The 2018 World Congress on
Advances in Civil, Environmental, & Materials Research (ACEM18)
Songdo Convensia, Incheon, Korea, August 27 - 31, 2018

Periodic mesoporous organosilicas with advanced applications

*Chang-Sik Ha[1)] and Sung Soo Park[2)]

[1), 2)] *Department of Polymer Science and Engineering, Pusan National University, Busan 46241, Korea*
[1)] *csha@pnu.edu*

ABSTRACT

Periodic mesoporous organosilicas (PMOs) are a new class of mesoporous silicas, where the organic groups are located within the channel walls as bridges between the Si centers. In this talk, a few interesting applications of PMOs are presented. Key applications of PMOs that were conducted in this laboratory include drug delivery and metal ion adsorption.

1. INTRODUCTION

Three groups (Ozin., Inagaki, and Stein) independently developed a novel class of organic-inorganic nanocomposites known as "periodic mesoporous organosilicas (PMOs)" in 1999. In PMOs, the organic groups are located within the channel walls as bridges between the Si centers {$(R'O)_3Si\text{-}R\text{-}Si(OR')_3$ (R' = methoxy or ethoxy, R = the bridged organic groups)}. Organic–inorganic hybrid materials can be synthesized by hydrolysis and condensation reactions of bridged organosilica precursors via the self-assembly process of a structure-directing agent corresponding to a similar process for the preparation of mesoporous silica materials.

The organic functionalization of these solids permits tuning of the surface properties (hydrophilicity, hydrophobicity, and binding to guest molecules), alterations of the surface reactivity; protection of the surface from attack; and modification of the bulk properties (e.g. mechanical or optical properties) of the material. In the first pioneering study of PMOs, the materials were synthesized using single bridged silane as the framework composition(Ha, 2014). In the advanced studies, two or multi-organo silane precursors were used to obtain PMOs with multi-functional or advanced functionality. The bridged organosilica precursors have contained hetero-elements (N, S, P, O…) in the organic moieties, metal complex and chiral bridges, etc. Generally, these PMOs were obtained with a powder or film type morphology. This review is limited mainly to the applications of PMOs. In this talk, I would like to review most of the recent

[1)] Professor
[2)] Research Professor

advances in the applications of PMOs, in particular for the applications in drug delivery system and metal ions adsorption.

2. Drug Delivery Application of PMOs

The potential use of PMO materials as efficient drug delivery vehicles should be noteworthy. The well-organized mesoporous organosilica network in materials, such as organosilane modified materials and PMOs allow fine control of the adsorption and release of drug molecules in a controlled manner, whereas for conventional drug administration such as simple intravenous injection, there is a lower drug concentration in the specific targeted sites because a certain amount of small drug molecules are lost on their way to the targeted sites. To employ mesoporous organosilica hybrid nanomaterials as an intracellular delivery system, it is important that the drug be released in controlled manner in the targeted site. The premature release of loaded cargos can cause severe side effects on healthy cells. In the ultimate scenario, the delivery of toxic anticancer agents will require (i) a zero premature release behavior (ii) the drug carrier system that is biocompatible, and (iii) a controlled and sustained release rate (Ha, 2014).

