Increased adsorbed amount and new shape of isotherm due to formation of micro-solution in the pore

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Molecules in the nanospace show different behavior from bulk due to the interaction with the pore wall and spatial limitation. Among them, we focused on the micro-solution formed in the pore. Solution plays an important role in chemistry, and combining it with nanospace is expected to create a new functional nanospace. In this study, we measured nitrogen, water, and diethyl ether adsorption isotherms of MCM-41 with dibenzyl as a solute, and elucidate the effect of the formation of micro-solution in the pore on the adsorption behavior.

Dibenzyl was introduced into the MCM pore by immersing the MCM in a dibenzyl-diethyl ether solution and then removing the diethyl ether. It was confirmed by nitrogen adsorption isotherm and X-ray diffraction (XRD) measurements. As the fractional filling (ϕ) increases, the nitrogen adsorption amount of MCM-dibenzyl composite (MCM_{Dib}) decreased (Figure). Furthermore, the XRD profiles of MCM_{Dib} didn't show the crystal peaks of dibenzyl. These results indicate that dibenzyl was introduced into the MCM pore.

The adsorption isotherms for water (in which dibenzyl is only slightly soluble), and diethyl ether (in which dibenzyl is well soluble) were completely different from the nitrogen adsorption isotherms (Figure). In water adsorption, the raw MCM ($\phi = 0$) exhibits a general type V adsorption isotherm. But MCM_{Dib} ($\phi =$ 0.28, 0.64) shows a new type of adsorption isotherm that is not in the IUPAC classification. As a result, the water adsorption amount is almost constant regardless of the amount of dibenzyl, and agreed with that of raw MCM. In the case of diethyl ether adsorption isotherms, the raw MCM exhibit type IV isotherm, but MCM_{Dib} ($\phi =$ 0.28, 0.64) show a specific increase in adsorption amount at high relative pressure with diethyl ether adsorption amount reached four times that of raw MCM in $\phi = 0.64$ sample. The adsorption amount increased with ϕ despite the decrease in available pore capacity. These results are related to the solubility of dibenzyl in adsorbate molecules and can be understood by considering the formation of a "micro-solution" in the pore.

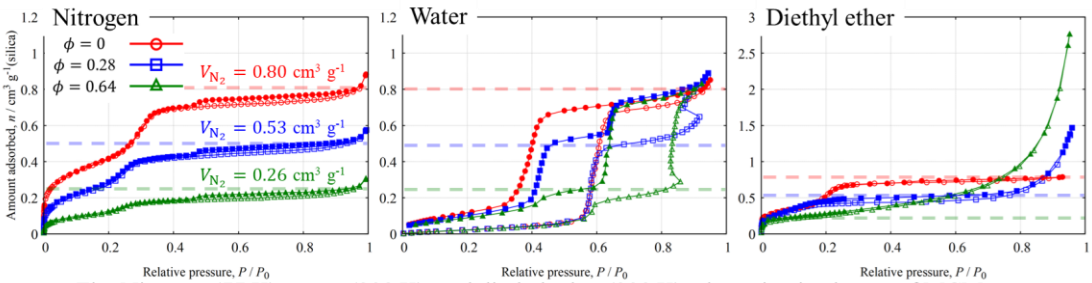

Fig. Nitrogen (77 K), water (298 K), and diethyl ether (298 K) adsorption isotherms of MCM_{Dib} (open: adsorption branch, fill: desorption branch)