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学位授与の要件	信州大学学位規程 第5条第1項該当
学位論文題目	Zn ²⁺ , トリアゾールおよびシュウ酸を含む多孔性配位高分子の磁場中合成とそれらの二酸化炭素吸着能 Synthesis of porous coordination polymers comprising Zn ²⁺ , triazole, and oxalic acid under magnetic fields and their adsorptivity for carbon dioxide.
論文審査委員	主査 尾関寿美男 教授 金継業 教授 飯山拓 准教授 松本明彦 教授 大木寛 教授

論 文 内 容 の 要 旨

Porous coordination polymers (PCPs) are a new class of porous crystalline materials that have extremely high porosity and selective adsorptivity for guest molecules. PCPs and metal organic frameworks (MOFs) are constructed from metal ions and organic linker ligands to give two- and three-dimensional frameworks. The highly designable frameworks and the variety of combinations of organic linkers and metal ions suggest the possibility of the creation of multifunctional porous materials, in which two or more physical/chemical properties are integrated in the crystal.

PCPs are attractive porous materials, because they are crystals which lead to homogeneous definite pores and their structure and function are easily controlled by changing organic ligands and metal ions. They are currently receiving attention because of their high surface area and large free cage volume, besides their interesting application as well as including gas purification, gas separation and catalysis. PCPs formed by the self assembly of metallic ions and organic ligands are crystalline materials and also have flexibility that arises from frameworks built with coordination bond. Designing structure and pore property is easy because components are selectable. Moreover, it is possible to modify pore walls surface by functional organic ligands which interact with specific molecules. Gas storage capacity in PCPs was promoted by introducing open metal sites, increasing surface area, and modifying pores with functionalized organic linker, etc.

As-synthesized $[Zn_2(Oxac)(Taz)_2] \cdot (H_2O)_{2.5}$, referred to ZOTW_{2.5}, was prepared from aqueous methanol solutions of $Zn_5(CO_3)_2(OH)_6$ and two kinds of ligands of 1,2,4-triazole (Taz) and oxalic acid (Oxac) at 453 K for 12 hours. The crystal structure was determined by the Rietveld method. The ZOTs pretreated at 383 K and 1 mPa over 4h, ZOTW_x($\geq 4h$), showed Type I adsorption isotherms for N₂ at 77 K having the saturation amount (*V*_s) of 180 mg/g, but those pretreated shortly showed only 1/10 in

adsorption amount. CO₂ was adsorbed at 303 K in sigmoid on non-porous ZOTW_x(0~2h) and in Langmuir-type on ZOTW_x(≥3h) to reach the adsorption amount of 120 mg/g at 700 Torr. N₂ adsorption on only ZOTW_x(0~2h) degassed after CO₂ adsorption was enhanced up to 1000 mg/g in *V*s. The metastable structure seems to be similar to the stable structure, but the positions and rotational angles of Taz ring and Zn-Oxac complex may be changed. The difficulty in our structural analysis may arise from swivelling motion around Zn-O bonds of the Zn-oxalate units, as observed in ZnOATW_{0.5}. The crystal structure specifies static pore size and volume, but adsorption amount depends on the dynamical sizes or flexibility of molecules and frameworks.

Magnetic fields (*H/T*) modify seriously structures and properties of materials, especially colloidal systems. Homogeneous magnetic fields affect them thermodynamically via magnetic energy, $(1/2)\chi H^2$, which may induce the magnetic orientation, phase transition, etc. Magnetic field gradient also brings about magnetic force, which causes convection, mass-transport, concentration change, etc. For molecules having lower symmetry than cubic symmetry, the magnetic susceptibility is anisotropic (dependent on direction), and the magnetic energy is anisotropic (different by direction).

[Zn₂(Oxac)(Taz)₂].(H₂O)_x, referred to ZOTW_x, was also prepared from aqueous methanol solutions of Zn₅(CO₃)₂(OH)₆ and two kinds of ligands of 1,2,4-triazole (Taz) and oxalic acid (Oxac) at 453 K under magnetic fields of up to 6 T. Magnetic fields changed markedly its morphology of irregular agglomerates at zero field to rectangular-prism crystals having smooth surfaces at 6 T, although its monoclinic crystal structure was only slightly deformed to triclinic one. As-synthesized ZOTW_x(*H*) prepared under magnetic fields of *H/T* ≥ 2T adsorbed large amount of N₂ at 77 K in rectangular Type I adsorption isotherm even without usual pretreatment at 383 K and 1 mPa. It suggests that high magnetic fields induced the formation of hydrophobic micropores having very uniform size. The hydrophobicity was consistent with the results that the CO₂-assisted micropore formation due to water-assisted CO₂ adsorption was depressed in as-synthesized ZOTW_x(*H*) containing small amount of water.