N-Formylation of amines utilizing CO₂ by a heterogeneous metal–organic framework supported single-site cobalt catalyst†

Rajashree Newar, Rahul Kalita, Naved Akhtar, Neha Antil, Manav Chauhan and Kuntal Manna ID*

Catalytic N-formylation of amines using CO₂ is considered pivotal for the sustainable synthesis of formamides, key chemical feedstocks for synthesizing heterocycles, pharmaceuticals and bioactive molecules. We report a single-site cobalt(II) hydride catalyst supported on an aluminum metal–organic framework (DUT-5-CoH), which is an active heterogeneous catalyst for transforming both primary and secondary amines, as well as anilines, into the corresponding N-formamides utilizing CO₂ and either H₂ or phenylsilane as a reducing agent. DUT-5-CoH is tolerant to a range of amine substrates bearing various functional groups under 10 bar CO₂. Various aromatic and aliphatic primary amines as well as secondary amines were readily converted to the corresponding N-formamides in excellent yields and selectivity. The MOF could be recycled and reused up to 15 times without decreasing the catalytic activity in the N-formylation of p-methoxybenzylamine. The kinetic, spectroscopic and density functional theory calculation studies suggest that the reaction of DUT-5-CoH and CO₂ forms cobalt-formate, which undergoes PhSiH₃ assisted formamide formation with benzylamine in the turnover limiting step. This work highlights the development of robust single-site earth-abundant metal catalysts based on metal–organic frameworks for efficient and chemoselective N-formylation of amines using CO₂.

1. Introduction

Carbon–nitrogen (C–N) bond formation utilizing carbon dioxide (CO₂) as a cheap C1 source has drawn much attention in recent years primarily due to the escalation of anthropogenic CO₂ in the atmosphere and its greenhouse effect.¹,² In particular, the construction of C–N bonds via reductive functionalization of CO₂ with amine is significant in producing N-formylated compounds, which are vital feedstocks in synthesizing dyes, fragrances, pharmaceuticals and bioactive molecules.³–⁵ However, because of the high thermodynamic stability and kinetic inertness of CO₂, the challenges in CO₂ activation remain. N-Formylation of amines using CO₂ is reportedly performed in the presence of H₂,⁶–¹⁹ hydrosilanes²⁰–⁴² or hydroboranes⁴³–⁴⁷ as reductants. In general, H₂ is the most economical and cleanest reducing agent. However, the use of H₂ requires comparatively harsher reaction conditions such as high temperature and pressure.

Alternatively, N-formylation of amines using hydrosilanes or hydroboranes normally requires milder reaction conditions due to the weaker and polar Si–H/B–H bond than the H–H bond in H₂.³⁹ Due to safety reasons, hydrosilanes are more convenient to use than H₂ as reductants in the laboratory syntheses. Furthermore, the by-products consist of strong Si–O bonds, which gives an extra thermodynamic driving force in the amine formylation reaction.

Numerous homogeneous catalysts based on precious and toxic late-transition metals such as Pt, Ru, Rh, Ir, and Pd have been developed for the N-formylation of amines.⁴⁸–⁵³ Various homogeneous earth-abundant metal catalysts have also been developed in recent years for economic and eco-friendly synthesis of N-formamides due to the low-cost and less toxicity of the abundant metals.³⁸,⁵⁴–⁶⁵ Compared to homogeneous catalytic systems, heterogeneous analogs are always preferred in industry owing to their inherent advantages of catalyst separation and reuse, and higher stability for sustainable synthesis of N-formamides.⁷,⁹–¹⁵,¹⁸,³³,³⁴,⁶⁶,⁶⁷ Despite significant development in heterogenizing molecular abundant-metal catalysts or traditional oxide-supported metal catalysts for formylation of amines, many of these systems suffered from poor selectivity, the presence of multiple active sites, non-uniformity, difficulty in characterization and non-tunability.⁶⁸–⁷¹
As porous solid supports, metal–organic frameworks (MOFs), constructed from metal-oxo cluster-based nodes or secondary building units (SBUs) and organic carboxylate-linkers, are of great interest for synthesizing crystalline, robust and single-site solid catalysts via active site-isolation with tunable properties. Metal-oxo nodes are reported to serve as an oxide-support for facile preparation of site-isolated single-site base-metal catalysts. Moreover, the hydroxyl group present in the SBU facilitates post-synthetic grafting of active metal-species. Herein, we report an easily synthesizable, single-site earth-abundant cobalt(ii) hydride catalyst for N-formylation of a range of primary and secondary amines, as well as anilines, using CO2 as a C1 source and either H2 or phenylsilane as a reducing agent to afford N-formamides with excellent yields and selectivity.

