Highly Selective Separation of Isoprene from C5 Hydrocarbons Mixture Using Pyridyl-based Metal-Organic Frameworks containing copper(I) iodide cluster

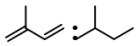
([1]*School of Science, Tokyo Institute of Technology*, [2]*ENEOS Corporation*) ○Joonsik Kim,[1] Pavel M Usov,[1] Yuki Wada,[1] Hiroyoshi Ohtsu,[1] Takaya Matsumoto,[1,2] Masaki Kawano[1]

Keywords: Metal-organic frameworks; Hydrocarbon separation; X-ray crystallography, Structural optimization calculations

Unsaturated hydrocarbons are widely used in industry as raw materials, but they typically require the use of extractive distillation processes for purification, which consume large amounts of energy. To address this challenge, several metal-organic frameworks (MOFs) based on copper iodide were developed.[1] The presence of accessible pores inside these frameworks could be used for separating and isolating specific molecules from hydrocarbon mixtures. However, there have not been many studies on the separation of olefin mixtures, especially including diene. Therefore, several pyridyl-based ligands were employed for MOF formation, providing promising candidates with high selectivity for olefins.

Three pyridyl-based (3- and 4-pyridyl) metal-organic frameworks (MOF) with copper(I) iodide cluster were used to selectively separate three structurally related C5 hydrocarbons (isoprene, 2-methyl-1-butene and 2-methylbutane). The separation is especially challenging due to close similarity of the molecules geometric shapes and have not been investigated in detail in the past. One of those MOF displayed over 3267 times higher selectivity for adsorption of isoprene over 2-methylbutane making it a promising candidate for industrial scale separation. Structural optimization calculations using Matlantis software, an atomistic simulator, revealed the reason of the high affinity for isoprene.

Table 1. Guest uptake and selectivity of each MOFs.

Material	Isoprene uptake, mmol/g	IAST Selectivity at 50 kPa  IP : 2MB	Reference
MOF1	1.7	**3267 : 1**	This work
MOF2	0.65	327 : 1	Previous work
MOF3	1.4	9.5 : 1	Previous work
MIL-125	4.4	1.1 : 1	2
NH_2-MIL-125	4.6	1.1 : 1	2

1) R. Robson, *J. Am. Chem Soc*. **1989**, *111*, 5962-5964.
2) S. Kim, W. Ahn, *Catalysis Today*. **2013**, *204*, 85-93.

© The Chemical Society of Japan