

ZSE Manuscript Outline

Jerry T. Crum^a, Justin R. Crum^b, William F. Schneider^{a,c}

^a Department of Chemical and Biomolecular Engineering, University of Notre Dame, 250 Nieuwland Science Hall, Notre Dame, IN 46556, USA

^b Department of Applied Mathematics, University of Arizona, 617 N Santa Rita Ave, Tucson, AZ 85721, USA

^c Department of Chemistry and Biochemistry, University of Notre Dame, 251 Nieuwland Science Hall, Notre Dame, IN 46556, USA

Introduction

- Topology of zeolite frameworks and associated tetrahedral sites (T-sites) are commonly characterized by their associated rings
- Rings are defined as a close cycle traversing the T-site and oxygen atoms of the framework, and cannot be decomposed into smaller cycles by a shortcut.¹
- A shortcut is defined as a path connecting two nodes of a cycle that is shorter than both the paths connecting those nodes along the cycle.
- See Figure 1 for example of rings
 - The blue highlighted cycle (8-3-4-5-6-7) is a 6-membered ring (6-MR)
 - The green highlighted cycle (1-2-3-8) is a 4-MR
 - The cycle following 1-2-3-4-5-6-7-8 is not an 8-MR because there is a shortcut connecting nodes 3 and 8.

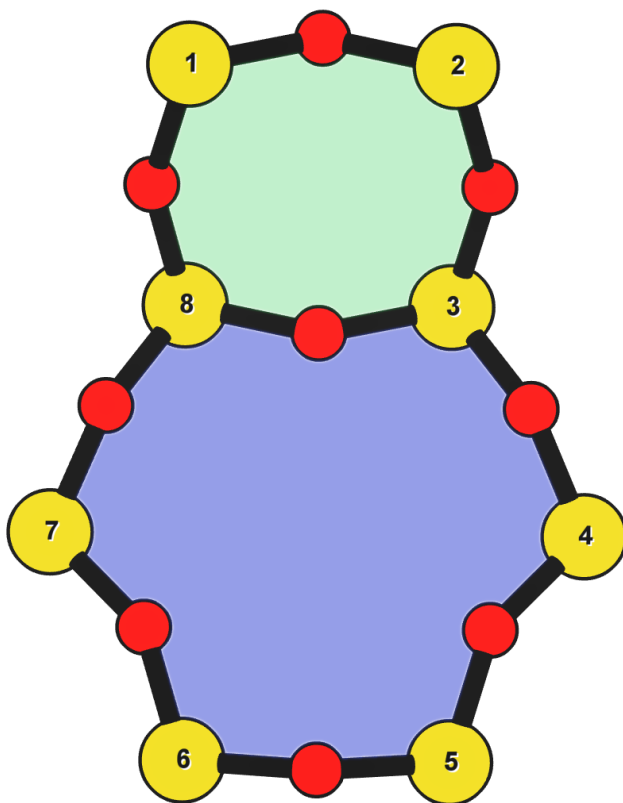


Figure 1: Cutout of the Chabazite framework showing a 6-MR in blue and a 4-MR in green. Yellow atoms are Si (T-sites), and red atoms are oxygen.

- Rings have been used to identify feasible zeolite topologies,² to describe the similarity and differences between zeolites,³ to identify sites or voids of catalytic relevance,^{4,5} and as machine learning finger prints [will get citations for this]
- Different methods exist to count rings present in a zeolite
- These methods return different sets of rings

- Vertex symbols are the set of shortest paths connecting the 6 oxygen-oxygen pairs around a T-site⁶
- Shortest path rings count all the vertex symbol rings that pass through a T-site or an oxygen atom⁷
- Or we can count all the rings that do not have a short cut¹
- Differences in ring counts leads to differences in how we describe the topology of zeolites. Therefore, when discussing the rings in a zeolite it is important to also state which method of ring counting is used.
- Here we report an analysis of rings and T-sites in a large number of zeolite frameworks using Zeolite Simulation Environment, a Python package that implements an efficient algorithm presented by Goetzke and Klein¹ for finding rings in arbitrary frameworks.
- We compare the results of a number of common and new ring definitions applied to a large number of common zeolite frameworks.⁴

Software Description

- All of the frameworks listed on the IZA Database of zeolite structures⁸ are included in a database with ZSE
- These structures are Atomic Simulation Environment Atoms objects,⁹ and can be used with any of the functions in ZSE
- ZSE also includes CIF tools to read structure files for frameworks not listed in the IZA website, such as hypothetical zeolites, and return an Atoms object that can be used with ZSE
- ZSE has 3 previously published rules for ring finding implemented
 - All cycles with out a shortcut¹
 - All shortest path cycles⁷
 - Cycles that compose the vertex symbol for a T-site⁶
- We have also implemented a new rule that finds all rings with out a shortcut, but excludes rings that are made by traversing a stacked set of rings.
 - Figure showing example of 8-MR in the d6r of CHA and 14-MR in AFI
- Each of the rules: shortest path, vertex symbols, and our new rule are a subset of the no shortcuts rule

