



Preparation of hierarchically porous diatomite/MFI-type zeolite composites and their performance for benzene adsorption: The effects of desilication



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HIGHLIGHTS

- Diatomite/zeolite composites prepared by vapor-phase transport and desilication.
- Desilication introduced mesoporosity and formed terminal silanol groups.
- The composites exhibited hierarchical porosity.
- The composites exhibited excellent benzene adsorption capacity.

ARTICLE INFO

Article history:

Received 11 December 2014

Received in revised form 7 February 2015

Accepted 16 February 2015

Available online 24 February 2015

Keywords:

Diatomite

Vapor-phase transport

MFI-type zeolite

Desilication

Hierarchical porosity

Benzene adsorption

ABSTRACT

Hierarchically porous diatomite/MFI-type zeolite composites were prepared by transforming the natural diatomaceous silica into MFI-type zeolite by a vapor-phase transport method, followed by a desilication treatment. The morphology and macroporosity of the diatomite were well preserved in the parent diatomite/MFI-type zeolite composite (Dt/Z). Treatment of Dt/Z by desilication in aqueous 0.2 M NaOH solution at 60 °C for 1 h resulted in a mesopore size distribution centered at approximately 7 nm, without significantly altering the macroporosity and microporosity of the resulting composite. Further desilication treatment (10 h) broadened the mesopore size distribution, whereas the macropores sourced from the diatomite support were significantly damaged and a fraction of the micropores was narrowed to approximately 0.49 nm. Under the optimal desilication condition (1 h), the desilication-treated Dt/Z sample (Dt/Z-A_{1h}) exhibited a higher adsorption capacity, better affinity, and faster adsorption kinetics toward benzene than the parent Dt/Z, as evaluated via a gravimetric method using an Intelligent Gravimetric Analyzer. The excellent benzene adsorption performance of Dt/Z-A_{1h} was attributed both to the increase in porosity and the formation of terminal silanol groups on the surface of newly developed pores after the desilication treatment.

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1. Introduction

Volatile organic compounds (VOCs) are the most common air pollutants emitted from the chemical, petrochemical, pharmaceutical, building materials, and printing industries. Most VOCs are toxic or even carcinogenic (such as benzene) and are the main sources of photochemical reactions in the atmosphere, which lead to various environmental hazards [1,2]. Many technologies are

available for VOCs control, such as adsorption [3], condensation [4], membrane separation [5], catalytic oxidation [6,7], and biological treatment [8], among which adsorption is the most applicable technology because of the flexibility of the system, low energy, and inexpensive operation costs [3,9].

Activated carbon has long been recognized as the most versatile adsorbent due to its low cost and excellent adsorption capacity [10]. However, several drawbacks are associated with its use in adsorption processes, such as hygroscopicity, pore clogging, and low thermal stability [11]. Hence, extensive efforts have been focused on finding alternative adsorbents [12–15]. MFI-type zeolites with low Al content or purely siliceous form (silicalite-1) have been proposed as potential VOCs adsorbents due to their high

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hydrophobicity/organophilicity, large surface area, and superior thermal stability [16,17]. However, these zeolites possess only micropore channels [18], resulting in both relatively slow mass transport and a high price, which is caused mainly by the need to use expensive organic templates and inorganic sources during the preparation process. These limitations have greatly hindered their use in adsorption processes.

Diatomite, also known as diatomaceous earth or kieselguhr, is a fine-grained, low-density biogenic sediment, consisting of amorphous hydrated silica ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$) derived from opalescent frustules of diatoms [19,20]. Diatoms are unicellular algae, microscopic plants that existed during tertiary and quaternary periods. One unique feature of diatoms is their highly developed porosity and, in particular, a macroporous structure with pore sizes ranging from the nanometric to micrometric domains [21–24]. Diatomite is relatively inexpensive because diatomaceous silica is the most abundant form of silica on Earth, and there are significant diatomite reserves worldwide. In previous investigations, diatomite has been used as a support to prepare diatomite/zeolite composites (supported zeolites) by offering two major advantages [25–27]: its macroporous structure can improve the efficiency of mass-transport and diffusion processes; and being made of silica, diatomite can act as an inexpensive inorganic silicon source for zeolite growth. For example, Anderson et al. [25] prepared a diatomite/ZSM-5 composite through the hydrothermal treatment of an ultrasonic seeded diatomite in a clear synthesis solution containing an adsorptive silicon source and observed a high diffusion rate of water; Wang et al. [26] prepared a hierarchically structured diatomite/MFI-type zeolite composite through a more economical and effective vapor-phase transport (VPT) method, in which the diatomaceous silica was partially transformed into zeolite. Although the overall diffusion performance of the aforementioned composites was improved due to the introduction of macroporosity by the diatomite support, the intracrystalline diffusion rate of diatomite-coated zeolite crystals may only yield a minor improvement compared to pure (unsupported) zeolites. Therefore, a possible strategy to further improve the diffusion performance of diatomite/zeolite composites is to enhance the intracrystalline diffusion rate of diatomite-coated zeolite crystals.

