

Thermochemistry of Amine-Templated Open Frameworks

Corine Gérardin,^{*,†} Thierry Loiseau,[‡] Gérard Férey,[‡] Francis Taulelle,[§] and Alexandra Navrotsky^{||}

Laboratoire de Matériaux Catalytiques et Catalyse en Chimie Organique, UMR 5618 CNRS ENSCM, 8 rue de l'École Normale, 34296 Montpellier Cedex 5, France, Institut Lavoisier, UMR 8637, Université de Versailles-Saint-Quentin-en-Yvelines, 78035 Versailles Cedex, France, Laboratoire de RMN et Chimie du Solide, UMR 7510, Université Louis Pasteur, 67070 Strasbourg, France, and Thermochemistry Facility, Department of Chemical Engineering and Materials Science, University of California at Davis, Davis, California 95616

Received February 27, 2002. Revised Manuscript Received May 9, 2002

The thermochemistry of pure-silica zeolites and other microporous compounds was extensively reported in the literature: high-temperature calorimetry experiments revealed that the enthalpy of formation of the molecular sieves is on the order of twice the thermal energy available at the synthesis temperature. However, a better knowledge of the role that the structuring agents used in the hydrothermal synthesis play in the stability and the selection of the structures is necessary. In this paper, the stability of hybrid organic–inorganic composites, precursors of microporous structures, is investigated. Amine-templated gallophosphates of the ULM-*n* series have been studied by high-temperature calorimetry combining transposed temperature drop and drop solution experiments. The heats of formation of the composites are about -1 and -10 kJ/mol GaPO₄ for ULM-4 and ULM-5 templated with diaminopropane and diaminohexane, respectively, and -202 kJ/mol GaPO₄ for ULM-3 where the template is the monohydrate of diaminopropane. The results for the ULM-*n* materials suggest an enthalpy of stabilization by the structuring agents on the order of what was found in the case of stabilization by adsorption of water in hydrated microporous aluminophosphates.

Introduction

Microporous materials are usually prepared under hydrothermal conditions with organic additives which act as structure directing agents. One of the main goals in the field of zeolites and other microporous compounds is to be able to synthesize new framework structures by rational design and selection of the template molecules.^{1–4} To guide the synthesis, the mechanisms of framework formation under the influence of additives must be elucidated. The role of the templating agents in the synthesis, the selection of the type of building units and the way these blocks assemble to form the framework are not well understood yet. The synthesis pathways seem to be controlled by the inorganic–organic interactions, but are the formation processes controlled by kinetics, thermodynamics, or a combina-

tion of both? It is still not known how thermodynamically stable the hybrid templated open frameworks, precursors of microporous structures, are. What has been demonstrated up to now is that microporous materials obtained after template removal are metastable phases relative to the isocompositional dense polymorphs.^{5–6} Microporous compounds are indeed metastable but the energy difference between their heat of formation and the heat of formation of the corresponding dense phase (SiO₂ quartz, for example, for silica zeolites) is rather small, on the order of two or three times the thermal energy at the synthesis temperature. Knowledge concerning the strength of the interaction of the extraframework species with the framework is fundamental to understanding the structure assembly process.

Much work has been done on the energetics of several families of nanostructured materials by high-temperature calorimetry. Microporous compounds such as zeolites, pure silica and aluminosilicates,⁷ or aluminophosphates⁸ were investigated using drop solution calo-

* To whom correspondence should be addressed. Telephone: 33 4 67 14 43 26. Fax: 33 4 67 14 43 49. E-mail: gerardin@cit.enscm.fr.

† UMR 5618 CNRS ENSCM.

‡ Université de Versailles-Saint-Quentin-en-Yvelines.

§ Université Louis Pasteur.

|| University of California at Davis.

