Metal-organic framework – nanostructured carbon composites

Thesis

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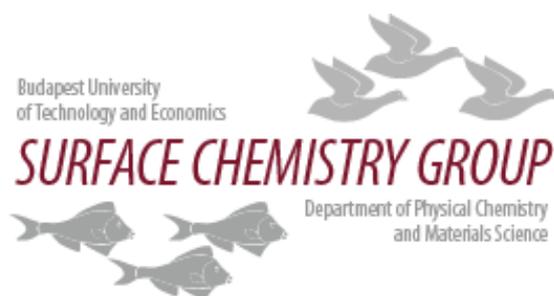
2020

1   Introduction

Natural gas and biogas or zero emission hydrogen as alternative fuels could significantly reduce the environmental pressures from carbon dioxide and other emissions. The current high pressure or cryogenic gas storage methods are not ideal for the economical storage of these gases for mobile (transport) application. Adsorption gas storage offers attractive solutions for the capture and portable storage of these gases if economically relevant nanoporous adsorbents are available [1]. The American Department of Energy (DoE) established the corresponding gravimetric and/or volumetric adsorption capacities of the adsorbents [2, 3].

Metal-organic frameworks (MOFs) with outstanding gas adsorption properties are one of the most promising materials for this purpose. In their hybrid structure, multivalent metal ions or clusters are connected by organic ligands via coordination bonds. Thus, constructing three-dimensional open framework, with ordered open pore structure. The wide variety of suitable metal ions and organic ligands provide excellent means to tune the porous structure best fitting to various applications such as gas storage (Fig. 1) [4].
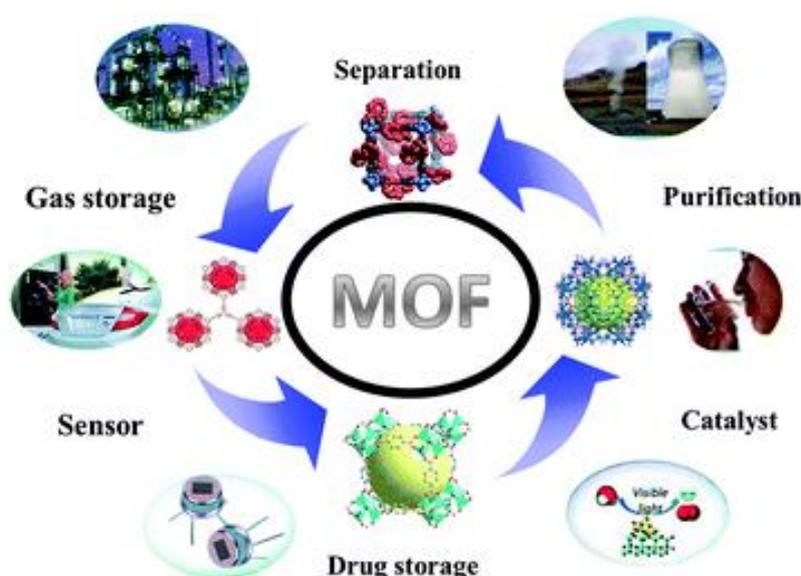

Figure 1. Widespread application of MOFs. [5]

[1] Kaneko, K. and Rodríguez-Reinoso, F. Eds.: Nanoporous Materials for Gas Storage.; Publisher: *Springer* **2019**. DOI: 10.1007/978-981-13-3504-4

[2] The Advanced Research Projects Agency – Energy of the U.S Department of Energy. Methane Opportunities for Vehicular Energy (MOVE). https://arpa-e-foa.energy.gov/Default.aspx?Search=move&SearchType=#FoaIddc1d731e-f2cf-4be9-b6ac-ab315582d000 Last time accessed: June 2020

[3] DoE Technical Targets for Onboard Hydrogen Storage for Light-Duty Vehicles. https://www.energy.gov/eere/fuelcells/doe-technical-targets-onboard-hydrogen-storage-light-duty-vehicles. Last time accessed: May 2020

[4] Kaskel, S. Ed: The Chemistry of Metal-Organic Frameworks: Synthesis, Characterization, and Applications. Publisher: *Wiley-VCH Verlag GmbH & Co. KGaA*. **2016**. DOI: 10.1002/9783527693078

[5] Chaemchuen, S. et. al: Metal-organic frameworks for upgrading biogas via CO_2 adsorption to biogas green energy. *Chem. Soc. Rev.* **2013**, 42, 9304-9332. DOI: 10.1039/c3cs60244c

The methane adsorption capacity of an iconic MOF namely copper benzene-1,3,5-tricarboxylate (Cu_3btc_2) abbreviated as CuBTC or HKUST-1 (after Hong-Kong University of Science and Technology [6]), reaches the volumetric DoE target of 263 cm^3 (STP) CH_4/cm^3 adsorbent at 25 °C and 65 bar [7]. Moreover, the production of HKUST-1 is also solved on an industrial level, which is an outstanding advantage. Unfortunately, HKUST-1 suffers from three main drawbacks. As most of the MOFs it is sensitive to humidity. Another problem is that the powder form is not really favoured for light duty mobile vehicle applications. Binder free pelleting would solve the latter matter, but the amorphization of the crystalline structure occurring during the compression process may result in porosity loss. The third challenge is the insufficient thermal conductivity of MOFs which compromises both the gas uptake and working capacity. Composites with an appropriate thermally conductive nanostructured material may provide a solution to all the three challenges. They could potentially enhance the mechanical stability and the water resistance as well as the thermal conductivity of the MOF – carbon associated systems [8].

In my thesis two of the above mentioned challenges, water sensitivity and the mechanical stability will be addressed. Nanostructured carbon support such as carbon aerogel and graphene oxide will be studied as potential associating materials. The water sensitivity of HKUST-1 will be revealed and the effect of the carbon supports will be demonstrated.

