

Base Metal Catalyst for Indirect Hydrogenation of CO₂

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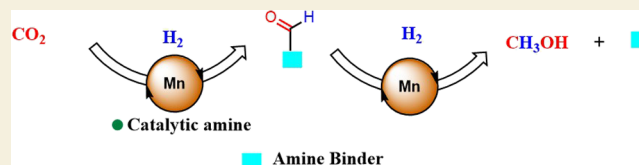
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ABSTRACT: We herein report a novel Mn-SNS-based catalyst, which is capable of performing indirect hydrogenation of CO₂ to methanol *via* formylation. In this domain of CO₂ hydrogenation, pincer ligands have shown a clear predominance. Our catalyst is based on the SNS-type tridentate ligand, which is quite stable and cheap as compared to the pincer type ligands. The catalyst can also be recycled effectively after the formylation reaction without any significant change in efficiency. Various amines including both primary and secondary amines worked well under the protocol to provide the desired formylated product in good yields. The formed formylated amines can also be reduced further at higher pressures of hydrogen. As a whole, we have developed a protocol that involves indirect CO₂ hydrogenation to methanol that proceeds *via* formylation of amines.

KEYWORDS: CCUS, hydrogenation, formylation, base metal catalyst, reductive elimination



Atmospheric CO₂ levels have been recorded with a significant hike (approx. 150%), since the modern industrialization era. The major cause of this hike can be attributed to the excessive use of fossil fuels, which is currently the backbone of industrial energy supply and vehicular transportation. Owing to this increased CO₂ level, devastating climate crises have been arising, *e.g.*, global warming and greenhouse effect. Global warming is a serious threat, which is directly affecting our lives; if not dealt with now, the outcomes could be excruciating. Consequently, controlling the hike of this CO₂ level is of utmost priority to the living community. In an earnest most attempt to overcome this; CCUS (carbon capture, utilization, and storage) has attracted significant attention in the past decade, as it has been proven to provide a solution to this CO₂ intermittency.^{1–3} One of the recent and most popular methods in CCUS is converting CO₂ to various chemical feedstocks, which are utilized on a bulk scale such as methanol, formic acid, and formaldehyde.^{4–6} Among these feedstocks, methanol is the most promising one. Since it offers a high hydrogen content and is an efficient alternative to fuels, methanol is used as a precursor in the synthesis of formaldehyde, acetic acid, and various other olefins.⁷ Despite all these advantages, CO₂ reduction to methanol is a difficult task to achieve, owing to the kinetic inertness associated with CO₂. Currently, methanol is produced from fossil fuels or *via* syngas (CO + CO₂ + H₂).⁸ However, direct reduction of CO₂ to produce methanol is a more viable and greener route, which can lead toward the foundation for a net zero carbon cycle.⁹ In this regard, heterogeneous catalysis is widely explored.¹⁰ However, harsh reaction conditions are required, which prevent it from being an affordable route to produce methanol. Methanol formation is an exergonic process, which becomes

unfavorable at higher temperatures, which is essential in heterogeneous catalysis. Water produced during hydrogenation deteriorates the surface morphology of heterogeneous catalysts. Therefore, water diffusion is a serious problem encountered in heterogeneous catalysis.¹¹ On the contrary, homogeneous catalysis offers mild conditions for this formidable task and is being explored since the past decade. Pioneering studies in the field of homogeneous catalysis were executed by Leitner, Sanford, and co-workers.^{12,13} These protocols opened an avenue for CO₂ hydrogenation in homogeneous catalysis. The ruthenium catalyst in the presence of PNP ligands enabled this transformation. Individually, the Leitner group performed direct CO₂ hydrogenation to methanol, whereas the Sanford group used cascade catalysis to generate methanol. However, harsh reaction conditions, lower TON and TOF, and expensive metal catalysts were some of the severe limitations of these protocols, which needed to be overcome. The Sanford group, again in 2015, reported CO₂ hydrogenation to methanol enabled by ruthenium catalysis.

