

APRIL 21, 2008 EDITED BY WILLIAM G. SCHULZ & LAUREN K. WOLF

SIZE-SELECTIVE ACID CATALYSIS

MICROPOROUS MATERIALS:
Framework pores control substrate access to exposed metal ions

METAL-ORGANIC FRAMEWORKS (MOFs), once synonymous only with hydrogen gas storage, are starting to show their potential as selective catalysts. In the latest development on this front, Jeffrey R. Long and coworkers at the University of California, Berkeley, have demonstrated how to take advantage of a MOF's pore size to precisely select substrates for heterogeneous catalytic reactions (*J. Am. Chem. Soc.*, DOI: 10.1021/ja800669j).

MOFs are porous crystalline materials typically made up of multimetal clusters interconnected by organic linkers. The researchers began their study by probing the catalytic activity of a manganese benzenetetracarboxylate MOF (Mn-BTT), a material Long's group first synthesized in 2006. This MOF started out as a record-setting H₂ storage material, with part of its success owing to two different types of unsaturated Mn²⁺ ions left exposed within the pore structure, Long says.

Besides being good at snagging H₂ molecules, the Mn²⁺ ions are Lewis acids and are well positioned to interact with guest molecules that are small enough to enter the framework pores, he adds. The team reasoned that Mn-BTT could function as a stand-in for zeolites, an industrially relevant class of microporous heterogeneous catalysts.

To prove the idea, Long and research group members Satoshi Horike, Mircea Dincă, and Kentaro Tamaki carried out two sets of reactions that rely on Lewis acid catalysts. One reaction was the cyanosilylation of aromatic aldehydes or ketones to form cyanohydrins, while the other was the Mukaiyama aldol reaction that couples aldehydes with silyl enol ethers to form β-hydroxyketones.

The MOFs turned out to function just as the researchers imagined they would. For example, cyanosilylation of an aryl aldehyde containing a small aryl group, such as a phenyl, went essentially to completion—a significant improvement in yield over other MOF catalysts. On the other hand, when the larger biphenyl group was used with an aryl methyl ketone substrate, the yield dropped to nearly zero, presumably because the substrate was too large to enter the MOF's pores and come in contact with the metal sites.

"Developing new catalysts is one of the most important challenges in the chemical industry, and the studies carried out by Long and coworkers illustrate well the power of being able to tailor active sites within MOFs," comments UCLA's Omar M. Yaghi, the world's leading authority on MOFs. "Their findings are along the lines of what many researchers have envisioned to be possible by designing MOFs."

Using MOFs for catalysis has enormous potential, Long says. Compared with zeolites, their surface area is much higher, leading to greater catalytic efficiency on a weight basis. And simple modification of the bridging ligands and the ability to readily exchange

the metal ions provide a tunability of properties that is lacking in zeolite chemistry, he says.

Zeolites are mostly made from silicon, aluminum, and oxygen—in essence they are nanoporous rocks and are very robust, explains Northwestern University's Joseph T. Hupp, another

MOF researcher. That's why they are used as catalysts in many high-temperature, gas-phase refinery processes, he says.

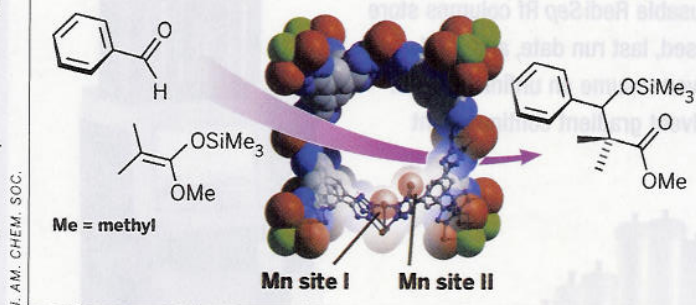
Where MOFs really shine is in permitting chemists to retain the inorganic character of zeolites while creating more versatile materials for condensed-phase catalysis, Hupp adds. And that makes MOFs promising for high-value transformations under milder conditions, such as enantioselective reactions for synthesizing pharmaceuticals and other fine chemicals, he says.

"Given the broad utility of zeolites in catalysis, I believe the possible applications for MOFs in this area have really only just begun to be explored," Long says.—STEVE RITTER

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—OMAR M. YAGHI

JUST PASSING THROUGH A portion of the Mn-BTT crystal structure illustrates the two types of Mn²⁺ sites—one five coordinate and the other two coordinate—that selectively catalyze reactions such as the Mukaiyama aldol synthesis shown.



J. AM. CHEM. SOC.