[6] Chui, S.S.-Y. et. al: A Chemically Functionalizable Nanoporous Material [$Cu_3(TMA)_2(H_2O)_3$]n. *Science* **1999**, 283, 1148-1150. DOI: 10.1126/science.283.5405.1148

[7] Peng, Y. et al: Methane Storage in Metal−Organic Frameworks: Current Records, Surprise Findings, and Challenges. *J. Am. Chem. Soc.* **2013**, 135, 11887-11894. DOI: 10.1021/ja4045289

[8] Liu, X.-W. et. al: Composites of metal-organic frameworks and carbon-based materials: preparations, functionalities and applications. *J. Mater. Chem. A* **2016**, 4, 3584-3616. DOI: 10.1039/c5ta09924b

2   State-of-the-art – *Motivation*

HKUST-1 was firstly synthetized by Chui et. al. in 1999 [9]. In the three-dimensional open framework of HKUST-1, copper(II) ions are linked by the btc^{3-} organic ligands via the formation of copper − carboxylate coordination bonds. In the so called secondary building unit (SBU) of HKUST-1 two copper(II) ions form coordination bonds with one-one carboxylate groups of the organic linker, therefore each copper has one coordinatively unsaturated site. The pore network of HKUST-1 is characterized by three pore sizes of 0.5, 1.1 and 1.35 nm (Fig. 2) [10, 11].
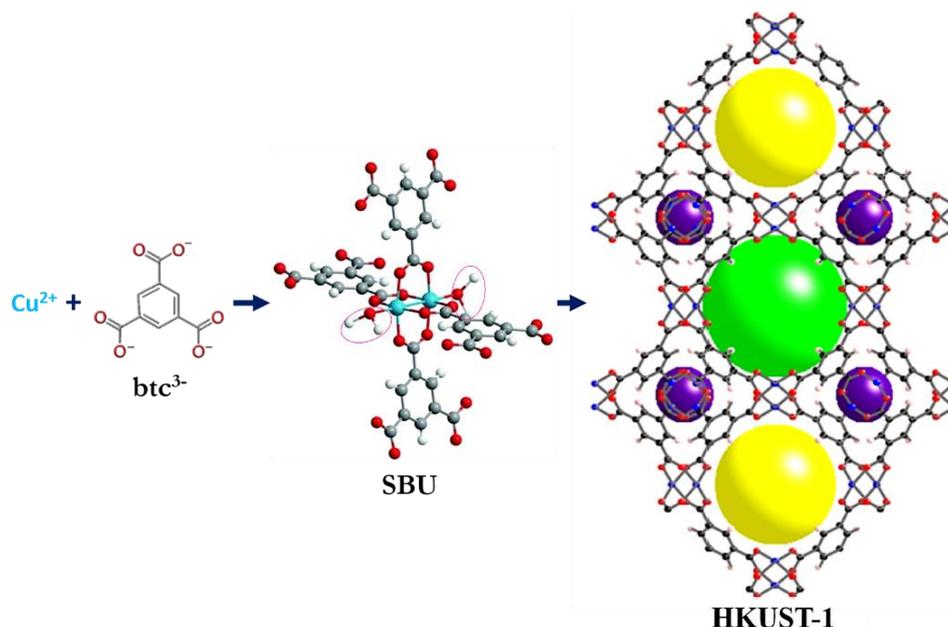

Figure 2. *Structural formation of HKUST-1. C: grey; O: red; Cu: blue; H: white, the H_2O molecules coordinated to the open metal sites in the secondary building unit (SBU) are highlighted in pink ellipse. The van der Waals spheres mark the size of the adsorption space: purple (0.5 nm); yellow (1.1 nm); green (1.35 nm). [after 10 and 11]*

HKUST-1 is most commonly prepared under solvothermal conditions using an inorganic copper salt and H_3btc in precursor solutions. After the reaction, the formed crystals are usually washed with pure solvent in several steps to remove the unreacted components and the turquoise powder product is obtained by filtration. The pore structure of the air dried material is partly occupied by solvent molecules. These solvent molecules can be completely eliminated at elevated temperature (100-180 °C) in vacuum (so called activation) [11].

[9] Worrall, S. D. et. al: Metal-organic framework templated electrodeposition of functional gold nanostructures. *Electrochim. Acta* **2016**, 222, 361–369. DOI: 10.1016/j.electacta.2016.10.187

[10] Gotthardt, M. A. et. al Synthesis and characterization of bimetallic metal–organic framework Cu–Ru-BTC with HKUST-1 structure. *Dalton Trans.* **2015**, 44, 2052-2056. DOI: 10.1039/c4dt02491e

[11] Chen, Y. et. al: High efficiency synthesis of HKUST-1 under mild conditions with high BET surface area and CO_2 uptake capacity. *Prog. Nat. Sci.* **2018**, 28, 584–589. DOI: 10.1016/j.pnsc.2018.08.002

Despite the fact that HKUST-1 is one of the most widely studied MOF, the reported TG/DTG studies have not revealed all the processes that take place during the thermal decomposition of HKUST-1. Literature references consistently state that until ca. 130 °C physisorbed water or solvent molecules are released from the framework which decomposes around 300 °C both in inert and oxidative atmospheres [12-14]. The explanations given to the minor, ca. 1-5 % mass loss between 130-250 °C is less solid. In some cases, it is simply neglected [12] or is considered as part of the first step [13]. It is also interpreted as the removal of chemisorbed water molecules or more strongly bound solvent [14], but these suggestions are hardly supported by experimental data. *One of the goals of my PhD work was to clarify the thermal behaviour of HKUST-1 which also might be relevant in its water sensitivity. Expanding the potential of TG/DTG with evolving gas analysis (with FTIR and MS techniques) allowed a deeper insight into the molecular structure of the MOF microcrystals.*

Water sensitivity is a well-known drawback of HKUST-1 [15]. It has been reported, that the activated HKUST-1 is sensitive to water vapour, despite the fact that it can be synthesised under hydrothermal conditions as well. *After observing the aging of the non activated HKUST-1 a systematic study was designed to reveal the role of water in the deterioration of the crystalline texture of this MOF. Air dried HKUST-1, obtained in solvothermal route from inorganic copper nitrate and organic ligand benzene-1,3,5-tricarboxylate and its activated form were exposed to relative humidity (RH 11% and RH 85%) for 21 days. The change of the morphology was followed by various imaging methods, powder XRD, TG/DTG and low temperature nitrogen adsorption techniques.*

Construction of composites is an attractive solution to overcome the drawbacks of HKUST-1, particularly if it can additionally improve its gas adsorption properties. Nanostructured carbons such as activated carbons (ACs), carbon aerogels (CAs), graphene (GN), graphene oxide (GO), reduced graphene oxide (rGO) and carbon nanotubes (CNTs) are promising associating materials thanks to their great chemical, thermal and mechanical stability [16].

