



A hierarchically porous diatomite/silicalite-1 composite for benzene adsorption/desorption fabricated via a facile pre-modification *in situ* synthesis route



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HIGHLIGHTS

- Diatomite/silicalite-1 composite was prepared by a mild pre-modification *in situ* coating route.
- This novel synthesized route increased the zeolite loading amount onto diatomite.
- The composite got macro-mesoporous structure with high specific surface area.
- The composite exhibited excellent static and dynamic benzene adsorption behavior.
- The composite presented good reusability for benzene adsorption.

GRAPHICAL ABSTRACT



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ABSTRACT

A novel, hierarchically porous diatomite/silicalite-1 composite with a high benzene removal efficiency was prepared via a facile coating process. Silicalite-1 nanoparticles (Sil-1_{nano}) were synthesized *in situ* on the surface of the pre-modified diatomite support by using a mild, low-temperature reflux reaction method. The obtained composite possessed a hierarchically porous structure, involving micropores and stacking mesopores from the silicalite-1 nanoparticles, and it retained the macropores from the diatomite support. The specific surface area and micropore volume of the composite were 348.7 m²/g and 0.127 cm³/g, respectively, with a zeolite loading amount of up to 60.2%. The diatomite/silicalite-1 composite exhibited considerably higher static and dynamic benzene adsorption capacities (94.9 mg/g (Sil-1_{nano}) and 246.0 mg/g (Sil-1_{nano}) respectively) per unit mass of zeolite than did the synthesized Sil-1_{nano} and commercial ZSM-5. Moreover, the introduced macroporosity of the diatomite reduced the mass transfer resistance of the nanoparticles because of their improved dispersity, and it provided more possible entryways for benzene molecules, leading to better penetration of benzene than for Sil-1_{nano} or commercial ZSM-5. The composite showed steady reversibility after 4 adsorption cycles, further demonstrating the promise of such a novel synthesized adsorbent for the removal of volatile organic compounds in industrial applications.

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1. Introduction

In recent years, the emissions of volatile organic compounds (VOCs) from industrial processes have received considerable attention because of the severe environmental hazards they create. Most VOCs are toxic, carcinogenic, or even mutagenic and are the primary contributors to photochemical pollution and secondary organic aerosols [1–4]. Various technologies have been developed for VOC abatement, such as catalytic oxidation [5], adsorption [6], membrane separation [7] and biofiltration [8]. Of these available techniques, adsorption is widely accepted as the most effective VOC removal method because of its flexible operation (possible even at low concentrations), low costs and low energy consumption [6,9]. A key solution for the problems associated with this method is to seek out an alternative adsorbent with a high VOC removal efficiency.

Activated carbon has conventionally been used as a gas adsorbent because of its high porosity and low cost [10,11]. However, its poor thermal stability and limited modification flexibility prevent its industrial application in VOC adsorption. In addition, it is difficult to regenerate the active material because the organic gas molecules adsorbed in the slit-like micropores of activated carbon are difficult to desorb [12]. Silicalite-1, the most well-known aluminum-free MFI-type zeolite, exhibits a significant adsorption capacity for VOCs because of its abundance of microporous structures with high specific surface areas and well-developed hydrophobicity [13,14]; in particular, silicalite-1 nanoparticles, are characterized as having high thermal and chemical stabilities and favorable reusability. Compared with activated carbon, the orderly straight or zigzag channels (sinusoidal pore size of 0.54 nm and elliptical pores with a pore size of 0.51 nm × 0.57 nm) of the micropores are advantageous for the desorption of gas molecules [15].

However, two major issues still exist in the application of silicalite-1 nanoparticles as adsorbents: (i) nanoparticle agglomeration is widely known to lower the effective surface area and reduce reaction activity, leading to a low VOC adsorption capacity; and (ii) silicalite-1 nanoparticles exhibit monomodal microporosity with a pore size smaller than 1 nm. These structural micropores of silicalite-1 readily limit the diffusion and mass transfer of certain macromolecules such as *m*-xylene and *o*-xylene [16–18]. Coating the silicalite-1 nanoparticles onto macroporous supports for the fabrication of the hierarchically porous composite is an alternative strategy to overcome these problems. Nanoparticles dispersed on a macroporous support are capable of diminishing their agglomeration. In addition, the macroporous structure of the support shortens the diffusion path and reduces the resistance to gas penetration, increasing the mass transfer efficiencies of guest molecules. Various porous materials, including α -alumina [19,20], stainless steel [21], porous carbon discs [22] and ceramics [23], have been developed as supports for the preparation of hierarchically porous composites. Nonetheless, the pre-synthesis or pretreatment process of such supports may increase the synthesis costs of the composites. Moreover, the low porosities, poor thermal stabilities or inferior renewable performance constrain their application in industrial processes. Consequently, identifying desirable porous supports that are economically viable and have high porosities and recyclability is important for improving the VOC adsorption performance of silicalite-1 nanoparticles.

