



# Study on the modified montmorillonite for adsorbing formaldehyde



Feng Lin<sup>a</sup>, Guangqi Zhu<sup>b</sup>, Yuenian Shen<sup>c</sup>, Zhenyi Zhang<sup>a</sup>, Bin Dong<sup>a,\*</sup>

<sup>a</sup> Key Laboratory of New Energy and Rare Earth Resource Utilization, State Ethnic Affairs Commission, School of Physics and Materials Engineering, Dalian Nationalities University, Dalian 116600, China

<sup>b</sup> State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian 116023, China

<sup>c</sup> Inner Mongolian Key Laboratory of Rare Earth Chemistry & Physics, School of Chemistry and Chemical Engineering, Inner Mongolian University, Hohhot 010022, China

## ARTICLE INFO

### Article history:

Received 8 May 2015

Received in revised form 30 June 2015

Accepted 25 July 2015

Available online 10 August 2015

### Keywords:

Modified montmorillonite

HCHO

Adsorption capacity

PVA

Pillared

## ABSTRACT

It is very important to develop a cost-effective and environmentally friendly adsorbent for the efficient removal of indoor formaldehyde (HCHO). Herein we present the modified montmorillonite as adsorbents for HCHO. A series of alumina cross-linked montmorillonite with surfactant modification (Al-SCLM) were synthesized in the presence of polyvinyl alcohol (PVA). These adsorbents are safe and cheap, in rich sources, acceptable appearance for daily use. By the characterization such as XRD, FTIR, HCHO adsorption/desorption capacity measurement, it is found that the interlayer environment is a key factor for the superior adsorption capacity of the modified montmorillonite. The introduction of surfactant molecules is very favorable for the improvement of the montmorillonite's adsorption capacity. With optimization, the adsorbing capacity of HCHO over Al-SCLM is obviously superior to conventional inorgano-montmorillonite and organo-montmorillonite, and can be over 80% of that over activated carbon with the same volume. We can conveniently recover the adsorbents by heating them to 353 K. The strategy that improving the adsorbing capacity by increasing the interlayer distance of materials with surfactant modification will be crucial for developing highly effective adsorbents for hazardous wastes, and has a good prospect for getting rid of HCHO in industrialization.

© 2015 Published by Elsevier B.V.

## 1. Introduction

Environment and energy have become one of the most important issues nowadays. Formaldehyde (HCHO) is a major indoor pollutant which is often emitted from personal care products, insulation materials, disinfectants, laminate floors, furniture and fabrics [1–5]. It is well known that long-term exposure to HCHO can cause many adverse effects including nasopharyngeal carcinoma, colorectal cancer, pregnancy syndrome, encephaloma, leukemia etc. [2]. HCHO is lethal at concentrations as high as 15 ppm [1]. In line with environmental safety, HCHO concentrations in residential dwellings, schools, hospitals and in the workplace must be strictly regulated, and the maximum permitted concentration of formaldehyde vapor for long-term exposure established by the World Health Organization (WHO) is 80 ppb [2–6].

There has been a lot of study suggesting some common ways for the removal of HCHO, such as air ionization method, air exchange method, physical adsorbing, material closing method, chemical

counteraction, catalysis technology [7–19]. However, some methods involve complex procedures, some cost more or can only be conducted in laboratory. Consequently, taking the practicality and cost in consideration, there are two ideal ways for the removal of HCHO, using a chemical reaction [20–24] and physical adsorption [25,26]. Adsorption is a simple and effective approach to remove gaseous HCHO under ambient conditions. A variety of adsorbents have been prepared, including potassium permanganate, aluminum oxide and ceramic materials [27,28], activated carbon [29,30], hydroxyapatite [31], titania [32–34], and celite [35,36]. Recently, activated carbon (AC) and mesoporous silica have been tested as HCHO adsorbents [37,38]. These adsorbents typically have a high surface area, tunable pore size and functionalized surfaces. However, as a typical polar molecule, HCHO is not efficiently adsorbed by AC-like materials [26]. The modification of AC and mesoporous silica with amine-containing compounds is an effective approach to improve their adsorption performance for HCHO [3–5,26], given that Schiff bases and amino groups can interact with HCHO effectively [39]. However, modified AC and mesoporous silica are unstable, especially at high temperature, and amine compounds probably lead to additional pollution. Meanwhile, the high cost and color of activated carbon are not extensively accepted

\* Corresponding author.