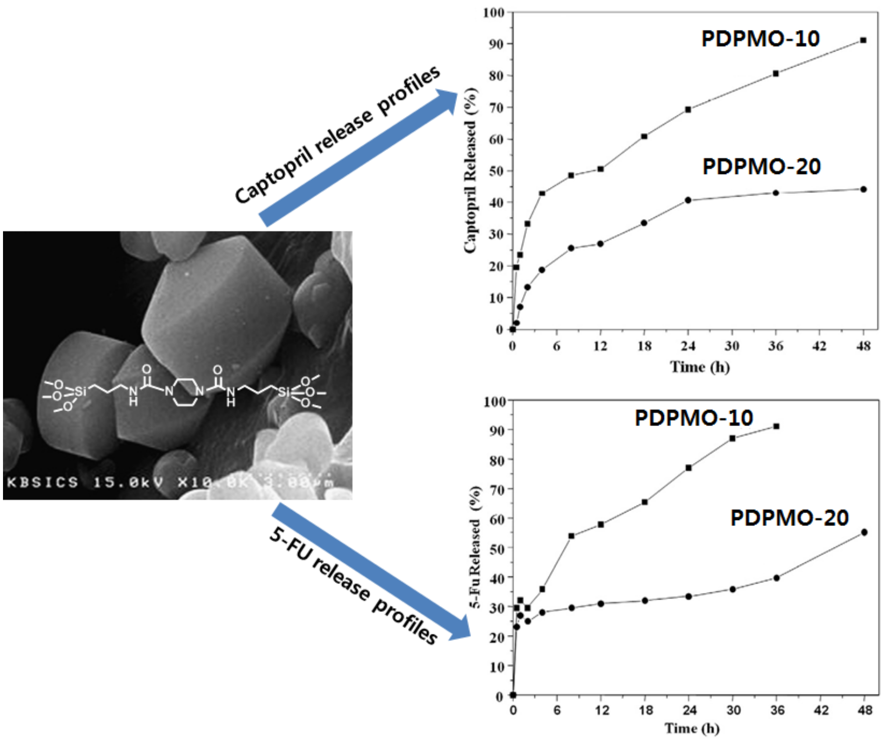


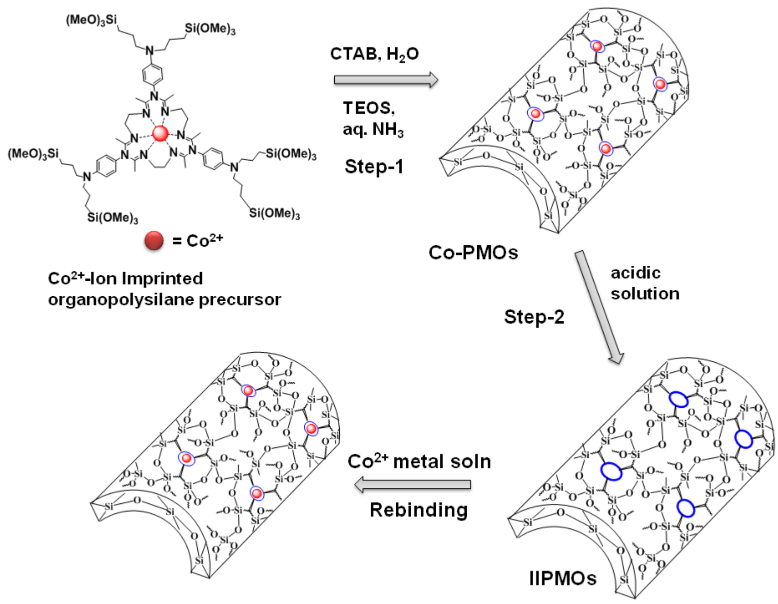
Figure 1 SEM image of diureylenepiperazine-bridged periodic mesoporous organosilicas (PDPMOs), and captopril and 5-fluorouracil release profiles from PDPMOs (Ha, 2011).

Mesoporous organosilica hybrid nanocarriers for drug delivery can be superior to traditional methods, because they can be designed to adsorb large amounts of drug molecules by interacting with the organic functionalities and release only at the specific sites with a controlled release rate. Many studies examined silica-based organic hybrid mesoporous materials with organosilane, capping molecules/nanoparticles or polymer functional groups, for the adsorption and delivery of drugs, genes, and enzymes under a range of internal/external stimuli such as temperature, redox, pH, light, magnetism, enzyme, ultrasound and etc. On the other hand, the studies using PMOs as a carrier of drug molecules are still limited. Special organic functional moieties within the PMOs can interact selectively with specific drug molecules and release them under specific physiological conditions.

In our group (Ha 2011), a bis-silylated precursor bearing sulphonamide and urea groups integrated into the PMO framework was prepared for the loading and release of two drugs, captopril and 5-fluorouracil. (Figure 1) For the same purpose, a PMO material was also prepared using ureylene and piperazine units containing PMOs as well as PMO materials with bridged organic moieties (the bridged amidoxime, the bridged pyridine) as a nanocarrier.

3. metal ion adsorption application of PMOs

Metal ion adsorption is one of the most explored research fields because of its importance in practical applications in the water treatment process. For instance, we reported a PMO material with imprinting sites for the highly selective recognition of Co^{2+} ions and PMO materials with pyridine bridged organosilane functional moieties (Scheme 1) and 3-(triethoxysilyl)propyl Isocynate(ICPES) functionalized PMOs for selective adsorption for Cr(III) ions (Figure 2), respectively.



Scheme 1. Preparation of ion-imprinted periodic mesoporous organosilica (Ha 2013).

