Microporous and Mesoporous Materials 206 (2015) 184–193

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromeso

Novel hierarchically porous nanocomposites of diatomite-based ceramic monoliths coated with silicalite-1 nanoparticles for benzene adsorption

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ARTICLE INFO

Article history:
Received 21 October 2014
Received in revised form 2 December 2014
Accepted 3 December 2014
Available online 10 December 2014

Keywords:
Diatomite-based ceramic support
Hierarchically porous nanocomposite
Benzene
Adsorption
Kinetics

ABSTRACT

Novel hierarchically porous nanocomposites of diatomite-based ceramic supports coated with silicalite-1 (Sil-1) nanoparticles for benzene adsorption were prepared via a facile preparation route. In this route, porous ceramic supports with three-dimensional reticulated structures were first prepared using the polymeric sponge method in which diatomite was used as the ceramic framework and polyurethane foam was used as the sacrificial template. This process was followed by facile *in situ* homogeneous coating of Sil-1 on the surface of the ceramic under mild conditions. The hierarchical porosity of the nanocomposites was due to the inherent micropores of Sil-1, the mesopores resulting from the stacking of Sil-1, and the hierarchical macropores of ceramic supports. The specific area and micropore volume of the nanocomposites were 122.9 m^2/g and 0.07 cm^3/g, respectively, with a high zeolite loading of 32.4%. The nanocomposites exhibited a much higher benzene adsorption capacity (133.3 mg/g(Sil-1)) compared with that of a commercial micron-sized ZSM-5 product (66.5 mg/g) and a synthesized Sil-1 (Sil_{SYN}, 94.7 mg/g). Moreover, adsorption–desorption rate constants of the nanocomposites were three and five times higher than those of the ZSM-5 and Sil_{SYN}, respectively, as evaluated via a gravimetric method using an intelligent gravimetric analyzer. The excellent benzene adsorption performance is ascribed not only to the *in situ* silicalite-1 coating process that facilitates the stability and dispersity of Sil-1 on the modified surface of the ceramic supports but also to the hierarchically porous monolithic structure of the nanocomposites, which is beneficial to the mass transfer efficiency for benzene adsorption.

1. Introduction

Silicalite-1, the most well-known aluminum-free MFI-type zeolite, has been extensively used in various industrial fields, such as catalysis, permeation, separation and purification [1–3], in the past two decades. In particular, silicalite-1 nanoparticles (abbreviated as Sil-1 hereafter) exhibit excellent adsorption capacity for volatile organic compounds (VOCs) because of their abundant microporous structures with high specific surface areas [4–7]. Activated carbon is conventionally used as an industrial adsorbent for gases because of its low cost [8,9]. However, poor thermal stability and limited modification flexibility of activated carbon inhibit its application in VOC adsorption. In addition, organic gas molecules adsorbed in the slit-like micropores of activated carbon are difficult to desorb and regenerate [10]. Sil-1 is characterized by high thermal and chemical stability and favorable reusability [11] compared with activated carbon. The regularly straight or zigzag channels of micropores in Sil-1 are advantageous for the desorption of gas molecules [12].

The agglomeration of nanoparticles is well known to lower their effective surface area and reduce their reaction activity, particularly their adsorption performance. Therefore, several methods have been developed to overcome this agglomeration problem [13–17]. Among these methods, the surface modification technique and the loading method have been well established to improve the dispersity of Sil-1. For example, in the surface modification route, Sil-1 was modified by microemulsions [15,18,19] which served as a thermodynamically stable dispersant. The surface of silicalite-1 nuclei were surrounded by nonionic or cationic microemulsions. Thus, the resulting Sil-1 nanoparticles were steadily and uniformly dispersed in the solution because of the strong van der Waals [15] or electrostatic forces [18,19] between the

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http://dx.doi.org/10.1016/j.micromeso.2014.12.004
1387-1811/

microemulsions and the nanoparticles. However, this surface modification route is only applicable in liquid-phase systems, limiting its feasibility in heterogeneous systems. The loading method, in which Sil-1 nanoparticles were coated onto organic or inorganic supports, is an alternative strategy to overcome the agglomeration problem. Non-porous supports such as metals, stainless steel [16,20,21], polymers [22] and inorganic fibers [23,24] have been used to prepare the nanocomposites. However, a drawback of non-porous supports is that the resulting nanocomposites formed from Sil-1 exhibit monomodal microporosity because the pores in Sil-1 are smaller than 1 nm. These structural micropores of silicalite-1 cause diffusion and the related mass transfer limitation of some guest molecules [25]. More recently, substantial efforts have been made to fabricate hierarchically porous Sil-1 nanocomposites. A hierarchically porous nanocomposite structure is capable of increasing the external surface area of Sil-1, shortening the diffusion path and minimizing the diffusion limitations of guest molecules. Assembling Sil-1 nanoparticles on macroporous supports such as porous α-alumina [26,27] enhance the gas adsorption and permeation efficiency of the resulting nanocomposites. However, the low porosity of the porous supports and the high calcination temperature (exceeding 1000 °C) used in their pre-synthesis potentially increases the preparation costs of the nanocomposites. Lu et al. [28] used inexpensive fly ash cenosphere (FAC), which is an aluminosilicate-rich waste produced from power plants, as a support for the coating of Sil-1. However, the readily caused secondary contamination of the FAC support, such as dusting problems, constrains the actual application of the resulting nanocomposites for VOC adsorption. Consequently, identifying desirable porous supports that are environmentally benign and economically viable is important for improving the gas adsorption performance of Sil-1.

