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Predicting Structural Feasibility of Silica and Germania Zeolites

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High throughput experimental techniques for zeolite synthesis, combined with the introduction of germanium in the synthesis gel, have allowed an increase in the number of new zeolites, especially of those containing large and extralarge pores. Zeolite phases containing Si/Ge as tetrahedral atoms stabilize certain unique topologies. One particular feature of Ge-containing zeolites is the stabilization of small TOT ($T = \text{Si, Ge}$) angles compared to their silica counterparts. This study employs computational chemistry techniques to calculate and rationalize the relative stability of zeolite phases as silicates and germanates. Atomistic force fields are used to simulate the structural properties of experimentally synthesized Si/Ge-containing zeolites, and an *ab initio* Hartree–Fock methodology is used to estimate the energetics of TOT angles. It is shown that each particular topology is only compatible with certain ranges of TOT angles, and, depending on the chemical composition, this induces stability or strain. A calculation of the energetic penalty associated with TOT angles for the different chemical compositions at each topology allows an estimate of their feasibility. The results are in agreement with experiments and allow one to make predictions about feasibility of new SiO_2 or GeO_2 zeolite structures.

1. Introduction

Germanium can isomorphically substitute silicon in zeolites, and many structures such as MFI, FAU, MON, NAT, RHO, SOD,¹ and, more recently, PKU-9² have been obtained as silico–aluminogermanates. Also gallium germanates such as BOF,³ BSV,³ and SBN⁴ or boron germanates such as SOS⁵ have been obtained. More than 30 years ago Lerot et al.⁶ showed that faujasite could be synthesized as silico–aluminogermanates with a high Ge content. Later, a series of pure GeO_2 zeolites were synthesized, where Ge was not only tetrahedrally coordinated but also penta- and hexacoordinated.^{7–9} The first tetracoordinated framework pure GeO_2 zeolites were synthesized by Li and Yaghi in 1998,¹⁰ and shortly after O’Keeffe and Yaghi argued how special symmetry requirements can make double four-ring (D4R) units compatible with either silicates or germanates.¹¹ One step forward in zeolite synthesis was achieved when it was recognized that Ge directs the crystallization of zeolites containing D4Rs as secondary building units.¹² Working with concentrated gels containing Ge, it was possible to synthesize a large number of new zeolite topologies with pores sizes ranging from 8-ring to 30-ring, all of them containing D4Rs as structural units.

New zeolite topologies first synthesized as pure GeO_2 zeolites or silicogermanates include ASV (ASU-7¹⁰), BEC(Beta-C¹³), ITQ-21¹⁴ (I21¹⁵), IWW (ITQ-22¹⁶), IWR (ITQ-24¹⁷), IWS (ITQ-26¹⁸), ITQ-33¹⁹ (I33²⁰), ITR (ITQ-34²¹), ITQ-37,²² SOF (SU-15²³), STW (SU-32²³), UOZ (IM-10²⁴), UTL (IM-12²⁵), and UOS (IM-16²⁶). Others initially synthesized without Ge have later been synthesized containing Ge such as AST,²⁷ ITH (ITQ-13²⁸), ISV (ITQ-7²⁹), and LTA,³⁰ to name just a few. In particular, the synthesis of ISV, initially obtained as pure silica,²⁹ was accelerated by 1 order of magnitude when Ge was introduced in the synthesis gel.^{31–33} In all of these structures,

the presence of D4Rs, which tends to accommodate preferentially low TOT ($T = \text{Si, Ge}$) angles, has been pointed out as one reason to favor their presence in the final material.^{12,32–42} Although most of the zeolites containing D4Rs have been synthesized with Ge in its composition, some exceptions exist such as ACO, AFY, -CLO, DFO, ITW (ITQ-12), IWV (ITQ-27), and UFI.¹ Following these developments, some of the new topologies recently synthesized containing Ge show potential interest for technical applications, and it is a challenge to achieve the synthesis of the Ge-free polymorphs. It would then be of much interest to be able to predict which of the zeolite structures synthesized as silicogermanates could be feasible in the pure silica form and/or as aluminosilicate or borosilicate.