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rimetry. Mesoporous silicates were also investigated. Some specific cases of porous structures containing some molecules in their cavities and channels, mainly water, were studied, too. The energetics of formation and hydration of ion-exchanged zeolites was investigated.⁹ In the case of aluminophosphates, the influence of water adsorption on the energetics was studied. Then, the case of framework and layered manganese dioxide phases filled with inorganic cations (alkali and alkaline earths) was investigated together with the effect of ion hydration on the energetics. The main results of these numerous studies are, first, that microporous compounds are metastable and their enthalpies of formation from the dense stable phases are endothermic on the order of +5 to +15 kJ/mol of tetrahedra. The heat of formation is mainly a function of the overall quality of packing of the microporous structure. Hydrated phases such as aluminophosphates are stabilized compared to dehydrated ones; they are energetically more stable than the dense phases plus water. The heat of formation of hydrated materials relative to the dense phase plus H₂O is on the order of -15 kJ/mol for the aluminophosphates. The case of tunnel or layered manganese dioxide phases is somewhat different, but it is interesting to point out here the main results. Cation-substituted MnO₂ phases are stable, and their heat of formation depends mainly on the hydration degree of the substituting ions, which may be Na, Ca, Cs, or Rb.^{10,11} The heat of formation of such phases varies between -10 and -70 kJ per mole of oxide depending on the number of water molecules per compensating cation.

The energetics of open frameworks templated with organic structuring agents has not directly been investigated yet, and the magnitude of the relative thermodynamic stability of the hybrid material is not known. It seems essential to energetically characterize the direct synthesis products, which are organic-inorganic composite precursors of the microporous phases. Such knowledge will help distinguish whether the self-assembly is driven by enthalpy, entropy, or purely kinetic factors.

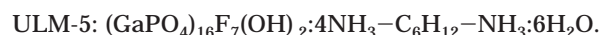
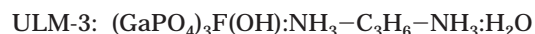
This paper presents a thermochemical study of oxyfluorinated gallophosphates templated with amines using high-temperature solution and reaction calorimetry. The purpose of the study is to measure the enthalpies of formation of the inorganic/organic mesostructures. In this study, the heats of formation of three GaPO₄-based open frameworks were measured. The materials are part of the ULM-*n* series.¹² The inorganic frameworks are oxyfluorinated gallophosphates, since fluorine ions are directly involved in the first coordination sphere of gallium. Depending on the amine, the composition, and the pH of the starting synthesis mixture, different framework structures were obtained. The thermochemistry of ULM-3, -4, and -5 was inves-

tigated here. The heats of formation were measured, and even if these materials cannot be emptied of organics without structure collapse, an estimate of the stabilization enthalpy due to host-guest interaction could be obtained.

Experimental Section

Samples. The ULM-*n* materials were prepared under hydrothermal conditions, typically at 180 °C for 24 h, starting from gallium oxide, phosphoric acid, hydrofluoric acid, and linear diamines, in water. The preparation methods were already reported elsewhere.

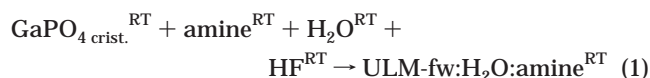
The structures of ULM-3,¹³ -4,¹⁴ and -5¹⁵ are presented in Figure 1. Grey polyhedra represent Ga atoms, while white tetrahedra represent P sites. White small circles represent water molecules, gray circles N atoms, and black circles C atoms of the amine molecules. The chemical formulas are given here:



ULM-3 and ULM-4 possess the same building units, which are assembled in different configurations. The materials were investigated by calorimetry as-synthesized, the templates were not removed. After thermal treatment of these ULM-*n* materials in order to remove the amines, the framework structures collapsed, and X-ray amorphous materials were obtained. For calorimetry experiments, the amine-templated materials were processed as pressed powder pellets of 15–20 mg.

