frequently used. However, it is reported that repeated heat treatment damage the crystallinity of the restored LDHs [94]. Furthermore, the restoration process is not necessarily topotactic, but involves dissolution and recrystallization and therefore cannot fully recover the original crystal shape [95, 96]. Thus, it is difficult to obtain LDHs containing various anions with a controlled crystal size and high crystallinity by the reconstruction method.

3.2.2. Acid–salt decarbonation method. From the early LDH studies, HCl and other inorganic acids were used for decarbonation [97, 98]. A CO$_3^{2-}$ LDH is decarbonated with the acid to give an LDH containing an anion which is a conjugated base of the acid. However, dissolution of the LDH layer results in a significant weight loss before attaining complete decarbonation. We reported that the addition of Cl$^-$ anion to the inorganic acid (HCl) improves the decarbonation reaction [99, 100]: Using aqueous HCl/NaCl mixed solution, CO$_3^{2-}$ are deintercalated from CO$_3^{2-}$LDH to yield Cl$^-$LDH without any weight loss or shape change under optimum conditions. This reaction is in a sense anion exchange under acidic condition, and it is topotactic. The obtained Cl$^-$LDHs can be subjected to a further ion exchange. Since the reaction can be conducted at room temperature and is very fast, this could be a convenient way for obtaining anion-exchangeable LDHs. However, complete decarbonation was observed only for Cl$^-$ and Br$^-$, whereas other anions such as NO$_3^-$ and ClO$_4^-$, which have lower affinity to LDHs, showed only partial exchange even at a very high concentration of the salt (about 8 M) [100]. Even for Cl$^-$, a NaCl concentration as high as 3 M was required for complete decarbonation. Because of the strong acidity of HCl and low tolerance of MgAl–LDHs to acids, the HCl/LDH ratio should be strictly controlled to avoid the LDH dissolution.

3.2.3. Acetate buffer–salt method. Subsequently we proposed a modified acid–salt method, in which an acidic buffer solution, i.e. the acetate buffer solution composed of acetic acid and sodium acetate, was used in place of HCl in the NaCl/HCl mixed solution. The acetate buffers supply protons needed for decarbonation while the pH remains almost unchanged at about 5.0–5.5. In this buffer/salt solution, a lower concentration (1 M) of NaCl was enough for complete decarbonation [101]. The LDHs did not dissolve under this pH condition and the acetate anion (AcO$^-$) was not incorporated in the LDH interlayer in the presence of a large amount of Cl$^-$. The acetate buffer alone could not decarbonate the LDHs; however, decarbonation of the LDHs was attained by adding NaCl, and because the anion selectivity for AcO$^-$ is much lower than Cl$^-$, the obtained product was Cl$^-$/LDH. The optimum conditions for decarbonation of the LDHs are: NaCl concentration above 1 mol L$^{-1}$, acetate buffer concentration 0.05–0.25 M, reaction time 3 min or longer. The decarbonation proceeds at room temperature (~25 °C).

These experiments were conducted in closed vials; however, a recent study demonstrated that under N$_2$ flow, a much lower concentration of NaCl was enough for the decarbonation [102]. By conducting the acetate-buffer decarbonation under N$_2$ flow, the conversion of CO$_3^{2-}$/LDH into ClO$_4^-$ and NO$_3^-$LDH became possible. The ClO$_4^-$ and NO$_3^-$LDHs are much more anion-exchangeable than Cl$^-$/LDHs, and are useful as the intermediates for a further anion exchange.

3.2.4. Mechanism of decarbonation. A possible mechanism of decarbonation of CO$_3^{2-}$/LDH using an acid/NaCl solution can be expressed as follows [99, 102]:

$$\text{H}^+(\text{aq}) + \text{Cl}^-(\text{aq}) + [\text{CO}_3^{2-}]\text{(LDH)} \leftrightarrow [\text{HCO}_3^-\text{, Cl}^-]\text{(LDH)}.$$  

(1)

$$[\text{HCO}_3^-, \text{Cl}^-]\text{(LDH)} + \text{H}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \leftrightarrow [2\text{Cl}^-]\text{(LDH)} + \text{H}_2\text{O} + \text{CO}_2(\text{aq})\text{.}$$  

(2)

