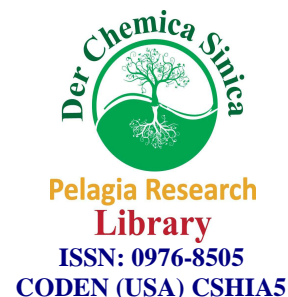




Pelagia Research Library

Der Chemica Sinica, 2015, 6(9):25-29



Storage of hydrogen: a future generation fuel, by metal organic frameworks

Usha Raju and Anil Kumar*

Department of Applied Chemistry, Delhi Technological University, Shahabad, Daulatpur, Bawana Road, Delhi, India

ABSTRACT

The continuous depletion of petroleum reserves with consequent carbon emission is a great area of concern and draws our attention towards the use of a cleaner fuel for transportation. Out of many alternative renewable energy sources, use of hydrogen seems to be the most preferred choice because of its high energy content as compared to gasoline and comparatively cleaner combustion products, which may save the earth from further pollution. However one of the major challenges in use of hydrogen as transportation fuel is the storage of this highly flammable gas, whereas stationary hydrogen storage has not been a big problem. Metal Organic Frameworks can serve as potential hydrogen storage and carriers for mobile applications.

Keywords: MOF, Hydrogen storage, Hydrogen interaction, Surface area.

INTRODUCTION

The article summarizes different research activities leading to the development of metal organic frameworks for use as mobile carriers of hydrogen- a future generation fuel. Different strategies leading to better yield, stability of metal organic frameworks, high porosity and surface area, enhanced hydrogen interaction and storage, post synthetic modifications and computational studies for improved design of MOFs with special emphasis on their hydrogen storage capacity, carried out by various prominent research groups in the last one decade have been presented. The future prospects for the synthesis of MOF complexes to be used as hydrogen storage materials for mobile applications, through green synthetic pathways have also been discussed.

Established hydrogen storage techniques:

Some of the established technologies for hydrogen storage include compressed hydrogen gas in high pressure hydrogen cylinders, liquid hydrogen in a specially designed cryogenic tank, underground hydrogen storage and pipeline hydrogen similar to natural gas network, carbon nanotubes and carbon nanofibres to name a few. These techniques make use of physical hydrogen storage where hydrogen gas is stored by compression or liquefaction under pressure. The liquefaction of hydrogen involves a great energy loss and tank must be perfectly insulated to avoid boil off. The chemical hydrogen storage makes use of Metal hydrides such as LiAlH_4 , NaAlH_4 , MgH_2 etc. However the use of complex metal hydrides as hydrogen carriers has limitations of poor hydrogen capacity, slow adsorption and release of gas and high cost. Most metal hydrides involve strong bonding with hydrogen and thus require high temperature for the release of hydrogen. The cheaper hydrogen production in high yield by enzymatic action from starch and water under mild conditions has been reported by Percival Zhang [1]. The method involves the use of starch or cellulose from biomass with a high energy density of 14.8 mass% as hydrogen carrier. Compounds named Liquid Organic Hydrogen Carrier (LOHC), where hydrogen in a cyclic fashion can be charged and discharged with considerable amount, have been proposed to be used as fuels which may replace the hydrocarbon fuels [2]. Hydrogen has been produced by catalytic decomposition of formic

