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Synthesis and characterisation of MIL-101(Cr) using different additives

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Abstract

MIL-101(Cr), a subgroup of metal-organic framework that has the capabilities as an adsorbent for CO_2 removal because of its large pore volume and high surface area. It is now commonly used to remove CO_2 from raw natural gas components as well as capture or lower CO_2 from flue gas or the atmosphere. The presence of CO_2 in raw natural gas will corrode the pipelines and lower the heating value which will lead to an increase in transportation costs. Therefore, it is significant to study the synthesis of MIL-101(Cr) with improved properties. Generally, the morphology and properties improvement of MIL-101(Cr) can be modified by the addition of additives or modulators (i.e., NaOH, HNO_3, HF). Hence, the objectives of this study are to synthesise the metal-organic framework of MIL-101(Cr) with different additives, and to characterise and analyse the synthesised MIL-101(Cr). The effect of adding modulators (additives) to MIL-101(Cr) was systematically discussed through X-Ray Diffraction (XRD), Scanning Electron Microscope (SEM), and Fourier Transform Infrared Spectroscopy (FTIR) analysis. The results showed that the Cr component was successfully integrated into each sample and MIL-101(Cr) – Non has a small particle size which indicates a larger surface area thus reflecting high porosity. It also has unsaturated metal sites which makes it excellent properties for gas adsorption.

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1.0 Introduction

Metal-organic frameworks (MOFs) are a new type of porous material that combines metal ions/clusters with organic ligands. It can be used as linkers/fillers for hybrid membranes, also known as mixed matrix membranes (MMM), that have been utilised widely in gas separations. Conventional fillers such as zeolites, carbon molecular sieves, and silicas were used to make the first MMM. In addition, carbon nanotubes, clay-layered silicates, MOFs, or graphene, are no stranger as filler in membrane fabrication (Taufiq Musa et al., 2021).

In comparison to rigid zeolite and activated carbon materials, MOFs have been able to replace conventional adsorbents due to their adjustability and flexibility in pore structure and framework building. Based on the literature review, MOF materials have been studied in a wide range of applications over the last decade and functions are abundance, including gas storage and separations by Lin et al., (2019), catalysis by Zhao et al., (2016), sensing by Wang et al., (2018), and medicine by He et al., (2015).

MIL-101(Cr) is an excellent form of MOF because of its great capabilities for adsorption, along with high surface area, large pore volume, and great chemical and thermal strengths. MIL-101(Cr) is formed by the coordination of the Cr_3O ionic cluster with terephthalic acid (H_2BDC), with the formula $[Cr_3(O)X(BDC)_3(H2O)_2]$. Hong et al., (2009) compared the adsorptive characteristics of 13X zeolite monoliths with MIL-101(Cr) monoliths for CO_2 adsorption where MIL-101(Cr) monoliths were fabricated using a hydrothermal process, and the results revealed that MIL-101(Cr) monoliths captured CO_2 better than zeolite monoliths. According to Yulia et al., (2019), another attraction of MIL-101(Cr)

is how easily functionalised ligands can be added during synthesis or how easily organic ligands may be treated chemically after synthesis. MIL-101(Cr) is a promising adsorber for future energy and good environmental applications due to its higher physicochemical features, chemical stability, and texture compared to other MOFs like MOF-5 and HKUST-1.

MIL-101(Cr) is extensively studied and used in a variety of scientific disciplines. The use of additives is frequently utilised in MOF synthesis in general to enhance the product's properties. In the synthesis of MIL-101(Cr), the impact of inorganic (mineral) and organic acid additives was carefully examined. Example of an inorganic compounds that are commonly used in previous studies are N,N′-dimethylformamide (DMF), and ethanol while an organic compound that is utilised in synthesising MIL-101(Cr) is terephthalic acid (H_2BDC). As a result of the chemical reaction between the inorganic and organic components, the material develops "pore templates" that are contoured by the solvent molecules and will be eliminated during high temperature washing and purification procedures (Kamal et al., 2020). Depending on the operating circumstances, the procedures may result in the obstruction of pores as a result of the incomplete removal of reactive medium from MOF products, such as the reaction solvents, remaining reactants, and side products. Terephthalic acid is a high-melting polymer, crystalline material that forms very strong fibres whereby it acts as a precursor for the formation of MIL-101(Cr). While ethanol and DMF are utilised during the purification process to remove any unreacted terephthalic acid.