Calorimetry. A custom-built Tian-Calvet twin microcalorimeter was used to run high temperature calorimetry experiments. Drop-solution calorimetry experiments in a molten oxide solvent were run at high temperature, they consist in dissolving an inorganic compound in a hot molten oxide solvent, namely 2PbO-B₂O₃ at 703 °C. Transposed temperature drop experiments were also run; they consist in dropping the sample in the hot calorimeter with no solvent present. The enthalpies of formation of compounds or the enthalpies of chemical reactions can be usually determined by the difference in heats of drop solution between materials under study and reference compounds. We checked that GaPO₄ was soluble in molten lead borate by separate experiments in a furnace. For each sample, the data for six to 10 drops of pellets were averaged in order to get the heat of reaction. The calibration factor for the calorimeter (J/μV) was obtained by dropping 15 mg pellets of alumina (Aldrich, 99.99%) stabilized in the corundum phase by heating them overnight at 1500 °C. The methodology is now standard and has been previously described.^{16,17}

The goal of this work was to measure the heat of formation of the ULM-*n* organic-inorganic composites relative to the standard components: dense GaPO₄, HF, water, and the amine at room temperature (RT). The reaction under study was then



GaPO_{4 crist.} is the cristobalite phase of GaPO₄. ULM-fw represents the oxyfluorinated gallophosphate inorganic framework. The method used in order to measure the heat of reaction

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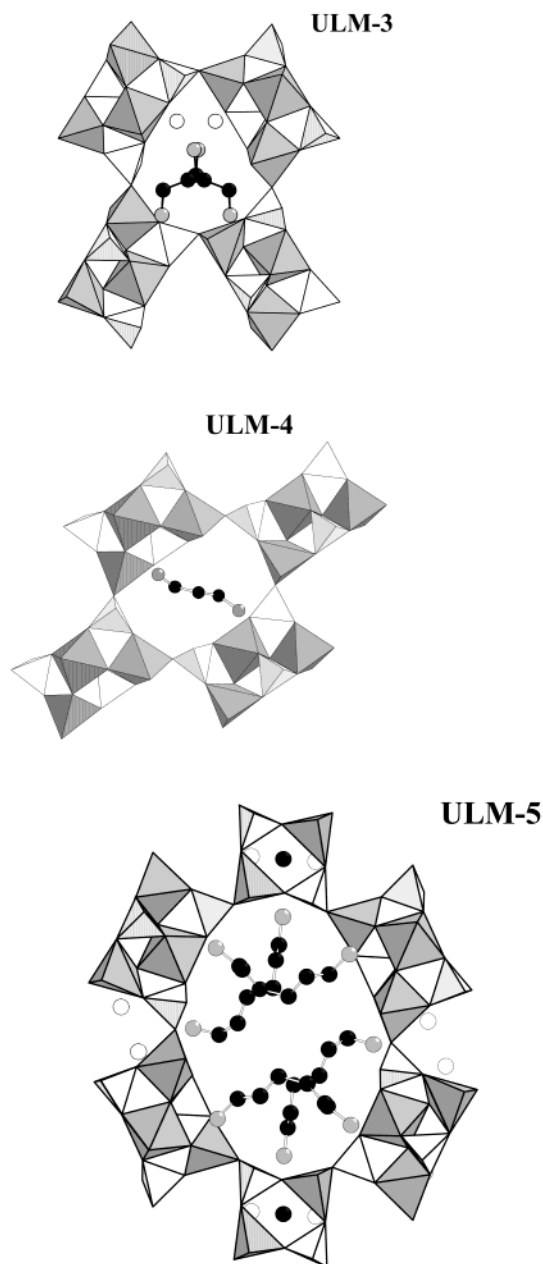


Figure 1. Representations of the ULM-*n* structures. The structures are viewed along the one-dimensional channels (10-membered ring for ULM-3 and ULM-4 and 16-membered ring for ULM-5). Opening windows: for ULM-3, 6.5×5.2 Å; for ULM-4, 6.1×3.6 Å; for ULM-5, 12.2×8.3 Å.

consists of transforming both the reactants and the products of the previous reaction into identical thermodynamic final states. Then the heat of reaction is calculated from the difference between the heats of reaction.

The heat of transformation of the standards is obtained as the sum of the heat of dissolution of GaPO_4 cristobalite plus the heats of evaporation and combustion of the organic entities. The heat of dissolution of GaPO_4 is obtained by drop solution calorimetry of GaPO_4 cristobalite into lead borate at 703°C . The heats of combustion are calculated with prediction models using additivity rules known for organic compounds; the combustion gases are H_2O , HF , CO_2 , and NH_3 .

