

Article

Zinc phthalocyanine as an efficient catalyst for halogen-free synthesis of formamides from amines via carbon dioxide hydrosilylation under mild conditions



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1. Introduction

ABSTRACT

The combination of a zinc phthalocyanine (ZnPc) catalyst and a stoichiometric amount of dimethyl formamide (DMF) provided a simple route to formamide derivatives from amines, CO_2 , and hydrosilanes under mild conditions. We deduced that formation of an active zinc-hydrogen (Zn-H) species promoted hydride transfer from the hydrosilane to CO_2 . The cooperative activation of the Lewis acidic ZnPc by strongly polar DMF, led to formation of activated amines and hydrosilanes, which promoted the chemical reduction of CO_2 . Consequently, the binary ZnPc/DMF catalytic system showed excellent yields and superior chemoselectivity, representing a simple and sustainable pathway for the reductive transformation of CO_2 into valuable chemicals as an alternative to conventional halogen-containing process.

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The use of carbon dioxide (CO_2) as a chemical feedstock has attracted considerable attention. Appropriate usage of CO_2 might help to elevate global warming in addition to yielding value-added organic compounds [1]. The activation of CO_2 is generally considered to be a key issue owing to its considerable thermodynamic and kinetic stability [2]. Depending on its different activation modes, chemical transformations of CO_2 are mainly classified into two pathways based on the valence-state-change of the carbon atom, as illustrated in Fig. 1: (1) CO_2 as a building block via functionalization, involving no change to valence state. For example transformations of CO_2 to urea [3], carbonates [4–6], and the other polymers/materials [7]; (2) CO_2 as a green feedstock via reduction, involving a change of its valence state: CO_2 to fuels and chemicals [8]. The synthesis of various fine and bulk chemicals through reduction of CO_2 has not been widely investigated [9,10]. Among these reports, the reductive *N*-formylation of amines with CO_2 and hydrosilanes to afford formamides or methylamines represents a promising approach for incorporating CO_2 into valuable chemicals [11].

Since 2012, various homo- and heterogeneous catalysts have been developed for this kind of reaction including organic

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Fig. 1. Green approaches to transforming CO₂.

bases [12], inorganic salts [13-16], strong polar solvents [17,18], ionic liquids (ILs) [19-21], copper-phosphine complexes [22-24], *N*-heterocyclic carbenes [25-29], IL-immobilized covalent organic frameworks (COFs) [30], organocatalysts [31-34], and metal-based catalysts [35-37]. Nevertheless, these catalytic systems often feature disadvantages, including: (1) the requirement for an organic solvent (e.g., CH_3CN , THF, CH_2Cl_2) to be added to the reaction [15]; (2) the use of toxic halogen- and phosphine-containing ligands to improve the catalytic activity [21,35]; (3) the sensitivity of the catalyst to air and moisture and the need for high catalyst loading [25]; (4) the expense of noble metal-based catalysts and the complexity of their preparation [36]. Recently, our group reported a simple Zn(salen) complex balanced by quaternary ammonium salts (e.g., tetrabutylammonium bromide, TBAB), which catalyzed solvent-free N-formylation reactions of amines from CO₂ and hydrosilanes under ambient conditions. The cooperative catalysis between the zinc center and bromide anion could activate both Si-H bonds within the hydrosilanes and N-H bonds of amines. This effect led to formation of active zinc-hydrogen (Zn-H) intermediates, which favored insertion and activation of CO₂, as illustrated in Scheme 1 [38-40]. Thus, the formation of a hypervalent silicon intermediate, originating from nucleophilic attack of a bromide anion, was a crucial step in the reduction of CO₂. However, this Zn(salen)/TBAB catalytic system required the use of a toxic halide anion, which could potentially cause environmental pollution problems. Thus, a halogen-, phosphine-, solvent-, and noble-metal-free catalytic system that shows excellent catalytic performance has yet to be developed [11].

