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# UiO-66 as an efficient catalyst for *N*-formylation of amines with CO<sub>2</sub> and dimethylamine borane as a reducing agent.

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# Abstract:

The most effective way to make the best use of CO<sub>2</sub>, is the reductive formylation of amines, as formamides have many applications in industry. A new protocol has been developed for reductive N-formylation of amines with CO<sub>2</sub> as a C1 carbon source and DMAB (Dimethylamine borane) as a reducing agent in the presence of Zr-containing metal-organic framework (MOF) as an efficient, heterogeneous recyclable catalyst. We used UiO-66 and UiO-66-NH<sub>2</sub> as catalysts for *N*-formylation of amines and observed that both the catalyst performs equally. Therefore, we continued our studies with UiO-66 as a catalyst. The UiO-66 MOF shows good catalytic activity and affording the desired formamides in good to excellent yield. This catalytic system is very efficient for several amines including primary and secondary aliphatic cyclic and aromatic amines. Moreover, the prepared catalyst was recycled up to four recycled without a considerable decrease in catalytic activity.

**Keyword:** One-pot reaction, *N*-formylation, Amines, CO<sub>2</sub> Utilization, UiO-66, Dimethylamine borane.

## 1. Introduction

From the last few decades, excessive emission of carbon dioxide is a major contributor gas for the greenhouse effect. Therefore, many efforts have been developed for capture and utilization of CO<sub>2</sub>.<sup>1-3</sup> Although the CO<sub>2</sub> is kinetically and thermodynamically stable molecule, several catalytic systems were developed for the construction of new C-C, C-O, and C-N bonds by chemical transformation of CO<sub>2</sub>.<sup>4-6</sup> As CO<sub>2</sub> is economical, abundant, non-flammable and renewable carbon source used for the synthesis of many valuable chemicals like carbonates,<sup>7</sup> carbamates,<sup>8</sup> formamides,<sup>9</sup> benzimidazoles,<sup>10</sup> urea,<sup>11</sup> methanol,<sup>12,</sup> etc. However, C-N bond formation reaction is one of the most efficient approach for transformation of CO<sub>2</sub> to formamide by using amines and suitable reductant. Formamides have many applications in organic synthesis such as solvents, key intermediates in drug molecules and in the agrochemical industry.<sup>13-14</sup>

Previous reports showed that the formylation of amines with CO<sub>2</sub> is mainly obtained in presence hydrogen and silanes as compared to boranes as a reductant. Recently, boranes and its derivatives attracted more attention as they have applications as they are cost-effective, easy to handle, less toxic and also have high H<sub>2</sub> storage capacity with high atom economy as compared to silanes.<sup>15-17</sup> Generally, LiAlH<sub>4</sub>, NaBH<sub>4</sub>, amine borane (NH<sub>3</sub>BH<sub>3</sub>) have been extensively used as a reducing agent. The dimethylamine borane (DMAB) is used as a H<sub>2</sub> substitute and it was not well explored in the previous reports. Also, DMAB has high stability, water solubility, and non-flammability. Thus, the DMAB is used as a greener reducing agent compare to silanes for formylation of amines.<sup>18-19</sup> Previous reports showed that several metals based homogeneous and heterogeneous catalysts had been studied for dehydrogenation reaction of amine borane.<sup>20-22</sup>

Conventionally, the formamides are prepared by using toxic CO and phosgene as a C1 reagent, instead, we use  $CO_2$  as a carbon source for N-formylation of amines as  $CO_2$  is an attractive and green approach for the synthesis of formamides.<sup>23-24</sup> In this context, expensive metal complexes Ru,<sup>25</sup> Pd,<sup>26-27</sup> Cu,<sup>28-29</sup> Rh,<sup>30</sup> Zn,<sup>31</sup> Ni<sup>32</sup> with respective ligands have been explored for the C-N bond formation, but these catalytic systems have some environmental issues and having complex catalyst synthesis processes. However, a metal-free catalytic system such as NHC carbene,<sup>33</sup> ionic liquids (ILs),<sup>34</sup> organic bases (TBD,<sup>35</sup> DBU,<sup>36</sup> guanidine<sup>37</sup>), B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub><sup>18</sup> has been proved to be an efficient catalyst for the synthesis of formamides. Also, basic catalysts like K<sub>2</sub>WO<sub>4</sub>, K<sub>2</sub>CO<sub>3</sub><sup>9</sup>, and CsCO<sub>3</sub><sup>38</sup> have been used for the *N*-formylation of amines. Considering the importance of recyclability and reuse of catalysts, some heterogeneous catalysts such as a zwitterionic covalent organic framework,<sup>39</sup> porous organic polymers with Nheterocyclic carbenes<sup>40</sup> and mesoporous imine-based organic polymer<sup>41</sup> have been developed for the synthesis of formamides, but complicated catalyst synthesis procedure limits its application. They also have some disadvantages like the requirement of an inert gas atmosphere, difficult catalyst separation, most of the catalyst requires high pressure (H<sub>2</sub> as reductant) and high temperature, use of expensive metals, less atom economy (Silane as a reductant), tedious work up procedure and difficulty in catalyst recyclability, etc.

