



## Research paper

# One-step green approach for synthesizing highly ordered pillaring materials via ultrafast transportation



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## ABSTRACT

The intercalation of guest molecules into layered materials is an important strategy to develop multifunctional hybrid nanocomposites and porous materials. The unique mesoporous structure and the intrinsic acidity of metal oxide intercalated porous clay heterostructure (PCH) make it a promising catalytic material. In contrast to the current synthesis methods of PCH that have complex procedures and structure-controlling difficulties, a novel one-step approach with supercritical CO<sub>2</sub> (scCO<sub>2</sub>) as medium was invented using montmorillonite (Mt) as the host matrix and cetyltrimethylammonium bromide as the structure-directing agent (SDA). In this simple and efficient approach, the high diffusivity of scCO<sub>2</sub> ensures the facile transportation of cationic SDA into the interlayer space of Mt via ion exchange, which eliminates a requirement for the high solubility of a SDA in scCO<sub>2</sub>. As a result, the co-assembly of the SDA and the oxide precursor controlled in the interlayer space of Mt leads to the highly ordered PCH. Furthermore, this unique approach provides a general technique to synthesize multi-functional intercalation compounds.

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## 1. Introduction

The intercalation of guest molecules into two-dimensional layered materials is a very important strategy to develop multifunctional hybrid nanocomposites and porous materials, which would have potential applications in electronics and catalysis (Baumgartner et al., 2008; Tsapatsis and Maheshwari, 2008; Chmielarz et al., 2011; Zhang et al., 2011; Rivera et al., 2012). Thus, the synthesis and application of intercalated layered materials have attracted considerable attention (Mohapatra et al., 2012; Coronado et al., 2010). For the preparation of intercalated layered materials, however, the strong interactions between the adjacent layers generally require complicated procedures with multi-steps (Chen et al., 2008). Moreover, the difficulties in confining the assembly of the guest species exclusively in the interlayer space make the structure of the intercalated materials disordered (Hao et al., 2012). Thus, the synthesis of highly ordered intercalated layered materials through a single-step/one-pot process is very necessary, but it is a great challenge.

Clay minerals, which are important layered materials, have been extensively studied as host matrixes to develop intercalated layered materials owing to their common availability and extraordinary

properties (Bergaya et al., 2006). Being an important intercalated layered material, porous clay heterostructure (PCH) was obtained by intercalating a surfactant and the precursor of a metal oxide and their subsequent co-assembly within the interlayer space of clay minerals, which is analogous to that applied to form ordered mesoporous silica (Galameau et al., 1995; Polverejan et al., 2000). The unique mesoporous structure and the intrinsic acidity of PCH constitute its promising applications for catalysis. However, current synthesis methods for PCH require relatively complicated manipulations (Hao et al., 2012; Cool and Vansant, 2004), i.e., 1) ion exchange of a cationic surfactant into the interlayer space of clay minerals; 2) the intercalation of the precursor of metal oxide (metal alkoxide in general); 3) the hydrolysis of the precursor with the interlayer water and its polymerization templated by the surfactant. More importantly, the requirement of confining the hydrolysis and assembly of the oxide precursor in the interlayer space of clay minerals makes the synthesis of an ordered PCH difficult. Following the current mechanism for the formation of PCH (Polverejan et al., 2000; Cool and Vansant, 2004), if an appropriate solvent is available, the well-structured PCH is expected to be efficiently synthesized in a one-step process.

