

Review

Dynamics, flow motion and nanopore effect of molecules present in the MCM-41 nanopores—An overview

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Abstract

Scientific studies on the chemical and physical processes in nanopores from various points of view were started intensively after the first synthesis of MCM-41 in 1992, whose nanopores are regularly ordered and well-defined. Understandings of the fundamental diffusion properties of organic molecules in the nanopores are particularly important in chemical industry. In addition, the molecular transport processes in nanopores have been important problem of long standing interest in heterogeneous catalysis, gas–solid reactions and adsorptive separations. So, the present review mainly focuses on the dynamics and flow properties of the molecules by various techniques to reveal the impressive phenomena which occur in the nanopore of MCM-41.

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1. Introduction

Nanoporous materials have attracted so much attention in recent years because they have found great utility as catalysts for industrial applications. Also, the understanding of molecular transport in narrow pores and molecularly confined spaces is an important problem of long standing interest in heterogeneous catalysis, gas–solid reactions and adsorptive separations [1]. Most of the experiments on freezing and melting of organic compounds confined in pores have been done in porous systems such as vycors, controlled porous glasses or porous silica [2–10]. But the large distribution of pore size and pore interconnectivity [11] in these three-dimensional confining porous systems induce disorder that may alter the properties of interest and complicate the

interpretation of the results. So, in recent years, the intense world-wide activity in applications of newly developed simple geometry templated porous media (MCM-41) in which the pore diameter can be accurately tuned in the range from 2 to 25 nm by Mobile researchers [12,13] has led to renewed interest in this subject.

MCM-41 is nanoporous silica walled materials that exhibit a regularly ordered two-dimensional hexagonal pore arrangement and narrow pore size distributions (Fig. 1). Also in MCM-41, pores are not interconnected and the surface contains hydroxyl groups which may experience specific interactions with molecules susceptible of having hydrogen bonds. Modifications of the surface of these materials could be achieved by grafting of hydrophobic groups. So, specific surface interaction effects on the properties of the confined compounds may be of interest to everyone. Hence, several works have been done to study the diffusion phenomena for the molecules in the nanochannel of MCM-41. Our main focus here is to review about the physico-chemical processes such as dynamics and flow properties

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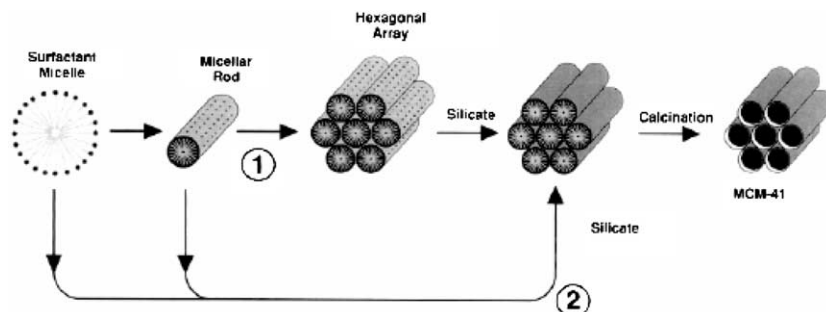


Fig. 1. Possible mechanistic pathways for the formation of MCM-41. (1) Liquid crystal phase and (2) silicate anion initiated. From Ref. [13].

for the systems included or adsorbed in the MCM-41 nanoporous materials and the nanospace effects are to be discussed because this material has an advantage for application towards chemical industry.

2. Molecular recognition in nanopores and their physical properties

Porous materials play an important role in many aspects of science and technology. Of which molecular recognition is becoming increasingly important for environmental protection. Extremely specific molecular selectivity is required for the removal of highly diluted pollutants in water; otherwise many coexisting compounds with higher concentrations will saturate the adsorption capacity. Inumaru et al. [14] reported evidence for a novel type of molecular recognition in the nanostructure where the organic moiety (4-*n*-heptylaniline) achieves high adsorption molecular selectivity in the nanostructure (alkyl grafted MCM-41) (Fig. 2). They provided IR spectra (Fig. 3) as the evidence for their model, in which the amino group of 4-*n*-heptylaniline interacts with the inorganic wall of the nanostructure. Thus, the above result when taken together demonstrates that organic and inorganic moieties cooperate in molecular recognition in the nanopore cavities.

Abundant amounts of literature on the physical properties of fluids confined in various environments are

available. Some leading issues include the phase transition behavior [15], glass transition, and dynamical properties of molecular liquids in nanometer scale porous materials [16]. In this respect, it is also required to elucidate how structural features are modified by confinement effect and at fluid–substrate interface. The confinement of a weakly interacting fluid in porous silicate may significantly affect its static properties, leading to glassy phases with different density at low temperature [17]. Moreover, confinement could eventually lead to new phases, the formation of which is driven by the balance between fluid–fluid and fluid–substrate interactions [18]. Also, it is established that some hydrogen bond bridges with the hydrophilic surface play a major role in defining the structure of the confined fluid [19–22]. Of which alcohols are considered as strongly hydrogen bonded organic liquids.

Methanol being the simplest one containing two crystalline phases [23] is of fundamental interest for studying the influence of H-bonds and fluid–substrate interaction on the properties of confined fluids. The α -phase is stable below 156 K, and the β -phase exists between 159 K and the melting point at 175.4 K. Within the nanoporous materials, the solidification of methanol into different structures was observed [24] based on the pore size i.e., β -phase may be stable in nanopores with radius $r = 7.0$ nm, the α -phase for $r = 5.3$ and 4.5 nm, and a glassy state for $r \leq 3.9$ nm. On cooling of methanol confined to the pores of $r = 7$ nm results in the formation of a crystalline solid with the same structure as that of the bulk β -phase and it does not transform into α -phase on further cooling down to low temperature, leading to the appearance of a glassy crystal with the same β -phase structure. Thus, vitrification of the confined methanol in the nanoporous materials results from a large freezing point depression due to the dynamical supercooling rather than the thermodynamical supercooling [24]. This suggests that the relative stability of the phases depends not only upon the temperature, but also upon the pore size.

Thus, the pore characteristics are known to play a key role in controlling the molecular sieving properties and the adsorption behavior of mesoporous materials.

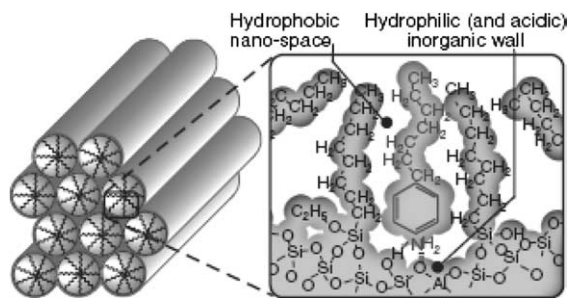


Fig. 2. Schematic illustration of a molecule adsorbed in the nanostructure. From Ref. [14].

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