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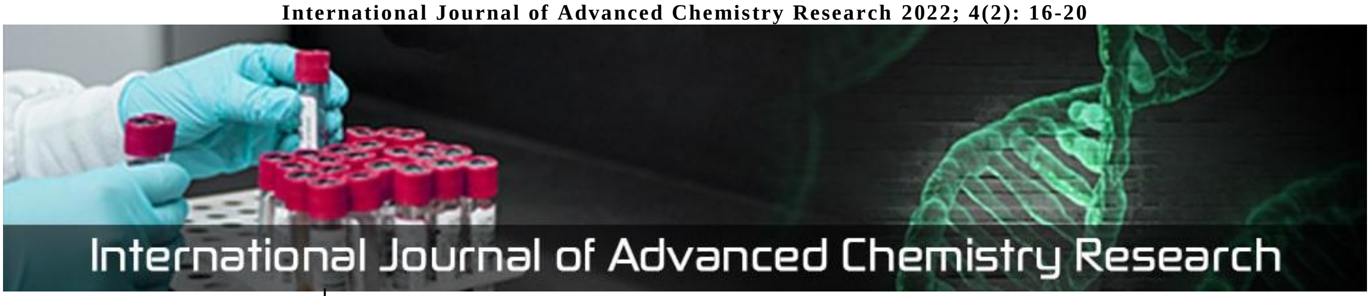

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Metal-organic frameworks as catalyst precursors in Catalytic Hydrogenation of Carbon Dioxide: Review

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Abstract

Catalytic hydrogenation of carbon dioxide to value-added chemicals is an attractive process to address both energy and environmental issues. Several approaches have been used to convert the greenhouse gas to useful products. This conversion has been done mainly through homogeneous catalytic systems of platinum group metal complexes. In recent years there has been a growing concern to design heterogeneous catalysts that are able to convert carbon dioxide to C1 products. The large surface area that metal-organic frameworks coupled with porosity make them better candidates for catalytic conversion of carbon dioxide to the desired products. Results from these studies indicate that metal-organic frameworks (MOFs) may answer both environmental and energy issues associated with the production of the greenhouse gas. This contribution will focus on the recent development in the design and application of MOFs in catalytic hydrogenation of carbon dioxide. Special emphases on tandem capture of carbon dioxide and hydrogen followed by subsequent hydrogenation of carbon dioxide in the presence of frustrated Lewis pairs functionalised MOF will be discussed.

Keywords: Carbon dioxide, catalysis, metal-organic framework, hydrogenation, heterogeneous catalysts

Introduction

Carbon dioxide (CO2) is a major contributor to the greenhouse effect and has an effect of trapping the sun's heat which is presently observed in climate change phenomena [1, 2]. Reducing CO2 emissions is an extensive and long-term task which involves finding strategies to reduce of the amount of CO2 produced, storage of CO2 and usage of CO2 stored [3]. The utilization and transformation of CO2 into value-added chemicals has attracted much attention in recent years thus, the development of efficient methods of CO2 reduction such as catalytic hydrogenation is highly desirable. Hydrogenation of CO2 has been more intensively investigated recently, due to fundamental and practical significance in the context of catalysis, surface science, nanotechnology, and environmental science. Catalysis provides tools for efficiently and selectively making and breaking chemical bonds that are crucial for converting CO2 to value-added chemicals [4, 7]. Homogeneous hydrogenation of CO2 to formic acid has been achieved in aqueous solutions using mainly rhodium and ruthenium catalyst/catalyst precursors [8]. Though homogeneous catalysts show satisfactory activity and selectivity, the recovery and regeneration of the catalysts has shown to be challenging. Alternatively, heterogeneous catalysts are preferable in terms of stability, separation, handling, and reuse, as well as reactor design, which reflects in lower costs for large-scale productions. However, most of these reactions are far from ideal in terms of selectivity and stoichiometric conversions which has led to further breakthrough technologies which proceed under mild conditions.

