Adsorption in heterogeneous porous media: Hierarchical and composite solids

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ABSTRACT

Experiment and molecular simulation are used to investigate adsorption in heterogeneous porous media consisting of hierarchical solids (combining different porosity scales) or composite solids (such as silver nanoparticles adsorbed at the external surface of zeolite). It is shown that adsorption in such heterogeneous materials can be written as a linear combination of the adsorption isotherms in its different domains (i.e. porosity scales for the hierarchical sample and constituents for the composite sample). In the case of the composite material, we also show that the linear combination can be used with weighing parameters obtained for a different adsorbate. Such a *superimposition principle*, which is validated using well-characterized experimental samples, is of interest for characterization purpose as well as industrial applications as they can be used to determine accurately the amount of phases in a given sample (volume corresponding to a given porosity scale or constituent). In contrast, significant departure between the experimental adsorption isotherm and the linear combination can be used to detect coupling effects between the different domains or restrained access to a given domain type. Such a characterization strategy of complex heterogeneous media is complementary to other experiments, such as those probing capillary hysteresis shapes, scanning curves and subloops, which allow determining the distribution of domains within the framework of the independent domain theory.

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1. Introduction

Owing to their large specific surface area and confining porosity, nanoporous media are at the heart of key applications in catalysis, separation and purification (refinery, chemistry), pollution abatement (car exhaust, water decontamination), environment (transport in soils and rocks), etc. [1,2] From a more fundamental point of view, porous materials can be used to investigate the effect of reduced dimension and confinement on the thermodynamics and dynamics of gases, liquids, and solids [3—7]. As a result, important research effort has been devoted to developing more and more accurate characterization techniques of porous media. In particular, fine characterization tools relying on adsorption are available to assess the pore size and specific surface area of porous materials but also pore connectivity, morphology and tortuosity [8—12].

While porous materials are selected for their large specific surface area and small pore size, many applications rely in fact on more sophisticated solids which are obtained by modifying the initial porous material (usually an aluminosilicate, silica or carbon solid). For instance, in catalysis, many processes rely on porous solids with a large specific surface area which is used to support catalytic species such as metal particles [13]. In filtration and decontamination, the host silica, carbon, or aluminosilicate surface can be used as prepared or is often modified using one-pot strategies or post-synthesis treatments to graft specific functional groups for a given application [14,15]. Finally, even when the host solid can be used without chemical treatment (or using simple

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ionic exchange such as with Faujasite zeolite used for xylene separation [16,17]), modification consisting of including a secondary pore network is needed to overcome the very slow diffusion and limited accessibility to the active sites located in the porosity [18–22]. To do so, important research efforts are devoted to design hierarchical porous media which combine different porosity scales [23–26]. The common point between the different modified samples described above is that they are complex media with strong short or long-range heterogeneity. Such materials, which are either composite materials (catalysts supported at the surface of a host porous medium or grafted porous solids) or hierarchical materials (solids combining different porosity scales/types), are disordered solids which strongly depart from their parent porous solid. We make clear here that the different domains in these solids are not necessarily disordered; for instance, zeolite, ordered mesoporosity (MCM-41 like), Ag nanoparticles, which are considered in the present paper, are ordered materials; However, the fact that composite and hierarchical materials are not strictly single-phase materials necessarily implies that some significant disorder can be present in the way the domains are distributed and at the boundary between domains.

Although such heterogeneous media share many structural and morphological properties with their parent solids, adsorption and transport in their porosity show some marked differences. Such departures raise the question of the characterization of these complex porous materials, including important issues about the validity of conventional adsorption-based characterization techniques. Recent works have suggested successful strategies to tackle such issues; For instance, using well-known techniques such as the t-plot method [29,30], combined adsorption/intrusion [31] or scanning curves [26,32,33], several authors were able to accurately probe the structure and morphology of hierarchical materials. Although expensive, time-consuming, and necessarily limited to small sample regions, FIB-SEM and tomography experiments are also very powerful characterization strategies of hierarchical materials [26–28]. In contrast, less attention has been devoted to the characterization of the morphology and topology of composite porous materials [34].

