# Hydrogen adsorption in Metal Organic Frameworks by hydrogen spillover

**Abhijit Krishna Adhikari, Kuen-Song Lin*, Kai-Che Chang, Mu-Ting Tu, and Wei Lu**
*Department of Chemical Engineering and Materials Science, Yuan Ze University, Chung-Li 320, Taiwan, R.O.C*
**Corresponding author: Fax: +886-3-4559373, E-mail: kslin@saturn.yzu.edu.tw*

**Abstract:** $Zn_2(bdc)_2dabco$ MOFs was synthesized and characterized. The catalytic properties of Pt/AC and Pd/AC were studied for hydrogen spillover in $Zn_2(bdc)_2dabco$ modified by 5 wt % of catalyst. The hydrogen adsorption capacity of modified $Zn_2(bdc)_2dabco$ was significantly enhanced up to 3.35 wt % by using the secondary spillover by carbon bridges measured at 1100 mmHg and 78 K. Moreover, the prepared MOFs was characterized by FE-SEM, XRD, XANES/EXAFS and BET $N_2$ sorption techniques.
**Keywords:** Metal Organic Frameworks, Spillover, Hydrogen adsorption.

## 1. Introduction

The negative impact of greenhouse gases and the eventual depletion of fossil fuel reserves have increased the importance of developing alternative fuel sources that are strong, viable, and emission free. Hydrogen is considered a clean fuel that has a minimum impact on the environment nearly eliminating the levels of carbon dioxide and other greenhouse gas emissions. It is safe to manufacture, reliable and environmentally friendly[1]. However, developing safe, reliable, compact, and cost-effective $H_2$ storage technologies is one of the most technically challenging barriers to the widespread use of hydrogen as a form of energy as well as onboard vehicle application. Concerning adsorbents, nanostructured carbon including activated carbon, carbon nanotubes and graphite nanofibers have been the major candidates for hydrogen storage. However, known carbon nanostructures cannot store a sufficient amount of $H_2$ required for transportation applications[2]. The use of dissociation/spillover for $H_2$ storage, which is defined as the dissociative chemisorption of hydrogen on the metal and the subsequent migration of atomic hydrogen onto the surface of the support such as activated carbon, alumina and so on[3], is possible to increase the storage capacities in nanostructured materials. Here we report, significantly enhanced hydrogen sorption in Metal Organic Frameworks (MOFs), the promising candidate for hydrogen storage due to light weight, tunable porosity and large surface area, by hydrogen spillover with bridges.

## 2. Experimental

$Zn_2(bdc)_2dabco$ samples (bdc: 1,4-benzenedicarboxylic acid, dabco: 1,4-diazabicyclo[2.2.2]octane) were prepared following the reported procedure[4] while we used the precursors twice in weight and more than 80% yield was received. The prepared MOFs sample was characterized by FESEM, XRD, EXAFS/XANES and $N_2$ adsorption analysis. Hydrogen adsorption isotherms were measured gravimetrically following the reported method by Eddaoudi et al[5].

## 3. Results and discussion

The particle size of synthesized $Zn_2(bdc)_2dabco$ sample was around 10 ~ 12 μm identified by FE-SEM micrographs. The intensive peaks appearing at small $2\theta$ angles (**Fig. 1**) in the XRD pattern are characteristics of porous materials which possess numerous pores or cavities. Nonspecific physical adsorption of the $Zn_2(bdc)_2dabco$ was carried out to measure the total surface area and pore size distribution, as shown in **Fig. 2**. The specific surface area of $Zn_2(bdc)_2dabco$ was 1433 $m^2g^{-1}$ with the pore volume of 0.769 $cm^3g^{-1}$. The near edge region of the XANES spectrum (**Fig. 3**) is very informative on both the oxidation and coordination states of Zn species. The edge positions of standard $Zn^{2+}$ and the central Zn metal of MOFs are 9661.79 and 9662.29 respectively. The offset is about 0.5 eV because of Zn ions are not entirely surrounded by oxygen atoms and form oxides ($OH^-$) with the covalent bond, it gives slight shift. However, the well-defined shoulders around 9661 eV are attributed to the 1s to $4p_{xy}$ transition that indicates

the existence of $Zn^{2+}$ species in MOFs. The EXAFS date shows that the MOFs have the Zn-O bond distance of 2.015 ± 01 with a coordination number of 3.42.