Recently, Metal-Organic Framework (MOF) attracted tremendous attention of chemist as it is porous material prepared from metal and organic linker through coordination bond.<sup>42-45</sup> It is well studied for

adsorption of gases such as for storage of H<sub>2</sub> and CH<sub>4</sub>.<sup>46</sup> It has many applications in catalysis,<sup>47</sup> gas storage and capture,<sup>46,48-49</sup> drug delivery,<sup>50</sup> magnetism<sup>51,</sup> etc. A various combination of metal and the organic linker has been used to develop many MOF. For *N*-formylation reaction system needs both acidic and basic sites in catalyst as Zirconium based MOF having these sites. Also, zirconium MOFs are easily prepared having good surface area, excellent chemical resistance for organic solvents and water. As zirconium-based MOF commonly called as a UiO-66 framework (UiO – University of Oslo) prepared from 1,4benzenedicarboxylate (BDC) linker and  $Zr_6O_4(OH)_{4.52}$  The UiO-66 is having good chemical, hydrolytic and thermal stability over many MOF as it having high coordinated zirconium metal in its framework. Considering these advantages, we selected UiO-66 and UiO-66-NH<sub>2</sub> as a catalyst for *N*-formylation reaction using CO<sub>2</sub> as a carbon source. The UiO-66 was well explored in literature as an efficient material for gas storage, transfer hydrogenation of levulinic acid and its esters.<sup>54</sup> Later, catalytic transfer hydrogenation of levulinic acid and its esters.<sup>54</sup> Later, catalytic transfer hydrogenation of levulinic acid and its esters.<sup>54</sup> Later, catalytic transfer hydrogenation of levulinic acid and its esters.<sup>54</sup> Later, catalytic transfer hydrogenation of levulinic acid and its esters.<sup>54</sup> Later, catalytic transfer hydrogenation of levulinic acid and its esters.<sup>54</sup> Later, catalytic transfer hydrogenation of levulinic acid and its esters.<sup>54</sup> Later, catalytic transfer hydrogenation and used for reduction of nitrobenzene to aniline using formic acid as a reducing agent.<sup>56</sup>

Considering these facts, this work is mainly focused on the use of heterogeneous recyclable catalyst which could effectively catalyze *N*-formylation reaction of amines with  $CO_2$  as a C1 source. To the best of our knowledge, Metal-Organic Frameworks (MOF) were not used for the formylation of amines with  $CO_2$ . Herein, we prepared UiO-66 which could be used as an efficient, cheap, non-toxic catalyst for the formamides synthesis from  $CO_2$  and amines with DMAB as a reducing agent (Scheme 1). Additionally, we used UiO-66 without immobilized metal or any support.



Scheme 1: Formylation of amines by using CO<sub>2</sub> and DMAB as a reducing agent.

# 2. Experimental

#### 2.1 Materials and methods

All chemicals were acquired from TCI chemicals, Alfa Aesar, Sigma Aldrich, and used for the reaction without purification.  $CO_2$  was obtained from Rakhangi Gases Ltd., Mumbai, India, with a purity of 99.99 %.