Similarities between SiO_2 and GeO_2 crystalline phases arise from the fact that Si and Ge have the same electronic structure in the valence shell, as well as similar ionization energies and electronegativities.⁴³ A relatively large number of germanates that are isostructural to rock-forming silicates have been synthesized and have similar physical properties⁴⁴ and similar pressure-induced phase transitions.⁴⁵ However, silicates and germanates differ in aspects such as a larger Ge–O than Si–O distance, by about 0.15 Å, and a smaller GeOGe than SiOSi angle, by roughly 15°. ⁴⁶ These differences can be ascribed to the fact that Ge is a third row element, larger than Si, a second row element, and that the GeO bond is more covalent than SiO. The narrower GeOGe angle can be explained as follows.

A study of the critical points of the electron density of the $\text{H}_6\text{Si}_2\text{O}_7$ and $\text{H}_6\text{Ge}_2\text{O}_7$ molecules reveals that the bridging anion on the latter molecule has two local maxima that can be ascribed to two nonbonded lone electron pairs, whereas that of the former molecule only has one ascribed to one nonbonded electron pair.⁴⁶ According to Gillespie’s VSEPR model,⁴⁷ nonbonded electron pairs produce larger repulsions than bonded electron pairs, and hence the $\text{H}_6\text{Ge}_2\text{O}_7$ molecule can be expected to exhibit a narrower bridging angle in minimizing bonded electron pair–nonbonded electron pair repulsions.

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GeOGe angles, therefore, tend to be narrower, but a proper characterization of the feasibility of a silicogermanate structure requires the knowledge of the energy vs GeOGe angle curve along the typical range in zeolites, about $[120^\circ, 180^\circ]$, and this also for the other two possible cases in silicogermanates, SiOSi and GeOSi. For a structure to be synthesized, stable TOT angles must be compatible with the topological constraints in the structure. The number of different TO_iT in a structure is equal to the number of different oxygens (*i*). The occurrence of each TO_iT angle, their preferential values (depending on the chemical composition, GeOGe, SiOSi, or GeOSi), and the topological constraints are the three main factors that determine the stability of a given structure. Apart from the total energy, topological features, in particular those related to TOT angles, can also be useful to assess feasibility. Force field methods are particularly good at reproducing structural traits, and hence their use will be a helpful tool throughout this study. It is the aim of the present work to analyze these factors by using computational chemistry techniques and to draw conclusions regarding the relative stability of different pure silica and pure germania phases.

2. Methodology and Models

2.1. Zeolites Studied. One objective of this study is to rationalize what is the likely outcome of a zeolite synthesis from a germanate or silicogermanate gel, and their corresponding limiting Si/Ge ratios. For this reason, an obvious choice of zeolites of interest are those which have been first obtained from such gels. They are known as “type materials” according to the International Zeolite Association (IZA), which—to date—include ASV (ASU-7¹⁰), BEC (Beta-C¹³), ITQ-21¹⁴ (I21), IWW (ITQ-22¹⁶), IWR (ITQ-24¹⁷), IWS (ITQ-26¹⁸), ITQ-33¹⁹ (I33), ITR (ITQ-34²¹), SOF (SU-15²³), STW (SU-32²³), UOZ (IM-10²⁴), UTL (IM-11²⁵), and UOS (IM-16²⁶). For the phases which are not included in the Atlas of Zeolite Framework Types, ITQ-21 and ITQ-33, the codes I21 and I33 have been used, while for the others the IZA code has been used to refer to the topology of the material. Far from being exhaustive, 11 out of the 13 above topologies have been included in our study.

Four zeolites which were not initially synthesized as germanates or silicogermanates have also been included in our study, namely, AST,²⁷ ITH (ITQ-13²⁸), ISV (ITQ-7²⁹), and LTA.³⁰ In particular, AST is one of the very few structures which has been synthesized over the entire range of Si, Ge composition.²⁷ Finally, we have also included in our study a recently synthesized pure silica phase called IHW (ITQ-32⁴⁸), whose feasibility for the incorporation of germanium we would like to consider. All together, we believe the above 16 structures comprise a representative set of zeolites to study their feasibility as germanates and silicates. Relevant compositional data of these structures are included in Table 1. It is considered throughout the calculations that the structures are perfect crystals, without defects, and hence proper comparison with experimental data should include samples as crystalline as possible.

