Template-Framework Interactions in Tetraethylammonium-Directed Zeolite Synthesis

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Abstract: Zeolites are often synthesized using organic templates, though their exact role in determining the final framework structure and composition remains unclear. We systematically examine tetraethylammonium by experimental and computational means in 8 zeolite frameworks, with compositional variations for 20 distinct materials. There are two distinct regimes of occluded conformer tendencies: 1) In frameworks with a large stabilization energy difference a single conformer exists. 2) In the frameworks with small stabilization energy differences a heteroatom-dependent distribution of conformers exists. These findings demonstrate that host–guest chemistry principles, including electrostatic interactions and coordination chemistry, can be as important as ideal pore-filling.

Keywords: host–guest systems, Raman spectroscopy, computational chemistry

1. Introduction

Microporous materials (MMs) are often synthesized with the use of organic structure-directing agents (OSDAs). These can be the cost-controlling factor in synthesis, motivating detailed investigations to explore their role in promoting the crystallization of a desired material so that lower-cost OSDAs can be used. It has been have found that in addition to space filling considerations, electrostatics lead to a complicated situation of OSDA-framework interactions, prompting further study to unravel the factors influencing the relationship between OSDA and the crystalline product. Tetraethylammonium (TEA^+), among the simplest OSDAs, is known to exist in two distinct conformers, designated *tt.tt* and *tg.tg*, which can be distinguished using Raman spectroscopy (highlighted in Figure 1). Crystalline TEA^+ salts are known as a single conformer, but in solution exist as an equilibrium of conformers. When occluded in MMs, TEA^+ has previously been shown to be present predominantly as a single conformer, experimentally demonstrated for AFI (*tt.tt* primarily), BEA (*tt.tt* exclusively), and CHA (*tg.tg* primarily).[1–3]

2. Experimental

Details regarding zeolite synthesis, Raman spectroscopy and computational methods can be found in our publication.[4]

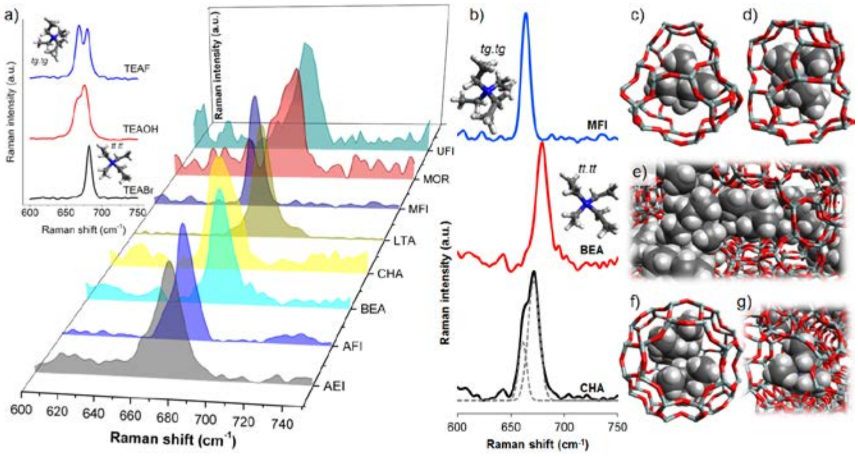

Figure 1. a) Representative Raman spectra of each framework showing the region of interest from 600 to 750 cm^{-1}. The inset graph shows the Raman spectra of the TEA^+ salts: solid TEABr, aqueous TEAOH and TEAF dihydrate, with the peaks corresponding to the *tg.tg* and *tt.tt* conformers indicated. b) A representative deconvolution of the Raman spectra for CHA, containing both conformers, as well as Raman spectra for BEA and MFI, which contain only a single conformer. For CHA, the collected data is in black and the Gaussian fits are in gray. c-g) The location of occluded TEA^+ molecules for AEI, CHA, BEA, LTA and MFI frameworks, respectively, as determined using molecular modelling.