Process to find rings:

1. To find rings in a zeolite, ZSE makes a custom connectivity matrix for the Si and O atoms in the framework
2. We use NetworkX¹⁰ to build a shortest path matrix for every atom pair in the zeolite framework
3. We then find all the rings up to some cutoff size base on the algorithm presented by Goetzke and Klein¹
4. Depending on the rule chosen by the user, ZSE then removes rings from this list that don't meet the qualifications of the rule

5. ZSE returns a list of the rings found, a list of the atom indices that compose each ring, Atoms objects for each ring that can be further analyzed or visualized by the user

Results

- Ring counts frequency plots
 - Plot showing how many frameworks on the IZA contain each size ring found using the various ring counting methods
 - This highlights the differences in the ring rules, and shows that results will vary depending on rule.

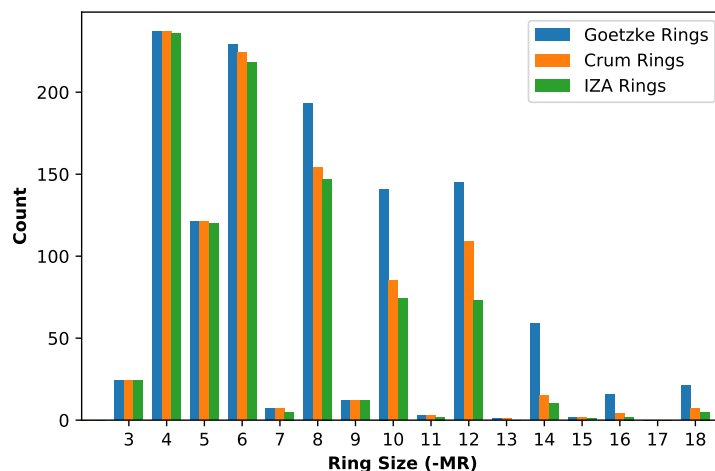


Figure 2: Number of IZA frameworks containing each size ring, using the various ring counting rules. [This will be updated with the Sastre method, vertex method, and the rings listed on the IZA website]

- Number of unique T-sites
 - There are 1460 T-sites through all the frameworks listed on the IZA website.
 - We can characterize those T-sites by the rings that pass through them
 - Sastre did this, and called the list of rings, the ring index
 - If we do this using different rules for ring finding how do the results change?
 - * See Figure 3
 - Most common T-site ring index using Goetzke method is: $5_6 \bullet 10_4$ showing up 23 times through the IZA frameworks.
 - Most common T-site ring index using Crum method is: $4_3 \bullet 8_4$ showing up 31 times through the IZA frameworks.
 - * Next most common T-site with Crum method is $5_6 \bullet 10_4$ showing up 25 times
 - This raises the question, if you want to use machine learning to correlate T-site rings to chemical properties, which ring method should you use?

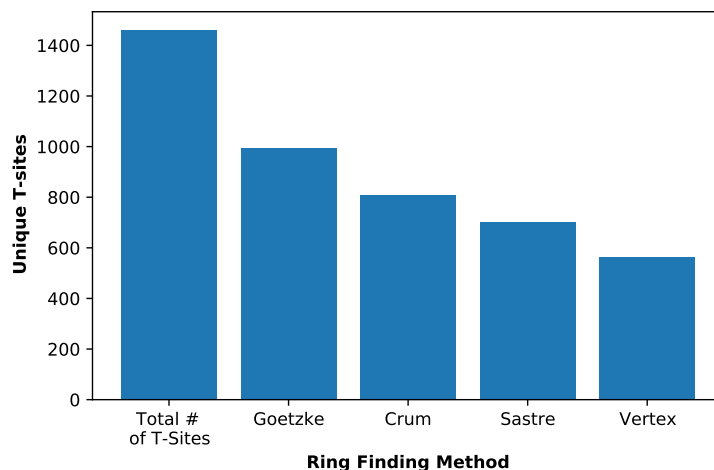


Figure 3: Number of unique T-sites when classified by the rings passing through them using varrious ring finding rules. [Sastre and Vertex method to be updated, still collecting data]

- Number of unique oxygen sites
 - We can repeat this method for the oxygen atoms in all the frameworks
 - There are 3219 oxygen atoms through all the frameworks listed on the IZA website
 - Figure here showing counts based on ring finding rules
- Reproduce the results from Sastre paper, show ring counts with the other rules, Table 1
 - Results in the Sastre column were found using ZSE but agree directly with the results shown by Sastre and Corma⁷
 - This provides an in depth look at some of the frameworks and the differences in rings found by each rule.
 - Leads into the next section discussing the specific rings of CHA and pentasil that do or don't get counted by each rule.