Here, (aq) indicates aqueous solution phase; (gas), gas phase; and (LDH), interlayer space of LDH. Acetate ions are not
LDH, and a higher [CO$_2$] and CO$_2$Nakayama of their chemistry. of various decarbonation techniques would provide the on its acidity. acidic compounds with ammonium salt and hydrochloride salts of amines [103] found that decarbonation is much easier a ClO$_3$ and NO$_3$; LDH are much more anion-exchangeable than Cl$^-$. These experiments were conducted in closed vials; however, our recent research demonstrated that under N$_2$ flow, a much lower concentration of NaCl was enough for the decarbonation [102]. By conducting the acetate-buffer decarbonation under N$_2$ flow, the conversion of CO$_3^{2-}$LDH into ClO$_3$ and NO$_3$;LDH became possible. The ClO$_3^-$ and NO$_3^-$;LDH are much more anion-exchangeable than Cl$^-$.LDH, and are useful as the intermediates for a further anion exchange.

3.2.5. Decarbonation in non-aqueous mediums. Anion exchange in hot glycerol was reported in [103]. Recently, a DMF–ethanol mixture was applied to CO$_3^{2-}$LDH [104], which caused not only decarbonation but also successive delamination. Furthermore, the carbonate ion was replaced by carboxylate via the action of carboxylic acid on CO$_3^{2-}$LDH in 1-propanol/toluene mixed solvent under solvothermal conditions [105]. These methods are not as versatile as the decarbonation in aqueous systems. However, Hayashi and Nakayama [106] found that decarbonation is much easier in alcohol than in water. They reported that CO$_3^{2-}$LDH with Mg/Al = 3 could be decarbonated to give Cl$^-$.LDH in NaCl/methanol at 50 ℃ within 3 h. We also found that CO$_3^{2-}$LDH was decarbonated in HClO$_4$/methanol solution at room temperature under N$_2$ flow, and the reaction was completed within 0.5–1 h [107, 108]. The amount of HClO$_4$ needed for decarbonation was 1.0–2.0 times the amount of CO$_3^{2-}$ in LDH ($f = [\text{H}^+]/(2[\text{CO}_3^{2-}]) = 1.0–2.0$). No appreciable dissolution of LDH occurred and no change in the Mg/Al ratio was detected up to $f = 8$. In contrast to the decarbonation in aqueous medium, the addition of ClO$_4^-$ salts is not necessary for decarbonation of LDHs in methanol. Other acids such as HCl, HNO$_3$ [107, 108], and even less acidic compounds with $pK_a$ values in the range of 0–12 such as ammonium salt and hydrochloride salts of amines [109] can also be used, though resistance of LDHs to acid depends on its acidity.

Thus, decarbonation and anion exchange in non-aqueous mediums warrant further investigation. The development of various decarbonation techniques would provide the foundation for application of LDHs and future development of their chemistry.

![Figure 10. Photodegradation of methyl orange (MO) and MO/LDHs monitored as normalized absorbance versus UV irradiation time [112].](image)

3.3. Catalytic activity of LDHs

LDHs have been attracting considerable attention as catalytic materials owing to their solid basicity [86] and ability to be modified by various polyacids [92]. Furthermore, mixed oxides formed by the calcination of LDHs can function as solid-base catalysts for many organic reactions. Thermally decomposed LDHs containing transition metal ions such as nickel, iron and copper have been particularly investigated as catalyst precursors [110–113].

Recently, attempts have been made to immobilize or stabilize functional species, such as fluorescent anions of methyl orange and xanthene dyes, by intercalation into LDHs. In addition, a photocatalytic LDH complex has been prepared by the intercalation of sulfonated indolinespirobenzopyran. To realize photocatalysts, polyoxometalate and semiconductor particles, such as TiO$_2$, ZnS and CdS, were immobilized in the interlayer space of LDHs. However, few studies [113, 114] have addressed the photocatalytic behaviors of LDHs in regard to organic substances. Patzko et al. [115] evaluated the photocatalytic properties of a calcined Zn–Al LDH intercalated with ZnO. Phenol [114] and/or 2,4 dichlorophenoxycetic acid [116] were photocatalytically degraded using calcined Mg–Zn–Al and Zn–Al–Fe LDHs, respectively. The photodegradation of a methyl orange dye on an untreated Zn–Al LDH was investigated, but the sample was contaminated by a ZnO phase during the synthesis [113], and thus the photocatalytic properties of uncalcined LDHs remain unclear.

