Applied Clay Science 88–89 (2014) 228–232

Contents lists available at ScienceDirect

Applied Clay Science

journal homepage: www.elsevier.com/locate/clay

Note

A facile in situ pillaring method—the synthesis of Al-pillared montmorillonite

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ARTICLE INFO

Article history:
Received 24 April 2013
Received in revised form 2 December 2013
Accepted 4 December 2013
Available online 23 December 2013

Keywords:
Al-pillared-montmorillonite
In situ
PEG400
One step

ABSTRACT

A facile pillaring method for Al-pillared montmorillonite (Al-pillared-MMT) has been established by the in situ formation polyoxocation $[Al_{13}O_4(OH)_{24}(H_2O)_{12}^{7+}]$ in the interlayer of montmorillonite (MMT). The result of X-ray diffraction (XRD) showed that the pillaring effect was consistent with that of the traditional method namely, the basal spacing was up to 18.8 Å. PEG400 in the synthesis system played a part of a layer extending agent which could promote the forming of Al_{13}^{7+} in the layer of MMT. The nitrogen adsorption–desorption measurement exhibited that the pore size and BET surface area of pillared montmorillonite(MMT) via an in situ way were 3.5–5 nm and 181 m^2/g, respectively. The BET surface area was larger than the conventional pillared MMT and the pore size was nearly the same with traditional methods. The process of synthesis Al_{13}^{7+} and pillaring MMT were completed in one step in this method, which was a facile and effective method for preparing pillared MMT.

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1. Introduction

Pillared interlayered clays (PILCs) have seen widespread application in the fields of plant growth, pollutant transfer, nutrient cycling and petroleum engineering (Bhattacharyya and Gupta, 2008; Brindley and Sempels, 1977; Kanda et al., 2009; Kloprogge et al., 2005; Vardoulakis et al., 2011) due to their high permanent porosity, excellent thermal stability and catalytic feature (Gil et al., 2000, Kloprogge 1998;). Therefore, more and more researchers have focused on the pillared interlayered clays, such as Fe(III) pillared montmorillonite (Martin-Luengo et al., 1989), mixed Al/Cu-pillared clays (Frini et al., 1997; Gil et al., 2000), Al-Fe-pillared clay (Storaro et al., 1996), and Al-pillared montmorillonite (Itadani et al., 2007; KhalaP et al., 1997; Kloprogge et al., 2002). However, the most studied is Al-pillared montmorillonite (Al-pillared-MMT), which not only possesses unique microporous structural characteristics, excellent thermal stability and a large BET surface area as an ideal catalyst supporting material, but also possesses a higher effective charge which is approximately +0.5 per Al exchanged with MMT (Kloprogge, 1998).

The pillaring of MMT with Al_{13} polyoxocation has been reported by Vaughan in 1977–1981 (Vaughan et al., 1979; Vaughan and Lussier, 1980; Vaughan et al., 1981a, 1981b). Katdare et al. (1999, 2000) have prepared Al-pillared-MMT by the ultrasonic-assisted method during the cation exchange process. Fetter et al.(1997) have proposed a pillaring method of microwave irradiation in order to shorten the time of pillaring. Del Riego et al. (1994) have reported a route of the Al-polyoxycations pillared interlayered clays (PILCs-Al) via dialysis bags. Storaro et al. (1996) have attempted to pillar natural saponite, calcium bentonite and laponite in acetone using solid chlorhydrol.

Based on the above-mentioned methods, pillared process includes two parts of the pillared agent preparation process and pillared process. In that way, it will consume a lot of time to prepare Al_{13}^{7+} and need large amounts of water during the cation exchange step (Aouad et al., 2005; Fetter et al., 1997; Sivaiah et al., 2010). Therefore, it's significant to develop a facile preparation method of Al-pillared-MMT. As we know, the Al_{13}^{7+} is formed during the hydrolysis of aluminum salts in aqueous solution (OH^-/Al^{3+} ratio 2.0 to 2.5) and it is composed of 13 aluminum ions, in which, one with a tetrahedral coordination is surrounded by 12 with octahedral aluminum ions (Shi et al., 2007). And the hydrolysis process has been obtained from ^{27}Al NMR studies (Kloprogge et al., 1995). If this hydrolysis process occurs in the interlayer of montmorillonite, Al-pillared-MMT will be prepared in situ by one-step.

A facile in situ pillaring method is developed for Al-pillared-MMT. In this process, PEG400 is employed as the layer extending agent. The Al-pillared-MMT is prepared using minimum expenditure of time and water.

2. Experimental

2.1. Materials

The raw MMT was from Jilin in the Northwest of China (Xia et al., 2010). The coarse particles were removed by sedimentation technique for obtaining the host material for pillaring. $AlCl_3 \cdot 6H_2O$ (Xilong Chemical Reagent Company, China), NaOH (Beijing Chemical Reagent Company, China) and the polyethylene glycol 400 (PEG400) (Beijing Chemical Reagent Company, China) were of reagent grade. And the water used was distilled by deionization.

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http://dx.doi.org/10.1016/j.clay.2013.12.004

2.2. Characterization techniques

The X-ray diffraction patterns of the clay materials were recorded on a Rigaku D/MAX 2550 diffractometer equipped with Ni-filtered CuK$_\alpha$ radiation ($\lambda = 0.154$ nm) and operated at 40 kV and 40 mA with a fixed slit. The XRD measurements were carried out in the 2θ range of 2–30° with a scan speed of 6°/min.

Nitrogen adsorption experiments were performed using a static volumetric apparatus (Micromeritics ASAP 2020 adsorption analyzer) at 77 K. The weight of each sample was 0.16 g and the sample was previously degassed for 24 h at 473 K. And the t-plot analysis was used to character the surface area and microporosity of the prepared sample (Gregg and Sing, 1982).