2.2. Analysis of the TOT Angles of Pure SiO₂ and GeO₂ Zeolites. Regardless of the Si/Ge range within which these structures (Table 1) have been experimentally synthesized, a first valuable information concerns their feasibility at the end range of compositions, as pure silica and germania. Apart from the obvious interest about the pure phases, energetic comparisons between structures can only be established for equal compositions, and this is another reason to consider the pure SiO₂ and GeO₂ polymorphs. Finally, any other compositional range different from the pure phases introduces the undesirable

TABLE 1: Zeotypes Studied Including Their IZA Code (Where Available), the Name of the Type Material, and the Chemical Composition Range Achieved in the Synthesis

code	material	composition
AST	octadecasil	pure silica, pure germania, any Si/Ge
ASV	ASU-7	pure germania
BEC	Beta-C	pure germania, Si/Ge, pure silica
I21	ITQ-21	Si/Ge = 1.9, Si/Al/Ge
I33	ITQ-33	Si/Al/Ge (Si/Ge = 2.2, (Si + Ge)/Al = 24.0)
ITR	ITQ-34	Si/Ge = 10.1
IHW	ITQ-32	pure silica
ISV	ITQ-7	pure silica, Si/Ge
ITH	ITQ-13	pure silica, Si/Ge
IWR	ITQ-24	Si/Al/Ge (Si/Ge = 9.5, (Si + Ge)/Al = 20.5)
IWW	ITQ-22	Si/Ge = 4.0
LTA	A	Si/Al = 1, pure silica, Si/Ge
SOF	SU-15	Si/Ge (Si/Ge = 1.4)
STW	SU-32a	Si/Ge (Si/Ge = 1.1)
UOZ	IM-10	pure germania, Si/Ge (Si/Ge ≤ 1.0)
UTL	IM-12	Si/Ge = 4.5

possibility of several Si, Ge distributions for each Si/Ge ratio, which complicates enormously the comparison of the energetic stability across structures at a given Ge/(Si + Ge) ratio different from 0 and 1.

As indicated in Table 1, most of the zeolites have not been synthesized at the pure end compositional ranges, and an evaluation of the GeOGe and SiOSi angles can only be approached by using computational techniques. A reasonable estimation of the resulting TOT angles can only be achieved by using periodic boundary conditions which take into account properly the topological restraints specific to each structure.^{49–58} Although a quantum-chemistry approach would be desirable, the large number of structures to be considered and the large size of some unit cells would result into a very expensive approach in terms of computational resources. Further, such a quantum-chemistry approach would need to optimize not only the atomic coordinates but also the unit cell parameters of both silica and germania cases, which will result in a very high demanding computational task even for large parallel computers. Instead, we have opted to use a force field approach, which we have successfully employed in previous similar studies.^{36,38,40}

One part of our previous work was devoted to parametrize a Si, Ge force field specially suited for the simulation of zeolites throughout any compositional range.^{59,60} Such a force field is based on a typical zeolite semiempirical shell model containing short-range Buckingham T–O and O–O terms and an Ewald-based treatment of the Coulombic interactions between the formally charged atoms of the system, where three specific oxygen polarizabilities have been considered for the cases GeOGe, SiOSi, and GeOSi. The force field functional is entirely similar to one of the most successful force fields to simulate structural properties of silicate zeolites developed by Leslie, Sanders, Jackson, and Catlow.^{61–63} Small discrepancies between experimental and calculated GeOGe angles have been found when using this force field, and a workaround has been devised for the particular case of purely germania structures. Once the optimization has been achieved, the geometry has been further refined with an updated force field which takes into account ab initio data on how the energy changes with GeOGe angles. This procedure achieves the high accuracy that this study requires for the calculation of structural properties of pure GeO₂ zeolites. More details are given as Supporting Information, where the experimental data from AST, ASV, BEC, and UTL germanates have been used to compare the predictions of our new force field and where comparison with previous force fields for GeO₂

are also included, showing a clear improvement in the description of Ge—O—Ge angles, Ge—O distances, and cell parameters. The RFO (rational functional optimizer) technique was used for the cell minimization scheme with a convergence criterion of a gradient norm below 0.001 eV/Å, with all the atomic coordinates and cell parameters being optimized in each calculation, and all these computational features being used as available from the GULP (General Utility Lattice Program) software tool.⁶⁴

P1—rather than symmetry constrained—unit cells were used for the calculations so not to introduce artificial constraints. The atomic coordinates of the optimized unit cells have been geometrically analyzed, with the help of zeoTsites software,^{39,65} in order to characterize, in particular, the TOT angles present in the structure.⁶⁶

2.3. Energetics of TOT (T = Si, Ge) Angles in Zeolites.

The above force field calculations do not allow an estimation of the energy associated with TOT angles because such a specific energetic term is not present in the functional form of the force field. On the other hand, force fields containing explicit TOT terms are available, but they are not specifically suited to reproduce accurately the structure of zeolites. Moreover, such force fields containing TOT terms are only available for silicates but not for germanates or silicogermanates, and hence it is not possible to evaluate the energetics of GeOT angles within a force field approach. Therefore an alternative to the force field approach seems mandatory.

