

 HETEROGENEOUS CATALYSIS

À la carte zeolites

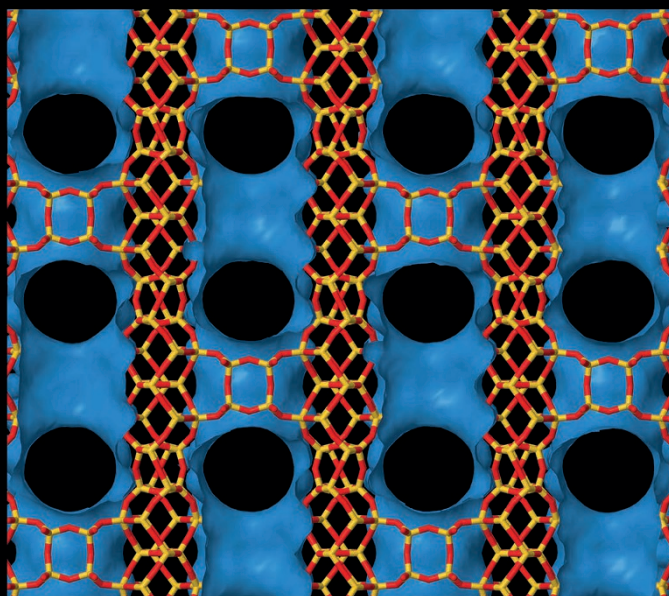


Image courtesy of A. Corma, Universitat Politècnica de València, Spain.

Knowing the structures of products and the transition states of organic reactions allows one to design catalysts with superior performance for these conversions. For example, with pre-established organic reactions in mind, one can develop optimal zeolite catalysts, as demonstrated by Avelino Corma and co-workers in *Science*.

The high active surface area of microporous materials, such as zeolites, makes them suitable as catalysts for various chemical reactions, including the treatment of toxic gases and refining of fuels. The high catalytic activity of zeolites stems from the confined and uniform nature of their pores — well-defined compartments in which reactions can occur. Rate enhancement occurs when the transition state is stabilized by weak interactions with the pore walls, thereby lowering the activation energy.

“The usual process to select a zeolite that acts as a catalyst for a specific reaction starts with the

synthesis of zeolites in the presence of organic structure-directing agents (OSDAs), which guide the formation of pores and cavities,” explains Corma. “Then, zeolites with different pore dimensions and topologies are screened as catalysts for different reactions, and the best catalysts are selected and optimized.” In this work, Corma and co-workers explored an inverse design approach by first choosing a certain organic reaction and then preparing a zeolite catalyst tuned for the particular transition state. The pore walls in the optimized catalyst interact effectively with the transition state, such that the activation energy of the reaction is minimized. Different approaches — including the use of imprinted antibodies or imprinted silica — exist to synthesize hosts with pores of given dimensions. Corma and colleagues decided to template their zeolites using OSDAs that mimic the transition state of a

specific reaction, resulting in zeolite–OSDA systems with structures that may or may not be new. Finally, the zeolite–OSDA product is subjected to high-temperature calcination to remove the organic template, leaving the crystalline zeolite intact (a process that would not be successful for imprinted amorphous silicas). The zeolite is now ready to be used as a catalyst for the organic reaction for which it was designed.

This new methodology was tested in the synthesis of catalysts for three reactions, namely: toluene disproportionation into benzene and xylenes, isomerization of ethylbenzene to xylenes, and *endo*-dicyclopentane isomerization to adamantane. Toluene disproportionation is catalysed by the zeolite ITQ-27, a known material that had never been used before for this reaction and one that was found to have a higher activity than the zeolite currently in commercial use. Another zeolite, ITQ-64, was optimized for ethylbenzene isomerization. Despite a lower conversion activity than that of the commonly used silica-based catalysts, ITQ-64 exhibits higher selectivity for *o*- and *p*-xylene rather than the undesirable *m*-xylene. Finally, zeolite MIT-1 was synthesized and used in *endo*-dicyclopentane isomerization. Corma points out that MIT-1 is similar in structure and overall selectivity to another zeolite discovered by the same group (ITQ-2).

“Our results show that, when possible, this methodology should allow us to make more selective solid catalysts in a rational manner,” explains Corma. He then concludes: “I believe that the main implication of this study is that it is possible to attempt a type of *ab initio* zeolite synthesis, opening new possibilities for making, at least in some cases, à la carte structures.”

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ORIGINAL ARTICLE Gallego, E. M. et al. “*Ab initio*” synthesis of zeolites for preestablished catalytic reactions. *Science* **355**, 1051–1054 (2017)

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