Metal-organic frameworks (MOFs) have some unique characteristics, such as high surface area, tunable pore size, and uniform-structured cavities, which make them promising candidates for diverse applications in gas storage, separation, catalysis, and sensing [9, 10]. In contrast to other crystalline porous solids, the high versatility of MOF design provides clear advantages for catalysis because of the possibility in rational and precise design of the active site. Wang and co-workers reported that a series of Fe-based MOF materials (MIL-101(Fe), MIL 53(Fe), and MIL-88 B (Fe) showed photocatalytic activity for CO2 reduction under visible light irradiation in the presence of triethanolamine as a sacrificial agent [11].

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Among these materials, MIL-101(Fe) showed the best activity for CO2 reduction due to the existence of the coordination unsaturated Fe sites in its structure and the synergetic effect of dual excitation pathways: i.e., an exciting NH2 functionality followed by an electron transfer from the excited organic linker to the Fe centre and the direct excitation of Fe−O clusters. Sun and Fu also reported photocatalytic reduction of CO2 to HCOO- in the presence of amino-functionalised NH2-Uio-66(Zr) MOF [5] and NH2-MIL-125 (Ti) MOF respectively [12]. Xu employed a very stable mesoporous zirconium- porphyrin MOF, based on tetrakis(4-carboxyphenyl)porphyrin ligand, for CO2 capture and reduction under visible light irradiation in the presence of triethanolamine [13]. The results revealed that the ligand behaves as a visible-light harvesting unit and recycling experiments demonstrated that no noticeable change occurs to the yield of HCOO- during the first three catalytic runs. Fei and co-workers [14] incorporated a manganese bipyridine complex, Mn(bpydc)(CO)3Br (bpydc = 5,5′-dicarboxylate-2,2′-bipyridine) into a highly robust Zr(IV)-based (MOF) for use as a CO2 reduction photocatalyst. The results revealed that Mn-incorporated MOFs efficiently catalyze CO2 reduction to formate in DMF/triethanolamine under visible-light irradiation. The photochemical performance of the Mn-incorporated MOF reached a turnover number of approximately 110 in 18 h, exceeding that of the homogeneous reference systems. The increased activity of the MOF-incorporated Mn catalyst is ascribed to the struts of the framework providing isolated active sites, which stabilize the catalyst and inhibit dimerization of the singly reduced Mn complex. The MOF catalyst largely retained its crystallinity throughout prolonged catalysis and was successfully reused over several catalytic runs [14]. While there are a few reviews on photo and electrocatalytic reduction of CO2, catalytic hydrogenation of CO2 by H2 with Lewis pairs functionalised MOFs has not been reviewed. Herein, this review reports on recent advances in MOF-catalysed hydrogenation of CO2 and mechanistic studies to produce valuable chemicals such as formic acid, formaldehyde and methanol. The final section summarizes the main conclusions and provides views related to future developments in the field.

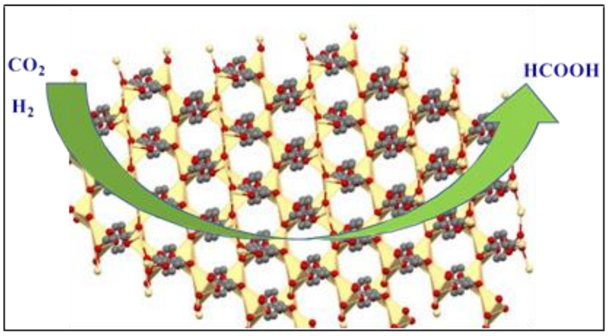

Fig 1: Graphical Abstract

Tandem capture of CO2 and H2 followed by subsequent hydrogenation of CO2 in the presence of frustrated Lewis pairs functionalised MOF

The most simple and direct route for CO2 reduction into valuable chemicals such as methanol is the addition of a proton (To the oxygen atom) and a hydride (To the carbon atom) to produce HCOOH [15, 16]. Conceptually, the required protic and hydridic hydrogens can be provided by Lewis bases and acids, respectively. Intra- or intermolecular Lewis acid–base combinations with bulky substituents at the active sites, capable of activating small molecules, such as H2, CO2, alkenes, etc., are known as frustrated Lewis pairs (FLPs) [17]. It has been experimentally shown that frustrated Lewis pairs (FLPs) can both bind CO2 and heterolytically dissociate H2 [18, 19]. As a result, FLPs have been considered as excellent candidates for both CO2 activation and subsequent stepwise hydrogenation for the production of hydrogen-rich C1 fuels [20, 21]. FLPs require significant steric hindrance to prevent the formation of Lewis acid/Lewis base adducts in solution, which would render them completely inactive.