Highly polar organic solvents can also activate the N-H bond



Scheme 1. *N*-Formylation of amines with CO_2 and $PhSiH_3$ over Zn(salen)/TBAB in our previous work and ZnPc/DMF in this work.

in amines through solvation and polarization [17,18]. Hence, we envisioned that strong polar solvents, such as dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO), might be capable of replacing quaternary ammonium salts as an efficient additive (either as a co-catalyst or a solvent) in the presence of a simple zinc-based catalyst. Thus, we considered this to be a good potential approach to a halogen- and noble-metal-free process for CO₂ conversion under mild conditions. Herein, we combined a catalytic zinc phthalocyanine (denoted ZnPc) with a stoichiometric amount of DMF in the N-formylation of amines with CO2 and hydrosilanes, as an alternative to halogen- and phosphine-based approaches. This synthetic process represents a promising method for using CO2 as a simple, inexpensive, and readily available raw material. Additionally, the commercial ZnPc complex showed high stability and exhibited enhanced catalytic performance compared with that reported of a Zn(salen) catalyst. We attributed the performance to the electronic structure of the catalyst, which improved the stability of the highly active Zn-H species.

2. Experimental

N-Methylaniline (**1a**), 4-methyl-*N*-methylaniline (1b), 3-methyl-*N*-methylaniline (1c), 4-bromo-*N*-methylaniline (1d), 2-methoxy-N-methylaniline (1e), dihexylamine (1f), morpho-1,2,3,4-tetrahydroisoquinoline line (1g), (1h), *N*-methylpiperazine (**1i**), proline (**1j**), cyclohexylamine (**1k**), 4-aminoacetophenone aniline (1I), (1m),*n*-butyl-4-aminobenzoate (1n), imidazole (1o) or 1H-indole (1p), N-methylformanilide, phenylsilane (PhSiH₃), diphenylsilane (Ph2SiH2), dimethylphenylsilane (PhMe2SiH), triethylsilane (Et₃SiH), poly(methylhydrosiloxane) (PMHS), and zinc phthalocyanine (ZnPc) were obtained from J&K Scientific Ltd.

N-Methylaniline (1.0 mmol), ZnPc (0.5 mol%), DMF (2.0 mmol), and PhSiH₃ (1.0 mmol) were added to a 10-mL stainless steel autoclave. The reactor was then charged with CO₂ to 0.5 MPa and heated in an oil bath. After the reaction, the autoclave was cooled quickly to 0 °C and depressurized to atmospheric pressure. The conversion and yield were determined against naphthalene as an internal standard and measured by a GC2010 gas chromatograph (Shimadzu) equipped with a capillary column (Rtx-5, 30 m × 0.32 mm × 0.25 µm) and FID detector. The structure and the purity of the corresponding formamides were identified by ¹H NMR, ¹³C NMR and GC-MS analysis.

3. Results and discussion

In our preliminary experiments, we performed a benchmark reaction based on *N*-formylation of *N*-methylaniline with CO₂ and PhSiH₃ to produce *N*-methylformanilide and examined the influence of different amounts of DMF at 35 °C and 1.5 MPa CO₂ pressure in the presence of 2.0 eq. of PhSiH₃ relative to the amine [17]. Initially, no reaction occurred without DMF as shown in Fig. 2(a). When the amount of DMF was increased from 1.0 to 15.0 mmol, we observed enhanced product yield under the above-mentioned conditions. *N*-Methylaniline could



Fig. 2. (a) Effects of the amount of DMF on the *N*-formylation reaction of *N*-methylaniline with CO₂ and PhSiH₃ (Reaction conditions: *N*-methylaniline 1.0 mmol, PhSiH₃ 2.0 mmol, CO₂ pressure 1.5 MPa, reaction time 3 h, reaction temperature 35 °C); (b) Kinetic curves from the DMF-promoted *N*-formylation reaction of *N*-methylaniline with CO₂ and PhSiH₃ with ZnPc as a catalyst (Reaction conditions: *N*-methylaniline 1.0 mmol, PhSiH₃ 1.0 mmol, ZnPc 0.5 mol%, DMF 2.0 mmol, CO₂ pressure 0.5 MPa, reaction temperature 25 °C).

be smoothly converted into *N*-methylformanilide with a yield of 95%, with the use of a ten-fold excess of DMF in 3 h. Similar to a report by Lei and coworkers [17], strong polar solvents, including DMF, promoted catalyst-free *N*-formylation of amines to produce the corresponding formamides in excellent yields and selectivity at ambient conditions. The DMF likely played an important role in activation of the amines and PhSiH₃ and contributed to the favorable insertion of CO₂. However, if the CO₂ pressure (1.5–0.5 MPa), reaction temperature (35–25 °C), and the amount of PhSiH₃ (2.0–1.0 eq.) were decreased, only a negligible yield was obtained with stoichiometric DMF (2.0 eq.). DMF shows moderate toxicity, thus, it would be desirable to improve its activity so that it may be used in only a stoichiometric or catalytic amount, rather than as a solvent.