acid in an aqueous solution at a temperature range of 15-220⁰ C using a catalyst preferably ruthenium by G. Laurenczy and co-workers [3], which they claim to be a suitable method for providing hydrogen for a motor, fuel cell or chemical synthesis. Imidazolium ionic liquids with Pd/C or Ir⁰ nano particle catalyst can be used for on board hydrogen storage, which can hold up to 30gL⁻¹ of hydrogen at atmospheric pressure as claimed by J. Dupont and co-workers [4]. The carbon materials are known to be adsorbents for gases like hydrogen and carbon dioxide which mainly depends upon micro pores in activated carbons. Thus pore structure in these materials needs to be governed, which can be carried out either by the process of activation or templating. Templating has the advantage of providing large number of homogeneous pores [5]. D.C Elias and co-workers reported that Graphene, an atomic layer of Graphite can react with atomic hydrogen reversibly to form Graphane and release hydrogen after heating to 450⁰ C [6]. R. T. Yang and co-workers have reported that Graphene has a characteristic property to dissociate hydrogen, which leads to increase in storage capacity. The group carried out their hydrogen isotope scrambling experiments at different temperature and pressure conditions to determine the potential applications of Graphene in hydrogenation and dehydrogenation catalysis [7]. Dillion and co-workers have provided the experimental evidence for storage of hydrogen in carbon nanotubes at room temperature [8]. Since then attempts have been made towards hydrogen storage in various nanotubes and nanostructures as summarized by George E. Froudakis in his review [9]. Chen, P. and co-workers have shown that carbon nanotubes doped with alkali metals exhibit high hydrogen uptake and have reported hydrogen adsorption of 20 wt. % and 14 wt. % by lithium and potassium doped carbon nanotubes respectively, between 1 atmosphere and 200-400⁰ C temperature for Li doped and near room temperature for potassium doped carbon nanotubes [10]. Later on Ralph T. Yang adopted the same procedure and measured hydrogen uptake in carbon nanotubes as carried out by Chen, P. and co-workers and concluded that the high hydrogen uptake was due to moisture contamination and actual adsorption by alkali doped carbon nanotubes was merely 2 wt % with dry hydrogen [11]. The results reported by one group could not be reproduced by another group due to sensitive experimental conditions and measurement procedures, which lead to controversy regarding efficient storage of hydrogen in carbon nanotubes. Rao and co-workers investigated the hydrogen storage on single and multi-walled nanotubes as well as aligned bundles of multi-walled nanotubes and found that maximum adsorption of 3.7 wt % was obtained with densely aligned bundles of acid treated multi-walled nano tubes [12]. They have verified the hydrogen storage capacities of materials through electrochemical studies and have claimed that their results were reproducible.

Metal organic frameworks and hydrogen storage:

Hydrogen a cleaner fuel can play an important role in pollution control once the challenges for safe and economical onboard hydrogen storage are overcome. This can be achieved by the synthesis of materials suitable for charging and discharging large quantities of hydrogen at appropriate rate under normal temperature and pressure conditions, which can attain the goal set by the US Department of Energy (DOE website-energy.gov). Metal Organic Frameworks seem to be the best possible option to serve the purpose as they can be tailored to meet the requirement of mobile hydrogen storage and carrier, because of their unique properties like, exceptionally large surface area, tunable structure, pore dimensions and reversible uptake and release of hydrogen. MOFs constitute a class of inorganic-organic hybrid materials with highly porous crystalline structure consisting of metal ions or their clusters, coordinated to organic ligands to form one, two or three dimensional crystal structures [13]. Their structures can be manipulated by introducing multiple metals with different coordination properties and appropriate choice of organic ligands with suitable functionalities for efficient uptake and storage of hydrogen for mobile applications. These materials have an added advantage of being synthesized by simple hydrothermal or solvothermal methods in which highly porous structure can be achieved by solvent evacuation without destabilizing the framework. The name "MOF" was first introduced by Yaghi group. The story of hydrogen storage by an MOF started in 2003 when Yaghi and co-workers claimed the first hydrogen storage by MOF-5 to be 4.5 wt. % at 78 K and 1.0 wt. % under conditions of room temperature and 20 bar pressure [14]. Jeong Yong Lee and co-workers have carried out low temperature gas sorption analysis on three dimensional micro porous MOFs and two dimensional layered complexes and studied the pore characteristics based on the argon adsorption-desorption isotherms at 87K and concluded that all micro porous metal organic frameworks have a relatively high hydrogen capacity [15]. Yaghi and co-workers while analyzing the behavior of MOFs towards low pressure hydrogen adsorption in contrast with their structures, have found that catenated materials display remarkable capacities for hydrogen adsorption on a molar basis whereas functionalization does not have much influence on adsorption. The hydrogen adsorption can be enhanced by providing larger charge gradient on the metal oxide units and by reducing the pore dimensions by adjusting link metrics [16]. Space and co-workers while studying the role of polarization interactions in hydrogen storage by a metal-organic framework, have demonstrated through their Monte Carlo Simulations, that highly ionic framework with narrow pores lead to strong hydrogen interactions and large hydrogen uptake by an MOF [17]. Li and co-workers have reported hydrogen spillover which involves atomic hydrogen adsorption, to be an appropriate method to enhance the hydrogen storage capacity of the covalent-organic frameworks and MOFs at room temperature [18]. A three dimensional MOF