2. Experimental section

2.1. Preparation of the MOF catalyst (DUT-5-CoH)

First, DUT-5 MOF was synthesized by a solvothermal reaction between AlCl3·6H2O and biphenyl-4,4’-dicarboxylic acid (H2-bpdc) in dimethylformamide (DMF). A mixture of H2-bpdc (0.05 g, 0.206 mmol), AlCl3·6H2O (0.032 g, 0.135 mmol) and DMF (3 ml) was stirred for 2 h in a 5 ml vial at room temperature. Then, the reaction mixture was transferred to a hydrothermal bomb with a Teflon liner and placed in a preheated oven at 120 °C for 48 h. It was then cooled to room temperature, and the resultant white crystalline solid of DUT-5 MOF was isolated via centrifugation and washed with DMF multiple times. Inside a glovebox, the post-synthetic metatation of DUT-5 was performed by treating DUT-5 (0.015 g, 0.052 mmol) with n-BuLi (0.047 ml, 1.65 M in cyclohexane) in THF, followed by addition of 1 ml THF solution of CoCl2 (0.094 g, 0.073 mmol). The reaction mixture was stirred slowly for 24 h at room temperature to furnish Al-node-supported cobalt chloride [DUT-5-CoCl] as a blue crystalline solid. DUT-5-CoCl (0.012 g, 0.038 mmol) was finally treated with NaEt3BH (15 μL, 1 M in toluene) inside the glovebox, and stirred at room temperature for 1 h to afford DUT-5-CoH as a black solid. DUT-5-CoH was washed with THF multiple times and stored in THF in the glovebox.

2.2. General procedure for DUT-5-CoH catalyzed N-formylation of amines using phenylsilane as the reductant

In a glovebox, a glass liner was charged with an amine substrate (0.375 mmol), phenylsilane (0.862 mmol) and DUT-5-CoH (0.5 mol% of Co) in 3 ml of THF. The liner was fitted in a high-pressure Parr reactor and sealed. The sealed reactor was taken out from the glovebox and purged with CO2 gas two times. The reactor was pressurized to 10 bar CO2 and heated at 25–100 °C for 20–40 h. After the completion of the reaction, the pressure of the reactor was released. The solid MOF was removed from the suspension via centrifugation inside the glove box, washed with THF three times, and reused. The combined organic extracts were concentrated in vacuo followed by column chromatography using hexane and ethyl acetate (50:1) as an eluent to yield the N-formaldehyde product.

2.3. General procedure for DUT-5-CoH catalyzed N-formylation of anilines using H2 as a reductant

In a glovebox, a glass liner was charged with an aniline substrate (0.375 mmol) and DUT-5-CoH (0.5 mol% of Co) in 3 ml of THF. Then, the liner was fitted in a high-pressure Parr reactor and sealed. The sealed reactor was taken out from the glovebox and purged with CO2 gas two times. The Parr reactor was pressurized to 10 bar CO2 followed by 10 bar H2 and heated at 100 °C for 40 h. After the completion of the reaction, the pressure of the reactor was released. The solid MOF was removed from the suspension inside the glove box, washed with THF three times, and reused. The combined organic extracts were concentrated in vacuo to yield the corresponding N-phenylformamide.

All the characterization techniques, including X-ray absorption spectroscopy (XAS) and X-ray photoelectron spectroscopy (XPS), and the computational methods to study the mechanism of formylation reactions are described in detail in the ESI.

3. Results and discussion

3.1. Characterization of the DUT-5-CoH MOF catalyst

The deprotonation of μ2-OH of nodes of the DUT-5 MOF followed by reaction with CoCl2 gave DUT-5-CoCl. It was subsequently reacted with NaEt3BH in THF to afford DUT-5-CoH via a halide-hydride exchange reaction (Fig. 1a). The similar PXRD pattern of freshly prepared DUT-5-CoH to that of simulated DUT-5 and pristine DUT-5 indicated that DUT-5-CoH has a three-dimensional porous framework with rhombic channels constructed from octahedrally coordinated aluminium oxo-nodes bridged with 4,4’-biphenyldicarboxylate bridging linkers (bpdc) (Fig. 1b). 29% Co-loading as analysed by inductively coupled plasma atomic emission spectroscopy (ICP-OES) of the digested DUT-5-CoH suggested its formula of Al(O)[bpdc][Li]0.71(CoCl)0.29. The Co2+ in DUT-5-CoH coordinates with two neutral carboxylate oxygens, one anionic μ1-O−, one hydride, and one THF to form a distorted square pyramidal [[μ1-O(carboxylate-O)2CoH][THF]] species.