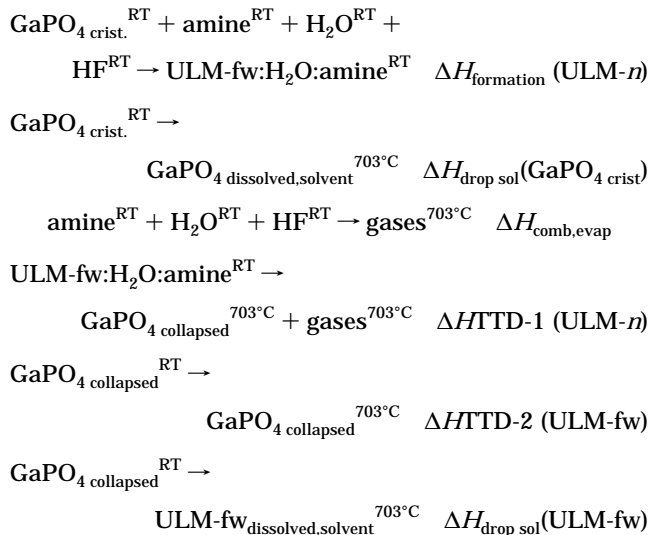
In the case of the inorganic-organic ULM-*n* composites, the final state also combines the inorganic part dissolved in lead borate at 703°C plus the organic additives transformed into the combustion products at 703°C . The hybrid material cannot be directly dropped into the solvent in the calorimeter because the amine molecule could lead to a reduction of the Pb^{2+}

cations in the solvent and thus change the final state. So, three experimental steps were necessary in order to transform the composite into the final state: first, a transposed temperature drop (TTD) is made, which is a drop into the hot calorimeter under O_2 flow, with no solvent present. In this first drop, the organic part is burnt and the sample analyzed. During the first drop (TTD-1) under O_2 , the material undergoes the following irreversible chemical changes upon dropping: breaking of the interactions between the framework and either template or water, combustion of the amine, evolution of water and HF and collapse of the crystalline open framework. The heat effects associated with this first drop include the heat content of the collapsed material from room temperature to 703°C . A second transposed temperature drop (TTD-2) from room temperature to 703°C is then necessary to measure that heat content. Finally, the transformed sample is dropped a last time into the calorimeter to be dissolved in lead borate. During that drop solution (DS) experiment, the resulting material is dissolved to a final dilute ionic state in the molten salt solvent.

The following equation (eq 2) was used to get the heat of formation, $\Delta H_{\text{formation}}(\text{ULM-}n)$, of the templated ULM-*n* samples; it includes the different enthalpies involved in the transformation pathways of the ULM-*n* sample on one hand and of the corresponding standards on the other hand, into the same final state.

$$\Delta H_{\text{formation}}(\text{ULM-}n) = \Delta H_{\text{drop sol}}(\text{GaPO}_4 \text{ crist.}) + \Delta H_{\text{comb, evap}} - \Delta H_{\text{TTD-1}}(\text{ULM-}n) + \Delta H_{\text{TTD-2}}(\text{ULM-fw}) - \Delta H_{\text{drop sol}}(\text{ULM-fw}) \quad (1)$$

The enthalpies mentioned in eq 2 correspond to the following reactions:



$\Delta H_{\text{drop sol}}(\text{GaPO}_4 \text{ crist.})$ is the heat of drop solution of the GaPO_4 cristobalite reference sample.

$\Delta H_{\text{comb, evap}}$ represents the heat of combustion of the amine, evaporation of H_2O , and evolution of HF . The resulting gases are CO_2 , H_2O , N_2 , and HF . $\Delta H_{\text{TTD-1}}(\text{ULM-}n)$ is the heat of the first transposed temperature drop of the ULM-*n* sample. $\Delta H_{\text{TTD-2}}(\text{ULM-fw})$ and $\Delta H_{\text{drop sol}}(\text{ULM-fw})$ are respectively, the heat of second transposed temperature drop and the heat of drop solution of the collapsed sample.