In the present study, MIL-101(Cr) will be synthesised through the hydrothermal method with different additives. The additives used for this study are limited to sodium hydroxide (NaOH), nitric acid (HNO_3), and hydrofluoric acid (HF). The samples will be characterised by X-Ray Diffraction (XRD), Scanning Electron Microscope (SEM), and Fourier Transform Infrared Spectroscopy (FTIR).

2.0 Methodology

2.1 Materials

Chromium nitrate nonahydrate ($Cr(NO_3)_3 9H_2O$, Sigma-Aldrich, 97%), 1,4 benzene dicarboxylic acid (H_2BDC, Merck, 98%), N,N′-dimethylformamide (DMF, Systerm, 99.5+%), hydrofluoric acid (HF, Merck, 48%), sodium hydroxide pellets (NaOH, R&M, 97%), nitric acid (HNO_3, Merck, 65%), ethanol (EtOH, Merck, 99.9%) and deionised water (DI).

2.2 Synthesis and purification of MIL-101(Cr)

MIL-101(Cr) was synthesised by using the hydrothermal method according to a well-documented procedure (Rajati et al., 2018). A solution comprising $Cr(NO_3)_3 \cdot 9H_2O$ (12 g) and H_2BDC (5 g) was prepared in H_2O (100 mL) in a conventional procedure. The solution was placed into a Teflon-lined stainless-steel autoclave and heated at 220 °C for 8 hours. The reaction mixture was then allowed to cool naturally to room temperature for 24 hours, and the resulting green solid was filtered to eliminate any unreacted crystalline terephthalic acid. The green powder was washed with hot DMF (100 mL) at 100 °C and hot ethanol (100 mL) at 80 °C and hot DI water (100 mL) after drying at 120 °C overnight. To activate the MIL-101(Cr) particles, the washed solid was dried for 4 hours to yield fine green MIL-101(Cr) powder. The experiment was repeated for other additives. Fig. 1 shows the method to synthesise MIL-101(Cr).

2.3 Synthesis and purification of MIL-101(Cr) with different additives

A solution comprising $Cr(NO_3)_3 \cdot 9H_2O$ (12 g), H_2BDC (5 g), and chosen additive (5 mL) was prepared in deionised water (100 mL). The mixture is then transferred into the Teflon-lined stainless-steel autoclave and heated at 220 °C for 8 hours. After the reaction, the mixture was then allowed to cool naturally to room temperature for 24 hours. The purification method of MIL-101(Cr) with different additives is repeated as described above.

2.4 Characterisation of MIL-101(Cr)

XRD patterns of the prepared materials were identified by the powder X-ray diffraction (XRD) using Cu Kα radiation in a range of 2θ from 5° to 65° at a scan speed of 8°/min (Zhang et al., 2018). The Hitachi S-3400N scanning electron microscope (SEM) with energy dispersive spectroscopy (EDS) was used to determine the morphology, topography, and composition of materials. Before the SEM and EDS analyses, the sample surface was coated with a thin layer of platinum to improve the sample conductivity (Hong et al., 2009). A Nicolet iS10 instrument was utilised to obtain the samples' FTIR spectra at wavenumbers 400 cm^{-1} to 2000 cm^{-1}.