In this report, NHMe₂ played a very crucial role, which reacted with CO₂ to form diethyl ammonium carbamate and also intercepted the formation of formic acid by converting it to diethyl formamide, which is subsequently reduced to methanol.¹⁴ Base metal catalysis for CO₂ hydrogenation

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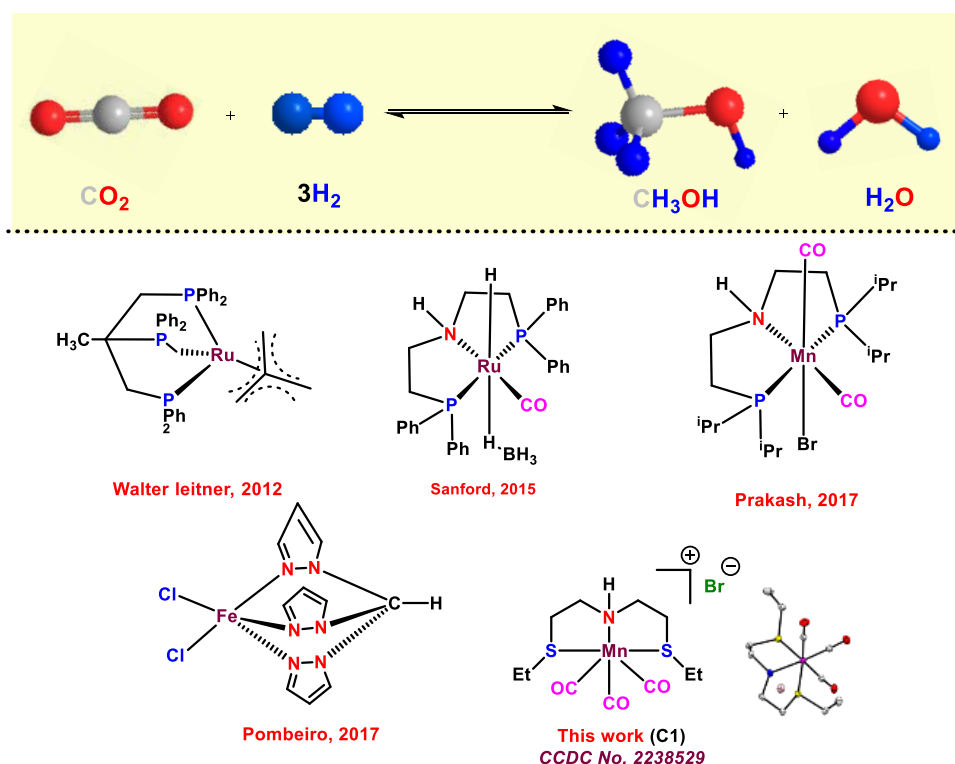


Figure 1. Transition metal catalysts for CO₂ hydrogenation.

originated in 2017 by Surya Prakash, Beller, and co-workers, utilizing manganese and cobalt catalysts in the presence of Triphos and pincer-type ligands.^{15,16} The work using the Mn-PNP catalyst followed an indirect CO₂ hydrogenation route, using morpholine as the mediator.¹⁵ Optimal conversion for morpholine was 95%, while we are able to produce 91% of formyl morpholine in our optimized conditions. They were able to achieve a maximum TON of 128 for methanol formation using their Mn-PNP catalyst. In contrast, we are observing 60% conversion of formyl morpholine under optimized conditions to produce methanol. However, the use of such expensive Triphos and pincer-type ligands was essentially required, which deteriorated the economic aspect of these protocols. Additionally, the lower TON and expensive ligand decreased the application of these protocols. Followed by these studies, some other protocols came up for CO₂ hydrogenation, which mainly utilized iron-based catalysts.^{17–19} These reports further expanded the scope with respect to base metals in the domain of CO₂ hydrogenation. So far, this genre of CO₂ reduction has witnessed a clear predominance by pincer-type ligands in cooperation with rare metal catalysis.^{20–23} Therefore, we envisioned to develop a protocol with base metal, which utilizes bench-stable cheap ligands.²⁴

Inspired from literature reports, we started our investigation with manganese catalyst C1 as shown in Figure 1. The SNS-tridentate ligand is bench-stable and can be easily synthesized from readily available cheap chemicals. Manganese also is an earth-abundant nontoxic metal. Consequently, this will aid to the greener and economic aspect of the methodology.

