

Xuehua Liu, Soledad Valero, Estefania Argente, Vicente Botti and German Sastre\*

# The importance of T··T··T angles in the feasibility of zeolites

**Abstract:** The database of prospective zeolites ([www.hypotheticalzeolites.net](http://www.hypotheticalzeolites.net)) has been screened in search of feasible zeolites. Previous criteria of zeolite feasibility have been reviewed, based on descriptors such as energy, density, average and distribution of ring sizes, and more importantly that of Li et al. (LID criteria) presented recently [*Angew. Chem. Int. Ed.* **2013**, *52*, 1673], based on Si–O, O··O, and Si··Si distances of SLC-minimised structures. In spite of the still large number of feasible zeolites according to this and other criteria, a number of researchers wonder why there are so many feasible and so few synthesised zeolites. Without answering this difficult question, a new criteria is proposed in this study based on the fact that T··T··T angles (T is tetrahedral atom) show specific ranges of values depending on the ring size to which they belong. Based on improved definitions to count and enumerate rings in zeolites, and with data from the IZA database, we introduce the TTT criteria, which we propose to use after the LID criteria, to further narrow the space of feasible zeolites.

**Keywords:** hypothetical zeolites; topology; zeolite feasibility.

DOI 10.1515/zkri-2014-1801

Received September 5, 2014; accepted December 4, 2014; published online January 21, 2015

## Introduction

The design of new materials within solid state chemistry is strongly based on our knowledge of the general rules that dictate order at the short and long range in matter. Hypothetical structures can be assessed as feasible or

unfeasible based on calculated energies or structural/topological considerations obtained from such knowledge. Hopefully, order can be recognised as a common element of stable structures [1–4], and this idea, applied to zeolites, is the topic of this study. Since the early times when zeolite science began to grow after the first zeolites were synthesised in the laboratory, there has been a certain concern in how to illustrate zeolites (in particular their channel systems) in order to make the most of their intrinsic beauty, but also with the idea that a good visualisation contributes to gain new knowledge. It comes as a well known fact that hiding the bitopic oxygens does not remove topological information and in fact the representation gains clarity, unveiling T··T··T angles. This has been a classical way to picture zeolites in a schematic yet accurate way, suggesting that further analysis might yield interesting insights.

The advent of databases of hypothetical (computer-generated) zeolites [5, 6] comes after breakthroughs regarding the systematic enumeration of zeolite nets [7–12], being the monte carlo or simulated annealing algorithms the most important part. From both approaches it is the general belief that there is a virtually infinite number of hypothetical zeolite structures, although for a given number of crystallographically nonequivalent tetrahedral sites this is a finite number. The question arises on how many zeolites can be potentially synthesised (feasible zeolites).

In addition to the classic solvothermal approach, where new gel compositions and new families of templates have contributed, among other, to the rising number of zeolites, novel methods such as ‘inverse sigma’ and ‘ADOR (assembly, disassembly, organisation, reassembly)’ approaches have been recently presented [13, 14]. They start from existing zeolites containing individual layers interconnected by D4Rs (double four rings) where a high concentration of Ge favours delamination by selective removal of the D4Rs, and where subsequent condensation may lead to one or several new fully condensed phases.

Currently, from the several million hypothetical zeolites reported in the databases, 209 uninterrupted (plus 9 interrupted) structures have been synthesised. It may be thought that the latter is a small number, but this depends

\*Corresponding author: German Sastre, Instituto de Tecnología Química U.P.V.-C.S.I.C. Universitat Politècnica de València, Avenida Los Naranjos s/n, 46022 Valencia (Spain), E-mail: gsastre@itq.upv.es

Xuehua Liu, Soledad Valero, Estefania Argente and Vicente Botti: Departamento de Sistemas Informáticos y Computación. Universitat Politècnica de València. Avenida Los Naranjos s/n, 46022 Valencia (Spain)

on the efforts dedicated to try to synthesise new zeolites. The narrow differences in their relative free energies [15] is a factor against increasing their number, although some new synthesis methods allow to overcome certain energetic barriers by following a less straight synthesis path [13, 14]. Assessing zeolite feasibility is a challenging issue and several attempts have been made [16–18]. An important result has been reported by Li et al. [19] who have been able to give eight mathematical equations involving O··O, T··T, and T··O distances (T is a tetrahedral atom), plus one more T··O based condition specifically for aluminosilicate composition. This is the so called LID criteria (local interatomic distances). Hypothetical structures fulfilling only eight criteria should be feasible pure silica zeolites, and if, in addition, the ninth condition is obeyed then the framework is feasible as aluminosilicate. Importantly, these conditions apply only to geometries minimised using the SLC force field [20]. In this study we will test if the LID criteria are enough to determine feasible structures within a database of hypothetical structures. If the LID criteria is not enough, we will add some more condition to further narrow the number of feasible structures, making the new criteria more closer to our common experience of a low number of possible zeolite framework types.