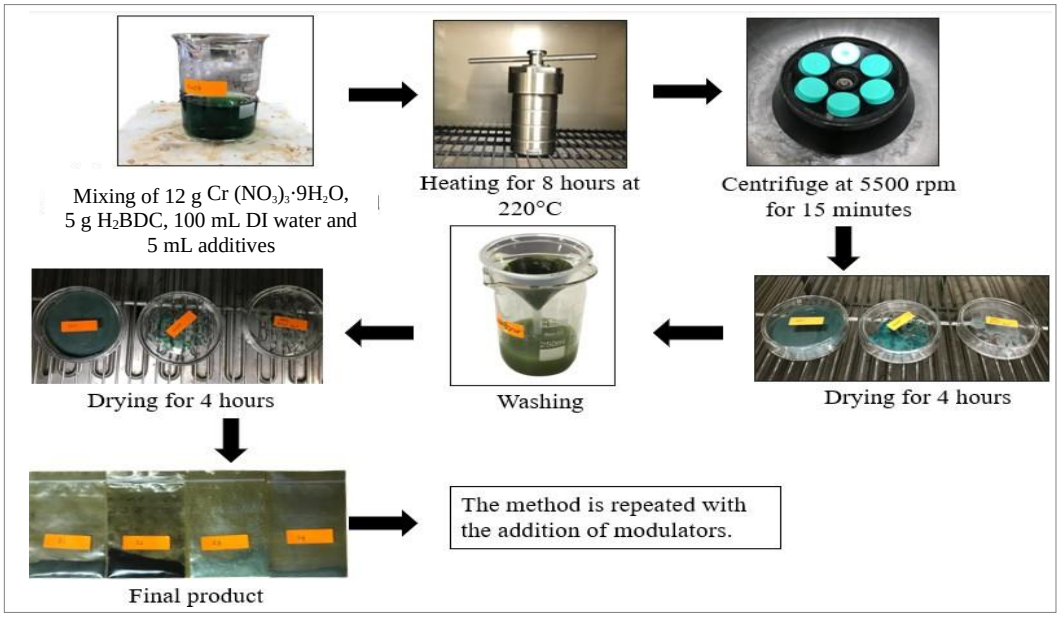


Fig 1: Method to synthesise MIL-101(Cr)

3.0 Results and discussion

3.1 Powder X-ray diffraction pattern

The XRD patterns of MIL-101(Cr)–Non, MIL-101 Cr)–NaOH, MIL-101(Cr)–HNO_3 and MIL-101(Cr)–HF are depicted in Fig. 2. The typical peaks of MIL-101(Cr)–Non can be seen at 9.53°, 10.82°, and 17.13° and the peaks are consistent with the literature (Bayazit et al., 2017). As for MIL-101(Cr)–NaOH, the peaks are observed at 5.08° and 12.23° wherein the pattern differs from the literature. However, the FTIR result exhibits that there are bands in which it corresponds to the symmetric (O–C–O) vibrations explaining the presence of dicarboxylate within the MIL-101(Cr) framework. In addition, NaOH has a high pH value that makes reagents more soluble and favourable for the production of benzene dicarboxylate and chromium trimers which shifted the equilibrium and led to the formation of MIL-101(Cr) (Zhao et al., 2018). As for MIL-101(Cr)–HNO_3 and MIL-101(Cr)–HF, the peaks observed at 18.03°, 17.87°, and 28.4°, respectively, exhibits that the presence of residuals of unreacted H_2BDC crystals in the sample framework.

The size of the particle is correlated with the breadth of the diffraction peak whereby a wider peak denotes a smaller particle (Chong et al., 2022). Hence, the XRD patterns indicated that MIL-101(Cr)–Non has the smallest particle size since it had the broadest diffraction peak compared to MIL-101(Cr)–NaOH, MIL-101(Cr)–HNO_3, and MIL-101(Cr)–HF.

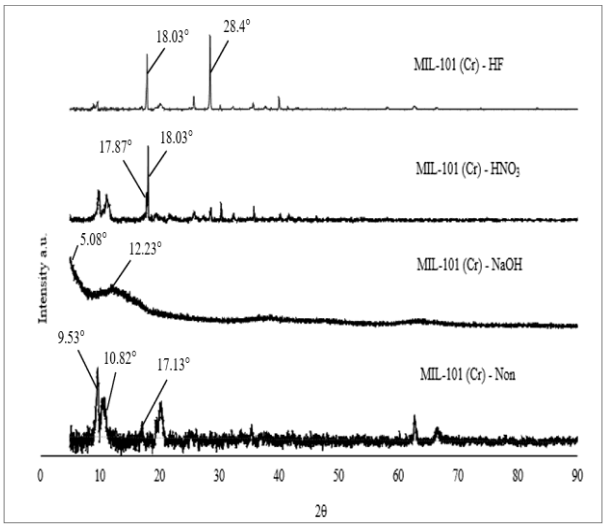


Fig 2: XRD patterns of MIL-101(Cr)–Non, MIL-101(Cr)–NaOH, MIL-101(Cr)–HNO_3, and MIL-101(Cr)–HF

3.2 Fourier transform infrared spectra analysis

3.2.1 MIL-101(Cr –Non

The FTIR plot for MIL-101(Cr)–Non is shown in Fig. 3. A significant absorption bands of about 745.56 cm^{-1} proved that it is due to the vibration of C–H group. Relevant C–H deformity was discovered at 1015.21 cm^{-1} indicating the presence of benzene rings (Chen et al., 2018).