UV–vis and IR studies of the catalyst and metal precursor Mn(CO)₅Br confirmed the complexation [Figure 2] [see the SI pages 8 and 9].

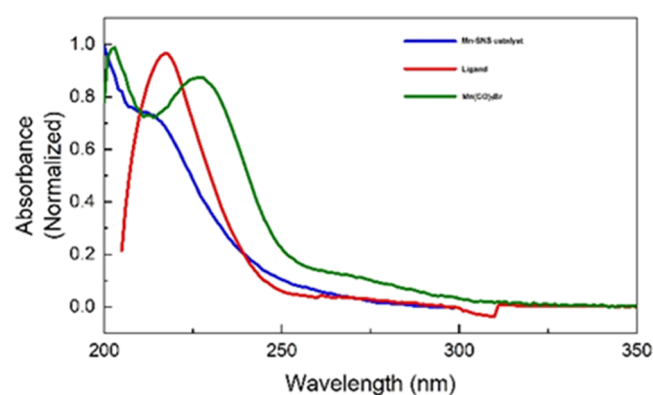
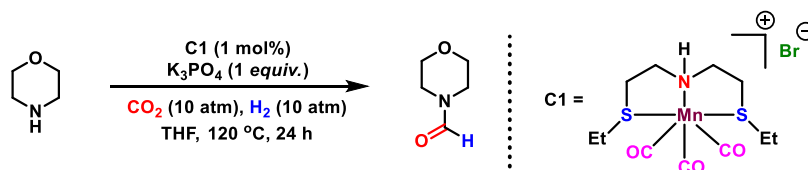


Figure 2. UV spectra of the synthesized catalyst.

Crystal Structure

The molecular form of C1 was authenticated by its crystal X-ray structure. It consisted of two independent units. The distorted octahedral arrangement around the metal ion was reflected in the deviation of cis and trans angles with respect to the ideal values of 90 and 180°, respectively. The average Mn–S bond length was found to be 2.33029 Å (14), while the Mn–N bond length was found to be 2.083 Å(4) [see SI Page 6].

From the previous knowledge of related literature reports, we initially carried out the reaction in the THF solvent in the presence of the K₃PO₄ base and morpholine as a capturing agent for CO₂ as shown in entry 2 (Table 1). However, we did not detect formation of methanol by conducting NMR and GC analysis of the crude reaction mixture. Nonetheless, formylation of amine was found to be occurring to a considerable extent as confirmed by ¹H and GCMS analysis of the reaction mixture. After confirming the formylated product of morpholine, we carried out some controlled

Table 1. Optimization Table for Formylation of Morpholine^a

entry	alteration from standard conditions	yield (%)
1	none	87
2	P(CO ₂) and P(H ₂) = 5 atm	68
3	Toluene as solvent	Trace
4	T = 140 °C	65
5	T = 130 °C	71
6	T = 110 °C	40
7	C1 = 2 mol %	89
8	C1 = 0.5 mol %	61
9	K ₃ PO ₄ = 2 equiv.	91

^aStandard reaction conditions: morpholine (2 mmol), C1 (1 mol %), K₃PO₄ (1 equiv) P(CO₂) = 10 atm, P(H₂) = 10 atm, THF, 120 °C, 24 h.