During the first TT drop of the ULM-*n* sample (TTD-1), the material has undergone irreversible changes; the heat effects associated with that process include the heats of transformation (collapse) of the sample at room-temperature plus the heat content of the transformed material from room temperature to 703°C . The second transposed temperature drop (TTD-2)

Table 1. Calculated Heats of Combustion of the Diamine, Evaporation of Water, and Evolution of HF from Room Temperature to 703 °C

	ULM-3	ULM-4	ULM-5
$\Delta H_{\text{comb}}^{703^\circ\text{C}}$ (kJ/mol amine)	-2095	-2095	-3828
$\Delta H_{\text{comb}}^{703^\circ\text{C}}$ (kJ/mol GaPO ₄)	-698	-524	-957
$\Delta H_{\text{evap}}^{703^\circ\text{C}}$ H ₂ O (kJ/mol GaPO ₄)	23	11.5	26
$\Delta H_{\text{evol}}^{703^\circ\text{C}}$ HF (kJ/mol GaPO ₄)	7	13	9
$\Delta H_{\text{tot}}(\text{comb, evap})$ (kJ/mol GaPO ₄)	-668	-499	-922

Table 2. Calorimetric Data Obtained for the Transposed Temperature Drops and the Drop Solution Experiments on the ULM-*n* Samples

samples	ULM-3	ULM-4	ULM-5
$\Delta H_{\text{TTD}-1}$	-366 ± 7 (10)	-396 ± 3 (10)	-803 ± 16 (12)
$\Delta H_{\text{TTD}-2}$	86.1 ± 0.8 (6)	87 ± 0.8 (6)	99 ± 2 (10)
$\Delta H_{\text{drop sol}}(\text{ULM-}n)$	29.2 ± 0.8 (8)	28 ± 0.9 (10)	33 ± 0.8 (12)

^a The data are given in kJ/mol GaPO₄. Errors are two standard deviations from the mean. Numbers in parentheses indicate the number of measurements carried out.

from room temperature to 703 °C gives the heat content of the transformed sample.

Results and Discussion

The heats of combustion of the amines were calculated using the predictions of the enthalpy of combustion of organic compounds by Cardozo.¹⁸ The heats associated with evaporation of water and evolution of HF from room temperature to 703 °C were also calculated. The relative errors on the calculated heats are estimated to be on the order of 1%. The details of the calculations are given in the appendix. The values of $\Delta H_{\text{comb, evap}}$ for the ULM-*n* samples are reported in Table 1, expressed in kJ/mol of GaPO₄. The calorimetric data obtained for the transposed temperature drops and the drop solution experiments are given in Table 2. The heat of drop solution of the GaPO₄ cristobalite reference was also measured and equals 43 ± 0.8 kJ/mol GaPO₄.

The samples were characterized after the first transposed temperature drop. Thermogravimetric analyses of the treated samples showed no weight loss up to 1000 °C, suggesting that the amine, water, and fluorine evolved during the first treatment. X-ray diffraction patterns of the samples after the first TTD reveal no peak due to the crystalline open framework; only small and broad peaks characteristic of the low temperature form of GaPO₄ (low cristobalite structure type) are observed. The transposed temperature drops lead to materials where the microstructures collapsed.

The heats associated with the TTD-2 characterize the heat contents of the ULM-*n* samples transformed into weakly ordered gallium phosphate. The heats associated with the drop solution experiments on the collapsed GaPO₄ samples equal 29 and 28 kJ/mol for ULM-3 and -4 and 33 kJ/mol GaPO₄ for ULM-5. Knowing that the heat of drop solution of the GaPO₄ cristobalite reference equals 43 kJ/mol, the conclusion can be drawn that collapsed and weakly ordered GaPO₄ samples are less stable than cristobalite by about 10 to 15 kJ/mol. This value is comparable to the heat of transition from amorphous silica to quartz (10–15 kJ/mol). In the case of silica zeolites, amorphous silica samples were shown

to be 3–5 kJ/mol SiO₂ less stable than crystalline zeolitic silicas.

