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ORIGINAL CONTRIBUTION

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Study on the preparation and structure of positive sol composed of mixed metal hydroxide

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Abstract Using precipitation method mixed metal hydroxide (MMH) positive sol was prepared. The preparation process and the properties of the sol were studied with powder XRD, TEM, particle size distribution determination system and microelectrophoresis instrument.

The preparation of MMH was made as follows: Diluted ammonia water was added to the mixed solution of aluminum and magnesium chlorides which was prepared in the molar ratio of 1:1 or 1:2, or 1:3; then the pH values of the suspension at different amounts of ammonia water were measured. After that, the precipitate was aged for 5 h in the mother solution at room temperature, and washed after filtering. Finally, the filter cake was peptized at constant temperature of 333 K.

The results showed that 1) preparation reaction was completed in three steps, 2) pH value was decisive factor, and 3) both the contents of magnesium and the ζ-potential of MMH sol particles increased with pH values and finally remained constant. The mechanism of the reaction was that magnesium ions intercalated $Al(OH)_3$ crystal lattice, forming mixed metal hydroxide. The results also showed that positively charged MMH colloidal particle belonged to hexagonal system and three-layer superposition structure.

Key words Mixed metal hydroxide – layered compounds – positive sol – precipitation

Introduction

In 1942, Feitknecht [1] and colleagues reported the preparation of mixed metal hydroxide (MMH) by coprecipitation method at high pH from a solution containing two different valent metal ions. Feitknecht stated that the structure of these compounds was double layers, one was regular triakisoctahedral layer containing divalent cations, in another regular dioctahedral layer containing trivalent cations. In the 1970s, Allmann [2] summarized the work of Feitknecht and others about these types of compounds and stated that the two cations were randomly distributed in the same octahedral hydroxide sheet with anions such as Cl^- and CO_3^{2-} and water occupying the region between these layers. This was not in agreement with the earlier idea that the structure consisted of alternate layers of the two individual hydroxides. These compounds possessed bigger surface area, and formed basic catalyst or catalyst carrier of specific composition. In addition, the compounds were used as a characteristic absorbent for ion exchange since they had specific layered structure.

In 1988, Burba et al. [3, 4] first applied MMH to oilfield chemistry; they suggested that MMH particles and sodium montmorillonite could form composite possessing quite superior suspension capacity, which was widely used in industry. Ref. [5] had summarized two methods of the preparation of MMH. One was coprecipitation and another was intercalation. The coprecipitation method was done by mixing proportionally different metal salt aqueous solutions, then adding precipitating agent contained hydroxyl ion; after that, washing, drying and crushing the precipitate. The intercalation method was done by forming a precipitate first, then intercalating another metal ion into the precipitate crystal lattice, or forming MMH in the pores of the macroporous ion exchange resin. We [6] had prepared montmorillonite particles charged positive by intercalation.

In the 1990s, we [7–11] synthesized positively charged MMH as transforming agent of electric property of clay suspension, which benefited oilfield development. At present, the structure of MMH has not been studied in detail. According to electron microscope photogram, only sheet-like particles were known. In view of the ever increasing application potential of MMH, we studied the method of preparation of MMH (Al-Mg) by inspecting the test condition, the shape, the particle diameter, the electric property and the structure of MMH with microelectrophoresis, electron microscope and XRD; and thought that it was probable to obtain the more positively-charged MMH sol by means of intercalating metal ions during coprecipitation.

Experimental

Reagents

$AlCl_3 \cdot 6H_2O$; $MgCl_2 \cdot 6H_2O$; $NH_3 \cdot H_2O$ were all C.P. reagents.

Apparatus

Powder x-ray diffraction patterns were obtained by the Japanese D/max-YB model at Cu target, 40 KV and 150 mA. The samples were step-scanned from 5° to 60° at the speed of 4°/min.

TEM micrograph was taken by JEM-100cxII model electron microscope. Particle size distribution was measured by Malvern II c model automatic particle diameter determination system.

The ζ-potential of MMH was measured by DXD-I model microelectrophoresis instrument.