$\text{Cu}_3(\text{BTC})_2$ HKUST-1, [BTC=benzene-1,3,5 tricarboxylate] in high yield and in less reaction time has been synthesized by Zong-Qun Li and co-workers by using ultrasonic method under ambient temperature and pressure conditions [19]. The method has been claimed to be an efficient and environmentally friendly. Bo Xiao and co-workers in their review have presented the development of nano porous metal-organic framework materials used for physical hydrogen storage [20]. According to them good MOF materials are achieved by judicious choice of metal cations and their counter ions, organic ligands and pH values. The solvent used not only helps to dissolve reactants, but also plays a role as a structure directing agent. To get good quality product in high yield temperature, pressure and reaction time are very crucial. Carbon nanostructures have been considered to be the most desired candidates for the storage of hydrogen reversibly, but physisorption of H_2 on pure carbon nanostructures does not fulfill the criteria prescribed by the U.S. Department of Energy (DOE), probably due to low hydrogen adsorption energy and weak $\text{H}_2\text{-H}_2$ interaction. B. Kuchta and co-workers have described the influence of various factors such as adsorption energy, pore dimensions, $\text{H}_2\text{-H}_2$ interaction, chemically substituting carbon by an atom like boron or Li^+ ion and quantum effects on the hydrogen adsorption capacity of the nano porous structures with the help of Grand Canonical Monte Carlo Simulations and have shown that chemically substituting boron atoms in place of carbon atoms enhances adsorption capacity of the material [21]. The extent of gas adsorption on metal-organic framework surface depends on temperature and pressure of the gas. The adsorption increases generally with decrease in temperature and increasing pressure. Furthermore, greater is the surface area, more is the adsorption of hydrogen. Another crucial factor is high enthalpy of hydrogen adsorption. Theoretically 22-25 kJ/mol energy interactions are sufficient for adsorption and quick de-sorption. MOFs with exposed metal sites are the best suited for adsorption, which can be achieved by the proper choice of ligands whose geometries do not allow the metal to be fully coordinated. The removal of volatile solvent molecules bound to metal, post synthetic modifications by metallation of MOFs or super critical carbon dioxide drying of MOFs synthesized by solvothermal techniques can enhance their hydrogen storage capacity. The super critically dried MOFs exhibit exceptionally high surface area and much enhanced hydrogen storage capacity as compared to MOFs dried by the thermal evaporation of the solvent [22]. Hongwei Yang and co-workers have carried out the mechano-chemical synthesis of a micro porous MOF $\text{Cu}_3(\text{BTC})_2$, [BTC=Benzen-1, 3, 5-tricarboxylate] also known as HKUST-1 from trimesic acid and various copper salts [23]. The water of hydration if present in the reactants improved the crystalline nature of $\text{Cu}_3(\text{BTC})_2$. Adding a little solvent prior to grinding further improved crystallinity and lead to increased specific surface area and hydrogen storage capacity. They have claimed the mechano-chemical synthesis to be a very fast method for the quantitative preparation of $\text{Cu}_3(\text{BTC})_2$. A rapid, inexpensive and environmentally friendly, solvothermal method for the synthesis of isorecticular metal-organic framework, IRMOF-8 has been reported by Samuel A. Orefuwa and co-workers [24]. They have claimed the product of this rapid synthesis route to have greater surface area, higher hydrogen storage capacity and larger pore volume compared to those prepared by the traditional solvothermal convection oven synthesis. P. Li and co-workers have studied the stability and hydrogen storage properties of metal-decorated benzene complexes and have reported that most metals from first to third period of the periodic table can be strongly adsorbed on the surface of benzene except Be, Na, Mg, K & Zn and found that Ca was the most suitable metal for hydrogen storage. Metals like Al, Ga & transition metals from Ti to Cu are not suitable for hydrogen storage [25]. According to them two Ca atoms prefer to be isolated on the benzene surface and each Ca can adsorb up to four hydrogen molecules, thus yielding a hydrogen uptake of 9.2 wt. %. Their whole work is based on first- principles calculations. Narae Jin and co-workers have synthesized two ultra micro porous MOFs based on pyrimidyl- 5-carboxylate using Cobalt II chloride and Iron III perchlorate and have reported their selective gas sorption properties [26]. One of them shows the selective sorption of H_2 against N_2 at 77 K and CO_2 against CH_4 at 195 K and for other the selective sorption has been observed only at 77 K and sorption is almost indiscriminate at 195 K. The difference is believed to originate from the different pore structures of both. Hussein Rasool Abid and co-workers have synthesized Zirconium metal-organic frameworks (Zr-MOFs) with or without ammonium hydroxide as an additive [27]. They have found that BET surface area, pore volume and crystal size of Zr-MOF was reduced after addition of ammonium hydroxide whereas crystalline structure and thermal stability were maintained. William A. Goddard and co-workers have calculated hydrogen uptake by Li, Na, K metalated metal-organic frameworks at 298K using Grand Canonical Monte Carlo Simulations and have reported MOF 200-Li and MOF 200-Na to attain DOE 2015 target of 5.5 wt. % at 298K [28]. Dewei Rao and co-workers have proposed Li-doped iso-reticular IRMOF-9 for hydrogen storage, having hydrogen uptake of 4.91 wt. % and 36.6g/L at 243 K and 100 bar pressure based on their Grand Canonical Monte Carlo Simulations, which is expected to achieve 2017 DOE target [29]. Atanu Santra and co-workers have reported gas storage in a partially fluorinated highly stable 3-D porous MOF $\{[\text{Zn}_4\text{O}(\text{bfbpdc})_3(\text{bpy})_{0.5}(\text{H}_2\text{O})] \cdot (3\text{DMF})(\text{H}_2\text{O})_n\}$ using 2,2'-bis-trifluoromethyl-biphenyl-4,4'-dicarboxylic acid $[\text{H}_2\text{bfbpdc}]$ [30]. Lalonde and co-workers have reported the synthesis and hydrogen storage properties of two MOFs with Zwitter ion structure formed from negatively charged $\text{Zn}_2(\text{CO}_2)_5$ nodes and N- heterocyclic azolium group in the linker, with the aim to increase the hydrogen- framework interaction and enhanced hydrogen adsorption due to free carboxylic acid sites [31]. A nitrogen rich MOF, NTU-105, having BET surface area of 3543 m^2/g having exceptionally high H_2 and

