



# Preparation of surface-functionalized porous clay heterostructures via carbonization of soft-template and their adsorption performance for toluene

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## ABSTRACT

A new type of surface-functionalized porous clay heterostructures (SF-PCH) was synthesized via carbonization of the template agents with sulfuric acid. The converted carbons deposited on the porous surface of the SF-PCH samples and changed their surface chemical properties. The composites possessed a maximum carbon content of 5.35%, a large specific surface area of 428 m<sup>2</sup>/g and micropore volume of approximately 0.2 cm<sup>3</sup>/g. The layered and porous structure of SF-PCH was retained after carbonization and calcination when sulfuric acid solution with a mild concentration was used. Analysis by XPS confirmed that the carbonaceous matter in the pore channels was functionalized with various organic groups, including carbonaceous, nitrogenous, and sulfated groups. Both the surface chemical property and structural characteristic of adsorbents have effects on the adsorption properties of SF-PCH for toluene. The SF-PCH samples exhibited a stronger adsorption affinity to toluene compared with untreated PCH in the low pressure region, which is more valuable in the practical applications. These results demonstrate that carbonization of soft-template is a feasible process for the surface modification of PCH, enabling the resulting composites to become promising candidates for application in toluene emission control.

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## 1. Introduction

The volatile organic compounds (VOCs) from anthropogenic emission has become a critical component of hazardous air pollutants. Volatile organic compounds have complex composition, and most of them are noxious for environment and human health, such as benzene, toluene, and formaldehyde, which are considered by many authorities to be proven or probable human carcinogens [1,2]. Considering their economic values, hardly complete removal or

causing secondary pollution in removal (e.g., combustion method), VOCs have to be trapped and recycled. Adsorption is one of the widely accepted methods for collecting these harmful compounds because of the flexibility of the system, low energy, and inexpensive operation costs [3]. Owing to the following properties, activated carbon is the most common materials used for adsorption of VOCs: highly developed surface area, large pore volumes, low price and wide range of raw material source [4–6]. However, some disadvantages of activated carbon usually encounter in practical gas adsorption, including flammability, pore clog, hygroscopicity, and other problems associated with regeneration [7].

Porous clay heterostructures (PCH) is a kind of pillared interlayered clays (PILC) according to the definition of IUPAC [8]. Because of possessing large surface area, inherent or enhanced solid acidity, and unique combined microporosity and mesoporosity, PCH is a promising candidate for applications as adsorbents [9–11], catalysts [12–14], carriers [15], and templates [16–18]. Compared with

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microporous PCH, the porous surface modification of macroporous adsorbents (e.g., diatomite) can be relatively easily performed by grafting silane or organophilic zeolite [19,20] to improve their affinity to VOCs without concerning about the blockage of macropores. The pore sizes of PCH distribute in the supermicropore to small mesopore domain. For such small pores, their porous surfaces are hard to be modified and functionalized. The micropores are more likely to become clogged by grafted molecules.

In some previous works focusing on improving the adsorption and catalytic performances of PCH, the native template agents or additional organic species were partially or completely retained to functionalize the internal surface of the porous silica. Depending on the calcination temperature and atmosphere, as well as the composition and concentration of extracting solvents, the surface chemical properties and the solid acidity were tuned through adjusting the contents of organic residues on the internal pore surface. The surface-functionalized materials with residual surfactant in their pores exhibited good hydrophobicity or catalytic activity [21,22]. However, their relatively low thermostability caused by the organic residues hindered the regeneration of the adsorbents. In some other reports, a variety of functional groups (e.g., methyl [23,24], phenyl [25–27], and thiol [28]) were incorporated into the framework through co-condensation methods by introducing silane with specific functional groups during the one-step synthesis of porous materials. The resultant materials exhibited greater thermostability by the greater stability of the Si–C bonds formed between functional groups and pore walls. However, part of the incorporated functional groups remained in the framework, which negatively affected the condensation of silicon species and further affected the crystallinity and the arrangement of pore network.

Recently, a synthesis route for preparing carbon materials from native template agents [29] or other carbon sources [30,31] was applied in the preparation of mesostructured silica–carbon composites. The surfactant in the pore channels was carbonized with the aid of sulfuric acid. Both the silica framework (hard template) and the template agent (soft template) were preserved in this method. The Si–framework and carbonaceous materials in the pores were acid-proof and relatively thermostable, which ensured the mesoporous structural ordering and enhanced the thermostability of the composite. The final products combined the textural characteristics of mesostructured silica and the surface chemical properties of carbon materials [29–31]. Such silica–carbon composites attract attention because of their potential applications in catalysis and liquid-phase adsorption. The suitability of the composites in these applications stems from their good textural and surface chemical properties [32,33], whereas their application for removing VOCs is rarely reported. Surface-functionalized porous silica may exhibit a greater adsorption affinity to VOCs, e.g., toluene, by the incorporation of converted carbon deposited inside the pores of silica. This feature inspires us to make an attempt on fabricating SF-PCH as gas-phase adsorbents for toluene removal.

