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Formation and Aggregation Kinetics of Mixed Metal Hydroxides Agglomerates

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Abstract: The aggregation and fractal structure of mixed metal hydroxides (MMH) agglomerates with increasing ionic strength have been studied by dynamic light scattering (DLS) and SEM techniques. The experiments indicate that the MMH agglomerates have two different structures in RLA regime and DLA regime, and also give the proof that the transition region between RLA and DLA may occur.

Keywords: Aggregation kinetics, fractal structure, the mixed metal hydroxides (MMH).

The mixed metal hydroxides (MMH) are very versatile materials and rarely existing in nature but it is relatively easy and inexpensive to synthesize [1,2]. In recent years, MMH have been widely utilized in many fields such as catalysts, antisettling agents, medicine, and rheology modifiers, *etc*. The aggregation kinetics and structure of colloidal agglomerates are the predominant factors to affect these applications. However, the study on the aggregation kinetics of this permanent positively charged and plate-like particle model has received less attention. This letter will report about aggregation behavior and fractal structure of MMH agglomerates with increasing ionic strength by dynamic light scattering (DLS) and SEM techniques.

In this study MMH were synthesized by a non-steady coprecipitation method[1] and the chemical composition determined by chemical analysis was $Mg_{0.48}Al(OH)_{3.52}Cl_{0.44}$. A near-monodisperse particle distribution was obtained by sequential centrifugation, decanting and filtering. Using a JEM-100cxII model transmission electron microscope (TEM), the average platelet diameter was determined to be 40±2 nm as shown in **Figure 1**. The mean hydrodynamic diameter determined by DLS was equal to 73.2 nm with the relative standard deviation of about 0.15 nm. Average particle concentration was 0.2408 ± 0.009 kg/m^3. pH value of the dilute dispersion was adjusted to 9.0. All experiments were performed at 25 °C.

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Figure 1 TEM micrograph of MMH (100k multiple)

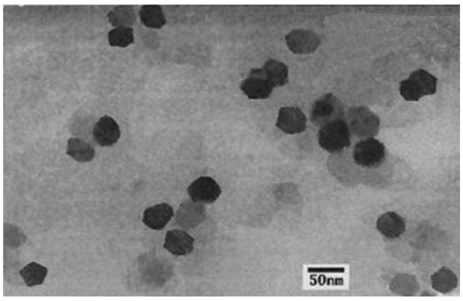
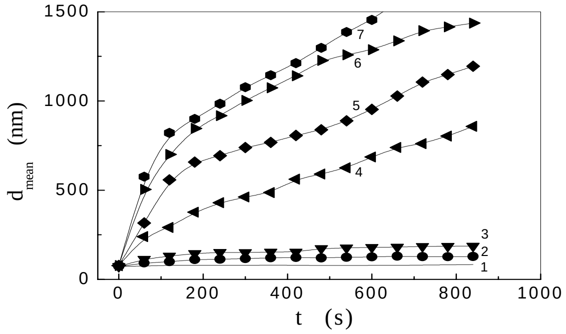


Figure 2 Hydrodynamic diameter of MMH agglomerates as a function of time



The concentrations of KCl: 1- 5 mmol/L，2 - 10 mmol/L，3 - 50 mmol/L，
4 - 120 mmol/L，5 - 180 mmol/L，6 - 210 mmol/L，7 - 300 mmol/L

Aggregation was induced by adding known amounts of solution of KCl into the prepared particulate dispersion to achieve a final KCl concentration with the range 1 to 300 mmol/L. The curves of mean hydrodynamic diameters (d_{mean}) *versus* time (t) have been detected by DLS and the rate constant for doublet formation (k_{II}) can be calculated from the equation $k_{\text{II}}=(\partial d_{mean}/\partial t)_{t\to 0}/(d_{\text{mean},0}\,\alpha N_{\text{I}(t=0)})$, where α is an optical factor and $N_{\text{I}(t=0)}$ is the initial number concentration of primary particles [3]. Then the stability ratio W can be obtained further from the equation: $W=k_{\text{Smol}}/k_{\text{II}}$. Here the theoretical rate constant for diffusion-limited aggregation k_{Smol} is calculated by the Smoluchowski equation $k_{\text{Smol}}=8\kappa_{\text{B}}T/3\eta$, where κ_{B} is the Boltzmann's constant, T is the absolute temperature and η is the viscosity of the medium [3]. DLS measurements were performed using the apparatus consisted of a BI-200SM goniometer and a BI-9000AT digital autocorrelator (Brookhaven, America). All data were gathered at a scattering angle of 90° with a wavelength of 488 nm. The SEM image of MMH agglomerates after supercritical drying in CO_2 was obtained by an S-520 model SEM (HITACHI, Japan) and the fractal dimensions of agglomerate surfaces were determined by box-dimension method [4].