Uncalcined LDHs have been studied for their degradation of dyes under ultraviolet (UV) irradiation [117, 118], particularly the decomposition of methyl orange, fast green and sulforhodamine B over Mg–Al-based LDHs and Zn–Al-substituted LDHs with different Zn/Al molar ratios. The photodegradation rates were monitored using an absorption spectrometer. Dyes decomposed faster in dye–LDH solid films than in pure films (figure 10). This result indicates the important role of LDH materials containing sensitized dyes in enhancing the generation of labile hydroxyl.
ions at the hydrophilic LDH surface. LDHs have both adsorption and degradation capabilities for anionic pollutants and can degrade very stable compounds such as phenol. Furthermore, LDHs are stable, economical, easy to prepare and are functional materials under ambient conditions. They can be reused after the reconstruction of calcined LDHs in organic anion solutions. Hence, the use of dye–LDH complexes for the removal of aqueous anionic contaminants is envisaged.

4. Zeolites and their composites

4.1. Basic properties

Zeolites are unique environmental remediation materials mainly composed of hydrated aluminosilicates. The aluminosilicate portion of the structure is a two- or three-dimensional open framework consisting of a network of AlO₄ and SiO₄ tetrahedra. The tetrahedra are linked by shared oxygen atoms. Zeolites have periodic, molecular size pores and channels, high specific surface areas and cation-exchange ability. Harmful cations such as ammonium, cadmium and lead ions, and molecules such as formaldehyde, benzene and toluene can be absorbed in the channels and pores of zeolites [119].

Table 1 lists the maximum ammonium ion-exchange capacities of two natural zeolites (clinoptilolite and mordenite) and three synthetic zeolites (RHO, LTA and FAU zeolites). Ammonium ion-exchange experiments were performed by the following procedure: 30 ml of ammonium chloride solutions with ammonium concentrations ranging from 1 × 10⁻⁴ to 3 × 10⁻² M were added to 0.1 g of the zeolites in polyethylene tubes. The tubes were shaken at 30 rpm at 25 °C for 7 days, and the obtained suspensions were filtered with a 0.45 μm membrane filters. The ammonium concentrations of the filtered solutions were determined using an ammonium-ion-specific electrode.

The measured ammonium ion-exchange capacities were higher than those of other materials, with the best results obtained for synthetic rather than natural zeolites. Most of these results can be explained in terms of the cation-exchange capacity (CEC) but not the CEC difference between the LTA (7.0 mmol g⁻¹) and FAU zeolites (6.4 mmol g⁻¹). The selectivity is higher for the FAU zeolite when the ammonium ion exchange exceeds 10%. The open pores of FAU zeolite (0.74 nm) are larger than those of LTA zeolite (0.42 nm), and

| Zeolite     | Cation exchange capacity (mmol/g) | Maximum pore size (nm) | Maximum ammonium ion exchange capacity (mmol g⁻¹) | Reference |
|------------|----------------------------------|------------------------|-----------------------------------------------|-----------|
| Clinoptilolite | 2.6                              | 0.72                   | 1.35                                          | [1]       |
| Mordenite  | 2.6                              | 0.70                   | 1.05                                          | [1]       |
| RHO        | 3.1                              | 0.36                   | 1.65                                          | [2]       |
| LTA        | 7.0                              | 0.42                   | 2.56                                          | [2]       |
| FAU(X)     | 6.4                              | 0.74                   | 3.20                                          | [2]       |

4.2. Zeolite/LDH composites

As mentioned in the previous section, LDHs have a high anion-exchange capacity. Harmful anions such as phosphate, arsenic and nitrate ions can be absorbed in the interlayers of LDHs [121–123].

We focused on preparing multifunctional composites with adsorption properties, which can be used to simultaneously remove harmful cations and anions. Thus we synthesized zeolite/LDH nanocomposites by precipitating a Mg₆Al₂(OH)₁₆Cl₂ LDH on a synthetic zeolite combined with a hydrothermal treatment as follows [124,125]. Aqueous solutions of magnesium and aluminum chloride hexahydrates were mixed together at a molar Mg/Al ratio of 3 while stirring at room temperature; the concentrations of the components in the starting solutions were 0.03 and 0.01 M, respectively. Then 50 ml of the homogeneous solution was added dropwise to 100 ml of a 1 × 10⁻³ wt% LTA or FAU zeolite suspension at pH of 10, which was adjusted using a 0.03 M NaOH solution. The suspensions were subsequently aged at room temperature for 24 h, placed in a Teflon cup fitted in a stainless-steel pressure vessel, and heated in an oven at 150 °C and autogenous pressure for 24 h. After cooling to room temperature, the product was filtered using a 0.45-μm membrane filter, washed with deionized water, and dried at 50 °C in an oven.