Most of the adsorption bands in the domain between 600 and 1600 cm^{-1} belonged to the functional groups and the benzene ring inside the BDC natural linker that cooperated in the establishment of MIL-101(Cr).

Furthermore, the peaks of about 1396.23, 1503.69, and 1587.71 cm^{-1} were due to the symmetrical vibration of the O–C–O of the benzene ring and dicarboxylate functional group, respectively, within BDC (Chong et al., 2022).

3.2.2 MIL-101(Cr)–NaOH

The FTIR plot for MIL-101(Cr) – NaOH is shown in Fig. 4. The band at 1739 cm^{-1} indicates the presence of absorbed water. In addition, the band at 1363.01 cm^{-1} corresponds to the symmetric (O–C–O) vibrations implying the presence of dicarboxylate within the MIL-101(Cr) framework.

3.2.3 MIL-101(Cr)–HNO_3

Fig. 5 shows the FTIR plot for MIL-101(Cr)–HNO_3. The peak at 584 cm^{-1} was attributed to the Cr–O stretching vibration presenting a successful connection of metal clusters to carboxylic groups of H_2BDC. Most of the absorption bands in the region between 600 and 1600 cm^{-1} were related to the H_2BDC and its aromatic rings whereby 651.77, 747.07, 829.58, and 1015.21 cm^{-1} related to the C–H vibration, 1398.62 cm^{-1} signifies to the O–C–O stretching vibration. The peak at 1622.88 cm^{-1} represents the presence of unreacted H_2BDC lying through the pores (Sheikh Alivand et al., 2019).

3.2.4 MIL-101(CR)–HF

The FTIR plot for MIL-101(Cr)–HF is shown in Fig. 6. The absorption bands at 1017.16 and 1216.46 cm^{-1} were attributed to benzene and deformation vibration (C–H) (Liu et al., 2013). The peak observed at 1400.05 cm^{-1} corresponds to the symmetric O–C–O vibrations of dicarboxylate (BDC) linker in the structure of MIL-101(Cr) (Rajati et al., 2018).

3.3 Scanning electron microscope (SEM) Analysis

Fig. 7 exhibits SEM images of MIL-101(Cr) – Non (a), MIL-101(Cr) – NaOH (b), MIL-101(Cr) – HNO_3 (c), and MIL-101(Cr) – HF (d). SEM images depicted the morphologies of several additives used to produce MIL-101(Cr). SEM images revealed that MIL-101(Cr) – Non consists of small crystal particles. The surface of MIL-101(Cr) – Non was found to have many small round-shaped particles. These round-shaped particles are assumed to be unreacted chromium particles because of an excess of chromium metal reactant. The surface morphology is correlated with particle size (Chong et al., 2022).

