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Effect of time on the reconstruction of the $Mg_4Al_2(OH)_{12}CO_3{\cdot}3H_2O$ layered double hydroxide in a Na_2CO_3 solution

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Abstract The effect of time on the reconstruction of an $Mg_4Al_2(OH)_{12}CO_3{\cdot}3H_2O$ LDH compound in a 0.1 M Na_2CO_3 solution have been investigated. It seems that the reconstruction phenomena of the $Mg_4Al_2(OH)_{12}CO_3{\cdot}3H_2O$ LDH after a moderate thermal treatment is a very fast process, as it is already completed after 5 min of soaking in a 0.1 M Na_2CO_3 solution. Indeed, the weight of the reconstructed samples after the centrifuging-washing-drying cycle, as well as the carbon content of the reconstructed samples, remains constant whatever the time of contact between the solution and the mixed oxides issued from LDH. Powder XRD patterns are also similar for all the reconstructed samples without significant FWHM variations. SEM and TEM observations coupled with granulometric and BET measurements show that all the samples, both mixed oxides and reconstructed LDHs, are composed by aggregates of small plate-like particles (less than 100 nm) with a sub-hexagonal morphology but with different porosities.

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Introduction

The $Mg_4Al_2(OH)_{12}CO_3{\cdot}3H_2O$ compound belongs to the wide family of compounds known as layered double hydroxydes (LDHs), anionic clays or hydrotalcite-like compounds. The general formula of the family is $[M(II)_{1-x}M(III)_x(OH)_2]\,[A^{n-}]_{x/n}\cdot mH_2O$ where M(II) and M(III) are metal cations and A^{n-} are anions. M(II) is a divalent cation that can be Mg^{2+}, Mn^{2+}, Zn^{2+}, Co^{2+}, Cd^{2+}, Cu^{2+}, Ni^{2+}, ... and M(III) is a trivalent cation that can be Al^{3+}, Fe^{3+}, Cr^{3+}, Ga^{3+}, ... [1]. The anion A^{n-} can be as simple as inorganic anions such as Cl^-, F^-, Br^-, OH^-, SO_4^{2-} or CO_3^{2-}, to complex as DNA [2, 3]. These possibilities of substitutions lead to a wide family of compounds. Their structure consists of brucite-like layers ($Mg(OH)_2$) with a partial substitution of the divalent cation by a trivalent cation resulting in a net positive charge balanced by interlayer anions associated with variable amounts of water [4].

These compounds have received a great attention since the 1970's due to their potential technological applications. These applications are numerous. They can be used as catalysts or catalyst precursors [5, 6]. Indeed, it has been shown that the calcination of LDHs at temperatures depending on the particular cations in the layers and anions in the interlayers, leads to mixed oxides, characterised by structural homogeneity and absence of chemical segregation, that present basic sites for catalysis [7–9]. LDHs can also be used as support for catalysts [10]. As anions in the interlayer space are necessary to counterbalance the positive charge of the brucite-like layers, LDHs are widely used as ion exchangers [2, 11, 12], for depollution [13–16] or in separation science [17]. LDHs can act as flame retardant by generation of non-combustible gases (water and CO_2) when heated [1]. They are also used as precursors for the synthesis of spinel compounds [18]. More recently, LDHs have been involved in the synthesis of new heterostructured nanohybrids such as inorganic/inorganic, organic/inorganic or bio/inorganic materials [3, 19–21].

One of the most interesting and useful property of LDHs is their regeneration ability after moderate heating, sometimes called ''memory effect''. Indeed, a moderate heating (near 300–500 °C, depending on composition) leads to the formation of mixed oxides often considered as amorphous, which are able to recover the layered structure when in contact with solutions containing anions [1]. First studies on reconstruction were dealing with the possibility for reconstruction to take place related to the composition of the LDHs and the temperature of the thermal treatment [22–24]. More recent papers have investigated the mechanisms that lead to reconstruction [25–28]. These authors claim that reconstruction occurs by a mechanism of dissolution-recrystallisation. This property of reconstruction has allowed to synthesise new compositions of LDHs [29, 30] but is very important for all processes that require recyclability. Avoiding the reconstruction can also be very important for some reactions catalysed by mixed oxides issued from LDHs, where LDHs show a drastically reduced catalytic activity compared to their mixed oxides. Thus, it appears important to know the effect of time on the reconstruction and whether it is a fast or slow process. So the aim of this paper, is to study the effect of time on the reconstruction of an LDH compound.