Figure 11 shows scanning electron microscope (SEM) images of LTA and FAU zeolites before and after hydrothermal treatment ((b) LTA, (d) FAU). They are also considerably larger than the ammonium ion diameter (0.29 nm); therefore, physical ammonium adsorption was maintained in the equilibrium state. The ammonium ion exchange activity of these zeolites is dependent on their open-pore sizes and CEC [120].
crystals 100–150 nm in diameter and 15 nm thick. The crystal morphology was very similar to that of a typical LDH (figure 11(b)). The molar Mg/Al ratio of the platy particles was about 3.0, which is typical for an LDH. The crystal structures of both zeolites were not altered by the hydrothermal treatment.

The adsorption of ammonium and phosphate ions on the obtained zeolite/LDH composites was studied in aqueous solutions. Ammonium and phosphate ion adsorption experiments were performed as follows: 30 ml of 0.001 M ammonium chloride solution and 0.001 M phosphate solution were added to 0.1 g of the samples in polyethylene tubes. The tubes were shaken at 30 rpm at 25 °C for 24 h. The suspensions were filtered using 0.45 μm membrane filters. The ammonium and phosphate concentrations of the filtered solutions were determined using an ammonium-ion-specific electrode and inductively coupled plasma atomic emission spectroscopy (ICP-AES), respectively. Table 2 shows the amounts of adsorbed ammonium and phosphate ions on the LTA–LDH and FAU–LDH nanocomposites. These composites adsorbed both ammonium and phosphate ions and can be used for removing them from rivers and lakes.

### Table 2. Ammonium ion and phosphate ion-exchange capacities of LTA zeolite, LDH, and LTA–LDH and FAU–LDH nanocomposites

|          | Ammonium ion exchange capacity (mmol/g) | Phosphate ion exchange capacity (mmol/g) | Reference |
|----------|----------------------------------------|----------------------------------------|-----------|
| LTA–LDH  | 1.80                                   | 0.72                                   | [3]       |
| FAU–LDH  | 1.10                                   | 0.83                                   | [3]       |
| LTA      | 1.77                                   | 0.40                                   | [3]       |
| LDH      | 0.10                                   | 1.41                                   | [3]       |

4.3. Zeolite/apatite composites

Hydroxyapatite (HA) [Ca_{10}(PO_{4})_{6}(OH)_{2}] has a very low solubility product of less than 1 × 10^{-100} and is particularly stable in alkaline solutions [126]. These properties make it very useful as a coating material for enhancing the solution stability of other materials and as a matrix for the long-term immobilization of harmful ions and molecules. Several researchers have grown HA crystals on wollastonite, alite and LDH surfaces for biological and medical applications [127–129]. We have also prepared HA nanocrystals on zeolite surfaces using the calcium ions at the ion exchange sites of zeolites for the long-term immobilization of radioactive ions and molecules [130–133]. Zeolites have periodic, molecular-sized pores and channels. They have high specific surface areas and cation-exchange capability. In particular, LTA zeolite is an efficient adsorbant of radioactive iodine and strontium. We have developed a long-term immobilization method for radioactive iodine molecules and strontium ions using a zeolite/apatite composite [134, 135]. This section describes the long-term immobilization method for iodine using zeolite/apatite composites.

An HA coating on I_{2}-doped LTA zeolite (I_{2}-zeolite A) was obtained as follows: 2.0 g of I_{2}-zeolite A was immersed in 200 ml of a 1 M (NH_{4})_{2}PO_{4} solution at pH 9.5 in a sealed Teflon bottle (500 ml). The suspension was then heated at 80 °C for 8 h. The resulting samples were filtered using a 0.45 μm membrane filter, rinsed with distilled water three times to remove excess cations, and dried at 100 °C for 24 h.

Figure 12 shows SEM images of I_{2}-zeolite A before and after HA coating. In both cases, cubic automorphisms (figures 12(a) and (b)) and about 200-nm-long needle-like HA crystals (figures 12(c) and (d)) are evenly distributed on the surface. These structures were formed in an ion exchange reaction of calcium ions on LTA with ammonium ions in the ammonium phosphate solution, followed by a reaction between the calcium ions and phosphate ions on the LTA surface. Thus, neither iodine adsorption nor HA coating affected the morphology of zeolite A. From the selected-area energy-dispersive x-ray (EDX) spectrum, the Ca/P ratio of HA was calculated to be 1.67, which is the same as the nominal HA composition. HA crystal growth proceeded in a similar manner on Ca-zeolite A and I_{2}-zeolite A.