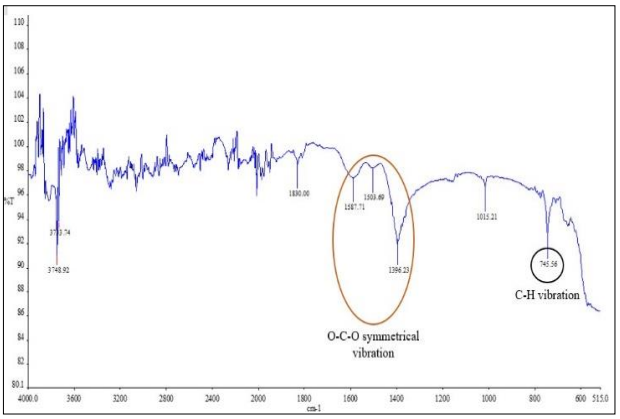


Fig 3: FTIR plots of MIL-101(Cr) – Non

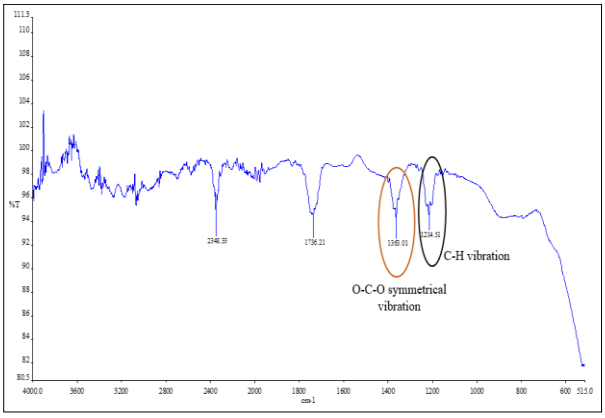


Fig 4: FTIR plot of MIL-101(Cr) – NaOH

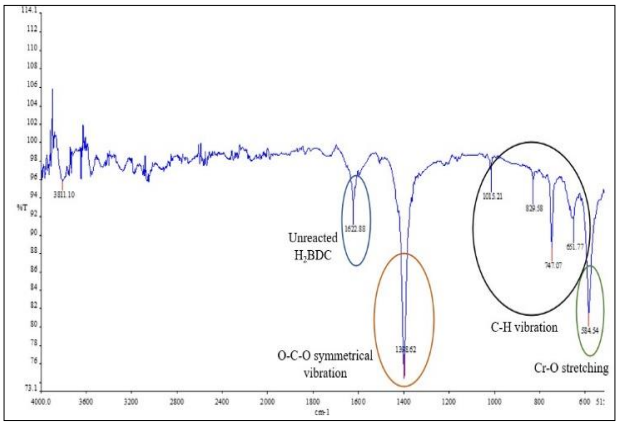


Fig 5: FTIR plot of MIL-101(Cr) – HNO_3

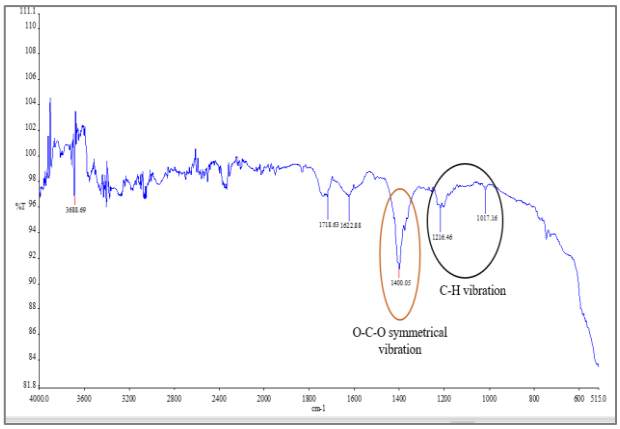
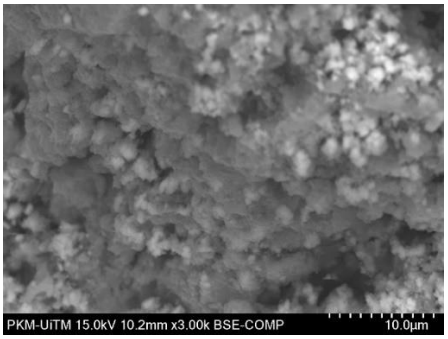
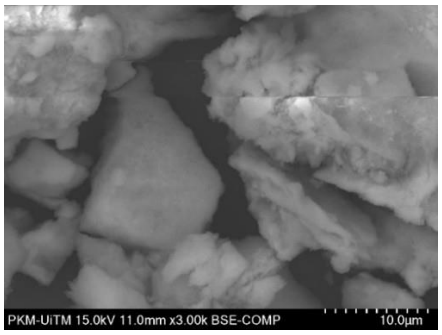


