Preparation of Zirconium Pillared Montmorillonite Composites

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Abstract. Zr-pillared montmorillonite (Zr-pmt) was obtained from which ZrOCl\textsubscript{2}.8H\textsubscript{2}O cross-linked Na-mt through Sol-gel means. Several important parameters of the preparation of Zr-pmt, such as the initial concentration of montmorillonite (mt), Zr/mt, aging time of the pillaring agent and cross-linking reaction time were investigated in detail to evaluate performances of Zr-pmt. Under the conditions of the montmorillonite initial concentration of 4\%, Zr/mt of 7.5 mmol/g, aging time of the pillaring agent for 3 h and cross-linking reaction time of 6 h, the maximum basal spacing (d\textsubscript{001}) of Zr-pmt is 2.06 nm. Zr-pmt material is expected to be used for adsorption of wastewater.

1. Introduction

The Natural montmorillonite is often used as the base material of the pillared montmorillonite materials, whose structural unit is composed by two Si-O tetrahedrals and one Al-O octahedral (Da Costa et al., 2013; Kitano et al., 2007; Tian et al., 2009; Khajehpour et al., 2015). The isomorphism substitutions could occur in the tetrahedral and octahedral molecular structures. There has more negative charge in sheet, which has a strong adsorption capacity and cation exchange capacity, and the substitution of Si\textsuperscript{4+} by Al\textsuperscript{3+} in the unit cell followed “Lowenstein's Rule”. As the result turns out, the montmorillonite unit cell becomes a large anion group, the cation between which can be interchanged. The interchange of the interlayer cation may lead to the charge reduction and the change of the physical and chemical properties of montmorillonite, such as cation exchange capacity, swelling volume and specific surface area etc( Varadwaj et al., 2013; Parida et al., 2011; Tavasoli et al., 2014). Pillared montmorillonite is a process that layered montmorillonite can be transformed into highly porous structure. The montmorillonite pillared has higher specific surface area, pore volume and other characteristics (Bahranowski et al., 2015) Pillared montmorillonite are becoming the potential absorbent, catalyst or catalyst support, and a lot of the pillared montmorillonite materials have been applied in the environment protection in recent years(Zhu et al., 2015; Serwicka and Bahranowski, 2004; Centi and Perathoner, 2008; Gil et al., 2010).

Some scholars have carried out the investigation of pillared montmorillonite. After Ti pillared montmorillonite was synthesized by Sterte(Sterte, 1986), it has been applied gradually into petro-chemicals, environmental protection area and cosmetics(Li et al., 2011; Pi et al., 2011). However, the reports on zirconium pillared mt (Zr-pmt) were very little. Only a few studies have reported the...
physical properties of Zr-pmt and its potential application in environmental protection. Guan et al. (Guan et al., 2006) found that Zr-pmt was a new kind of material to synthetic molecular sieve, which has the mesoporous molecular sieve structure of two-dimensional network. The further studies about the influence factors of Zr-pmt preparation have not yet been reported.

In this study, the influence factors of Zr-pmt preparation process involving the initial concentration $(C_{ic})$ of Na-mt, Zr/mt rate $(Zr/mt)$, aging time $(t_a)$ and cross-linking reaction time $(t_c)$ of the pillaring agent, which were investigated based on XRD. It is desirable to synthesize a Zr-pmt with layered structure, higher stability and adsorptivity by optimizing the preparation conditions.

2. Experiment

2.1. Materials

Raw montmorillonite used in the study was the sodium form of the less than 2μm particle size from Inner Mongolia, China, washed free of chloride ions by dialysis, and referred to as Na-mt. The main chemical compositions of raw montmorillonite were as follows: SiO$_2$ (64.59%), Al$_2$O$_3$ (13.12%), CaO (1.61%), MgO (3.11%), Fe$_2$O$_3$ (1.2%), MnO (0.017%), TiO$_2$ (0.129%), F (0.94%), K$_2$O (0.08%), Na$_2$O (1.848%), SrO (0.008%), P$_2$O$_5$ (0.092%), loss on ignition (13.44%). Fig.1 shows the XRD patterns of Na-mt and Zr-pmt. Raw montmorillonite swelling capacity and the colloid index were respectively 76.125 ml/g and 84ml/15g. The basal $(d_{001})$ spacing was 1.25 nm when the montmorillonite was transformed into Na-mt. The swelling capacity was 93 ml/g, the colloid index and the CEC were respectively 100 ml/15g and 106.25 mequiv./100g.

