Chemical Physics 448 (2015) 9–14

Contents lists available at ScienceDirect

Chemical Physics

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

# Investigation of structure formation mechanism of a mesoporous ZSM-5 zeolite by mesoscopic simulation

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ARTICLE INFO

*Article history:*
Received 29 September 2014
In final form 26 December 2014
Available online 5 January 2015

*Keywords:*
Mesoporous zeolite
Simulation
DPD
Surfactant
Self-assembly

ABSTRACT

Amphiphilic surfactant molecules have a profound influence in directing zeolite crystallization, while the self-assembly process between the functionalized surfactant and aluminosilicate species is the key factor in determining the structure of zeolites. However, such a complex process is extremely difficult to be characterized experimentally. A novel mesoporous ZSM-5 zeolite with hexagonal mesostructures and crystalline microporous frameworks has been synthesized in our previous work. In present research, dissipative particle dynamics (DPD), a mesoscopic simulation method, has been used to investigate the self-assembly process of a surfactant/tetraethylorthosilicate (TEOS)/water system in order to explore the structure formation mechanism of a mesoporous ZSM-5 zeolite. The simulation results show that under a certain composition, the specially designed bifunctional triquaternary ammonium-type surfactant and TEOS can form spherical core–shell micelles. The core (inner section) of a spherical micelle is occupied by hydrophobic beads, while the shell (outer section) is formed by hydrophilic beads. Besides, an ordered, uniform mesophase can be formed under a constant shear rate and transformed into mesoscale structure. The simulation results are consistent with the corresponding experimental results. Overall, the DPD simulation is a valuable tool to investigate the porogenic mechanism of surfactants. The present approach may open a window for investigating the formation mechanism of mesoporous zeolites that involves the surfactant-driven synthesis process.

## 1. Introduction

Zeolites are a family of crystalline aluminosilicate porous materials with pore sizes typically at 0.4–1.2 nm, which enables shape-selective transformations. Zeolites are among the most useful catalysts in industrial processes, such as oil refining and organic synthesis [1–3]. However, the shape-selectivity brings about some negative effects. For example, reactants and products with sizes beyond micropore dimensions are too bulky and therefore cannot diffuse into and out of zeolite crystals. This reduces the catalytic performance of zeolites due to limited mass transport to and from the active sites [4]. In recent years, a novel class of mesoporous zeolites has emerged as an important material with much better catalytic performance compared to conventional zeolites and traditional mesoporous materials [5–10]. This material possesses additional intra- or inter-crystalline mesoporosity as well as the inherent microporosity of zeolites. The mesopore walls are useful for catalyzing reactions involving bulky molecular species that cannot diffuse into the micropores.

Recently, various attempts to prepare mesoporous zeolites by the template synthesis method have been reported. The mesoscale templates can be classified into two groups: (i) soft templates, including amphiphilic organosilanes [7], polymers [11], and surfactants [12,13]; (ii) hard templates, such as carbon particles [14], carbon nanotubes [15,16], carbon nanofibers [17], and wood cells [18]. First, mesoporous zeolites with crystalline microporous frameworks can be generated by using these templates. Then, after the zeolite crystallization, the templates can be removed through a combustion process. However, it is difficult to disperse such hard templates homogeneously into the reaction gel owing to their hydrophobicity [19]. In comparison, soft templates give simpler prepared procedures by self-assembly with aluminosilicate during synthesis. Corma et al. [20,21] prepared a delaminated zeolite by exfoliation. After a complete swelling of the zeolite precursor with an intercalated surfactant, these randomly packed zeolite sheets formed a highly mesoporous material that preserved the microporous structure of the parent zeolite. Specifically, in 2011, Corma's

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http://dx.doi.org/10.1016/j.chemphys.2014.12.011
0301-0104/

group [22] synthesized a hierarchically connected meso-microporous zeolite that was found to generate the very opened structure.

It would be interesting to further study the synthesis of mesoporous zeolites using surfactants as it would give a fuller understanding the role that surfactants play during synthesis. Recently, a novel mesoporous ZSM-5 zeolite sample (MZS) was prepared using a specially designed dual-function surfactant in our laboratory [23]. The surfactant was composed of hydrophobic long-chain alkyl groups and hydrophilic quaternary ammonium groups, which played a key role in the mesoporous ZSM-5 zeolite synthesis process and determined its bimodal pore system. However, it is still difficult for researchers to find a direct relationship between the surfactant and the hierarchically structured zeolite, and to investigate the formation mechanism of mesoporous zeolites. With the aid of computer simulations, the surfactant phase behavior may be understood.

There is no doubt that computer simulation methods have proven to be valuable tools in the mechanism studies that involve the formation process of zeolites [24,25]. Many researchers such as Rao [26], Wu [27], Schumacher [28,29], Trinh [30], and their colleagues used molecular dynamics, the Monte Carlo method, and electronic structure calculations, respectively, to investigate the formation of zeolite materials at the atomic level. However, these atomic simulation tools are limited in the time and length scale in simulation. Additionally, it is not easy to observe the phase transformation process of a complex system. Therefore, atom-based simulations cannot predict more realistic structures on a mesoscopic scale. On a different scale, dissipative particle dynamics (DPD), one of the mesoscopic simulated methods, has been widely used to study mesostructures of complex systems [31,32], including flow in porous media [33], polymer mixtures [34,35], surfactant monolayers [36], micelles [37] and oil–water surfactants [38]. The advantage of DPD is the fact that DPD is a coarse-grained technique that preserves the hydrodynamic modes of the fluid by using a simple pair-wise potential.