3.2. DUT-5-CoH catalyzed N-formylation of primary amines

DUT-5-CoH is an active catalyst for N-formylation of primary and secondary benzylic- and aliphatic-amines using CO2 as a C1 source. The formylation reaction was first optimized using 4-methoxybenzyl amine (1a) as a primary amine substrate, CO2, and phenylsilane as the reductant (Table 1). Stirring a mixture of 1a, PhSiH3 (2 eq. with respect to amine), DUT-5-CoH (0.5 mol% Co) and 3 ml THF under 10 bar CO2 in a high-pressure batch reactor at room temperature for 24 h afforded N-(4-methoxybenzyl)formamide (2a) as the sole product (Table 1, entry 1). The yield of 2a decreased when less than 2.0 eq. of PhSiH3 was used (Table 1, entry 2). The
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Formylation reaction conducted in toluene afforded 2a in a lower yield under identical reaction conditions (Table 1, entry 3). The highest turnover frequency was acquired when the formylation reaction was conducted in THF as a solvent under 10 bar CO2 and 0.5 mol% DUT-5-CoH and 2.3 eq. of PhSiH3 with respect to the amine substrate for 20 h (Table 1, entry 4). It is noteworthy that 100% conversion and 81% yield of 2a were obtained upon decreasing the Co-loading to 0.1 mol% (Table 1, entry 5). Utilization of H2 as the reductant instead of PhSiH3 afforded only N-(4-methoxybenzylidene)-1-(4-methoxyphenyl)methanamine (2a) in 99% yield. Compared to electron-donating functional groups (1a, 1c–d), electron-withdrawing substituents (1e–f) on the phenyl ring significantly decreased the reaction rate. Therefore, a longer reaction time and elevated temperature were required for high conversion. At a 0.5 mol% Co-loading, primary aliphatic amines such as isopropyl amine (1h), n-butylamine (1i), hexylamine (1j), octylamine (1k), isobutylamine (1l), 2-ethylhexylamine (1m), cyclohexylamine (1n), and t-butylamine (1o) were selectively converted to the corresponding monoformylated amines (2h–o) in good yields.

Table 1 Optimization of reaction conditions for the N-formylation of p-methoxy benzylamine using CO2 and PhSiH3

<table>
<thead>
<tr>
<th>Entry</th>
<th>Co-loading (mol%)</th>
<th>Reductant (eq. w.r.t. the amine substrate)</th>
<th>Solvent</th>
<th>Time (h)</th>
<th>% GC-yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.5</td>
<td>PhSiH3 (2 eq.)</td>
<td>THF</td>
<td>24</td>
<td>80</td>
</tr>
<tr>
<td>2</td>
<td>0.5</td>
<td>PhSiH3 (1 eq.)</td>
<td>THF</td>
<td>24</td>
<td>50</td>
</tr>
<tr>
<td>3</td>
<td>0.5</td>
<td>PhSiH3 (2 eq.)</td>
<td>Toluene</td>
<td>24</td>
<td>63</td>
</tr>
<tr>
<td>4</td>
<td>0.5</td>
<td>PhSiH3 (2.3 eq.)</td>
<td>THF</td>
<td>20</td>
<td>90</td>
</tr>
<tr>
<td>5</td>
<td>0.1</td>
<td>PhSiH3 (2.3 eq.)</td>
<td>THF</td>
<td>72</td>
<td>81</td>
</tr>
<tr>
<td>6</td>
<td>0.5</td>
<td>H2</td>
<td>THF</td>
<td>24</td>
<td>0&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>7</td>
<td>0.5</td>
<td>(EtO)&lt;sub&gt;2&lt;/sub&gt;MeSiH (2.3 eq.)</td>
<td>THF</td>
<td>20</td>
<td>0&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup> Reaction conditions: DUT-5-CoH, 10 bar CO2, 0.375 mmol of amine, 3.0 mL solvent. <sup>b</sup> N-(4-Methoxybenzylidene)-1-(4-methoxyphenyl)methanamine was obtained in 99% yield. <sup>c</sup> N-(4-Methoxybenzylidene)-1-(4-methoxyphenyl)methanamine was obtained in 10% yield.

