Reactivity and applications of layered silicates and layered double hydroxides

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Layered materials, such as layered sodium silicates and layered double hydroxides (LDHs), are well-known for their remarkable adsorption, intercalation and swelling properties. Their tunable interlayers offer an interesting avenue for the fabrication of pillared nanoporous materials, organic–inorganic hybrid materials and catalysts or catalyst supports. This perspective article provides a summary of the reactivity and applications of layered materials including aluminium-free layered sodium silicates (kanemite, ilerite (RUB-18 or octosilicate) and magadiite) and layered double hydroxides (LDHs). Recent developments in the use of layered sodium silicates as precursors for the preparation of various porous, functional and catalytic materials including zeolites, mesoporous materials, pillared layered silicates, organic–inorganic nanocomposites and synthesis of highly dispersed nanoparticles supported on silica are reviewed in detail. Along this perspective, we have attempted to illustrate the reactivity and transformational potential of LDHs in order to deduce the main differences and similarities between these two types of layered materials.

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1. Introduction

Layered materials are a widespread class of inorganic solids which can be found not only in laboratories and man-made products but occur foremost in nature in the form of clays.^{1,2} They are responsible for the quality of our soil, especially for

the storage of water and fertilizers. In this respect, the naturally occurring layered silicates, clays and clay-like materials are the basis of our life. Scientifically, these materials are well-known for their remarkable adsorption, intercalation and swelling properties.^{3–5} Such properties pave the way for their use as functional materials like fillers in polymer nanocomposites,^{6–8} drug release systems or adsorbents in environmental protection applications.^{9,10} In addition, their tunable interlayers offer an interesting avenue for the fabrication of pillared nanoporous materials,¹¹ organic–inorganic hybrid materials¹² and catalysts or catalyst supports.^{13,14}

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Fig. 1 Schematic illustration of different layered materials.

The variety of layered structures is huge from the chemical point of view,³ but their common feature is at least the two-dimensional crystal extension with a similar bonding type and strength along these layers, whereas the third crystal direction is characterised by a different kind of bonding or interactive strength, resulting in a special reactivity in the third crystal dimension. In particular, most layered materials exhibit a regular alternation of anionic or cationic (bulk) layers interrupted by interlayers hosting the charge balancing ions, which are mostly solvated by water molecules. Typical representatives

are layered silicates, layered double hydroxides (LDHs), layered aluminium phosphates and clay minerals, whose structures and building units are depicted in Fig. 1. While layered aluminium phosphates and clay minerals are made up of a combination of metal tetrahedra and octahedra, layered silicates and LDHs are representatives for layered materials which contain exclusively metal tetrahedra and octahedra as the primary building units, respectively.

In the present review the reactivity and applications of layered materials will be discussed with a special focus on Al-free layered silicates and layered double hydroxides (LDHs) as typical examples of cationic and anionic layered materials made up exclusively of metal tetrahedra and octahedra, respectively. Note that layered zeolites (2D),^{15–17} which have nowadays become an important class of layered materials, fall outside the scope of the present review. The essential difference between the classical layered silicates and the ‘novel’ layered zeolites lies in the porosity of their layers. While layered zeolites exhibit a pore-like structure already in the layer itself, layered silicates (as well as LDHs) do not possess such porosity. Layered silicates (as well as LDHs) would actually become dense materials if the interlayer space would be removed without pillaring or an additional structural transformation.

The main characteristics of layered silicates and layered double hydroxides are summarized in Table 1. While metal (silicon) oxide tetrahedra in layered silicates are well-known for their excellent reactivity as building units for the development of ordered porous 3D SiO₂ networks, the metal hydroxide octahedra in LDHs are not known for such reactivity. Accordingly,

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Table 1 Important characteristics of layered silicates and layered double hydroxides (LDHs)

Characteristics	Layered silicates	Layered double hydroxides (LDHs)
Composition	$M_{2/n}^{n+}O \cdot xSiO_2 \cdot yH_2O^a$	$[M_{1-w}^{2+}M_w^{3+}(OH)_2]^{w+}(A_{w/n}^{n-}) \cdot mH_2O^b$
Primary building units	Tetrahedra	Octahedra
Building blocks	$[Si_nO_{2n+2}]_{\infty}^{4-}$	$[M(OH)_2]_{\infty}$
Layer thickness	~ 0.49 – 1.12 nm	~ 0.47 nm
Layer charge	Negative	Positive
Thermal stability	300 – 400 °C	~ 200 °C
Catalytic applications	Acid-catalysed	Base-catalysed

^a M^n = protons or cations with charge n , x = between 2 and 40 and y = between 1 and 20. ^b M^{2+} , M^{3+} = di-/trivalent metal cation, $w = M^{3+}/(M^{2+} + M^{3+})$ molar fraction (typically between 0.2 and 0.4), A^{n-} = charge balancing interlayer anion with charge n , m = amount of interlayer water molecules (approximately 150).

we would like to give an update on recent developments in the use of layered sodium silicates as precursors for the preparation of various materials including zeolites, ordered mesoporous materials, pillared layered silicates, organic–inorganic nanocomposites and the synthesis of highly dispersed nanoparticles supported on silica. Additionally, in order to depict the similarities and differences between these different groups of layered materials, the reactivity and transformational properties of layered double hydroxides are reviewed and finally summarized in a comparative conclusion.

2. Reactivity and applications of layered silicates

2.1. Layered silicates

Among the layered sodium silicates, kanemite, ilerite (RUB-18 or octosilicate) and magadiite are the most widely investigated, and their characteristics are summarized in Table 2. Kanemite ($NaHSi_2O_5 \cdot 3H_2O$) is a layered sodium silicate, which consists of single silicate sheets alternating with hydrated Na sheets (Fig. 2a).^{18–20} The local structures and dynamics of interlayer Na cations and water have also been studied by solid-state 1H -, ^{29}Si - and ^{23}Na -NMR.²¹ The interlayer water is present in two different states (bound as well as free) in kanemite, as revealed by quasi-elastic neutron scattering (QENS), thermogravimetry

Fig. 2 Structures of: (a) kanemite and (b) ilerite (RUB-18 or octosilicate).^{27,28,31}

(TG) and 2H -NMR measurements.²² It has also been found by 2H -NMR T_1 relaxation study that the hydrated water in kanemite is in the solid state (icelike) at room temperature.²³ Moreover, the existence of Si–O–Si linkages with a bond angle near

Table 2 Some of the important synthetic layered silicates and their characteristics

Layered silicates	Composition	Basal spacing (nm)	Proposed structural feature	Reference
Kanemite	$NaHSi_2O_5 \cdot 3H_2O$	1.0	Single layers of SiO_4 tetrahedra	18–20
Ilerite (RUB-18 ^a or octosilicate)	$Na_2Si_8O_{17} \cdot 9H_2O$	1.1	Four five-membered rings; thickness of double layers of SiO_4 tetrahedra	27,28,31
Magadiite	$Na_2Si_{14}O_{29} \cdot 11H_2O$	1.5	Triple layers of SiO_4 tetrahedra	31 ^b

^a RUB-18 (Ruhr-University of Bochum 18). ^b The exact crystal structure of Na-magadiite is not known yet, however, it is believed that magadiite contains triple layers of SiO_4 tetrahedra.

180° and six-membered rings of SiO₄ tetrahedra in kanemite is also shown by vibrational (IR and Raman) spectroscopic studies.²⁴ A layered octosilicate (Na₂Si₈O₁₇·9H₂O) was first synthesized by R. K. Iler in 1964.²⁵ Later such a layered octosilicate (chemical molar ratio SiO₂/Na₂O = 8) was named as ilerite to honour the findings of Iler.²⁶ Note that the structure of ilerite-like material was resolved by Gies and coworkers, and hence it is called RUB-18 (Ruhr-Universität-Bochum-18).^{27,28} The basic building unit of the RUB-18 consists of four five-membered ring [5⁴] cages, which is similar to the building unit of MFI and MOR type zeolites. Fig. 2b shows the structure of ilerite, which is composed of two silicate sheets alternating with hydrated Na sheets, instead of one as in the case of kanemite (Fig. 2a). Although the layered character and the swelling behaviour of Na-magadiite (Na₂Si₁₄O₂₉·11H₂O) are well documented in the literature, the exact crystal structure of Na-magadiite is not yet known. Nevertheless, on the basis of various diffraction (XRD) and spectroscopic techniques (NMR, IR and Raman), it has been assumed that each silicate layer in Na-magadiite may consist of three silicate sheets with a combination of five- and six-membered rings.^{29,30}

All these layered silicates (kanemite, ilerite, and magadiite)^{31–34} can be synthesized under conventional hydrothermal synthesis conditions using various silica sources, sodium hydroxide and water. SEM images of these layered sodium silicates are shown in Fig. 3. Kanemite is composed of crystallites (2–5 μm) with an irregular plate-like morphology (Fig. 3a), whereas ilerite crystallites (Fig. 3b) exhibit nearly a perfect square shaped plate-like morphology. The SEM image of the magadiite sample shows the typical lamellar morphology and aggregates of large spheres (8–10 μm) with a cauliflower-like morphology. Recently, the synthesis and characterization of various isomorphously substituted layered silicates including Al-, Ga- and Ti-kanemite,^{35–37} Al- and Sn-ilerite,^{38,39} and Al-, Mn-, Co- and Sn-magadiite^{40–45} have also been reported.