#### 2.2 Instrumental measurements

The X-ray diffraction images obtained with the use of a Shimadzu XRD-6100 with non-monochromated Cu K $\alpha$  radiation ( $\lambda$ =1.5405 Å). The scanning mode within the range of 10 to 80° with a step of 0.02°, with a scanning rate of 2 deg per min. Thermogravimetric analysis (TGA) curves were performed on a STA-6000 (Perkin Elmer), under N<sub>2</sub> atmosphere (20 mL min<sup>-1</sup>) between 30 °C to 900 °C, at a heating rate of 20 °C min<sup>-1</sup>. The morphology of samples was studied by SEM analysis using a TESCAN MIRA 3 model at a 10 kV field-emission scanning electron microscope. FTIR spectra were measured by using a Brucker PerkinElmer-100 spectrometer from 450 cm<sup>-1</sup> to 4000 cm<sup>-1</sup>. The reaction products were analyzed by the

thin layer chromatography (TLC). The gas chromatography (GC) of PerkinElmer Clarus 400 and GC-MS (Shimadzu QP 2010 ultra, Rtx- 17, 30 m  $\times$  25 mm ID column) were used to calculate yields for the products as well as for identification of the products. The column chromatography (100-200 mesh silica gel) was used for the purification of products. NMR spectra were recorded with an Agilent Technologies (<sup>1</sup>H NMR at 400 and 500 MHz, <sup>13</sup>C NMR at 101 and 126 MHz) spectrometer.

#### 2.3 Experimental procedure for the synthesis of formamides:

*N*-formylation of amines by  $CO_2$  and DMAB in the presence of UiO-66 as a catalyst was carried out in autoclave. The synthesis of formamides is as follows, Amines (5.0 mmol), UiO-66 (10 mg), DMAB (1.5 equiv.), DMF (7 mL) were added in the reactor at room temperature, reactor was closed, flushed two to three times by  $CO_2$  and 1 MPa  $CO_2$  pressure was introduced into reactor, then the reactor was heated to required temperature with continuous stirring. After the reaction was complete, the reactor was cooled, and the  $CO_2$  pressure was carefully discharged from the autoclave. The UiO-66 MOF was separated by centrifugation. The resultant mixture was concentrated by rotary evaporator and subjected to the column chromatography with ethyl acetate-petroleum ether used as an eluent to obtain the product. All the products are confirmed by GCMS

#### 2.3.1 Recycling test

Piperidine (5.0 mmol), UiO-66 (10 mg), DMAB (1.5 equi.), DMF (7 mL) were added in the reactor at room temperature, the reactor was closed and 1 MPa  $CO_2$  pressure was introduced into the reactor, then the reactor was heated to required temperature with continuous stirring. After completion of the reaction, the catalyst was recovered by centrifugation and dried at 60 °C then the catalyst was used for the further recycle run.

# 3 Result and discussion

## 3.1: Synthesis and characterization of UiO-66 and UiO-66-NH<sub>2</sub>

The UiO-66 and UiO-66-NH<sub>2</sub> were prepared by the reported method<sup>44,57</sup> and detailed procedure for the synthesis of UiO-66 and UiO-66-NH<sub>2</sub> are shown in the supplementary information (**SI**). The UiO-66 and UiO-66-NH<sub>2</sub> were characterized by IR, XRD, SEM, and TGA.

The structure of samples was confirmed by the powder X-ray diffraction method (**Fig. S2, SI**). The 2 $\theta$  peaks at 7.1, 8.3 and 25.54° are observed in the XRD patterns of UiO-66-NH<sub>2</sub> and UiO-66 that are in good accordance with the literature.<sup>57</sup> According to experimental, UiO-66-NH<sub>2</sub> and UiO-66 are highly crystalline materials. The average crystalline size of UiO-66 was found by Scherrer's formula Dhkl = 0.9 $\lambda/\beta$  cos  $\theta$  and found to be 23 nm, full-width half maxima (FWHM) is 0.3596, where,  $\theta$  is the Bragg angle and  $\beta$  is the line broadening at half the maximum intensity.

The morphology and particle sizes of UiO-66 were investigated by the Scanning electron microscope. SEM images of the UiO-66 are shown in **Fig. S3 (SI)**. These data point shows that UiO-66 consists of the relatively uniform aggregates with 7-9  $\mu$ m of the 6.49  $\mu$ m width and 8.67  $\mu$ m of the length.