[12] Schlichte, K. et. al: Improved synthesis, thermal stability and catalytic properties of the metal-organic framework compound Cu$_3$(BTC)$_2$. *Microporous and Mesoporous Mater.* **2004**, 73, 81-88. DOI: 10.1016/j.micromeso.2003.12.027

[13] Lin, et. al: Synthesis and characterization of porous HKUST-1 metal organic frameworks for hydrogen storage. *Int. J. Hydrog. Energy* **2012**, 37, 13865-13871. DOI:10.1016/j.ijhydene.2012.04.105

[14] Qiu, W. et. al: Effect of Activation Temperature on Catalytic Performance of CuBTC for CO Oxidation. *Chin. J. Catal.* **2012**, 33, 986–992. DOI: 10.1016/S1872-2067(11)60389-6

[15] DeCoste, et. al: The effect of water adsorption on the structure of the carboxylate containing metal–organic frameworks Cu-BTC, Mg-MOF-74, and UiO-66. *J. Mater. Chem. A* **2013**, 1, 11922-11932. DOI: 10.1039/c3ta12497e

[16] Sule, R. et al: MOFs-carbon hybrid nanocomposites in environmental protection applications. Environmental Science and Pollution Research **2020**, 27, 16004-16018. DOI: 10.1007/s11356-020-08299-x

Carbon aerogels generally possess a three-dimensional, hierarchical pore network built up from interconnected primary nanoparticles. They contain micro-, meso- and macropores [17]. Their hierarchical pore structure and surface chemistry can be controlled and modified in many ways. Their preparation includes three major steps. Firstly, a sol-gel polymerization reaction is applied to prepare hydrogels. Thereafter, the supercritical drying leads to the formation of polymer aerogels. Finally, carbon aerogels can be obtained by the carbonization of the polymer gels (Fig. 3).
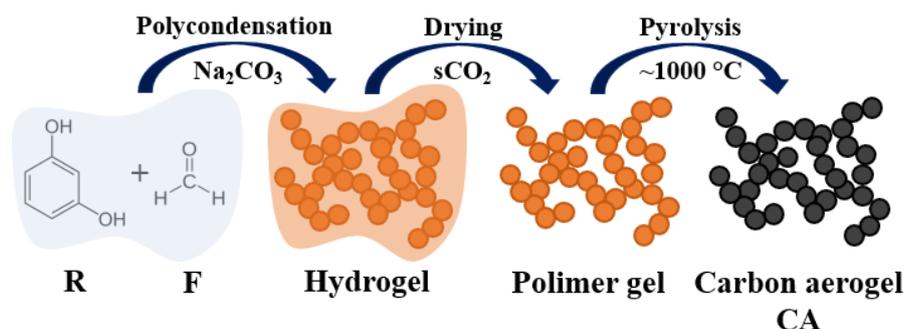

Figure 3. Schematic illustration of the synthesis of resorcinol (R) – formaldehyde (F) based carbon aerogels.

Graphene oxide is a derivative of the two-dimensional carbon allotrope, graphene. The single or few carbon layers are decorated with various oxygen-containing functional groups (Fig. 4) [18]. GO is commonly produced by the oxidative exfoliation of graphite and often used as an intermediate for graphene manufacturing.
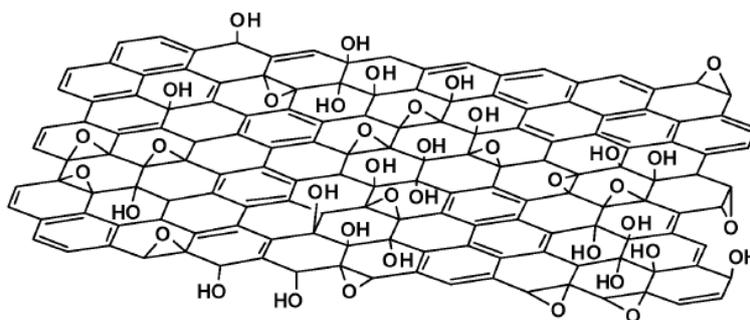

Fig. 4. The Lerf-Klinowski model of graphene oxide. [18]

I aimed to study the potential protective effect of GO and CA in HKUST-1 – nanostructured carbon binary materials. The associated systems were investigated regarding the problem of water sensitivity and/or pelletisation. The thermal conductivity of the carbon materials may also help to overcome the thermal management of the adsorption/desorption cycles during the adsorption gas storage. (Investigation of this problem was beyond the scope of this thesis.)

[17] Arenillas, A. et al. Fierro, V.; Maldonado-Hodar, F.J.; Bailón-Garcia, E.; Job, N. Organic and Carbon Gels. From Laboratory Synthesis to Applications. *Book Series: Advances in Sol-Gel Derived Materials and Technologies.* Springer, 2019 ISBN 978-3-030-13897-4
[18] Dreyer et al. The chemistry of graphene oxide. *Chem. Soc. Rev.*, **2010**, 39, 228–240. DOI: 10.1039/b917103g

3   Experimental methods

3.1   Sample preparation

HKUST-1 was synthesized under solvothermal conditions after Wang et al. [19] at 80 °C in the stochiometric reaction mixture of copper nitrate trihydrate ($Cu(NO_3)_2\cdot 3H_2O$) and benzene-1,3,5-tricarboxylic acid (H_3btc) in a one-to-one volumetric mixture of ethanol and water. The obtained turquoise crystals were washed with ethanol, dried in air (20 °C, 48h, 40-50% relative humidity: RH) and stored in a tightly closed container. Samples were outgassed at 110 or 180 °C in vacuum (activation) directly before certain measurements.

Carbon aerogel was prepared from resorcinol-formaldehyde (RF) polymer aerogel after Pekala and Czakkel et al. [20, 21]. Surface of the powdered carbon aerogel was altered from basic to acidic by oxidation with nitric acid to ensure optimal conditions for HKUST-1 crystal formation [22]. The improved Hummers method was used to prepare the graphene oxide [23]. The obtained GO suspension was concentrated to 1.1 wt%.

HKUST-1 – CA binary samples were obtained in two different routes. HKUST-1@CA was prepared when powdered CA was added to the precursor solution of HKUST-1 prior to the solvothermal synthesis. A thoroughly homogenized physical mixture (HKUST-1+CA) from powdered CA and HKUST-1 of similar composition (mass ratio 1:1) was used as comparison. HKUST-1@GO samples were prepared similarly to HKUST-1@CA. The GO content was changed between 6-24 wt% by adding 1-2.5 g/dm^3 GO to the precursor solution.

3.2   Methods

Scanning electron microscopy (SEM), conventional and high resolution transmission electron microscopy (TEM or HRTEM) and low temperature N_2 adsorption was used to characterize the morphology and the pore structure of the samples. Powder X-ray diffraction (XRD) was used for the phase analysis of the crystalline components. Simultaneous thermogravimetry/differential thermal analysis (TG/DTA) itself or combined with mass spectroscopy (TG/DTA-MS) or Fourier transform infrared spectroscopy (TG-FTIR) were applied to reveal the thermal decomposition of HKUST-1 and the binary samples. Methane, hydrogen and carbon dioxide adsorption capacity of selected samples was also compared.