The pH values of solution were obtained by DZ-2 model automatic electric potential titration instrument.

The contents of magnesium and aluminum in the precipitate were measured by electron spectroscopy for chemical analysis of JXA-840 model scanning electron micrograph.

Preparation of MMH sol

A mixed solution of magnesium and aluminum chlorides was prepared in the molar ratio of 1:1, or 1:2, or 1:3. Then diluted ammonia water (5:1 (V/V)) was added to the mixed solution at a speed of 15.0 ml/min. The pH values of the suspension at different amounts of ammonia water were measured. The precipitate was aged for 5 h in the mother solution at room temperature, and then washed with deionized water. After that, the filter cake was peptized at constant temperature of 333 K, forming the MMH positive sol. The ζ-potential, chemical composition, particle distribution and XRD of MMH sol prepared were measured.

Results and discussion

Effect of pH value on synthesis of MMH

Effect of the amounts of ammonia water on the pH value of reaction solutions

The pH value change diagram is shown in Fig. 1. It is evident that when ammonia water was added to the mixed solution (1:1) of magnesium and aluminum chlorides with total metal concentrations being $0.50\,mol \cdot dm^{-3}$ and $0.80\,mol \cdot dm^{-3}$, respectively, the curves were divided into three parts: 1) in the range of 3.0~4.0, pH value changed very little with increasing amounts of ammonia water, 2) in the range of 4.0~8.0, pH value increased rapidly, and 3) at pH above 8.0, the value increased gently.

The reaction mechanism of the mixed solution could be conjectured from the changes in the curve. At pH = 4.0, when the concentration of Al^{3+} reached only $1.3 \times 10^{-3}\,mol \cdot dm^{-3}$, the precipitation reaction should have started according to solubility product of aluminum hydroxide, $Ksp = 1.3 \times 10^{-33}$. However, the precipitation reaction did not start because of the following reaction:

$$Al(OH)_3 + H_2O \rightleftharpoons Al(OH)_4^- + H^+ , \quad (1)$$

i.e., the precipitate could be dissolved again and could not be reacted completely. In the first part, the reaction should go as follows:

$$NH_3 \cdot H_2O \rightleftharpoons NH_4^+ + OH^- \quad (2)$$

$$[Al(H_2O)_6]^{3+} + OH^- \rightleftharpoons [Al(OH)(H_2O)_5]^{2+} + H_2O \quad (3)$$

$$[Al(OH)(H_2O)_5]^{2+} + OH^- \rightleftharpoons [Al(OH)_2(H_2O)_4]^+ + H_2O . \quad (4)$$

Because the reactions consumed a lot of hydroxide ions, pH value increased gently. As for Mg^{2+}, the $Mg(OH)_2$

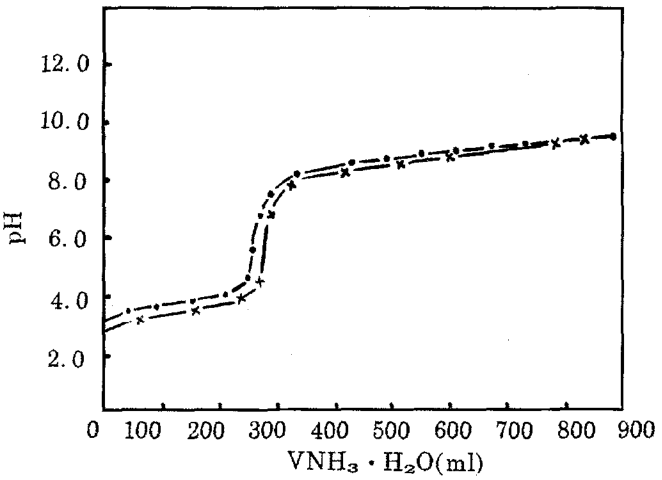


Fig. 1 Effect of the amounts of ammonia water on the pH value in precipitation. For reaction solution, the molar ratio of Mg to Al was 1:1, total metal concentrations were (·) 0.50 mol · dm^{-3}, (×) 0.80 mol · dm^{-3}

precipitate could not be formed according to the solubility product of $Mg(OH)_2$, $Ksp = 1.8 \times 10^{-11}$.