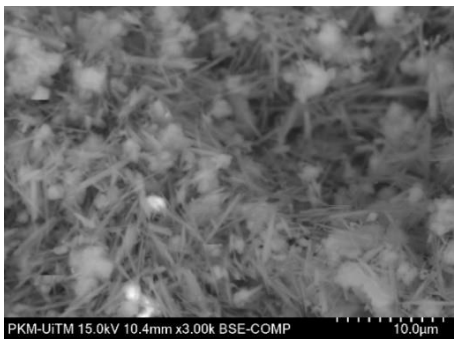
Fig 6: FTIR plot of MIL-101(Cr) –HF



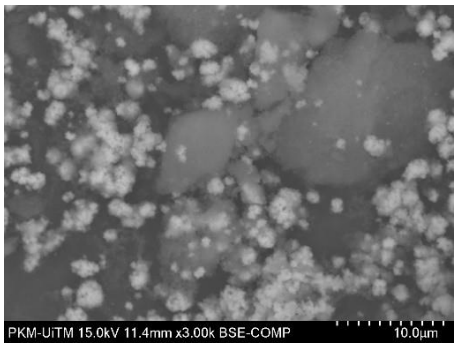
(a)



(b)



(c)



(d)

Fig 7: SEM images of (a) MIL-101(Cr)–Non, (b) MIL-101(Cr)–NaOH, (c) MIL-101(Cr)–HNO_3, (d) MIL-101(Cr)–HF

The SEM image of MIL-101(Cr)–NaOH demonstrated that it had a smoother surface compared to MIL-101(Cr)–Non whereby it determines that MIL-101(Cr)–NaOH has a bigger particle size which was consistent with XRD results. MIL-101(Cr)–NaOH is observed to have irregular, granular-shaped particles that aggregate between each other. Furthermore, MIL-101(Cr)–HNO_3 has needle-shaped crystals, which determined that the post- purification process did not completely remove the H_2BDC crystals (Sheikh Alivand et al., 2019). The surface of MIL-101(Cr)–HF was discovered to be vague due to the various-shaped particles that appeared.

4.0 Conclusion and recommendation

In this study, the hydrothermal method was employed to synthesise MIL-101(Cr) using different additives. It is concluded that all types of MIL-101(Cr) were successfully synthesised and characterised. Different additives were used as modulators to see the effect of properties enhancement of MIL-101(Cr). The type of additives added has a substantial effect on the structural properties of MIL-101(Cr). The integration of Cr components into each sample was accomplished. The result indicated that MIL-101(Cr)–Non has a small particle size which indicates a larger surface area thus reflecting high porosity. It also has unsaturated metal sites which makes it excellent properties for gas adsorption. However, for MIL-101(Cr)–NaOH, MIL-101(Cr)–HNO_3, and MIL-101(Cr)–HF it is recommended that the purification method to be revised in a subsequent study to obtain a clean final product without any unreacted components.

Authorship contribution statement

Effah Yahya: Conceptualisation, Methodology, Writing – Original draft, Investigation. **Nur Alia Mohd Samsul Anuar:** Writing – Original draft. **Ahmad Fauzi Ismail:** Supervision. **Nik Khairul Irfan Nik Ab Lah:** Writing – Reviewing and Editing. **Suriatie Mat Yusuf:** Validation, Writing – Reviewing and Editing. **Azzah Nazihah Che Abdul Rahim:** Visualisation, Writing – Reviewing and Editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

Bayazit, Ş. S., Danalıoğlu, S. T., Abdel Salam, M., & Kerkez Kuyumcu, Ö. (2017). Preparation of magnetic MIL-101 (Cr) for efficient removal of ciprofloxacin. *Environmental Science and Pollution Research*, *24*(32), 25452–25461. https://doi.org/10.1007/s11356-017-0121-0

Chen, C., Feng, N., Guo, Q., Li, Z., Li, X., Ding, J., Wang, L., Wan, H., & Guan, G. (2018). Template-directed fabrication of MIL-101(Cr)/mesoporous silica composite : Layer – packed structure and enhanced performance for CO_2 capture. *Journal of Colloid and Interface Science*, *513*, 891–902. https://doi.org/10.1016/j.jcis.2017.12.014

Chong, K. C., Ho, P. S., Lai, S. O., Lee, S. S., Lau, W.J., Lu, S. Y., & Ooi, B. S. (2022). Solvent-Free Synthesis of MIL-101(Cr) for CO_2 Gas Adsorption: The Effect of Metal Precursor and Molar Ratio. *Sustainability (Switzerland)*, *14*(3), 1–12. https://doi.org/10.3390/su14031152