Experimental

Raw powder of commercial heat treated $Mg_4Al_2(OH)_{12}CO_3 \cdot 3H_2O$ was used (Süd Chemie). First, a 0.1 M Na_2CO_3 aqueous solution has been prepared from solid Na_2CO_3 (Prolabo, 99.5% purity) in deionised water under vigorous stirring. Then 10 g of powdered heat treated $Mg_4Al_2(OH)_{12}CO_3 \cdot 3H_2O$ was added to the 500 ml of the 0.1 M Na_2CO_3 aqueous solution. Reactors have been closed to avoid evaporation during the experiment. The samples have been let in the solution at room temperature under vigorous stirring for duration times varying from 5 min to 28 days (5 min, 1 h, 24 h, 5 days and 28 days). At the end of each experiment, the slurry was centrifuged at 4000 rpm during 7 min (Jouan CR412) The supernatant was eliminated and the sample was washed three times with room temperature deionised water. Then, it was dried in a furnace at 43 °C for 24 h.

pH values have been recorded by a pH-meter Heitolab P310. CO_2 measurements have been performed with a Horiba carbon/sulfur analayzer EMIA-820 V. Powder X-ray diffraction (XRD) patterns have been performed on a Siemens D 500 diffractometer using Co-K_α radiation and operating at 40 kV and 30 mA at room temperature. The scans have been recorded from 4 to 84° (2θ) with a step of 0.02° and a counting time of 1 s per step. The specific surface areas of the samples were determined from the nitrogen adsorption isotherm at 77 K treated according to the BET method. Prior to the measurements, the samples were outgassed at 110 °C for 72 h. At the end of the outgassing process, the residual pressure was below 0.05 mbar. The measurements have been realised in a multipoint adsorptometer Micromeritics Tristar 3000. The size distributions of the particles composing the samples have been measured using a laser light scattering (λ = 632.8 nm) particle size analyser Malvern Mastersizer S. Prior to the measurements, 0.13 g l^{-1} of samples were dispersed in water containing 0.5 wt % of sodium hexametaphosphate and 0.5 wt % of sodium polyacrylate Dispex N40 (Allied Colloids). The solutions were then homogenised by mechanical stirring (1800 rpm) and an ultrasonic treatment of 5 min at 40 kHz. The results obtained are diameters of equivalent spheres expressed in volume. The scanning electron microscopy (SEM) observations have been realised on samples previously sputter-coated with a thin layer of carbon, using a Jeol 6100 coupled with an Energy Dispersive Spectrometer (Kevex Quantum) for chemical analysis, at 25 kV. The transmission electron microscopy (TEM) observations have been realised at 200 kV (Philips CM20 with a CCD Gatan camera). The TEM samples were prepared by dispersing the powder products in alcohol by ultrasonic treatment, dropping them onto a porous carbon film supported on a copper grid, and then drying them in air.

Results and discussion

First of all, the structure of the heat treated $Mg_4Al_2(OH)_{12}CO_3 \cdot 3H_2O$ compound has been checked by XRD. The thermal treated LDH exhibits an XRD pattern of a poorly crystalline compound (Fig. 1). This compound has a

