Hierarchical zeolite microspheres with flat sheets, wave sheets or agglomerates induced by gemini surfactant counterion

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ABSTRACT

The solution structure of a gemini surfactant, C_{22-6-6}, associated with various counterions was investigated with small-angle neutron scattering (SANS). Subsequently, C_{22-6-6} with various counterions (Br^-, $HC_2O_4^-$, $C_2O_4^{2-}$, CO_3^{2-}, $H_2PO_4^-$, HPO_4^{2-} and OH^-) was applied as a structure directing agent (SDA) in the synthesis of hierarchical zeolites. C_{22-6-6} gemini surfactants form robust prolate (rod) micelles that only exhibit small changes in size with varying counterion, concentration, temperature and salt. Hierarchical MFI successfully crystallized with C_{22-6-6} associated with various counterions as the SDA. The exception was for $HC_2O_4^-$ and $H_2PO_4^-$ which lowered the pH of the final synthesis solution. Different SDA counterions engender MFI zeolites with various morphologies, such as flat sheets, wave-like sheets, aggregates, micron sized spheres, and change the mesoporosity, total pore volume and silicon to aluminum ratio.

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1. Introduction

Zeolites are inorganic crystalline microporous aluminosilicates that have a negative framework balanced with exchangeable cations. When the cation is a proton, strong acid sites are engendered in the zeolite framework and such zeolites can be used for acid-catalyzed industrial reactions. Zeolites are also thermally stable and can be recycled by calcination for multiple uses making them economical materials for industrial use. Zeolites are thus widely used in industry as catalysts, membranes, ion-exchangers and absorbents [1–3]. Research on zeolite synthesis has generally focused on the synthesis of new zeolite framework types but in recent years, there has been growing interest in developing new zeolite morphologies such as zeolite nanosheets and two-dimensional zeolites [4,5]. Conventional zeolites are limited by slow diffusion rates because of their microporous and tortuous channels. New zeolite morphologies could improve these diffusion rates by either creating smaller nanocrystalline zeolites or introducing mesopores into the structure to form hierarchical zeolites. Theoretically, hierarchical zeolite architectures will have improved intracrystalline diffusion rates as the presence of mesopores would allow for facile micropore access and faster transport of bulky materials [6]. To date, hierarchical zeolites have been synthesized as-is with dual templates where typical structure directing agents (SDAs) act as the microporogen to template the zeolite micropores and either surfactants [7] or polymers [8–10] mesoporogens to template the mesopores, or are introduced via post-synthesis modification using acid-leaching methods [6,11,12].

More recently, single template methods using a gemini surfactant, a surfactant molecule with more than one hydrophobic tail and hydrophilic head group connected by a spacer, to template both the micropores and the mesopores have been demonstrated [13]. This new template method eliminates the need for two porogens (for micropores and mesopores) by using a gemini cationic surfactant as both the structure directing agent for the zeolite framework as well as the mesoporogen for mesoporosity in the zeolite. Further, the gemini surfactant is also able to influence the zeolite morphology, creating interesting structures such as lamellar sheets and unilamellar sheets in a one-pot process [4]. Ryoo et al. demonstrated that multilamellar MFI zeolite sheets could be synthesized using $C_{22}H_{45}-N(CH_3)_2-C_6H_{12}-N(CH_3)_2-C_6H_{13}Br_2$ ($C_{22-6-6}Br_2$) gemini surfactant and was able to control the zeolite interlayer spacing by varying the hydrophobic tail of the surfactant from $C_{12}-C_{22}$ [14].

Subsequent research with similar gemini surfactants reported changes in morphology from a "house of cards" to dense packing plates with the addition of tetrapropylammonium hydroxide [15] and the formation of thin zeolite plates with perpendicular intergrowth with a change in chain length between the quaternary ammonium groups [16]. Some have also reported improvements to the high silica to alumina ratios more commonly obtained with the use of gemini surfactants with the addition of zeolite seeds [17] or with the addition of NaF and a variation to the hexyl gemini end group [18]. Such hierarchical MFI zeolites synthesized with the use of gemini surfactants have also been widely tested and found to be efficacious for several reactions. For ethylene conversion and heptane cracking, slower catalyst deactivation rates were observed due to the zeolite morphology [19]. An increase in catalytic activity was reported for the cracking of decalin as the zeolite nanosheet morphology led to stronger acid sites on the external surfaces [20]. In the conversion of propanal to hydrocarbons, the nanosheet structure of MFI led to changes in olefin and aromatic selectivity, and a fivefold increase in catalyst stability [21]. Consequently, it is important to discover new ways to synthesize hierarchical zeolite morphologies that have better diffusion properties and outperform their conventionally synthesized counterparts.

This paper explores the ability to tune hierarchical zeolite morphology by changing the gemini surfactant counterion used in its synthesis and thoroughly characterizes the gemini surfactant solution structure to determine if it is directly responsible for the zeolite morphology. Presently, the mechanism by which the surfactant induces changes in zeolite morphology is still unclear and requires further elucidation. It has been proposed that the C_{22-6-6} surfactant forms a lamellar phase and the zeolite grows on the lamellar phase directly, thus the zeolite takes on a plate-like morphology [4,22]. If the zeolite morphology truly takes on the soft structures of the surfactants during synthesis, one can envision zeolites being synthesized into several other morphologies related to surfactant self-assembled structures such as micelles, cylinders/rods, bilayers, etc. However, there is a dearth of studies that investigate in detail, the structure of the surfactant and correlate this to the resulting zeolite morphology.