The Structure of UiO-66 and  $NH_2$ -UiO-66 also was analyzed by IR spectroscopy. IR spectra of samples are shown in **Fig. S1 (SI)**. In the spectra of samples, the sharp band at 1662 cm<sup>-1</sup> corresponds to DMF and the two intense peaks at 1585 and 1395 cm<sup>-1</sup> assigned to the in/out stretching modes of the

carboxylate group are observed. The peaks observed at 745, 700, 676, 552 and 487 cm<sup>-1</sup> assigned to the -OH and C-H bending peaks are overlapped with Zr-O peaks. The broad band in the region of 3000 to 3500 cm<sup>-1</sup> is observed in spectra of samples. This band can point to the existence of the -OH groups in SBU (secondary bonding unit) of UiO-66 and NH<sub>2</sub>-UiO-66.

The stability of samples was investigated by thermal gravimetric analysis (TGA). TGA curves of UiO-66 and  $NH_2$ -UiO-66 are shown in **Fig. S4 (SI)**. The first weight loss was observed from 38 to 115 °C and it was about 6.2 wt%. This may be corresponding to the initial loss of solvent. The second weight loss occurred from 180 to 300 °C and it was about 15.2 wt%. This weight loss related to water vaporization. The third weight loss observed from 460 to 610 °C and this is major weight loss about 24.4 wt% and corresponds to the decomposition of the organic linker. These data are in agreement with that reported in literature.<sup>58</sup>

## 3.2: Catalytic properties of UiO-66

In the first set of experiments, piperidine is selected as a model substrate for *N*-formylation of amines with  $CO_2$  as a C1 source to examined catalytic properties of UiO-66.

3.2.1: N-formylation of piperidine with CO<sub>2</sub>

Table 1: Optimization Table<sup>a</sup>

$ \begin{array}{c}                                     $									
Entry	Solvent	Catalyst (mg)	CO2	Temperature	Time (h)	Yield <sup>b</sup> (%)			
		(equiv.)		(MPa)	(°C)				
1	Toluene	DMAB (3)	UiO-66 (15)	2.0	80	20	10		
2	ACN	DMAB (3)	UiO-66 (15)	2.0	80	20	45		
3	THF	DMAB (3)	UiO-66 (15)	2.0	80	20	24		
4	1,4-dioxane	DMAB (3)	UiO-66 (15)	2.0	80	20	40		
5	DMF	DMAB (3)	UiO-66 (15)	2.0	80	20	90 <sup>c</sup>		
6	DMF	DMAB (3)	UiO-66-NH <sub>2</sub> (15)	2.0	80	20	92		
7	DMF DMAB (3)		UiO-66-NH <sub>2</sub> (15) 2.0		40	20	60		
Effect of Temperature									
8	DMF	DMAB (3)	UiO-66 (15)	2.0	60	20	88		
9	DMF	DMAB (3)	UiO-66 (15)	2.0	40	20	54		
10	DMF DMAB (3)		UiO-66 (15)	2.0	100	20	92 <sup>c</sup>		
Effect of Pressure									
11	DMF	DMAB (3)	UiO-66 (15)	1.5	60	20	89		
12	DMF	DMAB (3)	UiO-66 (15)	1.0	60	20	86		
13	DMF	DMAB (3)	UiO-66 (15)	0.5	60	20	62		

Effect of DMAB loading										
14	DMF	DMAB (2)	UiO-66 (15)	1.0	60	20	87			
15	DMF DMAB (1.5)		UiO-66 (15)	1.0	60	20	85			
16 DMF DMAB (1)			Uio-66 (15)	1.0	60	20	58			
Effect of Time										
17	DMF	DMAB (1.5)	UiO-66	1.0	60	16	90 <sup>c</sup>			
18	DMF	DMAB (1.5)	UiO-66	1.0	60	12	85			
19	DMF	DMAB (1.5)	UiO-66	1.0	60	8	48			
Effect of catalyst/substrate ratio										
20	DMF	DMAB (1.5)	UiO-66 (10)	1.0	60	12	92			
21	DMF	DMAB (1.5)	UiO-66 (5)	1.0	60	12	72			
22 <sup>d</sup>	2 <sup>d</sup> DMF DMAB (1.5)		UiO-66 (10)	1.0	60	12	90			
23eDMFDMAB (1.5)		UiO-66 (10)	1.0	60	12	82				
24 <sup>f</sup>	DMF	DMAB (1.5)	UiO-66 (10)	1.0	60	12	58			
Effect of other boron adduct										
25	DMF	NaBH <sub>4</sub> (1.5)	UiO-66 (10)	1.0	60	12	67			
26	DMF	NaBH <sub>3</sub> CN (1.5)	UiO-66 (10)	1.0	60	12	78			
27	DMF	Na(CH <sub>3</sub> COO) <sub>3</sub> BH	UiO-66 (10)	1.0	60	12	34			
		(1.5)								
Controlled Experiments										
28	DMF	1.5	-	1.0	60	12	15			
29	DMF	1.5	UiO-66	0.0	60	12	-			
Reaction conditions: a) Piperidine (2 mmol), DMAB (1.5 equiv.), CO <sub>2</sub> (1 MPa), UiO-66 (10 mg), DMF (7 mL) at 60 °C for 12 h. b)										

