Zeolite Synthesis Hot Paper

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Synthesis of a Specified, Silica Molecular Sieve by Using Computationally Predicted Organic Structure-Directing Agents**

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Abstract: *Crystalline molecular sieves are used in numerous applications, where the properties exploited for each technology are the direct consequence of structural features. New materials are typically discovered by trial and error, and in many cases, organic structure-directing agents (OSDAs) are used to direct their formation. Here, we report the first successful synthesis of a specified molecular sieve through the use of an OSDA that was predicted from a recently developed computational method that constructs chemically synthesizable OSDAs. Pentamethylimidazolium is computationally predicted to have the largest stabilization energy in the STW framework, and is experimentally shown to strongly direct the synthesis of pure-silica STW. Other OSDAs with lower stabilization energies did not form STW. The general method demonstrated here to create STW may lead to new, simpler OSDAs for existing frameworks and provide a way to predict OSDAs for desired, theoretical frameworks.*

Molecular sieves are crystalline, microporous materials (pores less than 2 nm) that consist of three-dimensional networks of oxide tetrahedra. These materials are used in a wide variety of applications, and, at present, over 200 different frameworks have been identified.[1,2] In many applications, only a single structure will give optimal performance. This specificity in the structure–property relationships is one of the major driving forces behind much of the research directed at creating new structures.[3] It is estimated from theory that there are well over a million possible frameworks,[4] but of the 200 that have been synthesized, fewer than 10 % are in commercial use.[5,6] As an example of the potential of these possible frameworks, recent studies on carbon capture have identified numerous predicted frameworks with calculated performances superior to known materials.[7] Thus, the motivation to create these structures is high.

The crystallization of a microporous material is a complicated process that is still not well understood.[2,8–10] The use of organic structure-directing agents (OSDAs), most of which are charged alkylammonium cations, offers some level of "design", for example, there is a correlation between the shape and size of the OSDA used and the resulting framework.[2,11–13] Despite extensive work in this area, there is currently little ability to target specific frameworks through the prediction of OSDAs, and much discovery continues to be based on trial and error,[14] which has provided only a small fraction of the many possible predicted frameworks.

A priori prediction of OSDAs to target the synthesis of desired frameworks is a long-standing challenge in microporous materials synthesis.[2,15–17] Many previous predictive examples have relied on scoring the framework interaction energies with the OSDA or leveraging methods developed for the pharmaceutical industry to design organic molecules that bind to proteins.[3,15,17,18] While these procedures do allow the de novo prediction of OSDAs, they suffer from many shortcomings; paramount among these is that many of the molecules can be difficult or impossible to synthesize.[15] A new method to predict chemically synthesizable OSDAs for crystalline molecular sieves has recently been reported.[3] Here, we provide the first experimental validation of this new method by using fluoride-mediated, pure-silica chemistry to create pure-silica frameworks. This system is selected to avoid the use of inorganic cations, heteroatoms such as aluminum, and other variables commonly encountered in the synthesis of microporous materials to more clearly test the structure–property relationships between the framework and the OSDA predicted by the new method.[8,19] To illustrate the method, we synthesized pure-silica STW (HPM-1).[20,21] HPM-1 was selected as the target framework, as prior to our study only a single OSDA (**2**) has been reported to produce HPM-1 under a very narrow range of synthesis conditions.

The previously published computational method was used to screen an evolving population of potential OSDAs.[3] The population was created by the application of known organic reactions to a library of available reagents by using a standard reagent library and a custom library of imidazole-based organic compounds. Each member of the evolving population of potential OSDAs was evaluated by calculating its stabilization energy in STW, which is the average difference in energy between the OSDA/STW composite and the isolated OSDA and the empty STW. A subset of particularly interesting compounds were subjected to a further eight evaluations of the stabilization energy to confirm results from a single run, and the compounds selected for experimental evaluation are shown in Figure 1 (**2** is reported to form HPM-1).