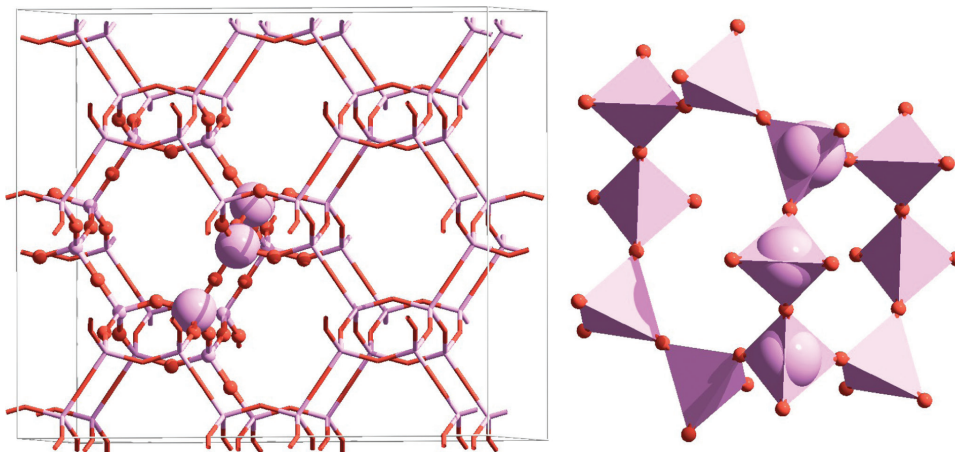
For the new criteria, we will explore T··T··T angles for the following reasons. Short-range-ordering-based criteria have been fully explored in previous studies [4, 5, 7, 9, 11, 18, 19] regarding T··O, T··T, and O··O distances, as well as O··T··O and T··O··T bonding angles. Long-range ordering parameters such as van der Waals and/or Coulombic energies seem not appropriate so as to define criteria based on zeolite topology. Criteria based on ring occurrence have not been defined

in previous studies. Instead, we believe T··T··T angles are somehow in between short and long-range criteria and they offer both a chemically intuitive justification as well as provide a direct relation to zeolite topology. The intuitive justification comes from a similar reasoning than that employed by O’Keeffe and Hyde [21] who show that Si...Si close distances in tectosilicates peak around 3.06 Å, this being related to the leading role of Si··Si non-bonding interactions [22].

If we consider a central Si ( $\text{Si}_x$ ) coordinated to four  $\text{Si}_y$  neighbours,  $\text{Si}_x$  ( $-\text{O}-\text{Si}_y$ )<sub>4</sub>, we can expect that the non-bonding interactions ( $\text{Si}_y \cdots \text{Si}_y$ ) will lead to a preferential tetrahedral distribution of the four  $\text{Si}_y$  atoms around the central  $\text{Si}_x$ , which will tend to give  $\text{Si}_y \cdots \text{Si}_x \cdots \text{Si}_y$  angles close to 109.47° [23, 24]. The three constraints mentioned have the relative strength of: “Si tetracoordination” > “Si...Si close distances close to 3.06 Å” >> “ $\text{Si}_y \cdots \text{Si}_x \cdots \text{Si}_y$  angles close to 109.47°”. The latter requirement is thus less tight, but in fact leads to the observed wide variety of zeolites and it originates from the Si...Si nonbonding (van der Waals) interactions between the extreme Si atoms ( $\text{Si}_y \cdots \text{Si}_y$ ) in each of the  $\text{Si}_y-\text{O}-\text{Si}_x-\text{O}-\text{Si}_y$  links resulting from considering any central  $\text{Si}_x$  in the zeolite.

## Methodology

The latest version of the zeoTsites software [25, 26] has been used throughout as the code is now able to: assess feasibility of a given SLC-minimised structure according to the LID criteria, list and count rings, locate T··T··T angles assigning the ring(s) to which they belong, and analyse the T··T··T angles of each ring. Special attention deserves the fact that some T··T··T angles belong, not only to one, but two rings (Figure 1).



**Fig. 1:** Two views of ABW framework. Left: A T··T··T link is highlighted which belongs to a 8-ring and to a 6-ring (both rings highlighted with ball and stick). Right: detail of the same T··T··T link.

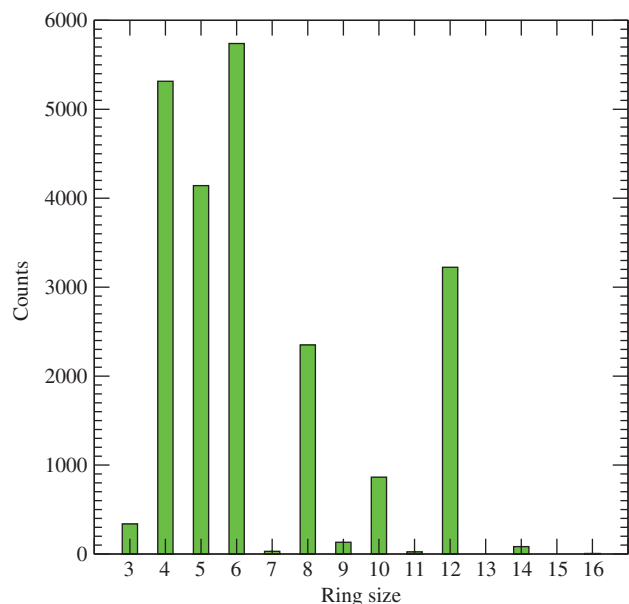
Because of that, the total number of T··T links in a zeolite framework is equal or smaller than the summation of  $n \times NR(n)$ , where  $NR(n)$  is the number of rings of  $n$ -size (formed by  $n$  T atoms and commonly called  $n$ -ring). The number of T··T links is equal to the summation of  $n \times NR(n)$  when (and only when) none of the vertex symbols contain subscripts. Subscripts in vertex symbols are treated in the work by O’Keeffe and Hyde [27]. For the definition of ring employed in this study, see our previous work [26] and literature cited. Rings have been counted in the unit cell as this is the smallest unit for which integer numbers are obtained. In unit cells the number of rings of each size are always integer numbers.

## Results and discussion

### IZA zeolites

209 IZA structures have been considered for this study [28]. Their IZA geometries (highest symmetry, DLS-optimised, pure silica composition) have been employed for the analysis of ring occurrences and Si··Si··Si angle distributions considered in this epigraph. Figure 2 shows the histogram of rings (up to a maximum size of 16-ring) found.

