

FROM "CLEAN ENERGY" CARS TO STRUCTURE OF METAL-ORGANIC FRAMEWORK MATERIALS (MOFs)

Hydrogen is able to replace petroleum in the future. However, hydrogen storage is a difficult problem which still has to be solved

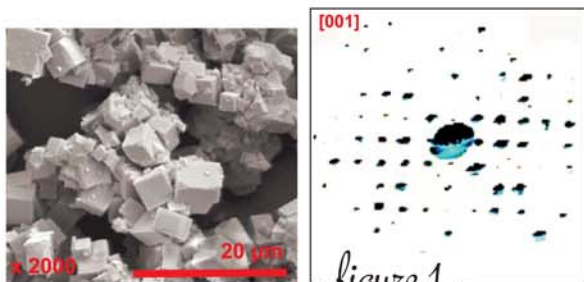
Fossil fuel energy sources and their burning emissions from vehicles have a very negative impact on the environment and on people's health. Furthermore, fossil fuels are not renewable, which means that if the world use them uncontrollably, fuel will be limited in the future. Hydrogen is an attractive energy carrier which could replace petroleum. However, hydrogen storage is a difficult problem which still has to be solved. Investigation of metal-organic



The challenge:	MOF are nanosized crystals & extremely beam sensitive
Solution:	3D Diffraction Tomography & precession electron diffraction with a cryo-holder used for keeping the temperature at ~100K

frameworks (MOFs) as porous materials for hydrogen storage is currently an important research field. Due to a recent requirement of United States Department of Energy, a hydrogen storage tank must contain 6 wt% of hydrogen. Hydrogen uptake depends on several properties of porous material. However, a material with a high surface area or free volume alone is not necessarily a good candidate for hydrogen storage. Pore size distribution of MOF strongly influences the heat of adsorption. Thus, frameworks with smaller pore sizes have higher heat of adsorption due to a stronger interaction between adsorbed hydrogen molecules and cavities. The desorption temperature of hydrogen increases likewise with decreasing pore size. Calculations showed that pores with diameter of 7 Å should be optimal for hydrogen adsorption. Additionally, the stability of metal-organic framework plays a very important role for its potential use as hydrogen storage material as well as for other applications.

Triazolate-based MOF featuring Kuratowsky-type secondary building units, have been studied thoroughly. MFU-4, constructed from benzobistriazolate linkers and $\{Zn_3Cl_4\}^{6+}$ cores, features a very high thermal and hydrolytic stability. Due to its small pore apertures (2.5 Å) it is highly selective for the adsorption of atoms or small molecules such as H_2 . However, in order to separate mixtures of larger molecular adsorbates for catalytic transformations, a porous framework featuring larger pore apertures is required. MFU-4l(arge) $[Zn_3Cl_4(BTDD)_3]$ constructed by a longer triazolate linker compared to



SEM IMAGE OF MFU-4L & 3D DIFFRACTION RECONSTRUCTION

MFU-4, is a novel member of isorecticular MFU-4-type frameworks that has been studied recently.

The crystal structure of MFU-4l has been solved *ab initio* from powder X-ray diffraction data by direct methods. An independent structure analysis was performed by 3D Electron Diffraction Tomography in parallel, using a cryo-holder to avoid sample melting due to beam exposure.

The crystal structure of MFU-4l is similar to that of MFU-4 in that it possesses a cubic six-connected net.

Thermogravimetric and VT-XRPD analyses indicate that MFU-4l possesses very high thermal stability (500 °C under nitrogen). Large pore apertures of 9.1 Å allow adsorption and free diffusion of different molecules. In contrast, MFU-4, presenting small pore apertures of 2.5 Å, is highly selective for the adsorption of atoms or small molecules such as He or H_2 . MFU-4l, which has a much higher surface area, is generally able to adsorb more hydrogen than MFU-4. However, at higher temperatures and lower pressures MFU-4 adsorbs more hydrogen than MFU-4l. Thus, MFU-4 is more suitable for hydrogen adsorption than MFU-4l. It has been demonstrated that MFU-4-type of frameworks have a huge potential for the development of functional materials for hydrogen storage, gas separation (MFU-4) and possible catalytic applications (MFU-4l).

Crystal Structure
 $Zn_3Cl_4(BTDD)_3$
Cubic Fm-3m
 $a=31.057 \text{ \AA}$

Experimental data
 tilt range: $\pm 60^\circ$ step: 1°
 No ind. reflections: 412
 No ind. atoms: 9
 $R = 32.1 \%$

