

Chemistry of Small Spaces

by Susumu Kitagawa

The fundamental science of materials and life, which has greatly contributed to humanity, lies in atoms and molecules. For two centuries, chemistry focused on synthesizing molecules or “skeletons assembled from atoms.” This approach led to the development of various substances (pharmaceuticals, foods, dyes, pesticides, clothes, plastics, etc.). In the late 20th century, this concept evolved into supramolecular chemistry, where molecules were used as constituents and eventually led to the nanoscience field.

Material with space

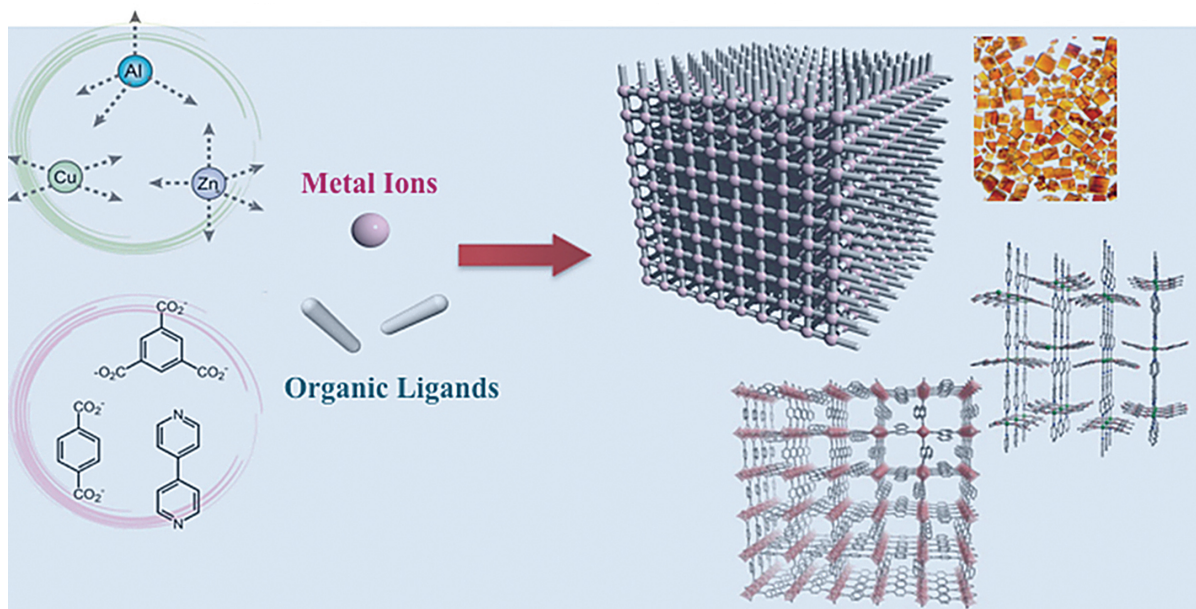
My work inverts the viewpoint from “skeletons” to “spaces” where atoms and molecules act as the surrounding space and partitions, which may realize another realm of science. My work considers space as the treasure trove where molecules and ions work instead of an empty void. My starting point lies in “the usefulness of the useless” (Chuang Tsu, 4th-century B.C.). That is, “everyone knows the usefulness of the useful, but no one knows the usefulness of the useless.”

What is a nanoscale space in the molecular-scale world? What happens when small spaces are arranged into a larger solid? Consider a 1-cm³ cube where the square frame is constructed by four 1-cm² panels and the inner surface area is 4 cm². What happens when 1-cm channels (0.8 × 0.8 nm² cross section and 0.4-nm

