

Enhanced hydrogen uptake by the inclined polycatenated dynamic Cu(II)-MOF

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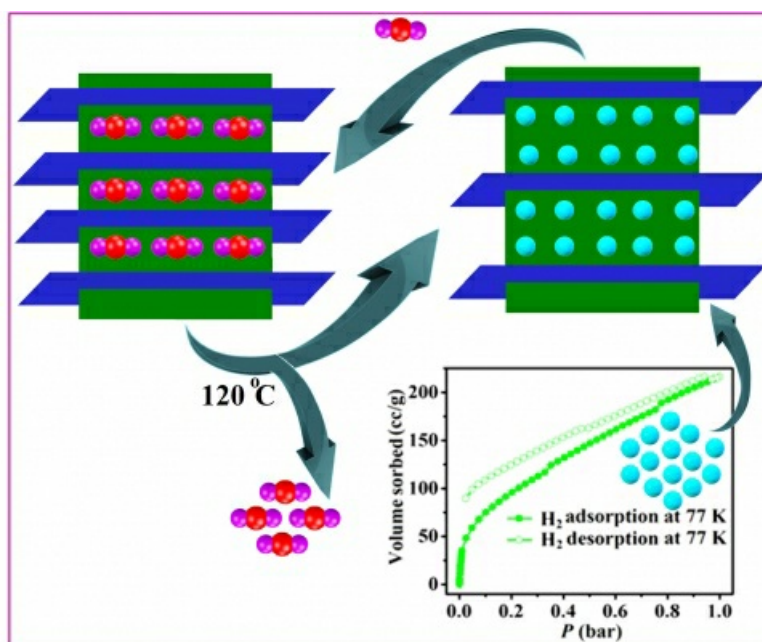
With the rapid diminution of fossil fuel energy and the escalating growth of human being's demand for energy, it is not only paramount important but also urgent, for mankind, to search for an alternative energy source; which can substitute the limited availability of fossil fuel energy sources. In this regard, the storage of hydrogen in metal-organic frameworks (MOFs) becomes a promising candidate for supplying appreciable amount of clean energy into the fuel-cell vehicles due to its highest energy density by weight.

Due to possessing of exceptionally high specific surface area, micro-porous channel with effective pore size and shape, polar pore wall, structural flexibility and/or framework entanglement; presently the MOFs are probably the most favourable candidates for the physisorption of tiny hydrogen gas molecules on the adsorbent surface. Notably, since long time the entangled (i.e. interpenetrated or polycatenated) MOFs [1] are believed to be nonporous and hence considered unsuitable for exhibiting the illustrious functionalities of the MOFs. But through last few couple of years, several stalwarts reported some interpenetrated metal-organic framework materials for exhibiting significantly enhanced hydrogen uptake capacity like the non-interpenetrated MOFs. However, although the interpenetrated MOFs has been implemented for the aforesaid H₂ adsorption study; but no such work on polycatenated class of metal-organic framework materials has been investigated for enhanced hydrogen adsorption study till date. It is worth to mention that our work first opened a new window through the execution of enhanced H₂ adsorption study [2] on an interesting 2D + 2D → 3D inclined polycatenated dynamic MOF, namely, {[Cu(4-bpe)(2-ntp)(H₂O)₂].2(H₂O)}_n [where, 2-ntp⁻ = 2-nitroterephthalate and 4-bpe = 1,2-bis-(4-pyridyl)ethane]. The dehydrated framework (at 120 °C) of the said compound exhibits significant amount of type I H₂ gas isotherm upto ~216 cc/g (i.e. 1.94 wt%) at 77 K and 1 bar pressure along with appreciable amount of different gas uptakes like for N₂ (~250 cc/g at at P/P₀ ≈ 0.99) and CO₂ (~153 cc/g at 195 K and 1 bar pressure). The dehydrated framework of the said compound also exhibit comparatively lower H₂ uptake capacity upto ~130 cc/g (1.17 wt %) at 77 K and 62 bar pressure; which is probably due to more partial rupture of the dynamic/flexible framework at high pressure. The dynamicity of the said compound has also been firmly confirmed by the variable temperature PXRD study; which exhibits the appearance of few new peaks due to framework transformation during degassing. The said compound also exhibits a reversible visual color change of blue-cyan-blue during the phase transformation from parent-to-dehydrated-to-rehydrated form.

This observation might explore the expanse of flexible MOFs that can undergo physical/chemical transformation in presence of external stimuli like pressure, heat/light energy leading to exhibit significant uptakes of preferred gases. Thus the development of flexibility in polycatenated structures would be the 'holy grail' of state-of-the-art synthetic chemistry research for the development of hydrogen storage materials.

[1] Su, C.-Y. et. al. (2004). Chem. Commun., 19, 2158–2159.

[2] Maity, D. et. al. (2017). Inorg. Chem., 56, 713–716.



Keywords: [Micro porous polycatenated framework](#), [structural dynamism](#), [hydrogen storage](#)