Using eq 2, the heats of formation of the ULM-*n* samples were calculated. They equal -202 ± 16 kJ/mol GaPO₄ for ULM-3, -1 ± 10 kJ/mol for ULM-4, and -10 ± 29 kJ/mol for ULM-5. These numbers are the result of the combination of three consecutive calorimetry experiments plus the estimation of enthalpies by calculations. The heats of formation of the hybrid composites are negative, showing that the formation reaction is exothermic, which means an increased stability of the organic–inorganic composites compared to the mixture of reference compounds. The template-containing open frameworks are more stable than the dense phases plus amine and water. These results are similar to the data obtained on water-stabilized AlPO₄s. Previous results obtained on microporous aluminophosphates showed that hydrated aluminophosphates phases were stable compared to the dense berlinite phase in the presence of water. The increased stability was about -14 kJ/mol AlPO₄. This value is of the same order of magnitude as the stabilization enthalpy that was measured for ULM-4 and ULM-5 composites. The anhydrous AlPO₄ frameworks, which are isocompositional to the dense phase, are unstable by about 16 kJ/mol compared to the dense phase. This revealed a stabilizing energy of about -30 kJ/mol of the microporous framework due to the interaction between water in the cages and the framework.

In the ULM-*n* series, the heat of interaction between the template and the framework cannot be directly measured since the frameworks cannot be emptied without collapse of the crystalline structure. In the thermochemical cycle corresponding to the first TTD experiment, there are two unknowns, the heat of framework–guest interaction ($\Delta H_{\text{inter}}^{\text{RT}}(\text{fwk-guests})$) and the heat of collapse ($\Delta H_{\text{collapse}}^{\text{RT}}$), which cannot be separated.

The thermodynamical cycle corresponding to the first transposed temperature drop of the ULM-*n* sample is detailed below and represented as a set of equations.

$$\begin{aligned}
 \Delta H_{\text{TTD}-1} &= -\Delta H_{\text{inter}}^{\text{RT}}(\text{fwk-guests}) + \Delta H_{\text{collapse}}^{\text{RT}} + \\
 &\quad \Delta H_{\text{TTD}-2} + \Delta H_{\text{comb, evap}}^{\text{RT} \rightarrow 703^\circ\text{C}} \\
 \text{ULM-fw:H}_2\text{O:amine}^{\text{RT}} &\rightarrow \text{ULM-fw}^{\text{RT}} + \text{amine}^{\text{RT}} + \\
 &\quad \text{H}_2\text{O}^{\text{RT}} - \Delta H_{\text{inter}}^{\text{RT}}(\text{fwk-guests}) \\
 \text{ULM-fw}^{\text{RT}} + \text{amine}^{\text{RT}} + \\
 &\quad \text{H}_2\text{O}^{\text{RT}} \rightarrow \text{ULM-fw}_{\text{collapsed}}^{\text{RT}} + \text{amine}^{\text{RT}} + \text{H}_2\text{O}^{\text{RT}} + \\
 &\quad \text{HF}^{\text{RT}} - \Delta H_{\text{collapse}}^{\text{RT}} \\
 \text{ULM-fw}_{\text{collapsed}}^{\text{RT}} + \text{amine}^{\text{RT}} + \text{H}_2\text{O}^{\text{RT}} + \\
 &\quad \text{HF}^{\text{RT}} \rightarrow \text{ULM-fw}_{\text{collapsed}}^{703^\circ\text{C}} + \text{amine}^{\text{RT}} + \text{H}_2\text{O}^{\text{RT}} + \\
 &\quad \text{HF}^{\text{RT}} - \Delta H_{\text{TTD}-2} \\
 \text{ULM-fw}_{\text{collapsed}}^{703^\circ\text{C}} + \text{amine}^{\text{RT}} + \text{H}_2\text{O}^{\text{RT}} + \\
 &\quad \text{HF}^{\text{RT}} \rightarrow \text{ULM-fw}_{\text{collapsed}}^{703^\circ\text{C}} + \\
 &\quad \text{gases}^{703^\circ\text{C}} - \Delta H_{\text{comb, evap}}^{\text{RT} \rightarrow 703^\circ\text{C}}
 \end{aligned}$$