In this study, we report the preparation of SF-PCH via the carbonization of native template agents with H<sub>2</sub>SO<sub>4</sub> and the effect of acid concentration on the physicochemical characteristics of SF-PCH. The adsorption performance of SF-PCH was evaluated on the base of the adsorption of toluene. The influence of the structural characteristics and surface chemical properties on the adsorption behaviors was also discussed.

## 2. Experimental

### 2.1. Materials

Montmorillonite (Mt) obtained from Inner Mongolia, China, showed the very high purity above 95% containing quartz as an impurity, confirmed by XRD measurement. Its chemical compositions (wt%) are listed in Table 1. The cation exchange capacity (CEC) was 110.5 mmol/100 g measured through [Co(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup> cation exchanging method [34,35]. Cetyltrimethylammonium bromide (CTAB, approx. 99%) was purchased from Nanjing Robiot Co., Ltd. Dodecanamine (DDA, approx. 98%) was purchased from Sigma-Aldrich chemistry Co., Ltd. Tetraethylorthosilicate (TEOS, chemically pure), hydrogen peroxide (≥30 wt%), Sulfuric acid (95.0–98.0%), hydrofluoric acid (≥40%), hydrochloric acid (36.0–38.0%), and toluene (used as adsorbate in adsorption experiments, ≥99.5%) were purchased from Guangzhou chemical reagent factory.

### 2.2. Synthesis of SF-PCH samples

The organo-montmorillonite (OMt) was prepared by the exchange of CTA<sup>+</sup>, whose amount was 1 time the cation exchange capacity (CEC) of Mt. The dispersion was stirred at 80 °C for 10 h. After filtration, the obtained OMt was washed with distilled water to remove excess water-soluble surfactant. The OMt was air dried at 80 °C and ground sufficiently to pass 100-mesh sieve. Subsequently, OMt was mixed and continuously stirred with DDA and TEOS with the mass ratio of OMt/neutral amine/TEOS of 1/1/120 for 4 h at 60 °C, centrifuged without washing and then air-dried overnight. The same procedure was also performed without OMt to fabricate silica materials as a reference to the PCH samples. The resultant materials are referred to as P-T. The product heated at 550 °C for 6 h in air is named P-air.

The PCH precursor (before calcination) was dispersed in H<sub>2</sub>O<sub>2</sub> (solid/liquid = 1 g/100 mL) for 15 h to oxidize the template agents in the pore channels. Subsequently, 2.5 g of the obtained materials were dispersed in H<sub>2</sub>SO<sub>4</sub> solutions with a concentration of *x* wt% (*x* = 0, 1, 2, 5, and 10). The dispersion was heated in air at 100 °C for 6 h and then at 160 °C for 12 h. Finally, the resulting gray or black solid was heated at 550 °C for 6 h. The process was under flowing nitrogen. The final product is designated as P/C-*x*H. Particularly, P/C-0H means that no H<sub>2</sub>SO<sub>4</sub> was used in the preparation of the corresponding SF-PCH.

To eliminate the influence of the base clay on the characterization of the converted carbon from the surfactant, carbonaceous materials were obtained by dissolving the mineral host and inter-layered Si-framework with HF and HCl. The templated carbon obtained from P/C-2H is labeled as C-2H.

### 2.3. Characterization methods

Major element oxides were analyzed using a Rigaku RIX 2000 X-ray fluorescence spectrometer (XRF) on fused glass beads. Calibration lines used in quantification were produced by bivariate regression of data from 36 reference materials encompassing a wide range of silicate compositions, and analytical uncertainties are mostly between 1% and 5%.

**Table 1**  
Chemical composition of the pristine Mt and P-air.

	SiO <sub>2</sub> (%)	Al <sub>2</sub> O <sub>3</sub> (%)	Fe <sub>2</sub> O <sub>3</sub> (%)	CaO (%)	MgO (%)	Na <sub>2</sub> O (%)	K <sub>2</sub> O (%)	MnO (%)	TiO <sub>2</sub> (%)	P <sub>2</sub> O <sub>5</sub> (%)	L.O.I. (%)
Mt	58.16	16.95	5.26	2.29	3.57	0.19	0.15	0.03	0.20	0.08	13.12
P-air	80.06	7.75	2.74	0.08	2.38	0.05	0.09	0.02	0.18	0.01	6.97

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