Journal of Colloid and Interface Science 324 (2008) 142–149

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

www.elsevier.com/locate/jcis

A combined study by XRD, FTIR, TG and HRTEM on the structure of delaminated Fe-intercalated/pillared clay

Peng Yuan [a,*], Faïza Annabi-Bergaya [b], Qi Tao [a,c], Mingde Fan [a,c], Zongwen Liu [d], Jianxi Zhu [a], Hongping He [a], Tianhu Chen [e]

[a] *Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China*
[b] *Centre de Recherche sur la Matière Divisée, CNRS-Université d'Orléans, 1b, Rue de La Férollerie, Orléans Cedex 2, France*
[c] *Graduate School of the Chinese Academy of Science, Beijing 100039, China*
[d] *The Australian Key Centre for Microscopy and Microanalysis, The University of Sydney, NSW 2006, Australia*
[e] *School of Natural Resources and Environment, Hefei University of Technology, Hefei 230009, China*

ARTICLE INFO

Article history:
Received 7 March 2008
Accepted 30 April 2008
Available online 10 May 2008

Keywords:
Montmorillonite
Pillared clay
Delaminated
Nanoparticles
Iron oxide

ABSTRACT

Fe-PILC samples were synthesized by the reaction between Na^+- and/or Ca^{2+}-montmorillonite (Mt) and base-hydrolyzed solutions of Fe(III) nitrate. Different from the known usual microporous pillared structure, a meso–microporous delaminated structure containing intercalated or pillared fragments was found in the respective resulting Fe-intercalated or -pillared clays. XRD patterns of Na^+-Mt-based Fe-intercalated/pillared clays show one large *d*-spacing above 6.4 nm corresponding to the mesoporous delaminated part, whereas another *d*-spacing of ca. 1.5 nm was indicative of the microporous pillared part. Fe-intercalated/pillared clays based on Ca^{2+}-Mt lead to similar results, but with a *d*-spacing less than 6 nm and a second low intense *d*-spacing less than 1.5 nm. In the delaminated Fe-intercalated clays, NO_3^- anions were retained even after thorough washing process. They play as counterions to neutralize the positive-charged iron aggregates in the delaminated structure, and can be exchanged by heteropolyanions as $[PW_{12}O_{40}]^{3-}$. The delaminated Fe-pillared clays show good thermal stability at 500 °C and exhibit at this temperature dramatically higher specific surface area and porosity than the starting montmorillonites. However, calcination at a higher temperature leads to the formation of nanocrystalline hematite. Air-drying after ethanol extraction (EAD) method has an advantage over air-drying (AD) method in preserving the delaminated structure.

1. Introduction

Pillared interlayered clays (PILC) have attracted continuously increased interest [1] since the first inorganic pillared clay mineral reported in the late 1970s [2]. Classified as a two-dimensional lamellar nanomaterial, PILC is prepared in two steps (i) by exchanging the charge-compensating cations between the swelling clay layers with larger polymeric or oligomeric hydroxy metal cations, leading to intercalated clay minerals, and (ii) by heat treatment of these intercalated clays, the metal hydroxy cations undergo dehydration and dehydroxylation and are transformed to metal oxide (e.g., Al_2O_3 and Fe_2O_3) clusters/nanoparticles, which act as pillars to prop the clay mineral layers apart, and to create a stable microporous pillared structure [1]. The resultant oxide-PILC has shown some promising prospects in the fields of adsorbents and catalysts [3–5].

Much research interests have been directed towards Fe_2O_3-PILC, due to the intrinsic catalytic activities (e.g., as a Fischer–Tropsch catalyst) and the magnetic properties of iron oxide [6–10]. A common route to synthesize Fe_2O_3-PILC is based on the intercalation of iron polycations [4], the base-hydrolyzed product of Fe(III) salts, such as $FeCl_3$ and $Fe(NO_3)_3$. Besides, a synthesis route by intercalation of the trinuclear Fe(III)-acetato complex was also reported in the literatures [11–13].