GC and GC-MS yield. c) isolated yield. d) Piperidine (4 mmol). e) Piperidine (6 mmol) f) Piperidine (10 mmol)

In the first set of experiments, piperidine is selected as a model substrate for N-formylation of amines with  $CO_2$  as a C1 source. Initially, the reaction was performed in the presence of various solvents (Table 1). When we used non-polar toluene as a solvent, lesser yield of 2a was obtained (Table 1, entries 1), while weak polar solvents like ACN, THF, 1,4-dioxane are also not appropriate solvents for the formylation reaction because of the unsatisfactory yield of 2a (Table 1, entries 2 to 4). A 90% yield of **2a** was achieved when we used DMF as a solvent at 80 °C for 20 h (Table 1, entry 5). This is probably due to the good solubility of CO<sub>2</sub> and DMAB in DMF. It is observed that polar solvent has a prominent effect on the formylation reaction, as the polar solvent can activate N-H bond of secondary amines through polarization and solvation. Then, we tried the reaction with UiO-66-NH<sub>2</sub>, also gave the formylated product in good yield (Table 1, entries 6) but at a lower temperature, the only 60% yield was obtained (Table 1, entry 7). Therefore, we continued our studies with UiO-66 as a catalyst. After the solvent study, the effect of temperature was studied. As we decreased the temperature to 60 °C, 88% yield of 2a was observed while at 40 °C low yield was noted (Table 1, entries 8 and 9). The 60 °C temperature is an optimal temperature used for next set of reaction. Next, the effect of  $CO_2$  pressure was investigated on the reaction system (Table 1, entries 11 and 13). The decrease in pressure from 2 MPa to 1 MPa, slightly decreased in the yield of 1-formylpiperidine (2a) was observed (Table 1, entries 11 and 12). At 5 bar CO<sub>2</sub> pressure, less yield of **2a** was observed. Next, the effect of DMAB loading was studied and 1.5 equivalent of DMAB provided 1-formylpiperidine (**2a**) in very good yield compare to 1 equivalent DMAB (Table 1, entries 14-16). Finally, we focused on the effect of time. The reaction time was lowered from 20 to 8 h and it was noted that the 12 h reaction time was enough to provide **2a** excellent yield (Table 1, entries 17-19). In the next set of experiments, the effect of substrate/catalyst ratio was studied. The catalyst loading was decreased from 15 to 5 mg and 10 mg of catalyst loading gave the good yield of the *N*-formylated product compared to 5 mg catalyst loading (Table 1, entries 20-21). Then 10 mg catalyst loading was used for further experiments. Next, we increased the piperidine from 2-10 mmol and it was observed that up to 6 mmol of **1a** gave the 1-formylpiperidine (**2a**) in good yield, (Table 1, entries 22-24). Effect of other hydrogen sources (boron adducts) was also studied. When we used NaBH<sub>4</sub> and NaBH<sub>3</sub>CN gave the 67 and 78% yield of **2a** respectively, while only 34% yield was obtained in presence Na(CH<sub>3</sub>COO)<sub>3</sub>BH as a reducing agent (Table 1, entries 25-27). In a control experiment we carried out a reaction in the absence of catalyst, only 15% yield of **2a** was obtained (Table 1, entry 28). Also, we examined the reaction in the absence of CO<sub>2</sub>, **2a** was not observed (Table 1, entry 29). The final optimized reaction condition is Piperidine (6 mmol), DMAB (1.5 equiv.), CO<sub>2</sub> (1 MPa), UiO-66 (10 mg), DMF (7 mL) at 60 °C for 12 h.

