



# Structure evolution of brick-red palygorskite induced by hydroxylammonium chloride

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## ABSTRACT

Brick-red clay mineral with palygorskite (PAL) as the main ingredient has huge reserves in the nature, but the congenital brick-red color limits its applications in industrial fields. In light of the prospective application value of such mineral, researchers have been looking for a feasible way to turn it into white one. Herein, a simple one-step reaction process in the presence of hydroxylammonium chloride (HAC) was developed and used to turn brick-red PAL into white one. The change of textural structure and physicochemical features of the brick-red PAL was investigated. It was shown that the brick-red PAL was converted to white after the reaction in 5 mol/L of aqueous solution of HAC at 80 °C. The rod-like crystal morphology of PAL still remain well after the reaction, and the associated minerals such as quartz, feldspar and muscovite did not change obviously. The dissolution of associated hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ) and the leaching of Fe(III) and Fe(II) in acidic and reductive HAC solution mainly contributed to the whitening of brick-red PAL, as confirmed by Mössbauer spectroscopy. This research would lay a theoretical basis for extending the industrial application of naturally abundant brick-red clay minerals.

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## 1. Introduction

Palygorskite (PAL, also called as attapulgite) is a natural hydrated aluminum, magnesium-rich silicate clay mineral with nanorod-like crystal morphology, nanopores and active silanol groups [1,2]. It is composed of talc-like tetrahedron-octahedron-tetrahedron (T-O-T) ribbons running parallel to the fibre axis, and each ribbon is connected to the others by inverted Si-O-Si bonds to form two continuous tetrahedral sheets and one discontinuous octahedral sheets [3,4]. The ordered linkage of ribbon-layer units by Si-O-Si bonds leads to the formation of tunnels with the cross-sectional area of  $0.37 \times 0.64 \text{ nm}^2$  [5]. Owing to the particular structure and surface properties, PAL has been widely applied in many fields, e.g., colloidal agents [6,7], adsorbents [8–11], catalysts [12–15], polymer composites [16–19], hybrid pigments [20–22], sealing materials [23], and fluorescent composite [24].

In theory, the intact PAL crystal should be a tri-octahedral mineral with the structure formula of  $\text{Si}_8\text{Mg}_8\text{O}_{20}(\text{OH})_2(\text{H}_2\text{O})_4 \cdot 4\text{H}_2\text{O}$ , and all the empty positions in the octahedral sheets were occupied by  $\text{Mg}^{2+}$  ions [25]. However, the practical structure formula of natural PAL is proposed to be  $(\text{Mg}_{5-y-z}\text{R}_y^{3+}\text{Al}_z)(\text{Si}_8-x\text{Al}_x\text{O}_{20}(\text{OH})_2(\text{OH}_2)_4\text{R}^{2+}_{(x-y+2z)/2}(\text{H}_2\text{O})_4$  (where,  $\square$  is a vacant site, and R represents Mg(II), Al(III), Fe(III) or Fe(II))

[26], or  $(\text{Mg}_2\text{R}^{3+}\square_1)(\text{Si}_8-x\text{Al}_x\text{O}_{20}(\text{OH})_2(\text{OH}_2)_4\text{R}^{2+}_{(x-y+2z)/2}(\text{H}_2\text{O})_4$  (where  $x = 0-0.5$ ) [27] due to the isomorphism substitution phenomenon occurred during the geological formation process, so that the chemical composition, physicochemical features and color of natural PAL clay mineral originated in different region or mine sites are quite different. For example, the PAL clay mineral in Mingguang city of China is white, and the PAL clay mineral in Huangnishan mine, Xuyi of China is gray, and the PAL clay mineral in Linze county of China is brick-red [28], and their geological causes or chemical composition are also different [29]. In recent years, the research and development of high-quality PAL clay mineral with intact rod-crystal structure, high whiteness and purity has made great progress, and a series of functional materials have been developed using high-grade PAL as the raw materials and applied in different areas [30]. However, the reserves of white high-grade PAL mineral are very limited in the nature, because it can only be formed by hydrothermal reaction mechanism.