In the second part (pH value was in the range of 4.0 ~ 8.0), pH value increased sharply with ammonia water added; we found that the viscosity of the solution rose, and that the thixotropy increased at this part. So hydroxyaluminum ions are considered to be able to polymerize by hydrogen bonds and coordinate bonds on the basis of properties of hydroxyaluminum ions, and to form multinucleate compounds. The pH value of the solution sharply increased since hydroxide ions only played the role of a catalyst. The reaction equation in this part was as follows:

$$2[Al(OH)(H_2O)_5]^{2+} \rightleftharpoons [Al_2(OH)_2(H_2O)_8]^{4+} + 2H_2O \,. \tag{5}$$

Similarly, the $Mg(OH)_2$ precipitate still could not be formed in second part according to the solubility product of $Mg(OH)_2$.

In the third part, pH value was above 8.0, aluminum and magnesium ions would be precipitated simultaneously, final pH value of the solution was same as the value of ammonia water and varied little.

Effect of pH value of precipitation on the contents of magnesium

The contents of magnesium and aluminum in the precipitate in different pH values were analyzed, the results are shown in Table 1. When pH values were below 6.50, the main metal composition of the precipitate was aluminum, and the contents of magnesium were very low (only 1% or so). The magnesium could be regarded as an inclusion in the precipitate of Al^{3+}. When pH values were in the range of 7.48 ~ 8.10, the contents of magnesium increased; however, according to the solubility product of magnesium hydroxide the precipitate of $Mg(OH)_2$ should not occur in this condition. This result showed that more magnesium ions had intercalated $Al(OH)_3$ crystal lattice. When pH values were above 8.56, a lot of $Mg(OH)_2$ precipitate occurred with contents of magnesium being 39% and remaining constant, which was in complete agreement with the results in Fig. 1.

Table 1 Effect of pH values on the contents of magnesium, the peptization and the appearances of the precipitate

pH values in precipitation	Mg (mol. %)*	peptization	appearances
4.65	1.68	no	gel
6.50	1.43	no	gel
7.48	12.2	no	gel
8.10	25.7	yes	viscous
8.56	39.3	yes	sol
9.30	39.7	yes	sol

* the contents of magnesium in the precipitate were expressed in the molar ratio of Mg to (Al + Mg). For reaction solutions, the molar ratio of Mg to Al was 1:1, total metal concentration was 0.5 mol · dm^{-3}.

The reasons why the contents of magnesium could not reach 50% were that:

1) $Al(OH)_3$ was dioctahedral structure [12], in which hydroxide ions stacked hexagonal close-packed lattice; however, aluminum ions occupied only two-thirds of the octahedral sites. The remaining one-third of the octahedral sites were occupied by Mg^{2+} during reaction, therefore, the contents of Mg^{2+} were limited (its theoretical value was 33.3%).

2) In the mixed solution of Al^{3+} and Mg^{2+}, when Al^{3+} was precipitated, some Mg^{2+} ions were also precipitated at the same time. According to the solubility product of $Mg(OH)_2$, $Mg(OH)_2$ precipitate should not appear when pH value was 7.48, but it appeared (the contents of Mg in precipitate was 12.2% (see Table 1)). This is the reason why the observed values were higher than the theoretical value.

3) Some Mg^{2+} ions which did not get into $Al(OH)_3$ crystal lattice were adsorbed onto the surface of the precipitate, and might be lost during washing. The reason why the content of Mg^{2+} was still higher than 33.3% was that the drop caused by washing was less than the gain caused by coprecipitation. According to the above-mentioned explanations, we thought that Al^{3+} and Mg^{2+} in MMH sol were distributed in the same octahedral hydroxide sheet,

not within the two individual hydroxide sheets. This view was further supported in Fig. 3.