Post-synthesis treatment of parent zeolites can increase the porosity due to the appearance of defect sites in the zeolite framework. Thus, it can improve the gas transport characteristics of zeolites. Well-known post-treatments include steaming at relatively high temperatures [28], acid leaching [29], and, more recently, alkaline treatment [30]. Alkaline treatment selectively removes silicon from the zeolite framework, whereas steaming and acid leaching lead to dealumination. Dealumination is mainly used to stabilize the zeolite structure or to create Lewis acidity, and increase in porosity is rather limited [31]. The desilication treatment is a more efficient method to induce mesoporosity in zeolite crystals [32,33]. As inferred in the above-mentioned studies, it would be of interest to combine the coating of zeolite crystals on the surface of diatomite with the desilication treatment to achieve an improvement on the mass-transport and diffusion efficiency. However, to the best of our knowledge, related studies have not been reported to date.

In this study, a diatomite/MFI-type zeolite composite was prepared through a VPT process, thus introducing macroporosity in the zeolite material. Then, the composite was treated by desilication in an alkaline medium to create mesopores in the zeolite crystals coated on the surface of the diatomite. Treatment of the parent diatomite/MFI-type zeolite composite in aqueous 0.2 M NaOH solution at 60 °C for 1 h resulted in a mesopore size distribution centered at approximately 7 nm, without significantly altering the macroporosity and microporosity of the resulting composite. Thus, the desilication-treated diatomite/MFI-type zeolite

composite exhibited a special trimodal porosity: macroporosity sourcing from the diatomite support, mesoporosity created by desilication treatment, and microporosity of MFI-type zeolite. This is a significant optimization in the pore structure compared with the previous reported diatomite [25–27] or other substrate (e.g., porous stainless steel, porous glass or solid foam monoliths) supported zeolites [34–36], which could be helpful for the improvement of the adsorption performance of such materials. Benzene was used as a model pollutant to evaluate the adsorption performance of the resulting composites for VOC. Benzene was specifically chosen, because it is released from multiple sources (e.g., petrochemical plants, petroleum tanks, coke ovens, printing office, and Chinese-style cooking) and has been proven to be carcinogenic [1,8]. The benzene static adsorption capacity and adsorption kinetics on the resulting composites were studied based on a gravimetric method using an Intelligent Gravimetric Analyzer (IGA), which have rarely been reported in previous studies concerning the similar diatomite/zeolite composites [25–27]. The influences of desilication on the structure and the benzene adsorption performance of the prepared composites were investigated.

2. Experimental

2.1. Reagents and materials

Tetraethoxysilane (TEOS, 99%) and diallyldimethylammonium chloride (PDDA, 20 wt% in the water) were purchased from Aldrich. Tetrapropylammonium hydroxide (TPAOH, 25 wt% in the water) was obtained from Zhejiang Kente Chemical Co., Ltd. Sodium hydroxide pellets (AR Grade) were purchased from Nanjing Chemical Reagent Co., Ltd. All reagents were used as received without any further purification. Distilled water was used in all experiments. The raw diatomite was obtained from Qingshanyuan diatomite Co., Ltd. (Jilin provinces, China), and purified via a sedimentation method [37]. The chemical composition (wt%) of the purified diatomite (hereafter denoted as Dt) is as follows: SiO_2 , 85.76; Al_2O_3 , 5.60; Fe_2O_3 , 1.74; K_2O , 0.99; CaO , 0.33; MgO , 0.01; Na_2O , 0.20; TiO_2 , 0.26; ignition loss, 4.64.

2.2. Preparation of the diatomite/MFI-type zeolite composite

The diatomite/MFI-type zeolite composite (Dt/Z) was prepared via a VPT process as previously reported by Wang et al. [26]. The aqueous suspension of 80-nm silicalite-1 seeds (Sil-1) was prepared following a procedure described in the literature [38]: a synthesis mixture with a molar ratio of $25\text{SiO}_2:9\text{TPAOH}:480\text{H}_2\text{O}:100\text{EtOH}$ was heat-treated in a polypropylene bottle under reflux in a silicone oil bath at 100 °C for 48 h. TPAOH acted as template; here, the silica source was TEOS, and EtOH (Ethanol) was the hydrolysis product of TEOS. A layer-by-layer electrostatic assembly technique was used to perform the seeding process [39]. Typically, 0.5 g of diatomite powder was immersed in 25 mL of 5 wt% PDDA solution for 30 min, and then, the solid phase in the resultant mixture was centrifuged (4000 rpm for 5 min) and washed four times with distilled water to remove the excess polyelectrolyte. Next, the modified sample was added to 25 mL of pH 9.5, 1.5 wt% Sil-1 suspension and left in contact with this solution for 30 min. The excess of Sil-1 was removed by washing four times with 0.10 M ammonia solution and centrifugation at 4000 rpm for 5 min. This layer-by-layer seeding procedure was performed only once, producing Sil-1 monolayer-seeded diatomite samples. Subsequently, 0.5 g of the seeded sample was placed on a porous Teflon board, that was placed horizontally in the middle of a Teflon-lined stainless steel autoclave and 5 g of a liquid mixture of ethylenediamine, triethylamine, and H_2O with a molar ratio of 2:9:6 was injected into the

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