[19] Wang, F. et. al: The controlled regulation of morphology and size of HKUST-1 by "coordination modulation method". *Microporous and Mesoporous Mater.* **2013**, 173, 181–188. DOI: 10.1016/j.micromeso.2013.02.023

[20] Pekala, R. W.: Organic aerogels from the polycondensation of resorcinol with formaldehyde. *Journal of Materials Science* **1989**, 24, 3221-3227. DOI: 10.1007/BF01139044

[21] Czakkel, O. et. al: Influence of drying on the morphology of resorcinol–formaldehyde-based carbon gels. *Microporous and Mesoporous Materials* **2005**, 86, 124–133. DOI:10.1016/j.micromeso.2005.07.021

[22] Domán, A.: The role of the chemical properties of the carbon surface is materials science. From the Schay-Nagy isotherm equation to reduced graphene oxide. (In Hungarian). *Magyar Kémiai Folyóirat*, **2018**, 124(4), 153-156. DOI: 10.24100/MKF.2018.04.153

[23] Marcano, D.C. et. al: Improved synthesis of graphene oxide. *ACS Nano* **2010**, 4, 4806 4814. DOI: 10.1021/nn1006368

4 Results and discussion

4.1 Characterisation of HKUST-1

The strictly microporous HKUST-1, the iconic metal organic framework capable for adsorptive gas storage was reproducibly obtained under solvothermal conditions with a yield of 84%. Its air dried light blue form (Fig. 5a) contains ca. 9.4 mol water/Cu_3btc_2 unit, bonded directly to the free sites of copper atoms (3 mol water/Cu_3btc_2 unit) and as bulk water filling the micropores. The pore network of the HKUST-1 can be liberated from these water molecules by the evacuation of the MOF at elevated temperature in vacuum (activation). The appearing dark blue colour (Fig. 5b) indicates the alternation in the coordination sphere of the copper(II) ions, namely the formation of open metal sites.
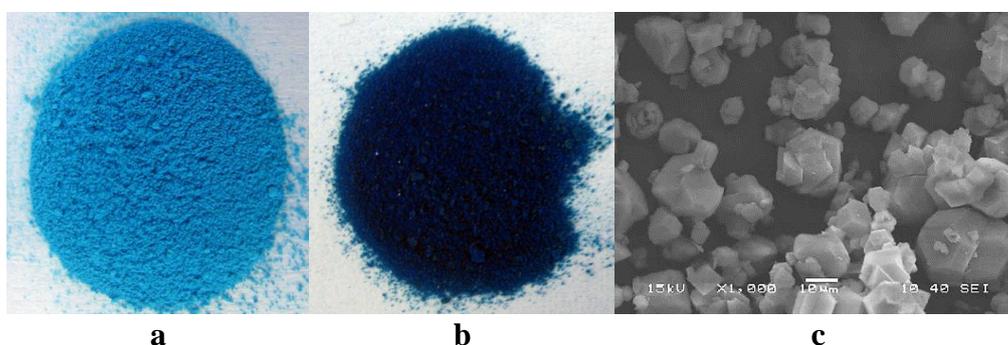

| a | b | c |

Figure 5. *Macroscopic appearance of (a) air dried and (b) activated (180 °C, vacuum) HKUST-1 and (c) SEM image of the characteristic polyhedral MOF crystals. [24]*

Based on the thermal analysis coupled with *in situ* evolving analysis I found that in the first stage up to 150 °C only water was released from the air dried system in spite of the fact that the crystal formation occurred in ethanol-water mixture and they were washed with ethanol prior to drying. During the thermal analysis of the air dried HKUST-1 a ca. 3% exothermic weight loss occurs between 150 and 250 °C which up to now has not been properly recognised in the literature (Fig. 6a: inset). Only ethanol was identified in the evolving gas phase in the mentioned temperature range under inert conditions. Due to the elevated temperature it is proposed that the ethanol originates from the thermal decomposition of mono-ethyl esters which may form during the solvothermal reaction between the ethanol and some of the carboxylic groups of the benzene-1,3,5-tricarboxylate ligands on the surface or edge positions of HKUST-1. Thus, ethanol molecules probably serve as barriers that limit the growth of the HKUST-1 crystal in the precursor solution [24].

[24] **Domán, A.** et. al: In situ evolved gas analysis assisted thermogravimetric (TG-FTIR and TG/DTA–MS) studies on non-activated copper benzene-1,3,5-tricarboxylate. *Thermochim. Acta* **2017**, 647, 62–69. DOI: 10.1016/j.tca.2016.11.013
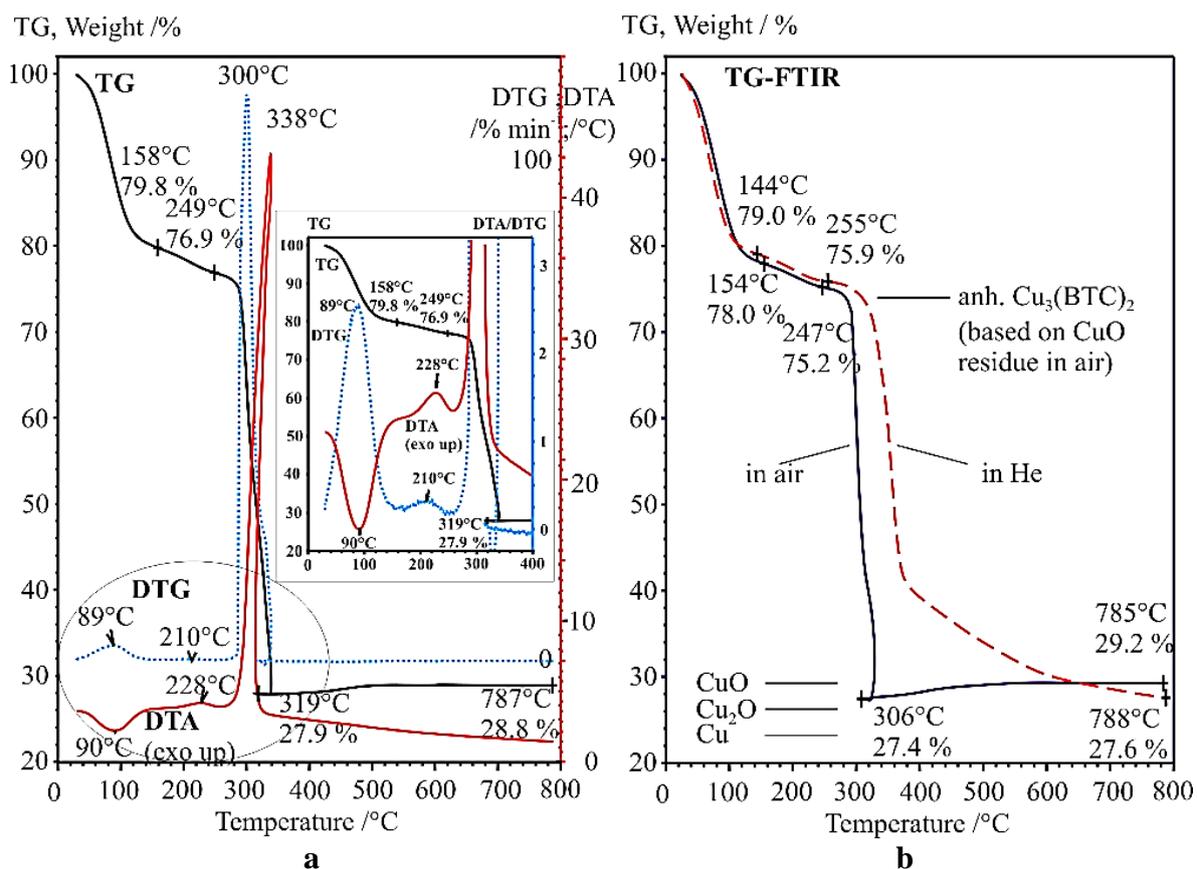
Figure 6. *Thermal analysis of HKUST-1. a) TG curve (black solid line), DTG curve (red solid line) and DTA curve (light blue dotted line) obtained by TG/DTA instrument (heating rate: 10 °C/min) in air (gas flow: 130 cm³/min); inset shows the DTG and DTA curves in enlarged view. b) TG curves obtained by TG instrument (heating rate: 10 °C/min) in air and helium (gas flow: 130 cm³/min). [24]*

