Short communication

Little energetic limitation to microporous and mesoporous materials

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Abstract

A series of pure-silica or high-silica zeolites, several mesoporous silicas, moganite, and the conventional silica polymorphs (tridymite, cristobalite, coesite, glass) are energetically, at most, 15 kJ/mol higher than quartz, with the energy versus volume curve leveling off about 15 kJ per mol of SiO_2 above quartz for large volumes. For $AlPO_4$ polymorphs, a similar trend holds, with energy leading off at an even less metastable value, namely about 10 kJ per mol of $Al_{0.5}P_{0.5}O_2$ above berlinite. These small energy differences are consistent with self assembly of these materials being geometrically and kinetically, rather than energetically, controlled. Thus there is very little energetic limitation to the possibility of synthesizing various micro- and mesoporous framework structures.

Keywords: Zeolite; Mesoporous material; Enthalpy; SiO_2; $AlPO_4$

Recently there has been increasing interest in synthesis of microporous and mesoporous materials using organic structure-directing agents. The ability to make mesoporous structures using surfactants and diverse inorganic constituents [1–5] suggests that this type of self assembly is a very general phenomenon. The mesophases formed, upon careful calcination, often produce inorganic frameworks with nanometer-sized pores arranged in a regular array. They may have novel applications as catalysts, molecular sieves, encapsulants, and composites. This work addresses the energetics

of the calcined porous inorganic frameworks, and shows that for both SiO_2 and $AlPO_4$ the enthalpy difference between the most stable polymorph (quartz structure) and the microporous and/or mesoporous forms is small, namely 5–15 kJ/mol. Further, this energy is not a strong function of molar volume and appears to level off with decreasing density. This implies the absence of a strong energetic driving force for decomposition, and suggests that the number of possible mesoporous frameworks is virtually limitless.

Evidence against zeolite frameworks being particularly unstable structures comes from a recent calorimetric study of six calcined high-silica

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zeolites [6]. All are found to be energetically metastable with respect to quartz by only 7–14 kJ/mol (see Table 1). This makes them only 0–5 kJ/mol less stable in energy than silica glass. Since amorphous silicas derived from gels are higher in energy than fused glass by 0–10 kJ/mol [7,8], silica zeolites and amorphous silicas occupy an overlapping range of energies. At 373 K the available thermal energy, RT, is 3.1 kJ/mol, so the formation of a zeolite from amorphous silica is not hindered energetically under typical synthesis conditions.

Recently, a new family of mesoporous materials, with pore diameters in the 2–10 nm range, has been synthesized using surfactants as structure-directing agents [1–5]. These phases have a periodic arrangement of regularly sized pores that can be tailored in size by the synthesis method but the arrangement of tetrahedra in the framework is disordered, as inferred from X-ray diffraction,

Table 1
Energetics of zeolitic and mesoporous silica and aluminophosphate materials

Material	Molar volume (cm³/mol)	Enthalpy relative to quartz structure (two-oxygen basis) (kJ/mol)
Silica zeolites		
ZSM-12[a]	31.05	8.7±0.8
ZSM-5[a]	33.65	8.2±0.8
ZSM-11[a]	34.02	8.2±1.0
SSZ-24[a]	34.42	7.2±0.9
ZSM-18 (three-membered rings)[b]	42.12	13.9±0.4
EMT (hexagonal faujasite)[a]	46.51	10.5±0.9
FAU (faujasite)[a]	47.43	13.6±0.7
Mesoporous silicas		
MCM-41 (28)[b,c]		14.8±1.0
MCM-41 (32)[b,c]		14.4±0.4
MCM-41 (35)[b,c]		14.6±0.6
MCM-41 (50)[b,c]		14.8±0.5
K(45) (from kanemite)[b,c]		15.3±1.8
Other silicas		
Glass[a]	26.32	9.2±0.5
MCM-41 (collapsed to glass-like material)[b]		11.2±1.0
Moganite (related to quartz by unit cell twinning)[b]	23.02	3.3±0.6
Quartz[a]	22.69	0
Cristobalite[a]	25.74	2.7±1.0
Tridymite (several types)[a,b]	26.53	3 to 7
Coesite (a high-pressure form)[a]	20.64	2.9±0.3
AlPO₄ polymorphs		
Berlinite (quartz)	23.23	0
Tridymite	26.95	2.6±0.7
Cristobalite	26.57	3.0±0.6
AlPO₄-5	34.27	7.0±1.0
AlPO₄-8	34.32	5.4±0.8
AlPO₄-11	30.44	6.2±0.5
AlPO₄-42	42.01	7.8±1.0
UPI-5	42.26	9.7±1.2

[a] Ref. [6].
[b] This work.
[c] Value in parentheses indicates d-spacing of first peak (d_{100}).