2.2. Synthesis of Zr-pmt

The preparation of Zr-pmt was as follows: firstly, raw montmorillonite (20 g) was added into 500 ml distilled water to form a clay suspension, and rest for 24 h. Secondly, (NaPO$_3$)$_6$ of 0.5% was added into clay suspension to disperse raw montmorillonite particles. Thirdly, after stirring for 30 min 200 mesh sieve was used to wipe off the upper suspension and the lower solution was precipitated for 2 h and centrifuged at 3600 rpm for 10 min. Fourth, the high purity slurry liquid was dried in an oven at 100 °C and ground into powder. Finally, the basal spacing $(d_{001})$ of Na-mt was 1.25 nm by X-ray diffraction analysis. ZrOCl$_2$.8H$_2$O of 3.225-8.056 g and HCl of 1% were poured into a 500 ml beaker. After adding distilled water to 500 ml, shaking 30 min and aging 0-4.5 h, the solution was Zr-pillaring agent.

The synthesis process of Zr-pmt was shown as followed. Zr-pillaring agent solution was slowly added to the Na-mt suspension (the initial concentration was 2.1%-5.7%) under the conditions of constantly magnetic stirring and maintained cross-linking reaction for 4-7 h. After gravity settling for 12 h, the mixture was centrifuged at 3600 rpm for 10 min to remove liquid phase. In addition, the upper liquid phase of centrifuge tube was washed with distilled water until it had no Cl$^-$ (tested with AgNO$_3$). Then the above solid product was dried at 70 °C in the oven to obtained Zr-pmt.

3. Results and discussion

3.1. Results

XRD patterns of Na-mt and Zr-Pmtn is shows in Figure 1. The interplanar spacing of the synthetic composites under different test conditions is shows in Table 1.

| Single factor | $C_{ic}$/% | Zr/mt rate (Zr/mt) |
|---------------|------------|-------------------|
| Basal spacing values | 1.64 | 1.69 | 1.82 | 1.76 | 1.63 | 1.68 | 1.86 | 1.78 | 1.75 | 1.72 |
| Aging time $(t_a)$ / h | | | | | | | | | | |
| Crossing time $(t_c)$ / h | | | | | | | | | | |
3.2. Discussion

3.2.1. Initial concentration of Na-mt
The initial concentration ($C_{ic}$) of Na-mt is a key factor of pillaring montmorillonite material. The lower concentration could improve ion exchange capacity between the Na-mt interlayer and prevent generating precipitate. However, low concentration is not conducive to industrialization.

When experimental condition was Zr/mt=10 mmol/g, $t_a=4.5h$ and $t_c=5h$, the effect of the Na-mt initial concentration on the basal spacing values of Zr-pmt was studied. The small angle XRD result (Table 1) of Zr-pmt shows that the basal spacing values ($d_{001}$) of Zr-pmt first rises then reduces with the increase of the initial concentrations of Na-mt. The $d_{001}$ values of Zr-pmt decline with the increase of the initial concentrations when the initial concentration of Na-mt was less than 4 %. The rise of initial concentration is beneficial to increase the concentration of zirconium polymeric-cationic and inhibit the hydrolysis of the polymeric hydroxyl cationic groups. So $d_{001}$ values of Zr-pmt increases when the polymeric hydroxyl cationic groups enter into the Na-mt interlayer.

3.2.2. Zr/mt rate
Zr/mt rate has a great influence on the basal spacing and physico-chemical properties of Zr-pmt. The effect of Zr/mt rate on Zr-pmt basal spacing is studied when experimental condition was $C_{ic}=4\%$, $t_a=4.5h$ and $t_c=5h$. XRD analysis (Table 1) of Zr-pmt at different Zr/mt rate shows that the basal spacing of Zr-pmt first increases and then decreases as the extension of time. The maximum basal spacing of Zr-pmt was 1.86 nm when Zr/mt is 7.5mmol/g.

The main reason of the basal spacing increase is that the higher Zr/mt rate, the more zirconium polymerization hydroxyl cationic are formed, which cause the more zirconium polymerization hydroxyl cationic to enter Zr-pmt layer, Zr-pmt presents the larger basal spacing and larger aperture structure. So the basal spacing of Zr-pmt increases in proper order when Zr/mt rate is less than 7.5mmol/g.

