On the origin of mesopore collapse in functionalized porous carbons

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Heteroatom functionalization of ordered mesoporous carbon (OMC) represents an important strategy towards electrocatalytic and battery applications. Such functionalization frequently leads to degradation or even collapse of mesopores, which is generally attributed to the harsh conditions used or the successfully doped functional groups or the entrapment of guest species into mesopores. However, in this report, we find the structural deterioration of functionalized OMC is mainly induced by the water evaporation during the drying process, beyond the usually accepted concept mentioned above. We report two types of well-defined OMCs as model carbons, resembling comparable pore architectures but varying in surface chemistry, namely the hydrophobic OMC (C_{meso}) and hydrophilic one (HC_{meso}). After the washing and drying processes, C_{meso} remains intact regardless of the drying processes. In sharp contrast, HC_{meso} shows gradual porosity deterioration or even a complete loss of structural ordering under continuous washing-drying cycles. Lyophilization can however well preserve the porosity of HC_{meso} due to the reduced stress exerted by water on the carbon walls. Such a distinct phenomenon is elaborately characterized by N_2 physisorption, H_2O physisorption, TEM and in situ small angle X-ray scattering and is further validated by a well-known OMC (CMK-3), which undergoes a surface functionalization by concentrated nitric acid. Our finding reveals an important but neglected issue addressing the drying process in particular for polar functionalized porous carbons.