3. Results and discussion

Herein, the relationship between framework structure, material composition, synthesis conditions and the conformation of occluded TEA^+, as probed with Raman spectroscopy, has been examined in eight distinct frameworks, with further variations in composition (e.g., addition of B, Co, Ti, Mn and Zn).[4] All materials studied are in Table 1, along with the experimentally determined occluded conformer distributions. Representative Raman spectra are given in Figure 1a, with examples of the deconvolution procedure in Figure 1b. The occluded conformer distribution has been simulated using molecular modelling to determine if optimal space filling is the primary driver influencing the observed distributions, and the results of the energy calculations are given in Table 1, with the calculated positions of TEA$^+$ in Figure 1c-g.

Framework	Material	$\Delta E_{tg.tg\text{-}tt.tt}$ (kJ/mol TEA$^+$)^a	*tg.tg* conformer (%)^b
AEI	AlPO$_4$-18	3.2	20
AFI	AlPO$_4$-5	0.0	17
	SAPO-5		12
BEA	AlSi^c (OH$^-$)	8.7	0
	AlSi (OH$^-$)		0
	Borosilicate (OH$^-$)		0
	Pure-silica (F$^-$)		0
	Ti-AlSi (OH$^-$)		0
	Titanosilicate (F$^-$)		0
	Zincosilicate (OH$^-$)		0
CHA	AlSi (OH$^-$)	3.4	23
	CoAPO-34		22
	MnAPO-34		29
	SAPO-34		25
	SAPO-34		16
	ZnAPO-34		79
LTA	UZM-9 (AlSi)	17.3	0
MFI	ZSM-5 (AlSi)	-9.8	100
MOR	MOR (AlSi)	2.1	12
UFI	UZM-5 (AlSi)	1.9	0

AlSi=aluminosilicate composition. The energy barrier in solution is $\Delta E_{tg.tg\text{-}tt.tt}$= 4.1 kJ/mol TEA$^+$.[5]

Table 1. Description of the 20 distinct materials prepared including framework, composition, calculated stabilization energy difference between the occluded conformers and the experimentally determined conformer distribution in each material.

In the frameworks with small calculated energy differences (AEI, AFI, CHA and MOR), less than the interconversion of TEA$^+$ in solution, a heteroatom dependent distribution of conformers was observed. This is most clearly illustrated for the CHA framework as 6 distinct materials were prepared, in which it is expected that the acid strength will follow: aluminosilicate > Si > Mn > Zn > Co. Combined with the fact that the *tt.tt* conformer allows the shortest interaction distance between the charged nitrogen and charged framework elements, a correlation between percent *tt.tt* conformer and the acid site strength emerges, with stronger acid sites leading to a greater proportion of *tt.tt* conformer. This same trend holds in AFI and MOR, where the charged composition caused a high proportion of the *tt.tt* conformer.

In frameworks with a large calculated stabilization energy difference, only a single occluded conformer was found (BEA, LTA and MFI). The influence of heteroatom interactions versus space filling was extensively studied in BEA, with materials prepared from both hydroxide and fluoride media, as well as with an all-silica framework and containing isoelectronic (Ti^{4+}) and charged (Al^{3+}, B^{3+}, Zn^{2+}) heteroatoms. In all samples, TEA$^+$ was occluded as only the *tt.tt* conformer, regardless of composition, demonstrating that when space filling considerations are significant that electrostatic interactions cannot overcome them. In LTA only the *tt.tt* conformer was observed, which is expected from the energy calculations, and in the MFI framework only the *tg.tg* conformer, which was found to be occluded at the channel intersections using molecular modelling, similar to tetrapropylammonium in MFI.

4. Conclusions

The results show that the phase that crystallizes is determined by a complex interplay of framework inorganic elements, OSDA conformation, OSDA-heteroatom interactions and framework stabilization by the space filling OSDAs. The two regimes of occluded conformer tendencies underscore the entangled nature of OSDA framework interactions and demonstrate the power of the molecular model used as it can accurately predict the occluded conformer in these systems.

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