A wealth of quantum-chemistry cluster-model work has been devoted, over the years, to the study of the energetics of SiOSi angles in zeolites.^{67–77} Our study requires a proper cluster model and a well-balanced methodology to study the three cases we are considering, i.e., GeOGe, SiOSi, and GeOSi.

Rings are the essential constituents and fingerprints of zeolites,^{66,78–86} not only because zeolites can be characterized by their number and size of rings but also because rings introduce an essential strain which strongly influences the value of the TOT angles. For this reason, we have selected a ring-shaped cluster in order to calculate the energy variation of the TOT angles. Three different models have been tested for which the best result has been obtained with the H₈T₄O₄ four-ring cluster. Details of the other models are given in the Supporting Information. In the four-ring cluster, three cases have been modeled, T_i = Ge (*i* = 1–4); T_i = Si (*i* = 1–4); T_i = Si, T_j = Ge (*i* = 1, 3; *j* = 2, 4), so that in the latter all linkages are GeOSi. One of the TOT angles has been kept fixed and scanned from 120° to 180° in steps of 5°, while the rest of the cluster has been totally optimized without any symmetry constraint. It is expected that when the TOT angle is scanned, the rest of the TOT angles of the four-ring cluster can find a minimum near the absolute minimum; if this is not possible (due to the particular constraints of a four-ring), then it is clear that the energy plotted at a given TOT is a function that depends on more than one variable. In other words, conceptually speaking it is not possible, under those circumstances, to separate variables, and, consequently, TOT angles cannot be considered as independent of each other in a real zeolite structure. However, the ring-cluster approach should be successful in taking into account the constraints of zeolites due to the presence of rings.

The results of the HF/6-31G(d) calculations are shown in Figure 1. Qualitatively speaking, the shape of the curves is as expected. Lower minimum TOT angles appear for SiOSi > GeOSi > GeOGe, with the respective values being 157.7°, 137.8°, and 133.3°. The energy minimum of the SiOSi curve is somewhat larger than expected, but it should be observed (Figure

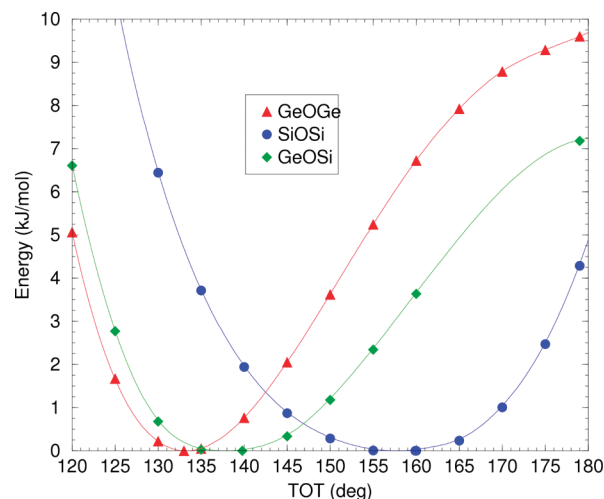


Figure 1. Plot of energetic stability of GeOGe, SiOSi, and GeOSi angles in zeotypes obtained from four-ring cluster ab initio HF/6-31G(d) results in the present study. TOT angles within 4 kJ above the minima include the following intervals (roughly): [122°, 150°] for GeOGe, [136°, 180°] for SiOSi, and [125°, 160°] for GeOSi. Minimum energies correspond to 133.3° for GeOGe, 157.7° for SiOSi, and 137.8° for GeOSi. The lines correspond to a fourth power fit whose details are given as Supporting Information.