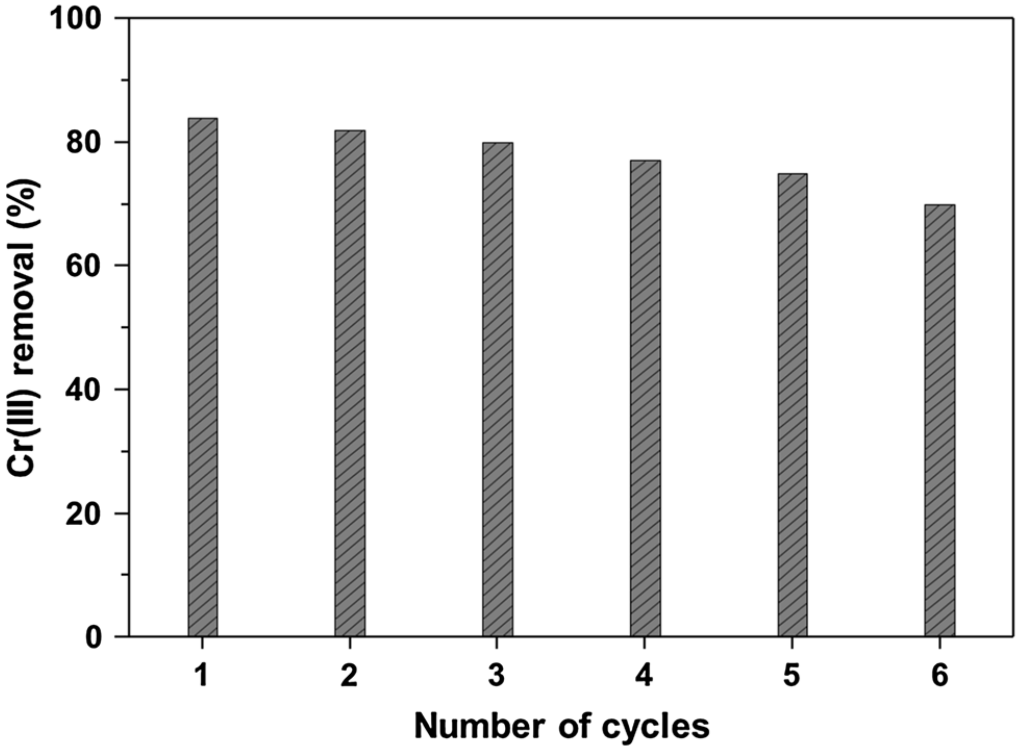


Figure 2. Adsorption/desorption cycles of Cr(III) on functionalized PMOs (Ha, 2015)

4. Conclusion

In this talk, I summarized a few typical advanced applications of PMOs. Though I mentioned only on the applications for drug delivery and metal ions adsorption, PMOs are really useful materials for a variety of applications, and many others can be envisaged in the near future. The current results and the forthcoming advances in PMOs will make them the materials of choice for some high-technology applications in strong competition with other highly porous solids (microporous and mesoporous silicas, non-siliceous mesoporous materials, metal–organic compounds, etc.)

Acknowledgments
The work was supported by the National Research Foundation of Korea (NRF) Grant funded by the Ministry of Science and ICT, Korea) {No. NRF–2017R1A2B3012961; Brain Korea 21 Plus Program (21A2013800002)}.

REFERENCES.

Asefa, T., MacLachlan, M. J., Coombs, N. and Ozin, G. A.(1999), “Periodic mesoporous organosilicas with organic groups inside the channel walls,”. *Nature* **402**, 867-871.

Inagaki, S., Guan, S., Fukushima, Y., Ohsuna, T. and Terasaki, O.(1999), “Novel mesoporous materials with a uniform distribution of organic groups and inorganic oxide in their frameworks," *J. Am. Chem. Soc*. **121**, 9611-9614.

Mathew, A., Parambadath S., Kim, S.Y. Park, S.S. and Ha, C.S.(2015), "Adsorption of Cr(III) ions using 2-(ureylenemethyl)pyridine functionalized MCM-41," *J. Porous Mater.* **22**, 831-842.

Melde, B. J., Holland, B. T., Blanford, C. F. and Stein, A. (1999), "Mesoporous sieves with unified hybrid inorganic/organic frameworks," *Chem. Mater.* **11,** 3302-3308.

Moorthy, M.S., Tapaswi, P.K., Park, S,S,, Mathew, A., Cho, H.J., and Ha, C.S.(2013), "Ion-imprinted mesoporous silica hybrids for selective recognition of target metal ions," *Micropor. Mesopor. Mater.*, **180**, 162-171.

Parambadath, S., Rana, V. K., Zhao, D. Y. and Ha, C.-S.(2011), "N,N'-diureylenepiperazine-bridged periodic mesoporous organosilica for controlled drug delivery," *Micropor. Mesopor. Mater*. **141**, 94-101.

Park, S,S., M.S. Moothy, and Ha, C.S. (2014), "Periodic Mesoporous Organosilicas for Advancd Applications," *NPG Asia Mater*.,**6**, e96, 1-21.