Diatomite is considered a good candidate for the preparation of hierarchically porous composites [24–31] because it occurs naturally and has a well-developed porosity. Diatomite, also known as diatomaceous earth or kieselgur, is a fossil assemblage of diatom shells composed of amorphous hydrated silica ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$) and is

classified as opal-A in mineralogy. It is characterized by a macroporous structure with pore sizes ranging from nanometers to micrometers [32–34]. As a fine-grained, low-density biogenetic sediment that is non-toxic and readily available in ton quantities at low cost, diatomite has been studied to evaluate its feasibility as a support for nanoparticle coating. Several reports have presented various preparation methods for zeolite nanoparticles coated onto diatomite. Anderson et al. [35,36] proposed a process involving ultrasonically loading silicalite-1 seeds onto diatomite, followed by a hydrothermal growth process of the seeds. The obtained composite showed a low specific surface area (S_{BET} , 29.2 m²/g) and micropore volume ($V_{\text{micropore}}$, 0.01 cm³/g). Wang et al. [28] proposed the layer-by-layer (LBL) zeolite deposition method in which silicalite-1 nanoparticles were assembled onto diatomite via electrostatic attraction. The resulting composite possessed an improved S_{BET} and $V_{\text{micropore}}$ of 44.0 m²/g and 0.016 cm³/g, respectively, but the loading amount of zeolite remained low, at 10%. To increase the zeolite loading amount, Wang et al. [29] then developed the LBL technique, and an effective vapor-phase transport (VPT) treatment was subsequently used to supplement the LBL procedure. The zeolite loading amount of the composite reached 51.4%, after a 10-day hydrothermal reaction and the composite also exhibited an excellent benzene adsorption capacity (46.0 mg/g). However, the extraordinarily long preparation period (more than 10 days) and laborious procedures constrain the industrial application of the synthesized adsorbent. In addition, the rigorously high temperature and pressure conditions required in the VPT treatment pose certain risks, making it less suitable for large-scale production. Thus, a facile synthesis method for silicalite-1 coating is urgently needed.

The VOC adsorption performance and industrial application of the adsorbents are typically evaluated in terms of the adsorption capacity, diffusion and mass transfer efficiency, and reusability. Adsorption capacity [37,38] has been recognized as the most common metric for testing the adsorption performance because of its ease of measurement, whereas the diffusion efficiency and reusability of adsorbents are rarely studied. Fletcher et al. [39,40] investigated the adsorption–desorption kinetics for vapors on activated carbon. Dou et al. [12] reported the mass transfer efficiency of benzene over carbon–silica composites. However, to date, few reports have systematically investigated the mass transfer efficiency of diatomite/zeolite composites, and there are no related reports regarding their reusability.

Therefore, the objective of this study is to develop a facile method for the preparation of a diatomite/silicalite-1 composite and to systematically assess the feasibility of applying such a novel synthesized adsorbent for the removal of VOCs. In the present study, silicalite-1 nanoparticles were synthesized *in situ* on the surface of the modified diatomite through a simple and mild low-temperature reflux reaction, yielding a diatomite/silicalite-1 composite with a high zeolite loading amount. Several techniques (X-ray diffraction, scanning electron microscopy, mercury intrusion tests and N₂ adsorption–desorption isotherms) were used to investigate the morphology and texture of the composite. Benzene was used as the model organic compound to systematically evaluate the adsorption–desorption performance of the obtained diatomite/silicalite-1 composite. Benzene, a typical VOC, is primarily released from building and decoration materials in indoor environments and leads to massive environmental problems in industrial and domestic settings [41,42]. In this work, the benzene adsorption capacity of the novel synthesized composite was studied. The diffusion and mass transfer kinetics and reusability were systematically investigated as well. A static benzene adsorption–desorption test was conducted using an accurate, intelligent gravimetric analyzer, and we adopted a method involving breakthrough

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