1) that the curve shape is very flat around the energy minimum, which partially agrees with the results in the literature which locate the minimum at a somewhat lower SiOSi angle, around 147°. ^{87–95} Our minimum at 157.7°, not far from previous calculations in zeolites,⁵³ can be attributed to the particular constraints of the four-ring and, even though an equilibrium SiOSi angle close to 147° seems an optimum choice for a wide range of zeolite structures, our equilibrium SiOSi angle (157.7°) looks like a reasonable choice for the particular case of zeolites containing a large number of four-rings. Another interesting aspect of the SiOSi curve (Figure 1) is the steep energy increase at angles larger than 165°. This is attributed to the fact that, during the optimization, several SiOSi angles within the four-ring cluster take a high value and the overall energy receives the energetic contribution of several strained SiOSi angles. This would be an anomalous behavior for a cluster free from ring constraints, but, again, we believe the present model considers properly the constraints of a zeolite structure. In any case, what is more important, the tail (high angles) of the SiOSi curve indicates that high SiOSi angles are more stable than their corresponding GeOSi and GeOGe, which corresponds to the general knowledge in zeolites.^{27,56,59} In fact, although the shape of the tail for SiOSi might be too steep, we find an energy increase of 4.3 kJ/mol from 160° to 180°, which compares very well with the value of 3.8 kJ/mol obtained by Kamakoti and Barckholtz.⁴² Finally, we point out that the present results (Figure 1) indicate a very good result for the energetic behavior of the GeOGe low angles, where an increase of only 5 kJ/mol is noted from 133° to 120°. Previous results⁴² indicated an energetic penalty of 15 kJ/mol for such an interval, which we assess as too high, taking into account the experimental GeOGe angles found in zeolites.^{27,56,59} This is the main reason which prompted us to try an improved calculation of the energetic variation of TOT angles in zeolites. A detailed comparison is given as Supporting Information. Although our results in SiOSi, while being satisfactory, may not be as good as previous results,⁴² we believe that the results regarding GeOGe angles, improved with respect to a previous study,⁴² justify the use of this model.

TABLE 2: Number of Unlikely TOT Angles (%) in Zeolites with SiO₂ and GeO₂ Compositions^a

	SiO ₂	GeO ₂
AST	0	0
ASV	40	0
BEC	0	0
I21	10	17
I33	33	0
ITR	0	9
IHW	4	0
ISV	0	6
ITH	0	0
IWR	0	4
IWW	0	5
LTA	0	10
SOF	0	0
STW	10	0
UOZ	40	0
UTL	24	8

^a Unlikely angles are defined as <140° (SiOSi) and >145° (GeOGe).

3. Results and Discussion

3.1. Structural Feasibility of Silica and Germania Zeolites.

As a first approximation, the feasibility of the silica and germania zeolites has been assessed from the SiOSi and GeOGe angles resulting from the force field calculations described in section 2.2. An inspection of Figure 1 shows that SiOSi angles lower than 140° and GeOGe angles larger than 145° involve an energetic penalty larger than 2 kJ/mol. Further from such angles, the energy becomes increasingly large. This estimation is in agreement with the literature regarding Si, Ge zeolites.^{27,56,59} The relative amount of unlikely angles in the calculated pure silica and germania structures is shown in Table 2, and this is taken as an approximation to structural unfeasibility. From the data in Table 2, as well as from a detailed list of all the angles and their values (given as Supporting Information), several conclusions can be drawn. For this simple analysis, the structures containing a relatively high percentage of unlikely TOT angles (Table 2) will not be considered as feasible.

AST and BEC look favorable as both pure silica and pure germania, and this means they possess flexible structures with topologies compatible with TOT angles close to 157° (as pure silica) and close to 133° (as pure germania). UTL looks unlikely at both pure end compositions and may only be synthesized at intermediate Si, Ge ranges. I21, ITR, ISV, and LTA look unfeasible as pure germania, and ASV, I33, and UOZ look unfeasible as pure silica.

3.2. TOT Energetic Penalty and Feasibility of Silica and Germania Zeolites. We now suggest a more strict approach in which the energy associated with every TOT angle is calculated, and from the resulting energy the structural feasibility is assessed. From the force-field-optimized geometries, the TOT angles are obtained, and then their corresponding energetic contribution is evaluated from the previous ab initio approach (section 2.3 and Figure 1).

Combining both results, we have calculated the energetic penalty associated with all the TOT angles present in each silicate and germanate structure, and the results are shown in Figure 2 (numerical values are given as Supporting Information). It is arbitrary to consider what is the threshold energy above which a structure becomes unfeasible. However, to assess that, we have used experimental information as follows.