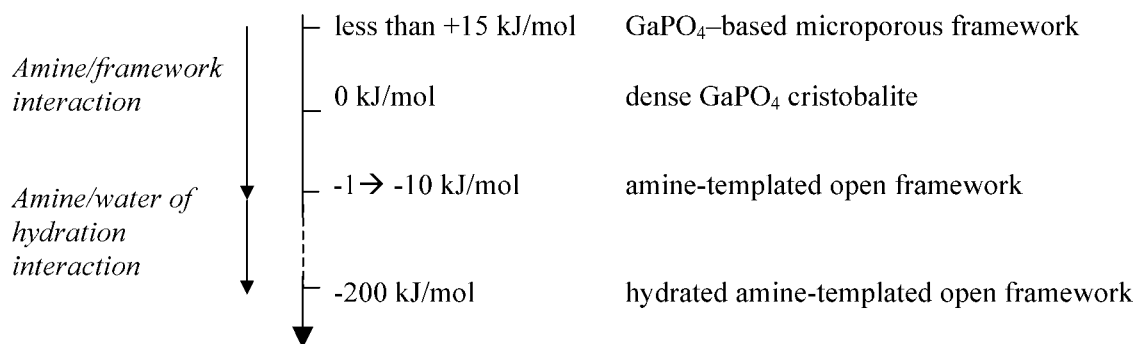


Figure 2. Schematic showing the metastability of ULM-*n* samples with the orders of magnitude of interaction energies involved in the hybrid materials.

Using the overall knowledge on energetics of microporous silica, aluminosilicates, and aluminophosphates, we can expect that the energetic difference between the crystalline microporous phase and the glass of same composition would be quite small (less than 5 kJ/mol tetrahedra (in our case $\text{Ga}_{0.5}\text{P}_{0.5}\text{O}_2$). This trend was also seen in the study of in situ crystallization of a zeolite; an exothermic heat of crystallization of about -2 kJ/mol tetrahedra was obtained from an amorphous precursor.¹⁹ That would mean that microporous gallophosphates would be about 10 kJ/mol of GaPO_4 less stable in enthalpy than GaPO_4 cristobalite. Then, an estimate of the stabilization energy due to host–guest interaction can be deduced. In the case of ULM-4 and ULM-5, the stabilization enthalpy would then be on the order of -10 to -25 kJ/mol, which is of the same order of magnitude as what was obtained for water–framework interaction in hydrated microporous aluminophosphates (-30 kJ/mol AlPO_4).

In the case of ULM-3, the host–guest interaction energy would be near -215 kJ/mol GaPO_4 . This value of the interaction energy is due to interactions between the framework and the amine, amine and water and water and the framework. Considering the structures of the ULM-*n*, the 200 kJ/mol difference in interaction energy between ULM-3 and ULM-4 may be assigned to an ion–dipole interaction corresponding to the hydration of the amine molecule in ULM-3. ULM-3 and ULM-4 have very similar structures, but the template in ULM-3 is the hydrated amine, while the template is anhydrous in ULM-4. Also, the frameworks in ULM-3 and ULM-4 are based on the same building units and the quality of packing is very similar in both structures. The enthalpy for the water–amine interaction is expected to be on the order of -100 kJ/mol molecule, which gives an order of magnitude of -250 kJ/mol amine. What is also expected is that the enthalpy of hydration (per mole of H_2O) of the first water molecule is much higher than the one corresponding to a higher hydration degree. The hydration enthalpy is known to depend strongly on the extent of hydration. In the case of a hydration number of 1 (first water molecule tightly bound to the amine), it is expected to be very high and thus leads to a considerable stabilization energy. The high value found here is consistent with the hydration discussion in the literature and with previous experimental results reported for example for hydrated MnO_2 based frameworks and obtained by high-temperature calorimetry. The heat of stabilization was calculated to be on the order of -60 to -70 kJ/mol MnO_2 for a degree

of hydration of the cation of 1; but the heat of stabilization calculated per mole of water is on the order of -200 kJ/mol H_2O for that same sample.