Table 1: Comparison of Ring Indices for the T-sites in Various Uninodal Zeolite Frameworks

Framework	Goetzke	Crum	Sastre ⁷
ABW	$4_2 \bullet 6_3 \bullet 8_4$	$4_2 \bullet 6_3 \bullet 8_4$	$4_2 \bullet 6_3 \bullet 8_4$
ACO	$4_3 \bullet 6_3 \bullet 8_6 \bullet 10_{15}$	$4_3 \bullet 8_6$	$4_3 \bullet 8_6$
AFI	$4_1 \bullet 6_{13} \bullet 12_1 \bullet 14_7$	$4_1 \bullet 6_{13} \bullet 12_1$	$4_1 \bullet 6_{13}$
ANA	$4_2 \bullet 6_2 \bullet 8_{16}$	$4_2 \bullet 6_2 \bullet 8_{16}$	$4_2 \bullet 6_2 \bullet 8_{16}$
ATO	$4_1 \bullet 6_9 \bullet 8_8 \bullet 12_{20}$	$4_1 \bullet 6_9 \bullet 12_{20}$	$4_1 \bullet 6_9$
BCT	$4_1 \bullet 6_6 \bullet 8_{20}$	$4_1 \bullet 6_6 \bullet 8_{12}$	$4_1 \bullet 6_6$
CHA	$4_3 \bullet 6_1 \bullet 8_6 \bullet 12_1$	$4_3 \bullet 6_1 \bullet 8_2 \bullet 12_1$	$4_3 \bullet 6_1 \bullet 8_2$
DFT	$4_2 \bullet 6_6 \bullet 8_{10} \bullet 10_{10}$	$4_2 \bullet 6_6 \bullet 8_{10}$	$4_2 \bullet 6_6 \bullet 8_{10}$
GIS	$4_3 \bullet 8_4$	$4_3 \bullet 8_4$	$4_3 \bullet 8_4$
GME	$4_3 \bullet 6_1 \bullet 8_6 \bullet 12_7$	$4_3 \bullet 6_1 \bullet 8_2 \bullet 12_1$	$4_3 \bullet 6_1 \bullet 8_2$
MER	$4_3 \bullet 8_4 \bullet 10_{10} \bullet 14_{14}$	$4_3 \bullet 8_4$	$4_3 \bullet 8_4$
MON	$4_1 \bullet 5_5 \bullet 8_6$	$4_1 \bullet 5_5 \bullet 8_6$	$4_1 \bullet 5_5 \bullet 8_6$
NPO	$3_1 \bullet 6_6 \bullet 12_{40}$	$3_1 \bullet 6_6 \bullet 12_{40}$	$3_1 \bullet 6_6$

- Show the cage belts results for CHA, AFT, etc... and discuss how those rings don't show up in previous literature, Figure 4

- Looking at results from CHA we see the Goetzke method finds $4_3 \bullet 6_1 \bullet 8_6 \bullet 12_1$
- This is different from the results in the Sastre paper,⁷ in that they only show 2 8-MRs and no 12-MRs
- The extra 8-MRs result from cycles traversing nodes in both 6-MRs of the d6r
- The 12-MR is a cycle that circumferences the CHA cage

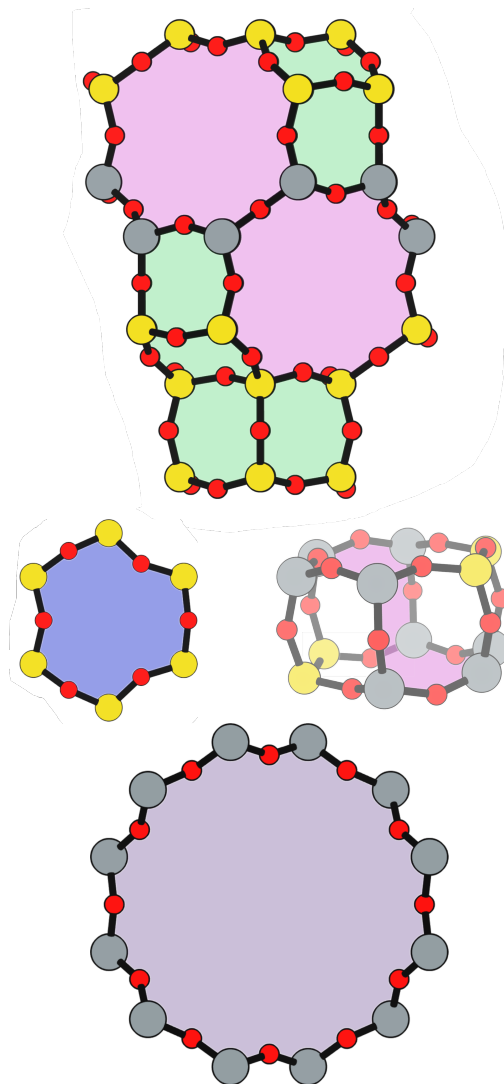


Figure 4: Chabazite framework with highlighted rings: 4-MR in green, 6-MR in blue, 8-MR in pink, 12-MR in purple. The 8-MR in the d6r and the 12-MR are rings not typically discussed in literature. This is a placeholder figure, I want to show the rings in CHA for discussion. Hoping to get your input on how best to do that.