The following silica zeolites have been synthesized, with their corresponding calculated SiOSi energy according to data in

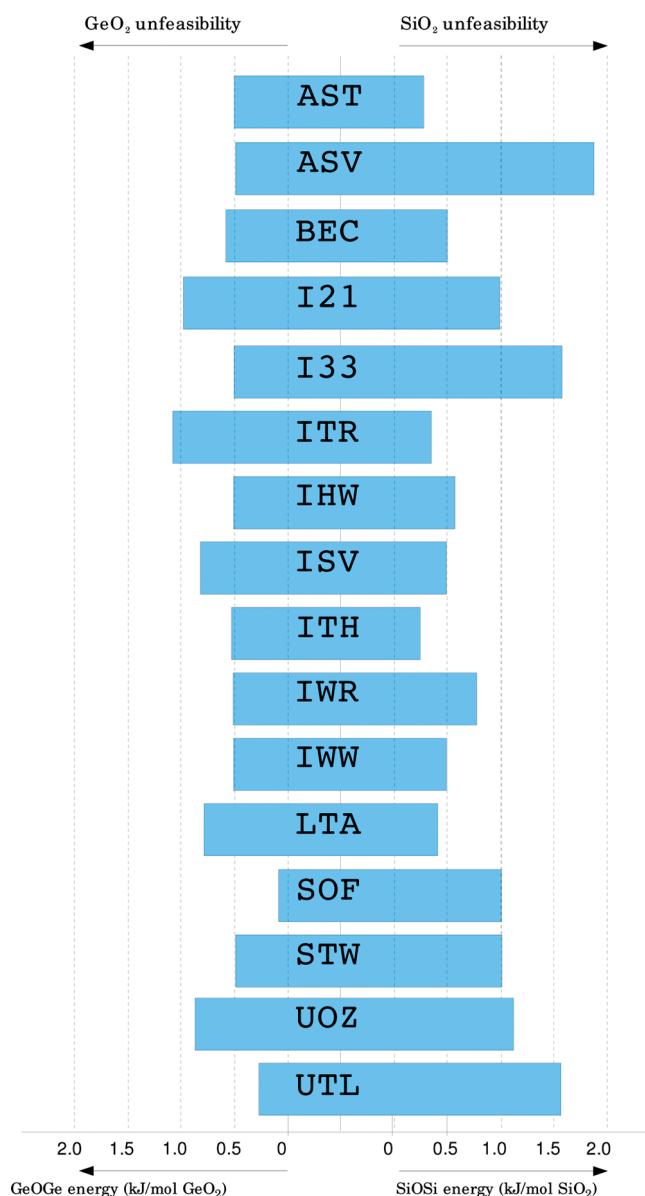


Figure 2. Feasibility of 16 different zeotypes with SiO₂ and GeO₂ compositions. TOT energies have been calculated by using the data in Figure 1. The numerical values are given as Supporting Information.

Figure 2 indicated: AST(0.3), BEC(0.5), IHW(0.6), ISV(0.5), ITH(0.3), IWR(0.8), and LTA(0.4). Using such information, 0.8 (kJ/mol SiO₂) is the maximum SiOSi energy found among the synthesized silicates. If we take structures above that value as zeolites difficult to be synthesized and below that value as experimentally feasible, an estimation about the feasibility can be made, and this is indicated in Table 3. From the data, possible silicates not yet synthesized are ITR and IWW. Also, zeolites that will be very difficult to be synthesized as silicates are estimated to be ASV, I21, I33, SOF, STW, UOZ, and UTL. According to the previous, less accurate, criteria of unlikely TOT angles (Table 2), I21, SOF, and STW were not ruled out as possible pure silicates, but the more stringent energetic criteria shown here indicate that I21, SOF, and STW could be excluded as stable pure silicates.