Compared to the histogram obtained by Earl and Deem [5], significant differences are observed, although here the number of counts is much larger, making difficult a direct comparison. Our ring counting is coincident with that of O’Keeffe and Hyde [27] and hence differences with



**Fig. 2:** Histogram of rings corresponding to 209 fully-connected frameworks in the Atlas of Zeolite Framework Types.

Earl and Deem may be due to a different definition of ring. Given the different definitions of rings in the literature [26], it is useful to include samples of ring countings for the sake of comparison. A full list of ring counting for all the 209 IZA structures explored is included as supplementary information.

It is clear that the histogram in Figure 2 will change as the number of IZA structures increase. The significant number of 3-rings only started to become prominent after Be, Ge, Zn, Ga, or combinations of them, were routinely incorporated in the synthesis gels in some laboratories. 16 out of the 23 frameworks containing 3-rings were synthesised by year 2000 or later. Individual frameworks such as BSV, LTN or PAU contain a large number of rings (2352 12-rings, 432 4-rings, 300 8-rings) and contribute notably to the histogram, hence this is another argument to show that a few new topologies could contribute to a noticeable change in the histograms in the near future. Structures with large unit cells also contribute more because rings are counted per unit cell. Hence, trends obtained from a reduced (and not random) set, such as that of synthesised zeotypes, must be drawn with care. An alternative ring counting is presented as Supplementary Information. From the set of IZA structures, a histogram of T··T angles is presented in Figure 3.

It can be guessed that peaks corresponding to maxima at 60, 90, 108, 120, etc, are due to  $180-360/n$ , where ‘ $n$ ’ is the ring size. This corresponds to the T··T angle of a planar (regular)  $n$ -ring. Although rings are not necessarily planar, a substantial number of rings deviate little from planarity, giving the peaks above. T··T angles of unplanar rings tend to be lower than  $180-360/n$  [29] and that is why the distributions do not follow symmetric gaussians but rather a Maxwell–Boltzmann function. This does not mean that we suggest that T··T angles should follow a Maxwell–Boltzmann statistics, but rather we are simply using this function for fitting purposes. The distribution of T··T angles corresponding to each  $n$ -ring ( $n=3-16$ ) has been fitted to a Maxwell–Boltzmann distribution centred at  $180-360/n$ , with an area corresponding to the total number of  $n$ -rings. The resulting envelope is only an approximation to the actual distribution of T··T angles, which indicates a more complex distribution of the ring puckering (see Figures S1, S2, Supplementary Information). Other than rationalising the distribution of T··T angles, we are just interested in obtaining approximated ranges of T··T angles (for each ring size) in feasible frameworks, those of the IZA Atlas.

For this task we have analysed the data corresponding to rings of  $n$ -size ( $n=3-16$ ), where the number of  $n$ -rings

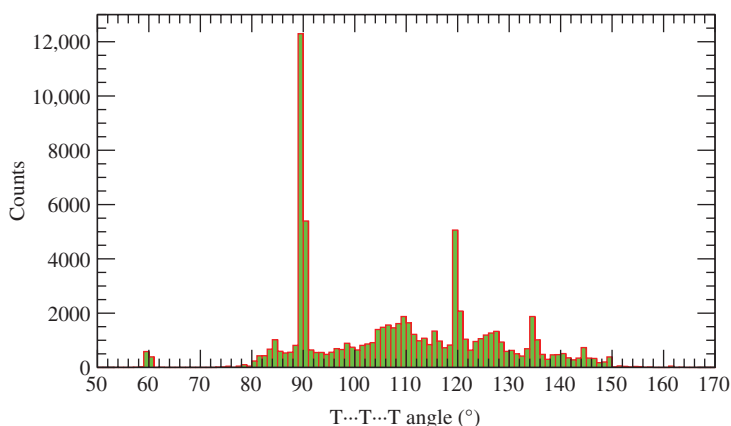


Fig. 3: Histogram of T··T··T angles corresponding to 209 fully-connected frameworks in the Atlas of Zeolite Framework Types.

analysed corresponds to the data in Figure 2. For each ring of  $n$ -size, we register the maximum T··T··T angle (maxTTT), the minimum T··T··T angle (minTTT), and the corresponding span (spanTTT = maxTTT – minTTT). The fact that some IZA frameworks have not been synthesised as pure silica or aluminosilicate is an advantage for the analysis because it leads to a larger variability of T··T··T angles. This means that the variability of T··T··T angles (for each ring size) obtained from this analysis will include all the chemical composition range of the structures currently reported.

Just for clarification let us consider an example. VNI has only been synthesised as a zincosilicate since the authors reported the structure in 1996 [30]. The structure contains some of the oddest 8-rings across the IZA database, with a minTTT = 80° in the IZA pure silica DLS-minimised (Figure S3), which can be clearly assessed as highly unusual and very far from the most frequent value of 135° in 8-rings (Figure S2). By including this as a feasible T··T··T angle for 8-rings, we are allowing the range of ‘feasible’ towards this and other zincosilicates which may be prone to show similarly shaped 8-rings. In summary, our method allows to tabulate the extreme (maxTTT, minTTT) and span (spanTTT) of T··T··T angles found for each ring size across the entire IZA database by using the data from the pure silica DLS-minimised frameworks. The fact that not the type materials but rather the pure silica have been used is not a shortcoming, but a desirable feature for two reasons. In the first place because little deviations in T··T··T angles are observed with the type material, and secondly because it provides a uniform and equivalent criteria for all frameworks regardless their chemical composition. Table 1 contains the information obtained from the analysis regarding the range of feasible T··T··T angles for rings of each size. Using the range of values for maxTTT, minTTT

and spanTTT (this will be called TTT criteria), hypothetical feasible structures (those hypothetical frameworks which pass the LID criteria) will be screened and those not passing the TTT criteria will be analysed. In light of the analysis of hypothetical frameworks (next section), conclusions regarding their feasibility will be extracted in order to justify whether or not they can be discarded as feasible zeolites.