During the past decade, several research groups have focussed on the synthesis and characterization of aluminium-free layered sodium silicates.^{31,46} They possess high purity and a high ion-exchange capacity and were found to be stable both under acidic and basic conditions. They provide interesting alternatives to the different forms of silica, such as precipitated silica, fumed silica and silica gel. In particular, owing to the presence of interlayer sodium ions, layered sodium silicates are currently under increased investigation for the development of a large variety of novel intercalation complexes and/or compounds, organic–inorganic nanocomposites, polymer–inorganic nanocomposites with a unique combination of properties.⁴⁷ In addition to fundamental intercalation studies, intercalated layered silicates are being investigated for important applications, for example, selective adsorption of Zn²⁺ from seawater⁴⁸ and highly selective adsorption of CO₂.⁴⁹ Moreover, they are well-suited for use as precursors for the synthesis of various materials including novel layered silicates,^{50,51} pillared layered silicates,^{52,53} already known and new zeolites⁵⁴ and mesoporous materials.^{55–57} Fig. 4 depicts the

Fig. 3 SEM images of: (a) kanemite, (b) Na-ilerite and (c) Na-magadiite.

possibilities for the preparation of various advanced functional and catalytic materials using layered sodium silicates as precursors.

2.2. Transformation of layered silicates into zeolites

Zeolites are microporous crystalline aluminosilicates with uniform pores (pore size < 2 nm) and cavities of molecular dimensions, which have found application in various industrial (ion-exchange, adsorption, separation and catalytic) processes.⁵⁸ They are mainly synthesized from a synthesis gel containing silica, alumina, alkali cations, organic template (optional) and water under hydrothermal conditions at 80–200 °C.⁵⁹ During the past few decades, there has been a growing activity in the area of zeolite synthesis using layered sodium silicates as precursors. The types of zeolites that have been synthesized *via* solid-state, hydrothermal, topotactic condensation and solvothermal methods using layered sodium silicates as precursors are summarized in Table 3. As can be

Fig. 4 Preparation pathways of various materials using layered sodium silicates as precursors.

Table 3 Synthesis of various types of zeolites using layered silicates as precursors

Layered silicate	Template	Method	Zeolite	Reference
Kanemite	TPAOH, ^a TBAOH ^b	Solid-state	Silicalite-1, Silicalite-2	60–62
Kanemite	TPAOH	Solid-state	Al-MFI	63
Kanemite	TPAOH	Solid-state	Cu-, Co-Silicalite-1	64
Kanemite ^c	Piperidine	Solid-state	FER	65
Kanemite	TEAOH ^d	Hydrothermal	BEA	66
Kanemite	TEAOH	Solid-state	BEA	67
RUB-18 ^e	Triethylenetetramine	Topotactic condensation	RUB-24 (RWR)	54,68
RUB-18	TMAOH ^f	Topotactic condensation	RWR	69
Octosilicate ^e	Acetic acid	Topotactic condensation	RWR	70
RUB-18	—	Hydrothermal	MOR	71
Magadiite ^c	TPAOH, TBAOH	Hydrothermal	MFI, MEL	72
Magadiite ^c	Piperidine	Solid-state	FER	73
Magadiite	Ethylenediamine	Hydrothermal	FER	74
Magadiite ^c	TEAOH	Solid-state	Al- and B-BEA	75,76
Magadiite	TPABr, ^g TPAOH	Hydrothermal	Silicalite-1	77
Magadiite ^h	TPAOH	Hydrothermal	Mn-Silicalite-1	43
Magadiite	TPAOH	Hydrothermal	Co-Silicalite-1	78
Magadiite ⁱ	TPABr, TEAOH	Hydrothermal	Co-ZSM-5, Co-BEA	44
Magadiite	—	Hydrothermal	MOR	79,80
Magadiite	Cyclohexylamine	Hydrothermal	MOR	81
Magadiite	TABr ^j	Hydrothermal	OFF, MOR, MFI	82,83
Magadiite	Mononitrogen surfactants	Hydrothermal	MFI-nanosheets	84
Magadiite	Glycerol	Solvothermal	Omega (MAZ)	85

^a Tetrapropylammonium hydroxide. ^b Tetrabutylammonium hydroxide. ^c Al-containing. ^d Tetraethylammonium hydroxide. ^e RUB-18, octosilicate and ilerite are identical materials. ^f Tetramethylammonium hydroxide. ^g Tetrapropylammonium bromide. ^h Mn-containing. ⁱ Co-containing. ^j Tetraalkylammonium bromide (TEABr, TPABr and TBABr).

seen, numerous zeolite types can be synthesized using kanemite, RUB-18/octosilicate and magadiite as precursors. In 1996, Kiyozumi and co-workers introduced a solid-state method for the synthesis of silicalite-1 and silicalite-2 *via* the transformations of kanemite intercalated with tetrapropylammonium (kanemite-TPA) and tetrabutylammonium (kanemite-TBA) cations, respectively.^{60–62} In comparison with the conven-

tional synthesis of zeolites, the main advantages of this method are shorter crystallization time, smaller crystals and a convenient way to prepare binder-free pre-shaped zeolites in different forms (pellets and discs). This method of preparation has been extended to the synthesis of various other zeolite types including Al-MFI,⁶³ Cu- and Co-silicalite-1,⁶⁴ and FER.⁶⁵ In line with the above mentioned studies, we have studied the

transformation of kanemite into large-pore zeolite Beta (BEA) under hydrothermal⁶⁶ as well as solid-state⁶⁷ conditions, using tetraethylammonium hydroxide (TEAOH) as the structure directing and/or intercalating agent. The hydrothermal transformation of kanemite yielded a highly crystalline and phase-pure zeolite Beta but required a high consumption of the relatively expensive template (TEAOH/SiO₂ = 0.35–0.45), whereas the solid-state method required only moderate amounts of TEAOH (TEAOH/SiO₂ = 0.11–0.23).

It is more likely that kanemite tends to dissolve in the presence of alkaline solutions and/or structure directing agents during the hydrothermal transformation process,⁶⁶ and thus creates the conditions necessary for nucleation and crystal growth of zeolite Beta (BEA) *via* a solution-mediated process. Note that zeolite Na-P1 (GIS) was found as an intermediate during the hydrothermal transformation process.⁶⁶ However, an amorphous phase was identified during the initial stages of the solid-state (quasi-hydrothermal) transformation process.⁶⁷ It is imperative to mention here that most of the starting synthesis mixtures for the solid-state transformations of layered silicates into zeolites generally contain a small amount of water, which is necessary for the successful transformation of layered silicate into zeolite.

Topotactic transformations of layered silicates into microporous zeolitic frameworks have been demonstrated for a number of systems.⁵⁴ This type of synthesis strategy has led to the generation of new zeolite structures. For example, Gies and co-workers performed the topotactic condensation of the layered silicate RUB-18 intercalated with triethylenetetramine into RUB-24 (RWR),⁶⁸ which is a new pure silica zeolite with 8-membered ring pore openings. Recently, similar topotactic conversions of RUB-18 and/or octosilicate into RWR-type zeolites using tetramethylammonium hydroxide (TMAOH)⁶⁹ and acetic acid⁷⁰ as the intercalating agents have also been reported. In fact, high-silica mordenite (Si/Al = 14–23) (MOR) has now been prepared by hydrothermal condensation of the RUB-18 using Al[OCH(CH₃)₂]₃ or Na₂Al₂O₄ as the aluminium sources.⁷¹ Additionally, several known zeolites (MFI,⁷² MEL,⁷² FER,^{73,74} Al- and B-BEA,^{75,76} silicalite-1,⁷⁷ Mn-silicalite-1,⁴³

Co-silicalite-1,⁷⁸ Co-MFI and Co-BEA,⁴⁴ MOR,^{79–81} OFF^{82,83}) have been synthesized using the layered silicate magadiite as the precursor and respective structure directing agents (Table 3). In recent years, zeolites such as MFI-type nanosheets⁸⁴ and omega (MAZ)⁸⁵ have been synthesized using magadiite as the precursor under hydrothermal and solvothermal conditions, respectively. Despite intensive research efforts, the application of layered silicates (kanemite, ilerite and magadiite) in the manufacture of zeolites is very limited, even though their potential is considered to be high, for example, zeolite RUB-24 (RWR), which can only be synthesized using a layered silicate RUB-18 as a precursor.

Here it is worth mentioning that the so-called layered zeolites (2D) can also be transformed into 3-dimensional materials including novel zeolite structure types.^{86–90}

2.3. Transformation of layered silicates into ordered mesoporous materials

Ordered mesoporous materials have been extensively studied because of their large, well-defined and controllable pore sizes (2–10 nm), and high surface areas (~1000 m² g^{−1}).⁹¹ They are especially attractive due to their potential applications in different fields, such as adsorption, separation, chromatography, sensor technology, catalysis and drug delivery. These materials are generally synthesized under mild hydrothermal conditions using different silica sources in the presence of long-chain alkyltrimethylammonium halides as structure-directing agents.