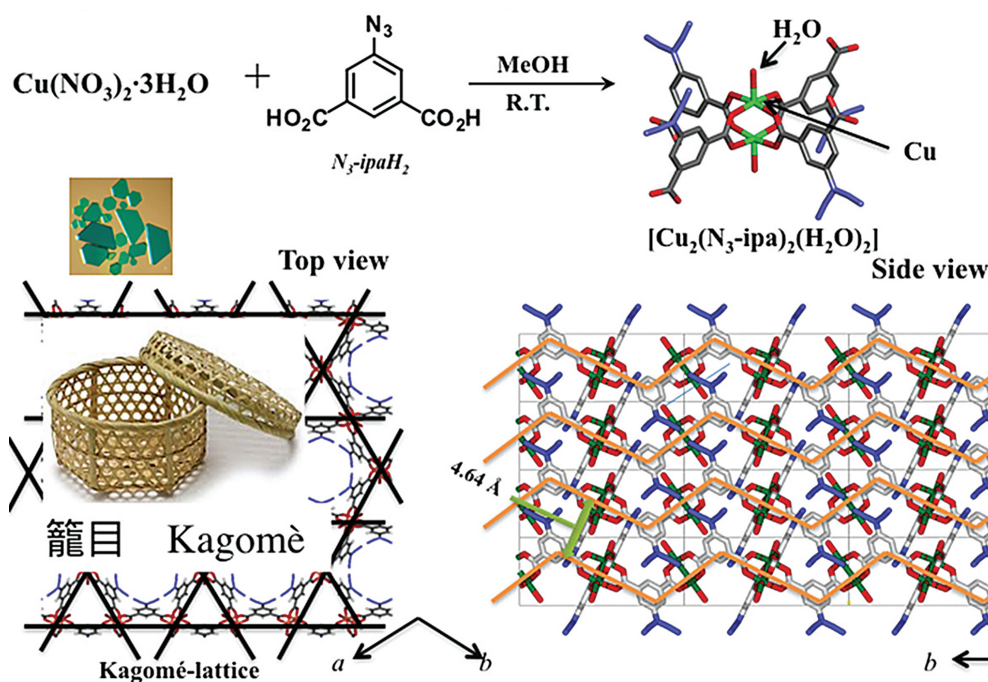
channel distance) are uniformly arranged in the cross section (1 cm²) of the frame? A cross-section of one channel can accommodate only four methane molecules (0.38 nm in size). If all the inner surface areas of the small channels are summed, it totals 2200 m². This forms a space with an enormously large inner surface area (about half a soccer field) inside a 1-cm³ cube. Thus, a 1-cm³ cube can hold 150 times its volume of densely packed methane molecules.

How can this happen? When small molecules enter a large space, they are influenced by the attractive force from only one side of the dividing frame. However, when small molecules enter a narrow space, they are influenced by attractive forces from multiple surfaces. Consequently, guest molecules are easily trapped. Since the late 1980s, my research has focused on “the chemistry of coordination space.” In 1997, we discovered an innovative porous material, which differs from conventional porous materials, and demonstrated a robust porous coordination network that adsorbs methane, oxygen, and nitrogen reversibly.

Materials with nanosized spaces occur naturally and are commonly used as porous materials in diverse applications, including storage, separation, purification, and catalysis. The concept of a “pore” was recorded in the world’s oldest Chinese character dictionary around A.D. 100, and the concept of a “void” was also written about 2000 years ago. Interestingly, papyrus records indicate that activated carbon, a conventional porous material used today (e.g., water purification),



Chemistry of Coordination Space: Porous Coordination POLymers (PCPs) and Metal-Organic Frameworks (MOFs)



Synthesis and structure of Kagomé-N₃. From Science, 2014, 343, 167. DOI: 10.1126/science.1246423

was used for medical purposes in ancient Egypt (B.C. 1550). In the 18th century, zeolite, another conventional porous material, was discovered from a natural ore and artificially synthesized in the 20th century. These materials have become indispensable, but they require a calcination process at high temperatures, which makes it difficult to design and produce the desired pore size and shape. Realization of porous materials with tailor-made pore shapes and sizes as well as storage and separation capacities beyond conventional materials will create a paradigm shift in the lives of humankind.

