Application of POMOF composites for CO\textsubscript{2} fixation into cyclic carbonates.

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Abstract. The problem of global warming is one of the major concerns in the world today as there has been continuous rise in temperature resulting from increase in the emission of anthropogenic carbon dioxide (CO\textsubscript{2}). Recently, carbon dioxide is considered as an abundant C\textsubscript{1} feed-stock for organic transformations, due to its free availability, non-toxicity, and simplicity in handling. The synthesis of metal-organic framework/polyoxometalates supported composites (POM@MOF), were prepared by incorporation of Keggin type-polyoxometalate groups via impregnation method. The as-synthesized composites were characterized by powder X-ray diffraction (PXRD), fourier-transform infrared spectroscopy (FT-IR), and field emission scanning electron microscope (FESEM), which confirm the presence of the polyoxometalates group after formation of the composites. The composites were employed as catalyst for the conversion of CO\textsubscript{2} and epichlorohydrin into cyclic chloropropylene carbonate. The reaction was carried out under mild condition of atmospheric pressure in a schlenk tube without addition of any co-catalyst or solvent and the yield have shown progressive increase over time as indicated by GC results from 30\% at 6 h duration to 87\% over a period of 48 h of continuous siring.

1. Introduction
Carbon dioxide (CO\textsubscript{2}) is one of the major greenhouse gas that contributes significantly to the current global climate change situation. The increase in the release of carbon dioxide into the atmosphere as a byproduct from different industries and the use of fossil resources has significantly resulted in rising CO\textsubscript{2} globally, and has since exceeded the tolerable limit with 410 parts per million in 2018 and that would lead to global warming \cite{1-7}. Carbon capture and utilization is the most promising alternative among other several processes in reducing the produced CO\textsubscript{2} due to fossil fuel combustion \cite{8-12}. In the recent years the attention of the researchers has dwelled in to utilizing CO\textsubscript{2} as C\textsubscript{1} feedstock for chemical conversion into various useful products \cite{13-16} in the presence of highly selective and task-specific catalysts \cite{9,17,18}.

Among the various conversion processes, more attention is given to the conversion of CO\textsubscript{2} into cyclic organic carbonates due to its potentials to produce several value-added chemicals which can be utilized as intermediates and solvents for the pharmaceutical and other production industries and as an electrolytes in lithium batteries \cite{17,19}. Recently, nanomaterial integrated MOF-composites are increasingly receiving attention by incorporating different nanoparticles, such as quantum dots, graphene or polyoxometalates \cite{20-23} and their functional abilities were evaluated in the areas of
adsorption [24,25], catalysis [26-28], environment remediation [29] and many other potential applications [30,31]. When compared to their pristine counterparts, MOF composites with this advanced architecture reveal unique physicochemical features and significantly increase their functionality [20]. In this article we present the synthesis of POM@MIL-101 composites denoted as PW11@MIL-101 and the synthesis of the MOF and the corresponding composites were confirmed by various spectroscopic techniques. The utilization of the as-synthesized composite as catalyst in the conversion of CO2 into cyclic organic carbonate compounds by cycloaddition reaction was also investigated.

2. Experimental

2.1 Materials

In the synthesis procedure, chemicals such as nitrate salts of chromium (Cr(NO3)3·9H2O, Merck), cobalt (Co(NO3)3·6H2O, Merck) and zinc (Zn(NO3)2·6H2O, Sigma Aldrich, 98%), manganese (II) sulfate monohydrate (MnSO4·H2O, Merck) terephthalic acid, nitric acid (HNO3, Merck, 65%), tungstophosphoric acid hydrate (H3PW12O40·nH2O, Merck) and tetra-n-butylammonium bromide (TBABr, Merck) were obtained from commercial sources and used in their original form. Additionally, solvents such as acetonitrile (Merck, 99.8%), methanol (Merck, 99.99%) and ethanol (Merck, 99.9%) were used without further purification.

2.2 Experimental procedure

2.2.1 Synthesis of MIL-101(Cr). The MOF, MIL-101 was hydrothermally prepared as described by Ferey et al. with some little modifications [32]. A chromium nitrate (8 g, 20 mmol) and terephthalic acid (3.32 g, 20 mmol) were mixed in 100 ml distilled water (DI) under continuous stirring for 30 mins. This was followed by drop-wise addition of nitric acid (0.83 ml, 20 mmol) and continued stirring for another 30 mins. The mixture was then moved into a Teflon autoclave with stainless steel casing and placed in an oven for 8 hours at a temperature of 220°C and was allowed naturally to cool down. The resulting green solid was then filtered on a dense paper filter and dried at 80°C.