- Show the pentasil 6-membered cycle (MFI) and discuss how that is often considered a ring by catalysis researchers, but not a ring by the Goetzke definition

Conclusions

- The method used to find rings in a zeolite will provide different ring counts
- When discussing rings in a zeolite it is import to disclose by which method those rings were found

- Using ZSE we can find rings based on various methods
- This provides a foundation for using ring fingerprints in machine learning models to correlate chemical properties and topology

References

- [1] Goetzke, K. and Klein, H.-J. Properties and efficient algorithmic determination of different classes of rings in finite and infinite polyhedral networks. *Journal of Non-Crystalline Solids*, 127(2):215–220, February 1991. ISSN 0022-3093. doi: 10.1016/0022-3093(91)90145-V. URL <https://linkinghub.elsevier.com/retrieve/pii/002230939190145V>.
- [2] Li, X. and Deem, M. W. Why Zeolites Have So Few Seven-Membered Rings. *The Journal of Physical Chemistry C*, 118(29):15835–15839, July 2014. ISSN 1932-7447, 1932-7455. doi: 10.1021/jp504143r. URL <https://pubs.acs.org/doi/10.1021/jp504143r>.
- [3] Curtis, R. A. and Deem, M. W. A Statistical Mechanics Study of Ring Size, Ring Shape, and the Relation to Pores Found in Zeolites. *Journal of Physical Chemistry B*, 107:8612–8620, 2003.
- [4] Li, S., Li, H., Gounder, R., Debellis, A., Müller, I. B., Prasad, S., Moini, A., and Schneider, W. F. First-Principles Comparison of Proton and Divalent Copper Cation Exchange Energy Landscapes in SSZ-13 Zeolite. *The Journal of Physical Chemistry C*, 122(41):23564–23573, October 2018. ISSN 1932-7447, 1932-7455. doi: 10.1021/acs.jpcc.8b07213. URL <https://pubs.acs.org/doi/10.1021/acs.jpcc.8b07213>.
- [5] Kester, P. M., Crum, J. T., Li, S., Schneider, W. F., and Gounder, R. Effects of Brønsted acid site proximity in chabazite zeolites on OH infrared spectra and protolytic propane cracking kinetics. *Journal of Catalysis*, 395:210–226, March 2021. ISSN 00219517. doi: 10.1016/j.jcat.2020.12.038. URL <https://linkinghub.elsevier.com/retrieve/pii/S0021951721000191>.
- [6] O’Keeffe, M. and Hyde, S. Vertex symbols for zeolite nets. *Zeolites*, 19(5-6):370–374, November 1997. ISSN 01442449. doi: 10.1016/S0144-2449(97)00133-4. URL <https://linkinghub.elsevier.com/retrieve/pii/S0144244997001334>.
- [7] Sastre, G. and Corma, A. Topological Descriptor for Oxygens in Zeolites. Analysis of Ring Counting in Tetracoordinated Nets. *The Journal of Physical Chemistry C*, 113(16):6398–6405, April 2009. ISSN 1932-7447, 1932-7455. doi: 10.1021/jp8100128. URL <https://pubs.acs.org/doi/10.1021/jp8100128>.
- [8] Baerlocher, C. and McCusker, L. B. *Database of Zeolite Structures*. URL <http://www.iza-structure.org/databases/>.
- [9] Larsen, A. H., Castelli, I. E., Christensen, R., Du, M., Groves, M. N., Jennings, P. C., Jensen, P. B., Kermode, J., Kitchin, J. R., Kolsbjerg, E. L., Kubal, J., Kaasbjerg, K., Lysgaard, S., Maxson, T., Olsen, T., Pastewka, L., Peterson, A., Rostgaard, C., Schi, J., Thygesen, K. S., Vegge, T., Vilhelmsen, L., Walter, M., Zeng, Z., and Jacobsen, K. W. The atomic simulation environment—a Python library for working with atoms. *J. Phys.*, page 31, 2017.
- [10] Hagberg, A. A., Schult, D. A., and Swart, P. J. Exploring network structure, dynamics, and function using networkx. In Varoquaux, G., Vaught, T., and Millman, J., editors, *Proceedings of the 7th Python in Science Conference*, pages 11 – 15, Pasadena, CA USA, 2008.