Chemistry to make new porous materials

The challenge of porous materials is precisely controlling the shape and size of the spatial structure while maintaining the desired pore function in the nanosized regime. Nature provides various examples such as stones that form mountains. Humankind has emulated this construct. Examples include the Parthenon temple (a pillared-layer structure) and the Egyptian Pyramids (square-pyramidal structure). On the other hand, Escher's drawings of cubic space on a two-dimensional plane are a blueprint for an infinite structure. Theoretically, such an infinite structure can be realized by preparing vertical lines of the same size and linking them with connectors in six isotropic directions. In reality, however, the strength of the material of the components is vital, and repeatedly assembling units is difficult. In contrast, such atomic and ionic structures commonly occur as nanosized inorganic compounds,

but there is currently not an equivalent to the line, which changes the existing chemical bonds.

As an example, consider the Parthenon, which is divided into pillars, floors, and ceiling units with adhesive cement built based on a blueprint. The space surrounded by these components becomes a construct with spaces for residence. Downsizing to the nanoscale, the pillar, floor, and ceiling are organic molecules, their linking materials, and metal ions that possess cementing ability (called coordination bonds in chemistry), respectively. Metal ions have a positive charge, while organic molecules tend to bear negatively charged atoms, forming coordination bonds. Although nanoscale designs are conceptually the same as macroscale buildings, how are nanoscale designs assembled? They cannot be assembled by hand. Chemistry is needed to incorporate structural information into organic molecules of the components. Specifically, the pillar structure forms a straight-type organic molecule and the ceiling entity forms a two-dimensional network of metal ions and molecules. All components are dissolved in a solvent and dispersed in a liquid where the components automatically recognize and bind to each other. This realizes a skeletal structure with numerous spaces where the coordination bonds serve as adhesives. For example, although the cross section of the hole is on the order of 1 nm, the solid (crystal) size exceeds 1 micrometer (1 μm) on one side with 1 million (1000 x 1000 pieces) holes in a 1 x 1 μm^2 cross section. Moreover, rational design without large energy consuming

Chemistry of Small Spaces

processes is possible. Similar to building with LEGO[®], this type of chemistry realizes nanoworld architecture in a flask. Such materials are called Porous Coordination Polymers (PCPs) or Metal-Organic Frameworks (MOFs), which are unlike conventional porous materials because they form structures where numerous molecules are regularly connected via coordination bonds. Since MOFs have excellent designability and involve low-energy fabrication processes, they are studied worldwide. In 2017, more than 8000 research reports were published. As a typical conventional porous material, 1 g of zeolite has a surface area equivalent to a basketball court, while 1 g of activated carbon is about half of a soccer field. In contrast, 1 g of MOFs provides a

surface area equivalent to a whole football field. MOFs are promising because they may provide various functions such as capturing, storing, separating, detecting, and responding to gases and chemical substances to address environmental, energy, and biological issues.

Age of gas

During the Industrial Revolution, humans began creating technologies that consumed huge amounts of energy. Initially, energy came from coal (solid) but the 20th century ushered in the age of petroleum (liquid). As petroleum depletion becomes a concern, gases (e.g., natural gas, biogas, and air) should play important roles in the 21st century. Based on this trend, society

Chemistry for the Future Solvay Prize

The 2017 ceremony and following reception for the “Chemistry for the Future Solvay Prize” took place in Brussels on 22 November 2017 to reward Professor Susumu Kitagawa for “The Development of Metal Organic Frameworks,” a new class of nanoporous materials with unprecedented morphological characteristics and promising new applications in the future.

The laureate received the award from His majesty King Philippe of Belgium and Jean-Pierre Clamadieu, CEO of Solvay during the ceremony in presence of a fascinated and prestigious audience.

And what about Science?

The formal moment of the Prize presentation was followed by a lecture by Vincent Ginis, the young Belgian physicist (Solvay Award in 2014) designated as



Meet the Jury: Standing from Left to right: Christophe Dobson, Patrick Maestro, Anne de Wit, Paul Baekelmans, Jean-Marie Lehn, Paul Chaiki; sitting, Håkan Wennerström (president of the Jury) and Gerhard Ertl



one of the top 50 tech pioneers in Belgium in 2017. His particular area of study is optics, but he made a strong case for the combination of different scientific disciplines, or “languages,” to drive progress in research.