The interlayer space of Fe_2O_3-PILC synthesized by base-hydrolyzed route appears to be diverse in different reports. Basal spacings $d_{(001)}$ of ca. 2.5 ± 0.4 nm (corresponding to the interlayer space of ca. 1.5 ± 0.4 nm) were reported by several researchers [4,14,15]. In some other reports, however, the basal spacing of Fe_2O_3-PILC is found to be lower than 1.47 nm [7,16,17]. Furthermore, Burch and Warburton and Chen et al., reported the complete disappearance of the regular basal spacing of Fe_2O_3-PILC [18,19], which was proposed to correspond to a delaminated pillared structure. Therefore, some further work are deserved to be done to investigate the structure of Fe_2O_3-PILC, especially the specific formation mechanism of delaminated or pillared structure.

---

[*] Corresponding author. Fax: +86 20 85290130.
E-mail address: yuanpeng@gig.ac.cn (P. Yuan).

0021-9797/$ – see front matter © 2008 Elsevier Inc. All rights reserved.
doi:10.1016/j.jcis.2008.04.076

In this work, by using powder X-ray diffraction (PXRD), nitrogen adsorption–desorption isotherms, thermogravimetric (TG) analysis, high-resolution transmission electron microscope (HRTEM) and FTIR spectroscopy, the detailed structural properties were studied, as well as the related anion-exchangeability, of a series of Fe intercalated/pillared montmorillonite samples with delaminated structure. Effects of the starting montmorillonite (Na^+- or Ca^{2+}-Mt) characteristics, drying methods and calcination temperature on the structure of the resultant Fe-PILC samples were also investigated.

2. Materials and methods

2.1. Materials

The calcium-montmorillonite (Ca^{2+}-Mt), supplied by Nanhai Mining Ltd., China, was purified and classified by sedimentation, then the <2 µm fraction was collected for pillaring experiment. The structural formula of the obtained Ca^{2+}-Mt as determined from chemical analysis is:

$$Ca_{0.19}Mg_{0.06}Na_{0.01}(Si_{3.96}Al_{0.04})(Al_{1.44}Fe_{0.09}Mg_{0.47})O_{10}(OH)_2\cdot nH_2O.$$

The cationic exchange capacity (CEC) of the Ca^{2+}-Mt is 66.5 mmol/100 g. The Na^+-montmorillonite (Na^+-Mt) was prepared by ion exchange reaction between Ca^{2+}-Mt and Na_2CO_3, as previously described [20]. Both Ca^{2+}-Mt and Na^+-Mt were used as the starting materials for the pillaring reactions.

The Keggin-type heteropolyanion $[PW_{12}O_{40}]^{3-}$ was prepared by titration of the $H_3PW_{12}O_{40}$ solution (with a pH of ca. 2.0) into a solution of NH_4OH.

2.2. Preparation of iron pillaring solutions and synthesis of PILC

Following a procedure similar to that reported by Rightor et al. [14], Na_2CO_3 powder was slowly added to an aqueous solution of 0.2 M iron(III) nitrate with vigorously stirring (ca. 1100 revs/min). The amount of added base includes six OH/Fe molar ratios in the range of 0.5–2.5. The resulting translucent solution was aged for 24 h at room temperature before addition to the Mt dispersion.

A dispersion of 2 g of starting Mt in 100 ml of deionized water was used. The iron pillaring solution was added dropwise into the vigorously stirred clay dispersion kept in a water bath at 60 °C, with a ratio of 10 mmol Fe per gram of clay. After addition of the pillaring solution, the reaction mixture was stirred for 2 h, and then aged for 20 h at room temperature. The mixture was centrifuged and washed 12 times by successive agitations/centrifugations with deionized water. The obtained wet cakes corresponding to intercalated clay minerals were ready for drying.

2.3. Drying and calcination

Two drying methods, air-drying (shortened hereafter as AD) and air-drying after ethanol extraction (EAD), were used to dry the obtained wet cakes. Under AD condition, wet cakes were dried at 105 °C for 16 h. Under EAD condition, wet cakes were immersed into absolute ethanol, washed and centrifuged with ethanol for 3 times to replace the water by ethanol, then followed by the same steps as for AD condition. A part of the dried intercalated products was ground into powder with mortar for further characterization.