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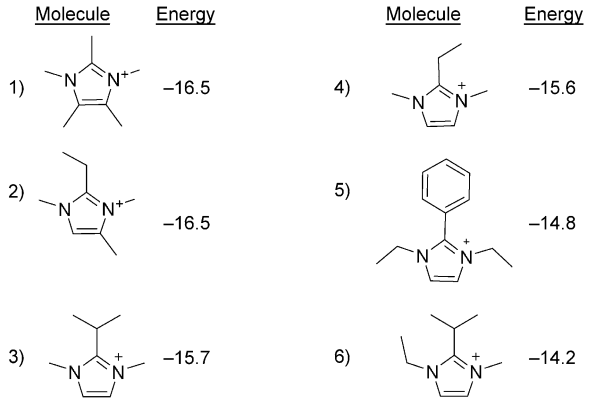

Figure 1. OSDAs used to prepare pure-silica molecular sieves and their calculated stabilization energies in the STW framework (stabilization energies in kJ (mol Si)$^{-1}$).

Synthesis reactions were conducted with OSDAs **1**–**6** at temperatures and H_2O/SiO_2 ratios typical for pure-silica, fluoride-mediated syntheses. In general, reactions were allowed to proceed until a crystalline product was observed or all the reaction material had been consumed, as evident by taking aliquots for analysis. A summary of the experimental results is provided in Table 1, and a complete listing of experimental results can be found in the Supporting Information, along with the experimental and characterization details (representative powder X-ray diffraction patterns for each of the as-made materials are shown in Figure S1).

Table 1: Summary of experimental results (a complete listing is given in the Supporting Information)

OSDA	H_2O/SiO_2	*T* [°C]	*t* [days]	Results[a]
1	4, 7	140, 160, 175	5–23	STW
1	14	140, 175	35, 16	U, dense
1	14	160	7	STW
2	4	140, 160, 175	40, 16, 16	STW
2	7	140, 160	70, 41	STW
2	7	175	20	HPM-2[22]
2	14	140, 160	70, 47	HPM-2[22]
2	14	175	20	dense
3	4, 7, 14	140, 160, 175	9–80	MTW, STF, A
4	4	160	16	STW + ITW
4	7, 14	160	22–44	ITW, MTW
4	4, 7, 14	140, 175	10–49	ITW, MTW, STF, A
5	4, 7, 14	140, 160, 175	13–60	MFI, A
6	4, 7, 14	140, 160, 175	5–56	STF, A

[a] A = amorphous, U = unidentified.

The computational screening identified **1** as the only molecule with a stabilization energy comparable to the published OSDA, **2**. When **1** was used in the synthesis reactions, it was shown to be more strongly directing than **2** towards STW, as it produced this framework across a greater range of synthesis conditions and in shorter times. To conclusively demonstrate that **1** and not a decomposition fragment was responsible for producing HPM-1, ^{13}C CP-MAS NMR spectroscopy was used to determine that **1** was occluded intact (see Figure S2 in the Supporting Information). This result provides the first experimental evidence that validates the new computational method for predicting chemically synthesizable OSDAs.

As **1** and **2** have similar stabilization energies in HPM-1, additional factors must account for the reasons that **1** forms HPM-1 across a greater range of synthesis conditions. In contrast to **2**, **1** does not possess any rotational degrees of freedom. OSDAs with many conformational degrees of freedom tend to be less effective at structure direction than OSDAs with fewer conformational degrees of freedom.[9,23] The rotational degrees of freedom in **2** likely allow many different conformations in solution, and therefore lead to a decrease in the probability that a molecule has the correct conformation to structure-direct the formation of HPM-1. As a consequence, and since the stabilization energies of compounds **1** and **2** are roughly the same, we expect the stabilization free energy of **1** will be more favorable than that of **2**.

A critical parameter of the computational algorithm used in this study is the occupancy of OSDAs per unit cell, as this is treated as a fixed value when determining the stabilization energies. With **1**, we iterated across OSDA occupancies and found stabilization energy values of −11.3, −14.2, and −16.5 kJ (mol Si)$^{-1}$, for 4, 5, and 6 OSDAs per unit cell, respectively. It was not possible to fit 7 OSDAs per unit cell. Thermogravimetric analysis showed that the HPM-1 made using **1** was 20.7 wt % organic and fluoride (see Figure S3 in the Supporting Information). The theoretical mass loss assuming 6 molecules per unit cell and one fluoride anion per OSDA molecule is 20.0 wt %, which agrees well with the experimental value. If either 5 or 7 molecules of **1** per unit cell were occluded in HPM-1, the mass losses would be 17.2 wt % and 22.6 wt %, respectively. The fact that the occupancy determined by the algorithm matches the experimental value provides another point of validation for the computational screening method. A view of the conformation of the organic species in the STW framework as calculated from the molecular simulations is shown in Figure 2.