He delivered a speech on a topic as fascinating as unexpected: how interdisciplinary science is on the verge of making invisibility a reality!

Then came Professor Susumu Kitagawa on stage.

Professor Susumu Kitagawa is Director of the Institute for Integral Cell-Material Sciences at Kyoto University. As a pioneer and leading scientist in the field of porous coordination polymers and, more specifically, “Metal Organic Frameworks” (MOFs), he gave a comprehensive voyage in the world of pore/size/shape controlled innovative technology giving access to materials with a specific area twice as big as a football ground but a mass of just 1 gram!

Chemistry of Small Spaces

will enter the “age of gas” and eventually ubiquitous gases such as air will be utilized as a resource. However, gases are difficult to handle due to ease of dispersion, propensity to form mixtures, low concentrations under normal conditions, and invisibility. Conventional transportation, storage, and conversion of gases consume massive amounts of energy under harsh conditions (e.g., high pressure and extremely low temperature). Science and technology must realize the means to handle gases under mild conditions (e.g., normal temperature, low pressure, and low energy). As technologies were initially developed using easiest-to-access resources, gases are an untapped resource. In this regard, porous materials have potential in numerous

practical applications and fields, suggesting that they will be vital to advances in science and technology.

Gases, especially atmospheric air [e.g., carbon dioxide (CO_2), oxygen (O_2), and nitrogen (N_2)] and water (e.g., rain, fresh, and ocean water) are ubiquitous and are composed of fundamental elements necessary for fuel and chemical products. To sustain humankind and the global environment, it is essential to develop science and technology that is independent of underground resources. In this context, porous materials with nanosized spaces will contribute significantly to the science and technology that handle gases *ad arbitrium*. The discovery of innovative porous materials with extraordinary features will revolutionize society.

The potential range of future applications for MOFs is rather large and is mainly related to their absorption capability. They include gas storage and release (methane, CO , CO_2 , hydrogen, etc.), specific catalysis, drug delivery, insulating material, the management of indoor air quality, etc.

Prof. S. Kitagawa's achievements meet very well the Solvay prize objectives, created in 2013 to celebrate its founding 150 years earlier by Ernest Solvay and to perpetuate his commitment as a dedicated and inspired supporter of scientific research. Every two years, the prize of € 300,000 aims to recognize a major scientific discovery that lays the foundation for the chemistry of the future, while promoting human progress.

Designation of Prof. S. Kitagawa as the third laureate, by the jury, following a long process with the target



Vincent Ginis gives a lecture promoting interdisciplinary science.



His majesty King Philippe of Belgium (left) and Jean-Pierre Clamadieu, CEO of Solvay (right) present the award to Prof. Kitagawa.

of excellence, as was described in *Chemistry International* Vol 38, No 5 (2016) is well in line with his predecessors, Prof Peter Schultz (Scripps Inst.) and Prof Ben Feringa (University of Groningen) Nobel Laureate 2016.

On the following day, Solvay young scientists and the Solvay Research Fellows met Prof. S. Kitagawa to discuss about his career and his outstanding research work. They brainstormed about the potential applications of MOFs at industrial scale. “There is still a lot of work to be done between academic and industrial people to develop the good process to make MOFs available industrially in an economical way and with the good properties.” Industry must first, however, overcome the technology challenges of MOFs large scale production.

By Dr. Paul Baekelmans
Science Adviser Solvay

Current world problems and porous materials

The United Nations (UN) has set out to achieve 17 sustainable development goals (SDGs) by 2030, which are crucial for the global environment and human health. Moreover, food is indispensable. The global population in the early 20th century was approximately one billion, and Crooks of the Royal Society (UK) said that even if the best technologies of the 1800s are employed and all productive land produces crops, the Earth cannot feed more than four billion people. Today there are more than seven billion people, due in part to Fritz Haber and Carl Bosch's pioneering work that led to mass production of the nitrogen fertilizer. Taking advantage of the 80 % nitrogen content in air, 140 million tonnes of ammonia is produced annually worldwide. This has made it possible to produce large amounts of nitrogen fertilizer, increasing agricultural output and the human population while simultaneously reducing starvation. This is a stellar example of chemistry contributing to humanity.