Figure 2 shows the increase of the hydrodynamic diameter with time for the MMH dispersions at different KCl concentrations. The initial slope of the curve of hydrodynamic diameter versus time increases with increasing electrolyte concentration. The electrolyte concentrations higher than 210 mmol/L leads to the same slopes and the aggregation rate, which can be expressed by $(\partial d_{mean} / \partial t)_{t\rightarrow 0}$ **,** reaches maximum.

Figure 3 shows the stability ratios determined from the slope of the mean hydrodynamic diameter with time at different ionic strengths. The shape of the curve is typical colloids stabilized by electrostatic repulsions [3]. The slope of the reaction limited aggregation (RLA) regime as a function of electrolyte concentration has been divided on the left-hand side of **Figure 3** and the plateau regime of the diffusion limited aggregation (DLA) on the right-hand side. The critical electrolyte concentration (C_c) for this particle was found to be 205 mmol/L.

When a suspension of plate-like particles aggregates, three different modes of particle association may occur: face-to-face (FF), edge-to-face (EF) and edge-to-edge (EE). EF and EE association can lead to three-dimensional 'card-house' structures, while FF association leads to thicker and larger flakes. **Figure 4** are SEM micrographs of MMH agglomerates obtained from dispersions at different electrolyte concentrations. **Figure 4a** shows the compact and fine grape-like agglomerates, which can be described by the card-house structure formed at low electrolyte concentration in RLA region. In **Figure 4c** the agglomerates consist of loose MMH flakes described by FF association at

Figure 3 Stability curve of MMH particles as a function of KCl concentration

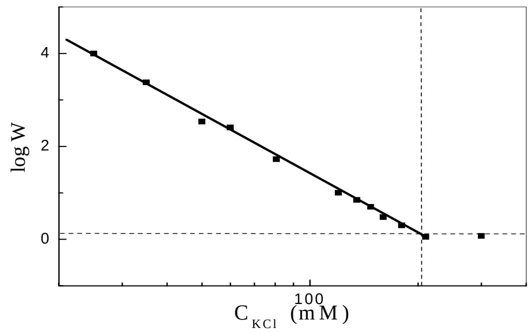
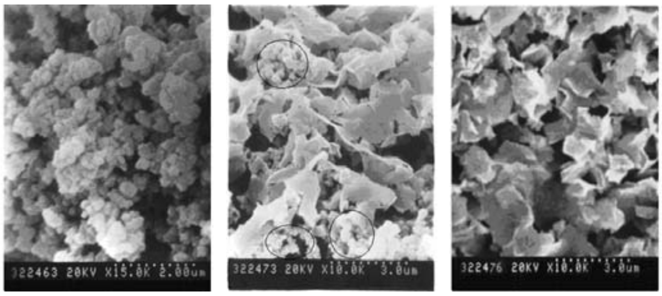


Figure 4 SEM micrographs of MMH agglomerates (t = 600 s)



(a) C_{KCl} = 10 mmol/L, (b) C_{KCl} = 180 mmol/L, (c) C_{KCl} = 300 mmol/L high electrolyte concentration in DLA region. Just as shown in **Figure 4b**, the complex of two different structures appears at the KCl concentration of about 160~220 mmol/L, which names as the transition region between RLA and DLA.

By SEM image analysis[4], the fractal dimension of agglomerates decreases gradually from 2.26, 1.92 to 1.76 with the increase of electrolyte concentration. The evolvement of fractal dimension also approves that the agglomerate structures grow from compact and fine agglomerates to loose-flake agglomerates. Odriozola and Di Biasio[5,6] supported the existence of a vast transition region and considered that repulsive particle interactions not only reduced the sticking probability but also introduced additional effects, such as multiple cluster-cluster contacts, which need not be considered for pure DLA.

Acknowledgments

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