^bYields are determined by ¹H NMR.

experiments, which are described in Figure 3. In the absence of CO₂ or H₂, no formylated product was observed and in the

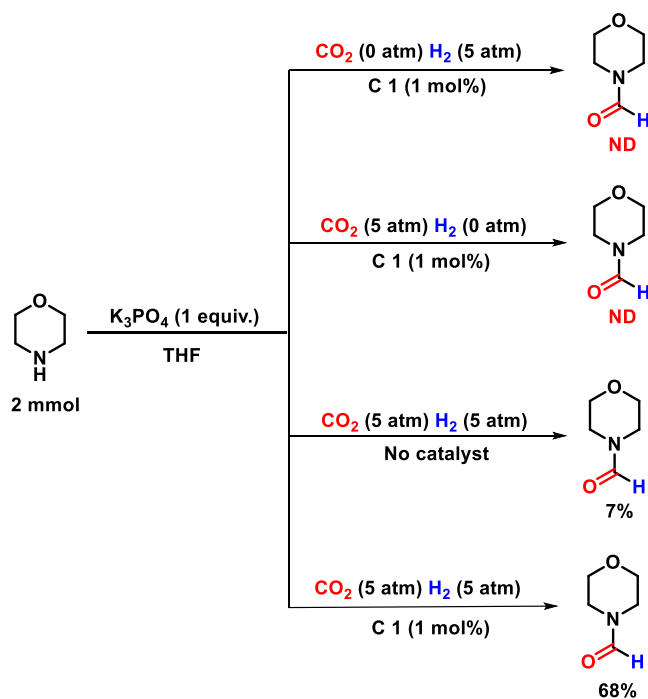


Figure 3. Control experiments for formylation of morpholine (yields are calculated by ¹H NMR using trimethoxybenzene (TMB) as an internal standard).

absence of the catalyst, the trace amount of the formylated product was observed, which can be attributed to the background reaction in the presence of base. Various other optimizations were carried out including variation of the solvent, change of pressure and temperature, and amount of the catalyst to generate the formylated product in good yield as shown in Table 1. When toluene was used as the solvent, very little/no formylated product could be detected. Temperature variation concluded 120 °C to be the optimal temperature for this transformation.

Increasing the amount of base from 1 to 2 equiv did not affect the fate of the reaction much; only a slight increase in yield was observed.

Variation of reaction time was also tested; 24 h was found to be optimal for the reaction conditions. In a longer reaction time, formation of other side products was observed. Increasing the catalytic amount from 1 to 2 mol % showed only a slight increase in yield. Therefore, we continued with 1 mol % of catalyst loading for our subsequent studies, Entry 7 (Table 1). Reaction conditions as depicted in Entry 9 were found to be optimal for formylation of morpholine, where almost full conversion was observed.

With these optimized conditions, we tested some other amines that could be successfully transformed. We started with piperidine, and it worked well in our methodology to give the desired product *N*-formyl piperidine in 80% yield. Subsequently, we planned to test primary amines in our protocol. Initially, we started with benzylamine, which offered the desired product *N*-benzyl formamide in 65% yield [Figure 4]. Conversion was somewhat less as compared to secondary amines such as morpholine and piperidine. Other benzyl amines like 3,4-dimethylbenzyl amine also worked well to give the desired formylated product in good yields. Along the way, we also tested 3-methoxybenzyl amine, which worked fine to give the desired product. However, 3-methyl benzylamine showed less conversion for formylation. Some starting materials remained unreacted, and increasing the pressure of hydrogen or increasing the reaction time led to a complex reaction mixture. GCMS analysis indicates the formation of imine, which might be because of condensation of the formed formyl morpholine. After having this one-step reduction of CO₂ to -CHO, we again focused on methanol formation. As catalyst C1 and morpholine were working best for formylation, we preferred morpholine over other amines for methanol generation. As pressure of hydrogen is a critical parameter to decide the fate of the reaction, we moved to higher pressures of hydrogen to produce methanol. We increased the pressure to 20–30 atm using the same reaction conditions. However, no sign of formation of methanol was observed as confirmed by GC analysis of the reaction mixture. At 60 atm hydrogen pressure and 10 atm CO₂ pressure with catalyst C1, methanol formation was observed as confirmed by GC analysis of the