On the basis of our previous work on N-formylation of amines with hydrosilanes and CO₂ [38], the biocompatible ZnPc was used as an efficient catalyst to improve the activity of the DMF-promoted N-formylation reaction. A kinetic curve of the reaction is shown in Fig. 2(b). A quantitative yield of N-methylformanilide was achieved with a catalyst loading of 0.5 mol% ZnPc in combination with 2.0 eq. of DMF and 1.0 eq. of PhSiH₃, within 6 h at 25 °C and 0.5 MPa. The by-product N,N'-dimethylaniline could not be detected and an excellent chemoselectivity of >99% was obtained. The cooperative effects between the weak Lewis base (DMF) and Lewis acidic metal center likely promoted the reductive transformation of CO2 under milder conditions, thus leading to the low catalyst loading and reductant requirements. This finding can be attributed to the activation of amines and hydrosilanes through the strong polarization induced by DMF. The coordinative interaction between the electron-deficient zinc center and the lone electron pairs of the organic amines (i.e., electron-rich donors) could tune the basicity/nucleophilicity of the amines and activate the N-H bond [18]. The formation of an active Zn-H species could be attributed to nucleophilic attack on the

hydrosilanes by activated amines via the Lewis acid-base Si-N interaction, which might activate the Si–H bond simultaneously [17]. *In situ* generated Zn-H species exhibited high nucleophilicity, leading to the insertion of CO_2 into the active Zn–H bond [41,42]. As a result, we believe that these two components, i.e., ZnPc and DMF, might promote the nucleophilic addition of the hydrogen atom from hydrosilane to the C=O bond of CO_2 , which is a key step in the *N*-formylation reaction [21].

To further understand the cooperative effects between the ZnPc and DMF, factors influencing the catalytic performance were studied, including the type of ligand and metal active center, to determine the mechanism of CO₂ conversion, as elaborated in Fig. 3(a). The N-formylation reaction proceeded in low yields with simple zinc salts, such as ZnO or ZnBr2 in DMF (2.0 eq.), within 6 h at 25 °C and 0.5 MPa, owing to their heterogeneity. Only a 10%-yield of the formanilide product was obtained without any additional catalyst under identical conditions; thus, a stoichiometric amount of DMF might also catalyze the transformation to a certain extent. Conventional organic zinc catalysts, i.e., ZnTPP, Zn(salen), Zn(acac)₂, and Zn(OAc)₂ exhibited low-to-moderate yields of <1%, 4%, 15%, 39%, respectively, and much lower than that of the optimal catalyst, ZnPc. These observations strongly suggested that the structure of the organic ligand and its electronic properties influenced the catalytic activity. We introduced electron-withdrawing nitro groups (-NO₂) into the porphyrin-based frameworks, and an enhanced yield of 36% was observed for the catalyst ZnTPP-NO₂ under the same conditions. Notably, the activity of the metallophthalocyanine catalyst was closely related to the type of metal active center, which promoted activation of the Si-H bond. The formation of an active Zn-H species was regarded as a key step in the Zn-catalyzed CO₂ hydrosilylation reaction, and the enhanced nucleophilicity of the Zn-H species resulted in higher N-formylation reactivity. When commercial metallophthalocyanine complexes, including copper (CuPc),



Fig. 3. (a) Effects of the ligand type and active metal center on DMF-promoted *N*-formylation reaction of *N*-methylaniline with CO₂ and PhSiH₃ over various catalysts; (b) Effect of additives on ZnPc-catalyzed *N*-formylation reaction of *N*-methylaniline with CO₂ and PhSiH₃ (Reaction conditions: *N*-methylaniline 1.0 mmol, PhSiH₃ 1.0 mmol, catalyst 0.5 mol%, additives 2.0 mmol, reaction temperature 25 °C, CO₂ pressure 0.5 MPa, reaction time 6 h).