The decomposition of the organic ligand occurred at around 300 °C in agreement with literature data. In air, the degradation products can burn out completely, while in helium this step is followed by a long, monotonically decreasing tail up to the end of the experiment at 800 °C (Fig. 6b). The XRD phase analysis of the residual masses obtained at 325 °C and 800 °C revealed that the mass increase above 320 °C in air corresponds to the oxidation reaction of Cu_2O:
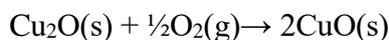
$$Cu_2O(s) + \tfrac{1}{2}O_2(g) \rightarrow 2CuO(s)$$

[24] **Domán, A.** et. al: In situ evolved gas analysis assisted thermogravimetric (TG-FTIR and TG/DTA–MS) studies on non-activated copper benzene-1,3,5-tricarboxylate. *Thermochim. Acta* **2017**, 647, 62–69. DOI: 10.1016/j.tca.2016.11.013

4.2 Effect of storage conditions (relative humidity) of HKUST-1

It is well known that HKUST-1 is not stable under humid condition, however the mechanism of its deterioration is not fully understood. The apparent surface area decreased but no sign of the hydrolysis of the mono-ester groups was detected by TG/DTG on the air dried HKUST-1 sample stored in sealed container. The half-life of our air dried sample was found 33 month from regular nitrogen adsorption measurements. Samples with different pre-history i) simply air dried ii) activated at 110 °C or 180 °C in vacuum were exposed to humid atmospheres (RH 11% and RH 85%) at 20 °C for 21 days. SEM imaging, low temperature nitrogen adsorption (Figs. 7a and b), powder XRD (Figs. 7c and d) and TG/DTG (Figs. 7e and f) measurements were used to reveal the extent of deterioration and the degraded structures. It was found that the water molecules withheld after air drying significantly stabilize the exclusively microporous structure of HKUST-1. To maximize the gas adsorption capacity the removal of the water molecules cannot be circumvented. Once all the water is removed the re-exposition to humid gas/air results in the enhanced decomposition/transformation of the crystalline structure (Figs. 7a and b: 110_11 and 110_85 curves) and corrupts the adsorption properties. Depending on the relative humidity this may lead to the partial (Fig. 7a: 110_11 and 180_11 curves) or total (Fig. 7b: 110_85 and 180_85 curves) loss of the microporosity, in the former case along the development of mesopores. HKUST-1 is transformed into a mixture of several, up to know not identified crystalline compounds at high RH (Fig. 7b: 110_85 and 180_85 curves). Water molecules with five different binding strengths were distinguished in the activated samples after exposure to RH 85% for 21 days (Fig. 7f: 110_85 and 180_85 curves). I succeeded to identify one of the minor products as hydrogen triaqua benzene-1,3,5-tricarboxylate copper(II) $[Cu(OOC)_2(C_6H_3COOH) \cdot 3H_2O]$ based on XRD database (PDF_00-064-1336). My finding implies that the re-adsorbing water attacks the copper – carboxylate bonds [25, 26].