Finally, trans-1,2-cyclohexanediamine (1r) gave the diformamide product in 92% yield. Pure formamide products were isolated by removing the solid MOF via centrifugation, followed by evaporation of the volatile organics when the selectivity and conversion of the reactions were 100%. In other cases, the products were purified by silica gel column chromatography using hexane and ethyl acetate (50:1) as the eluent. Surprisingly, anilines were inactive in the formylation reactions under identical catalytic conditions using PhSiH3 as the reductant.
3.3. DUT-5-CoH catalyzed N-formylation of secondary amines

DUT-5-CoH is also efficient in catalyzing N-formylation of various secondary amines utilizing CO₂ and PhSiH₃ under similar optimized reaction conditions of primary amines (Scheme 2). At a 0.5 mol% Co-loading, DUT-5-CoH catalysed the N-formylation of different aliphatic secondary amines, namely, diethylamine (3a) and diisopropylamine (3b), to furnish the corresponding N-formamides in 90% and 99% yields, respectively. Excellent yields (62–99%) and selectivity were found in the formylation of various cyclic amines such as pyrrolidine (3d), piperidine (3e), indoline (3f), 1,2,3,4-tetrahydroquinoline (3g) and 1,2,3,4-tetrahydroisoquinoline (3h). The formylation of morpholine (3i), substituted piperazine (3j–k), and bis(trimethylsilyl)amine (3l) proceeded smoothly at room temperature within 20 h to yield the corresponding formyl products (4i–l) as the major products.

Scheme 2  DUT-5-CoH catalyzed N-formylation of secondary amines using CO₂ and PhSiH₃.a,b aReaction conditions: DUT-5-CoH (0.5 mol% Co), 0.375 mmol of amine, 10 bar CO₂, 0.862 mmol of phenylsilane, 3.0 mL of THF, 25 °C, 20 h. Isolated yield in the parentheses, regioselectivity was determined by GC-MS. bReaction was carried out at 100 °C.

3.4. Heterogeneity and recycling of DUT-5-CoH in N-formylation of amines

We also performed different experiments to test the heterogeneity of the DUT-5-CoH MOF catalyst. Further, the catalysis reaction was stopped when the solid MOF material was removed from the reaction mixture, thus indicating that the supernatant liquid was unable to catalyse the reaction (Fig. S4, ESI†). Also, metallic mercury did not interfere in the reaction medium, confirming that no Co-nanoparticles or leached Co-particles were responsible for the catalysis; instead, the solid DUT-5-CoH MOF was the actual catalyst that was catalysing the reaction. Moreover, Co-nanoparticles generated from CoCl₂ and NaEt₃BH could not catalyse the N-formylation of morpholine at all, whereas DUT-5-CoH under exact conditions yielded morpholine-4-carbaldehyde in 100% yield and selectivity (Fig. S8, ESI†).

The DUT-5-CoH MOF could be recycled and reused at least 15 times for N-formylation of p-methoxybenzylamine (Fig. 2a). We also evaluated the percentage of metal-leaching during the recycling experiments, where the % leaching values of Co and Al after run 1 were 0.02% and 0.9% respectively, while after run 14 they were 0.08% and 2.01%, respectively. The PXRD pattern after the run of N-formylation of p-methoxybenzylamine remained intact with respect to the pristine DUT-5 MOF as well as the DUT-5-CoH MOF, which indicates the robustness of the catalyst under reaction conditions (Fig. 1b). We also tested the...
The effect of pore size on the catalysis reaction by comparing the catalytic activity of the DUT-5-CoH MOF with that of an MIL-53 AlCoH MOF that has a smaller pore size than the DUT-5 MOF with a similar topology. Under similar reaction conditions, the MIL-53 AlCoH MOF is almost 2 times less active than the DUT-5-CoH MOF, confirming that the catalysis reaction occurs both on the surface and inside the pores (Fig. S7, ESI†). The superior activity of the larger pore-sized MOF was due to the facile diffusion of the reactant and product inside the large pores (Fig. 1).