The choice of the MOF that is used for functionalization with the FLP must be thermally stable and must not be easily poisoned by water [22]. The MOF must have high affinity for both CO2 and H2 with large pores which can accommodate bulky FLPs. The choice of the FLPs used should be guided by their ability to dissociate the H2 molecules as well as high affinity for CO2 adsorption [23]. However, care must be taken to prevent the dimerization of the FLP as this will render it non-reactive [24]. In this regard, FLPs with bulky substituents will be used to mutual quenching of a pair of LP moieties within the channels. LP can be grafted successfully into a MOF (Figure 1) by anchoring the LP first into the open metal sites within the MOF through coordination interaction followed by the introducing the corresponding acid moiety of the LP [25]. Given the strong coordination interaction, it is anticipated that the LP would be stabilized within the MOF yet accessible to substrates of interest. The drawback of using FLPs is that there will be a competitive binding for the Lewis sites between the CO2 and H2 molecules. The production of HCOO- species requires that H2 is dissociated first then react with CO2 to give the required product. However, it is also possible for CO2 to be activated and the activated state may react with H2 to give a wrong product. One way to get around this issue is to introduce the H2 to the FLP-MOF first which will be followed by addition of CO2. The fact that MOFs can be readily functionalised, it should be possible to introduce complementary binding sites which can selectively bind H2 without binding CO2 significantly.

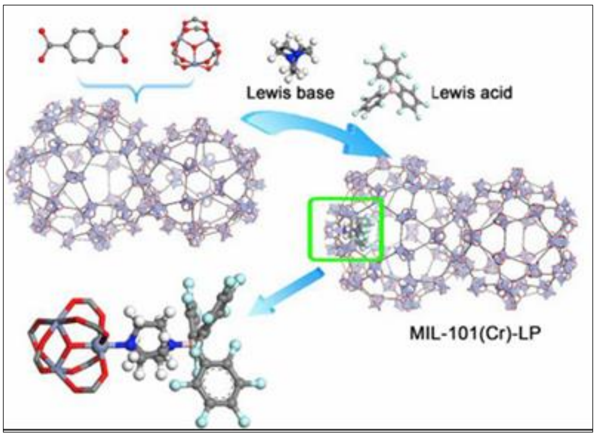

Fig 2: Illustration of anchoring strategy of Lewis pair on MIL-101 MOF [25].

Carbon dioxide Hydrogenation Mechanistic Studies in the presence of FLPs functionalised MOFs According to density functional theory (DFT) studies by Yang on CO2 hydrogenation to CH3OH in the presence of FLP-UiO-66 MOF, the hydrogenation proceeds in three stages [26]. The three stages are shown in Figure 2, namely formation of HCOOH from the hydrogenation of CO2 followed by conversion of HCOOH to HCHO *via* hydrogenation and dehydration, and lastly HCHO hydrogenation into CH3OH. Ye and Johnson [27] demonstrated that functionalised FLP-(UiO-66-P-BF2) could capture CO2 and also transform it into HCOOH *via* a two-step reaction of chemically binding CO2 and heterolytically dissociating H2. In practice, one would have to expose the material first to H2 and then to CO2 to avoid the competing reaction and potential poisoning of the catalyst. This requirement is a major drawback for UiO-66-P-BF2 that would preclude its practical use.

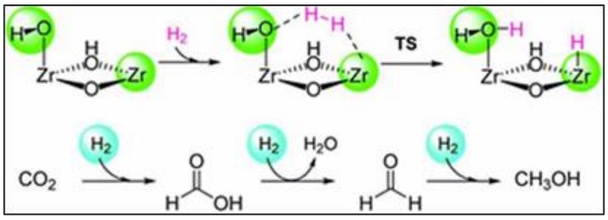

Fig 3: Hydrogenation of CO2 to CH3OH in the presence of FLP-UiO-66 MOF [26]