The advantages of mesoporous materials derived from layered silicates like kanemite are many, including higher thermal/hydrothermal stabilities due to their quasi-crystalline frameworks and thicker pore walls in comparison with the most extensively studied MCM-41 (hexagonal, *p6mm*)⁹² material. Mesoporous materials derived from layered silicates as precursors are listed in Table 4. Discussion of their synthesis conditions, structures and applications can be found in several review articles.^{55–57}

A typical example of a mesoporous material obtained from a layered precursor is KSW-1⁹³ (mesoporous silica derived

Table 4 Synthesis of mesoporous materials using layered silicates as precursors

Layered silicate	Surfactant	<i>T</i> /°C	pH	Material	BET surface area (m ² g ^{−1})	Reference
Kanemite	C _n TMA ^a	65	8.0–9.0	KSW-1	900	93
Kanemite	C ₁₆ TMACl ^b	70	8.5	FSM-16	1070–1100	94,95
Kanemite	C ₂₂ TMABr ^c	70	8.5	Lamellar	—	96
Kanemite	C ₂₂ TEABr ^d	80	8.5	FSM-16	820	96
Kanemite	C ₁₆ TMACl	50–90	10.4–11.4	Lamellar	—	97
Kanemite	C ₁₆ TMACl	25	4.0–6.0	KSW-2	1192	98,99
Kanemite	C ₁₆ TMACl	25	5.5	Al-KSW-2	830	100
Kanemite ^e	C ₁₆ TMACl	25	6.0	Ti-KSW-2	1047–1211	37
Kanemite	C ₁₆ TMABr ^f	100	10.0–11.8	Al-FSM-16	638–788	101,102
Kanemite ^g	C ₁₆ TMACl	80	8.0–12.0	Mesoporous ^g	—	35
RUB-18 ^h	C ₁₆ TMACl	150	11.5	Mesoporous-plate-like	242	103,104
RUB-18	C ₁₆ TMACl, C ₁₆ TMAOH ⁱ	150	—	Mesoporous-plate-like	150–260	105–107

^a Alkyltrimethylammonium halides (*n* = 12, 14, 16 and 18). ^b Cetyltrimethylammonium chloride. ^c Docosyltrimethylammonium bromide. ^d Docosyltriethylammonium bromide. ^e Ti-containing. ^f Cetyltrimethylammonium bromide. ^g Al- and Ga-containing. ^h RUB-18, octosilicate and ilerite are identical materials. ⁱ Cetyltrimethylammonium hydroxide.

from Kanemite Sheets at Waseda University). It was first synthesized by intercalation of the layered sodium silicate kanemite with long-chain cetyltrimethylammonium (CTMA) ions at 70 °C, followed by adjustment of the pH of the suspension to 8.5 and then calcination of the resulting CTMA-kanemite complex at 550 °C in air. Another example is the FSM-16-type mesoporous silica with a hexagonal array of channels,^{94,95} which is formed *via* layered intermediates composed of fragmented silicate sheets and CTMA ions.⁵⁷ Moreover, lamellar and FSM-16 materials have also been synthesized using docosyltrimethylammonium-kanemite and docosyltriethylammonium-kanemite complexes, respectively.^{96,97} On the other hand, mesoporous silica with square channels (KSW-2)^{98,99} has been obtained by adjusting the pH of the layered CTMA-kanemite complex to a pH of 4.0–6.0 with 1 M acetic acid. The formation mechanism of KSW-2 is different from that found in FSM-16, and proceeds mainly through the bending of individual silicate sheets and subsequent intralayer and interlayer condensation.⁵⁷ Recently, the syntheses of mesoporous Al- and Ti-containing KSW-2 materials with potential applicability in catalysis have also been reported.^{37,100}

We have also synthesized Al-rich FSM-16 materials (Si/Al = 14–226), possessing a slightly disordered hexagonal packing of channels, by treating a mixture of kanemite, cetyltrimethylammonium bromide (CTMABr) and Na-aluminate (pH = 10.7–11.8) at room temperature followed by hydrothermal treatment at 100 °C.^{101,102} Furthermore, Al- and Ga-containing kanemite have been used as precursors for the synthesis of Al- and Ga-containing mesoporous materials³⁵ with potential applicability in heterogeneous catalysis.

Recently, the layered sodium silicate RUB-18 has been successfully used for the synthesis of mesoporous materials with plate-like morphology.^{103–107} One of the main advantages of mesoporous materials obtained from RUB-18 is that they exhibit a plate-like morphology similar to that of the crystalline precursor (RUB-18). In particular, mesoporous materials with a plate-like morphology are attractive for several reasons: shorter diffusion path length, improved mass transport, and changes in selectivity for the desired product, thereby improving the performance of the catalysts. Publications dealing with the preparation of ordered mesoporous materials from the layered silicate magadiite (composed of triple layers of SiO₄ tetrahedra) are scarce, indicating the importance of layered silicates composed of the more flexible SiO₄ single layers (as in the case of kanemite) for the preparation of ordered mesoporous materials.⁵⁷

2.4. Preparation of delaminated/exfoliated layered silicates

In general, it is possible to intercalate/swell and subsequently delaminate/exfoliate all types of layered silicates,¹⁰⁸ irrespective of their layer thickness and layer charge density, *etc.* Nevertheless, several important parameters, such as intercalating/swelling agent, pH and temperature, play a major role for the successful delamination/exfoliation of the layered silicates.¹⁰⁸ Surprisingly, only a few reports on the preparation of delaminated/exfoliated layered sodium silicates (kanemite,

ilerite (RUB-18/octosilicate) and magadiite) are available in the literature. The lack of interest in delamination/exfoliation of layered sodium silicates in comparison with other layered materials could be due to several reasons, for instance, high layer charge density and relatively strong hydrogen bonds between hydrated interlayer cations and silanol groups on the surface.⁴⁷ Despite these limitations, the delamination/exfoliation of magadiite has been sufficiently studied for its potential benefits in the preparation of hybrid organic–inorganic nanocomposites¹⁰⁹ and optically transparent monoliths.¹¹⁰ Moreover, Bi *et al.* have successfully obtained high surface area (microporous/mesoporous) materials^{111–113} *via* an intermediate delamination of magadiite induced by an intercalation of cetyltrimethylammonium bromide (CTMABr) and tetrapropylammonium hydroxide (TPAOH), ultrasonication in water, followed by acidification, drying and calcination. Similarly, recent developments have shown that the exfoliation of layered sodium octosilicate can also be performed by intercalation of 1-butyl-3-(3-triethoxysilylpropyl)-4,5-dihydroimidazolium and didecyldimethylammonium ions, followed by an ultrasonication in water¹¹⁴ and pentane,¹¹⁵ respectively. In spite of these successful reports, the limited interest in research about delaminated or exfoliated aluminium free layered silicates might also be due to their special morphology with relatively large single plates (*e.g.* ilerite) or their aggregation behavior (*e.g.* magadiite) resulting in a reduced applicability as composite materials in polymers. However, there has been considerable work on the preparation of magadiite-based pillared materials, which will be discussed in the forthcoming section.

2.5. Pillaring of layered silicate materials

There is growing interest in pillared materials because of their high surface areas with two levels of porosity (micro and meso) and potential applications as selective gas adsorbents and catalysts.^{116–119} These materials are commonly prepared by the insertion of guest species (inorganic or organic compounds as pillars) into the interlayer space of layered materials through ion-exchange/intercalation/swelling and pillaring processes. Various strategies have been developed during the past few decades to obtain pillared materials with different pore-sizes by modifying the interlayer spaces of layered materials by ion-exchange and intercalation of long-chain surfactants or amine compounds prior to the pillaring process and changing the nature/size of the pillars. In recent years, layered sodium silicates have been widely used as starting materials for the preparation of microporous and mesoporous materials or a combination of both by the pillaring method.

The characteristics and applications of pillared kanemite, ilerite and magadiite are summarized in Table 5. Silica-pillared kanemites have been prepared by intercalation of either dilauryldimethylammonium (C₁₂DADMA; surface area: 1281 m² g^{−1}) or dimethyldipalmitylammonium (C₁₆DADMA; surface area: 1099 m² g^{−1}) ions followed by pillaring with tetraethyl orthosilicate (TEOS) as the silica source.¹²⁰ However, silica-pillared Al-kanemites using dimethyldistearyl ammonium (DMDSA) ions exhibited moderate to high surface areas

Table 5 Preparation of pillared materials using layered silicates as precursors

Layered silicate	Pillars	Intercalating agent	BET surface area (m ² g ⁻¹)	Application	Reference
Kanemite	SiO ₂	C ₁₂ DADMA ^a	1281	—	120
Kanemite	SiO ₂	C ₁₆ DADMA ^b	1099	—	120
Kanemite ^c	SiO ₂	DMSABr ^d	572–756	—	121
Kanemite	—	DMDOACl, ^e DMDSACl ^f	—	Tribology	122
Ilerite ^g	Cu, Zn, CuO/Zn, ZnO/Cu	Octylamine	450–500	Synthesis of dimethyl ether from synthesis gas	123,124
Ilerite	SiO ₂	Octylamine	580–1000	—	125
Ilerite	Si, Ti, Al, Zr	Octylamine	486–728	Epoxidation reaction	126
Ilerite	Ti, Fe, Zr	Octylamine	147–338	—	127
Ilerite	Si, Ta	Octylamine	358–395	Beckmann rearrangement	128,129
	Si/Ta	Octylamine	320–520	—	
Ilerite	Si, Ta, Nb	Octylamine	144–180	Beckmann rearrangement	130
Ilerite	Pt/Ta, Pd/Ta	Octylamine	256–269	Beckmann rearrangement	131
Ilerite	Pt/Nb, Pd/Nb	Octylamine	—	Beckmann rearrangement	132
Magadiite	Ta	Octylamine	155–314	Beckmann rearrangement	133
Magadiite	SiO ₂	Octylamine	480–670	—	134
Magadiite	SiO ₂	Dodecylamine	607–830	—	135
Magadiite	SiO ₂	C ₁₆ TMA ^h	778	—	136
Magadiite	SiO ₂	C ₁₆ TMABr ⁱ	644–753	—	137,138
Magadiite	SiO ₂	Dodecylamine	1057	Partial oxidation of methane	139

^a Dilauryldimethylammoniumbromide. ^b Dimethyl dipalmitylammoniumbromide. ^c Al-containing. ^d Dimethyldistearylammonium bromide.