3.5. DUT-5-CoH catalyzed N-formylation of anilines using CO2 and H2

As mentioned earlier, DUT-5-CoH catalyzed N-formylation of anilines did not occur when PhSiH3 was used as the reductant. We, therefore, tested the formylation of anilines using CO2 and H2. Heating a mixture of aniline and DUT-5-CoH (0.5 mol% Co) in THF at 100 °C under 10 bar CO2 and 10 bar H2 furnished the N-phenylformamide (6a) product in 61% conversion (entry 1, Table 2). Under these reaction conditions, several mono-, di- and tri-methyl-substituted anilines such as p-toluidine (5b), 3,5-dimethylaniline (5c), and 2,4,6-trimethylaniline (5d) were converted to the corresponding N-formamides in moderate yields (entries 2–4, Table 2). Electron-rich anilines such as 4-methoxyaniline (5e) and 2-methoxyaniline (5f) were readily converted to N-(2-methoxyphenyl)formamide (6f) in quantitative yields. In addition, DUT-5-CoH was also active for N-substituted anilines such as N-methylaniline (5g) to give N-methyl-N-(2-methoxyphenyl)formamide (6g) in 35% isolated yield.

3.6. Mechanistic investigation of DUT-5-CoH catalyzed N-formylation of amines using CO2 and PhSiH3

We also scrutinized the mechanism of DUT-5-CoH catalyzed N-formylation of benzylamine by identifying the catalytic species after catalysis, control experiments, and kinetic and computational studies. The XPS spectrum of DUT-5-Co recovered after N-formylation of benzylamine using CO2 and PhSiH3 showed that the Co 2p3/2 and 2p1/2 binding energies are located at 781.2 eV and 797.1 eV, respectively, which indicates the +2 oxidation state of the Co ion like DUT-5-CoH (Fig. 2b). The +3 oxidation state of aluminium in MOF-nodes was also unchanged during catalysis as revealed by the XPS result (Fig. 2c). The absence of characteristic peaks of Co-nanoparticles at higher 2θ in the PXRD pattern of the recovered MOF rules out the formation of metallic cobalt and its role in catalysing amine formylation (Fig. 1b).

The cobalt species formed after catalysis was further characterized by extended X-ray absorption fine structure (EXAFS) analysis of the recovered DUT-5-Co. The EXAFS at the Co K-edge was well fitted with the DFT-optimized structure of a DUT-5 node-supported cobalt-formate, indicating the formation of (μ3-O)OC(O)H species after
catalysis (Fig. 2d). The calculated Co–(...O) distance of 1.86 Å, Co–Ocarboxylate distances of 1.96 and 1.98 Å, and Co–OC(O) distance of 1.88 Å are similar to those measured by EXAFS fitting (1.83, 1.94, 1.95, 2.21 and 1.87 Å, respectively). We surmise that DUT-5-Co–OC(O)H is formed via insertion of CO2 into Co–H of DUT-5-CoH. The reaction between DUT-5-Co–OC(O)H and H2 or silane could form formic acid or silyl formate, respectively, which were reported to react with amines to produce the corresponding formamides.111 However, no formic acid or silyl formate was detected during the catalysis as analyzed by GCMS and 1H NMR. In addition, the control experiment in the absence of amine showed that DUT-5-CoH does not catalyze the reaction between CO2 and H2 or silane to give formic acid or silyl formate, respectively. These experiments suggest that DUT-5-CoH catalyzed N-formamide formation likely occurred directly from benzylamine, CO2 and H2 instead of the reaction between the silyl formate intermediate and benzylamine.

To further elucidate the reaction pathway, we determined the empirical rate law of DUT-5-CoH catalyzed formylation of benzylamine using CO2 and PhSiH3 by the initial rate method at 25 °C. The concentration of benzylamine was calculated by GC-FID using mesitylene as the internal standard. The initial rate of formylation is first order in [Co] and [benzylamine] and zero-order in both [PhSiH3] and [CO2] (Fig. S9, ESI†). The empirical rate law suggests that both the Co-catalyst and benzylamine are involved in the turn-over limiting step (TLS). Based on the spectroscopic and kinetic results, we