In this paper, we address the question of adsorption-based characterization of hierarchical or composite media by investigating by means of experimental and molecular simulation techniques the adsorption of simple gases in: (1) a hierarchical porous solid consisting of a microporous material (zeolite) in which a secondary mesoporous network is added [35] and (2) a composite material consisting of a microporous solid (zeolite) with its external surface partially covered by metal nanoparticles and nanoparticles entrapped in zeolite defects [36]. Throughout this paper, we coin zeolite solids with hierarchical micro/mesoporosity as hierarchical zeolites or mesoporous zeolites. For both these hierarchical and composite materials, we show that the adsorption properties of the heterogeneous medium obey a superimposition principle since they can be written as the sum of the adsorption properties for the different domains. In contrast, if the porosity volume of a given domain is modified by the presence of the other domains (such as nanoparticles supported in mesoporous solids which necessarily decrease the amount of initial mesoporous surface/volume), strong departure is observed with respect to such a linear combination since the domains do not behave independently. In this case, other strategies such as the independent domain theory, which allows probing the degree of heterogeneity of such complex disordered media, can be used. The independent domain theory, proposed by Everett in 1958, is a very powerful tool which consists of probing the distribution of domains in a porous medium by performing adsorption and desorption scanning curves within capillary hysteresis loops. The way such scanning curves meet the main

capillary hysteresis loop boundary indicates whether or not the porous domains behave independently of each other. For instance, in the case of hierarchical porous materials, the independent domain theory can be used to assess whether or not mesoporous domains have direct access to the external surface. Many authors have revisited/reviewed the independent domain theory and its applications to probe complex porous media [4,32,33,37,38] including to characterize hierarchical zeolites using Ar adsorption at 77 K [26]. Finally, in the case of samples containing mesoporosity, the distribution of porous domains can also be checked from the shape of the adsorption/desorption hysteresis loops. Symmetrical hysteresis loops are indicative of mesoporosity where the mesopores have direct access to the external surface. In contrast, if these pores are separated from the external phase through necks or constrictions, two possible scenarios are possible. (A) if the desorption pressure is larger than the cavitation pressure of N_2 at 77 K ($P = 0.42$ P0), the constrictions have a size that corresponds to this desorption pressure. (B) if the desorption pressure is equal to the cavitation pressure of N_2 at 77 K, the constriction size cannot be exactly determined but is at least smaller than the minimum size that can be probed with N_2 adsorption. Very recent reviews are available on such characterization techniques [4,9,10,39]. Further refined, adsorption-based characterization techniques include the use of different probes such as argon and water [40].

Experiment and molecular simulation in this work are carried out at 77 K or room temperature as these two temperatures pertain to characterization of porous media or gas capture/sensing applications. The use of different temperatures allows assessing the validity of the superimposition principle at different temperatures where adsorption behavior can vary greatly. While further work is needed to fully clarify adsorption in such heterogeneous samples, the present study provides simple means to characterize heterogeneous samples including their morphology/topology.

2. Experimental and computational details

2.1. Experimental samples

2.1.1. Hierarchical porous media

As far as the hierarchical samples are concerned, different samples consisting of a Faujasite zeolite (FAU) in which some ordered mesoporosity (type MCM-41) has been introduced were considered following an adapted procedure of Garcia-Ramirez [26] (Fig. 1). These samples, which have the same microporosity type but different mesopore sizes, have been described in details elsewhere [29]. In brief, alkyltrimethylammonium bromide surfactant (CnTAB with n = 10–18 from Aldrich) was first dissolved in sodium hydroxide aqueous solution under stirring at 50 °C until complete dissolution. FAU-Y zeolite powder was then added to this solution and stirred for 1 h. Multiple mixtures were prepared with increasing quantities of NaOH, corresponding to molar ratios of 1 Si/0.07 Al/0.1 CnTAB/0.05–0.25 NaOH/50 H_2O in order to increase the mesoporous volume fraction of the final sample. After 24 h at 115 °C in an autoclave in static conditions, the slurry was filtered, rinsed with water until neutral pH, dried at 80 °C and finally calcined at 550 °C under air-flow for 8 h. For comparison purpose, we also considered the native commercial FAU zeolite (CBV720 Zeolyst, Si/Al = 15) and Al-MCM-41 samples with the same mesopore sizes and the same Si/Al ratio as those of the hierarchical samples to maintain similar surface chemistry.

2.1.2. Zeolite supported silver nanoparticles

As far as the composite material is concerned, a commercial Na-ZSM-5 zeolite (ratio Si/Al = 12) was used to prepare the silver exchanged zeolite Ag@ZSM-5 (Fig. 1). Sodium zeolite powder was