The synthesis of ULM-3 can be done with linear C-3 to C-5 diamines. When diaminopropane or diaminopentane are used, the templates are just the amine molecules, whereas when diaminopropane is used, the template is the hydrate of the amine, due to the space available in the pore and the possibility to fit a water molecule in the ten-ring channel. Interactions between the template and the ULM-3 host have been studied.²⁰ Hydrogen bonds exist between fluorine atoms of the network and one terminal amino group, while the second amino group is linked to the hydration water molecule, which is itself bound to the inorganic network by another hydrogen bond to a F/OH site (a partial occupancy between OH and F is shared). The monohydrate of amine links two opposite hexameric building units in a same structural layer, and also two adjacent hexamers in two adjacent layers. In the case of ULM-4, the absence of water molecule tightly bound to the diamine may be due to the absence of a stable cation–water arrangement in the pores.

A schematic (Figure 2) summarizes the metastability of the ULM-*n* samples with the relative orders of magnitude of interaction energies involved in the hybrid material. These experimental results confirm the theoretical simulation study of the framework stability of gallophosphate polymorphs, recently described by G.F. In particular, the “anomalous” behavior of ULM-3 compared to ULM-4 and ULM-5 is explained.

Conclusions

Using high-temperature calorimetry, it was possible to determine heats of formation of amine-templated open frameworks. The amine–gallophosphates systems called ULM-3, -4, and -5 are stable. They are more favorable than the GaPO_4 phase in the presence of water and the organic additive.

Calorimetric data allowed to confirm that the template in ULM-3 is the monohydrate of amine, which leads to a huge stabilization energy of the composite. The comparison of the measurements on both ULM-3 and ULM-4 prepared with the same amine lead to an

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estimate of the hydration enthalpy of diaminopropane in the ULM-3 structure.

In this ULM-*n* series, since the open frameworks are unstable upon template removing, the host–guest interaction energy could not be precisely measured independent from the network energetics. Nevertheless, using the overall knowledge on energetics of microporous silica, aluminosilicates, and aluminophosphates, an estimate of the stabilization energy due to host–guest interaction could be obtained. The stabilization enthalpy is on the order of -20 kJ/mol, which is similar to that obtained for water–framework interaction in hydrated microporous aluminophosphates. The findings of this paper are again consistent with the scheme already proposed and supported by calorimetry measurements, explaining that host–guest interactions do not help to stabilize highly unstable porous structures. However, the presence of organic structuring agents would rather allow one to favor specific organic–inorganic composite configurations and corresponding building unit topologies. High-temperature calorimetry can be very powerful to investigate the energetics of complex organic–inorganic composites and to probe interaction energies of different orders of magnitude, from hydrogen bonds to strong hydration energies.

Appendix

Cardozo proposes a simple and accurate method to estimate the enthalpies of combustion of organic compounds at room temperature. Cardozo's prediction model relies on the principle saying that, for most homologous

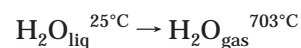
series, there is a first-order correspondence between the total number of carbon atoms and the enthalpy of combustion. A formula is deduced from the more general formula for liquid *n*-alkanes derived organic products. The following relation was used for a diamine, $\text{NH}_2\text{-C}_n\text{H}_{2n}\text{-NH}_2$, involved in the combustion reaction:



$\Delta H_{\text{combustion}}(298 \text{ K}) = -196.98 - 610.13N$ kJ/mol diamine. *N* is the equivalent alkane chain length of the amine obtained by adding the number of carbon atoms in the alkyl chain plus a correction factor taking into account the presence of functional groups. In the case of primary amine functions, the correction factor for *N* is 0.21 kJ/mol NH_2 . Thus, for linear diamines, we take $N = n + 0.42$.

The $\Delta H_{\text{combustion}}$ values thus obtained are at 703°C , and then, the heat contents from 25 to 703°C of the gases, N_2 , CO_2 and H_2O must be added.

For evaporation of water, the following reaction is considered:



and the heat is $\Delta H_{\text{evaporation}} = 69.13$ kJ/mol.

For evolution of HF, the following heat content is considered:



CM020098B