^e Dimethyldioctylammonium chloride. ^f Dimethyldistearylammonium chloride. ^g RUB-18, octosilicate and ilerite are identical materials.

^h Cetyltrimethylammonium. ⁱ Cetyltrimethylammonium bromide.

(572–756 m² g⁻¹).¹²¹ A recent study shows that kanemite pillared with dimethyldioctylammonium or dimethyldistearylammonium ions is useful for tribological application with a good load-carrying capacity and friction-reducing properties.¹²² Ahn *et al.*^{123,124} demonstrated the synthesis of metal-pillared (Cu and Zn) ilerites using octylamine and metal oxide (CuO and ZnO) modified metal-pillared ilerites by impregnation. It has been shown that the CuO/Zn ilerite catalyst, with a surface area of 450 m² g⁻¹, showed good catalytic activity for the synthesis of dimethyl ether (DME; 89% selectivity) from synthesis gas (CO conversion: 62%). In the past decade, a wide variety of silica¹²⁵ as well as mixed oxide (Si, Ti, Al and Zr;¹²⁶ Ti, Fe and Zr;¹²⁷ Si, Ta and Si/Ta;^{128,129} Si, Ta and Nb;¹³⁰ Pt/Ta and Pd/Ta;¹³¹ Pt/Nb and Pd/Nb¹³²) pillared ilerites have been synthesized using octylamine as the intercalating/swelling agent. In this respect, Kim and coworkers reported that metal oxide pillared ilerites^{128–132} are efficient catalysts for vapor phase Beckmann rearrangement of cyclohexanone oxime (conversion: ~98%) to ϵ -caprolactam (selectivity: 96%). In addition to the above studies, Ta-pillared magadiite was also reported to be highly active for the Beckmann rearrangement reaction.¹³³ Furthermore, silica-pillared magadiites^{134–138} have been reported to possess moderate to high surface areas (Table 5). They are also known to be effective catalysts for the oxidation of methane.¹³⁹

From the viewpoint of the preparation of micro/mesoporous materials by a pillaring process of layered silicates, layered-like zeolite (*e.g.* MCM-22(P)) will also offer an interesting alternative preparation pathway to well-ordered mesopore containing material (*e.g.* MCM-36).^{140–142} Recently, another type of highly ordered layered zeolites, the so-called multilamellar MFI-type

zeolites, have also been pillared by using tetraethyl orthosilicate (TEOS) in order to preserve the ordered structure of the layered zeolites.^{143,144}

2.6. Organic–inorganic nanocomposites from layered silicates

Organic–inorganic nanocomposites with tunable hydrophobicity/hydrophilicity have been extensively studied for their potential applications as adsorbents, ion-exchangers and functional materials.¹⁴⁵ They are also expected to exhibit selective recognition abilities for target molecules due to the controlled spatial distribution of specific functional groups within the interlayers.¹² In general, surfactant-swollen layered sodium silicates are commonly used as intermediates for the preparation of organic–inorganic nanocomposites through various organomodifications (intercalation, grafting, silylation and esterification) of their interlayer silanol groups. In recent years, many investigations have been carried out using the layered sodium silicates kanemite, ilerite (RUB-18 or octosilicate) and magadiite as precursors (Table 6). Takahashi *et al.*¹⁴⁶ prepared poly(oxyethylene)alkyl ether (C_nEO_m) intercalated kanemite (C_nEO_m-kanemite) using cetyltrimethylammonium-swollen kanemite (C₁₆TMA-kanemite) as the intermediate followed by the removal of C₁₆TMA ions by acid (1.0 M HCl) treatment. Such nanocomposites, containing hydrophobic alkyl chains and hydrophilic poly(oxyethylene) (EO) chains, are potentially applicable for the reversible adsorption of *n*-decane and water. Subsequently, Guerra *et al.*¹⁴⁷ reported the organofunctionalization of dimethyl sulfoxide (DMSO) modified kanemite with *N*-propyldiethylenetrimethoxysilane

Table 6 Preparation of organic–inorganic nanocomposites using layered silicates

Layered silicate	Intercalating agent	Functional group	Application	Reference
Kanemite	C ₁₆ TMACl ^a	Poly(oxyethylene) alkyl ether	Adsorption of <i>n</i> -decane and H ₂ O	146
Kanemite	DMSO ^b	<i>N</i> -PDETMSi ^c	Adsorption of uranyl(II) cation	147
		3-APTEOS ^d		
RUB-18 ^e	DAO ^f	—	Proton conductor	148
RUB-18	—	Methoxy	—	149
RUB-18	C ₁₆ TMABr ^g	N ^h , 2N ⁱ , 3N ^j	—	150
RUB-18	C ₁₆ TMABr	N, 3N	Cu-, Ni- and Co-sorption	151
RUB-18	—	N, 3N	Cu-, Ni- and Co-sorption	152
RUB-18	C ₁₆ TMABr	3-Cyanopropyltrichlorosilane	Cu-, Ni- and Co-sorption	153
RUB-18	C ₁₆ TMABr	3-Trimethoxysilylpropylurea	Textile dye removal	154
Ilerite ^e	C ₁₆ TMABr	Mercaptopropyltrimethoxysilane	Chelating heavy metal cations	155
Ilerite	<i>n</i> -Hexylamine	4,4'-Biphenyl-bridged alkoxy-silanes	Toluene adsorptivity	156,157
Ilerite	<i>n</i> -Hexylamine	<i>p</i> -Aminophenyltrimethoxysilane	Toluene adsorptivity	158
Octosilicate ^e	C ₁₆ TMABr, DTMABr ^k	Alkoxytrichlorosilanes, Dialkoxydichlorosilane	Molecularly ordered silica nanostructures	159,160
Octosilicate	C ₁₆ TMACl	1,4-Bis(trichloro- and dichloromethyl-silyl)-benzenes	Bifunctional microporous hybrids	161
Octosilicate	C ₁₆ TMACl	Sulfonic acid	—	162
Magadiite	C ₁₆ TMAOH ^l	Bridged silsesquioxanes ^m	Sensors, optical devices	163,164
Magadiite	C ₁₆ TMABr	BBDMS ⁿ and diarylethene ^o	Photochromic	165,166
Magadiite	C ₁₂ TMACl	Propylsulfonic or arylsulfonic acid	Synthesis of bisphenol A	167

^a Cetyltrimethylammonium chloride. ^b Dimethyl sulfoxide. ^c *N*-Propyldiethylenetriethoxysilane. ^d 3-Aminopropyltriethoxysilane. ^e RUB-18, octosilicate and ilerite are identical materials. ^f Dodecyldimethylamine oxide. ^g Cetyltrimethylammonium bromide. ^h 3-Aminopropyltriethoxysilane. ⁱ *N*-3-Trimethoxysilylpropylethylenediamine. ^j *N*-3-Trimethoxysilylpropyldiethylenetriamine. ^k Dodecyltrimethylammonium bromide. ^l Cetyltrimethylammonium hydroxide. ^m 4,4'-Bis-(trimethoxysilylpropyl)viologen and 4-nitro-*N,N'*-bis(3-trimethoxysilyl)propylaniline. ⁿ 4-Bromobenzyltrimethylsilane. ^o 1,2-Bis(2-methyl-5-(4-dimethylaminophenyl))perfluorocyclopentene.

(*N*-PDETMS) and 3-aminopropyltriethoxysilane (3-APTEOS) for the adsorption of uranyl(II) cations.

Ishimaru *et al.*¹⁴⁸ further investigated the intercalation of partly or fully ionized dodecyldimethylamine oxides (DAO) in RUB-18. An important feature of this composite is its ability to act as a proton donor or acceptor due to the presence of silanol and silanolate groups. In addition, the grafting of methoxy groups into the interlayers of RUB-18 (H-form) has been achieved by Kiba *et al.*¹⁴⁹ They revealed that the transformation of the RUB-18 crystal system from tetragonal to monoclinic is mainly due to the repulsion between the grafted methoxy groups. Airolidi and coworkers conducted a series of functionalization reactions with RUB-18 using different types of silylating agents (Table 6)^{150–153} under mild conditions. The results indicate that these nanocomposites containing one (N) or three (3N) basic nitrogen atoms attached to pendant chains and cyanopropylsilyl groups have interesting applications as sorbents for Cu, Ni and Co cations from aqueous solution owing to their excellent complexing properties. Similarly, 3-trimethoxysilylpropylurea-RUB-18¹⁵⁴ and mercaptopropyl-trimethoxysilane-ilerite¹⁵⁵ have been effective for the removal of textile dyes and chelating heavy metal (Cd and Pb) cations, respectively. Ishii *et al.* have also employed hexylamine-swollen ilerites for the development of 4,4'-biphenyl-bridged alkoxy-silanes^{156,157} and *p*-aminophenyltrimethoxysilane-modified¹⁵⁸ ilerites, followed by the extraction of *n*-hexylamine *via* HCl-ethanol treatment, having high microporosities and toluene adsorption capacities. The use of 4,4'-biphenyl-bridged alkoxy-silanes and aminophenyltrimethoxysilane (APHS) is very inter-

esting in the synthesis of organic–inorganic nanocomposites, as they possess two functional groups on both ends, leading to the condensation with the silanol groups on both surfaces between the silicate layers, and hence the formation of interlayer microporosities. Kuroda and coworkers^{159–161} used surfactant-swollen octosilicates and bifunctional alkoxytrichlorosilanes, dialkoxydichlorosilane and 1,4-bis(trichloro- and dichloromethyl-silyl)benzenes as silylating agents for the preparation of novel organic–inorganic nanocomposites. This method is especially useful for the fabrication of 2D and 3D silicate nanostructures. Very recently, an octosilicate-based nanocomposite¹⁶² with sulfonic acid groups has been prepared using phenethyl(dichloro)methylsilane followed by sulfonation of the phenethyl groups with chlorosulfonic acid. These results show the possibility of developing organic–inorganic nanocomposites having ion-exchangeable acid groups and variable layer charge densities.