[25] **Domán, A.** et al.: Role of water molecules in the decomposition of HKUST-1: evidence from adsorption, thermoanalytical, X-ray and neutron scattering measurements. *Appl. Surf. Sci.* **2019**, 480, 138 – 147. DOI: 10.1016/j.apsusc.2019.02.177
[26] **Domán, A.** et al: Graphene Oxide Protected Copper Benzene-1,3,5-Tricarboxylate for Clean Energy Gas Adsorption. *Nanomaterials* **2020**, 10, 1182. DOI: 10.3390/nano10061182
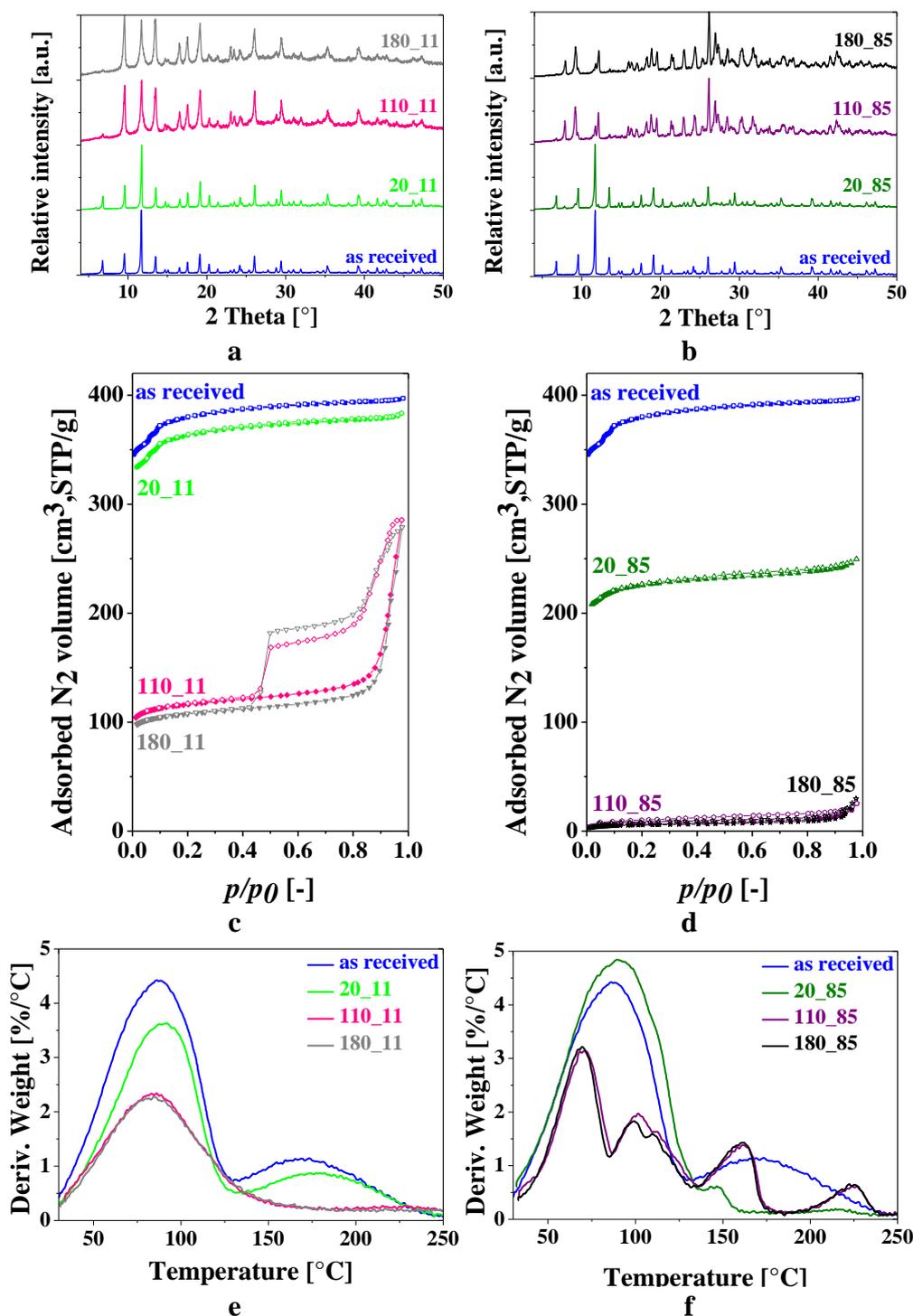
Figure 7. *Comparison of (a, b) XRD patterns, (c, d) low temperature (-196 °C) N₂ adsorption/desorption isotherms and (e, f) DTG curves up to 250 °C of the HKUST-1 samples with different prehistory. The samples were designated by drying temperature and relative humidity (a, c, e: RH 11%; b, d, f: RH 85%). 110_11 thus refers to the sample evacuated at 110 °C in vacuum before exposure to RH 11%. For XRD and TG (air flow: 130 cm³/min; heating rate: 10 °C/min) samples were directly measured after the treatment. Prior to the low temperature N₂ adsorption measurements (-196 °C), the cured samples were outgassed in the same manner as HKUST-1, at 180 °C for 24 h in vacuum.*

[25] **Domán, A.** et al.: Role of water molecules in the decomposition of HKUST-1: evidence from adsorption, thermoanalytical, X-ray and neutron scattering measurements. *Appl. Surf. Sci.* **2019**, 480, 138 – 147. DOI: 10.1016/j.apsusc.2019.02.177

[26] **Domán, A.** et al: Graphene Oxide Protected Copper Benzene-1,3,5-Tricarboxylate for Clean Energy Gas Adsorption. *Nanomaterials* **2020**, 10, 1182. DOI: 10.3390/nano10061182

4.3   Compression of HKUST-1 powder

HKUST-1 binder free pellets were successfully formed using an OL57 hydraulic press under 25-200 bar external pressure. However, there is a high price to pay for compacting as a drastic loss in the crystallinity and the porosity of HKUST-1 occurred even at the lowest pressure applied [27].

4.4   Associated systems with nanostructured carbon materials

HKUST-1 formation in the presence of amorphous mesoporous carbon aerogel (CA) and practically two dimensional graphene oxide (GO) under solvothermal conditions was equally successful. The Cu – benzene-1,3,5-tricarboxylate self-assembly was influenced by the amount of the associating material, challenging the purity of the HKUST-1. Higher (2.5 g/dm^3) GO content led to the formation of not identified side-product(s) with different crystal structure and porosity. The distinctive nature of the nanostructured carbon materials resulted in dissimilar composite systems, HKUST-1@CA and HKUST-1@GO. The apparent surface area of HKUST-1@CA was less than expected from additivity as HKUST-1 partially occupies the pores of the aerogel. The micropores of the HKUST-1 and the wider pores of the CA form a micro-meso-macroporous system. The surface area of the formed HKUST-1@GO systems was practically unaffected by the presence of GO at a suitable concentration of 1-2 g/dm^3 in the precursor solution. During the association the excellent adsorption properties characteristic of HKUST-1 were preserved [26, 27].

The water resistance and pressure tolerance of the selected HKUST-1 – nanostructured carbon materials were further investigated under the similar conditions as HKUST-1. HKUST-1@CA is able to form pellets at 100 and 200 bar, however, the high pressure corrupts the HKUST-1 structure and suppresses the adsorption capacity. The nanoscale structure of the physical mixture of HKUST-1 and CA with similar composition (50 wt%) cannot be pelletized up to 200 bar and its HKUST-1 content is more sensitive to external pressure than in the co-synthetized HKUST-1@CA. GO may protect the copper – carboxylate coordination bonds in HKUST-1@GO systems against water, at least temporarily, by sacrificing the ester groups formed during the solvothermal synthesis between ethanol and the carboxyl groups on the GO sheets. The HKUST-1@GO forms pellets already at 25 bar. The porosity loss is less than that of the "free" HKUST-1 and not influenced by the pressure. The flexible GO sheets with high mechanical stability may act as compressible spacers between the HKUST-1 crystals thus preventing their amorphization [26, 27].

[26] **Domán, A.** et al: Graphene Oxide Protected Copper Benzene-1,3,5-Tricarboxylate for Clean Energy Gas Adsorption. *Nanomaterials* **2020**, 10, 1182. DOI: 10.3390/nano10061182

[27] **Domán, A.** et al: Pressure resistance of copper benzene-1,3,5-tricarboxylate-carbon aerogel composites. *Appl. Surf. Sci.* **2018**, 434, 1300–1310. DOI: 10.1016/j.apsusc.2017.11.251

5 Application possibilities

The multifaceted applications of MOFs is illustrated in Figure 1. Among the MOFs HKUST-1 is one of the most promising adsorbents for gas storage and gas separation applications. It has a remarkable methane uptake meeting the volumetric DoE target. Moreover, HKUST-1 is already produced on industrial scale. The chemical modification of HKUST-1 or its application in associated systems are routes to overcome the problem of water sensitivity, pelletisation and thermal conductivity.