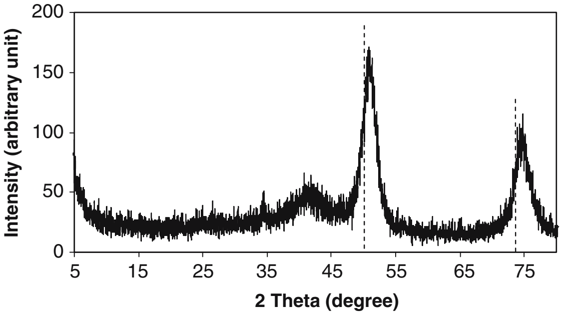


Fig. 1 XRD pattern of the oxides issued from the thermal treatment of $Mg_4Al_2(OH)_{12}CO_3 \cdot 3H_2O$ (dotted lines indicate the position of the strong lines of MgO)

structure similar to that of MgO, but with the strong lines of MgO shifted to higher 2θ. This indicates smaller lattice parameters due to the partial substitution of Mg by Al, 0.72 Å and 0.535 Å respectively [31]. This result is in agreement with the mixed oxides usually obtained after a moderate heat treatment of MgAl LDHs compounds [1].

The only parameter recorded during the reconstruction experiments is pH value of the solutions. Figure 2 exhibits the pH values measured for duration times varying from 0 to 15 h. It shows an increase of the pH value when increasing the duration time in solution, from 11.7 for the initial 0.1 M aqueous Na_2CO_3 solution ($t = 0$) up to a value near 13.1 reached after 12 h in solution. After 12 h, and up to 28 days, this pH value remains constant.

This seems to indicate that a phenomenon occurs as soon as the mixed oxides issued from the moderate heat treatment of the LDH are put in the aqueous Na_2CO_3 solution. An equilibrium seems to be reached circa 12 h, i.e. when the pH becomes constant.

After the centrifuging-washing-drying cycle, the weight of samples obtained has been checked. Figure 3 shows that whatever the time of contact between the solution and the oxides, the weight of samples obtained is constant between 16.02 and 16.22 g. The observed increase of mass is consistent with the restructuration process, i.e. the transformation of mixed oxides in a LDH phase, i.e. an uptake of protons, hydroxides and carbonates species. Indeed, this mass increase is consistent with the weight loss measured in thermogravimetric studies: a mass loss of 35–46% is usually observed for carbonate LDHs depending on the water content and the Mg/Al ratio [32]. The mass increase recorded during the reconstruction experiments (10 g of mixed oxides to circa 16.1 g of LDH) would correspond to a weight loss of 38%. This mass increase is consistent with a fully reconstructed LDH.

Figure 4 exhibits the carbon content measured in the samples for duration times varying from 0 to 28 days. This figure shows that the carbon content of the oxides is lower than the carbon content of the samples after contact with the Na_2CO_3 solution, 0.64 and 2.29% respectively. Moreover, it shows that the carbon content of the samples after contact with the Na_2CO_3 solution is constant irrespective to the duration time spent in solution. This value is consistent with the theoretical carbon content value of 2.56% calculated for the $Mg_4Al_2(OH)_{12}CO_3{\cdot}3H_2O$ formula. This means that the LDH is mainly reconstructed with CO_3^{2-} anion, even for the shortest contact times with the Na_2CO_3 solution. Indeed, for the shortest contact time with the solution (5 min), a possible reconstruction with OH^- could have been feared during the centrifuging-washing process as the sample stays 3× longer in deionised water (3 × 5 min) than in the Na_2CO_3 solution (5 min). The carbon content measurements show that reconstruction with OH^- does not occur for the sample staying 5 min in contact with the Na_2CO_3 solution, as this sample presents the same carbon content than the samples reconstructed during longer periods.

Powder XRD patterns of the resulting solids after 5 min, 1 h, 24 h, 5 days and 28 days in the Na_2CO_3 solution are presented in Fig. 5. This figure confirms that the patterns of all the samples are similar whatever the time spent in the solution. All the samples are single-phased and this phase correspond to the $Mg_4Al_2(OH)_{12}CO_3{\cdot}3H_2O$ LDH. The XRD patterns of the different samples are exhibiting peak areas (from 152 to 166 counts × degrees for the (110) peak of the samples soaked in the Na_2CO_3 solution 24 h and 1 h respectively) and full-width half-maximum (FWHM) very similar (from 1.44 to 1.66° for the (110) peak of the