Density functional theory (DFT) studies by Ye and Johnson [28] revealed that hydrogen dissociation reaction can be correlated as a function of the chemical hardness of the Lewis acid site during CO2 hydrogenation. These correlations provided a computationally efficient method for screening functional groups for their catalytic activity toward CO2 hydrogenation. The relationships are further utilized to carry out a Sabatier analysis on a simplified model of the reaction to generate contour plots of the Sabatier activity that can be used to identify properties of the functional groups for maximizing the reaction rate [28]. Maihom and co-workers carried out DFT mechanistic study of the hydrogenation of CO2 to HCOOH over Cu-alkoxide-functionalized MOF and revealed that the reaction proceeds *via* two different pathways, namely, concerted and stepwise mechanisms [29]. In the concerted mechanism, the hydrogenation of CO2 to HCOOH occurs in a single step and requires high activation energy of 67.2 kcal/mol. For the stepwise mechanism, the reaction begins with the hydrogen atom abstraction by CO2 to form a HCOO- intermediate which is further hydrogenated to form HCOOH. The activation energies were calculated to be 24.2 and 18.3 kcal/mol for the first and second steps, respectively. Because of the smaller activation barriers associated with this pathway, it therefore seemed to be more favoured than the concerted one. The catalytic effect of Cu-MOF-5 was also highlighted by comparing it with the gas-phase uncatalyzed reaction in which the reaction takes place in one step with a barrier of 73.0 kcal/mol. This study also demonstrated that the metal-functionalized MOF can be utilized for the greenhouse gas catalysis in addition to using it to capture and activate CO2. It was also noted that the catalytic activity of the MOF was sensitive to the charge transfer between the catalyst and the adsorbing molecules. The charge transfer played a twofold crucial role that is activating CO2 as to promote its hydrogenation as well as assisting the H-H bond cleavage of the H2 molecules. Another study by Tshuma and co-workers [30] proposed that the formate formation at RuII sites is proposed as follows (Figure 3), the first step involves reduction elimination of the Cl. This step provides open metal sites for the coordination of H2 molecules to give a dihydrogen complex [Ru(H2) (*p*-cymene)]. The active species, the ruthenium hydride RuH(*p*-cymene) is formed upon splitting of the coordinated H2 molecules with simultaneous elimination HCl. The insertion of CO2 *via* associative addition into the ruthenium hydride complex generates the formate complex which readily dissociates the formate.

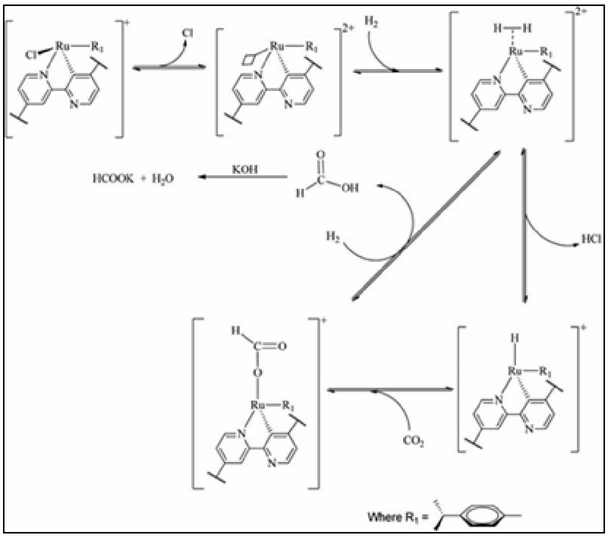

Fig 4: Proposed mechanism for HCOOH formation in the presence of RuII catalytic active species

Conclusion and perspective

As a major greenhouse gas, carbon dioxide, with increased concentration in the atmosphere is being considered responsible for the global warming and climate changes. Its conversion into fuels and chemicals offer opportunities to mitigate the increasing build up. The present study has analysed the current status of metal- organic frameworks as candidates for catalytic hydrogenation of CO2. The review has covered a number MOF supported (pre)catalysts for CO2 hydrogenation and various mechanistic studies involved. These technologies are still in research but are potential candidates for mitigating the still increasing atmospheric CO2 concentrations. On the basis of abundant reported examples to use MOFs as heterogeneous catalysts under various conditions, it can be concluded that the crystalline and porous MOFs are good candidates for catalytic hydrogenation of CO2.

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