## Hypothetical zeolites

For our study we have selected the database of hypothetical zeolites from Treacy’s group [6], of which we will screen the so called Silver database, containing all 230 space groups and 1–6 crystallographically different T-sites. Several operations were carried out for the first screening: duplicate structures were identified as those containing equal characteristics (stoichiometry, ring counting, number of T-sites, vertex symbols, and were removed. Resulting structures were energy-minimised using two different force fields. The first forcefield (BS) was specifically parameterised to reproduce energies of pure silica zeolites [31]. The second forcefield (SLC) [20] is the most universally employed in zeolites and it gives very accurate structural parameters as well as mechanical properties of high density silica polymorphs, but not so good energetics of pure silica zeolites. The latter can be seen in a previous study in our group (Figure 2B in [31]). However, the energies calculated with both forcefields were taken into account and structures with BS-energy and SLC-energy lower than 0.25 eV/SiO<sub>2</sub> with respect to quartz were selected (second screening). Then, non-porous -chlatrasil- structures were removed as they are not interesting for this study (third screening). From the

**Tab. 1:** Definition of TTT criteria. A structure is not feasible if one (or more) rings do not fulfil the three conditions. To fulfil each condition, the corresponding T··T··T angle should be in the interval indicated. The conditions have been obtained from the analysis of 209 structures in the IZA Atlas.

3-Ring: MaxTTT = [60.0, 62.3]	MinTTT = [57.5, 60.0]	Span-TTT = [0.0, 4.8]
4-Ring: MaxTTT = [75.4, 97.2]	MinTTT = [73.8, 90.0]	Span-TTT = [0.0, 19.1]
5-Ring: MaxTTT = [101.1, 125.2]	MinTTT = [77.1, 106.8]	Span-TTT = [1.1, 35.5]
6-Ring: MaxTTT = [102.5, 151.3]	MinTTT = [77.7, 120.0]	Span-TTT = [0.0, 63.4]
7-Ring: MaxTTT = [119.2, 137.2]	MinTTT = [90.0, 122.7]	Span-TTT = [11.6, 47.2]
8-Ring: MaxTTT = [108.9, 163.5]	MinTTT = [78.9, 135.0]	Span-TTT = [0.0, 76.4]
9-Ring: MaxTTT = [138.2, 148.1]	MinTTT = [84.8, 124.5]	Span-TTT = [16.6, 53.4]
10-Ring: MaxTTT = [113.9, 151.7]	MinTTT = [88.1, 138.3]	Span-TTT = [4.6, 55.2]
11-Ring: MaxTTT = [146.9, 146.9]	MinTTT = [123.6, 123.6]	Span-TTT = [23.3, 23.3]
12-Ring: MaxTTT = [133.3, 161.5]	MinTTT = [81.8, 150.0]	Span-TTT = [0.0, 67.9]
14-Ring: MaxTTT = [146.7, 155.5]	MinTTT = [105.4, 127.9]	Span-TTT = [26.7, 46.5]
16-Ring: MaxTTT = [148.3, 155.0]	MinTTT = [103.1, 108.8]	Span-TTT = [45.2, 46.3]

resulting set, the LID criteria was calculated using the SLC-minimised geometry and only structures fulfilling eight LID criteria [19] were selected (fourth screening), resulting in 2332 structures which, initially, should be feasible as zeolites. Some of these zeolites may not ‘look’ feasible zeolites (Figure S4) according to the Potter-Stewart criterion [32], a subjective and intuitive yet widely employed human recognition of feasibility according to perception of beauty and chemical knowledge. Hence, in order to introduce this criterion in a still subjective albeit more systematic and rationalised form, we propose that T··T··T angles tend to show a different and characteristic distribution depending on the ring size they belong to. From the previous analysis in IZA zeolites, Table 1 shows the intervals of T··T··T angles (maxTTT, minTTT and spanTTT) that should be obeyed for each n-ring ( $n=3-16$ ) to be considered feasible. This new criterion has been applied to the above set of 2332 structures and 349 of them have been found not to pass the TTT criteria, which means at least one of the criteria is not passed. This subset of 349 structures passing the LID criteria but not passing the TTT criteria should be discarded from the list of feasible zeolites. All structures in Figure S4 belong to this subset. An analysis of the subset indicates that 22

