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EMERGING RESEARCH FRONTS - 2009

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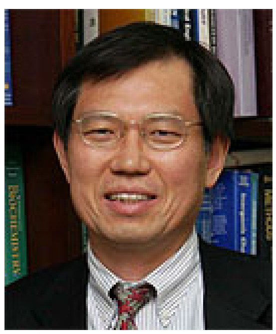
Kimoon Kim talks with ScienceWatch.com and answers a few questions about this month's Emerging Research Front Paper in the field of Chemistry. The author has also sent along images of their work.



Article: Rigid and flexible: A highly porous metal-organic framework with unusual guest-dependent dynamic behavior
Authors: Dybtsev, DN;Chun, H;**Kim, K**
Journal: ANGEW CHEM INT ED, 43 (38): 5033-5036 2004
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SW: Why do you think your paper is highly cited?

Metal-organic frameworks (MOFs) are an emerging field with a rapid growth of the number of publications about this discipline in recent years. MOFs have drawn special attention because of their potential in many areas including separation, catalysis, and gas storage, particularly hydrogen for their applications in fuel cells. In our paper "Rigid and flexible: A highly porous metal-organic framework with unusual guest-dependent dynamic behavior," as published in *Angewandte Chemie* in 2004, we reported on the rigid nanoporous framework, $Zn_2(bdc)_2(dabco)$ (Figure 1), with the highest hydrogen storage capacity at that time.

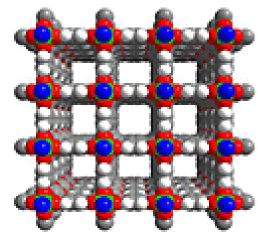
Another striking feature of the reported framework is its unusual guest-induced structural changes—the framework expands upon guest release and shrinks upon guest uptake, a rare phenomenon in this class of materials. The unique combination of such conflicting properties such as rigidity and flexibility in the framework makes our results remarkable. Therefore, researchers working on either gas storage or flexible frameworks often cite our paper as one of the first and representative milestones in this area.

SW: Does it describe a new discovery, methodology, or synthesis of knowledge?

In our paper, we described the facile synthesis of $Zn_2(bdc)_2(dabco)$, which has a rigid framework and permanent porosity, from low-cost chemicals in a one-pot reaction. What surprised us at that time was that the material exhibited exceptionally high surface area and hydrogen storage capacity compared with conventional porous materials such as zeolites and activated carbons.

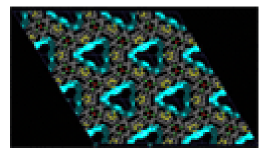
Another surprising discovery was the unusual flexibility of the framework during guest exchange. In particular, unlike conventional porous materials, the framework of this material shrinks upon an uptake of guest molecules. These structural changes depend on the nature of guest molecules, which suggested its potential applications in sensor.

Figure 1 [+] enlarge



Crystal structure of Zn2 $(bdc)_2(dabco)$ with a rigid and flexible framework.

Figure 2 [+] enlarge



First homochiral MOF, POST-1, demonstrating enantioselective sorption and catalysis.

SW: Would you summarize the significance of your paper in layman's terms?

In our daily lives, everyone uses porous materials—for example, a sponge to remove moisture from a kitchen table. In our paper we described the synthesis of a nanoporous material, where the pores are so small that it can absorb even small single molecules in a similar way. Therefore, with the help of such a "nanosponge," one can do cleaning on a molecular level!

Another unique property of such nanoporous materials is their ability to absorb a large amount of volatile gases. We all recognize the importance of hydrogen as a green fuel which should replace conventional fossil fuels in the not-too-distant future. One of the biggest obstacles to charge cars with hydrogen today is the very low capacity of hydrogen fuel tanks. For example, a regular 60 liter car tank can store about 500 grams of compressed hydrogen, which is enough only for a 50 km drive.

The same fuel tank made of our nanoporous material, however, is able to store several times more hydrogen under the same conditions. Although today's hydrogen storage capacity of nanoporous materials still does not meet the US DOE's guideline, the use of such "nanosponges" is one of the promising ways to achieve hydrogen-powered cars in the future.

SW: How did you become involved in this research and were any particular problems encountered along the way?

Design, synthesis, and applications of metal-organic porous materials have been one of the main research interests of our group at POSTECH. We successfully synthesized the first homochiral MOF, named as POST-1 (Figure 2), and demonstrated its enantioselective sorption and catalytic properties as reported in *Nature* in 2000.

Although the potential of MOFs in gas storage, selective sorption, separation, catalysis, etc., had been well demonstrated, one of the challenging issues in MOFs at that time was the synthesis of stable frameworks with permanent porosity upon removal of solvent molecules trapped in the pores.

To tackle this problem we used simple rigid organic linkers such as terephthalate, dabco, and formate, which allow us to synthesize a number of stable porous frameworks. Interestingly, these stable frameworks synthesized from rigid organic building units showed extraordinary gas sorption properties compared with conventional porous materials. These exciting results from our lab have been published in premier journals such as *Nature, Angewandte Chemie, Journal of American Chemical Society*, and *Chemical Communications* over the past 10 years.

SW: Where do you see your research leading in the future?

Shortly after our publication, other researchers took advantage of the extraordinary guest sorption properties and facile synthesis of $Zn_2(bdc)_2(dabco)$. For example, Professor Susumu Kitagawa (University of Kyoto, Japan), used this material to synthesize polymers inside channels with a better control of molecular weight. Such host-assisted polymers were shown to have a more regular length and structure. As mentioned above, this work demonstrated the potential of MOFs as a hydrogen storage material, which prompted many researchers to seek MOFs with higher hydrogen sorption capacity.

Although MOFs have not met the guideline set by DOE in terms of hydrogen sorption capacity, our efforts in searching for MOFs with higher hydrogen sorption capacity still continue. Another application of MOFs being explored is CO_2 capture and storage to solve an important environmental issue. We are also actively working on other challenging projects such as the synthesis of well-defined metal clusters inside the pores of MOFs and growth control of MOFs on surfaces for memory devices.

SW: Do you foresee any social or political implications for your research?

The field of MOFs has undergone explosive developments over the past decade. With emerging properties and functions, MOFs have already shown great promise in many applications including gas storage, separation and catalysis. The successful applications of MOFs in hydrogen storage and carbon dioxide capture would contribute greatly to a green and sustainable society. Also, MOFs' usefulness for separation and catalysis would make a great impact on the fine chemical and pharmaceutical industries. These are only a few examples. Other applications of MOFs are yet to be explored and their social and/or economical implications may be beyond our present imagination.

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