Available online at www.sciencedirect.com

ScienceDirect

Natural Gas Industry B 4 (2017) 382−389

www.elsevier.com/locate/ngib

Research Article

Adsorptive performance of chromium-containing ordered mesoporous silica on volatile organic compounds (VOCs)☆

Fan Jianwei[a,*], Gou Xiao[a], Sun Yu[b], Ran Xianqiang[a], Teng Wei[a], Wang Xiaomin[a]

[a] College of Environmental Science and Engineering, Tongji University, Shanghai 200092, China
[b] Shanghai Tongji Clearon Environmental Protection Equipment & Engineering Co., Ltd., Shanghai 200092, China

Received 16 March 2017; accepted 25 April 2017
Available online 20 November 2017

Abstract

Volatile organic compounds (VOCs) are the primary poisonous emissions into the atmosphere in natural gas exploitation and disposing process. The adsorption method has been widely applied in actual production because of its good features such as low cost, low energy consumption, flexible devices needed, etc. The commonly used adsorbents like activated carbon, silicon molecular sieves and so on are not only susceptible to plugging or spontaneous combustion but difficult to be recycled. In view of this, a new adsorbent (CrSBA15) was made by the co-assembly method to synthesize the ordered mesoporous silica materials with different amounts of chromium to eliminate VOCs. This new adsorbent was characterized by small-angle-X-ray scattering (SAXS), nitrogen adsorption/desorption, scanning electron microscopy (SEM), and transmission electron microscopy (TEM). Its adsorption performance to eliminate VOCs (toluene, benzene, cyclohexane and ethyl acetate used as typical pollutants) was also tested systematically. Research results indicate that this new adsorbent of CrSBA-15(30), with the silicon/chromium ration being 30, owns the maximum micropore volume, and shows a higher adsorption performance in eliminating toluene, benzene, cyclohexane and ethyl acetate. Besides, it is cost-effective and much easier to be recycled than the activated carbon. In conclusion, CrSBA-15(30) is a good adsorbent to eliminate VOCs with broad application prospects.

Keywords: Mesoporous materials; Silicon dioxide; Synthesis; Adsorption; Volatile organic compounds (VOCs); Recyclability; Energy saving

1. Introduction

Volatile Organic Compounds (VOCs) are the main pollutants emitting into the atmosphere during natural gas extraction and utilization [1,2]. There are a variety of definitions for VOCs in different regions and different industries. The World Health Organization (WHO) defines VOCs as volatile organic compounds that have a melting point below room temperature and a boiling point of 50−260 °C. ASTM D3960-98 defines VOCs as any organic compounds capable of participating in atmospheric photochemical reactions. In the *Technical Guidelines for the Preparation of List of Atmospheric Volatile Organic Sources (Trial)* released by the Ministry of Environmental Protection of the People's Republic of China in 2014, VOCs are defined as the organic compounds with a boiling point below 260 °C or a saturated vapor pressure greater than 70.91 Pa at room temperature. In scientific research, VOCs are usually defined as organic compounds that have a boiling point between 50 °C and 260 °C and a saturated vapor pressure greater than 133 Pa at room temperature [3]. According to their different chemical structures, VOCs can be divided into 5 categories, i.e., alkanes, olefins, aromatic hydrocarbons, halogenated hydrocarbons and oxygen-containing organic matters [4]. Most VOCs are harmful to humans, and some of them are carcinogenic [5]. In addition, in a certain meteorological condition, VOCs will produce photochemical reaction

☆ Project supported by the Independent Theme of the State Key Laboratory of Pollution Control and Resource Reuse (No. PCRRK16009).
* Corresponding author.
E-mail address: fanjianwei@tongji.edu.cn (Fan JW.).
Peer review under responsibility of Sichuan Petroleum Administration.

https://doi.org/10.1016/j.ngib.2017.10.003

to form secondary pollutants, including photochemical smog. Their products will further react to form secondary aerosol which is one of the main sources of $PM_{2.5}$ in the air [6–9].

There are many ways to remove VOCs, such as catalytic oxidation [10,11], adsorption [12,13], absorption [14], photocatalysis [15] and so on. The adsorption method has been widely applied in actual production because of its good features such as low cost, low energy consumption, and flexible devices needed. The commonly used adsorbents include activated carbon, silicon molecular sieves, etc. Activated carbon is low in price, large in surface area and better in adsorption properties [16], but it also has some shortcomings that cannot be overcome, which limit its use, such as easy clogging, spontaneous combustion risk and difficult recyclability [17,18]. Silicon molecular sieve is stable in performance, but its adsorption capacity for organic matter is low.