Because it is a naturally occurring mineral with well-developed porosity, diatomite is considered as a potential candidate for the synthesis of hierarchically porous nanocomposites [29–32]. Diatomite, also known as diatomaceous earth or kieselgur, is a fossil assemblage of diatom shells. It is characterized by a macroporous structure with pore sizes ranging from the nanometric to micrometric domains [33,34]. Diatom shells are composed of amorphous hydrated silica ($SiO_2 \cdot nH_2O$) and are classified as opal-A in mineralogy. Because biogenetic mineral aggregates are readily available in ton-scales at low cost and are non-toxic, diatomite has been studied to evaluate its feasibility for use as a support for Sil-1 coating. Wang et al. [35] reported the synthesis of Sil-1/diatomite nanocomposites; they hydrothermally synthesized Sil-1 nanoparticles and assembled them on a modified surface of diatomite using layer-by-layer (abbreviated as LBL hereafter) electrostatic deposition. However, the zeolite loading amount of the resulting nanocomposites was low (10%) because of the weak electrostatic interaction between the nanoparticles and the diatomite. Lu et al. [36] proposed a secondary hydrothermal method for the fabrication of Sil-1/diatomite nanocomposites; in their approach, the hydrothermal growth process was supplemented after the LBL procedure, which resulted in a slightly increased zeolite loading amount (12%). However, the common disadvantages of these two preparation routes are that they require a long synthesis period and need to be conducted under rigorous conditions such as high temperature and high pressure. These disadvantages complicate the preparation and make it less suitable for use in lot-sized production. Clearly, the development of a facile method for coating Sil-1 is needed.

Moreover, in previous studies, the as-synthesized Sil-1/diatomite nanocomposites were in powder form, and their gas adsorption performance was readily disturbed by fluid resistance [35,36]. In particular, the nanocomposites presented a loose two-dimensional (2D) structure and exhibited a low adsorption capacity and low diffusion rate because of the confinement of mass transfer in the 2D space. Mechanically stable monolithic supports with 3D structures, such as porous ceramic supports, have been beneficial in minimizing dusting problems and mass transfer limitations encountered in the gas adsorption process [25,37–39]. Compared with powdered materials, the 3D reticulated structure of the macroporous ceramic monoliths enlarges the contact area between adsorbents and adsorbates, making adsorption and mass transfer of the adsorbates effectively expand to the 3D space and improving the adsorption efficiency of the adsorbents. Among a variety of processing routes [39,40], the polymeric sponge method, also known as the replica technique [39], offers a simple and flexible strategy for the synthesis of macroporous ceramic monoliths. The great versatility of this method is attributed to its simplicity in the fabrication of high-porosity ceramic monoliths and its adaptability to any admirably dispersed ceramic materials. In this sense, testing and verifying the feasibility of using diatomite as a framework material for the preparation of macroporous ceramic monoliths via the polymeric sponge method would be interesting. However, to the best of our knowledge, such studies have not been reported thus far.

In this work, a novel hierarchically porous nanocomposite incorporating advantages from both hierarchically macroporous ceramic supports with unique 3D reticulated structures and a microporous Sil-1 coating was synthesized using a facile method. The simple polymeric sponge method was selected for the fabrication of diatomite-based porous ceramic supports. Then considering that the isoelectric point of SiO_2 is at pH 2 or 3 [41,42], a facile and economic Sil-1 *in situ* coating route on such supports under mild conditions with the aid of electrostatic interaction was adopted instead of the conventional LBL technique or secondary hydrothermal method.

Benzene was used as a model organic compound to evaluate the adsorption performance of the hierarchically porous nanocomposites. Ranked top on the list of VOC pollutants as a human carcinogen, benzene is mainly released from building and decoration materials in indoor environments; it is hazardous to human health and leads to massive acute environmental problems [43–45]. In this work, the benzene adsorption of the novel hierarchically porous nanocomposites was investigated and the structure-adsorption relationship was studied. In particular, an accurate gravimetric method based on the use of an intelligent gravimetric analyzer was applied to assess not only the static adsorption capacity of benzene on the nanocomposites but also the adsorption kinetic parameters [46], which have rarely been reported in previous studies concerning the mechanism of VOC adsorption onto molecular sieves.

2. Experimental section

2.1. Reagents and materials

Tetrapropylammonium hydroxide (TPAOH, 25% aqueous solution, Kente Chemical Co.) and tetraethoxysilane (TEOS, 99%, Aldrich) were used as zeolite synthesis solutions. The ceramic framework material, raw diatomite powder (denoted as Dt), was obtained from the Changbai deposit in Jiling Province, China, and its chemical composition in percent by mass of the respective oxide forms (SiO_2, 86.18; Al_2O_3, 3.08; Fe_2O_3, 1.47; MgO, 0.33; CaO, 0.37; Na_2O, 0.05; K_2O, 0.51; MnO, 0.01; P_2O_5, 0.06; TiO_2, 0.17; and loss on ignition 8.56) was determined by chemical analysis. The ceramic additives were composed of sodium silicate powder (AR grade, Fuchen Reagent Co.) and sodium chloride (AR grade, Sinopharm Reagent Co.). A polyurethane (PU) foam without cell membranes (97% porosity, 50 pores per liner inch) was used as a