#### 3.2.2: N-formylation of aromatic and aliphatic amines with CO<sub>2</sub>

After the optimization study, the substrate scope was also explored. The various primary and secondary aromatic and aliphatic amines which having different functional groups were tested for the N-formylation reaction (Scheme 2). Initially, cyclic aliphatic secondary amines namely piperidine, pyrrolidine, morpholine, piperazine were examined for the formylation of amines and the excellent yield of the corresponding products were obtained respectively (Scheme 2, 2a to 2d). A primary cyclic aliphatic amine (cyclohexyl amine), also provided the desired formamide 2e in good yield. The bulkier secondary aliphatic amines such as di-n-butylamine and di-tert-butylamine furnished the 2f and 2g in low yields. This is due to the steric hindrance of alkyl substituent (isobutyl) around the nitrogen of respective amines. The formylation of imidazole and indoline were examined for the optimized reaction condition and good yield of respective formamide was obtained (Scheme 2, 2h & 2i). Then, we tested aromatic substrates such as aniline and its derivatives for the formylation reaction. Primary aromatic amine (aniline) also provided N-formylaniline in excellent yield (Scheme 2, 2j). Then, we study the electronic effect on the aniline and methoxy and dimethoxy substituted aniline gave a good yield compared to withdrawing substrates like flouro and OCHF<sub>2</sub> substituted aniline (Scheme 2, 2k to **2n**). Moreover, the N-methylaniline, N-methylbenzylamine and  $\alpha$ -methylbenzyl amine were examined and the corresponding N-formylated products obtained in excellent yield (Scheme 2, 20 to 2q). Only 34% yield of 2r was observed when we used N-benzyl-2-methylpropan-2-amine as a substrate. The dibenzyl amine was tested and moderate yield of the desired formamide was noted (scheme 2, 2s). Then, we utilized o-phenylenediamine as a substrate and cyclized product benzimidazole was obtained in excellent yield (Scheme 2, 2t).



#### Scheme 2: Substrate Study

a) Reaction condition - 1a (5 mmol), CO<sub>2</sub> (1.0 MPa), Catalyst (10 mg), DMAB (1.5 equiv.), Solvent (DMF) at 60 °C for 12 h, Isolated yield.

## 3.2.3: Stability of UiO-66 in N-formylation of amine with CO2

We also investigated the reusability and recyclability of UiO-66 in N-formylation of piperidine with CO<sub>2</sub>. After each catalytic test, the catalyst was recovered by centrifugation, dried (in air), and reactivated at 60°C for 1 h.<sup>44</sup> and then used in the next cycle. It was found that activity of UiO-66 decreases from cycle to cycle (Fig. 1). The catalyst was found to be recyclable up to four recycle without considerable loss in the yield of the product. UiO-66 sample after the four recycle was examined by XRD, IR spectroscopy and TGA (**Figs S1, S2 and S4, SI**). The XRD pattern of the recycled UiO-66 shows that all peaks were maintained in its existing state with a slight decrease in intensity of



peaks, compared to the fresh catalyst and this result is also confirmed by IR spectra that the there is no significant changes was observed in the catalyst.

Figure 1: Catalyst recycles study of *N*-formylation reaction.

#### 3.2.4: Mechanism of formylation of amines

Moreover, the tentative reaction mechanism for the synthesis of formamides catalyzed by UiO-66 as a heterogeneous recyclable catalyst has been developed based on previously reported methods (Figure 2).<sup>18,44</sup> UiO-66 and UiO-66-NH<sub>2</sub> possess acid and basic sites which takes part in the reaction mechanism. Basic sites are sites for the CO<sub>2</sub> activation which favour the appearance of the positive charge on the carbon atom of CO<sub>2</sub> molecule. In UiO-66 there is no nitrogen atoms in the structures but also exhibited basicity, probably by the oxygen atoms in the organic ligands connected to metal clusters via covalent bonding.<sup>55,59-60</sup> Then attack of atom of carbon of CO<sub>2</sub> by molecule of amine (NH2-R) leads to the formation of intermediate 1. Next, Lewis acid sites (Zr atoms) are active sites for the degradation of dimethylamine borane, activates the B-H bond which leads to form intermediate 2, Intermediate 2 gave the formylated product and NMe<sub>3</sub>.H<sub>2</sub>B–OH as a side product. Both step A and B (rate of these steps) depend on the amount and strength of active sites and their accessibility. UiO-66 has larger amount of strong acid sites in compared with NH<sub>2</sub>-UiO-66 that should favour the higher rate of degradation of dimethylamine borane. In spite the larger number of basic sites in NH<sub>2</sub>-UiO-66 the accessibility of acid sites for dimethylamine borane is low.