Corma and coworkers^{163,164} have employed cetyltrimethylammonium-swollen magadiite as the precursor and two different bridged silsesquioxanes including 4,4'-bis(trimethoxysilylpropyl)viologen (BTMPVi) and 4-nitro-*N,N'*-bis(3-trimethoxysilyl)-propylaniline (BTMPNA) as pillars to prepare porous and thermally stable organic–inorganic nanocomposites. Furthermore, such nanocomposites containing viologen units (electron transfer ability) and nitroaniline groups (chromophores) have been used as thermal/luminescence sensors and optical devices, respectively. Shindachi *et al.*^{165,166} investigated the preparation of thermally stable magadiite/diarylethene (Mag-DE) derivatives using BBDMS (4-bromo-

benzyltrimethylsilane) intercalated cetyltrimethylammonium-swollen magadiite as the intermediate. Such composites show improved reversible photochromic behavior in comparison with the conventional DE/layered double hydroxide (LDH-DE) composites. Recently, Sano and coworkers synthesized silylated derivatives of magadiite modified with propylsulfonic and arylsulfonic acids.¹⁶⁷ The resulting organic-inorganic composites (sulfonated magadiites) were found to be efficient catalysts for the regioselective synthesis of bisphenol A.

In the context of organic-inorganic hybrid materials, it is worth mentioning that layered like zeolite of the MCM-22 type (MWW) has also been used as precursors for the preparation of organic-inorganic hybrid materials.^{168,169}

2.7. Nanoparticles/nanocomposites from layered silicates

Nanoparticles supported on various supports such as silica, alumina, microporous and mesoporous materials are of immense importance in the field of heterogeneous catalysis.^{170,171} Although many synthetic methods (ion-exchange, impregnation and sol-gel)¹⁷² are available to immobilize nanoparticles on various suitable supports, significant challenges still remain related to the preparation of highly dispersed and thermally stable nanoparticles with controlled particle size distributions, which are essential from a catalytic point of view. Therefore, it is important to develop new strategies for the fixation of nanoparticles on supports, which can stabilize the nanoparticles against sintering at high temperatures. In this context, layered silicates could play a key role in the preparation of nanoparticles and nanocomposites because of their high cation exchange capacity as well as thermal and hydrolytic stability. We have prepared $[\text{Pt}(\text{NH}_3)_4]^{2+}$ -ilerite¹⁷³ (Fig. 5A) by intercalation of Na-ilerite at room temperature using the required amount of $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$. Subsequent calcination (380 °C) of the intercalated products led to the formation of highly loaded (20 wt%) and highly dispersed Pt nanoparticles supported on silica (Fig. 5B). In particular, excellent catalytic performances of the bifunctional catalysts (silica-supported Pt nanoparticles derived from Na-ilerite in combination with zeolite catalysts)¹⁷⁴ were observed in hydration, dehydration and isomerization reactions of hydrocarbons.

Like Na-ilerite, Na-magadiite has also been used as a support for the preparation of Pt nanoparticles supported on silica.^{175,176} Recently, homogeneously distributed Pd nanoparticles within a silica matrix have also been synthesized by intercalation of palladium complexes ($\text{Pd}(\text{NH}_3)_4\text{Cl}_2 \cdot \text{H}_2\text{O}$; TAPdCl and $\text{Pd}(\text{NH}_3)_4(\text{CH}_3\text{COO})_2$; TAPdAc) into Na-ilerite (IL)¹⁷⁷ followed by calcination of the intercalated products (TAPdCl/IL, TAPdAc/IL) at 550 °C for 5 h under air (Fig. 6). In addition, Ide *et al.*¹⁷⁸ reported the preparation of Au nanoparticles (disc or plate-like morphology) in the interlayer space of the mercaptopropylsilylated Na-octosilicate (Na-ilerite or RUB-18). Furthermore, methods to prepare Ag-nanoparticles (3–5 nm)¹⁷⁹ and ZnO-nanoparticles (2.6–4.6 nm, depending on the calcination temperature)¹⁸⁰ from magadiite have been explored and they have always led to uniform particle sizes.

Fig. 5 (A) TEM images of the $[\text{Pt}(\text{NH}_3)_4]^{2+}$ -ilerite sample (as-synthesized): (a) low magnification, (b) high magnification, (B) TEM images of the $[\text{Pt}(\text{NH}_3)_4]^{2+}$ -ilerite sample (calcined at 380 °C): (a) low magnification and (b) high magnification. (Reprinted with permission.)¹⁷³

Fig. 6 HRTEM images of (a) TAPdCl/IL, (b) TAPdCl/IL cal (air), calcined at 550 °C under air, (c) TAPdAc/IL, and (d) TAPdAc/IL cal (air), calcined at 550 °C under air. (Reprinted with permission.)¹⁷⁷

The above mentioned results indicate that layered silicates are attractive supports for the preparation of supported nanoparticles/nanocomposites.

3. Reactivity and applications of LDHs

3.1. Layered double hydroxides (LDHs)

LDHs are crystalline anionic clays, which are – like the naturally occurring brucite ($\text{Mg}(\text{OH})_2$) – composed of metal hydroxide sheets, where the metal cations are octahedrally coordinated by hydroxide ions. As depicted in Fig. 1, the metal hydroxide octahedra are edge-connected, thus three octahedra share one “OH corner”. In this way every divalent cation obtains 1/3 of a negatively charged hydroxyl group and the overall charge of the brucite-like structure is neutral. If some of the divalent cations are isomorphously substituted by trivalent cations, a positive excess charge is created, which is compensated by the introduction of anions (e.g. CO_3^{2-} , NO_3^- , OH^- , SO_4^{2-} , Cl^- , and Br^-) into the interlayer region. For example, the cationic sheets of the naturally occurring mineral hydrotalcite ($\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$) are composed of Al^{3+} and Mg^{2+} ions, with charge compensating carbonate anions in the interlayer space. Because of the similar structure, LDHs are also called hydrotalcite-like compounds (HTLcs) whereas the cationic metal hydroxide sheets are sometimes denominated as brucite-like sheets. The general chemical formula of LDHs is given together with some other characteristics in Table 1.

The brucite-like LDH layers can contain combinations of various cations (e.g. Mg^{2+} , Ni^{2+} , Mn^{2+} , Zn^{2+} , Cu^{2+} , Co^{2+} , Al^{3+} , Fe^{3+} , Cr^{3+} , and V^{3+}),¹⁸¹ but the cation radii should be similar and in the range of 0.65 and 0.8 nm to obtain stable structures.¹⁸² In addition, for phase-pure LDH structures the molar portion of trivalent cations with respect to the total cation content (w) should be between 0.2 and 0.4, which equals $\text{M}^{2+}/\text{M}^{3+}$ molar ratios of 1.5 to 4.0.¹⁸² Very substantial surveys about the different LDH compositions as well as their synthesis, properties and applications can be found in the books of Rives¹⁸² and Cavani *et al.*¹⁸³

In sufficiently diluted synthesis solutions, LDHs crystallize in the form of hexagonal platelets. However, in order to increase the yield of LDH, syntheses are usually performed in more concentrated reaction media. Depending on the degree of supersaturation and precipitation method, LDH crystals of different sizes can be obtained. Typical SEM images are shown

in Fig. 7. LDH platelets are approximately 75 nm thick and thus consist of around 100 metal hydroxide layers.¹⁸⁴ Furthermore, selected area electron diffraction (SAED) showed that the distribution of divalent and trivalent cations within the LDH structure is extremely homogeneous,¹⁸⁵ which is one of the reasons for the use of LDHs as catalysts and catalyst precursors.¹⁸⁶ A big advantage of LDH derived materials is their high compositional flexibility. The kind of divalent and trivalent metal cations, their molar ratio and the type of interlayer anion can vary in a wide range without changing the structure or morphology of the material.¹⁸⁷ Because of this flexibility and the specific properties of each LDH variant also the industrial applications of these materials are very manifold and range from catalysis to biology, medicine and soil rehabilitation to flame retardants and additive for polymers.^{182,188,189} Furthermore, the various LDH types can be used as precursors for the manufacture of a broad range of related materials, which are summarized in Fig. 8 and will be discussed in the following subsections.

3.2. Thermal stability of LDHs and conversion into mixed metal oxides

The thermal stability of the LDH structure is limited to temperatures up to about 200 °C. Thermal treatment (calcination) above this temperature converts LDHs into amorphous mixed metal oxides (MMOs). MMOs obtained in this way exhibit a very homogeneous distribution (“solid solution”) of the different cations within the mixed oxide structure, which is an important reason for the use of LDHs as a precursor for mixed metal oxide catalysts and catalyst supports.^{182,183} MMO catalysts were used for a large variety of reactions (mostly in the gas phase), including hydrogenations and dehydrogenations over Ni/Al and Cu/Al MMOs, decomposition of N_2O over Co/Al, Rh/Mg/Al and Ni/Al MMOs,¹⁸² conversion of methane into syngas over Ni containing MMOs¹⁸² and various alkylations, condensations and transesterifications.¹⁹⁰ Also LDHs themselves can be used as catalysts, but mainly in liquid phase acid–base reactions like aldol condensation of citral with acetone and MEK over Mg/Al LDHs¹⁹¹ or isomerization of alkenyl aromates over Mg/Al and Ni/Al LDHs.¹⁹² Due to the low specific surface area and limited thermal and chemical stability, the catalytic applicability and industrial importance of

Fig. 7 SEM image of small (left) and large (right) LDH platelets.