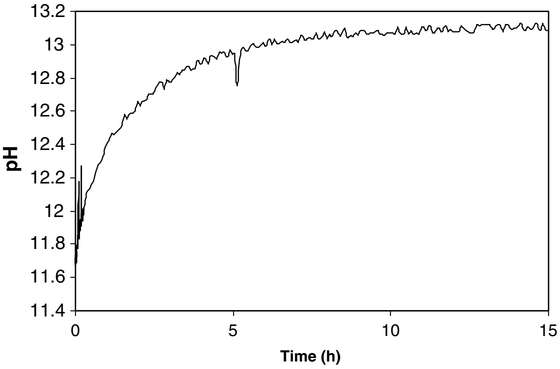


Fig. 2 pH value of the LDH + Na_2CO_3 solution as a function of time

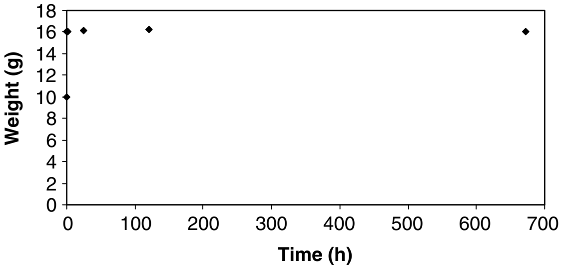


Fig. 3 Weight of solid samples obtained after centrifuging-washing cycle, after 5 min, 1 h, 24 h, 5 days and 28 days in the Na_2CO_3 solution

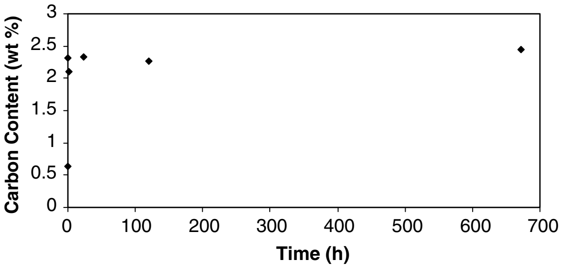


Fig. 4 Carbon content of the solid samples after 5 min, 1 h, 24 h, 5 days and 28 days in the Na_2CO_3 solution

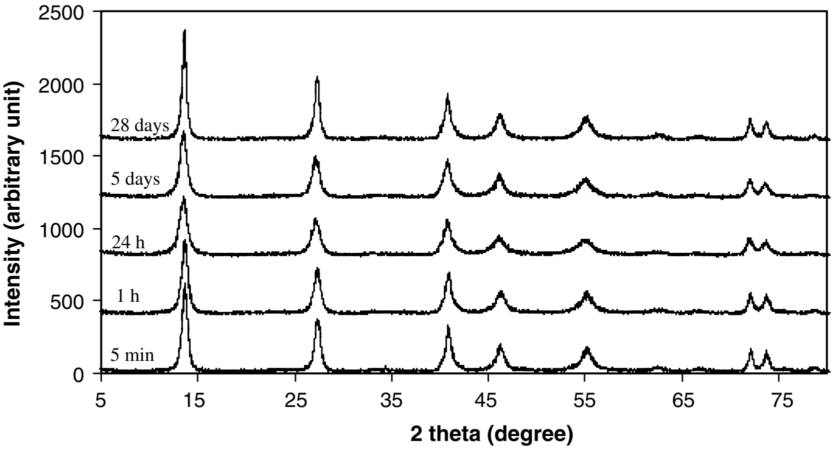


Fig. 5 Powder XRD pattern of solid samples after 5 min, 1 h, 24 h, 5 days and 28 days in the Na_2CO_3 solution

samples soaked in the Na_2CO_3 solution 5 days and 5 min respectively). This means that the crystallite size of the samples does not evolve significantly when increasing the time spent in the solution. This result is in disagreement with those found by Millange et al. [25]. Indeed, from time-resolved in-situ Energy Dispersive XRD experiments, these authors have observed a decrease of the FWHM of the (003) peak and have concluded to an increasing particle size as the reconstruction proceeds.