The contents of magnesium had great influence on properties of MMH sol. As was seen from Table 1, when the pH value was at 8.10 (namely, the contents of magnesium dropped to 25.7%), the precipitate could not be transformed from gel into sol. Only if the contents of magnesium reached 39.3%, the precipitate could turn into sol.

Effect of pH value in precipitation on ζ-potential of sol particles

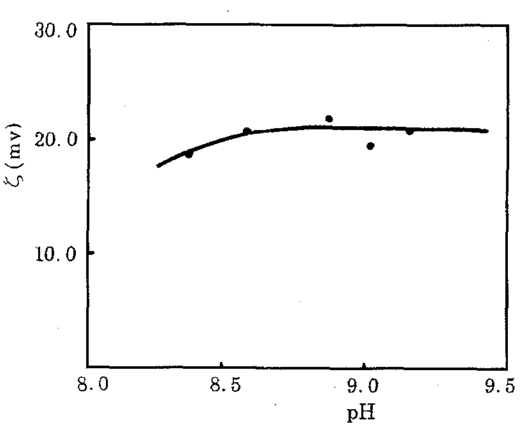
The ζ-potential of the sol particles increased gradually with the pH values in precipitation, and did not change again when pH values exceeded 8.80 (Fig. 2).

The results in Fig. 2 showed that MMH particles bore positive charge. We thought that the positive charge came from magnesium ions which intercalated $Al(OH)_3$ crystal lattice, and that some hydroxide ions did not enter into the precipitate but adsorbed on the surface of the colloidal particles. After peptizing, hydroxide ions and MMH colloidal particles formed electric double layer, which enabled MMH to be positively-charged colloidal particles.

From the above analysis, one can make the conclusion that the ζ-potential increased with increasing the contents of magnesium in the precipitate. In addition, the contents of magnesium in the precipitate increased with increasing the pH values in precipitation (see Table 1). Therefore, the ζ-potential of the sol particles increased with the pH values in precipitation.

The results in Fig. 2 could be successfully used to explain why the precipitate could not be peptized when pH values were below 8.10 (see Table 1). The peptization related directly to the ζ-potential, and the ζ-potential also related to the contents of magnesium ions in the precipitate. The higher the ζ-potential, the stronger the repulsive interaction of colloidal particles, and the easier the peptization. Thus, the peptization became easier and easier with the increase of the pH values in precipitation.

Fig. 2 Influence of pH value in precipitation on the ξ-potential of MMH positive sol particles. For reaction solution, the molar ratio of Mg to Al was 1:1, total metal concentration was 0.50 mol·dm^{-3}



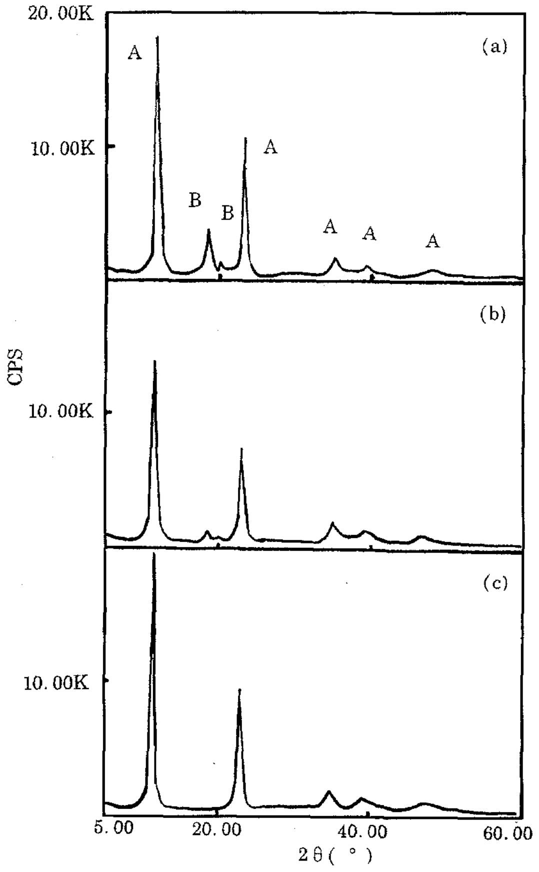
The structure of MMH powder particle

XRD Patterns of MMH powder

The sol was transformed into powder by heat treatment at 353 K for 24 h. Powder x-ray diffraction patterns are shown in Fig. 3.

