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BEHAVIOUR OF HYDROTALCITE AND ITS $Fe(CN)_6^{4-}$ PILLARED DERIVATIVE ON HEAT TREATMENT

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Abstract

Mg–Al L(ayered) D(ouble) H(ydroxide) was prepared and its thermal behaviour was characterized by thermoanalytical methods (TG, DTG, DTA), ^{27}Al M(agic) A(ngle) S(pinning) NMR spectroscopy, X-ray diffractometry (XRD) and S(canning) E(lectron) M(icroscopy). Heat treatment destroyed the layered structure, which could only be partially reconstituted by rehydration. On calcination mixed oxide with the predominance of basic sites were formed. Pillaring the LDH with $Fe(CN)_6^{4-}$ anions was also performed. The material was characterized by XRD and BET measurements. Heat stability of the pillared substance was investigated, too. Pillaring proved to be successful, however, decreased heat resistance was found in the intercalated material relative to the guest LDH.

Keywords: dehydration/rehydration and stability characterization, $Fe(CN)_6^{4-}$ anion pillared layered double hydroxide, Mg–Al layered double hydroxide, thermal behaviour

Introduction

Layered double hydroxides (LDHs) may be represented by the general formula: $M_a^{2+}M_b^{3+}(OH)_{2a+2b}(X^-)_b \cdot xH_2O$, where M^{2+} may be Mg^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+} and M^{3+} may be Al^{3+}, Cr^{3+}, Fe^{3+} [1]. Although these anionic clays are found in nature, for most applications they are synthesized. Various synthetic approaches are known for the preparation of these substances. They are reviewed in Ref. [1], together with available pillaring methods.

We have synthesized Mg–Al LDH (hydrotalcite) and investigated its thermal and dehydration/rehydration properties. Then, the material, which possesses anion exchange properties was applied as host and its layers were propped open by an inor-

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ganic anion. The heat stability of the pillared structure was studied by XRD. Results of this investigation are detailed in this contribution.

Experimental

Materials

Mg–Al LDH (hydrotalcite, Mg:Al=3:1)

Mg–Al LDH (hydrotalcite, Mg:Al=3:1) was prepared by pH controlled co-precipitation of the corresponding metal nitrate salts. Preparation was based on the method of Corma and co-workers [2]. A solution containing 0.02 mol of $Al(NO_3)_3 \cdot 9H_2O$ and 0.06 mol of $Mg(NO_3)_2 \cdot 6H_2O$ in 100 cm^3 water was prepared (solution A). Solution B contained 0.8 mol Na_2CO_3 and 1.6 mol NaOH in 1 dm^3 water. Solutions A and B were added simultaneously to 200 cm^3 water dropwise under vigorous stirring at room temperature. The addition of solution B was to keep the pH between 8.0 and 9.0. The gel formed was autoclaved at 458 K for 18 h in a teflon-coated container.

Mg–Al–$Fe(CN)_6^{4-}$(Mg.Al=3.1)

The original method was described by Mao *et al.* [3]. Here, a modified version of that recipe is given. Solution A was obtained by dissolving 0.05 mol $Al(NO_3)_3 \cdot 9H_2O$ and 0.15 mol $Mg(NO_3)_3$ in 100 cm^3 water. Then, an aqueous solution containing 2 mol dm^{-3} NaOH and 0.1 mol dm^{-3} $K_4Fe(CN)_6$ (solution B) was added to solution A under continuous stirring until Al^{3+}:$Fe(CN)_6^{4-}$=1 and pH about 9 was attained.

Double-distilled, chloride-free water and an inert atmosphere (Ar) was used throughout the synthesis of both substances.

Treatments of the materials

Calcination of Mg–Al LDHs was performed in vacuum at 723 K for 3 h. All characterization measurements were carried out after this treatment. Rehydration after calcination was performed with water vapour for 24 h.

Before BET measurements the pillared material was treated like the host substance except for a run, when 473 K was applied instead of 723 K.

For studying the durability of Mg–Al double hydroxide pillared by $Fe(CN)_6^{4-}$ ions, XRD spectra were taken after each 3-hour evacuation at 323, 423 or 473 K.

Methods for structural characterization

For studying the thermal behaviour of Mg–Al LDH a computerized Derivatograph Q instrument was used. The powdered material (100 mg) was placed on a platinum sample holder and was heated under inert gas flow (Ar) from 250 to 1300 K with 10°C min^{-1} temperature ramp.