The pillared clay samples were obtained by heating the dried intercalated products for 3 h at different temperatures (300, 400, 500, 600, 700, 800 and 900 °C). The final intercalated or pillared samples were differentiated on the basis of the kind of starting Mt, the OH/Fe molar ratio, the drying method and the calcination temperature. For example, Na^+-Mt-1.0 (AD) denotes the Fe intercalated clay sample, obtained from Na^+-Mt, air-dried, and with a OH/Fe molar ratio = 1.0, while Na^+-Mt-1.0 (AD, 500 °C) represents the pillared counterpart of Na^+-Mt-1.0 (AD) which underwent calcination at 500 °C.

2.4. Exchange reaction

The exchange reaction between the Keggin-type heteropolyanions $[PW_{12}O_{40}]^{3-}$ and the Fe-intercalated sample was carried out by titrating the $[PW_{12}O_{40}]^{3-}$ solution into the Na^+-Mt-1.0 (Fe-intercalated wet cake) with a ratio of 0.4 mmol of heteropolyanions per gram of Na^+-Mt-1.0. The mixture was then stirred for 3 h at 80 °C. The product was separated by centrifugation, washed with deionized water and dried at 105 °C for 16 h.

2.5. Characterization methods

The powder X-ray diffraction (PXRD) patterns were taken on a Rigaku D/max 2550 PC X-ray diffractometer equipped with Ni filter and Cu$K\alpha$ radiation ($\lambda = 0.154$ nm) using a generator voltage of 40 kV and a generator current of 300 mA, and a scan rate of 3° (2θ)/min were applied for the determination.

The chemical composition of the samples was determined using a PE-3100 atomic absorption spectrometer (AAS). The FTIR spectra of the samples were recorded on a Perkin–Elmer 1725X FTIR spectrometer. Specimens for measurement were prepared by mixing 0.9 mg of the sample powder with 70 mg of KBr and pressing the mixture into a pellet. The average over 9 scans was collected for each measurement with a resolution of 2 cm^{-1}.

Conventional TEM images were obtained in a Philips CM120 electron microscope operating at 120 kV. HRTEM characterization and selected-area electron diffraction analysis were preformed on a JEOL 3000F transmission electron microscope with an accelerating voltage of 300 kV. For TEM observation, the clay sample was ultrasonically dispersed in ethanol for 5 min, and then a drop of sample suspension was dropped onto a carbon-coated copper grid, which was left to stand for 10 min and transferred into the microscope.

N_2 adsorption–desorption isotherms were measured at liquid nitrogen temperature with a gas sorption analyzer (Quantachrome, NOVA 1000). Prior to measurement, samples were outgassed at 250 °C at a pressure less than 10^{-3} Torr for at least 3 h. The specific surface area was calculated by the BET equation [21] and the total pore volume was evaluated from nitrogen uptake at a relative pressure of 0.985. The t-plot according to de Boer's method was used to calculate the micropore volume and external surface area [22]. The Barrett–Joyner–Halenda (BJH) method was used to evaluate the average pore diameter (APD) [23]. And the pore size distribution (PSD) curves was fitted by the non-local density functional theory (NLDFT) method [24].

Thermogravimetric (TG) analysis was performed on a Netzsch STA 449C instrument. Approximately 50 mg of finely ground sample was heated in an open corundum crucible. Samples were heated from 40 to 1300 °C at a heating rate of 10 °C/min under highly pure nitrogen atmosphere (20 cm^3/min).

3. Results and discussion

3.1. PXRD and TEM results

Shown in Fig. 1 are the XRD patterns of the starting montmorillonites and the resultant Fe-intercalated samples and Fe-PILC in the low 2θ angle region.

Already, starting Na^+-Mt shows two reflections (Fig. 1a). The first unusual one corresponds to a large d-spacing of 8.2 nm, and the second to a d-spacing of 1.25 nm, attributed to the (001) reflection of Na^+-Mt in temperature and pressure normal conditions. In the cases of Na^+-Mt based Fe-intercalated samples (both AD