

Synthesis and characterization of Linde A zeolite coated with a layered double hydroxide

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Abstract

Linde type A zeolite (zeolite-LTA) coated with layered double hydroxide (LDH) was synthesized by a precipitation of LDH on zeolite-LTA and a hydrothermal treatment. When aqueous solutions containing magnesium chloride, and aluminum chloride were added dropwise to zeolite-LTA suspension at the constant pH of 10 using sodium hydroxide solution and then treated at hydrothermal conditions, LDH-coated zeolite-LTA was obtained. Scanning electron micrograph confirmed that the surface of zeolite-LTA was covered completely by fine LDH particles. The crystal structure of zeolite-LTA was retained even after the hydrothermal treatment and the coating with LDH particles, showing the possible application of the present multifunctional material for simultaneous uptake of harmful cations and anions, such as ammonium and phosphorous ions from wastewater.

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1. Introduction

The global environmental problems of today were brought by the rapid expansion of human and industrial activities. In river and lake systems, the eutrophication was generated by the considerable amounts of ammonium and phosphate ions in domestic wastewater which subsequently pass into freshwater. The groundwater and soil system were also contaminated with arsenic anion, cadmium and lead cations. In order to solve the environmental problems, it is essential for us to develop environment purification materials with high-sensibility and intelligent response to harmful pollutants.

Zeolites are crystalline, hydrated aluminosilicate with exchangeable cations. More than 100 different species of zeolites have been identified.¹ The aluminosilicate portion of the structure is a three-dimension open framework consisting of a

network of AlO_4 and SiO_4 tetrahedra linked to each other by sharing all the oxygen.² They have periodic and molecular-sized pores and channels in their structures. They have high cation exchange capacity, ion adsorption, and especially high selectivity for ammonium ion. The high affinity of zeolite for ammonium ion and the possibility of releasing it over time are of special interest for minimizing environmental pollution during municipal and industrial water management.^{3–8}

Layered double hydroxides (LDHs) are a class of layered materials with the ideal formula $[\text{M}_{1-x}^{2+}\text{M}_x^{3+}(\text{OH})_2][\text{X}_{x/m}^{m-}]_n\text{H}_2\text{O}$, where M^{2+} and M^{3+} are metal cations, X^{m-} is intercalated exchangeable anion.⁹ The structure consists of brucite-like layers constituting $\text{M}(\text{OH})_6$ octahedra. Partial M^{2+} to M^{3+} substitution induces a positive charge for the layers, balanced with the presence of the interlayer exchangeable anions.¹⁰ Because of their anion exchange property, they are expected to be one of potential water treatment agents for phosphate removal.^{11–16}

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In the present work, we focused on the preparation of multifunctional composite with adsorption properties, that is, simultaneous removal of harmful cations and anions. We synthesized the novel Linde type A zeolite (zeolite-LTA) coated with LDH of $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3\cdot 4\text{H}_2\text{O}$, by precipitation of LDH on zeolite-LTA and a hydrothermal treatment. We also investigated the effects of the synthesis parameters, including the concentration of starting solution and temperature, on the formation of LDH layers on the surface of zeolite-LTA and speculated the formation mechanism of LDH on the surface.

2. Experimental procedures

2.1. Materials

Linde type A zeolite (zeolite-LTA) powder (<200 mesh) with Na ion as an exchangeable cation was purchased from Wako Pure Chemicals Industries, Ltd., Japan. Magnesium and aluminum chloride hexahydrates, and sodium hydrate were also purchased from Wako Pure Chemicals Industries, Ltd., Japan. These chemicals were used without further purification.