All of the other OSDAs selected for experimental validation had stabilization energies at least 0.8 kJ (mol Si)$^{-1}$ less favorable than **1**. They were evaluated to elucidate the range in the stabilization energies between the OSDA and the target structure that leads to structure direction of the predicted phase. Based on our accumulated experience of

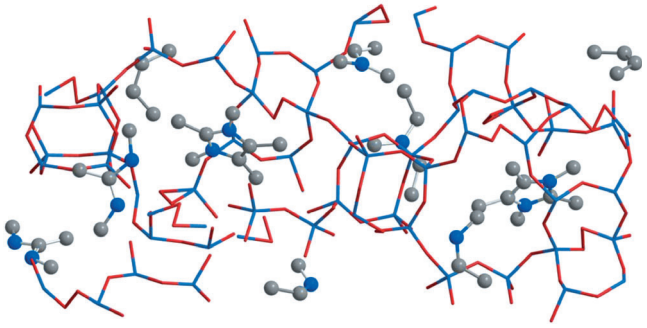

Figure 2. Unit cell of STW with the conformation of the occluded pentamethylimidazolium determined from molecular simulations.

calculated energies, differences of 2 kJ (mol Si)$^{-1}$ are considered significant. With the four remaining OSDAs, HPM-1 was never observed as a pure product, although it was encountered as a phase mixture with OSDA **4** (see complete results in the Supporting Information). Our results on the synthesis of molecular sieves agree with those from other studies involving OSDAs that demonstrate small structural differences can completely change product selectivity.[24–27]

In addition to STW, several other products were observed, including ITW, MFI, MTW, STF, and others that could not be identified or consisted of phase mixtures or organosilicate layered materials. The synthesis of ITW, MFI, and MTW is not surprising, as these are commonly observed in the syntheses of microporous materials and have been previously reported with similar OSDAs.[25,28,29] Pure-silica STF would not be expected as a product using the OSDAs in this study, but as our work highlights, stabilization can occur under conditions that may not be apparent from simple visual comparisons of OSDAs.[12,30,31]

In conclusion, we have demonstrated experimental validation of a computational method that is not only able to screen a large number of OSDAs, but is also able to construct OSDAs in an automated manner by using known chemical reactions so that they will be synthetically accessible. The results of our study have provided experimental evidence that this method is able to 1) successfully predict OSDAs for a specified framework by using known chemical reactions, and 2) yield predicted occupancies that are measured in the products. The ability to provide theoretical guidance to the creation of a crystalline molecular sieve is valuable, as it reduces the scope of an impossibly large synthetic problem in the quest to synthesize a desired framework. As this method has been applied to prepare a framework that is difficult to access, it is likely that the method can be extended to other, desired frameworks.

Experimental Section

All computations were conducted using the method described in Ref. [3]. The Dreiding forcefield was used in the GULP molecular modeling program to calculate the stabilization energies. Six OSDAs were first placed in sterically optimal locations in the microporous material unit cell and energy minimized. Molecular dynamics was performed at 343 K for 30 ps, and averages were collected over the last 5 ps of the run. A custom library was also used that contained the 4 aklylating reagents methyl iodide, ethyl iodide, 1-propyl iodide, 2-propyl iodide, as well as 47 imidazole derivatives available from Sigma–Aldrich, 17 additional commercially available imidazoles, and 25 imidazolium-based OSDAs that could be synthesized from commercially available materials in one or two steps.

Detailed synthesis and characterization details for each of the experimentally tested OSDAs can be found in the Supporting Information. In general, organic compounds were quaternized with iodomethane or iodoethane, purified by recrystallization, exchanged to the hydroxide form by using a hydroxide-exchange gel, and titrated.

Pure silica syntheses were performed by using standard methods, and details can be found in the Supporting Information. The final molar ratios of the gel were: 1 SiO_2:0.5 ROH:0.5 HF:x H_2O (x = 4, 7, 14). Each composition was run at 140, 160, and 175 °C and aliquots were taken periodically by first quenching the reactor in water and then removing enough material for powder X-ray diffraction analysis.

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