

Energy-efficient olefin separation by coordination networks using tetrahedral ligands

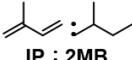
(¹*School of Science, Tokyo Institute of Technology*, ²*ENEOS Corporation*) ○Joonsik Kim,¹ Pavel M Usov,¹ Yuki Wada,¹ Hiroyoshi Ohtsu,¹ Takaya Matsumoto,^{1,2} Masaki Kawano¹

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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.² 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.

Currently, we succeeded in obtaining two types of MOF structures, which were investigated for their ability to separate olefin mixtures. Specifically, two ligands containing a rigid tetrahedral core were synthesized, and then combined with copper iodide to generate two MOFs comprised of helical copper iodide chains (denoted as MOF1 and MOF2). These materials were activated using two-step solvent exchange and vacuum treatment prior to guest sorption measurements. The mixture adsorption isotherms were calculated from the single component data using IAST (ideal adsorbed solution theory), which was used to determine guest selectivity. Remarkably, MOF1 showed a 327-fold selectivity of isoprene over 2-methylbutane (Table 1), which is considerably higher than previous studies.³

Table 1. Guest uptake and selectivity of each MOFs.

Material	Isoprene uptake, mmol/g	IAST Selectivity at 50 kPa	Reference
		 IP : 2MB	
MOF1	0.65	327 : 1	This work
MOF2	1.4	9.5 : 1	This work
MIL-125	4.4	1.1 : 1	3
NH ₂ -MIL-125	4.6	1.1 : 1	3

1) R. Robson, *J. Am. Chem. Soc.* **1989**, *111*, 5962-5964. 2) O. M. Yaghi, *J. Am. Chem. Soc.* **1998**, *120*, 2186-2187. 3) S. Kim, W. Ahn, *Catalysis Today*. **2013**, *204*, 85-93.