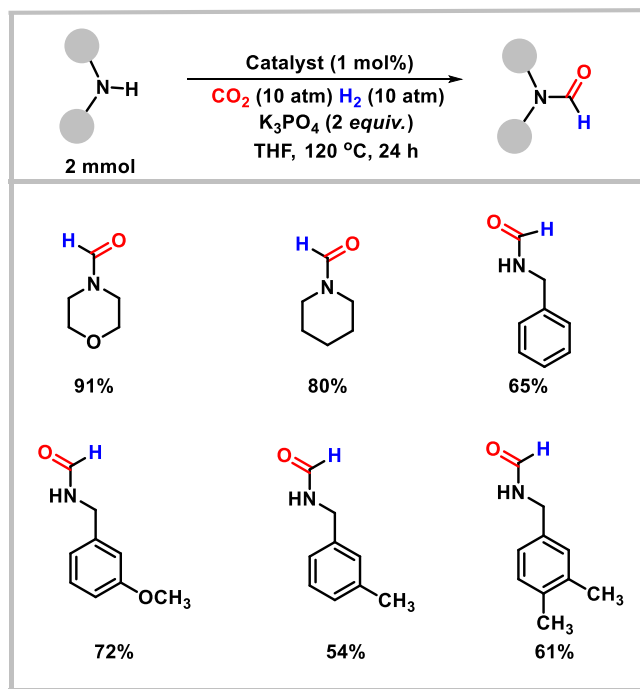


Figure 4. Formylation of amines using the Mn-SNS catalyst.

reaction mixture. We also tried toluene in the place of THF. However, no sign of methanol was observed. With the metal precursor $\text{Mn}(\text{CO})_5\text{Br}$ also, the reaction fails to generate methanol. One of the most important observations that we observed is with regard to morpholine and formyl morpholine, both being chemically competent, and the catalyst is quite active toward both of them, resulting in the formation of methanol.

Thus, we conclude that formyl morpholine is formed during the catalytic cycle and is further reduced to methanol at high pressures of hydrogen. Initially, when we subjected formyl morpholine to the reaction, it was significantly consumed in the reaction. NMR analysis of the reaction mixture showed a considerable decrease in $\text{p}-\text{CHO}$ proton of formyl morpholine. Based upon this decrease in the intensity of the $-\text{CHO}$

proton, we calculated a TON value of 60. Our experiments involving the hydrogenation of formylmorpholine have led to an interesting observation. We found that under lower pressures of hydrogen 10–20 atm, the substrate remains unreacted with no conversion taking place. Based upon the literature knowledge and our observations, we propose a catalytic cycle, which is shown in Figure 5. The cycle begins with the abstraction of a proton by a base, resulting in the formation of an active catalyst I. Subsequently, hydrogen addition occurs, leading to the formation of intermediate II. This intermediate undergoes CO_2 insertion into the $\text{Mn}-\text{H}$ bond, yielding intermediate III. Finally, reductive elimination takes place, leading to the formation of formylmorpholine. Formylmorpholine is hydrogenated by II to produce methanol. In the same step, morpholine is regenerated. However, to produce methanol, higher pressures of hydrogen are mandatory; with lower pressures of hydrogen, no trace of methanol is found, as confirmed by GC analysis of the reaction mixture.

As a whole, we have developed a protocol, which utilizes a bench-stable cheap ligand and base metal catalyst for CO_2 hydrogenation to methanol. The developed Mn-SNS catalyst is also applicable for formylation of various amines. At lower pressures of hydrogen, selective formylation is observed, while at higher pressures of hydrogen, the formed formyl amine is also sequentially reduced to produce methanol. Application of abundant and nontoxic transition metal catalysts can open a new avenue for CO_2 reduction to chemical feedstocks *via* homogeneous catalysis and can help us in establishing a net zero carbon cycle.