Table 2  DUT-5-CoH catalyzed N-formylation of anilines using CO2 and H2\(^{a,b}\)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Products</th>
<th>Time</th>
<th>Conversion (yield)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5a</td>
<td>6a</td>
<td>40 h</td>
<td>61%</td>
</tr>
<tr>
<td>2</td>
<td>5b</td>
<td>6b</td>
<td>40 h</td>
<td>72%</td>
</tr>
<tr>
<td>3</td>
<td>5c</td>
<td>6c</td>
<td>40 h</td>
<td>56%</td>
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<tr>
<td>4</td>
<td>5d</td>
<td>6d</td>
<td>40 h</td>
<td>40%</td>
</tr>
<tr>
<td>5</td>
<td>5e</td>
<td>6e</td>
<td>40 h</td>
<td>100% (99%)</td>
</tr>
<tr>
<td>6</td>
<td>5f</td>
<td>6f</td>
<td>40 h</td>
<td>100% (99%)</td>
</tr>
<tr>
<td>7</td>
<td>5g</td>
<td>6g</td>
<td>40 h</td>
<td>35%</td>
</tr>
</tbody>
</table>

\(^a\) Reaction conditions: DUT-5-CoH (0.5 mol% Co), 0.375 mmol of amine, 10 bar CO2, 10 bar H2, 3.0 mL of THF, 100 °C, 40 h. \(^b\) Isolated yield in the parentheses, regioselectivity was determined by GC-MS.
propose that the insertion of CO$_2$ into Co-H of DUT-5-CoH forms the corresponding Co-formate intermediate (INT-1) (Fig. 3). Then, the coordination of PhSiH$_3$ to the Co-formate gives INT-2 and also increases the electrophilicity of the carbonyl carbon, which facilitates the subsequent nucleophilic attack of benzylamine on the carbonyl in the TLS to produce (benzylamino)(phenylsilyl)oxy)methanol. Finally, (benzylamino)(phenylsilyl)oxy)methanol is converted to N-phenylformamide upon elimination of silanol (Fig. 3). The inactivity of aniline substrates to form N-formamides using CO$_2$ and PhSiH$_3$ is attributed to their poor nucleophilicity, which inhibits the nucleophilic addition of anilines to the carbonyl carbon of INT-2.

Computational studies of DUT-5-CoH catalyzed N-formylation of amines using CO$_2$ and PhSiH$_3$

To further shed light on the reaction pathways and turnover limiting step, DFT calculation was performed using B3LYP/6-311G+(d,p) in the Gaussian 09 software suite. The DFT-calculated energy profile diagram, as shown in Fig. 4, revealed that the transformation of DUT-5-CoH to DUT-5-Co–OC(O)H (INT-1) is exergonic by 29.3 kcal mol$^{-1}$. The subsequent coordination of PhSiH$_3$ to INT-1 gives INT-2, which is 18.5 kcal mol$^{-1}$ higher in energy than INT-1. Then, the nucleophilic attack by benzylamine on the carbonyl carbon of INT-2 furnishes (benzylamino)(phenylsilyl)oxy)methanol and regenerates DUT-5-CoH via TS-2. The DFT calculation showed that the nucleophilic addition of benzylamine to the carbonyl of Co-formate in TS-2 has the highest activation barrier of 24.3 kcal mol$^{-1}$, and therefore, this step is the turnover limiting step. The assignment of TLS is also consistent with the first-order dependency of [Co] and [benzylamine] in the empirical rate law. The energy profile diagram also suggests INT-1 as the catalyst resting state, which was also experimentally confirmed by EXAFS analyses of the recovered DUT-5-Co after catalysis.

4. Conclusions

In conclusion, we have demonstrated an easily affordable and highly active catalytic system based on MOFs for N-formylation of amines using CO$_2$ as a C1 source. The MOF-node supported cobalt(II)-hydride had a wide range of functional group tolerance and broad substrate scope, converting structurally diverse amines to their corresponding N-formamide products with high yields and excellent selectivity utilizing CO$_2$ and phenylsilane/H$_2$. The use of earth-abundant metals and the advantages of recycling and reusing the MOF-Co catalyst make the N-formylation process...
cost-efficient. The coordination environment around the cobalt centre within the MOF catalyst was expounded using EXAFS and DFT models. Theoretical and experimental data assisted each other in recognizing the catalytic species and the catalyst’s resting state and thus provided guidance to propose the mechanism of N-formylation reactions. This work, therefore, features the development of cost-effective catalytic technologies based on MOF-supported earth-abundant metal catalysts for efficient N-formylation of amines to produce synthetically crucial chemical feedstocks.

**Author contributions**

K. M. conceived the project; R. N. and R. K. performed the experiments; R. N., N. A., and M. C. characterized all the compounds and analysed the experimental data. Naved performed the computational studies. K. M. and R. N. wrote the manuscript taking inputs from all other authors.

**Conflicts of interest**

There are no conflicts of interest to declare.

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