The thermal stability of iodine adsorbed into zeolite A was evaluated using a combination of mass spectrometry and thermogravimetry/differential thermogravimetric analysis (TG-DTA). The TG-DTA curve and mass spectra are, respectively, shown in figures 13(a) and (b) for the I_{2}-zeolite and in figures 13(c) and (d) for the I_{2}-zeolite after HA coating. The weight of the I_{2}-zeolite A decreased by 22.3% upon heating from room temperature to 1300 °C. The broad endothermic peak at 150 °C is attributed to adsorbed water in the zeolite A cavities and the exothermic peaks at 923 and 1036 °C are due to the formation of amorphous and feldspar phases, respectively [119].

Iodine was removed from the zeolite cavities upon heating from 50 to 450 °C, as confirmed by the m = 127 peak in the mass spectrum (figure 13(b)). This elimination temperature is lower than the sintering temperature. However, the elimination behavior of iodine molecules from I_{2}-zeolite A with the HA coating is completely different, except for the weight loss of 23.3% and the vaporization of water with an endothermic peak at 183 °C. The elimination of N_{2} from
Zeolite A was confirmed by the $m = 14$ peak in the mass spectrum that appeared upon heating from 150 to 600 °C and above 950 °C, with two exothermic peaks at 973 and 1050 °C (figures 13(c) and (d)). The N$_2$ removal in the temperature range 150–600 °C is attributed to the elimination of NH$_3$ from NH$_2$-zeolite A cavities. This occurred during the formation of amorphous phase as revealed by x-ray diffraction (XRD). The evolution of N$_2$ upon heating to 950 °C is probably due to the amorphous phase on the zeolite A surface acting as an effective barrier, and the elimination of N$_2$ at 1223 °C is due to the phase change to feldspar.

The removal of iodine from zeolite A at 980 °C was confirmed via the $m = 127$ mass spectrum peak, and a weight loss of 3.8% was observed above 980 °C with two endothermic peaks at 1159 and 1209 °C (figures 13(c) and (d)). The broad exothermic peak at 892 °C is due to complete amorphization and that at 980 °C is due to the formation of feldspar (figure 13(c)), as confirmed by XRD. Thus, the elimination of iodine occurred during crystallization.

A three-component sintered body consisting of I$_2$-zeolite A, an HA nanolayer, and hydroxyfluorapatite (HFA) was fabricated at 950 °C by pulsed electric current sintering (PECS) method [136–138]; it had a relative density of up to 98.1±2.2%, which was calculated by considering the HFA/zeolite weight ratio. The sintered body was brown owing to the retained iodine (figure 14(I)). In contrast to the previously reported results, no breaking or cracking was observed during the sintering, probably owing to the presence of the HA nanolayer. Figure 14(II) shows a scanning TEM (STEM) image of the boundary region between the three

Figure 13. TG-DTA curves and mass spectra for the I$_2$-zeolite before (a, b) and after coating with HA (c, d), respectively (reproduced with permission from [134] ©2009 ACS Publications).

Figure 14. Three-component sintered body of I$_2$-zeolite A, HA nanolayer and HFA. Photograph (I), STEM image of the boundary region between the three components (II) and EDX analysis of the HFA matrix (III) (reproduced with permission from [134] ©2009 ACS Publications).
components. The grain size in the HFA matrix is smaller than 300 nm, which is typical for the PECS method, and results in high sinterability. EDX analysis of the HFA matrix revealed the absence of silicon and aluminum (figure 14(III-a)). A unique nanolayer structure at the interface between the HFA matrix and I$_2$-zeolite was clearly observed, and chemical analysis in this region indicated the presence of small amounts of silicon and alumina, were clearly detected by EDX as shown in figure 14(III-c). Iodine was also clearly detected from the regions of dark contrast in figures 14(II), (III-c) and (III-d).