As compared with the diffraction patterns of hydrotalcite ASTM 22–700, aluminum hydroxide ASTM 12–460, and magnesium hydroxide ASTM 7–239, respectively, we found that the patterns were assigned to two compounds

Fig. 3 XRD patterns of MMH positive sol particles. For reaction solutions, the molar ratios of Mg to Al were (a) 1:1, (b) 2:1 and (c) 3:1. Final pH values of reaction solutions were all 9.24



– one compound (A) was the same structure with hydrotalcite, another (B) was gibbsite, which possessed monoclinic crystal structure; however, the diffraction peaks of magnesium hydroxide did not appear in these patterns. In the mixed solution of aluminum and magnesium ions, two groups of diffraction peaks could at most occur. As was seen from XRD patterns, diffraction peaks of (A) were neither peak of $Al(OH)_3$ nor of $Mg(OH)_2$, but it had the same crystal structure as hydrotalcite. The hydrotalcite is composed of Al^{3+} and Mg^{2+}, which are randomly distributed within the same octahedral hydroxide interstice and are not within corresponding layers of the two individual hydroxides. The positive charge on the metal hydroxide sheets was balanced by interlayer anions. The biggest difference between hydrotalcite and MMH was the composition of anions. From this connection, (A)'s peaks were the diffraction peaks of MMH sol particles and its crystal structure was hydrotalcite-like.

When MMH sol was produced, the contents of magnesium in MMH sol depended upon the concentration of magnesium ion of a solution and the pH value in preparation. According to the intercalation reaction mechanism, the precipitate was mainly composed of $Al(OH)_3$ when pH value was below 7.48. When pH value was above 7.48 the contents of magnesium remarkably increased. These results showed that aluminum hydroxide changed gradually into MMH during reaction. As we can see from Fig. 3(a) (b) (c), when the concentration of magnesium ion of the solution increased, the height of (B)'s diffraction peaks became smaller and smaller, and finally disappeared completely, which indicated that (B)'s peaks were the diffraction peaks of aluminum hydroxide.

Table 2 Comparison of the interplanar distance d(Å) of samples (a)~(c) with those of the hydrotalcite

hkl	hydrotalcite* d(Å)	(a)	(b)	(c)**
			d(Å)	
003	7.84	7.875 4.854 4.396	7.701 4.833 4.388	7.742
006	3.90	3.821	3.843	3.857 3.811
009	2.60	2.59	2.587	2.586
012		2.546		2.539
015	2.33	2.311	2.303	2.309
018	1.990	1.95	1.938	1.959

* hydrotalcite ASTM 22-700.
** the interplanar distance d(Å) of diffraction peaks of samples (a), (b) and (c) in Fig. 3.

The crystal structure of MMH sol particles

According to the fact that MMH sol particles and hydrotalcite had the same crystal structure, they belonged to the same hexagonal system. We compared the interplanar distance d of MMH sol particles with that of the hydrotalcite (see Table 2). According to the formula of the hexagonal system:

$$\frac{1}{d^2} = \frac{4}{3} \times \left(\frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2} ,$$

where hkl – diffraction index; a, c – lattice constants (Å); d – interplanar distance (Å).

Lattice constants of MMH sol particles obtained are listed in Table 3.