cobalt (CoPc) and iron (FePc), were used as alternative catalysts, low-to-moderate yields from 7% to 87% were obtained with a 0.5 mol% catalytic loading. The product yield over the catalyst FePc was lower than that of the Zn-based catalyst, although iron(II)-phosphine complexes, reported by Cantat and coworkers [35], were able to promote the reductive functionalization of CO₂. The Cu-based catalyst CuPc could not catalyze the DMF-promoted N-formylation reaction although a copper-catalyzed transformation has been reported to occur under ambient conditions [22]. The formation of an active Zn-H intermediate might be more favorable for the reductive transformation of CO₂ owing to the shorter length of the M-H bond (0.1602 nm, as calculated by DFT) and the electronic structure of the complex. These findings indicate that the Zn-based catalyst with a phthalocyanine ring acted as a good ligand for N-formylation. We found that our catalytic system enabled catalysis of the N-formylation reaction of amines at 25 °C under 0.1 MPa of CO₂ with PhSiH₃ as a reducing agent, which is of particular relevance for industrial scale applications.

Afterwards, the effect of various additives, having different polarities, on the catalytic performance was investigated. We examined DMSO, ε -caprolactone, CH₃CN, THF, CH₂Cl₂, and toluene, under conditions of 25 °C and 0.5 MPa. The results are summarized in Fig. 3(b). No reaction occurred without any additive in the ZnPc-catalyzed *N*-formylation reaction, and reaction proceed slowly in the presence of non- or weakly-polar additives, such as THF, CH₂Cl₂, and toluene, which were considered to be unsuitable for this transformation. However, in the case of CH₃CN, a moderate yield (24%) of the *N*-methylformanilide was achieved after 6 h [18]. These experimental results were in accordance with a previous report on Cs₂CO₃-promoted formylation and methylation of amines with CO₂ and hydrosilanes [15], and indicate that additives markedly affect the reactivity. Notably, the polarity of the additives affected the reactivity of the ZnPc-based catalytic system. Thus, a comparable yield (97%) was obtained by replacing DMF with DMSO, a highly polar aprotic solvent [17], and a moderate yield of 63% was achieved with the use of a polar biomass-derived ϵ -caprolactone under identical conditions [18].

Moreover, the chemical structure of the hydrosilanes, i.e., the steric bulk around the Si–H bonds, has a marked impact on the reductive *N*-formylation. When bulkier hydrosilanes, including diphenylsilane (Ph₂SiH₂), triethylsilane (Et₃SiH), dimethylphenylsilane (PhMe₂SiH₂), and polymethylhydrosiloxane (PMHS), were used in the reaction, negligible yields were achieved at 25 °C and 0.5 MPa (Table 1, entries 1–5). Furthermore, the yields of the formamide product could not be increased by extending the reaction time. However, satisfactory results were achieved by increasing the reaction temperature from 25 to 80 °C with the inexpensive PMHS as a reducing

Table 1

Results of the *N*-formylation reaction of *N*-methylaniline with CO_2 with various hydrosilanes as reductants in the ZnPc/DMF system ^a.

Entry	Hydrosilane	T∕°C	p(CO ₂) /MPa	t/h	Yield ^b /%
1	PhSiH₃	25	0.5	6	99
2	Ph ₂ SiH ₂	25	0.5	6	<1
3	Et₃SiH	25	0.5	6	<1
4	PhMe ₂ SiH	25	0.5	6	<1
5	PMHS	25	0.5	6	<1
6 ^c	PMHS	80	1.0	8	99
7 ^c	PMHS	60	1.0	8	21
8 d	PMHS	80	1.0	8	<1
9	PhSiH₃	100	0.5	6	88:12 e

^a Reaction conditions: *N*-methylaniline 1.0 mmol, Si-H group of hydrosilane 1.0 mmol, ZnPc 0.5 mol%, DMF 2.0 mmol, reaction temperature 25 °C, CO₂ pressure 0.5 MPa, reaction time 6 h; ^bDetermined by GC; ^cZnPc 5.0 mol%; ^dZnPc 2.0 mol%; ^eMolar ratio of *N*-methylformanilide to *N*,*N*'-dimethylaniline.

agent, which is an abundant and nontoxic byproduct of the silicone industry [25]. A 99%-yield of the formamide product was obtained with 5.0 mol% ZnPc after 8 h at 80 °C and 1.0 MPa (Table 1, entry 6), indicating the effectiveness of our developed catalytic system [22]. If the catalyst loading (2.0 mol%) or reaction temperature (60 °C) were decreased, the catalytic performance declined owing to the low activity of PMHS (Table 1, entries 7, 8). Notably, a high reaction temperature might result in the formation of methylamines, thus, it was necessary to perform the *N*-formylation reaction under mild conditions to control the chemoselectivity (Table 1, entry 9) [43,44].