In order to check this point, a granulometric study has been performed. Figure 6 shows the size distribution of the particles of all the samples from the untreated mixed oxides to the sample soaked 28 days in the Na_2CO_3 solution. Roughly, Fig. 6 shows that for all the samples, 90% of the particles are smaller than 9 μm. Moreover, it seems that 3 different populations exist in the different samples: the first population has an average size of 0.36 μm, the second one has an average size of 1.7 μm, and the last one presents an average size of 4.9 μm. The particle size distributions are similar for the untreated mixed oxides and the samples soaked 5 min, 1 h, 24 h, and 5 days in the Na_2CO_3 solution. The sample soaked 28 days in the Na_2CO_3 solution presents a slightly different particle size distribution as the second population is more important than in other samples and as the third population is nearly absent. Figure 7 exhibits the corresponding specific surface areas obtained with the BET method. It shows that the untreated mixed oxides present an important specific surface area of 191 $m^2\ g^{-1}$, whereas the reconstructed LDHs have much lower specific surface areas (between 67.9 and 84.3 $m^2\ g^{-1}$ for the samples soaked in the Na_2CO_3 solution 5 min and 24 h respectively). There is an apparent discrepancy between granulometric and BET results. Indeed, the untreated mixed oxides present a particle size distribution similar to the LDH soaked 5 min in the Na_2CO_3 solution, but a specific surface area nearly three times larger. Moreover, while the samples soaked 1 h and 28 days in the Na_2CO_3 solution present similar specific surface area (77 and 76 $m^2\ g^{-1}$ respectively), the sample soaked 28 days in the solution exhibits a lower average particle size (near 1.5×) compared to the sample soaked 1 h in the solution.

SEM observations of the untreated mixed oxides (Fig. 8) show that the solid is mainly composed of grains from a few tenth of micron to several microns, consistent

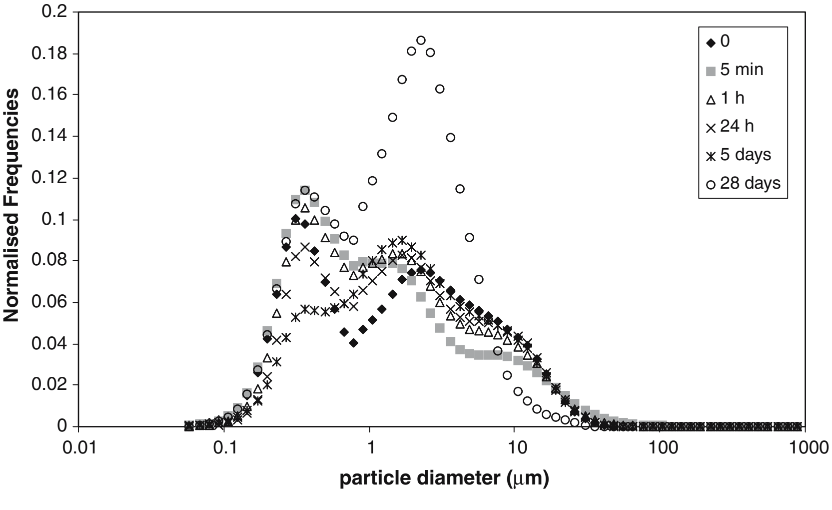


Fig. 6 Size distribution of the particles measured by laser granulometry, of the mixed oxides and of the samples after 5 min, 1 h, 24 h, 5 days and 28 days in the Na_2CO_3 solution

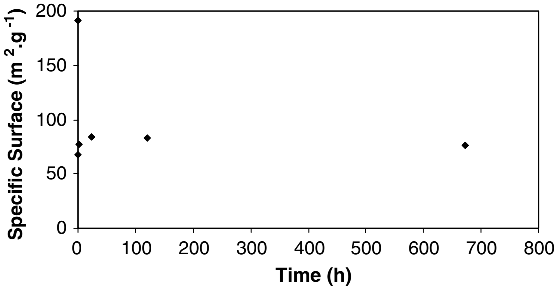


Fig. 7 Specific surface area (BET method) of the mixed oxides and of the samples after 5 min, 1 h, 24 h, 5 days and 28 days in the Na_2CO_3 solution