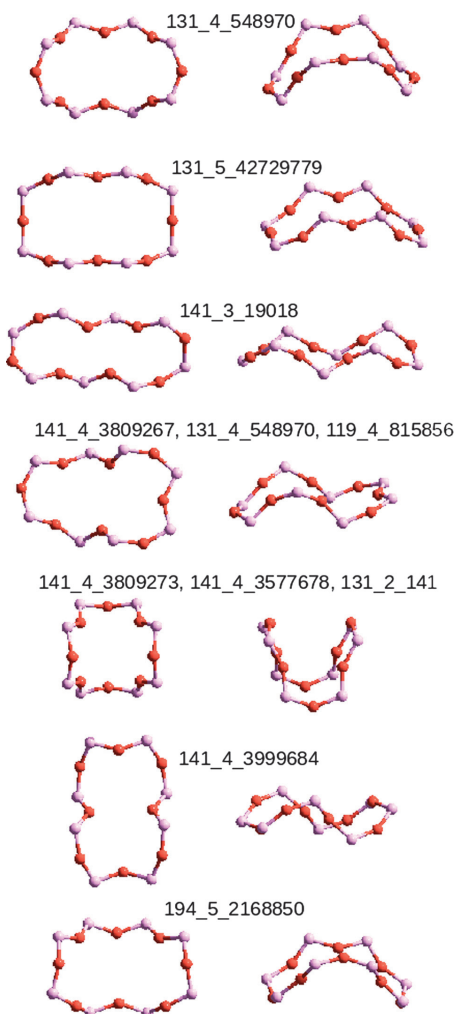
structures contain at least one 4-ring whose T··T··T angles do not pass the criteria. For the other rings, the number of structures in the subset are: 31 (5-rings), 23 (6-rings), 68 (7-rings), 10 (8-rings), 21 (9-rings), 83 (10-rings), 65 (12-rings), 24 (14-rings) and 39 (16-rings). Ten structures contain 8-rings not passing the criteria and those rings are shown in Figure 4.

All the 8-rings in Figure 4 do fulfill all chemically-based criteria such as Si–O distances, O–Si–O and Si–O–Si angles, which are well within those usually found in zeolites, and, as a consequence, energies of the structures are also within the range of feasible structures.

However, the main aspect of this study is to highlight that synthesised zeolites also show a characteristic distribution of T··T··T angles and hence we discard from the list of feasible structures those not fulfilling what we have called the TTT criteria. This does not invalidate the LID criteria of feasibility but rather we present the TTT criteria as a further refinement of the LID criteria.

Hence we suggest to employ the TTT criteria to structures screened with the LID criteria. From an intuitive viewpoint, our proposed TTT criteria provides a justification for the unfeasibility of pseudo-stable hypothetical zeolites containing abnormal rings.





**Fig. 4:** The 8-rings (two views of each ring, left and right) not passing at least one of the criteria defined in Table 1. The rings are found in the structures indicated on top. Such structures pass the LID criteria of feasibility but fail to pass the TTT criteria and hence they are not considered feasible zeolites.

## Discussion

The boundaries of what is (and not) chemically feasible are always difficult to draw. More success can be expected if we predict something that can be synthesised than if we predict something that can not, for in the latter case, time has many times discredited ‘authorised’ opinions. In the field of zeolites, the number of predicted structures is so high that we need methods to assess which ones can not (or are not likely to) be synthesised. By this, the aim is to extract the chemically feasible zeolites among the huge number of hypothetical structures in databases. A wrong prediction by one of the authors [31, 33], based on energetic criteria, established that STW would not be feasible

as pure silica due to high energy, and it was shortly after synthesised [34], and even again more recently using a different template [35]. Three reasons can be invoked to rationalise the failed prediction. ‘High energy’ is always a relative concept: higher than the highest achieved is not a too safe assumption. The ‘high energy’ should refer to the synthesis system which includes the organic template, many times omitted in the calculation of energies. Finally, many force fields do not assess energies of zeolites properly as most of them have been parameterised to reproduce structural properties.

Energetic criteria are, most of the times, restricted to pure silica zeolites and they can not be applied to structures whose tetrahedral atoms are chemically different to Si/Al such as Be, Ga and others. Other than energetic criteria, structural aspects have been collected to define the LID criteria which we have analysed in detail in this work. This happens to be, in the opinion of the authors, the most important criteria existing so far.

Previously, criteria based on density were given in connection to energy by Akporiaye and Price [36] and later by Henson et al. [37], but, the feasibility criterion is valid only for aluminosilicates. The criterion has been exploited more recently [18] and a parameter related to distance to the fitted line has been defined as feasibility factor, together with an energetic threshold considered to be 30 kJ/SiO<sub>2</sub>, and a suggested range of densities 11–21 Si atoms/1000 Å<sup>3</sup>. These are also useful criteria to assess zeolite feasibility.

An alternative approach based on the rigidity of the O–Si–O angles has been presented by Zwijnenburg et al. [38]. The authors define and quantify the tetrahedral distortion of zeolites under the ideal SiO<sub>2</sub> composition and found small values, below 0.025 Å<sup>2</sup>. For the hypothetical zeolites analysed, many of them were found above that threshold, which can be suggested as a criterion to assess zeolite feasibility, without the need of energy calculations.

Without including energetics, density was pointed out as the only parameter needed to assess feasibility in a landmark paper by Brunner and Meier [39] where a feasibility window was defined across an indicated range of densities and a parameter consisting on the average size of the smallest rings in each vertex site. This criterion has remained valid now for 25 years with almost negligible corrections. The updated version in the IZA Atlas [28] shows a line with a slightly corrected (lower) slope.

In a remarkable paper in 1993 [40], Brunner relates feasibility (pure silica and aluminosilicate) to the loop configurations, a widely known parameter in zeolites reported in the IZA Atlas [28]. Among other predictions, frameworks with the same loop configuration than FAU

are not expected as pure silica. In fact, from the 12 predicted as improbable pure silica (AEI, AFT, CHA, EMT, FAU, GIS, GME, KFI, MER, PAU, PHI and RHO), only one (AEI) has been synthesised as pure silica, SSZ-39 [41]. CHA and FAU, although reported as pure silica contain a significant number of defects. These predictions are in part made on the basis of synthesis-driven concepts and are valuable as they provide a complementary approach to those more recent which tend to be purely based on topological approaches.