2.2. Sample preparation

A typical synthesis procedure is as follows: Aqueous solution of magnesium and aluminum chloride hexahydrates were mixed together at the molar Mg/Al ratio of 3:1 with magnetic stirring at room temperature. The concentrations of the components in the starting solutions were 3×10^{-2} M and 1×10^{-2} M, respectively. 50 ml of the homogeneous solution added dropwise to 100 ml of a 1×10^{-3} wt.% zeolite-LTA suspension at a constant pH of 10 adjusted by 3×10^{-2} M NaOH solution. The suspensions were subsequently aged at room temperature for 24 h, and then placed in a Teflon cup fitted into a stainless steel pressure vessel and heated in an oven at 150°C and autogeneous pressure for 24 h. After cooling to room temperature, the product was filtered with a 0.45 μm membrane filter, washed with 500 ml deionized water, and dried at 50°C in an oven. Effects of the solution concentration and temperature on the products were investigated employing the synthesis conditions summarized in Table 1. The reaction time of hydrothermal treatment was fixed for 24 h.

2.3. Characterization

The powder X-ray diffraction (XRD) patterns were obtained on a Rigaku Rint 2200 diffractometer using monochromatic Cu $K\alpha$ radiation. A scanning electron microscopy fitted with an energy dispersive spectrometer (SEM-EDS by JEOL S-5000) was used to characterize the products after Pt-coating. The products were also characterized by transmission electron microscopy (JEOL JEM-1010).

Table 1
Synthesis conditions employing in the present study

Sample	Concentration of solution (mol/L)		Reaction temperature ($^\circ\text{C}$)
	MgCl ₂	AlCl ₃	
A	1×10^{-2}	$1/3 \times 10^{-2}$	150
B	2×10^{-2}	$2/3 \times 10^{-2}$	150
C	3×10^{-2}	1×10^{-2}	150
D	5×10^{-2}	$5/3 \times 10^{-2}$	150
E	1×10^{-1}	$1/3 \times 10^{-1}$	150
F	3×10^{-2}	1×10^{-2}	25
G	3×10^{-2}	1×10^{-2}	50
H	3×10^{-2}	1×10^{-2}	100
I	3×10^{-2}	1×10^{-2}	200

3. Results and discussion

3.1. Characteristics of typical LDH-coated zeolite-LTA

Fig. 1 shows the SEM images of zeolite-LTA with cubic morphology and smooth surface (a), and the obtained product from the typical synthesis procedure (b) (condition C in Table 1) with the corresponding EDS spectra. The hydrothermal treatment did not destroy the cubic morphology, but changed its surface morphology with a homogenous covering of tiny particles. The tiny particles were aggregated with platy crystals, 100–150 nm in diameter and 15 nm thickness. The crystal morphology was very similar to that of typical LDH.⁹ EDS analysis of zeolite-LTA was the same as that of ideal zeolite-LTA with Na as exchangeable cation. The comparison between the EDS data of zeolite-LTA and the treated product indicated that the Mg:Al ratio of platy particles (i.e. 3:1) is similar to that of general LDH.^{9,17}

The XRD patterns of zeolite-LTA and the product prepared by condition C are shown in Fig. 2. The crystal structure of zeolite-LTA in the product was maintained, and was stable after hydrothermal treatment since the XRD patterns of zeolite-LTA of original and in the product were not significantly different in the full-width at half maximum. After the hydrothermal treatment, a broad and weak reflection was observed as emphasized by the inset in Fig. 2. The broad peak corresponded closely to that of the basal reflection ($d_{(003)}$) of LDH, although the position of the broad peak was difficult to determine exactly, because the intensity of the peak was very weak and overlapped with those of zeolite-LTA.

Fig. 3 shows the TEM image and selected electron diffraction (SAED) pattern of the platy particles covered on the surface of zeolite-LTA after the treatment by condition C. SAED revealed that the platy particles that grow on the surface of zeolite-LTA were LDH, because the SAED pattern of the platy particle corresponded to that of LDH. The LDH was about 6 nm thick and had a sharp interface with zeolite-LTA, which indicated that LDH grew without marked dissolution of zeolite-LTA. The SAED patterns show sharp Debye rings, which suggest that the weak and broad peak in XRD pat-