Ordered mesoporous silicon materials have a large specific surface area and uniform adjustable pore sizes and passages, which make it have good application prospects in the field of adsorption and catalysis [19,20]. SBA-15, as a typical ordered mesoporous silicon material, has a more superior hydrothermal stability, and simple synthesis step. The pore walls of SBA-15 contain micropores, which makes it have a greater adsorption capacity for some VOCs than other silicon-based molecular sieves (MCM-41, etc.) [21,22]. Studies have revealed that the addition of salts during the synthesis will affect the formation and self-assembly process of the silica micelle, and thus affect the structure of the ordered mesoporous silica material. The structure of the material has a great influence on the adsorption capacity for VOCs. In addition, Sinha et al. [23] found that chromium oxide can be used as an effective adsorbent to selectively adsorb VOCs. Accordingly, the authors selected $Cr(NO_3)_3 \cdot 9H_2O$ as the chromium source, and introduced Cr into SBA-15 skeleton as the adsorbent by a co-assembly method, and selected toluene, benzene, cyclohexane and ethyl acetate as the target VOC contaminants, to test the static and dynamic adsorption performance of SBA-15 on the contaminants, and analyzed the experimental results.

2. Materials and methods

2.1. Chemical reagents

Chemical reagents include triblock copolymers (PEO-PPO-PEO, P123), tetraethoxysilane (TEOS), hydrochloric acid, chromic nitrate nonahydrate, ethanol, toluene, benzene, cyclohexane, ethyl acetate, and toluene gas.

2.2. Synthesis of material

The ordered mesoporous silicon material SBA-15 was prepared according to the method described in Ref. [24]. CrSBA-15 was synthesized according to the following procedures. First, 4.0 g triblock copolymer (P123) was dissolved in 150 mL hydrochloric acid at pH = 3, and stirred at room temperature for 4 h until P123 was completely dissolved; the solution was denoted as A. Then, 8.6 g tetraethoxysilane (TEOS) and a certain amount of $Cr(NO_3)_3 \cdot 9H_2O$ (the initial molar ratio of silicon and chromium is 30 and 10 respectively) was dissolved in 10 mL hydrochloric acid at pH = 3; the samples obtained were donated as CrSBA-15(30) and CrSBA-15(10), respectively, and stirred at room temperature for 4 h; the solution was record as B. Solution B was added into solution A during vigorous stirring and stirred at 40°Cfor 24 h. The mixture was transferred to a high temperature and high pressure reaction kettle with polytetrafluoroethylene liner, then placed into the oven, and crystallized for 24 h at 100 °C. The mixture was then naturally cooled to room temperature, and filtered to obtain white solids. The solids were dried at 100 °C for 24 h. Then, they were placed into a muffle furnace, and heated to 550 °C in the air at 0.5 °C/min. They were kept at 550 °C for 5 h. After the template agent was removed, CrSBA-15 was obtained.

2.3. Characterization of materials

The chemical composition of the materials was determined by ICP-MS (Agilent 7700). Small Angle X-ray Scattering (SAXS) was measured by DMAX2500 scatterometer (Cu Kα ray), with the tube voltage of 40 kV and current of 35 mA. N_2 adsorption/desorption isotherm was measured by using the Micromeritics Tristar-II 3020 analyzer at 77 K. Before measurement, the sample was degassed at 180 °C of vacuum condition for more than 8 h. The specific surface area was calculated by using the BET model. The specific surface area of the micropores was calculated by using the *t*-plot equation. The pore volume was calculated from the adsorption quantity at a relative pressure of 0.995. The pore size was calculated by using the BJH model. A Philip XL30 microscope was used for the scanning electron microscopy (SEM), with a working voltage of 20 kV. Before test, the sample was placed on a conductive adhesive, stuck on the sample stage, and placed in a test chamber and vacuumed for observation. JEOL 2011 microscope was used for the transmission electron microscopy (TEM), with a working voltage of 200 kV. Before test, the sample was subject to ultrasonic dispersion in ethanol solvent, and hang was hung on the copper wire for drying.

2.4. Adsorption experiment

2.4.1. Static adsorption experiment

Static adsorption experiment was carried out on the Hiden's 002 Intelligent Gravimetric Analyzer (IGA). This device consists primarily of test system, molecular pump, and analysis system. In this experiment, IGA weight accuracy can reach 0.1 ug, which can accommodate the sample mass of 0–100 mg, with the minimum control step of 0.05% and vacuum of 10^{-6} mbar (1 mbar = 100 Pa). Before the start of the adsorption experiment, a 50–80 mg sample was degassed at 150 °C of vacuum conditions until the sample mass no longer changed. During the test, the vapor of the VOCs gradually entered the test system, making the system pressure increase to the saturated vapor pressure of the target contaminant. The adsorption capacity of SBA-15 with different