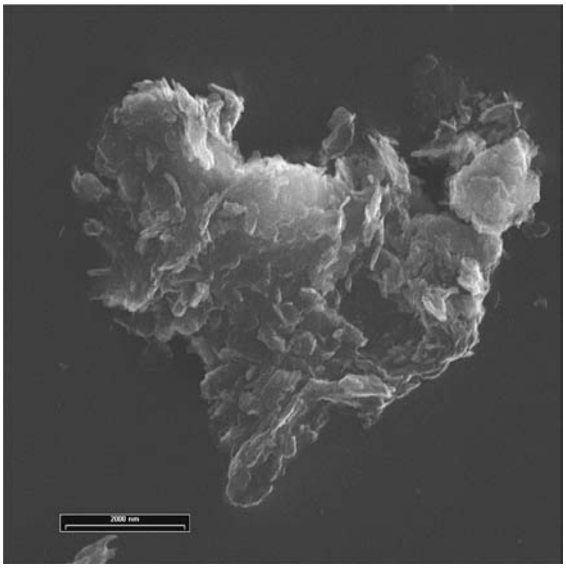


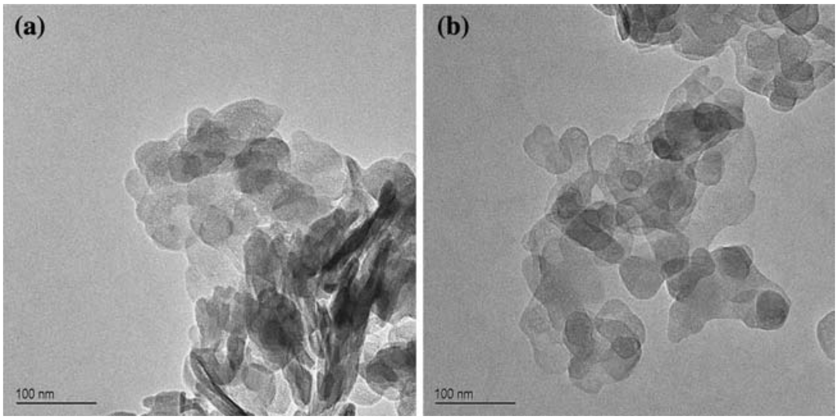
Fig. 8 SEM micrograph (secondary electrons) of the untreated mixed oxides

with the granulometric data. However, Fig. 8 also shows that these grains are in fact aggregates of smaller plate-like particles. A TEM study confirms that the grains are effectively constituted from small plate-like particles. Indeed, Fig. 9a clearly shows the small particles (less than 100 nm) exhibiting a sub-hexagonal morphology, constituting the grains observed by SEM. Figure 9b shows that the sample soaked 28 days in the Na_2CO_3 solution exhibits the same kind of small particles. The morphology and size of these particles are similar to those constituting the untreated mixed oxides (Fig. 9a). This result is consistent with the X-ray diffraction data described above that do not show significant change of the crystallite size. Figure 10 exhibits a SEM micrograph of the grains constituting the sample soaked 28 days in the Na_2CO_3 solution. The size of these grains is similar to the size of the grains observed in Fig. 8 for the untreated mixed oxides. They are also composed of small plate-like particles as shown in Fig. 9b. However, the grains seem more dense than the grains observed in the untreated sample. This means that the porosity of the grains of the sample soaked 28 days in the Na_2CO_3 solution is surely less important than the porosity of the grains of the untreated mixed oxides. This can explain the apparent discrepancy between granulometric and BET results.

Indeed, for all the samples, from the untreated mixed oxides to the reconstructed LDH after 28 days in the Na_2CO_3 solution, small plate-like particles (less than 100 nm) with a sub-hexagonal morphology are constituting aggregates. Granulometric measurements are giving indications of the size distribution of these aggregates whereas BET is related to their porosity. This model is consistent with all the data presented above.