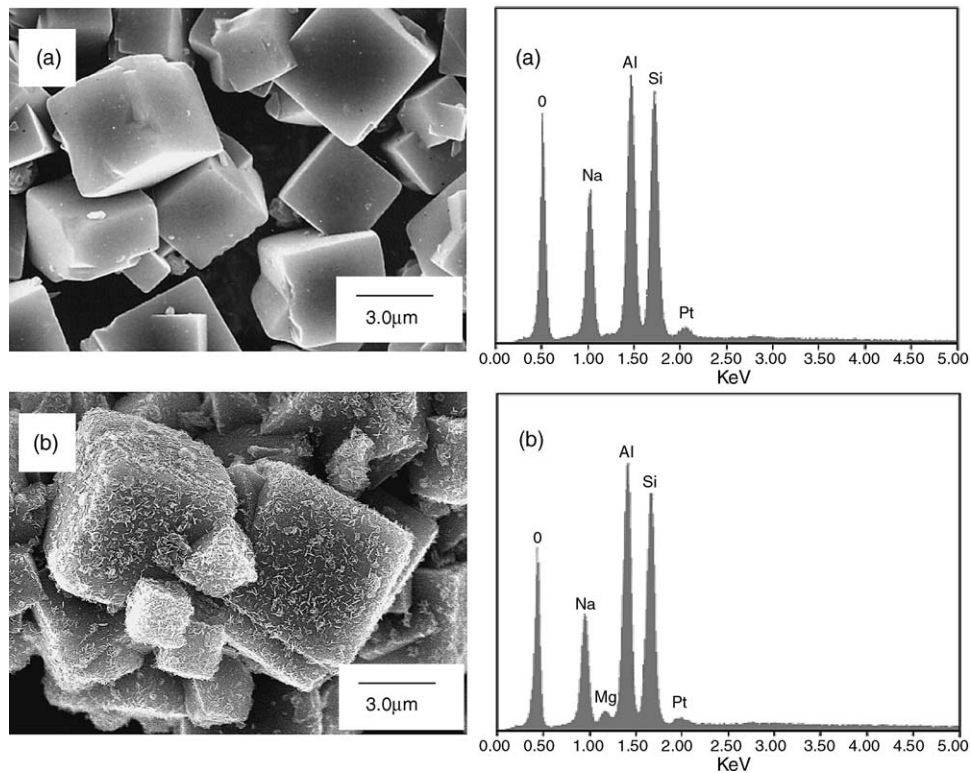


Fig. 1. SEM images and the corresponding EDS spectra of untreated zeolite-LTA (a) and zeolite-LTA after hydrothermal treatment by condition C (b).

tern was formed by fine crystallites but not by a defective structure. Those observations by SEM-EDS, XRD, TEM and SAED confirmed that the present product was a novel zeolite-LTA coated with platy LDH.

3.2. Synthesis conditions of LDH-coated zeolite-LTA

To vary the formation of the LDH layer on the surface of zeolite-LTA, experimental conditions (solution concentration and temperature) were varied as summarized in Table 1.

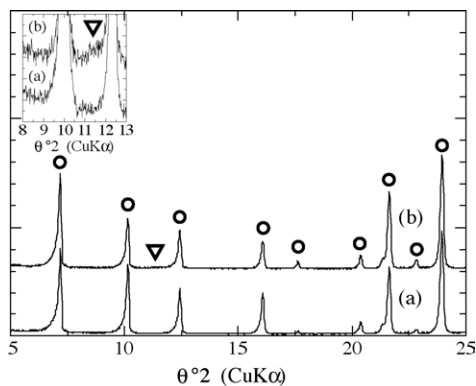


Fig. 2. The XRD patterns of zeolite-LTA (a) and the product prepared by condition C (b). The circle and arrow indicate the diffraction due to zeolite-LTA and LDH, respectively.

Irrespective of the reaction conditions, the formation of nano-LDH crystals on the surface of zeolite-LTA was confirmed by SEM-EDS, XRD, TEM and SAED.