EXPERIMENTAL SECTION

Procedure 1 (N-Formylation)

In a nitrogen-filled chamber, amine (2 mmol), the catalyst (1 mol %), K_3PO_4 (2 mmol), and dry THF (15 mL) were added to a 250 mL autoclave equipped with a mechanical stirrer, thermocouple, and piezoelectric pressure transducer. The vessel was then filled with CO_2 to half of the desired pressure (10 bar), followed by H_2 filling till the desired pressure was achieved (20 bar). The reaction mixture was heated up to 110–140 °C in an autoclave equipped with a mechanical stirrer at 750 rpm. After heating for a given period of time (24 or 36

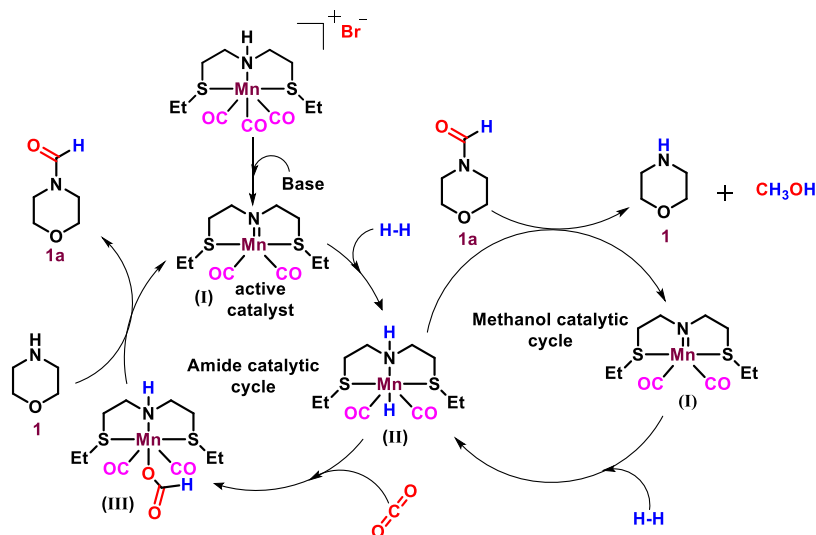


Figure 5. Plausible mechanism for CO_2 hydrogenation to methanol.

h), the reactor was cooled to room temperature. The vessel was then cooled in an ice bath for 30 min, and the gas inside was slowly released. Upon opening the reaction vessel, a brown-yellow solution was obtained with a powdery solid of K_3PO_4 . For the results reported in Table 1, the solvent was evaporated from this reaction mixture with a rotavap, and a known amount of TMB (trimethoxybenene) was added as an internal standard. The reaction mixture was then analyzed by 1H and ^{13}C NMR with $CDCl_3$ as the deuterated solvent. Yields were determined through 1H NMR from integration ratios between the formyl peaks (~ 8 ppm) and TMB (trimethoxybenene) aromatic proton peak (~ 6.12 ppm).

Procedure 2 (Methanol Generation)

In a nitrogen-filled chamber, amine (2 mmol), the catalyst (1 mol %), K_3PO_4 (2 mmol), and solvent dry THF (15 mL) were added to a 250 mL autoclave equipped with a mechanical stirrer, thermocouple, and piezoelectric pressure transducer. The vessel was then filled with CO_2 up to 10 bar pressure, followed by H_2 filling till the desired pressure was achieved (60 bar). The reaction mixture was heated up to 110–140 °C in an autoclave equipped with a mechanical stirrer at 750 rpm. After heating for 24 h, the reactor was cooled to room temperature. The vessel was then cooled in an ice bath for 30 min, and the gas inside was slowly released. Upon opening the reaction vessel, a brown-yellow solution was obtained with a powdery solid of K_3PO_4 ; then, the liquid part was taken out, and GC analysis was performed to confirm methanol.

■ ASSOCIATED CONTENT

Data Availability Statement

The data underlying this study are available in the published article and its Supporting Information.

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsorginorgau.3c00023>.

Experimental details including optimization details, crystal details, UV and IR details, characterization data, and 1H and ^{13}C NMR spectra of all the isolated compounds (PDF)

Accession Codes

CCDC 2238529 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Author Contributions

The article was written through contributions of all authors. All authors have given approval to the final version of the article.

Notes

The authors declare no competing financial interest.

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