**Figure 2:** Proposed reaction mechanism for the synthesis of formamides from amines and dimethylamine borane in the presence of  $CO_2$ .

# 3.2.5: Comparison of our method with other approaches

**Table 1:** Comparison of UiO-66 with other recent catalysts used for N-formylation reaction with  $CO_2$ and piperidine

Sr.no	Catalyst	Base/ Ligand	CO₂ (bar)	H <sub>2</sub> source (bar)	Temperature (°C)	Time (h)	Ref
1	Carpy-CMP@Ru	-	40	H <sub>2</sub> (40)	130	24	61
2	Co-pincer complex	KtBuO	30	H <sub>2</sub> (30)	150	36	62
3	Pd@HMP-1		10	Diphenylmethylsilane	60	20	64
4	$Co(ClO_4)_2$ . $6H_2O$ , $PPh_3$	K <sub>2</sub> CO <sub>3</sub>	30	H <sub>2</sub> (30)	140	24	63
5	Imine-POP@Pd	K <sub>3</sub> PO <sub>4</sub>	30	H <sub>2</sub> (30)	100	24	41
6	$B(C_6F_5)_3$	-	10	Me <sub>2</sub> NH.BH <sub>3</sub>	80	4	18
7	DBU	-	1	PMHS	30	72	36
8	FIP-IM@QA	-	10	PhSiH₃	35	14	65
9	FeN₃/KCC1/APTPOSS/ TCT/PVA/Cu(II) MNPs	-	15	H <sub>2</sub> (20)	90	1.5	68
10	Ru complex	KtBuO	40	H <sub>2</sub> (40)	90	30	69
11	NHC-Ir COD complex	-	30	H <sub>2</sub> (30)	100	20	70
12	$Cu_2(OH)_2CO_3$	Ph <sub>2</sub> CyP	1	PhSiH₃	60	12	66
13	Pd/NC-800-6.9%	-	30	H <sub>2</sub> (40)	130	24	67
14	UiO-66	-	10	Me <sub>2</sub> NH.BH <sub>3</sub>	60	12	This

				work

The comparisons of the catalytic activity of UiO-66 with other recent catalysts used for *N*-formylation amines with utilization of CO<sub>2</sub> as a C1 source (Table 1). Although the usage of hydrogen as a clean energy source has various reports as a reducing agent for *N*-formylation reaction, but the use of H<sub>2</sub> is problematic because of explosive nature, requirement elevated temperature and pressure and also used of expensive transition metal complexes.<sup>41,61-63,68-70</sup> Although, silanes are well explored in literature for *N*-formylation reaction but they are less atom-economical and generally require expensive catalyst.<sup>36,64-67</sup> Also, most of the reported methods are non-recyclable and costly as compared to boranes. In case of heterogeneous recyclable catalysts, use of silane as a hydrogen source require tedious work procedure as it generates solid waste. Considering the above circumstances, use of borane as a reducing agent is ideal compared to H<sub>2</sub> and silanes. As borane having high hydrogen storage capacity, moisture and air stability and easy to handle.

## 4 Conclusion:

In summary, we have prepared, characterized UiO-66 and UiO-66-NH<sub>2</sub> MOFs and its application for the *N*-formylation of amines with CO<sub>2</sub> to the corresponding formylated product. The DMAB is used as a greener reducing agent (compare to silane) for the *N*-formylation of amines. The synthesized catalyst UiO-66 shows excellent activity for a series of amines including aliphatic, cyclic and aromatic amines to obtain the formamides in good to excellent yield. Advantageously, the UiO-66 MOF is reused up to four consecutive cycles without a significant decrease in catalytic activity.

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# **Graphical abstract**



# Highlights

- $\triangleright$  CO<sub>2</sub> was used as an ideal C1 carbon source for *N*-formylation reaction.
- ➤ Zr MOFs (UiO-66 and UiO-66-NH<sub>2</sub>) were employed for *N*-formylation of amines.
- First time MOF was used for *N*-formylation reaction using  $CO_2$  as a carbon source.
- > Dimethylamine borane (DMAB) used as a reducing agent.
- ➢ Good to excellent yields were obtained with Primary and secondary amines.

# Journal Pre-proofs

**Conflict of interest** 

No conflict of interest.