So it seems that the reconstruction phenomena of LDH after a moderate thermal treatment is a very fast process, as it is already completed after 5 min of soaking in a Na_2CO_3 solution. Moreover, during the reconstruction process, the size of the constituting plate-like particles (mixed oxides or LDH) does not seem to change significantly, and the crystallinity of the reconstructed LDH phase does not seem to evolve with the time of contact with the solution. The main change occurring during the reconstruction process is the specific surface area decrease from the mixed oxide to

Fig. 9 TEM micrograph of (**a**) the untreated mixed oxides, (**b**) the reconstructed LDH after 28 days in the Na_2CO_3 solution



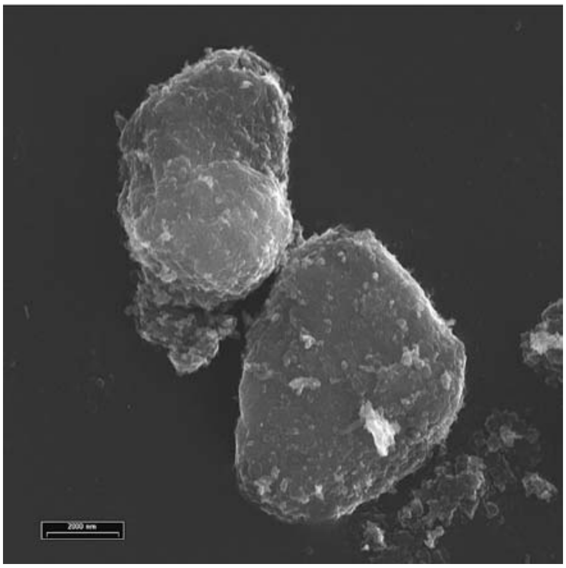


Fig. 10 SEM micrograph (secondary electrons) of the sample after 28 days in the Na_2CO_3 solution

the LDH phase, correlated to the porosity of the aggregates formed by the small plate-like particles.

The kinetics of the reconstruction process observed in this study is faster than the one observed by Stanimirova and Kirov [28], who consider that the reconstruction process is very slow and completed after 24–48 h at room temperature, faster than the one observed by Rajamathi et al. [26], who found a complete reconstruction in less than 5 h at 65 °C, and faster than the observations of Millange et al. [25], who have observed a complete reconstruction in 3 h at room temperature.

All these elements (no morphological changes of the particles, no change of the XRD patterns, ...), seem more in agreement with the conclusions of Sato et al. [33] who have suggested that the reconstruction of hydrotalcite proceeds topotactically without dissolution of the sample, than with the dissolution-recrystallisation process described by Millange et al. [25], Rajamathi et al. [26], Stanimirova et al. [27], Stanimirova and Kirov [28]. However, simple comparisons are difficult to make, because of the huge differences in experimental conditions presented in the different papers devoted to reconstruction of LDHs (pure water, Na_2CO_3 solutions, temperature, pH, concentrations, solid/liquid ratio...). Further investigations with in-situ characterisation techniques are in progress to study the first steps of the reconstruction process.

Conclusion

The kinetics of the reconstruction of an $Mg_4Al_2(OH)_{12}CO_3{\cdot}3H_2O$ LDH compound in a 0.1 M Na_2CO_3 solution have been investigated. The pH measurements of the solutions have shown an increase of the pH up to a value near 13.1 reached after 12 h in solution. After 12 h, and up to 28 days, this pH value remains constant. The weight of the reconstructed samples, after the centrifuging-washing-drying cycle, remains constant whatever the time of contact between the solution and the oxides, as well as the carbon content of the reconstructed samples. Powder XRD patterns are also similar for all the reconstructed samples without significant FWHM variations. There is an apparent discrepancy between granulometric and BET results as samples with similar specific surface area can present different particle size distributions and samples with similar particle size distributions can present specific surface area from simple to triple. However, SEM and TEM observations show that all the samples, both mixed oxides and reconstructed LDHs, are composed by aggregates of small plate-like particles (less than 100 nm) with a sub-hexagonal morphology but with different porosities. So, granulometric measurements are giving indications of the size distribution of the aggregates whereas BET measurements are related to their porosity. So it seems that the reconstruction phenomena of LDH after a moderate thermal treatment is a very fast process, as it is already completed after 5 min of soaking in a 0.1 M Na_2CO_3 solution. It occurs without affecting the size of the constituting plate-like particles. Moreover, the crystallinity of the reconstructed LDH phase does not seem to evolve with the time of contact with the solution. The main change occurring during the reconstruction process is the specific surface area decrease from the mixed oxide to the LDH phase, correlated to the porosity of the aggregates formed by the small plate-like particles.