The XRD measurements were performed on a DRON 3 powder X-ray diffractometer using the CuK_α radiation. Diffractograms of the freshly prepared, the calcined as well as the rehydrated samples were recorded. As to the pillared material,

Table 1 Characteristic data on Mg–Al LDH and its $Fe(CN)_6^{4-}$ pillared derivative

Materials	d(003)/nm[a]	BET surface area/$m^2\ g^{-1}$[b]	
Mg–Al LDH[c]	0.76	360	
Mg–Al–$Fe(CN)_6^{4-}$	1.05	63.8	80.0*

[a]air-dried material
[b]723 K, 3 h, except*, which is 473 K, 3 h
[c]Mg/Al=3:1

the spectra of the air-dried and the heat-treated material were recorded, too. Basal spacings were determined from the position of the d(003) reflection. Data are listed in the second column of Table 1.

For S(canning) E(lectron) M(icroscopy) a Hitachi S-800 scanning electron microscope was used. Platinum coating was applied to make the samples conductive. The accelerating voltage was 15 kV.

The ^{27}Al MAS NMR spectra were recorded on a Bruker MSL400 NMR spectrometer at 104.2 MHz (spinning rate was 3.8 kHz, pulse lengths: 1.0 μs, $\theta=\pi/12$). Chemical shifts were referenced to $Al(NO_3)_3$ solution. In initial measurements variable waiting time was applied and finally, 10 s seemed to be the most appropriate. The NMR spectra of the freshly prepared, the calcined and the rehydrated samples were taken.

BET measurements were performed in a conventional volumetric adsorption apparatus at the temperature of liquid nitrogen (77 K). Before measurements the samples were treated in various ways (for details, see above). Data are in the third and fourth columns of Table 1.

Results and discussion

Dehydration/rehydration behaviour of Mg–Al LDH, effects of heat treatment

XRD measurements revealed that the preparation of the Mg–Al hydrotalcite was successful and a substance with high crystallinity was obtained. Diffractogram (Fig. 1/a) typical of the layered structure was acquired (d(003) values are in the second column of Table 1). The ^{27}Al MAS NMR spectrum (Fig. 2/a) clearly showed that most of the aluminium is in octahedral position. Calcination destroyed the layered structure attested by the corresponding X-ray diffractogram (Fig. 1/b). The Mg–Al LDH transformed into slightly crystalline MgO, characterized by diffuse XRD pattern. ^{27}Al MAS measurement also indicated major structural rearrangement, i.e., a large portion of aluminium became tetrahedrally coordinated (Fig. 2/b). However, octahedral coordination was still predominant. The resulting partially mixed double oxide had large specific surface area (Table 1). After rehydration, the original layered structure was partially reconstituted (Fig. 1/c). Nevertheless, the rehydrated sample was less crystalline than it was before the heat treatment.

The ^{27}Al MAS NMR spectra of rehydrated Mg–Al hydrotalcite showed measurable decrease and corresponding increase in the spectral area for tetrahedrally and

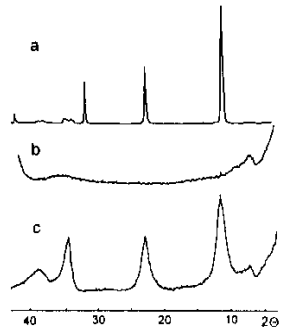


Fig. 1 XRD spectra of Mg–Al LDH (a) as prepared (air-dried), (b) calcined (vacuum, 723 K, 3 h), (c) rehydrated (water vapour, 24 h)

octahedrally coordinated aluminium, respectively (Figs 2/b and 2/c). It means that part of the tetrahedral aluminium was transformed back to octahedral form.

It is to be noted that the extent of reversibility in the dehydration/rehydration behaviour of LDH is a controversial topic. Similar behaviour to our finding was experienced by Corma *et al.* [4] on calcination of Mg–Al LDH (the counterion was hydroxide), however, they did not study rehydration, although they mention that it should be fully reversible.

Processes taking place on heat treatment were followed by thermoanalytical methods. TG, DTG and DTA curves reveal important details. All these functions for the Mg–Al LDH are displayed in Fig. 3.

Near 390 K an endothermic process, the loss of adsorbed water (between the layers) and the crystal water takes place. The second and third, overlapping mass loss steps between 700 and 800 K are the combination of the decomposition of carbonate

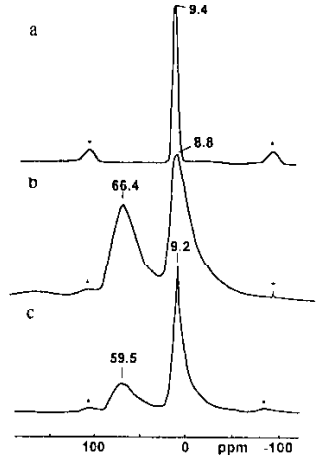


Fig. 2 ^{27}Al NMR spectra of Mg–Al LDH (a) as prepared (air-dried), (b) calcined (vacuum, 723 K, 3 h), (c) rehydrated (water vapour, 24 h)