In this work, the DPD simulation technique is employed to understand the self-assembly process of a gemini-type surfactant ($C_{16}$–$N_3$–$C_{16}$) and tetraethylorthosilicate (TEOS) in an aqueous solution based on the recent work reported by our group [23], which is critical for investigating the formation mechanism of the mesoporous ZSM-5 zeolite. Evolution of the mesoscale structure is monitored through observing 3D density fields, and the effect of the shear rate on the mesoscale structure is also investigated.

## 2. Method and simulation details

### 2.1. DPD theory

DPD is a mesoscale modeling method for simulating equilibrium and dynamical properties of fluids subjected to soft potentials and governed by predefined collision rules [39]. The simulation strategy is to group atoms together into single dissipative particles, each called a "bead," which represent small regions of fluid that is large on the atomistic scale but still macroscopically small [40]. These dissipative particles can be tied together by harmonic springs: $F^S_{ij} = Cr_{ij}$ if $i$ is connected to $j$. Thus, a particle is larger than or equal to a Kuhn's segment, and the surfactant is fully flexible on this length scale. Although these particles represent many internal degrees of freedom, once the atoms are grouped together into one new entity, the normal statistical mechanical rules should apply again to these "quasiparticles" and their corresponding effective Hamiltonian. However, when the particles are connected by harmonic springs and are not restricted to lattice positions, they can form a much more realistic representation of a lump of surfactant than Flory–Huggins segments. The number of segments that represent a realistic surfactant need not be large [35]. These dissipative particles comply with Newton's equation of motion through a modified velocity-Verlet algorithm [41]. For simplicity, the masses of all particles are taken to be equal to 1 DPD unit [42]. The force between each pair of beads is a sum of a conservative force ($F^C_{ij}$), a dissipative force ($F^D_{ij}$), and a random force ($F^R_{ij}$) [43]:

$$f_i = \sum_{j\neq i}\left(F^C_{ij} + F^D_{ij} + F^R_{ij}\right) \tag{1}$$

$$F^C_{ij} = \begin{cases} a_{ij}(1 - r_{ij}/r_c)\hat{r}_{ij} & (r_{ij} < r_c) \\ 0 & (r_{ij} \geqslant r_c) \end{cases} \tag{2}$$

$$F^D_{ij} = \frac{\sigma^2(\omega(r_{ij}))^2}{2kT}(\upsilon_{ij}\cdot\hat{r}_{ij})\hat{r}_{ij} \tag{3}$$

$$F^R_{ij} = \frac{\sigma\omega(r_{ij})\hat{r}_{ij}\zeta}{\sqrt{\delta_t}} \tag{4}$$

where $a_{ij}$ is the maximum repulsion between bead $i$ and bead $j$, $r_{ij} = r_i - r_j$, $r_{ij} = |r_{ij}|$, $\hat{r}_{ij} = r_{ij}/|r_{ij}|$, $\upsilon_{ij} = \upsilon_i - \upsilon_j$, $r_c$ is the cutoff radius, $k$ is the Boltzmann constant, $T$ is the system temperature, $\sigma$ is noise amplitude, $\zeta$ is a randomly fluctuating variable with zero mean and unit variance, and $\delta_t$ is the time step used. The $r$-dependent weight function is defined as $\omega(r) = 1 - r$ for $r < 1$ and $\omega(r) = 0$ for $r > 1$.

### 2.2. Coarse-Grain Description and DPD Parameters

In the DPD simulation, the system is composed of the surfactant $C_{16}$–$N_3$–$C_{16}$, TEOS, and water. The coarse-grain models are shown in Fig. 1. The molecular structure of surfactant $C_{16}$–$N_3$–$C_{16}$ is divided into two types of beads ($S_a$ and $S_b$). One molecule of TEOS is represented as a bead T. One molecule of water is represented as a bead W.

Each bead is enclosed by dashed lines. The liquid compressibility that determines the free energy change associated to density fluctuations is first matched in DPD simulation. To keep the compressibility of water at room temperature, the repulsion parameter in Eq. (2) is calculated according to [44]:

$$a_{ii}\rho = 75k_BT \tag{5}$$

where $a_{ii}$ is the repulsion parameter between particles of the same type and $\rho$ is the particle density. Here, density $\rho = 3$ has been used and hence the repulsion parameter $a_{ii} = 25k_BT$. Additionally, we have chosen $k_BT = 1$, in the same way as Hoogerbrugge and Koelman [40]. The value of repulsion between different types of beads is linearly related with the Flory–Huggins $\chi$-parameter, which can be obtained by the Groot and Warren [41] at $\rho = 3$ according to

$$a_{ij} \approx a_{ii} + 3.27\chi_{ij} \tag{6}$$

Here, the values of $\chi_{ij}$ can be calculated from the solubility parameters by

$$\chi_{ij} = \frac{(\delta_i - \delta_j)^2V}{RT} \tag{7}$$

where $V$ is the arithmetic average of molar volumes of two beads, $\delta_i$ and $\delta_j$ are the solubility parameters of beads $i$ and $j$, which depend on the chemical nature of species and can be obtained by experiments or molecular dynamics simulations. In this study, Flory–Huggins parameters ($\chi_{ij}$) are calculated by Amorphous Cell and Discovery [45–47] in Materials Studio 5.0 (Accelrys Inc.). The interaction parameters $a_{ij}$ are shown in Table 1.

In addition, an appropriate value of spring constant C (C = 4) has been used so that the average bead-bead distance along the chain