Based on a ring (face-size) definition different to that in this work and related to tiling theory, Zwijnenburg et al. [42] found that the lowest energy frameworks are those with the lowest face-size variance and within an average face-size range of 4.95–5.25. However, if the energetic criterion is used to screen the database [6] and a threshold value of  $\sim 30$  kJ/mol  $\text{SiO}_2$  [18] is used, the number of unlikely structures obtained is too high (too many unlikely structures are predicted to be feasible), even if the criterion of face-size variance and average are included. On the other hand, some IZA zeolites do not fall in the average face-size range of 4.95–5.25. The analysis of Zwijnenburg et al. [42] explains that silica polymorphs of relatively high energies can be feasible if their variance of face-size distribution is relatively large. Again a warning should be raised in how accurate are the energies depending on the forcefield used. For instance Zwijnenburg et al. [42] give 13 and 20 kJ/mol  $\text{SiO}_2$  for SGT and RTH, whilst Bushuev and Sastre [31] give 9 and 10 kJ/mol  $\text{SiO}_2$  respectively. A benchmark on calculated zeolite energies with different forcefields can be found in the S.I. of Zwijnenburg et al. [42] and section 3.2 of [43], thus the role and accuracy of zeolite energetics probably deserves more attention. Another study, not using energetics, but using a similar approach than that above based on tiling theory [16] tried to correlate zeolite feasibility with the presence of certain composite building units that can be described as natural tiles, but unfortunately no clear relation was found as only 51 known zeolites (of the total set of 201 at the time of writing) can be decomposed in natural tiles, which correspond to minimal cages of the framework. This approach has the advantage of relate tiles with entities that might be not only the topological bricks but perhaps also the synthetic bricks through which the synthesis process might evolve. However, even from the synthetic viewpoint there is no clear evidence on which building units form during the nucleation.

Also in connection with synthesis methods, a definition of flexibility has been related to zeolite feasibility [17]. Such definition, in simple terms, assess zeolites as either flexible or rigid with respect to possible reorientation of

rigid regular  $\text{SiO}_{4/2}$  tetrahedra linked by force-free spherical joints at the vertices, or in other words flexible  $\text{SiOSi}$  and rigid  $\text{OSiO}$  and  $\text{SiO}$ . This is a simplification of the real flexibility of zeolites which shows three ways of deformation through  $\text{SiOSi}$  angles,  $\text{OSiO}$  angles and  $\text{SiO}$  distances [44]. However the simplification is consistent with the fact that  $\text{SiOSi}$  is the preferred mechanism of distortion. With this method, and incorporating improved algorithms to search flexibility through the symmetry modes of the crystal, practically all (at the time 201) synthesised zeolites were predicted to be flexible as pure silica or in mixed composition (GOO, CZP, ITR, IWS, ISV and STW), with the exception of 6 zeolites (including IWW and RRO). Hence, a few shortcomings are noted by the authors such that ISV and STW have been obtained as pure silica, and also RRO. Possible ways to explain the discrepancies are that: a) the method still needs improved searching algorithms, b) these structures relax through  $\text{OSiO}$  and/or  $\text{SiO}$  deformations, or c) some of the reported pure silica samples contain defects. Also an explanation would be needed on why six existing frameworks can not be calculated as flexible in mixed compositions. In any case the discrepancies are little and the approach allows to link flexibility with synthesis because frameworks showing flexibility will display more versatility in fitting (and later expelling) templates [17]. In terms of flexibility, structures 191\_2\_38, 191\_4\_3293, 191\_6\_142373, 194\_4\_62593, and 194\_5\_3301037 from the database are calculated as feasible [17]. A further analysis of these 5 structures, as minimised using SLC [20], shows that only one of them (194\_5\_3301037) is not feasible as pure silica according to the LID criteria. Using our TTT criteria, all of them are feasible, although 194\_5\_3301037 contains a very unusual 4-ring with T··T angles 89.5(2) and 73.6(2), the latter being a rare value as can be seen from Figure S2. An energetic analysis using BS [43] shows that 191\_6\_142373 is the only unfeasible structure as pure silica, showing an energy 26 kJ/mol  $\text{SiO}_2$  above that of quartz.

## Conclusions

Topological concepts help to understand, systematise, and envisage chemical applications of zeolite nets. The database of Foster and Treacy has been used in yet another attempt to find chemically feasible zeolites. A discussion of previous studies is given with the conclusion that a combination of them might yield the best possible perception of what zeolites are possible if proper synthesis conditions are enforced. A classic correlation between

density and energy is still valid although the maximum deviation from the fit has not been defined. A revision of energetics accuracy is recommended as it will improve the result of this and other analysis. The presence of certain loop configurations and/or composite building units as criterion for feasibility has been suggested or attempted but this still requires further insights both from computational and synthetic viewpoints. Average ring sizes, as calculated either from smallest vertex indices or from tiling theory (face-size) also allow to establish certain ranges of feasibility when confronted to either framework density or variance of the face size distribution. In relation to synthesis and the role of templates, a definition of flexibility that can be calculated from structural parameters allows to assess zeolite feasibility with a large rate of success among the IZA structures (~97%). And very recently a well established geometrical criterion involving T–O, O–O and T–T distances gives apparently 100% success within the IZA structures. One common shortcoming of all approaches, including ours below, is the fact that, when applied to hypothetical zeolites, the list of feasible is still huge and suspiciously too large. Recently synthesised zeolites have been many times claimed to be within the list of feasible extracted from some database, but few times failed predictions have been pointed out: those where an ‘unfeasible’ zeolite has indeed been synthesised. Exchange of predictions from different research groups may help considerably by studying in depth lists of structures that are predicted as feasible and unfeasible by different groups.