2.3. Synthesis of in situ Al$_{13}$-pillared-montmorillonite

0.6060 g MMT powder was added into 30 ml 0.4 mol/L $AlCl_3$ $6H_2O$ solution at 80 °C and stirred continuously for 10 min. 5 ml PEG400 was added and stirred continuously for another 5 min. And then 69 mL 0.4 mol/L NaOH solutions were dropwise added slowly with vigorous stirring. The final ratio of $[OH^-]/[Al^{3+}]$ was 2.3. After that, stirring was needed for another 2 h. Then the solution was aged at 60 °C for 24 h. The product was deposited for 0.5 h and dumped the supernatant. The solid at the bottom was washed by distilled water following a centrifugation at 10,000 revolutions per minute (rpm) for 7 min, and this step was repeated 6 times until free of chloride. The precipitate was dried at 60 °C in drying oven, then rubbed into powder, finally placed into a desiccator. This sample was denoted as Al-(PEG)In-MMT. The Al-(No PEG)In-MMT prepared by the same method, which was not added 5 ml PEG400. And the sample was denoted as Al-MMT prepared by the conventional pillared method. The detailed steps of the conventional pillared method and the in situ pillared method were showed in Fig. 1.

3. Results and discussion

3.1. X-ray diffraction analysis

The XRD patterns of Al-MMT (conventional method), Al-(PEG)In-MMT (in situ Al-pillared montmorillonite) and Al-(PEG)In-MMT after calcinations under 400 °C are showed in Fig. 2. The basal spacing of Al-(PEG)In-MMT (Fig. 2c) is 18.8 Å, which is consistent with Al-MMT (Fig. 2a) prepared by the conventional pillared method. Furthermore, the basal (d_{001}) peak is more symmetrical and intense in Al-(PEG)In-MMT (Fig. 2c) than that of the Al-MMT (Fig. 2a). This phenomenon demonstrates that the Al-(PEG)In-MMT possesses a more ordered or higher crystallinity (Aouad et al., 2005; Fetter et al., 1997). The basal spacing of Al-(PEG)In-MMT after calcinations under 400 °C (Fig. 2b) is 17.8 Å which is lower than that of Al-(PEG)In-MMT without calcinations because of altering Al$_{13}$ to Al_2O_3 during calcination, which also proves that Al-(PEG)In-MMT does not collapse after calcinations (Kloprogge, 1998). However, the in situ pillared process is easier than conventional methods for the same effects.

3.2. Action of layer extending agent PEG400

The photos of PEG400, Al-(PEG)In-MMT and Al-MMT after calcinations under 400 °C are shown in Fig. 3(Up). From Fig. 3 (Up) we can

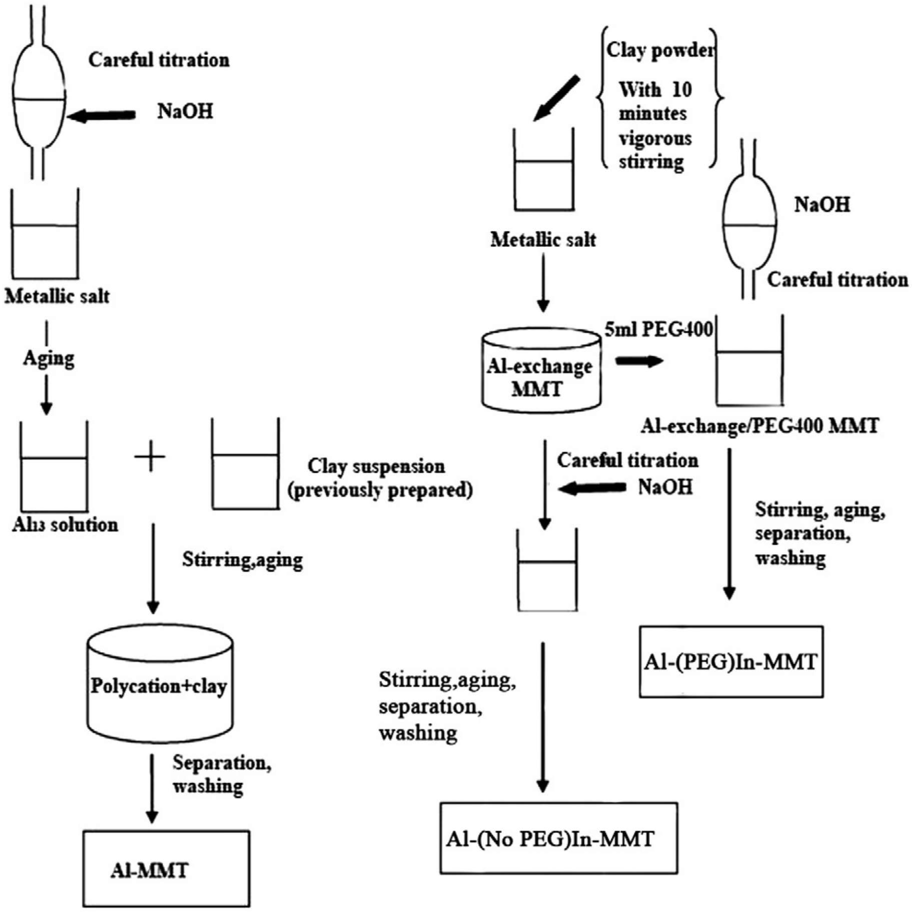

Fig. 1. The detailed step of the conventional pillared method (left) and the in situ Al-pillared montmorillonite (right).

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