Supercritical carbon dioxide (scCO<sub>2</sub>) has been promoted as a sustainable and green solvent to replace organic solvents because of its non-toxicity, non-flammability, and natural abundance (Cooper, 2003; Beckman, 2004). Furthermore, its low viscosity, high diffusivity, and

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near-zero surface tension make it very useful for transporting substances into nanospaces (Hao et al., 2012; Yoda et al., 2005). In our previous work (Hao et al., 2012),  $\text{scCO}_2$  was found favorable for introducing the tetraethoxysilane (TEOS) into the interlayer space of the surfactant-intercalated montmorillonite (Mt) with a good dispersion, leading to the highly ordered PCH. However, it is generally recognized that hydrocarbon-based cationic quaternary ammonium surfactants are unlikely to be intercalated into the interlayer space of clay minerals in the medium of  $\text{scCO}_2$  due to their very small equilibrium solubility in  $\text{scCO}_2$  (Fan et al., 2005). Thus, extensive efforts have been devoted to enhance the solubility of these surfactants in the  $\text{scCO}_2$  medium either by adding a co-solvent (Naveau et al., 2011) or designing and synthesizing ionic hydrocarbons with  $\text{CO}_2$ -philic fluorinated (Newman et al., 1993), silicone-based (Fink and Beckman, 2000) or oxygenated (Fan et al., 2005) tails. In contrast, herein, we report a novel strategy based on a single-step process with  $\text{scCO}_2$  medium, leading to highly ordered metal-oxide-intercalated clay mineral.

The general recognition, in which the small solubility of hydrocarbon-based cationic quaternary ammonium surfactants in  $\text{scCO}_2$  greatly limits their ability to enter the interlayer space of clay minerals, would be challenged by this work. The high diffusivity and the zero surface tension of  $\text{scCO}_2$  create a faster transportation of dissolved surfactant. Therefore, even if the equilibrium solubility in  $\text{scCO}_2$  is very low, the dissolved surfactant can quickly transport via ion exchange and deposit in the interlayer space of clay minerals before it reaches the equilibrium in  $\text{scCO}_2$ . As a result, the continuous dissolution of the solid surfactant would occur. Based on this hypothesis, the low-solubility surfactant in  $\text{scCO}_2$  can be expected to transfer into the interlayer space of clay minerals at the cation exchange capacity (CEC) of the clay minerals. Furthermore, in this work, this hypothesis was confirmed by one-pot synthesizing the  $\text{SiO}_2$ -intercalated PCH with Mt as the starting clay mineral and cetyltrimethylammonium bromide (CTAB) as the structure-directing agent (SDA). Our strategy, as shown in Scheme 1, is accomplished by the simultaneous transportation of CTAB molecules and soluble tetraethoxysilane (TEOS) into the interlayer space of Mt due to the high diffusivity and zero surface tension of  $\text{scCO}_2$ . After hydrolysis of the TEOS in the interlayer space of Mt templated by SDA micelles and the subsequent removal of SDA molecules by high-temperature calcination, a highly ordered PCH is obtained. This would create a novel one-step approach with  $\text{scCO}_2$  medium for pillaring layered materials. Moreover, its facile and easily controlled nature can allow us to overcome the limitations of the current complicated multiple-step approaches and to synthesize various ordered intercalated materials with tunable acidity

and mesopore sizes by simply changing the molecular size of the SDA, starting layered materials, and the precursor of intercalated oxides.

## 2. Experimental

### 2.1. PCH preparation

The sodium-type montmorillonite ( $\text{Na}^+$ -Mt) with a CEC of 110 meq/100 g (Zhejiang Sanding Group Co., Ltd.) was used directly without further purification. To 200 mL of 1 wt%  $\text{HNO}_3$  aqueous solution, a desired amount of  $\text{Na}^+$ -Mt was added under vigorous stirring to obtain a 2 wt%  $\text{Na}^+$ -Mt dispersion. Then, the prepared slurry was stirred at 80 °C for 5 h. After this, the slurry was centrifugated, and sufficiently washed with deionized water until pH = 6–7. Finally, the acid activated Mt ( $\text{H}^+$ -Mt) was obtained by drying the solid at 32 °C and a relative humidity of 65%.