The iodine content in the sintered body (weight ratio of HFA to I$_2$-zeolite A after HA coating= 15 : 85) was 0.51 ± 0.03 wt%, indicating that more than 99% of the iodine was retained. Upon sintering at 1000°C the iodine content decreased to 67%. Furthermore, iodine was removed by heating an I$_2$-zeolite without an apatite coating in a two-component (I$_2$-zeolite A and HFA) sintering process. Thus, zeolite/apatite composites are very useful for the long-term immobilization of radioactive iodine and other radioactive ions and molecules in reprocessing plants for nuclear fuel.

5. Conclusions

The development of environment-friendly materials is essential to solve the global environmental problems. By mimicking the minerals developed during the 4.6 billion year history of the Earth, we have produced geomaterials that have perfect circulation and high functionality with the minimum load on the environment.

Here we reviewed three groups of excellent geomaterials, smectites, LDHs and zeolites. Smectites are useful for removing harmful waste, as functional catalysts, for catalyst support, and as polymer nanocomposites. Novel synthesis methods for anion-exchangeable LDHs have been developed and their application in catalysis has been investigated. Zeolites and their composites with LDHs or apatite are useful for wastewater treatment and radioactive waste control. Geomaterials should help solve the environmental problems through their environmental purification and remediation capabilities. Their ability to remove radioactive substances from water and soil is potentially useful for radioactive contaminated sites such as the Fukushima No. 1 nuclear power plant.