CO₂ uptake capacity, due to favourable interaction between the nitrogen rich triazole units and gas molecules, as proved by experimental measurements and molecular simulations has been reported by Xiao. Jun Wang and co-workers [32]. Light porous material with high stability required for onboard hydrogen storage can be achieved by using light weight alkali & alkaline earth metals. Among the light metals Al draws special attention. Various Al-MOFs, MIL-53, MIL-96, MIL-100, MIL-110 have been synthesized and studied by Ferey and his group [33]. Mannuela Gaab and co-workers have reported that synthesis of an Al-MOF named Basonite A520 can be carried out in a water based route with 90% yield and the method is both economical & environmentally compatible [34]. The properties such as surface area, crystallinity of the material obtained by water based synthesis are the same as those synthesized by DMF based method. While synthesizing HKUST-1 and MOF-5 by the procedure known in literature, Bin Mu has reported that raising the temperature, longer reaction time, use of N,N- dimethyl formamide (DMF) in place of N,N- diethyl formamide (DEF) produces MOF with lesser surface area. Whereas use of fresh anhydrous DEF, minimum exposure to moisture and controlled temperature for solvent evacuation offer better yield, porosity and surface area of the product [35]. Recently Hiroshi Kitagawa and co-workers have reported that capacity and speed of hydrogen storage gets enhanced and storage capacity becomes double when Pd nano crystals are covered with MOF HKUST-1 [(Copper (II) 1, 3, 5 benzene tri carboxylate)] [36]. To improve the binding energy of hydrogen with metal-organic framework Yaghi group has synthesized MOF-649 and MOF-650 using polarized linker 2, 6-azulenedicarboxylate which results in polar pore walls and enhanced hydrogen interaction with the framework. MOF-650 adsorbs 14.8 mg g⁻¹ of hydrogen at 77 K and 1 bar [37]. Mario Wriedt and co-workers are in the process of designing frameworks with pores which can selectively adsorb hydrogen [38]. The team has synthesized two micro porous zwitterionic metal-organic frameworks {[M(bdc bpy)(OH₂)₄].4H₂O}_n with M = Mn, Ni, designing the anionic Viologen derivative, 1,1'-bis(3,5-dicarboxybenzyl)-4,4'-bipyridinium dibromide dehydrate solvate (H₄bdc bpyBr₂.2H₂O) and its self assembly with metal II acetate in an aqueous medium. Both contain three dimensional hydrogen bonded supramolecular frameworks with one dimensional channel pores, the pore surfaces are lined with charge gradients leading to adsorption of hydrogen due to polarization effects. Yaghi group has synthesized MOFs containing plurality of metal clusters having one or more metal ions in each cluster and plurality of ligands with sufficient number of available sites for adsorption of gases so that the surface area of the MOFs is larger than 5500 m²/g [39]. Quite recently Yaghi group has synthesized multivariate MOF-177 derivatives incorporating different functional groups in the organic linker [40]. They have concluded that presence of more than one functional group in the MOF results in enhanced gas adsorption by the MOF and an increase in volumetric hydrogen uptake takes place in all multivariate MOF-177 as compared to unfunctionalized MOF-177.