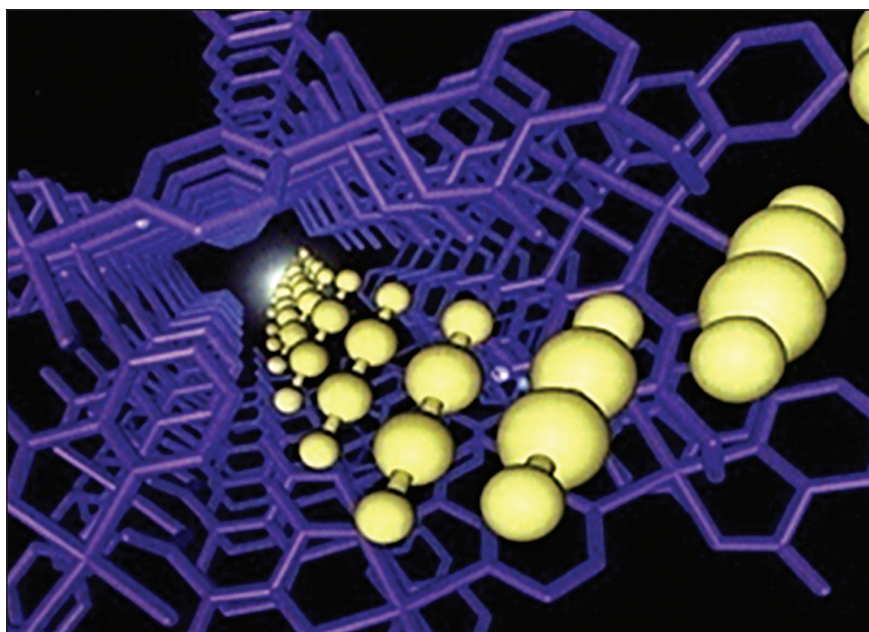
The world's population continues to increase. The UN predicts a global population of 9.8 billion in 2050. Although the population of developed countries is stagnant, developing countries are growing rapidly. Thus, developing countries are competing for resources and energy that have been monopolized by developed countries. As nationalism of resources and energy increases, so has the number of conflicts worldwide. Developed economies have relied on underground resources, especially petroleum. To reduce

the demand on underground resources, materials independent of subsurface resources must be developed. "Science and technology" must be established as a gift to future generations so that they can live with a sense of security.

Seawater and air, which contain the main elements for organic substances, are ubiquitous. It is important to develop science that uses such resources to pursue technological innovations. The Haber-Bosch method, which uses nitrogen in the air, provides inspiration to chemists to pursue new disciplines. However, the Haber-Bosch method is not perfect as the hydrogen comes from underground resources and the high-temperature and high-pressure process consumes a huge amount of energy.

Gas science and technology with new porous materials

As an example of a porous material application, consider a chemical separation process. About 40 % of the total energy consumed by the chemical industry is used for separation and purification processes (e.g., distillation). Although about 15 % of today's energy produced worldwide is used to separate and purify industrial commodities (e.g., gases and water), the demand for such commodities is expected to increase three-fold by 2050. To meet today's demand for energy savings and safety, materials that achieve mass storage and highly efficient separation of gases cannot be realized by simply improving conventional



The functionalized surface of a metal-organic microporous material (purple) permit the stable storage of acetylene at a density 200 times the safe compression limit of free acetylene at room temperature. Acetylene is normally highly reactive and explodes when compressed at more than 2 atm at room temperature.

Nature 436, 238–241 (14 July 2005); <https://doi.org/10.1038/nature03852>. See also 'Chemistry Highlights 2005', C&EN 19 Dec 2005, pp. 15–20; <https://cen.acs.org/articles/83/i51/Chemistry-Highlights-2005.html>
Courtesy of Susumu Kitagawa

materials. A porous material with precisely controlled structure and function is needed. MOFs have a high designability, which can realize rational coordination of the active points for adsorbed molecules, an extremely high porosity, which is enabled by the metal ion and organic molecule structure, and a regular structure without wasted space.