In fact, majority of the natural PAL clay minerals were mainly formed in the Tertiary sediments by the common deposition mechanism in marine, bay, lagoon, or lake conditions [31]. Such minerals usually show deep color (i.e., brick-red, brown, gray-yellow, and cinerous color), resulting from the isomorphism substitution of different cations (i.e., Fe(III), Fe(II)) for the octahedral Mg(II) or Al(III) ions [32,33]. The substitution of Fe(III) for octahedral Mg(II) or Al(III) ions make PAL showing brick-red color [34,35]. Xie et al. [36] reported firstly authigenic PAL in the sediments of the Lingtai red clay, and they [34]

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also reported that there were huge reserves of red PAL clay minerals in western China, which was mainly resulted from the wind-blown sediments and formed by the lacustrine deposition causes, and so many associated minerals such as quartz, feldspar, illite, chlorite and muscovite were also present in the brick-red clay minerals [29]. Although such clay minerals are extremely abundant in the nature (more than ten billion tons), the deep color, complex composition and poor performance make them hardly to be used in industries as colloidal agent, adsorbent and reinforcing filler. Moreover, the basic research on the structure and properties of brick-red PAL has not received enough attention in both academic and industrial fields.

As mentioned above, the main reason for the formation of brick-red PAL is the substitution of Fe(III) for Mg(II) or Al(III) in its octahedral structure. The Fe(III) in the skeleton structure of PAL is difficult to be transformed or removed by conventional purification, surface modification or mechanical treatment methods. Our previous studies found that hydrothermal process was an effective approach to change the structure of PAL and improve its properties [37,38]. The brick-red PAL can also be turned into white by one-step solvothermal reaction using dimethyl sulfoxide/water mixture as the solvents [39]. But the solvothermal reaction generally requires high temperature and pressures, and the sulfides have to be used to achieve this reaction process. So, we have been committed to develop a new process to change the color of brick-red PAL to white at ambient pressure, despite that is still challenging.

Our research found that the hydroxylammonium chloride (HAC) with strong reduction capability was helpful to convert the brick-red PAL to white, even under ambient pressure. This paper mainly studied the change of microscopic structure, physicochemical properties and color of PAL after the reaction in HAC solution by using Fourier transform infrared spectrometry (FTIR), X-ray diffraction (XRD), thermogravimetric analysis (TGA), scanning electron microscopy (SEM), BET analysis, X-ray fluorescence (XRF) analysis, solid state nuclear magnetic resonance (MAS NMR), and Mossbauer spectroscopy techniques.

## 2. Experimental

### 2.1. Materials

Natural brick-red PAL clay mineral, with the chemical composition of SiO<sub>2</sub> 54.28%, MgO 6.06%, Al<sub>2</sub>O<sub>3</sub> 16.75%, CaO 5.99%, Na<sub>2</sub>O 3.75%, Fe<sub>2</sub>O<sub>3</sub> 7.46% and K<sub>2</sub>O 3.72%, was taken from Linze mine located in Linze County of Gansu Province of China. The natural PAL was pretreated according to the following procedure: natural brick-red PAL was dispersed in 5% of HCl solution at the solid/liquid ratio of 1/10 (*m/v*), and then the mixture was mechanically stirred at 800 rpm for 240 min to remove the carbonates. The resultant solid product was fully washed, dried and smashed to obtain the powder with the particle size below 74 μm. Hydroxylammonium chloride (HO-NH<sub>2</sub>·HCl, abbreviated as HAC) is of analytical grade and purchased from Tianjin Chemical Reagent Co., Ltd. (Tianjin, China), and its molecular structure was illustrated in Fig. S1 (Supplementary Materials). Hydroxylamine hydrochloride is easy to deliquesce and is easily decomposed by high heat (above 152 °C), which is mainly used as reducing agent and imaging agent. So, it is necessary to operate closely and pay attention to ventilation. All other reagents are of analytical grade, and deionized water was used to prepare all the aqueous solutions.