References

[1] Brindley G W and Brown G 1984 *Crystal Structures of Clay Minerals and their X-ray Identification* (London: Mineralogical Society).
[2] Bailey E S 1988 *Hydrous Phyllosilicates (Exclusive of Micas)* (Washington, DC: Mineralogical Society of America).
[3] Velde B 1992 *Introduction to Clay Minerals* (London: Chapman and Hall).
[4] Bergaya F, Theng B K G and Lagaly G 2006 *Handbook of Clay Science* (Developments in Clay Science 1) (Amsterdam: Elsevier).
[5] Sparks D L 1999 *Soil Physical Chemistry* (Boca Raton, FL: CRC Press).
[6] Triantafyllou H, Christodoulou S E and Neou-Syngouna P 1999 *Clays Miner.* 47 567.
[7] Wypych F and Satyanarayana K G 2004 *Clay Surfaces: Fundamentals and Applications* (Amsterdam: Elsevier).
[8] Echeverria J C, Churio E and Garrido J J 2002 *Clays Miner.* 50 614.
[9] Miranda-Trevino J C and Coles C A 2003 *Appl. Clay Sci.* 23 133.
[10] Auerbach S M, Carrado K A and Dutta P K 2004 *Handbook of Layered Materials* (New York: Marcel Dekker).
[11] Ogawa M and Kuroda K 1995 *Chem. Res.* 95 399.
[12] Ogawa M, Handa T, Kuroda K and Kato C 1990 *Chem. Lett.* 19 71–4.
[13] Ogawa M, Hagiwara A, Handa T, Kato C and Kuroda K 1995 *J. Porous Mater.* 1 85.
[14] Ogawa M, Fuji K, Kuroda K and Kato C 1991 *Mater. Res. Soc. Symp. Proc.* 233 89.
[15] Ogawa M, Kimura H, Kuroda K and Kato C 1996 *Clay Sci.* 10 57.
[16] Ogawa M, Ishii T, Miyamoto N and Kuroda K 2001 *Adv. Mater.* 13 1107.
[17] Okada T and Ogawa M 2002 *Chem. Lett.* 31 812.
[18] Okada T and Ogawa M 2003 *Chem. Commun.* 1378.
[19] Okada T, Watanabe Y and Ogawa 2005 *J. Mater. Chem.* 15 987.
[20] Tagaki S, Shimada T, Matsui D, Tachibana H, Ishida Y, Tryk D A and Inoue H 2010 *Langmuir* 26 4639.
[21] Nagase T, Takahashi Y, Suzuki T M, Ebina T, Wakui Y and Onodera Y 2002 *Chem. Lett.* 8 776.
[22] Okada T, Ehara Y and Ogawa M 2006 *Chem. Lett.* 35 638.
[23] Lutsch B V and Ozin G A 2008 *Adv. Mater.* 20 4079.
[24] Theng B K G 1974 *The Chemistry of Clay–Organic Reactions* (London: Adam Hilger).
[25] Laszlo P 1987 *Preparative Chemistry using Supported Reagents* (New York: Academic).
[26] Brown D R and Rhodes C N 1997 *Catal. Lett.* 45 35.
[27] Urabe K, Koga M and Izumi Y 1989 *J. Chem. Soc. Chem. Commun.* 807.
[28] Nishiyama Y, Arai M, Guo S, Sonohara N, Naito T and Torii K 1993 *Appl. Catal.* A 95 171.
[29] Guelou E, Barrault J, Fournier J and Tatibouët J M 2003 *Appl. Catal. B* 41 41.
[30] Guelou E, Barrault J, Fournier J and Tatibouët J M 2003 *Appl. Catal. B* 41 41.
[31] Guelou E, Barrault J, Fournier J and Tatibouët J M 2003 *Chem. Lett.* 107 126.
[32] Belver C, Vicente M A, Fernández-García M and Martínez-Arias A 2004 *J. Mol. Catal. A* 219 309.
[33] Elsner M, Schwarzenbach R P and Haderlein S B 2004 *Environ. Sci. Technol.* 38 799.
[34] Varma R S 2002 *Tetrahedron* 58 1235.
[35] Varma R S, Naicker K P and Liesent P J 1998 *Tetrahedron Lett.* 39 3977.
[36] Yamanaka S and Makita K 1995 *J. Porous Mater.* 1 29.
[37] Ramaswamy V, Krishnan S M and Ramasamy A V 2002 *J. Mol. Catal. A: Chem.* 181 81.
[38] Yagi M and Narita K 2004 *J. Am. Chem. Soc.* 126 8084.
[39] Tani S, Yamaki H, Sumiyoshi A, Suzuki Y, Hasegawa S, Yamazaki S and Kawamata J 2008 *J. Nanosci. Nanotech.* 8 1.
[40] Cheng M, Song W, Ma W, Chen C, Zhao J, Lin J and Zhu H 2008 *Appl. Catal. B: Environ.* 77 355.
[41] Giannelis E P 1994 *Adv. Mater.* 8 29.
[42] Paul D R and Robeson L M 2008 *Polymer* 49 3187.
[124] Yamada H, Watanabe Y, Hashimoto T, Tamura K, Ikoma T, Yokoyama S, Tanaka J and Moriyoshi Y 2006 J. Eur. Ceram. Soc. 26 463
[125] Yamada H, Tamura K, Tanaka J, Ikoma T, Moriyoshi Y, Watanabe Y and Hashimoto T 2005 Japan Pat. Pend. 2005-263596
[126] Moreno E C, Kresak M and Zaharadnik R T 1974 Nature 24 64
[127] Liu X Y and Ding C X 2002 Mater. Lett. 57 652
[128] Liu X Y, Ding C X and Wang Z Y 2001 Biomaterials 22 2007
[129] Moriyoshi Y, Chiba Y, Monma H and Ikegami T 2000 Trans. Mater. Res. Soc. Japan 25 1143
[130] Watanabe Y, Moriyoshi Y, Hashimoto T, Suetsugu Y, Ikoma T, Kasama T, Yamada H and Tanaka J 2004 J. Am. Ceram. Soc. 87 1395
[131] Watanabe Y, Ikoma T, Suetsugu Y, Yamada H, Tamura K, Komatsu Y, Tanaka J and Moriyoshi Y 2006 J. Eur. Ceram. Soc. 26 469
[132] Watanabe Y, Ikoma T, Yamada H, Tamura K, Komatsu Y, Tanaka J and Moriyoshi Y 2004 Phosph. Res. Bull. 17 174
[133] Watanabe Y, Ikoma T, Yamada H, Tanaka J and Komatsu Y 2010 J. Ion Exch. 21 294
[134] Watanabe Y, Ikoma T, Yamada H, Suetsugu Y, Komatsu Y, Moriyoshi Y, Stevens G W and Tanaka J 2009 ACS Appl. Mater. Interfaces 1 1579
[135] Watanabe Y, Miwa Y, Ikoma T, Yamada H, Suetsugu Y, Tanaka J, Moriyoshi Y and Komatsu Y 2010 J. Ceram. Soc. Japan 118 1044
[136] Watanabe Y, Ikoma T, Monkawa A, Suetsugu Y, Yamada H, Tanaka J and Moriyoshi Y 2005 J. Am. Ceram. Soc. 88 243
[137] Gu Y W, Loh N H, Khor K A, Tor S B and Cheang P 2002 Biomaterials 23 37
[138] Nakahira A, Tamai M, Aritani H, Nakamura S and Yamashita K 2002 J. Biomed. Mater. Res. 62 550