When Zr/mt rate is more than 7.5mmol/g, the main reason of the basal spacing reduction is that the excess zirconium polymerization hydroxyl cationic groups increases the probability of ion collisions. The high activity of cationic groups makes fully exchange reaction with montmorillonite interlayer cationic and worsens the interlayer ion-exchange process. So, the excess zirconium polymerization hydroxyl cationic groups blocks the intercalation reaction and reduces the amount of insertion, resulting in the basal spacing($d_{001}$ values) of Zr-pmt decrease.
3.2.3. Aging time of the pillaring agent
The effect of the pillaring reagent aging time on Zr-pmt performance was investigated. When experimental condition was $C_{ic}=4\%$, $Zr/mt=7.5\ mmol/g$ and $t_с=5 h$. XRD analysis of Zr-pmt (Table 1) reveals that Zr-pmt presents a different basal spacing when the aging time of pillaring reagent is different. The basal spacing of Zr-pmt first increases and then decreases as the extension of time. The maximum basal spacing of Zr-pmt was 1.96 nm when aging time of pillared agent was 3 h. There are two main reasons. First a large number of zirconium polymerization hydroxyl cationic would aggregate and settle if the aging time of pillaring agent was too long, which will deteriorate structure and performance of Zr-pmt. Second the excessive aging time will result in the polymerization of the pillared agent, and the structure water will be lost. The high polymer was transformed into oligomer and made the basal spacing of Zr-pmt became smaller.

Therefore, the structure and performance of the material would be affected as aging time exceeds 3h. Appropriate aging time can promote ions exchange reaction between solution and montmorillonite interlayer, increase the basal spacing ($d_{001}$) of Zr-pmt and improve the pillared effect. Appropriate aging time of pillaring agent was 3 h.

3.2.4. Cross-linking reaction time
The effect of cross-linking reaction time on Zr-pmt performance was studied when experimental condition was $C_{ic}=4\%$, $Zr/mt=7.5\ mmol/g$ and $t_с=3 h$. XRD analysis (Figure 1, Table 1) reveal that the $d_{001}$ values of Zr-pmt increase from 1.83 nm to 2.06 nm when cross-linking reaction time is less than 6 h. The $d_{001}$ values of Zr-pmt is reduced to 1.76 nm as cross-linking reaction time is extended to 8 h. Its main reason is that too long cross-linking time will increase the hydrolyzing degree of zirconium polymerization hydroxyl cationic in non-interlayer and decrease zirconium polymerization hydroxyl cationic of montmorillonite interlayer. So it cannot make more zirconium polymerization hydroxyl cationic enter the interlamination. Too short cross-linking time to exchange between zirconium polymerization hydroxyl cationic and montomillorite interlayer cationic.

In conclusion, the appropriate cross-linking time can make zirconium polymerization hydroxyl cationic fully enter into montmorillonite interlayer and generate ion exchange reaction. The appropriate cross-linking reaction time was 6 h.

4. Conclusion
Zr-pmt with large basal spacing, microporous structure and high thermal stability could be synthesized by using Na-montmorillonite and pillaring precursor (zirconium polyhydroxy ions). The large basal spacing, microporous structure and thermal stability have been confirmed by XRD analyses.

The characteristics of prepared Zr-pillared montmorillonite were closely correlated with the condition parameters in the preparation, the initial concentration of Na-montmorillonite, aging time of the pillaring agent, $Zr/mt$ and cross-linking reaction time, etc. Under the condition that the initial concentration of montmorillonite was 4 %, $Zr/mt$ was 7.5 mmol/g, aging time of the pillaring agent was 3 h and cross-linking reaction time was 6 h, the $d_{001}$ value of Zr-pmt was 2.06 nm.

The parameters have to be optimized in order to prepare a high-quality Zr-pillared montmorillonite effectively and economically. The result suggests that Zr-pillared montmorillonite with large basal spacing and layered structure integrity have strong potential application in the field of environmental protection.

Acknowledgments
This research was supported by the National Natural Science Foundation of China (51464007), the Science and Technology Cooperation Plan LH Word of Guizhou Province ([2015]7684), Dr. Funds of Guizhou University (X131051).

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