

*Coordination exchanges in metal-organic frameworks*Nak Cheon Jeong¹¹*Department Of Emerging Materials Science, DGIST, Daegu, Korea, Rep.*

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Open coordination site (OCS) on intersectional metal ion has shown considerable potential in its role for the applications in i.e., high ion transport and efficient gas adsorption. Thus, the activation of MOFs, the removal of solvent molecules (typically used in during the synthesis) from the OCSs has been thought as a prerequisite process for those applications. To date, several strategies for activating MOFs have been suggested: (i) thermal activation; (ii) freezing-drying; (iii) supercritical CO₂ exchange; (iv) acid treatment. Among them, the thermal activation, which is normally performed by applying heat and vacuum, has been a unique way to remove the OCS-coordinated solvent molecule, whereas the other four methods are useful only for removing pore-filling solvents. Given that the high temperature (e.g., >150 C) can lead to structural damage to MOFs, conceivable low-temperature process will be a considerably promising way, compared to the cumbersome, pricey heat-and-vacuum technique.

In this presentation, we will discuss how to control the activation condition for maintaining structural integrity during the activation process. As an example, I will show a new activation method, "chemical activation", where methylene chloride (MC) plays a substantial role in removing both metal-coordinating and pore-filling solvents even at room-temperature. While MC treatment is surely a well-known method for replacing pore-filling solvent prior to thermal activation process in order to lower the activation temperature, the role of MC for breaking the metal-solvent coordination has never been demonstrated. We found that the chemical activation by MC arises via (i) replacement of pre-coordinated solvent by MC (the step before MC coordination) and (ii) spontaneous decooordination of MC (the step after MC coordination) with low activation energy which corresponds to room temperature. Also, we show that this low-temperature activation technique is more suitable for large-area MOF films.

Meanwhile, although this chemical activation method is substantially effective even in low-temperature, strongly coordinated solvents such as dimethylformamid (DMF) and dimthylsulfoxide (DMSO) cannot be adaptable to this method because they are not readily replaced by MC which coordination is very weak. To exceed this limit in the chemical activation, we further developed an advanced chemical activation method, "multistep chemical activation". This process includes an intermediate step, solvent exchange. Thus, the process consists of (i) multiple exchange (equal to or more than two-step exchange) of precoordinated solvent molecules by other solvent molecule such as methanol, ethanol, or acetonitrile which coordination bondings are relatively weak, (ii) exchange of the post-coordinated solvents by MC, and (iii) lastly, spontaneous decooordination of the coordinated MC molecules. With this strategy, we could completely remove the DMF solvent coordinated to the OCS sites in HKUST-1 without structural damage.

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