2.2.2 MIL-101 Post-synthesis Purification. An extensive procedure for purification was applied as reported by Sheikh et al. to remove any unreacted terephthalic acid in the crude sample [33]. The as-synthesized MIL-101 crude sample was first washed several times with boiling water to dissolve the chromium salt unreacted. It was then suspended in DMF at 80°C and stirred for 8 h to remove the remaining H2BDC from MIL-101(Cr) structure. After filtration, the powder was spread in aqueous NH4F solution for 5 h at 60°C. The resulting powder was washed again using hot boiling water to remove residual NH4F. The as-synthesized product was then suspended in a centrifuge at 9000 rpm for 15 min and soaked in methanol at room temperature, having low volatile property to eliminates all other solvents trapped within the pores of MIL-101. The methanol was regularly changed twice a day over the period of three days. Finally, the product was treated at 150°C in a vacuum for 12 h to evaporate all remaining impurities and cause the breaking of Cr-OH bonds which was due to MeOH presence. The activated MOF crystals was soaked for 18 h in dry ethanol at 80°C by reflux and the final product was dried and reactivated overnight at 150°C vacuum.

2.2.3 Synthesis of α-[(C4H9)2N]4H3[(PW11O39)·nH2O]. (TBA)4H3[(PW11(OH)O39)].nH2O was synthesized as previously reported [34,35] starting with the preparation of [PW11O39]3− solution prepared by dissolving Na3HPO4 (0.33 g, 9.1 mmol), Na2WO4·2H2O (3.33g, 90 mmol) in 80 ml DI water adjusting the pH to 4.8 by addition of 1M HNO3 solution. An aqueous solution of TBABr (2.90 g, 45 mmol) was then added drop wise and in excess under continuous stirring at 80°C. The white precipitates formed was filtered off and recrystallized from acetonitrile and the resulting powder was dried at 80°C overnight.

2.2.4 Preparation of Composite (PW@MIL-101). The PW11@MIL-101 composite was synthesized by immobilizing the polyoxometalates, TBA-PW11 into the MOF component, MIL-101(Cr) by modifying the procedure described by Rebeiro et al. [30]. The PW11 was dissolved in acetonitrile (5 mM, 30 ml),
0.25 g of MIL-101 was then added in a 50 ml vial. The mixture was stirred for 24 h at room temperature (RT), filtered off and washed several times with acetonitrile and the resulting powder was dried in a desiccator over silica gel.

2.3 Characterization
The MIL-101(Cr), PW_{11} and their composite material were characterized using different analytical techniques. Field emission scanning electron microscopy (FESEM), Tescan, Mira II instrument, was applied using a high resolution micrographs to obtained the crystal morphology and size of the samples. Crystallinity and phase structure was analyze using X-ray diffraction method (XRD). The functional groups and ligand-cluster formation was investigated using Perkin Elmer transform infrared spectroscopy (FTIR) in the range 400 to 4000 cm^{-1} with KBr pellets. The nitrogen adsorption-desorption isotherms at 77.3 K was investigated with micrometrics apparatus to determined the surface area and pore size distribution. The samples were degassed for 48 h at a temperature of 140 °C to evaporate the moisture and other undesired substances adsorbed in the micropores. The Brunauer, Emmett and Teller (BET) method was employed to find the specific surface area.

3. Results and Discussions
Field emission scanning electron microscopy (FESEM) was used to examine the morphology of the prepared MIL-101(Cr), as shown in Figure 1. The MOF has an equally dispersed octahedral porous structures with a smooth surface of approximately 400 nm, as shown in the image. Majority of the crystals were observed to have similar surface morphologies, with only a few with broken or lacking angles, and these findings were consistent with prior reports [34-36]. Furthermore, no needle-shaped crystals (representing unreacted H_{2}BDC) were present in the powder, indicating the effect of the additional purification steps. The EDX peaks also validate the purity level, demonstrating that the structure contains all of the predicted constituents in appropriate proportions.

The structure of MIL-101(Cr) was studied using FT-IR, as illustrated in Figure 2. The presence of relatively negligible unreacted H_{2}BDC residues in the pores was indicated by an intense absorption band in the spectrum at 1400–1600 cm^{-1}, which is due to the C–O stretching vibration peak of the benzene ring, indicating the effectiveness of the purification and post-treatment procedure. Monosubstituted benzene is responsible for the moderate intensity peak at 746 cm^{-1}, whereas Cr–O stretching vibration is responsible for a comparable peak at 578 cm^{-1}. This finding is in line with what has been described in the literature [33-35] thus confirming the formation of MIL-101(Cr).