Fig. 8 Preparation pathways of various materials using LDHs as precursors.

LDHs do not reach that of the calcined (MMO) counterparts. However, post-synthetic modifications like delamination, reconstruction and pillaring can significantly enhance the catalytic performance of LDHs and thus broaden their applicability.^{5,191}

The chemical composition of the MMOs is predetermined by the composition of the cationic layers in the LDH structure. During the thermal treatment the LDH structure loses its crystallinity as well as anions and other guest molecules from the interlayer region. The removal of the interlayer species enables access to the interlayer surface. However, covalent bonds between adjacent metal oxide layers are formed upon thermal treatment, which leads to the situation that only a part of the initial interlayer region will be accessible (compare Fig. 9). The layered nature of LDHs is passed on to the respective MMOs and creates (together with simultaneously formed mesopores, compare Fig. 9) a relatively large accessible specific surface area in the range of $>100 \text{ m}^2 \text{ g}^{-1}$.

The thermal transformation of LDHs into MMOs has been investigated especially for Mg/Al LDHs by means of thermogravimetry, *in situ* XRD and IR spectroscopy.^{193–195} It was found that the decomposition of LDHs and formation of MMOs proceed mainly in 4 stages, which partly overlap each other. Thus, the following temperature ranges are only approximations.

-stage I ($T < 200 \text{ }^\circ\text{C}$): loss of physically bound, structural water from the interlayer region

-stage II ($T = 200\text{--}300 \text{ }^\circ\text{C}$): hydroxyl groups attached to Al condense and the crystalline LDH structure gets lost in the course of the MMO formation

-stage III ($T = 300\text{--}400 \text{ }^\circ\text{C}$): hydroxyl groups attached to Mg condense and the transformation into MMO structure continues

-stage IV ($T = 400\text{--}600 \text{ }^\circ\text{C}$): interlayer anions (carbonate) decompose and leave the structure, the formation of the amorphous Mg/Al MMO structure is finalized at around $580 \text{ }^\circ\text{C}$.

Further increase of the temperature above *ca.* $600 \text{ }^\circ\text{C}$ leads to the crystallization of spinel phases and pronounced demixing of the formed mixed oxides (*e.g.* formation of nanoparticles within the MMO structure¹⁹⁶), which is accompanied by a loss of specific surface area.

Investigations of LDHs containing Zn, Ni, Fe and Cr with carbonate as the interlayer anion showed that the decomposition stages found for the Mg/Al system are also valid for other metal combinations, while the deviance of the respective temperature ranges amounts to 50 to $100 \text{ }^\circ\text{C}$ for some LDH species.^{194,197,198} Also the type of interlayer anion has an effect on the structural transformation of LDHs upon thermal treatment, which was shown for Zn/Al LDHs containing different interlayer anions.^{198,199}

Furthermore, it is noteworthy that many LDH variants exhibit the special feature called the “memory effect”, *i.e.* after thermal treatment up to a certain temperature (usually 200 to $500 \text{ }^\circ\text{C}$) it is possible to re-establish the LDH structure through exposure to water steam or aqueous solutions of certain lost or desired interlayer anions.^{195,200} The memory effect facilitates the introduction of bulky interlayer anions as well as the increase of the specific surface area and the modification of the morphological and catalytic properties of the LDHs.¹⁹¹ This effect seems to be especially pronounced for Mg/Al LDHs, but was also observed with other cation combinations like Zn/Al,²⁰¹ whereas *e.g.* Ca/Al LDHs show only a little memory effect.²⁰² In general it seems that the thermal migration of cations into tetrahedral positions and formation of spinel structure or single-phase nanoparticles within the sample have to be avoided in order to enable a successful reconstruction of the LDH structure.²⁰⁰

Fig. 9 Schematic illustration of intra-layer mesopores in MMOs obtained through thermal treatment of LDHs (a), respective nitrogen physisorption isotherms (b, c) and DFT pore size distribution curves (d, e) from the adsorption branch.

3.3. Anion exchange in LDHs

Because of their positive layer charge, LDHs are appropriate anion exchangers. Furthermore, anion exchange is the central step for the intercalation of functional anions as well as for pillaring and delamination of LDHs. However, a precondition for the anion exchange is the presence of interlayer anions with lower affinity to the interlayer region compared to the anion which will be intercalated.²⁰³ The interlayer affinity of anions increases in the order:^{204,205}

The above order of affinities was mainly experimentally determined for Mg/Al LDHs, but should also be valid for other cation combinations. It can be seen that carbonate anions have the highest interlayer affinity and are thus not easy to exchange. Furthermore, it was observed for the example of Mg/Al and Ca/Al LDHs with nitrate as the interlayer anion that the LDH structure can be destroyed in some cases, where phosphate or carbonate should be intercalated. There, new

structures like calcium carbonate or ammonium magnesium phosphate were formed instead of anion exchanged LDHs.²⁰⁶ The charge balancing interlayer anion can have a remarkable structural, morphological, reaction engineering and physico-chemical influence on the properties of the LDHs and the respective mixed metal oxides.^{199,207} Naturally occurring LDHs (e.g. hydrotalcite) usually contain carbonate as an interlayer anion because of its high affinity to the interlayer region. In contrast, various anions (e.g. nitrate, chloride, sulfate, phosphate and organic anions like dodecylsulfate or terephthalate) can be synthetically inserted into the LDH structure depending on the synthesis conditions and cation combination. In general, there are three central options for the specific introduction of various anions into LDHs:

- direct synthesis,
- post-treatment of carbonate containing LDHs with an acid containing the desired anion (decarbonisation),
- post-synthetic anion exchange.

The direct synthesis of LDHs containing specific interlayer anions is the simplest and most time-saving method. Additionally, this method enables to influence the LDH layer

morphology through addition of certain surface-active anions.²⁰⁷ For the direct synthesis, the metal salts should contain the desired anion when they are added to the synthesis mixture, thus avoiding a concurrent intercalation of other anions. If the required metal salt is not available, the desired anion has to be added separately and preferably as a salt where the respective cation cannot be integrated into the LDH structure. Similarly, the required cations have to be added as salts with anions which have a very low affinity to the interlayer region.

The post-synthetic anion exchange is applicable in such cases where the target interlayer anion exhibits a higher affinity to the interlayer space compared to the already present anion. A change of the LDH platelet morphology *via* post-synthetic anion exchange is usually not observed because the anion exchange seems to be a topotactic process and not based on a dissolution/reconstruction mechanism. This was shown for the example of Zn/Al LDHs, where an *in situ* anion exchange of nitrate for carbonate proceeded during the LDH synthesis *via* the urea method.²⁰⁸ Also, for the anion exchange of nitrate for dodecyl sulfate the number of stacked layers was retained, from which the authors concluded that the anion exchange proceeded through a topotactic mechanism.²⁰⁹

In order to insert less-affine anions also into carbonate containing LDHs, Bish *et al.*²¹⁰ presented a post-treatment method where the target anion is added in its acid form to the LDH sample. This method is based on the fact that carbonate reacts with acid to CO₂, which then leaves the LDH structure (decarbonisation) and enables the target anion to enter the interlayer space. The disadvantage of this method is the instability of the LDH structure against acids, which leads to a partial dissolution of the LDH and thus loss of material upon this acid treatment.²¹¹ However, the dissolution problem could be almost completely suppressed by using the acid together with the respective sodium salt²¹² or the use of an acetate buffer–sodium salt mixture.²¹³

A large variety of organic anions has been introduced into the LDH interlayer space, mostly using them as model substances for pharmaceutically or biochemically interesting molecules with the aim to investigate the correlation between the structure and composition of the LDHs and their tendency to intercalate organic anions. Often, nitrate containing LDHs were used as precursors for the intercalation of organic anions like carboxylates or sulfonates.²¹⁴ LDHs with cation combinations of Li/Al, Mg/Al and Ca/Al were successfully used as matrices for the controlled release of pharmaceuticals like diclofenac, ibuprofen and naproxen.²¹⁵ Folic acid and methotrexate (MTX) were intercalated into Mg/Al LDHs, which led to an improved efficiency of this drug against tumor cells.²¹⁶ Moreover, the intercalation of DNA, nucleotides, 4-biphenyl-acetic acid, β -cyclodextrins and several agrochemicals like 3-indoleacetic acid was briefly reviewed by Williams and O'Hare.²¹⁵ A very recent review by Rives *et al.*²¹⁷ also discusses the latest progress in the use of LDHs as drug release systems.

Besides organic, biochemical and common inorganic anions, the diversity of possible interlayer anions also covers polymeric and complex anions, macrocyclic ligands and their metal complexes as well as catalytically interesting iso- and heteropolyoxometalates (compare section 3.6 about pillaring). Respective examples were summarized by Braterman *et al.*²⁰⁵ The above list shows that LDHs are a very attractive, effective and thus widely studied host system for the ion-exchange and/or intercalation of various anions.