E-mail address: [dong@dlnu.edu.cn](mailto:dong@dlnu.edu.cn) (B. Dong).

for daily use. Therefore, it is necessary to develop a cost-effective and environmentally friendly adsorbent for the efficient removal of indoor HCHO.

Since the early study using inorganic polymeric hydroxyl cation to prepare pillared montmorillonite by Vaughan et al. [40], the research on the adsorbing capacity of pillared montmorillonite had been extensively carried out [41–45]. Montmorillonite have such advantages as rich sources, low cost, acceptable appearance, and superior adsorbing capacity and so on [46–51]. Based on these studies, we focused on synthesizing a modified montmorillonite that can adsorb or eliminate HCHO efficiently. A number of researchers devote to improve the properties of montmorillonite in many different ways, among which preparing the cross-linked montmorillonite in the presence of surfactant attracted researchers' interest [41,45]. Because of the bigger size of the surfactant molecules, the material prepared has bigger aperture, layer space and good stability even when heated [45]. However, the adsorbing capacity for removing indoor HCHO over this kind of modified montmorillonite was not studied yet. Through exploitation, we prepared alumina cross-linked montmorillonite with surfactant modification (Al-SCLM), and investigated their adsorbing capacity for indoor HCHO. The relationship between the structure and performance of adsorbents was found and concluded, this is crucial for developing highly efficient adsorbents for adsorbing HCHO in both preparation of adsorbents and environmental protection processes.

## 2. Experimental

### 2.1. Materials

Calcium montmorillonite (Ca-M) was obtained from Xinghe county of Inner Mongolian.  $(\text{CH}_2\text{:CHOH})_n$  (PVA-124) was purchased from Beijing Chemical Reagents Company.  $\text{AuCl}_3 \cdot \text{HCl} \cdot 4\text{H}_2\text{O}$  was purchased from Goya Chemical Reagents Company. All chemicals used in the experiments were of analytical reagent grade without further treatment.

### 2.2. Adsorbents preparation

#### 2.2.1. The pretreatment of montmorillonite

Ca-M was added into 1.0 M NaCl (aq) with the ratio 10 g/1 L. Then the above solution was stirred at 60 °C for 3 h. After that, the precipitate was separated by filtration, and then washed several times with distilled water until there was no residue of  $\text{Cl}^-$  in the filtrate (tested with  $\text{AgNO}_3$  (aq)). Finally, the obtained precipitate was dried at 328 K overnight. The sodium montmorillonite (Na-M) was obtained immediately.

Na-M was dispersed into the distilled water to form a suspension with a concentration 2.5%, then the acidification treatment was carried out as following: we added  $\text{H}_2\text{SO}_4$  (15% aq) to the above suspension, heated and refluxed the system at  $(95 \pm 2)^\circ\text{C}$  for 4 h. The precipitate was separated by filtration, then washed several times with distilled water until the pH of filtrate was 4. Finally the sample was dispersed into the distilled water to form a suspension with a concentration 1.0%.

#### 2.2.2. Al cross linking agent preparation

0.1 M NaOH (aq) was slowly dropped into 0.2 M  $\text{AlCl}_3$  (aq) under vigorous stirring at 80 °C ( $[\text{OH}^-]/[\text{Al}^{3+}] = 2.4$ ), and the suspension was stirred for 2 h further, finally aged for 2 days at 60 °C.