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References

1. Cavani F, Trifiro F, Vaccari A (1991) Catal Today 11:173
2. Miyata S (1983) Clays Clay Miner 31:305
3. Choy J-H (2004) J Phys Chem Solids 65:373
4. Reichle WT (1986) Solid States Ionics 22:135
5. Kagunya W, Hassan Z, Jones W (1996) Inorg Chem 35:5970
6. Vaccari A (1998) Catal Today 41:53
7. Constantino VRL, Pinnavaia TJ (1995) Inorg Chem 34:883
8. Sanchez Valente J, Figueras F, Gravelle M, Kumbhar P, Lopez J, Besse J-P (2000) J Catal 189:370
9. Alejandre A, Medina F, Rodriguez X, Salagre P, Cesteros Y, Sueiras JE (2001) Appl Catal B: Environ 30:195
10. Giannelis EP, Nocera DG, Pinnavaia TJ (1987) Inorg Chem 26:203
11. Bish DL (1980) Bull Mineral 103:170
12. Ookubo A, Ooi K, Hayashi H (1993) Langmuir 9:1418
13. You Y, Vance GF, Zhao H (2001) Appl Clay Sci 20:13
14. Seida Y, Nakano Y (2002) Water Res 36:1306

15. Das DP, Das J, Parida K (2003) J Colloid and Interf Sci 261:213
16. Orthman J, Zhu HY, Lu GQ (2003) Sep Purif Technol 31:53
17. Lotsch B, Millange F, Walton RI, O'Hare D (2001) Solid State Sci 3:883
18. Moroz T, Razvorotneva L, Grigorieva T, Mazurov M, Arkhipenko D, Prugov V (2001) Appl Clay Sci 18:29
19. Kwak S-Y, Jeong Y-J, Park J-S, Choy J-H (2002) Solid State Ionics 151:229
20. Chen W, Feng L, Qu B (2004) Solid State Commun 130:259
21. Leroux F, Gachon J, Besse J-P (2004) J Solid State Chem 177:245
22. Tichit D, Lhouty MH, Guida A, Chiche BH, Figueras F, Auroux A, Bartalini D, Garrone E (1995) J Catal 151:50
23. Kooli F, Depege C, Ennaqadi A, De Roy A, Besse JP (1997) Clays Clay Miner 45:92
24. Puttaswamy NS, Kamath PV (1997) J Mater Chem 7:1941
25. Millange F, Walton RI, O'Hare D (2000) J Mater Chem 10:1713
26. Rajamathi M, Nataraja GD, Ananthamurthy S, Kamath PV (2000) J Mater Chem 10:2754
27. Stanimirova TS, Kirov G, Dinolova E (2001) J Mater Sci Lett 20:453
28. Stanimirova TS, Kirov G (2003) Appl Clay Sci 22:295
29. Chibwe K, Jones W (1989) Chem Mater 1:489
30. Kooli F, Rives V, Ulibarri MA (1995) Inorg Chem 34:5114
31. Shannon RD (1976) Acta Cryst A 32:751
32. Prinetto F, Ghiotti G, Graffin P, Tichit D (2000) Micropor Mesopor Mat 39: 229
33. Sato T, Fujita H, Endo T, Shimada M, Tsunashima A (1988) React Solid 5:219