The structure of surfactant self-assemblies or surfactant soft structures is related to the surfactant's molecular dimensions, hydrocarbon chain length (l_c), volume (v), and effective headgroup area (a_0). The relationship between these parameters gives the surfactant packing parameter, $v/a_0 l_c$ and its value correlates to the types of structures that can form in solution [23]. It has been well established that for ionic surfactants, the identity of the counterion affects its self-assembly behavior and adsorbed layered structures at interfaces [24–28]. For ionic surfactants, the identity of the counterion mediates electrostatic interactions between the headgroups which can significantly alter a_0. Hydrolysable counterions have been shown to exhibit peculiar phase behavior and universally form the once-rare hexagonally close-packed (HCPS) micellar liquid crystal phase in alkyltrimethyalammonium salts due to their high degree of solvation [29,30]. An extensive range of microstructures including mesh phases, which are pH dependent were observed when such ions are associated with the double-chained didodecyldimethylammonium surfactant cation [31]. The effect of different counterions on gemini surfactants remain largely been unexplored [32]. Recently, Manet et al. investigated the effect of various Hofmeister and alkylcarboxylate counterions on the melting temperature and Krafft point of C_{n-2-n} gemini surfactants [33]. They found that the transition from a crystalline solid phase to a liquid crystalline phase and an isotropic liquid phase is strongly dependent on the counterion type. Ultimately, the identity of the counterion could be exploited as a potential means of controlling

the delicate balance of forces controlling solution properties and aggregate morphology in the zeolite synthesis solution.

In this study, a range of surfactant counterions associated with the C_{22-6-6} gemini surfactant SDA were applied to MFI synthesis — Br^-, $HC_2O_4^-$, $C_2O_4^{2-}$, CO_3^{2-}, $H_2PO_4^-$, HPO_4^{2-} and OH^-. To the best of our knowledge, all of the gemini surfactant-zeolite syntheses reported have been conducted with only bromide or hydroxide surfactant counterions, and morphological changes that are induced by gemini chain length or side group substitutions. Consequently, this is the first investigation into the effects of other counterions types such as carbonate, oxalate and phosphate on the resulting morphology of the zeolites synthesized. In addition, by using small-angle neutron scattering (SANS) we present a novel study that compares the solution structures formed by the surfactant SDA to the resulting zeolite morphology. Finally, the feasibility of engendering different zeolite morphologies by changing surfactant counterions is discussed.

2. Materials and methods

2.1. Materials

Orthophosphoric acid (85%, Sigma-Aldrich), oxalic acid (anhydrous, >99%, Fluka), 1-bromodocosane (>98.0%, TCI), 1-bromohexane (98.0%, TCI), N,N,N',N'-tetramethyl-1,6-diaminohexane (98.0%, TCI), acetonitrile (>99.5%, Sigma-Aldrich), toluene (99.8%, Tedia), diethyl ether (anhydrous, Tedia), tetraethylorthosilicate (99%, Merck), aluminum sulfate (hydrated, 98%, Sigma-Aldrich), sodium hydroxide (99%, Merck), sulfphuric acid (95–97%, Honeywell), sodium aluminate (Sigma-Aldrich), fumed silica (99.80%, Aerosil 200), sodium hydroxide (98%, Sigma-Aldrich), and tetrapropylammonium bromide (98%, Sigma-Aldrich) were used as received. The water used in all protocols refers to Milli-Q water with a conductivity of 18 MΩ^{-1}.

2.2. Surfactant synthesis

$C_{22-6-6}Br_2$ gemini surfactant was synthesized as previously reported [22]. $C_{22-6-6}OH$ was obtained by ion-exchange with Amberlite IRN78 (hydroxide form) (Supelco) resin. Phosphate ($C_{22-6-6}(H_2PO_4)_2$, $C_{22-6-6}HPO_4$) and oxalate ($C_{22-6-6}(HC_2O_4)_2$, $C_{22-6-6}C_2O_4$) surfactants were prepared by titration with orthophosphoric acid and oxalic acid respectively, to an appropriate equivalence of $C_{22-6-6}OH$ solution and is similar to a previously reported protocol for other cationic surfactants [29]. The bicarbonate-carbonate form (denoted as $C_{22-6-6}CO_3$) was generated by adding 2–3 cubes of dry ice to the hydroxide solution. The pH (Metrohm Biotrode) of the final solution was 6.5 indicating the successful neutralization of the hydroxide ions. Clear solutions of C_{22-6-6} phosphate, oxalate and carbonate surfactants were obtained, freeze-dried and isolated as fine white powders. C_{22-6-6} surfactants with different counterions were then used for the synthesis of MFI zeolites.

For surfactants with hydrolysable counterions, hydrolysis in solution leads to a distribution of counterion species which can be determined from the solution pH based on acid-base equilibria equations and the K_a of the respective acids. Table 1 summarizes the distribution of species for surfactants associated with hydrolysable counterions at the equivalence point of the titration. Although there is a fractional distribution of 1^- and 2^- counterion species in the majority of our systems, we denote the surfactant counterion as the one with the higher fraction. For example, $C_{22-6-6}CO_3$ in solution comprises of 58% 2^- and 41% 1^- counterions. The respective zeolite synthesized from the corresponding surfactants will be denoted as Z-counterion (with charges omitted).