SEM images of the products prepared by the reactions obtained from different $\text{MgCl}_2\text{-AlCl}_3$ mixed-solutions (conditions A, B, D and E, respectively) at 150°C are shown in Fig. 4. As seen in Fig. 4, the hydrothermal treatments did not destroy the cubic morphology of the original zeolite-LTA. The amount of platy particles grown on the surfaces of zeolite-LTA increases with higher concentrations of the solutions used in the synthesis. At the condition A, the surface of zeolite-LTA was covered by LDH heterogeneously. At the condition B and D, a homogeneous coating occurred as under condition C. At higher concentration, LDH crystals covered the surface of zeolite-LTA, and furthermore, LDH was formed as aggregates among zeolite-LTA crystals. It indicated that LDH particles were nucleated and grown freely from the solution at higher concentration.

In addition to the solution concentration, the reaction temperature affects the formation of LDH on the surface of zeolite-LTA. SEM images of the reacted products prepared at $25, 50, 100$ and 200°C (conditions F, G, H and I, respectively) are shown in Fig. 5. At these conditions, the zeolite-LTA with cubic morphology was completely covered by tiny LDH crystals. The particles sizes of LDH on the surface of zeolite-LTA changed from 100 to 300 nm in diameter, depending on the

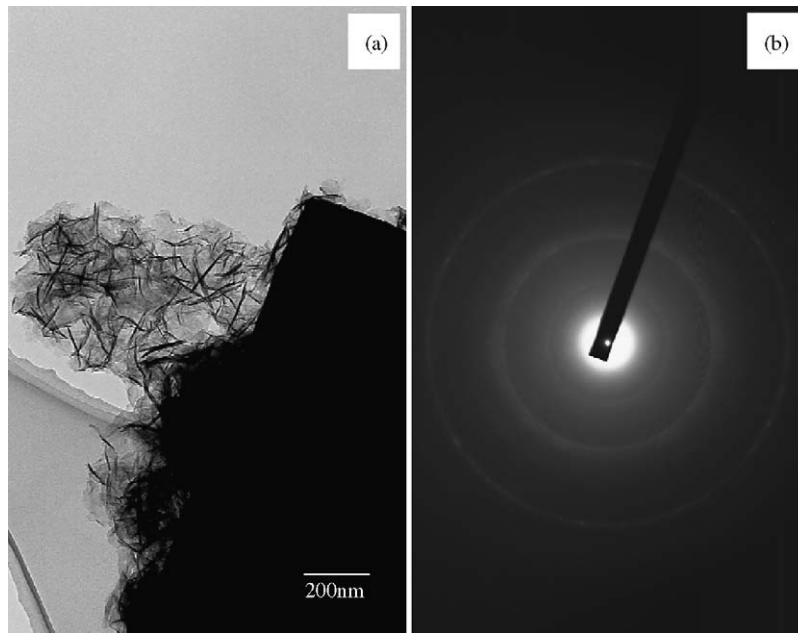


Fig. 3. TEM image (a) and SAED pattern (b) of the platy particles covered on the surface of the zeolite-LTA after the treatment by condition C.

temperature of hydrothermal treatment. The results indicated that the size of particles is controllable by changing the synthesis temperature during hydrothermal treatment.

3.3. The formation mechanism of LDH on the surface of zeolite-LTA

Recently the hydroxyapatite layers on the surface of zeolite-LTA were synthesized in $(\text{NH}_4)_3\text{PO}_4$ solution at 120°C for 8 h under autogeneous pressure.¹⁸ The thin layers of hydroxyapatite crystals, 100–200 nm in diameter and

30 nm in thickness, were formed on the surface of zeolite-LTA by a reaction between discharged Ca^{2+} ions from zeolite-LTA and an $(\text{NH}_4)_3\text{PO}_4$ solution. The ion exchange of Ca^{2+} on zeolite-LTA for NH_4^+ in an $(\text{NH}_4)_3\text{PO}_4$ solution was the driving force for the formation hydroxyapatite. The present nanocomposite was not obtained using a concept based on an ion-exchange reaction. But the cation exchange capacity of zeolite-LTA might play an important role to gather Mg^{2+} and Al^{3+} cations and form LDH nanocrystals. A detailed study is necessary to explain the formation mechanism of LDH layers on zeolite-LTA.