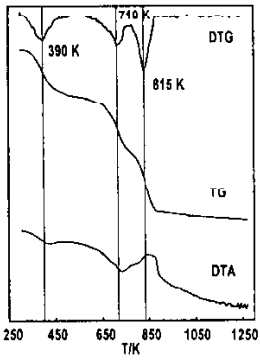
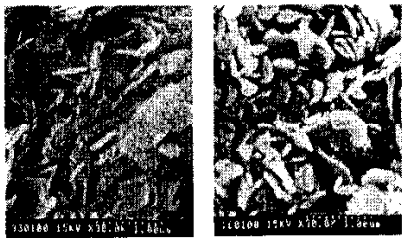


Fig. 3 Thermal characteristics of Mg–Al–CO_3^{2-} LDH (temperature ramp: 10°C min^{-1})

ion (with CO_2 evolution) and the ever deeper dehydroxylation of the LDH. The two endothermic processes lead to the collapse of the layered structure. This structural rearrangement is indicated by an exothermic peak in the DTA curve in the vicinity of 850 K. The layered structure is completely destroyed by 900 K and the result is an amorphous mixed oxide with lots of dislocations – ideal for a potential catalyst.

A recent study [5] concerning the thermal characteristics of Mg–Al LDH (Mg:Al=4:1, the counterion was CO_3^{2-}) gives a less complicated TG pattern, with two endothermic (by DTA) mass losses. Signs of dehydroxylation (an exothermic process) were not observed.



A B

Fig. 4 SEM images: (A), Mg–Al LDH, air-dried (B), Mg–Al LDH, heat-treated (vacuum, 723 K, 3 h)

Indeed, SEM images reveal that the air-dried Mg–Al LDH forms well-developed, thin hexagonal flat crystals indicating the layered structure (Fig. 4, image A), while the heat-treated LDH loses crystallinity as well as the original crystal form (Fig. 4, image B). The collapse of the layered structure is clearly in a highly advanced stage.

Mg–Al LDH pillared with $Fe(CN)_6^{4-}$ anions

Propping up the layers of LDHs was attempted by pillaring during the synthesis of LDH. The method proved to be successful, as the substantial increase in d(003) distance attests (Table 1).

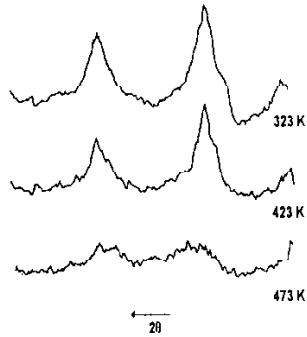


Fig. 5 The structural changes in Mg–Al LDH pillared by $Fe(CN)_6^{4-}$ ions – XRD spectra after 3 h treatments at various temperatures

One may expect that Mg–Al LDH pillared with organic anions has low heat stability, however, somewhat surprisingly, this was also found for that pillared with inorganic anion, as well. BET surface areas were low (Table 1), indicating that the pillared material does not survive even mild heat treatment (3 h evacuation at 473 K). This heat sensitivity is clearly demonstrated in Fig. 5. XRD spectra show that crystallinity ceases after the 3 h evacuation at 473 K. Obviously, the layered/pillared structure collapsed. Signs of detrimental changes can be observed after the 3 h evacuation at 423 K, too. Reflections are not so sharp as after a similar treatment at 323 K and their intensities also decrease.

Conclusions

Calcination destroys the layered structure of Mg–Al LDH. On increasing the temperature, the loss of adsorbed water and the crystal water occurs first, then dehydroxylation and the decomposition of carbonate occur, finally, the layered structure collapses. The resulting mixed oxides are basic in character. Rehydration only partially restores the original layered structure.

Experiments revealed that the *in situ* method led to pillaring of the LDH. Due to the success of intercalation, the basal spacing increased substantially, however, heat stability diminished.

References

1 W. Jones and M. Chibwe in Pillared Layer Structures: Current Trends and Applications, (I. V. Mitchell ed.) Elsevier Applied Science, London and New York 1991, p. 67.
2 A. Corma, V. Fairness, R. M. Martín Aranda and F. Rey, J. Catal., 134 (1992) 58.
3 G. Mao, M. Tsuji and Y. Tamaura, Clays and Clay Minerals, 41 (1993) 731.
4 A. Corma, V. Fornès and F. Rey, J. Catal., 148 (1994) 205.
5 E. Kanezaki, Solid State Ionics, 106 (1998) 279.