The crystallinity and phase purity of MIL-101(Cr) were evaluated using the powder X-ray diffraction method, and the energy-dispersive X-ray spectra (XRD) of the synthesized MIL-101(Cr) represents information on the crystallinity and phase purity of MIL-101(Cr) as shown in Figure 3, which are also in consistent with prior studies [35, 36], confirming the similarity of crystallite structure of materials.

The Cr oxidation state was determined using X-ray photoelectron spectroscopy (XPS). The wide-scan (a) and Cr2p (b) energy spectra of MIL-101 are shown in Figure 4. (Cr). A shoulder seen on the main peak at 583 eV (Figure 4b), which is ascribed to Cr(III) species, confirms the presence of Cr(III) in MIL-101(Cr).

The as-synthesized MIL-101(Cr) has a BET surface area of 1439.95 m^{2} g^{-1} and an average pore size of 2.146 nm with a pore volume of 0.7725 cm^{3} g^{-1}. The inclusion of a benzene ring in the structure and the nature of metal-ligand interaction in the MIL-101 structure account for the high porosity [32].
The PW11@MIL-101 composite material's FTIR spectra exhibited visible bands in the 700–800 cm\(^{-1}\) range, which are attributable to contributions from the vibrations of W–O–(M\(^{2+}\)) (Figure 5). The bands 800–850 cm\(^{-1}\) are caused by the vibrations of W–O–W (on the oxygen atoms connecting the edge-
sharing WO6 octahedra) and 850–950 cm\(^{-1}\) are caused by the contributions from the vibrations of W–O–W (on the oxygen atoms connecting the edge-sharing WO6 octahedra). The asymmetric vibrational stretching of P–O in the central PO\(_4\) unit occurs at 1050–1100 cm\(^{-1}\) [31]. The band were shifted and split into basically two components, one with a peak maximum at 1078 cm\(^{-1}\) and the other with a double band at 1045 and 1035 cm\(^{-1}\), respectively, when the symmetry of the PO\(_4\) tetrahedron in the structure of PW11 decreases. These FTIR findings are consistent with those reported in the prior study [37], indicating that the structures of the primary heteropoly tungstophosphate anions remain intact after assembling with the quaternary ammonium cations.

![Figure 5](image_url)

**Figure 5.** FT-IR spectra of PW\(_{11}\)@MIL-101.

### 4. Cycloaddition of CO\(_2\) with epoxide

The composite were employed without the addition of a co-catalyst or a solvent, the PW11@MIL-101 catalyst was used to cycloaddition epichlorohydrine oxide under atmospheric conditions of temperature and pressure (Table 1). The reaction was carried out in a vial totally covered with a rober cock using a schlenk flask with balloons attached to it carrying the CO\(_2\). As indicated in Table 1, the catalyst has a high conversion and selectivity. It was observed that when reaction time reduces, the conversion drops. The reaction can also be catalyzed by pristine MOF of MIL-101(Cr) and TBA-PW11, however with slightly lower efficiency. The inclusion of tetrabutyl-n-ammonium bromide, which plays an important role in the epoxide ring opening, can be linked to the considerable improvement in PW11 performance over MIL-101(Cr).

| Catalyst       | Catalyst loading (mg) | Time (h) | Conversion (%) | Selectivity (%) |
|----------------|------------------------|----------|----------------|-----------------|
| MIL-101(Cr)    | 20                     | 48       | 38             | 37              |
| PW11           | 20                     | 48       | 56             | 49              |
| PW\(_{11}\)@MIL-101 | 20                  | 48       | 87             | 72              |
| PW\(_{11}\)@MIL-101 | 20                  | 24       | 52             | 43              |
| PW\(_{11}\)@MIL-101 | 20                  | 6        | 30             | 42              |

Reaction conditions: 30 mmol epichlorohydrin (ECH) epoxide, room temperature, atmospheric pressure.

### 5. Conclusion

The catalytic activity of PW11@MIL-101 catalysts for cycloaddition of CO\(_2\) with epichlorohydrin was examined after encapsulation of teta-n-butylammonium salts (TBA) of Keggin-type polyoxotungstates, [-PW11O39]\(^{7-}\) in the metal-organic framework MIL-101(Cr). Different analytical approaches were used to access the successful synthesis and comprehensively analyze the MIL-101, MOF, and PW11@MIL-101 composites, they include; FESEM, EDX, BET, XRD and XPS which shows the presence of the...
POM material encapsulated into the MOF material. The cycloaddition reaction was successfully carried using a schlenk flask set-up under atmospheric condition of temperature and pressure with relatively high conversion rate with time increase. The moderate TOF and selectivity was obtained without any co-catalyst presence and the catalyst can be reused easily. This achievement demonstrates that encapsulating POM catalysts in MOF is a novel way to create catalysts that are highly active, selective, and easily recoverable. For prospective future industrial applications, more research is required.

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