As we can see from Table 3, lattice constants of MMH particles varied with the proportion of aluminum and magnesium. Theoretically, the ionic radius of magnesium ion (0.66 Å) was bigger than that of aluminum (0.51 Å) [13], so lattice constants a and c of MMH particles both should increase with the contents of magnesium, lattice constant a related only to the contents of magnesium. While lattice constant c related not only to the contents of magnesium, but also to the contents of interlayer water and the ionic radius of interlayer anions. Therefore, lattice constant a increased, and c varied with the contents of magnesium. If monolayer thickness of MMH particles was 7.603 Å [14], the crystal structure of MMH particles should be a three-layer superposition structure; in every monolayer, Mg^{2+} and Al^{3+} were randomly distributed within the same octahedral hydroxide sheet. Because of

Table 3 X-ray diffraction data for samples (a)~(c)

samples	Al: Mg molar ratio		Phases detected by XRD	MMH particles structure lattice constants (Å)	
	precipitation	in samples		c	a
(a)	1:1	1:0.66	Hydrotalcite-like + Gibbsite	23.63	3.010
(b)	1:2	1:0.98	Hydrotalcite-like + Gibbsite	23.10	3.018
(c)	1:3	1:1.17	Hydrotalcite-like	23.23	3.065

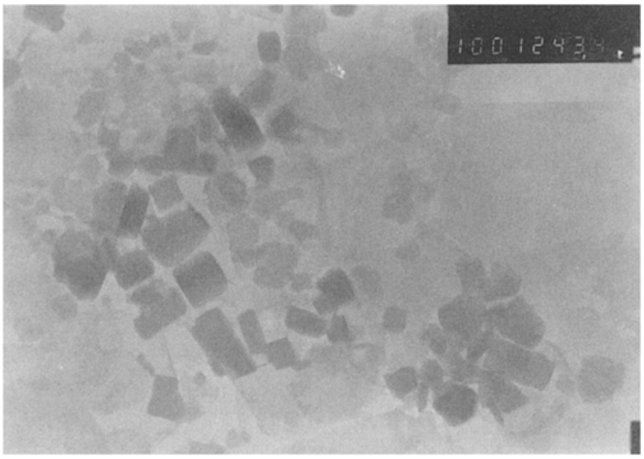


Fig. 4 TEM micrograph of MMH positive sol particles. (100000 ×). For reaction solution, the molar ratio of Mg to Al was 1:1, total metal concentration was 0.50 mol·dm^{-3}, final pH value was 9.24

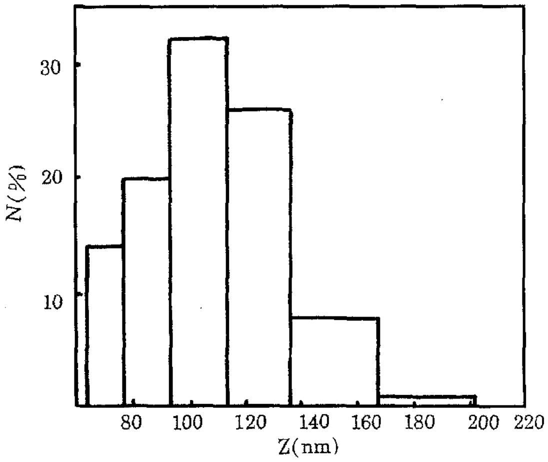


Fig. 5 Particle size distribution diagram of MMH positive sol particles. For reaction solution, the molar ratio of Mg to Al was 1:1, total metal concentration was 0.50 mol·dm^{-3}, final pH value was 9.24

magnesium ion intercalation, MMH sol particles was charged positive, and the positive charge was balanced by interlayer exchangeable anions such as Cl^- and OH^-. From TEM micrograph (Fig. 4) and particle size distribution diagram (Fig. 5), MMH sol particle was plated and the mean particle size of MMH sol was 110.9 nm.

Conclusion

The reaction in preparing MMH sol by precipitation was divided into three parts. A pH value was the decisive factor. The content of magnesium and the ξ-potential of MMH sol particles both increased with pH values and fiinally reached balancing value, respectively.

The mechanism of the synthetic reaction was that magnesium ion first intercalated $Al(OH)_3$ crystal lattice, and then formed mixed metal hydroxide. The MMH sol thus obtained was composed of positively charged colloidal particles, which belong to hexagonal system and have a three-layer superposition structure. The lattice constants of MMH powder changed somewhat with the proportion of the concentration of aluminum and magnesium ions.

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