Computational Study of the Reversible Opening and Closing of the COK-14 zeolite.

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Abstract

Recently, a new zeolite was synthesized by acid leaching of the layered IM-12 zeolite (UTL topology) [1,2]. First, germanate four-rings are dislodged, allowing the framework to contract. The Ge-4R subsequently shift into the channels (Ge-COK-14) and are later eliminated, resulting in a systematically interrupted framework, indicated by -COK14. The newly discovered COK14 framework shows some remarkable properties.

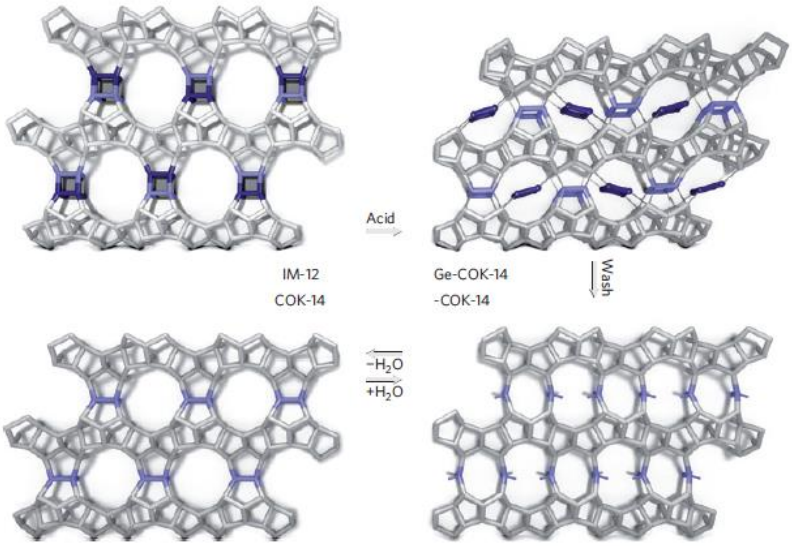

Fig. 1 | Acid leaching of IM-12 zeolite dislodges germanate four-rings. The Ge-4R units are shifted into the channels of Ge-COK-14 and later removed (-COK-14). The systematically interrupted framework can be closed upon calcination (COK14).

First of all, the as-synthesized material is a systematically interrupted framework, exposing silanol (-OH) groups along the 12-membered ring, **Static Density Functional Theory calculations** and **partial vibrational analysis** show that water is strongly bound as it bridges two silanol groups, explaining experimental observations from **Thermogravimetric Analysis** and **Infra-red spectroscopy**.

Secondly, when heating the zeolite above 700 K, the silanol groups condense and the systematically interrupted structure closes. Exposing the closed framework to ambient air will result again in the opening of COK-14. COK-14 is the first zeolite framework that can reversibly open and close and it is hence also the first time that this unique behavior has been investigated with computational techniques.

First, we treated this opening/closing behavior with static **calculations** and assigned a transition state for the first hydrolysis step with the **climbing-Nudged Elastic Band** method. This 0 K reaction profile could however not explain the experimental observations.

Full vibrational analysis of the interrupted -COK14 and the fully connected COK14 framework confirmed that the entropy of the entire framework plays a role in the reversible opening and closing of the framework. Aside geometrical optimization, an **optimization along the imaginary vibrational modes** was also necessary to obtain a framework free of imaginary frequencies.

Furthermore, **Metadynamics Simulations** provide deeper insight in the reaction path while treating the framework fully flexible. As expected the potential energy landscape changes drastically at high temperature.

In conclusion: a wide variety of computational techniques was used to explain some of the remarkable features of this novel material. Theoretical results were linked to experimental results and the different types of simulations were compared among each other. This provided a better understanding of the reversible opening and closing behavior of the COK14 topology.

References:

[1] Nature Materials 11 (**2012**) 1059
[2] Chemical Communications 50 (**2014**) 4610