RESULTS AND DISCUSSION

Though much of the work has been done and studied regarding uptake and storage of hydrogen by metal-organic frameworks for mobile applications as automobile fuel by different groups of researchers, but still there exists a gap between efficiency of those MOFs for hydrogen storage and targets set by US Department of Energy (DOE). Committed to provide a cleaner environment to the future generation, President Barack Obama has recently announced a new \$ 1 billion Department Of Energy loan guarantee program in addition to the existing one for investment in renewable energy sources and storage systems [41].

CONCLUSION

Complexation of organic linkers with a combination of metal ions using green synthetic pathways involving the use of water as a solvent, organic solvent free synthesis, microwave assisted reaction conditions, ultrasonic synthesis of MOFs, post synthetic modifications and super critical CO₂ drying of the material can serve the purpose for obtaining a suitable material for onboard storage of hydrogen, a clean fuel in transportation and to prevent further damage to the environment and consequent global warming caused by the use of hydrocarbon based fuels.

REFERENCES

- [1] Zhang, Y. H. P. *Energy & Environmental Science*, **2009**, 2, 272.
- [2] Teichmann, D., Arlt, W., Wsatterscheid, P., Freymann, R. *Energy & Environmental Science*, **2011**, 4, 2767.
- [3] Patent: Laurenczy, G., Fellay, C., Dyson, P. *US 20100068131 A1*, (**2010**).
- [4] Stracke, M. P., Ebeling, G., Cataluna, R., Dupont, J. *Energy Fuels*, **2007**, 21, 1695.
- [5] Inagaki, M., Kang, F., Toyoda, M., Konno, H. *Advanced Materials Science and Engineering of Carbon: Tsinghua University Press*, **2014**.