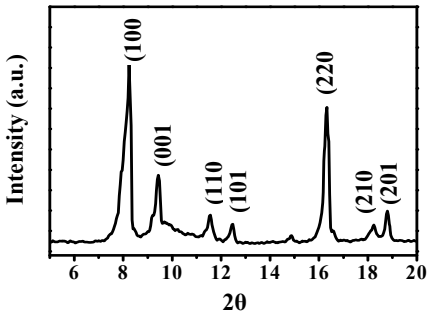


**Figure 1.** XRD pattern of $Zn_2(bdc)_2dabco$ MOFs.

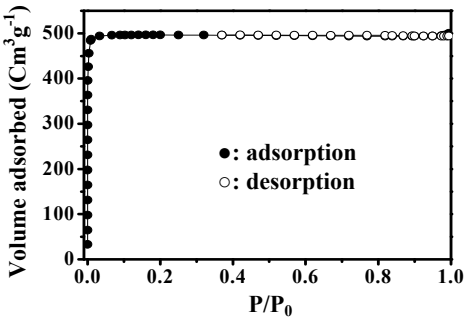


**Figure 2.** Nitrogen isotherms of $Zn_2(bdc)_2dabco$.

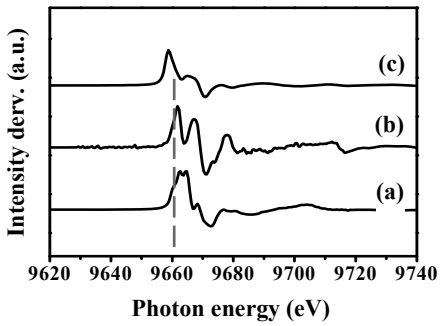


**Figure 3.** XANES spectra of (a) $Zn_2(bdc)_2dabco$, (b) ZnO and (c) Zn.

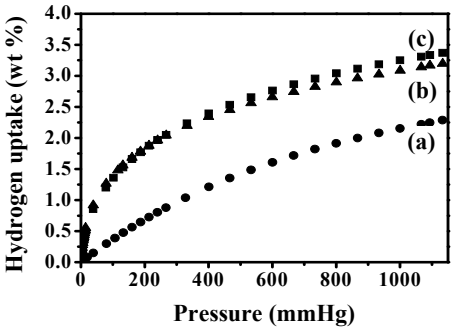


**Figure 4.** Hydrogen sorption isotherms of (a) $Zn_2(bdc)_2dabco$, (b) Pt/Ac- $Zn_2(bdc)_2dabco$ and (c) Pd/Ac- $Zn_2(bdc)_2dabco$ at 78 K.

$H_2$ can be stored via spillover in nanostructured materials. Secondary spillover is also possible to increase the $H_2$ storage capacity by using a catalyst that is capable of dissociating $H_2$. In this work, we used a catalyst containing 5 wt % Pt or Pd on active carbon (Pt/AC or Pd/AC) as the source for $H_2$ dissociation. Here, active carbon was the primary receptor for hydrogen spillover. The catalyst and the $Zn_2(bdc)_2dabco$ (secondary spillover receptor) were introduced into a physical mixture. The high pressure hydrogen adsorption in Pt/AC-$Zn_2(bdc)_2dabco$ and Pd/AC- $Zn_2(bdc)_2dabco$ at 78 K are shown in **Fig. 4**. In addition, to determine the enhancing effect of spillover, adsorption in unmodified $Zn_2(bdc)_2dabco$ also carried out at the same condition. The reversible $H_2$ storage capacity were markedly increased to 3.20 and 3.35 wt % at 1100 mmHg by mixing $Zn_2(bdc)_2dabco$ with Pt/AC or Pd/AC catalyst respectively than that of unmodified $Zn_2(bdc)_2dabco$. This significant enhancement is clear evidence of the hydrogen spillover by carbon bridges. These results indicated that the creation of carbon bridges has remarkably importance for achieving higher hydrogen adsorption by secondary spillover.

## 4. Conclusions

The obtained results revealed that hydrogen storage by spillover is a promising technique to achieve higher hydrogen storage in MOFs. The highest measured $H_2$ uptake was 3.35 wt % at 1100 mmHg and 78 K. The secondary spillover technique by carbon bridge can be applied in other MOFs and higher sorption capacity can be expected.

## References


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