Developing new efficient separation techniques will realize solutions to energy problems. The criteria to separate gas mixtures are boiling point, molecular size, and shape. CO₂ and methane are a relatively easy combination to separate because their physico-chemical properties differ, whereas separating mixtures of C₂H₂/CO₂, CO/N₂, C₂H₄/Xe, O₂/Ar, and alkane/alkene is extremely difficult. Introducing functional groups into the pore surface and/or soft porosity (*i.e.*, a flexible framework) may overcome this challenge. For example, introducing amine (hydrogen) bonding sites has successfully realized selective recognition and effective trapping of CO₂ (acetylene). Flexible MOF frameworks can control channel pore gates to selectively introduce a target molecule, affording an excellent CO/N₂ separation capacity. Another excellent MOF feature is a high designability. However, separation of a very diluted component from a mixture is another difficult case. CO₂ is a renewable carbon feedstock. Combustion engines' exhaust gas has a CO₂ concentration of about 15 %, which is relatively easy to separate, but CO₂ in air is 400 ppm, making direct capture from air difficult. However, MOFs should realize an innovative low-energy separation process.

Mass storage and transport of gases are also important. Gas storage currently requires a large space, high-pressure condensation, or low-temperature liquefaction. Mass storage near ambient conditions is a dream technology. Since we first demonstrated gas storage using a MOF in 1997, many researchers have worked on developing MOFs. To date, high capacity storage of CO₂, CH₄, O₂, and N₂ has been realized. Additionally, dangerous gas storage is an important issue. We successfully synthesized MOFs to store pure C₂H₂ gas, which usually explodes at 2 bar at room temperature (0.2 MPa or 200 kPa), and reported guidelines for safe storage. For corrosive and toxic dopant gases such as AsF₅, PH₃, and SiF₄ used in electronic industries, cylinders containing MOFs are being developed in the United States.

MOFs can effectively capture and remove harmful substances. For example, MOFs, which selectively

capture and detoxify plant hormones (ethylene) involved in spoilage of foods such as fruits are marketed in Europe. Sustained release of biologically active gases such as NO and CO is effective for both cell biology basic research and medical application (drug delivery).

Toward the future

Because the global supply of petroleum is finite, the demand for substitutes of underground resources is increasing. Consequently, chemistry using ubiquitous gases will greatly contribute to solutions such as converting gases into useful substances under mild conditions.

One strategy, the so-called "methanol economy," is a fascinating scenario for a future sustainable world. Technologies separating and concentrating CO₂ from air and synthesizing fuel and/or feedstocks such as methanol from renewable energy and water are presently a dream. An efficient low-energy process using dilute CO₂ from air is important to make this dream a reality. Additionally, developing a conversion catalyst that does not use hydrogen from underground resources is imperative.

Since an efficient reaction under the dilute state of raw material gases has yet to be realized, high pressure conditions are adopted. The advantage of using porous materials is that gas molecules are effectively incorporated and confined into the pores. Thus, a low-pressure system may be constructed. Another advantage is the rational design of catalytically active sites within the pores where catalytically active metal complexes are incorporated or hybridized in the pores. Therefore, MOFs are promising as effective gas conversion catalysts.

Compared to the long history of conventional porous materials, MOFs are young. However, they should significantly contribute to low energy processes that solve issues facing humankind. In the Orient, it is said that "hermits live by eating haze." Soon this will not be a fantasy. A future where materials are intentionally made from air and water is rapidly approaching due to advances in gas science and technology. 

Susumu Kitagawa <kitagawa@icems.kyoto-u.ac.jp> was awarded the Chemistry for the Future Solvay Prize 2017 for his research in molecular architecture. Kitagawa is Director of the Institute for Integrated Cell-Material Sciences (iCeMS), and Distinguished Professor at the Institute for Advanced Study (KU-IAS) at Kyoto University, Kyoto, Japan.