- [6] Elias, D. C., Nair, R. R., Mohiuddin, T. M., Morozov, S. V., Blake, P., Halsall, M. P., Ferrari, A. C., Boukhalov, D. W., Katsnelson, M. I., Geim, A. K., Novoselov, K. S. *Science*, **2009**, 323, 610.
- [7] Stuckert, N., Yang, R. T. 12 AIChE Annual Meeting, Conference Proceedings, Pittsburgh, PA; United States. 28Oct. - 2Nov. **2012**.
- [8] Dillion, A. C., Jones, K. M., Bekkedahl, T. A., Kiang, C. H., Bethune, D. S., Heben, M. J. *Nature*, **1997**, 386, 377.
- [9] Froudakis, G. E. *Materials Today*, **2011**, 14, 324.
- [10] Chen, P., Wu, X., Li, J., Tan, K. L. *Science*, **1999**, 285, 91.
- [11] Yang, R. T. *Carbon*, **2000**, 38, 623.
- [12] Gundiah, G., Govindaraj, A., Rajalakshmi, N., Dhathathreyan, K. S., Rao, C. N. R. *Journal of Materials Chemistry*, **2003**, 13, 209.
- [13] Kaskel, S. Porous Metal-Organic Frameworks, p.1190-1249, in Handbook of Porous Solids (**2002**), Wiley Online Library.
- [14] Rosi, N. L., Eckert, J., Eddaoudi, M., Vodak, D. T., Kim, J., O'Keeffe, M., Yaghi, O. M. *Science*, **2003**, 300, 1127.
- [15] Lee, J. Y., Li, J., Jang, J. *Journal of Solid State Chemistry*, **2005**, 178, 2527.
- [16] Rowsell, J. L. C., Yaghi, O. M. *Journal of the American Chemical Society*, **2006**, 128, 1304.
- [17] Belof, J. L., Stern, A. C., Eddaoudi, M., Space, B. *Journal of the American Chemical Society*, **2007**, 129, 15202.
- [18] Li, Y., Yang, R. T. *AIChE Journal*, **2008**, 54, 269.
- [19] Li, Z. Q., Qiu, L. G., Xu, T., Wu, Y., Wang, W., Wu, Z. Y., Jiang, X. *Materials Letters*, **2009**, 63, 78.
- [20] Xiao, B., Yuan, Q. *Particuology*, **2009**, 7, 129.
- [21] Kuchta, B., Firlej, L., Cepel, R., Pfeifer, P., Wexler, C. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **2010**, 357, 61.
- [22] Xiang, Z., Cao, D., Shao, X., Wang, W., Zhang, J., Wu, W. *Chemical Engineering Science*, **2010**, 65, 3140.
- [23] Yang, H., Orefuwa, S., Goudy, A. *Microporous and Mesoporous Materials*, **2011**, 143, 37.
- [24] Orefuwa, S. A., Yang, H., Goudy, A. J. *Microporous and Mesoporous Materials*, **2012**, 153, 88.
- [25] Li, P., Deng, S. H., Liu, G. H., Zhang, L., Huang, J., Yu, J. Y. *Journal of Power Sources*, **2012**, 211, 27.
- [26] Jin, N., Seo, J., Hong, K., Chun, H. *Microporous and Mesoporous Materials*, **2012**, 150, 32.
- [27] Abid, H. R., Pham, G. H., Ang, H. M., Tade, M. O., Wang, S. *Journal of Colloid and Interface Science*, **2012**, 366, 120.
- [28] Mendoza-Cortes, J. L., Han, S. S., Goddard, W. A. *Journal of Physical Chemistry A*, **2012**, 116, 1621.
- [29] Meng, Z., Lu, R., Rao, D., Kan, E., Xiao, C., Deng, K. *International Journal of Hydrogen Energy*, **2013**, 38, 9811.
- [30] Santra, A., Senkovska, I., Kaskel, S., Bharadwaj, P. K. *Inorganic Chemistry*, **2013**, 52, 7358.
- [31] Lalonde, M. B., Getman, R. B., Lee, J. Y., Roberts, J. M., Sarjeant, A. A., Scheidt, K. A., Georgiev, P. A., Embs, J. P., Eckert, J., Farha, O. K., Snurr, R. Q., Hupp, J. T. *Crystal Engineering Communications*, **2013**, 15, 9408.
- [32] Wang, X. J., Li, P. Z., Chen, Y., Zhang, Q., Zhang, H., Chan, X. X., Ganguly, R., Li, Y., Jiang, J., Zhao, Y. *Scientific Reports*, **2013**, 3, 1149.
- [33] Ferey, G., Haouas, M., Loiseau, T., Taulelle, F. *Chemistry of Materials*, **2014**, 26, 299.
- [34] Gaab, M., Trukhan, N., Maurer, S., Gummaraju, R., Muller, U. *Microporous and Mesoporous Materials*, **2012**, 157, 131.
- [35] Mu, Bin. Ph. D Thesis, Georgia Institute of Technology, Atlanta, Georgia. United States. **2011**.
- [36] Li, G., Kobayashi, H., Taylor, J. M., Ikeda, R., Kubota, Y., Kato, K., Takata, M., Yamamoto, T., Toh, S., Matsumura, S., Kitagawa, H. *Nature Materials*, **2014**, 13, 802.
- [37] Barman, S., Khutia, A., Koitz, R., Blacque, O., Furukawa, H., Iannuzzi, M., Yaghi, O. M., Janiak, C., Hutter, J., Berke, H. *Journal of Materials Chemistry A*, **2014**, 2, 18823.
- [38] Aulakh, D., Varghese, J. R., Wriedt, M. *Inorganic Chemistry*, **2015**, 54, 1756.
- [39] Patent: Yaghi, O. M., Kim, J., Ko, N., Choi, S. B., Furukawa, H. *US 8841471B2*, (**2014**).
- [40] Zhang, Y. B., Furukawa, H., Ko, N., Nie, W., Park, H. J., Okajima, S., Cordova, K. E., Deng, H., Kim, J., Yaghi, O. M. *Journal of the American Chemical Society*, **2015**, 137, 2641.
- [41] Chemical & Engineering News: Volume 93, Issue 34, p. 5, News of the Week, Issue date: **August 31, 2015**.