3.4. Delamination of LDHs

The main motivation to delaminate layered materials is to increase the specific surface area available for interactions with the surrounding medium. As stated in subsection 3.3, anion exchange enables the modification of the interlayer space with various functional anions. But the strong attraction between the metal hydroxide layers and the interlayer anions often hinders bulky anions from gaining access to the interlayer space. In this case, delamination of LDHs into single layers and successive restacking with the desired functional anion is one of the solutions to this problem.²¹⁸

Furthermore, delaminated LDHs (LDH nanosheets) can be used for the fabrication of a wide variety of functional nanostructured materials.²¹⁹ In this respect, delaminated layered solids have already shown practical importance for applications like polymer reinforcement,²²⁰ emulsion stabilization²²¹ as well as the preparation of self-assembling monolayers (SAM) and Langmuir–Blodgett films.²²² Since delamination increases the dispersion of LDH sheets, it is the main objective when LDHs shall be used as composite partners, *e.g.* in the manufacture of LDH/polymer composite materials.^{223,224} Also inorganic–inorganic hybrid materials have been prepared by using delaminated LDHs,²²⁵ *e.g.* PbS nanoparticles stabilized in the LDH interlayer space²²⁶ or functional LDH spheres with a magnetic core for use as an easily-separable support for photocatalysts or an absorbent for anionic drugs.²²⁷ A recent review by Wang and O'Hare²²⁸ gives a comprehensive overview of routes to delaminated LDHs as well as the various fields of application.

In contrast to many cationic clays like montmorillonite, LDHs are not that easy to delaminate due to the higher formal charge density and attraction strength between adjacent layers.²²⁸ Accordingly, systematic research in this area started only in the beginning of the new millennium. In general, the process of LDH delamination consists of 3 steps:

1. inserting an anion into the interlayer space which supports swelling,
2. increasing the distance between adjacent LDH layers through swelling with an appropriate solvent,
3. delaminating the swollen LDH structure through energy input in an appropriate solvent/dispersant.

Table 7 summarizes various LDH types (metal combinations), interlayer anions, solvents and conditions which were successfully used to obtain delaminated LDHs. The upper LDH/solvent ratios for stable suspensions of delaminated LDHs are also given. From these studies it turns out that

Table 7 Examples of successfully delaminated LDH materials and respective conditions

Initial LDH	Interlayer anion for delamination	Delaminated with	Stable ^a dispersion up to [g l ⁻¹]	Reference
Zn/Al-Cl	Dodecyl sulfate (= DS)	Butanol or higher alcohols at boiling temperature	1.5	209
Zn/Al-DS	DS	LLDPE ^b in xylene	n.i. ^c	235
Mg/Al-Cl	DS	2-Hydroxyethyl-methacrylate, high-speed stirring at 70 °C	~10	223
Mg/Al-lactate	Lactate	Standing in water, 12 h 60 °C	10–20	218
Mg/Al-CO ₃	NO ₃ ⁻	Vigorous shaking in formamide	>0.5	232
Mg/Al-NO ₃	NO ₃ ⁻	Formamide, ultrasound treatment at room temperature	40 (5)	231
Mg/Al-AA	Various amino acids (AA) like glycine, alanine, leucine, lysine, <i>etc.</i>	Formamide, stirring	n.a. ^d	229
Zn/Al-glycine Ni/Al-glycine Co/Al-glycine	Glycine	Formamide, stirring	n.a.	229
Mg/Al-glycine	Glycine	Formamide, reflux	3.5	234
Mg/Al-borate	Borate	Acetone or other aqueous miscible organic solvents (AMOS)	∞	233
Zn/Al-borate				

^a Stable = transparent homogeneous dispersions (mass of LDH added to volume of solvent) with stability of weeks to months, lower limit for gel formation in brackets. ^b LLDPE = linear low density poly ethylene. ^c n.i. = determination not intended (exfoliation only as a short-term transition state during the preparation of composite materials). ^d n.a. = not assigned.

the success of the delamination procedure mainly depends on the following parameters:

- charge occupation of the interlayer anions and accessibility of the interlayer space for the solvent/swelling agent (role of hydrogen bonding),²²⁹
- solubility of the interlayer anions in the solvent,
- delamination conditions (energy input by high shear, ultrasound, temperature, *etc.*; time),
- morphology of the LDHs (intergrown LDH sheets cannot be completely delaminated).

The exchange of inorganic anions by organic and thus organophilic anions such as anionic surfactants or fatty acid anions has been found to be a successful strategy for the delamination of LDHs because it proceeds fast²³⁰ and leads to a substantial modification of the LDH surface properties and layer–layer interaction (*e.g.* polarity, hydrogen bonding, *etc.*). The insertion of organic anions like dodecyl sulfate (=C₁₂H₂₅SO₄) creates strong van der Waals forces within the interlayer space, which leads to a weaker stacking of the layers and enhanced interactions with non-aqueous solvents.²⁰⁹ Furthermore, due to their larger size, organic anions widen the interlayer space and thus make it more accessible for solvent molecules. For example, Adachi-Pagano *et al.*²⁰⁹ used butanol as the dispersant. Shorter alcohols did not lead to stable dispersions whereas higher alcohols like pentanol and hexanol also worked well. The key process for a complete exfoliation was assumed to be the rapid replacement of all the intercalated water molecules by solvent molecules. For this reason, solvents with boiling points higher than that of water (*e.g.* butanol, under reflux) were most effective for delamination. However, in the case of amino acids intercalated in LDHs, delamination in formamide (boiling point: 210 °C) did not work if the interlayer charge occupation by the amino acids

was too high.²²⁹ It was assumed that under these conditions the amino acids were too closely packed and hydrogen bonding between interlayer species as well as with the host layers did not allow formamide to sufficiently penetrate the interlayer space.

It is noteworthy that also other polar solvents were tested for their ability to induce delamination in amino acid containing LDHs.²²⁹ The solvents ranged from amphiprotic solvents to aprotic solvents and included water, methanol, ethanol, methylene glycol, ethylene-diamine, triethanolamine, *N*-methylformamide, *N,N*-dimethylformamide, ethyl formate, methyl acetate, propylene carbonate and acetone. Among these solvents, formamide was the only solvent that induced delamination. This finding was explained with the strong hydrogen bonding ability of formamide and it was assumed that hydrogen bonding is the driving force for delamination.²²⁹ Later it was found that lactate as the interlayer anion enabled delamination also in water.²¹⁸ However, delamination of lactate LDHs in water took much longer (several hours to days depending upon the temperature) compared to the instantaneous delamination of LDHs containing the amino acid glycine in formamide. In formamide some LDH dispersions were stable and transparent up to a concentration of 40 g l⁻¹, but formation of transparent gels was observed at concentrations higher than 5 g l⁻¹.²³¹ The delaminated LDHs could be restacked by adding sodium carbonate or ethanol.²³¹

Li *et al.*²³² delaminated large crystals (10 μm) of Mg/Al LDH with a nitrate as the interlayer anion by simple shaking for 12 h in formamide. As one application example the obtained dispersion was subsequently used for a layer-by-layer self-assembly of the LDH nanosheets and anionic polymers to produce multilayer nanocomposite films. Also, dodecyl sulfate containing LDH was delaminated in acryl monomers under

high shear at 70 °C and subsequently embedded in a polymer matrix by *in situ* polymerisation.²²³

However, even successfully delaminated LDH dispersions exhibit the inherent problem of immediate aggregation or even restacking of the LDH layers as soon as the solvent is removed. This hinders all applications where the use of delaminated LDHs in the dry state would be advantageous, *e.g.* for heterogeneous catalysis where a high dispersion and porosity would enable LDHs to expose more active sites to reagents. A solution to this fundamental problem was very recently introduced by Wang *et al.*²³³ with the so-called AMOST (Aqueous Miscible Organic Solvent Treatment) method. This method comprises the synthesis of Zn/Al-borate and Mg/Al-borate LDH powders by a conventional coprecipitation and the subsequent re-dispersion and washing of the obtained solid with an aqueous miscible organic (AMO) solvent prior to the final filtration and drying step in order to keep the hydrophobicity and thus dispersion of the LDH platelets. For this purpose the solvent needs to be completely miscible with water (*e.g.* acetone and methanol). The specific surface area of the delaminated Zn/Al-borate LDH powders was reported to reach 459 m² g⁻¹, which is more than 30 times higher compared to the conventional stacked LDH form ($A_{\text{BET}} \sim 13 \text{ m}^2 \text{ g}^{-1}$). For Mg/Al-borate the specific surface area reached 263 m² g⁻¹ compared to 1 m² g⁻¹ for the stacked LDH variant. When the delaminated LDH powders were contacted with Na₂CO₃ solution, highly crystalline Zn/Al-CO₃ or Mg/Al-CO₃ LDHs were obtained.