We propose a new structural criteria, called TTT criteria, which is suggested as post-criteria to LID criteria to further trim the list of feasible zeolites. Our criteria is based on the well known fact that T–T–T angles show a characteristic range of allowed variability depending on the ring to which they belong. Structures showing some ring not meeting at least one of the TTT criteria are assessed as unfeasible. As in many other studies, the range of allowed values is obtained from our limited synthetic knowledge, but most of the criteria have been extracted from data with as large statistical confidence as allowed by the limited number of zeolites synthesised. In relation to that, the criteria defined for rings with lower occurrences (7-, 9-, 11-, 14- and 16-rings) will be significantly less confident and may need to be taken with more care if ‘unfeasibility’ is going to be decided from results on those rings. An interesting point of the TTT criteria is that it includes all the compositional ranges in the current IZA structures. A further work may consist on splitting the TTT criteria for certain chemical compositions.

**Acknowledgments:** We thank ASIC computational centre of UPV for making available their computational resources. UPV is acknowledged by funding through project PAID-05-12. G. S. thanks the Spanish government for the provision of Severo Ochoa project (SEV 2012-0267) and MAT2012-31657 project. Professors Mike Treacy and Christian Baerlocher are gratefully acknowledged for useful discussions. Laurent Baumes is thanked by initial training with the database.

**Supporting information available:** List of the 209 IZA structures analysed. CIF (and XTL) files of the subset of 349 zeolites which fulfil the LID criteria but not the TTT criteria. Also, details of some of the networks analysed as well as the definition of the TTT criteria are given.

## References

- [1] W. H. Baur, One hundred years of inorganic crystal chemistry—a personal view. *Cryst. Rev.* **2014**, *20*, 64.
- [2] Y. Li, J. Yu, New stories of zeolite structures: their descriptions, determinations, predictions, and evaluations. *Chem. Rev.* **2014**, *114*, 7268.
- [3] G. Ferey, C. Mellot-Draznieks, T. Loiseau, Real, virtual and not yet discovered porous structures using scale chemistry and/or simulation. A tribute to Sten Andersson. *Solid State Sci.* **2003**, *5*, 79.
- [4] J. Klinowski, Hypothetical molecular sieve frameworks. *Curr. Opinion Solid State Mater. Sci.* **1998**, *3*, 79.
- [5] D. J. Earl, M. W. Deem, Toward a database of hypothetical zeolite structures. *Ind. Eng. Chem. Res.* **2006**, *45*, 5449.
- [6] M. D. Foster, M. M. J. Treacy, Database of hypothetical zeolite structures: [http://www.hypotheticalzeolites.net/NEWDATABASE/SILVER\\_UNIQ/query.php](http://www.hypotheticalzeolites.net/NEWDATABASE/SILVER_UNIQ/query.php).
- [7] J. V. Smith, Enumeration of 4-connected 3-dimensional nets and classification of framework silicates. I. Perpendicular linkage from simple hexagonal net. *Am. Miner.* **1977**, *62*, 703.
- [8] M. Sato, Framework topology of tectosilicates and its characterization in terms of coordination degree sequence. *J. Phys. Chem.* **1987**, *91*, 4675.
- [9] M. O’Keeffe, N. E. Brese, Uninodal 4-connected 3D nets. I. Nets without 3- or 4-rings. *Acta Cryst. A* **1992**, *48*, 663.
- [10] M. M. J. Treacy, K. H. Randall, S. Rao, J. A. Perry, D. J. Chadi, Enumeration of periodic tetrahedral frameworks. *Zeit. Krist.* **1997**, *212*, 768.
- [11] M. M. J. Treacy, I. Rivin, E. Balkovsky, K. H. Randall, M. D. Foster, Enumeration of periodic tetrahedral frameworks. Polynodal graphs. *Micropor. Mesopor. Mater.* **2004**, *74*, 121.
- [12] O. Delgado-Friedrichs, D. H. Huson, Tiling space by platonic solids. *Discrete Comput. Geom.* **1999**, *21*, 299.
- [13] E. Verheyen, L. Joos, K. Van Havenbergh, E. Breynaert, N. Kasian, E. Gobechiya, K. Houthoofd, C. Martineau, M. Hinterstein, F. Taulelle, V. Van Speybroeck, M. Waroquier,