I have shown that of the two studied associating materials, graphene oxide – in optimal amounts – is able to provide protection to the HKUST-1 structure during pelletization and against moisture in HKUST-1@GO associated systems.
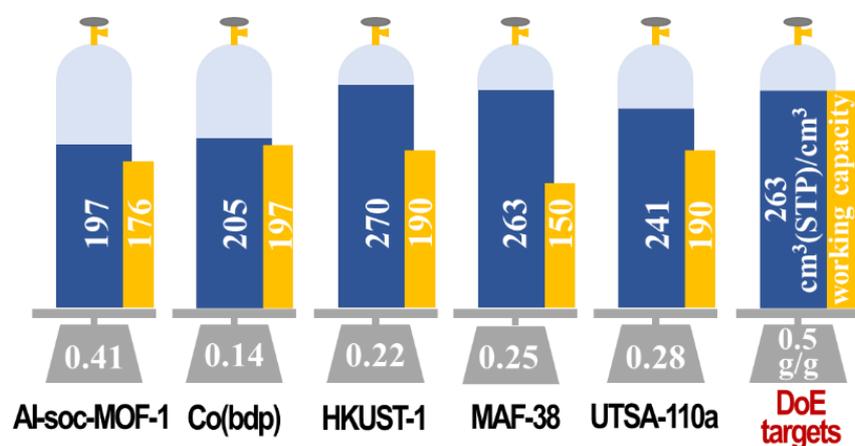

Figure 8. *HKUST-1 is outstanding among the MOFs approaching the DoE targets of gravimetric (grey balance), volumetric (blue cylinder) and volumetric working (yellow column) CH₄ adsorption capacities.*

6   New results

1. I was able to identify an until now neglected region in the TG/DTG curve of copper benzene-1,3,5-tricarboxylate (Cu_3btc_2 or HKUST-1) metal-organic framework prepared in water-ethanol binary solvent under solvothermal conditions. In situ evolving gas analysis and mass spectrometry revealed that the mass loss between 150 and 250 °C originates from the thermal decomposition of mono-ethyl esters which were formed during in the reaction between the ethanol and the carboxyl groups of the benzene-1,3,5-trycarboxylic acid organic ligand situated on the HKUST-1 crystal surface or in edge positions during crystal growth.

2. The air dried HKUST-1 contains ca. 9.4 mol water/Cu_3btc_2 unit. Part of this water fills the pores as "bulk" water and 3 mol/Cu_3btc_2 unit is related to the free Cu sites. The presence of the water results in a slow decay of the MOF with an estimated half-life of about 33 months. Exposition of these samples to 11 and 85% relative humidity (RH) for 21 days at 20 °C revealed that these water molecules provide a certain level of protection to the framework even against RH 85%. The samples keep their exclusively microporous character, but their pore volume is reduced according to RH conditions.

3. The samples activated in vacuum either in 110 or 180 °C lost both types of water. After exposing these activated samples to RH 11% for 21 days at 20 °C the re-adsorbing water molecules result in the partial disintegration of the isoreticular structure of the HKUST-1. The formerly exclusive microporosity is suppressed and mesopores with a size distribution maximum of 25 nm develop.

4. After exposing the activated samples to RH 85% for 21 days at 20 °C the re-adsorbed water molecules have five different binding strengths. The water molecules result in the complete disintegration of the isoreticular structure of the HKUST-1. The porosity is practically completely lost and several up to now unknown disintegration products are formed. I succeeded to identify one of the minor products as hydrogen triaqua benzene-1,3,5-tricarboxylate copper(II) [PDF_00-064-1336: $Cu(OOC)_2(C_6H_3COOH) \cdot 3H_2O$]. This product implies that the re-adsorbing water molecules attack the copper – carboxylate coordinative bonds.

5. I found that carbon aerogel (CA) is able to form an associated system (HKUST-1@CA) when added to the precursor solution of HKUST-1 prior to its solvothermal synthesis. The apparent surface area of the product is less than the area expected from additivity as HKUST-1 partially occupies the pores of the aerogel. The material forms compact pellets at 100 and 200 bar, however, the high pressure corrupts the HKUST-1 structure and suppresses the adsorption capacity. Nanoscale structure of a physical mixture with similar composition cannot be pelletized up to 200 bar and its HKUST-1 content is more sensitive to external pressure than in the co-synthetized HKUST-1@CA the porosity of which gradually decreases with pressure.

6. I found that graphene oxide (GO) is able to form an associated material with HKUST-1. GO – in an optimal concentration – is able to protect the copper – carboxylate coordination bonds in HKUST-1@GO systems against water, at least temporarily, by sacrificing the ester groups formed during the solvothermal synthesis between ethanol and the carboxyl groups on the GO sheets. HKUST-1@GO forms pellets already at 25 bar. The porosity loss was less than that of the "free" HKUST-1 and not influenced by the pressure. The flexible GO sheets with high mechanical stability may act as compressible spacers between the HKUST-1 crystals thus preventing their amorphization.

7 Publications

Publication part of the dissertation (Impact factors and Quartile categories from WoS)

1. **Domán, A.**; Madarász, J.; László, K. In situ evolved gas analysis assisted thermogravimetric (TG-FTIR and TG/DTA–MS) studies on non-activated copper benzene-1,3,5-tricarboxylate. *Thermochim. Acta* **2017**, 647, 62-69. DOI: 10.1016/j.tca.2016.11.013 (IF 2017: 2.189 (Q2); independent citiations: 6)

2. **Domán, A.**; Nagy, B.; Nichele, L.P.; Srankó, D.; Madarász, J.; László, K. Pressure resistance of copper benzene-1,3,5-tricarboxylate-carbon aerogel composites. *Appl. Surf. Sci.* **2018**, 434, 1300-1310. DOI: 10.1016/j.apsusc.2017.11.251 (IF 2018: 5.155 (Q1); independent citiations: 5)

3. **Domán, A.**; Czakkel, O.; Porcar, L.; Madarász, J.; Geissler, E.; László, K. Role of water molecules in the decomposition of HKUST-1: evidence from adsorption, thermoanalytical, X-ray and neutron scattering measurements. *Appl. Surf. Sci.* **2019**, 480, 138-147. DOI: 10.1016/j.apsusc.2019.02.177 (IF 2019: 6.182 (D1); independent citiations: 5)