3.5. Organic-inorganic nanocomposites from LDHs

The vast majority of organic-inorganic nanocomposite materials involving LDHs as the inorganic phase contain polymers as the organic composite partner. The main motivation behind the preparation of LDH/polymer composites is to enhance the mechanical, optical, chemical and thermal properties of polymers. Also the preparation of conductive LDH/polymer nanocomposites is an emerging field of investigation.²³⁶ In contrast to conventional organic-inorganic composite materials, in nanocomposites the LDHs are used in a delaminated form²⁰⁵ to facilitate a higher dispersion of the LDH phase and thus more interaction between the composite partners. Depending on the ratio between both composite partners, the LDH phase can be highly dispersed in the polymer matrix or the polymer can fill the interlayer space between the LDH layers.²³⁶

For the composite preparation, the monomers are usually added during the delamination step of the LDHs and then the polymerization is subsequently initiated. In other cases, the LDH material is swollen with a monomer solution (*e.g.* styrene) and polymerization itself leads to the delamination of the layers.²²⁴ Several examples of LDH/polymer nanocomposites can be found in the book chapter of Braterman *et al.*²⁰⁵ In 2012, the latest developments concerning the use of delaminated LDHs in polymeric composites were summarized in a review paper.²²⁸ However, other organic nanocomposite partners which have been successfully incorporated into the LDH

interlayer space are several biopolymers like DNA as well as dyes, *e.g.* methyl orange and carbohydrates.¹⁸⁸

3.6. Pillaring of LDHs

Pillaring chemistry of LDHs is a well-established field due to the importance of this method for the preparation of multifunctional catalysts. Additionally, LDHs are pillared in the course of immobilizing large molecules in the LDH interlayer space. Apart from delamination, pillaring is the only option to gain access to the large LDH interlayer surface area through micropores between the pillars.²³⁷

Because LDHs are anionic clays, the pillars have to be anionic. The most important pillars for LDHs are polyoxometallates (POMs), *e.g.* polyoxovanadate. Whereas the thermal treatment of LDHs converts them into basic mixed metal oxide catalysts, POM pillars implement acidity and in several cases also redox activity into LDHs and MMOs, respectively. Other important pillars are phthalocyanines (PCs) yielding redox catalysts.²⁰⁵ In this regard, POM and PC pillared LDHs and MMOs have been investigated in a huge variety of heterogeneously catalyzed reactions, reaching from esterification, thiol oxidation, alkane dehydrogenation and isobutene alkylation to photocatalytic degradation of hexachlorocyclohexane and aldol condensations.^{9,205}

Furthermore, LDHs can be pillared with dicarboxylate anions like terephthalate.²³⁸ Whereas the introduction of POM and PC pillars usually requires an initial anion exchange with hydrophobic anions like dodecyl sulfate and subsequent swelling of the LDH host in order to widen the interlayer space for these large anions,²³⁹ the smaller dicarboxylates can be directly intercalated during the LDH synthesis.²³⁸ Besides, hexacyanoferrate pillars are commonly applied for the introduction of micropores into the LDH interlayer space, which creates LDHs with specific surface areas of up to *ca.* 400 m² g⁻¹.¹⁸²

3.7. Mesoporous and macroporous materials from LDHs

LDH platelets are stacks of alternating (brucite-like) metal hydroxide layers and interlayer anion layers. The platelets themselves are usually not porous because the interlayer space is tightly occupied by anions and water molecules and thus not accessible. As discussed in the previous sections, access to the interlayer space can be gained through delamination or widening the interlayer space by pillaring. In contrast, thermal removal of the interlayer molecules leads to collapse of the interlayer space and formation of mixed metal oxides (MMOs). However, MMOs are mesoporous and thus exhibit a significantly higher specific surface area compared to LDHs. The mesopores in MMOs arise during the thermal treatment of LDHs because of OH group condensation and thus shrinkage of the LDH layers, which seems to lead to local contractions and thus formation of structural holes, *i.e.* pores, in the dimension of mesopores. Schematic illustrations as well as nitrogen physisorption isotherms representing the non-porous nature of LDH platelets and the mesopores in MMO platelets, respectively, are depicted in Fig. 9.

Fig. 10 SEM (left) and TEM (right) images of delaminated LDH sheets after (a, b) coating on PS spheres, (c, d) PS removal by calcination at 480 °C, (e, f) after treatment in humid air to yield LDH hollow shells. Reproduced from ref. 240 with permission from the Royal Society of Chemistry.

However, LDH platelets can be used as building blocks for the preparation of LDH materials with defined inter-platelet pores. For example, a method was reported for the preparation of LDH hollow spheres by deposition of about 20 delaminated LDH layers on polystyrene spheres, thermal polystyrene removal and subsequent recovery of the LDH structure by rehy-

dration.²⁴⁰ Electron micrographs of such LDH layers enwrapping one large macropore are depicted in Fig. 10. Such a coating method might also be applicable for the deposition of LDH layers on (macro) porous substrates. This is a well-known strategy for the preparation of hierarchically porous zeolitic composite materials²⁴¹ and a few examples for LDH coatings on macroporous metal foams can already be found,^{242–244} which also involves the direct (*in situ*) crystallization of LDHs on such porous supports.²⁴² An example of LDHs on porous (foam) supports is shown in Fig. 11. However, in this case the LDH coating consists of the typical individual LDH aggregates and not of LDH single layers, which does not help to increase the accessible LDH surface area. In contrast, an example of an extremely homogeneous attachment of very thin LDH layers on porous supports is biotemplated Zn/Al LDH, which was obtained *via in situ* growth of the LDH structure on an alumina coated legume template, which was then subsequently converted into a hierarchically porous Zn/Al mixed metal oxide.²⁴⁵ The SEM image of this material is depicted in Fig. 12.

4. Comparative conclusion and outlook

Aluminium free layered silicates and layered double hydroxides are the two end-types of the series of layered materials because they contain just a single type of primary building blocks, namely tetrahedra and octahedra, respectively. With the previous subsections we intended to demonstrate that these two types of layered materials can be used as functional materials for various applications. Due to the differences in structure and composition, the obtained target materials have been shown to be different, although the fields of their application were in many cases similar. In Table 8 an attempt is made to generalise and compare the properties of these two specimens. Both the aluminium free layered silicates and LDHs are very attractive owing to their inherent layered struc-

Fig. 11 SEM images of an aluminium foam before (a–c) and after (d) coating it with Mg/Al LDH particles (e); (f) EDX of the LDH coating. Reprinted with permission from ref. 244. Copyright 2012 American Chemical Society.

Fig. 12 SEM image of the hierarchically porous Zn/Al MMO framework obtained through *in situ* crystallization of Zn/Al LDH on a legume bio-template. Reprinted with permission from ref. 245. Copyright 2009 American Chemical Society.

ture-based characteristics such as intercalation and swelling. A general finding with respect to the reactivity is that both materials can be delaminated and pillared because both are composed of charged layers. But due to the higher charge density both the layered silicates and the LDHs are more difficult to delaminate compared to the well-known clay based layered aluminosilicate (*e.g.* montmorillonite), which can easily be delaminated after intercalation of a large variety of substances like long-chain surfactants. For the layered silicates and the LDHs, one has to support this exfoliation process by an additional input of energy like an ultrasonication.

Furthermore, both materials can act as a precursor for the formation of 3D structures applicable as an ion-exchanger, an adsorbent or mainly as a catalyst or a catalyst support. However, the process which leads to such a new structure is completely different for both structure types. The different primary building units lead to the situation that layered silicates (composed of SiO_4 tetrahedra) can be converted into various 3D siliceous structures (*e.g.* zeolites and ordered mesoporous silica, *etc.*, which are also built up of SiO_4 tetrahedra) by a hydrothermal transformation process. In contrast, LDHs (octahedral metal hydroxide building units) have to undergo a thermally induced destruction process to form the three-dimensional amorphous mixed metal oxides (MMOs).

The advantage of using layered materials as precursors for the preparation of micro- or mesoporous materials with other functions or properties than the layered precursors appears to be not only the option to obtain layered morphologies. To make use of the different (pre-formed) building blocks also reduces the crystallization time compared to conventional syntheses with molecular educts and leads to higher chemical and thermal stabilities in the case of ordered mesoporous materials, because the pore walls of these usually amorphous materials are then partially crystalline. Furthermore, some types of zeolites can only be obtained with layered precursors, *e.g.* RUB-24.

Besides, the layered nature of layered silicates enables the stabilization of nanoparticles and the controlled introduction of guest species with catalytic functions. In contrast to layered silicates, the metal composition of layered double hydroxides is extremely flexible and enables the implementation of the catalytic function already directly into the layer. Also, mixed metal oxides prepared from LDHs as precursors exhibit a very homogeneous metal distribution on the molecular level ("solid solution"), which cannot be obtained *via* other preparative routes.

Furthermore, the layered nature of these materials is very ideal to use them as hosts for various guest molecules. Pillaring chemistry of layered silicates and LDHs is a well-established field due to the importance of this method for the preparation of multifunctional catalysts having high surface areas.

Both groups of layered materials are able to exchange their interlayer ions, but due to the different layer composition, layered silicates are cation exchangers, whereas LDHs are anion exchangers. The different charge of layered materials opens a route to direct the local arrangement and interaction of these layers with other charged species in order to fine-tune *e.g.* composite materials. Because of the different character of the bulk layer – anion or cation – the respective reactivities might even complement each other. Recently, both types of layered materials – montmorillonite layers as the anion and LDH layers as the cation – could be combined to form one inorganic–inorganic composite material consisting of periodically alternating anionic and cationic layers through exfoliation with cationic and anionic surfactants, respectively, which facilitated the mixing of both types of hydrophobic sheets in the same non-polar surfactant.²⁴⁶

Table 8 Comparison of important reactivities of the two types of layered materials

Reaction	Layered silicates	Layered double hydroxides (LDHs)	Process driven by
Intercalation	Yes	Yes	Layered character
Pillaring	Yes	Yes	Layered character
Delamination	Yes, but limited	Yes	Surface charge density
3D precursor	Yes, by direct hydrothermal, solid-state and topotactic rearrangement of the tetrahedral building blocks	Yes, but only by destruction of the octahedral building blocks	Building blocks
Ion exchange	Cations	Anions	Chemical composition

As already mentioned in the present perspective article, in recent days many efforts have been made in the field of preparing two dimensional extended materials with zeolitic structural features, the so-called layered zeolites. In particular, the driving force for these developments is more on the reduction of the necessary length of the diffusion pathway for guest molecules in the zeolitic framework.¹⁴³ However, they might exhibit also some typical layered like reactivities like pillar-ing.¹⁴⁴ Future studies will show that such a combination of zeolitic and layered like characteristics might be useful for important catalytic applications.

In this light we believe that the nature, reactivity and flexibility of layered materials will continue to be intensively explored in order to discover novel materials and composites with interesting properties. For this purpose, the understanding and predictability of the reactivities of the different types of layered materials, systematically starting with the left and right chain links (layered silicates and LDHs), appear to be important.

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