### 2.2. Modification of brick-red PAL with HAC solution

The pretreated brick-red PAL powder was uniformly dispersed in 100 mL of 5 mol/L HAC solution at a solid/liquid ratio of 1/10 (*m/v*) under continuous mechanical stirring. The resultant suspension was heated to 80 °C under stirring, and the reaction runs at 80 °C for 4 h, 8 h, 12 h, 24 h or 48 h, respectively. After the resultant suspension was cooled to room temperature, the solid product was separated from the suspension by centrifugation at 5000 r/min, fully washed

with deionized water and then dried to constant weight at 60 °C in a vacuum oven. The dry solid product was smashed and passed through a 200-mesh sieve for further use. The pretreated brick-red PAL was coded as RPAL, and the modified PAL with HAC were coded as HAC-PAL-*x*, where *x* represents the reaction time (h).

### 2.3. Characterizations

FTIR spectra were recorded on a Fourier transform infrared spectrometer (Thermo Nicolet NEXUS TM, USA) in the wavenumber range of 4000–400 cm<sup>-1</sup> after the sample was prepared as KBr tablets (the mass ratio of sample/KBr is 1/150). The surface morphologies of samples were observed using a scanning electron microscopy (SEM, JSM-6701F, JEOL, Ltd. Japan) after fixed the sample on copper stub and coated with gold film. X-ray diffraction (XRD) patterns were collected using an X'pert PRO X-ray power diffractometer equipped with a Cu-Kα radiation source (40 kV, 40 mA) (PAN analytical Co., Netherlands) from 3 to 70° with a step interval of about 0.167°, using Cu-Kα radiation of 0.1542 nm. The chemical composition was determined using a Minipal-4 X-ray fluorescence spectrometer (PANalytical, Netherland). Zeta potential was measured on a ZEN3600 Zeta voltmeter (Malvern, Britain), and the sample was prepared as an aqueous dispersion (0.5 mass%) by a high-speed stirring before test. The specific surface area (*S*<sub>BET</sub>) was measured on ASAP 2010 analyzer (Micromeritics, USA) at 77 K and the values were determined by the Brunauer-Emmett-Teller (BET) method. The total pore volumes (*V*<sub>total</sub>) and the micropore volume (*V*<sub>micro</sub>) were obtained from the volume of liquid N<sub>2</sub> held at the relative pressure *P/P*<sub>0</sub> = 0.95 and estimated by the *t*-plot method ultimately. Mossbauer spectra were obtained at room temperature with a MS-500 (Oxford Company, Britain) electromechanical spectrometer working in a constant acceleration mode. A <sup>57</sup>Co/Pd source and a Fe standard were used. The experimentally obtained spectra were fitted to mathematical processing according to the least squares method. The parameters of hyperfine interaction such as isomer shift (IS), quadrupole splitting (QS), hyperfine magnetic field (*H*<sub>hf</sub>), and the relative area of the partial components in the spectra were determined.

## 3. Results and discussions

### 3.1. Apparent and microscopic morphologies

Fig. 1 shows the digital photos of RPAL and the modified PAL with HAC solution at different reaction time. It was clearly observed from Fig. 1a that RPAL shows brick-red color. After the reaction in HAC solution < 12 h, the color of PAL slightly becomes lighter, but it still is brick-red. However, the brick-red PAL turns into white when the reaction time is equal to or longer than 24 h, and the whiteness of the HAC-PAL-48 h reached 70.01 (the whiteness of RPAL is zero) (Table S1, Supplementary Materials). The change of microscopic morphology of PAL after treated with HAC solution for different time was studied and the results were shown in Fig. 1b-f. As can be seen, the PAL rod crystals and the plate- or particle-like associated minerals were observed in the SEM images of RPAL. The plate-like matters are mainly chlorite and feldspar [40], and the particle-like matters are mainly quartz [41, 42] (also confirmed by XRD results). After being treated with the HAC solution, the longer rod crystals slightly become shorter; whereas the length of the rods becomes uniform in contrast to the uneven rod crystals of RPAL. As prolonging the reaction time, the rods become more homogeneous after the reaction in HAC solution for 48 h.

### 3.2. XRD analysis

Fig. 2 shows the XRD patterns of RPAL and the modified PAL with HAC solution at different reaction time. The characteristic reflections of PAL crystal at  $2\theta = 8.47^\circ$  ( $d = 1.0441$  nm, 110 crystalline plane),  $2\theta = 13.62^\circ$  ( $d = 0.6496$  nm, 200 crystalline plane),  $2\theta = 19.80^\circ$

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