4. **Domán, A.**; Klébert, Sz.; Madarász, J.; Sáfrán, Gy.; Wang, Y.; László, K. Graphene Oxide Protected Copper Benzene-1,3,5-Tricarboxylate for Clean Energy Gas Adsorption. *Nanomaterials* **2020**, 10, 1182. (Feature Paper) DOI: 10.3390/nano10061182 (IF 2019: 4.324 (Q2); independent citiations: 0)

Publications not strictly related to the dissertation

5. **Domán, A.**; Ábrahám, D.; Nagy, B.; László, K. The role of the chemical properties of the carbon surface in materials science. From the Schay-Nagy isotherm equation to reduced graphene oxide. (Original title in Hungarian: A szénfelület kémiai tulajdonságainak szerepe az anyagtudományban. A Schay-Nagy izoterma egyenlettől a redukált grafén-oxidig). *Magyar Kémiai Folyóirat* **2018**, 124(4), 153-156. DOI: 10.24100/MKF.2018.04.153 (IF: -)

6. Imre, A.; Szentannai, P.; Kustán, R.; László, K.; Groniewsky, A.; **Domán, A.**. Design of a Power-to-Gas based complex energy storage research and development center - challenges, related research (Original title in Hungarian: Egy Power-to-Gas alapú komplex energiatárolási kutatófejlesztőközpont terve – kihívások, kapcsolódó kutatások). *EnergiaGazdálkodás* **2019**, 60, 8-12. (IF: -)

7. Manek., E.; Berke, B.; Miklósi, N.; Sajbán, M.; **Domán, A.**; Fukuda, T.; Czakkel, O.; László, K. Thermal sensitivity of carbon nanotube and graphene oxide containing responsive hydrogel composites; *Express Polym. Lett.* **2016**, 10, 710-720. (IF 2015: 2.965 (Q1); independent citiations: 9).

8. Nagy, B.; Bakos I.; Bertóti, I.; **Domán, A.**; Menyhárd, A.; Mohai, M.; László, K. Synergism of nitrogen and reduced graphene in the electrocatalytic behavior of resorcinol - Formaldehyde based carbon aerogels. *Carbon* **2018**, 139, 872-879. (IF 2018: 7,466 (Q1); independent citiations: 7)

9. Nagy., B.; **Domán, A.**; Kállay-Menyhárd, A.; László, K. Influence of Graphene Oxide Incorporation on Resorcinol-Formaldehyde Polymer and Carbon Aerogels; *Period. Polytech. Chem. Eng.* **2018**, 62, 441-449. (IF 2018: 1,382 (Q3); independent citiations: 0)

10. Sebestyén, Z.; Jakab, E.; **Domán, A.**; Bokrossy, P.; Bertóti, I.; Madarász, J.; László, K. Thermal degradation of crab shell biomass, a nitrogen-containing carbon precursor. *J. Therm. Anal. Calorim.* **2020**. DOI: 10.1007/s10973-020-09438-9 (IF 2019: 2.731 (Q2); independent citiations: 0)

8   Conference presentations

Oral presentations

11. **Domán, A.**; Madarász, J.; László, K. Investigation of HKUST-1 metal organic framework by adsorption and in situ TG-FTIR and TG / DTA-MS methods (Original title in Hungarian: HKUST-1 fémorganikus térháló vizsgálata adszorpciós és in situ TG-FTIR és TG/DTA-MS módszerrel). *Collaborative meeting of MTA (Hungarian Academy of Sciences) Scientific Committee on Technical Chemistry, Material Science and Silicate Chemistry Working Committee and the MKE (Hungarian Chemical Society) Department of Colloid Chemistry and Nanotechnology*. BME, Budapest, Hungary; 09 Jan **2017**

12. **Domán, A.**; Madarász, J.; László, K. Synthesis and characterisation of copper benzene-1,3,5-tricarboxylate. *11th Conference on Colloid Chemistry*. Eszterházy Károly University; Eger, Hungary; 28-30 May **2018**

13. **Domán, A.**; Madarász, J.; László, K. Thermal analysis of copper benzene-1,3,5-tricarboxylate metal organic framework. (Original title in Hungarian: A réz-benzol-1,3,5-trikarboxilát fémorganikus térháló termoanalitikai vizsgálata.) *Collaborative meeting of Thermoanalytical Working Committee and the MKE (Hungarian Chemical Society) Thermal Analysis Group*. Hungarian Academy of Sciences (MTA), Centre of Natural Science (TTK), Budapest, Hungary; 26 Nov **2018**

14. **Domán, A.**; Madarász, J.; Klébert, Sz.; László, K. Effect of surface chemistry of graphene oxide (GO) derivatives on the formation of copper benzene-1,3,5-tricarboxylate 3D network (Original title in Hungarian: Grafén oxid (GO) származékok felületkémiájának hatása réz-benzol-1,3,5-trikarboxilát 3D térháló kialakulására.). *BME 2019/2020. academic year online ÚNKP Conference.* 7 May **2020**

Poster presentations

15. **Domán, A.**; Madarász, J.; László, K. In situ evolved gas analysis assisted thermogravimetric (TG-FTIR and TG/DTA–MS) studies on non-activated copperbenzene-1,3,5-tricarboxylate. *XIV. George Olah Doctoral Conference*, Budapest, Hungary, BME, 02 Feb **2017**

16. László, K.; **Domán, A.**; Madarász, J. Protective effect of a carbon aerogel in metal organic framework/carbon aerogel systems. *Carbon 2018, the World Conference on Carbon.* Madrid, Spain, 1-6 July **2018**

17. **Domán, A.**; Czakkel, O.; Porcar, L.; Madarász, J.; Geissler, E.; László, K. Role of water molecules in the decomposition of HKUST-1. *XV. George Olah Doctoral Conference* Budapest, Hungary, BME, 31 Jan **2019** (Best poster prize)

18. **Domán, A.**; Czakkel, O.; Porcar, L.; Madarász, J.; Geissler, E.; László, K. Role of water in the decomposition of HKUST-1. *Summer School and Workshop in Calorimetry and Thermal Analysis 2019 Calorimetry and thermal methods in material science*. Lyon, France, 16-21 June **2019** (Best poster prize)

19. **Domán, A.**; Madarász, J.; Klébert, Sz.; Dobos, G.; Sáfrány, Gy; László, K. Copper benzene-1,3,5-tricarboxylate@graphene oxide composites. *Okinawa Colloids 2019*. Okinawa, Japan, 03-08. Nov. **2019**