He, C., Liu, D., & Lin, W. (2015). Nanomedicine Applications of Hybrid Nanomaterials Built from Metal-Ligand Coordination Bonds: Nanoscale Metal-Organic Frameworks and Nanoscale Coordination Polymers. *Chemical Reviews*, *115*(19), 11079–11108. https://doi.org/10.1021/acs.chemrev.5b00125

Hong, D. Y., Hwang, Y. K., Serre, C., Férey, G., & Chang, J. S. (2009). Porous chromium terephthalate MIL-101 with coordinatively unsaturated sites: Surface functionalization, encapsulation, sorption, and catalysis. *Advanced Functional Materials*, *19*(10), 1537–1552. https://doi.org/10.1002/adfm.200801130

Kamal, K., Bustam, M. A., Ismail, M., Grekov, D., Shariff, A. M., & Pré, P. (2020). Optimization of washing processes in solvothermal synthesis of nickel-based mof-74. *Materials*, *13*(12), 1–10. https://doi.org/10.3390/ma13122741

Lin, R. B., Xiang, S., Xing, H., Zhou, W., & Chen, B. (2019). Exploration of porous metal–organic frameworks for gas separation and purification. *Coordination Chemistry Reviews*, *378*, 87–103. https://doi.org/10.1016/j.ccr.2017.09.027

Liu, Q., Ning, L., Zheng, S., Tao, M., Shi, Y., & He, Y. (2013). Adsorption of Carbon Dioxide by MIL- 101(Cr): Regeneration conditions and influence of flue gas contaminants. *Scientific Reports*, *3*, 1–6. https://doi.org/10.1038/srep02916

Rajati, H., Navarchian, A. H., & Tangestaninejad, S. (2018). Preparation and characterization of mixed matrix membranes based on Matrimid/PVDF blend and MIL-101(Cr) as filler for CO_2/CH_4 separation. *Chemical Engineering Science*, *185*, 92–104. https://doi.org/10.1016/j.ces.2018.04.006

Sheikh Alivand, M., Hossein Tehrani, N. H. M., Shafiei-Alavijeh, M., Rashidi, A., Kooti, M., Pourreza, A., & Fakhraie, S. (2019). Synthesis of a modified HF-free MIL-101(Cr) nano adsorbent with enhanced H_2S/CH_4 , CO_2 $/CH_4$, and CO_2 $/N_2$ selectivity. *Journal of Environmental Chemical Engineering*, *7*(2), 102946. https://doi.org/10.1016/j.jece.2019.102946

Taufiq Musa, M., Shaari, N., & Kamarudin, S. K. (2021). Carbon nanotube, graphene oxide and montmorillonite as conductive fillers in polymer electrolyte membrane for fuel cell: an overview. *International Journal of Energy Research*, *45*(2), 1309–1346. https://doi.org/10.1002/er.5874

Wang, H., Lustig, W. P., & Li, J. (2018). Sensing and capture of toxic and hazardous gases and vapors by metal-organic frameworks. *Chemical Society Reviews*, *47*(13),4729–4756. https://doi.org/10.1039/c7cs00885f

Yulia, F., Nasruddin, Zulys, A., & Ruliandini, R. (2019). Metal-organic framework-based chromium terephthalate (MIL-101 Cr) growth for carbon dioxide capture: A review. *Journal of Advanced Research in Fluid Mechanics and Thermal Sciences*, *57*(2), 158–174.

Zhang, L. J., Li, F. Q., Ren, J. X., Ma, L. B., & Li, M. Q. (2018). Preparation of metal organic frameworks MIL-101 (Cr) with acetic acid as mineralizer. *IOP Conference Series: Earth and Environmental Science*, *199*(4). https://doi.org/10.1088/1755-1315/199/4/042038

Zhao, M., Yuan, K., Wang, Y., Li, G., Guo, J., Gu, L., Hu, W., Zhao, H., & Tang, Z. (2016). Metal- organic frameworks as selectivity regulators for hydrogenation reactions. *Nature*, *539*(7627), 76–80. https://doi.org/10.1038/nature19763

Zhao, T., Li, S. H., Shen, L., Wang, Y., & Yang, X. Y. (2018). The sized controlled synthesis of MIL- 101(Cr) with enhanced CO_2 adsorption property. *Inorganic Chemistry Communications*, *96*, 47–51. https://doi.org/10.1016/j.inoche.2018.07.036