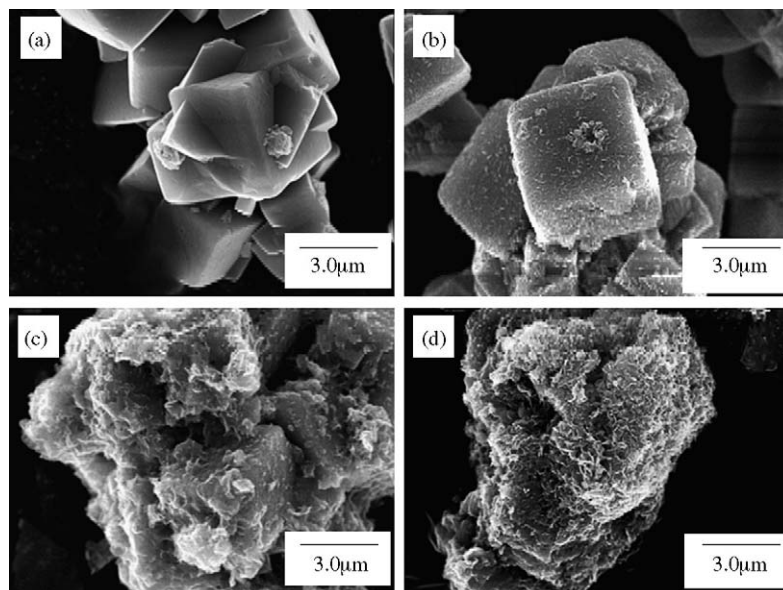


Fig. 4. SEM images of zeolite-LTA after hydrothermal treatment by conditions: A (a); B (b); D (c) and E (d).

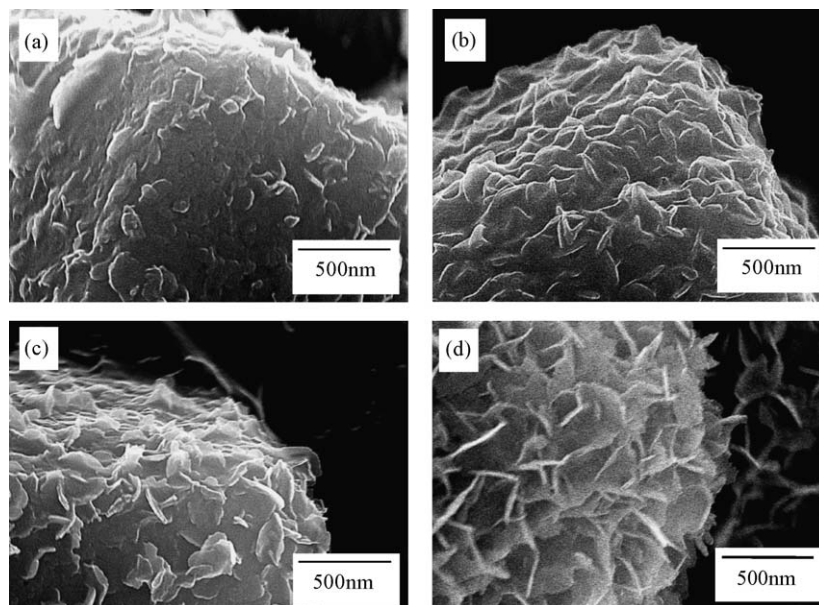


Fig. 5. SEM images of zeolite-LTA after hydrothermal treatment by conditions: F (a); G (b); H (c) and I (d).

4. Conclusion

We successfully synthesized nanocrystals of LDH on the surface of zeolite-LTA under hydrothermal treatments. When homogeneous aqueous solutions containing magnesium and aluminum chloride hexahydrates were added to zeolite-LTA suspension at pH of 10 and then treated at hydrothermal conditions, LDH-coated zeolite-LTA was obtained. The size and amount of LDH crystals coated on zeolite-LTA depend on the solution concentration and the reaction temperature. The present material should be a promising one for remove both harmful cations and anions at the same time.

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