Similarly, for the case of pure GeO₂ zeolites, AST, ASV, BEC, and UOZ have been recently synthesized, with the following respective calculated energies (from Figure 2): 0.5, 0.5, 0.6, and 0.3 kJ/mol GeO₂. Zeotypes well above such values, which are thus assessed to be very difficult to synthesize as

TABLE 3: Estimation of the Experimental Feasibility of 16 Different Zeotypes with SiO₂ and GeO Compositions^a

	SiO ₂	GeO ₂
AST	yes ^b	yes ⁱ
ASV	no	yes ⁱ
BEC	yes ^c	yes ^j
I21	no	no
I33	no	yes
ITR	yes	no
IHW	yes ^d	yes
ISV	yes ^e	no
ITH	yes ^f	yes
IWR	yes ^g	yes
IWW	yes	yes
LTA	yes ^h	no
SOF	no	yes
STW	no	yes
UOZ	no	yes ^k
UTL	no	no

^a Underlined estimations correspond to materials already synthesized: these are of no predictive power but are in agreement with experiments. ^b Caullet, P.; Guth, J. L.; Hazm, J.; Lamblin, J. M.; Gies, H. *Eur. J. Solid State Inorg. Chem.* **1991**, 28, 345. ^c Corma, A.; Navarro, M. T.; Rey, F.; Rius, J.; Valencia, S. *Angew. Chem., Int. Ed.* **2001**, 40, 2277. ^d Cantin, A.; Corma, A.; Leiva, S.; Rey, F.; Rius, J.; Valencia, S. *J. Am. Chem. Soc.* **2005**, 127, 11560. ^e Villaescusa, L. A.; Barrett, P. A.; Cambor, M. A. *Angew. Chem., Int. Ed.* **1999**, 38, 1997. ^f Corma, A.; Puche, M.; Rey, F.; Sankar, G.; Teat, S. J. *Angew. Chem., Int. Ed.* **2003**, 42, 1156. ^g Cantin, A.; Corma, A.; Diaz-Cabañas, M. J.; Jorda, J. L.; Moliner, M. J. *Am. Chem. Soc.* **2006**, 128, 4216. ^h (a) Bibby, D. M.; Dale, M. P. *Nature* **1985**, 317, 157. (b) Corma, A.; Rey, F.; Rius, J.; Sabater, M. J.; Valencia, S. *Nature* **2004**, 431, 287. ⁱ Li, H.; Yaghi, O. M. *J. Am. Chem. Soc.* **1998**, 120, 10569. ^j Conradsson, T.; Dadachov, M. S.; Zou, X. D. *Microporous Mesoporous Mater.* **2000**, 41, 183. ^k Mathieu, Y.; Paillaud, J.-L.; Caullet, P.; Bats, N. *Microporous Mesoporous Mater.* **2004**, 75, 13.

pure GeO₂ zeolites, are I21, ITR, ISV, LTA, and UTL. Also, pure GeO₂ zeolites not yet synthesized but feasible from our data are I33, IHW, ITH, IWR, IWW, SOF, and STW. Interestingly, IHW appears low in GeOGe energy in spite of not having double four rings in its structure. As indicated previously, small GeOGe angles (close to the equilibrium 133°) are the criteria for feasibility. Such small angles can always be found in double four rings, but not only in them. In fact, some zeolites show smaller angles outside the D4R than in the D4R, such as AST and ASV (details are given as Supporting Information).

Considering the large number of D4R-containing zeolites synthesized from gels with Ge, it is reasonable to think that a large number of D4Rs could be a sufficient condition for a new topology to be experimentally feasible as germanate or silicogermanate. An analysis of the percentage of D4Rs in each structure (see Table 4) shows a large range of values such as 16–21% (UTL, ITR, ITH, IWR, IWW), 38–50% (BEC, ISV, I33, I21), 60% (AST, ASV, SOF, STW, UOZ), and 75% (LTA). Going from low to high Ge-content, once a certain Ge-content is achieved, incoming Ge tends also to locate outside the D4R, and this is a favorable process if the corresponding GeOGe (or GeOSi) angles outside the D4R are sufficiently low. In that sense, structures with relatively large values of GeOGe angles not in the D4R (see Table 4) are I21, ITR, ISV, LTA, and UTL, and these structures seem to be poor candidates to be feasible as pure GeO₂ zeolites. In agreement with this result for LTA, O’Keeffe and Yaghi also argue about LTA as a bad candidate for a pure GeO₂ zeolite structure.¹¹ This condition (low GeOGe angles required outside the D4R) is in total agreement with our previous energetic criteria, which pointed out the same structures