In a 30.0 mL high-pressure autoclave with magnetic stirring, 0.50 g of the dried  $\text{H}^+$ -Mt, 10 mL of TEOS, and 0.30 g of CTAB were loaded. After purging with  $\text{CO}_2$  (99.999% purity) for 10 min, the reactor was sealed, and  $\text{CO}_2$  was pumped into the reactor until 20 MPa. Simultaneously, the system was heated to 80 °C, and the synthesis was performed for 5–72 h. After cooling the reactor to room temperature, it was slowly depressurized to atmosphere. Subsequently, the mixture was centrifugated, and dried under atmospheric conditions for 72 h. Finally, PCH was obtained by calcining the solid at 600 °C for 5 h at a temperature ramp of 2 °C/min.

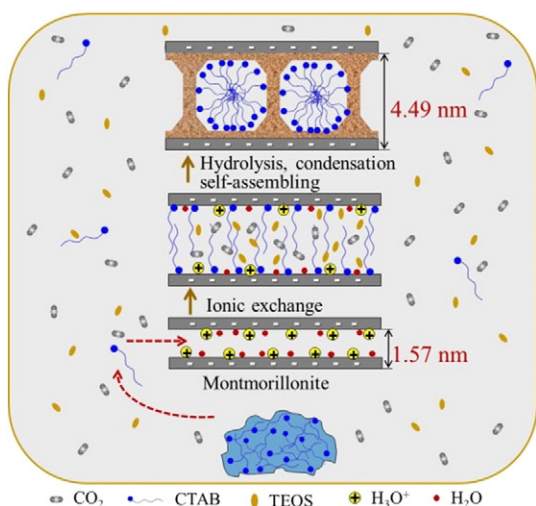
### 2.2. Characterization techniques

X-ray diffraction (XRD) patterns were recorded on a X-ray diffractometer (D8 Advance, Bruker) equipped with Cu K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ) and Ni filter. The applied voltage and current were 40 kV and 40 mA, respectively.  $\text{N}_2$  adsorption-desorption isotherms were measured with a BelSorp-Max (Bel Japan Inc.). Before measurement, the samples were degassed at 300 °C for 12 h, and the  $\text{N}_2$  adsorption/desorption was performed at  $-196 \text{ }^\circ\text{C}$ . TEM micrographs were obtained on an FEI Tecnai G2 F20 electron microscope operated at 200 kV, and SEM observations were performed on a Philips-FEI model Quanta 200 instrument. Fourier Transform Infrared Spectroscopy (FT-IR) measurements were performed on a PerkinElmer Spectrum 400 spectrometer. FT-IR spectra in the transmittance mode were recorded in the range of 2700–3500  $\text{cm}^{-1}$  at a resolution of 1  $\text{cm}^{-1}$  using the KBr pressed disk technique (1 wt% sample).

## 3. Results and discussion

### 3.1. Textural and structural properties

The obtained PCH was subjected to XRD measurement. As shown in Fig. 1A, the  $d_{001}$ -value of the dried  $\text{H}^+$ -Mt is only about 1.57 nm. In contrast, the PCH exhibited a very sharp 001 reflection peak at  $2\theta$  of 2.15°, corresponding to the  $d_{001}$ -value of 4.05 nm, which is similar to the PCH prepared with the traditional methods (Hao et al., 2012; Galarneau et al., 1995; Polverejan et al., 2000). Taking the Mt layer thickness (0.96 nm) into account, the interlayer space of Mt was increased from 0.61 to 3.09 nm. This suggests that the SDA and TEOS can really be transported into the interlayer space of Mt in  $\text{scCO}_2$  medium, leading to the highly ordered PCH in a single-step process. This was further supported by the  $\text{N}_2$  adsorption-desorption isotherms and BJH pore size distribution of PCH (Fig. 1B). The PCH showed a linear relationship of nitrogen uptake with pressure in the relative pressure ranges of 0.05–0.35 and a very sharp pore size distribution curve with peak pore size of 2.44 nm (the inset of Fig. 1B). This can be attributed to the framework change from supermicropores to small mesopores directed by the SDA micelle formed within the interlayer space of Mt. Moreover, there is no triangular shape in the desorption branch falling steeply to the lower



**Scheme 1.** Illustrative scheme of one-pot process for the formation of PCH in the medium of  $\text{scCO}_2$ .

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