- S. Bals, G. Van Tendeloo, C. E. A. Kirschhock, J. A. Martens, Design of zeolite by inverse sigma transformation. *Nat. Mater.* **2012**, *11*, 1059.
- [14] W. J. Roth, P. Nachtigall, R. E. Morris, P. S. Wheatley, V. R. Seymour, S. E. Ashbrook, P. Chlubna, L. Grajciar, M. Polozij, A. Zukal, O. Shvets, J. Cejka, A family of zeolites with controlled pore size prepared using a top-down method. *Nat. Chem.* **2013**, *5*, 628.
- [15] A. Navrotsky, O. Trofymuk, A. A. Levchenko, Thermochemistry of microporous and mesoporous materials. *Chem. Rev.* **2009**, *109*, 3885.
- [16] V. A. Blatov, G. D. Ilyushin, D. M. Proserpio, The zeolite conundrum: why are there so many hypothetical zeolites and so few observed? A possible answer from the zeolite-type frameworks perceived as packings of tiles. *Chem. Mater.* **2013**, *25*, 412.
- [17] C. J. Dawson, V. Kapko, M. F. Thorpe, M. D. Foster, M. M. J. Treacy, Flexibility as an indicator of feasibility of zeolite frameworks. *J. Phys. Chem. C* **2012**, *116*, 16175.
- [18] D. Majda, F. A. Almeida Paz, O. Delgado Friedrichs, M. D. Foster, A. Simperler, R. G. Bell, J. Klinowski, Hypothetical zeolitic frameworks: in search of potential heterogeneous catalysts. *J. Phys. Chem. C* **2008**, *112*, 1040.
- [19] Y. Li, J. Yu, R. Xu, Criteria for zeolite frameworks realizable for target synthesis. *Angew. Chem. Int. Ed.* **2013**, *52*, 1673.
- [20] M. J. Sanders, M. Leslie, C. R. A. Catlow, Interatomic potentials for SiO<sub>2</sub>. *J. Chem. Soc. Chem. Commun.* **1984**, *19*, 1271.
- [21] M. O'Keeffe, B. G. Hyde, On SiOSi configurations in silicates. *Acta Cryst. B* **1978**, *34*, 27.
- [22] M. O'Keeffe, B. G. Hyde, The role of nonbonded forces in crystals. *Structure and Bonding in Crystals*, Academic Press, New York, Vol. 1, Chapter 10, pp. 227–254, 1981.
- [23] M. W. Deem, J. M. Newsam, Determination of 4-connected framework crystal structures by simulated annealing. *Nature* **1989**, *342*, 260.
- [24] G. O. Brunner, Criteria for the evaluation of hypothetical zeolite frameworks. *Zeolites* **1990**, *10*, 612.
- [25] G. Sastre, J. D. Gale, ZeoTsites: a code for topological and crystallographic tetrahedral sites analysis in zeolites and zeotypes. *Micropor. Mesopor. Mater.* **2001**, *43*, 27.
- [26] G. Sastre, A. Corma, Topological descriptor for oxygens in zeolites analysis of ring counting in tetracoordinated nets. *J. Phys. Chem. C* **2009**, *113*, 6398.
- [27] M. O'Keeffe, S. T. Hyde, Vertex symbols for zeolite nets. *Zeolites* **1997**, *19*, 370.
- [28] (a) Ch. Baerlocher, L. B. McCusker, D. H. Olson, Atlas of Zeolite Framework Types, 6<sup>th</sup> Revised Edition, Amsterdam: Elsevier **2007**. (b) The current version of the Atlas in the web [<http://www.iza-structure.org>] at the time of writing contains 218 structures, of which 9 interrupted structures will not be considered in this study. A list of the 209 frameworks included in this study is given as supplementary material.
- [29] L. Stixrude, M. S. T. Bukowinski, Rings, topology, and the density of tectosilicates. *Am. Miner.* **1990**, *75*, 1159.
- [30] L. B. McCusker, R. W. Grosse-Kunstleve, Ch. Baerlocher, M. Yoshikawa, M. E. Davis, Synthesis optimization and structure analysis of the zinco-silicate molecular sieve VPI-9. *Micropor. Mesopor. Mater.* **1996**, *6*, 295.
- [31] Y. G. Bushuev, G. Sastre, Feasibility of pure silica zeolites. *J. Phys. Chem. C* **2010**, *114*, 19157.
- [32] Are all of these structures really prospective zeolite structures? <http://www.hypotheticalzeolites.net/wordpress/>.
- [33] G. Sastre, A. Corma, Predicting structural feasibility of silica and germania zeolites. *J. Phys. Chem. C* **2010**, *114*, 1667.
- [34] A. Rojas, M. A. Cambor, A pure silica chiral polymorph with helical pores. *Angew. Chem. Int. Ed.* **2012**, *51*, 3854.
- [35] J. E. Schmidt, M. W. Deem, M. E. Davis, Synthesis of a specified, silica molecular sieve by using computationally predicted organic structure-directing agents. *Angew. Chem. Int. Ed.* **2014**, *53*, 8372.
- [36] D. E. Akporiaye, G. D. Price, Relative stability of zeolite frameworks from calculated energetics of known and theoretical structures. *Zeolites* **1989**, *9*, 321.
- [37] N. J. Henson, A. K. Cheetham, J. D. Gale, Theoretical calculations on silica frameworks and their correlation with experiment. *Chem. Mater.* **1994**, *6*, 1647.
- [38] M. A. Zwiijnenburg, A. Simperler, S. A. Wells, R. G. Bell, Tetrahedral distortion and energetic packing penalty in zeolite frameworks: linked phenomena? *J. Phys. Chem. B* **2005**, *109*, 14783.
- [39] G. O. Brunner, W. M. Meier, Framework density distribution of zeolite-type tetrahedral nets. *Nature* **1989**, *337*, 146.
- [40] G. O. Brunner, Which frameworks will form SiO<sub>2</sub> analogs? The significance of loop configurations. *Zeolites* **1993**, *13*, 592.
- [41] P. Wagner, Y. Nakagawa, G. S. Lee, M. E. Davis, S. Elomari, R. C. Medrud, S. I. Zones, Guest/host relationships in the synthesis of the novel cage-based zeolites SSZ-35, SSZ-36, and SSZ-39. *J. Am. Chem. Soc.* **2000**, *122*, 263.
- [42] M. A. Zwiijnenburg, S. T. Bromley, M. D. Foster, R. G. Bell, O. Delgado-Friedrichs, J. C. Jansen, T. Maschmeyer, Toward understanding the thermodynamic viability of zeolites and related frameworks through a simple topological model. *Chem. Mater.* **2004**, *16*, 3809.
- [43] Y. G. Bushuev, G. Sastre, Atomistic simulations of water and organic templates occluded during the synthesis of zeolites. *Micropor. Mesopor. Mater.* **2009**, *129*, 42.
- [44] G. D. Gatta, Extreme deformation mechanisms in open-framework silicates at high-pressure: evidence of anomalous inter-tetrahedral angles. *Micropor. Mesopor. Mater.* **2010**, *128*, 78.

**Supplemental Material:** The online version of this article (DOI: 10.1515/zkri-2014-1801) offers supplementary material, available to authorized users.