TABLE 4: Average GeOGe Angles (deg) Belonging and Not Belonging to D4R in 16 Different Zeotypes with GeO₂ Composition

	no-D4R	D4R	%D4Ra ^a
AST	133	140	60
ASV	132	140	60
BEC	135	132	38
I21	141	136	50
I33	137	133	39
ITR	142	137	18
IHW	136	—	0
ISV	141	137	38
ITH	137	133	21
IWR	137	133	21
IWW	138	138	21
LTA	142	140	75
SOF	134	133	60
STW	137	139	60
UOZ	136	132	60
UTL	139	139	16

^a %D4R is the percentage of GeOGe linkages belonging to D4R in the structure.

as unfeasible pure GeO₂ zeolites. According to the same principle, structures containing small GeOGe angles outside the D4R may be feasible as pure GeO₂ zeolites, and an analysis of the data (Table 4) points to structures such as AST, ASV, BEC, SOF, and UOZ, all of them containing non-D4R angles within 132°–136°. This is in agreement with experimental results for the cases of AST, ASV, BEC, and UOZ, which have been synthesized as pure GeO₂ zeolites. In addition to contrasted experiments, our results predict that SOF—with 60% of GeOGe bonds belonging to the D4R and low GeOGe angles outside the D4R—could be synthesized as pure GeO₂ zeolite, and also IHW (without D4R) could be stable as pure GeO₂ zeolite. Structures with GeOGe angles ca. 137°–138° in non-D4R (Table 4) should also be feasible, and this includes I33, ITH, IWR, IWW, and STW as possible germanates, also in agreement with the conclusions from the energetic criteria.

According to the previous conclusions, we have already established the following structures as suitable for germania compositions: AST, ASV, BEC, I33, IHW, ITH, IWR, IWW, SOF, STW, and UOZ. A related question is, what is the maximum Ge-content achievable in the remaining structures I21, ITR, ISV, and UTL? From the present results it is not possible to evaluate accurately the maximum Ge-content achievable for each zeotype, but some comparative trends can be outlined based on approximations, whose details are shown in the Supporting Information. Considering unlikely Ge-sites as those giving a large GeOGe average, the maximum Ge-content of each structure has been roughly estimated. The approximate estimations show the following maximum capacity of Ge: I21 (89%), ITR (28%), ISV (50%), and UTL (74%).

4. Conclusions

Computational chemistry techniques have been used to implement a method to calculate the relative energetic stability of silicates and germanates. This consists of a full cell optimization with an appropriate force field and, in a second step, the energetics of the resulting TOT (T = Si, Ge) angles are evaluated through functions obtained from ab initio quantum-chemistry calculations. The method relies on the assumption that the feasibility/unfeasibility of pure GeO₂ zeolites can be estimated from the distribution of TOT angles in a zeolite structure.

Equilibrium angles of 157.7°, 137.8°, and 133.3° are found for SiOSi, GeOSi, and GeOGe angles, respectively. The data of the minima, as well as the shape of the energy vs TOT plots, indicate that pure GeO₂ zeolites can only be viable with small TOT angles. The feasibilities of 16 zeolite topologies as pure silicates and germanates have been evaluated. The results show that several structures would not be feasible as pure silicates: ASV, ITQ-33, UOZ, and UTL. Structures feasible or borderline as pure silicates not yet synthesized include ITR, IWW and ITQ-21, SOF and STW, respectively. On the other hand, pure germania structures are favorable in the cases of AST, ASV, BEC, and UOZ (in agreement with experiments), as well as ITQ-33 and SOF (not yet synthesized as pure GeO₂ zeolites). Other structures feasible as pure GeO₂ zeolites, according to their distributions of GeOGe angles, close to 133°, and their low energy, are IHW, ITH, IWR, IWW, and STW.

Double four rings (D4Rs) are a common structural unit in most of the Ge-containing synthesized zeolites, and this has previously been explained due to the low angles in such building units. An analysis of TOT angles belonging and not belonging to D4Rs has been carried out, as well as a study of D4R abundance. It is proposed that the presence of a D4R is a sufficient condition to stabilize a Ge-containing zeolite. Further, the amount of D4R, as well as the values of the TOT angles not belonging to the D4R, determines the maximum Ge-content that can be achieved in the structure, which has been approximately estimated. This approach can be applied to hypothetical zeolites in order to assess their stability as silicates or germanates.

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Supporting Information Available: CIF (and XTL) files of the zeolites simulated; complete description of the cluster results; full list of the TOT force-field-optimized angle values; compressed (ZIP) files with relevant structural data and results from geometry optimizations. This information is available free of charge via the Internet at <http://pubs.acs.org>

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