#### 2.2.3. Modified montmorillonite (Al-SCLM) preparation

Surfactant polyvinyl alcohol (PVA) with 2400–2500 polymerization degree was used as the pillared precursor. A 3.6 wt% aqueous PVA was added to the suspension with a concentration 1.0% prepared in step (1), then the above solution reacted for

4 h under vigorous stirring at room temperature. After that the Al cross linking agent solution prepared in step (2) was added dropwise into the above mixture under vigorous stirring for 12 h. The final adsorbent was washed with deionized water until there was no residue of  $\text{Cl}^-$  in the filtrate (tested with  $\text{AgNO}_3$  (aq)), finally dried at 343 K overnight. The adsorbents with different mole ratios of Al/montmorillonite and PVA/montmorillonite were coded as Al(3.5)-SCLM(1.5) (Al/M = 3.5 mmol/g, PVA/M (g/g) = 1.5), Al(3.5)-SCLM(1.0) (Al/M = 3.5 mmol/g, PVA/M (g/g) = 1.0), Al(2.5)-SCLM(1.0) (Al/M = 2.5 mmol/g, PVA/M (g/g) = 1.0) [41].

For comparison, we also prepared other adsorbents respectively, including hydroxyl iron aluminum pillared montmorillonite, organic intercalated hydroxyl aluminum pillared montmorillonite (ORPMT) modified with cetyltrimethylammonium bromide, organic intercalated montmorillonite (ORMt) without hydroxyl aluminum pillared [41–48].

### 2.3. Adsorbents characterization

#### 2.3.1. Bulk density

The bulk density of adsorbents was tested as follows. We take the adsorbents with same volume, then test their masses. Consequently the bulk density can be calculated by the formular,  $\rho = m/V$ .

#### 2.3.2. Fourier transform infrared spectroscopy (FT-IR)

Infrared spectra (IR) were recorded on a Nicolet NEXUS 470 FT-IR Spectrometer in ambient air at room temperature. The spectra of different adsorbents were collected in KBr pellets from 400 to 4000  $\text{cm}^{-1}$  with 4  $\text{cm}^{-1}$  resolution and averaged 10 times.

#### 2.3.3. X-ray diffraction (XRD)

The prepared samples were characterized by X-ray powder diffraction (XRD) on a Bruker AXS D8 Advance Bragg–Brentano geometry powder diffractometer. Each sample was scanned using Cu-K $\alpha$  radiation with an operating voltage of 40 kV and an operating current of 200 mA. The scan rate of 0.4°/min was applied to record the patterns in the range of 0°–60° at a step of 0.02°.

### 2.4. Adsorption and desorption experiment

The schematic diagram of adsorption experiment is shown in Fig. 1. The adsorbents' adsorbing capacity of HCHO was investigated in a glass tube with a diameter 6 mm at room temperature. Firstly, after purification air got across the HCHO aqueous solution (37%), and then the above gas was passed through the adsorbents (40–60 mesh) addressed in the glass tube, the space velocity was 96000  $\text{ml h}^{-1} \text{g}^{-1}$ . According to the "public health standard" published by Chinese technical supervision bureau and the ministry of health: formaldehyde concentration in air should be lower than 0.12  $\text{mg m}^{-3}$ . In other words, it should be less than 0.0978 ppm at 25 °C. The HCHO concentration in our experiments is four times of this formaldehyde concentration standard in air (ca. 0.42 ppm). The residual HCHO in the gas system was measured by formaldehyde monitor (Interscan 4160, produced by the Interscan Company in the United States, the resolution of which is 10 ppb).

The temperature programmed desorption (TPD) of formaldehyde adsorbed on adsorbents was investigated on the above equipment. Firstly high pure nitrogen (99.999%) was got across the entire pipeline for 30 min to remove oxygen in the system, and then formaldehyde desorbed from the adsorbents when the temperature programmedly varied from the room temperature to 350 °C. We monitored the desorbed HCHO concentration in the system by formaldehyde monitor (Interscan 4160). Thus the desorption of formaldehyde on adsorbents as a function of temperature can be achieved.

Download English Version:

<https://daneshyari.com/en/article/5348907>

Download Persian Version:

<https://daneshyari.com/article/5348907>

[Daneshyari.com](https://daneshyari.com)