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Uniform nanoparticles of hydrotalcite-like materials and their textural properties at optimized conditions of urea hydrothermal treatment

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HIGHLIGHTS

- The efficient urea hydrothermal synthetic technique of hydrotalcites was optimized.
- A series of single-phase Mg–Al hydrotalcites was successfully obtained.
- The chemical composition, crystallinity data, and textural properties were investigated.
- The highest uniformity of particle size was recorded at urea/metals molar ratio of 3.0.
- The reduction of hydrothermal aging led to a narrow particle size distribution.

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ABSTRACT

The efficient urea hydrothermal synthetic technique for hydrotalcite (HTlc) was optimized to prepare uniform HTlc nanoparticles that exhibit high performance in variety of applications. Experimentally, a series of single-phase Mg–Al HTlc(s) with good textural properties was successfully obtained under optimized urea/metals molar ratio and hydrothermal aging conditions. The X-ray analysis confirmed the purity and the high crystallinity of the prepared HTlc(s). The chemical composition, crystallinity, and textural properties of the optimized HTlc(s) were investigated and compared to those of the conventionally prepared HTlc(s). The increase in the urea concentration decreased the crystallite size of the HTlc(s). The reduction in the hydrothermal aging time led to a narrow particle size distribution. The greatest uniformity of particle size was achieved at a urea/metals molar ratio of 3.0 and at a hydrothermal aging time of 12 h. An increase in the urea/metals molar ratio to 3.0 increased the micropore volume available for adsorption, and the BET surface area consequently increased. The hydrothermal aging of the HTlc(s) significantly decreased the amount of nitrogen the samples adsorbed.

1. Introduction

Driven by the promise for new technological applications and by our belief that advances in nanotechnology demand the development of new materials, layered materials are of particular interest. An interesting category of layered materials is hydrotalcites (HTlcs). HTlcs are used as adsorbents of pollutants [1,2], as catalysts [3], as catalyst precursors [4], as nanocarriers of bioactive materials [5–7] and as additives for polymers [8].

HTlc is an anionic clay. It consists of layers of edge-sharing hydroxyl octahedra. HTlc has a general formula of $[M^{II}_{1-x}M^{III}_{x}(OH)_2](A^{n-})_{x/n}$-$^{II}_{1-x}M^{III}_{x}(OH)_2](A^{n-})_{x/n}\cdot mH_2O$, where M^{II} and M^{III} represent divalent and trivalent metal ions, respectively, and A^{n-} is the anion between the layers. Replacement of some fraction of the divalent ions by a trivalent ion of comparable size leads to a net positive charge on the layers. This positive charge is balanced by anions in the interlayer. M^{II} can be, for example, Mg^{2+}, Ca^{2+}, Zn^{2+}; and M^{III} can be Al^{3+}, Cr^{3+} and Co^{3+}. The interlayer anions A^{n-} can be inorganic (e.g. halides, oxoanions, oxometalates or polyoxometalates) or organic anions (e.g. polymers, anionic drugs, hormones or amino acids) [9,10].

However, the nature of HTlc application is influenced by its physicochemical properties, and the present conventional synthesis methods (such as coprecipitation technique) do not allow a large

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Table 1
Synthetic conditions of HTlc(s) prepared by conventional and urea hydrolysis techniques[a] at 120 °C, and their chemical analysis data.

Sample name	Urea/metals molar ratio (Urea/(Mg^{2+} + Al^{3+}))	Reaction time (h)	Mg/Al[b] molar ratio	pH[c]	N weight (%)	CO_3^{2-} weight (%)	Yield (%)
U0.5-24	0.5	24	0.61	5.4	–[d]	–[d]	12
U1-24	1.0	24	0.86	6.0	–[d]	–[d]	13
U1.5-24	1.5	24	1.52	7.1	–[d]	–[d]	22
U2-3	2.0	3	0.98	6.6	–[d]	–[d]	41
U2-6	2.0	6	1.65	7.3	–[d]	–[d]	45
CV-12	–	12	1.90	8.5	0.000	7.81	75
U2-12	2.0	12	1.94	7.5	0.041	5.18	82
U3-12	3.0	12	1.98	7.9	0.056	6.19	84
U3.5-12	3.5	12	1.97	8.2	0.103	6.31	89
CV-18	–	18	1.91	8.5	0.000	7.42	78
U2-18	2.0	18	1.98	7.8	0.011	5.51	84
U3-18	3.0	18	1.99	8.2	0.051	6.18	87
U3.5-18	3.5	18	1.93	8.3	0.090	6.45	91
CV-24	–	24	1.91	8.5	0.000	7.36	80
U2-24	2.0	24	1.98	7.9	0.000	5.20	86
U3-24	3.0	24	1.88	8.4	0.040	6.20	90
U3.5-24	3.5	24	1.80	8.9	0.084	6.31	92

[a] Metal ions conc. (mol/L) = 0.5, Metal ions molar ratio (Mg^{2+}/Al^{3+}) = 2.
[b] Metals molar ratio in the product materials after the reaction.
[c] pH of HTlc dispersion after reaction.
[d] Not selected for analysis.