Raman spectroscopy, and nuclear magnetic resonance [9]. We have recently measured the enthalpy of formation of several of these materials, by the same high-temperature oxide melt solution calorimetric technique used for zeolites [6] and found them to be only 14–15 kJ/mol less stable than quartz at room temperature (see Table 1). Thus, even such large-pore silicas are similar in energy to zeolites and to amorphous sol–gel silica.

The above MCM-41 materials were made using amorphous silica. Similar mesoporous silicas can be made starting with a layered polysilicate, kanemite ($NaHSi_2O_5 \cdot 3H_2O$) [10]. We have measured the enthalpy of formation of one such material K(45) with $d_{100} = 4.507$ nm (pores diameter 3.5 nm, assuming 1-nm walls) and found it to lie 15.3 ± 1.8 kJ/mol above quartz. Thus the starting material does not play a major role in the energetics, and all the mesoporous silicas studied so far are similar in enthalpy.

Fig. 1 shows the enthalpy relative to quartz of zeolitic and mesoporous silicas as a function of pore diameter. The energy appears to reach a plateau at about 15 kJ/mol higher than quartz for pores greater than about 0.8 nm. This suggests a transition from a regime in which cages or pores are an integral part of the crystal structure and affect its energetics to a regime in which large

pores act energetically as an inert volumetric diluent. That is, the large pores are effectively a second phase, and further increase in pore diameter does not influence the energy. It is remarkable that this transition appears to occur at a pore diameter near 1 nm, and that the plateau in energy is only 15 kJ above the most stable polymorph (quartz). It is also noteworthy that the mesoporous materials, despite their large pore size and lack of complete crystallinity, have enthalpies very similar to those of many silica zeolites, for example silica faujasite.

Preliminary calorimetric data for several aluminum phosphates have been obtained very recently in our laboratory (see Table 1 and Fig. 2). It is striking that the enthalpy of $AlPO_4$ polymorphs, on a two-oxygen basis, $Al_{0.5}P_{0.5}O_2$, appears to level off with increasing volume at values only about 10 kJ/mol above berlinite, the quartz form. This low energetic cost, even less than for SiO_2, may explain the very extensive family of large-pore $AlPO_4$ materials which has been synthesized, and suggests that a wealth of surfactant coassembled materials should be possible.

Recent studies suggest that the process of self assembly is complex [1–5,11,12]. Formation of the surfactant mesophase does not precede silica pre-

Fig. 1. Enthalpy of zeolitic and mesoporous silicas as a function of diameter of largest pore in the calcined material.
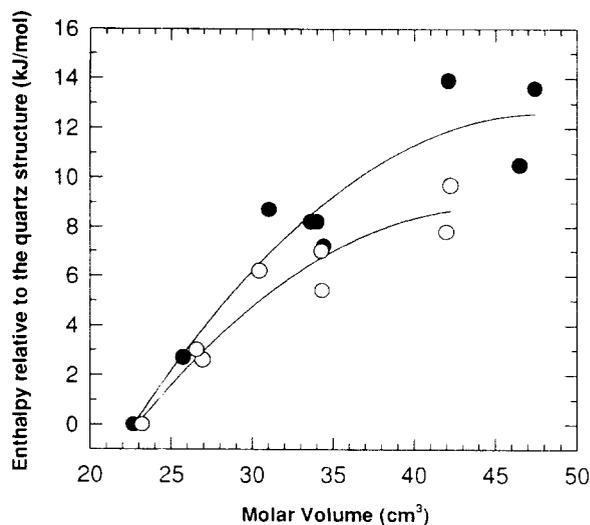
Fig. 2. Enthalpy of dense and zeolitic silicas (solid circles) and aluminophosphates (open circles) as a function of molar volume.

cipitation; the silica does not merely petrify a preexisting organic framework. It has been argued that charge matching between the inorganic and micellar structures at the interface is an important driving force in synthesis [4,11,12]. We have shown that the energy differences between various calcined frameworks are small and on the order of thermal energy. Thus, although the bonding within an organic molecule and within a silicate or aluminophosphate is strong, as is the electrostatic interaction between charged species in solution and in the evolving inorganic framework, the energy differences among alternative mesoscopic configurations are likely to be small, and the change in energy of the framework during synthesis is probably only a very weak driving force. This scenario of small energy differences between competing strongly bonded species sets the stage for mesoscopic self assembly. These small energy differences are the key to why so many different structures can form. Indeed, were the differences in energy between alternative frameworks or mesostructures large, only one or a few structures would form, rather than the large number seen. The formation of porous mesostructures in a variety of systems, (e.g. silica, antimony, iron, and lead oxides [4] and titanosilicates [5]) suggests that the specific chemical composition does not play a crucial role in making mesoscopic self assembly possible, though it does dictate the details of the structure that forms. This is only possible if the energetic cost of these mesostructures is small relative to polymorphs of normal density. The number and variety of structures that can be formed is thus not seriously constrained by the energetics of the final inorganic product and is limited only by the ingenuity of the chemist in applying suitable structure-directing agents and synthesis conditions.

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