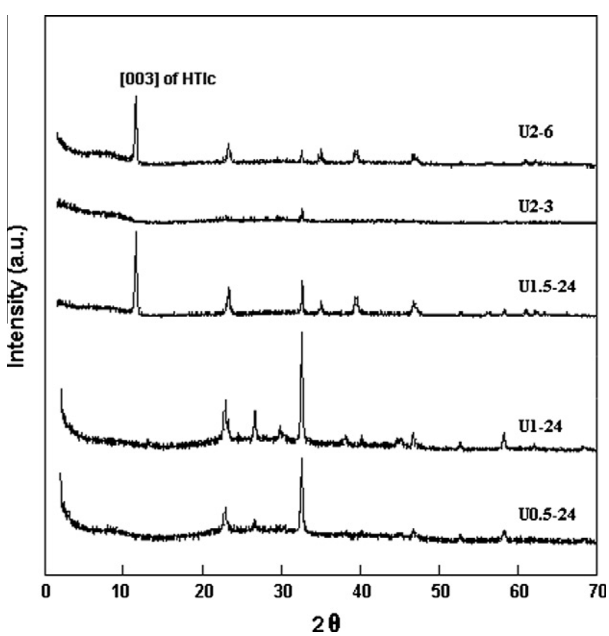

Fig. 1. X-ray diffraction patterns of the HTlc samples synthesized at insufficient conditions of urea and reaction times.

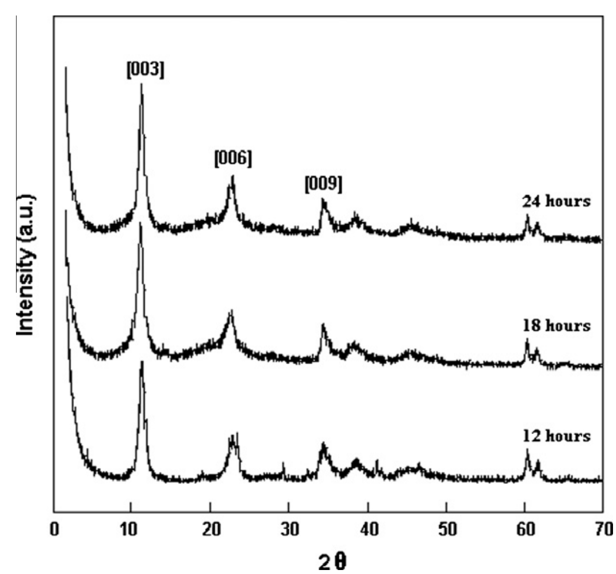

Fig. 2. X-ray diffraction patterns of the conventionally prepared HTlc materials.

degree of control of the HTlc textural properties in terms of morphology, particle size and adsorption capacity. Therefore, HTlc(s) deserve increased interest in the identification and optimization of the synthetic parameters that affect their textural properties. In addition, detailed structural information with respect to HTlc can improve the performance of HTlc(s) in various applications. Toward this end, several approaches have been attempted because well-defined HTlc particles have yet to be developed. Tichit et al. [11] studied the effects of microwave irradiation on co-precipitated HTlc gels and found that microwaves induced a higher number of surface defect sites, which affected the specific surface area and the crystallite particle size. Seida et al. [12] found that HTlc synthesized under ultrasonic conditions exhibited a larger crystallite size and a larger adsorption capacity. Consequently, the degree of adsorption of HTlc correlated well with the crystal size. Choudary et al. [13] have developed an innovative aerogel method that produces nanobinary and nanoternary HTlc(s) with large surface areas and small particle sizes. Based on these investigations and the use of HTlc(s) as efficient precursors, the optimization of the textural properties of HTlc(s) is a fruitful area of research and can extend the range of applications of these interesting materials.

HTlc(s) can be prepared using a variety of techniques [14–17]. The urea hydrothermal method is used to synthesize HTlc(s) [18] because urea promotes the precipitation of metal hydrous oxides with uniform size when a homogenous aqueous solutions that contains soluble metal salts is heated. Despite the strong potential of the urea method, the delicate control of the urea/metal ratio is required to prepare well-ordered single phase HTlc(s). To the best of our knowledge, a detailed study about the effects of the urea/metals ratio on the physicochemical and textural properties of the obtained HTlc(s) has not been previously reported.