Finally, the N-formylation reaction was performed with a wide range of amines to evaluate the substrate scope. The reaction conditions included 0.5 mol% ZnPc in the presence of 2.0 eq. of DMF and 1.0 eq. of PhSiH₃, as listed in Table 2. Initially, only 2.0 eq. of DMF were used and low yields were generally obtained under the same conditions. We showed that not only aromatic secondary amines (1a-1e), but also aliphatic (1f) and cyclic secondary amines (1g-1i) underwent the transformation to the corresponding formamides in excellent yields at 25 °C and 0.5 MPa (Table 2, entries 1-9). Unfortunately, the N-formylation reaction did not proceed with proline (1j) owning to the deactivating carboxyl group (COOH) on the adjacent carbon atom of the amine (Table 2, entry 10). For cyclic or aromatic primary amines (1k, 1l) having two reactive N-H bonds, only mono-formylated products were obtained under mild conditions and no di-formylated analogues were observed (Table 2, entries 11, 12). However, our previous Zn(salen)/TBAB catalytic system produced mixtures of these products owing to the different activation mechanism of the Si-H and N-H bonds [38].

To clarify the cooperative effect of the bi-component ZnPc/DMF system, the reaction mechanism was investigated through control experiments. First, we found that the CO2-mediated metathesis reactions between amines and DMF to synthesize formamides could be performed smoothly at 100 °C in the absence of hydrosilane, as reported recently by Wang and coworkers [45]. This strategy used CO_2 as a mediator to activate the amine and DMF as a solvent and substrate under non-reductive conditions, as determined by in situ NMR in Wang's previous work. Nevertheless, the metathesis reaction could not proceed under ambient conditions, and reductive N-formylation of the amines occurred when hydrosilane was added as a reductant, as shown in Fig. 4(a). A product yield of up to 99% was achieved in the presence of a catalytic amount DMF (20 mol%) under similar conditions when the reaction time was extended to 36 h, as shown in Fig. 4(b). We note that reactions had a long induction period (\sim 24 h) at the initial stage owing to the low polarity of the reaction solution. However, over the following 12 h, the reaction proceeded rapidly because of the high polarity of the formamide product. Thus, the polarity of the reaction mixture had a great influence over the N-formation reaction. Strongly polar DMF could tune the nucleophilicity of the amines in their reaction with CO₂ owing to the effects of solvation and polarization.

Moreover, ¹H NMR analysis revealed the interactions among DMF, PhSiH₃ and *N*-methylaniline, as shown in Fig. 4(c) and (d).

Table 2

Results of DMF-promoted chemoselective reduction of CO_ and various amines to formamides with PhSiH_3 and with/without ZnPc $^{\rm a}.$

Entry	Substrate	Product ^b	DMF ^c	ZnPc/DMF ^d
1	H 1a		10 (93) ^e	99
2	H ₆ C 1b		<1 (98) ^e	99
3	H ₀ C		17 (68) ^e	99
4	Br 1d	Br 2d	5	53
5	П ССН _о сн _о		<1	86
6	Hex ^{-N} Hex 1f	Hex ^N Hex Hex	<1	78
7	L J 1g	P N 2g	11	92
8	NH 1h	2h	<1 (20) ^e	57
9			<1 (94) ^e	99
10	HN HN 1j		<1	<1
11	NH ₂ 1k		67 (95) ^e	91
12	NH ₂		<4	63

^a Reaction was performed in a 10 mL autoclave with the amine (1.0 mmol) as a substrate; ^{b-e} Determined by GC or GC-MS with naphthalene as the internal standard; ^c Reaction conditions: DMF 2.0 mmol, PhSiH₃ 1.0 mmol, reaction temperature 25 °C, CO₂ pressure 0.5 MPa, reaction time 6 h; ^d ZnPc 0.5 mol%, DMF 2.0 mmol, PhSiH₃ 1.0 mmol, reaction temperature 25 °C, reaction time 6 h, CO₂ pressure 0.5 MPa; ^e Reaction conditions for values in parentheses: DMF 10 mmol, PhSiH₃ 2.0 mmol, reaction temperature 35 °C, reaction time 3 h, CO₂ pressure 1.0 MPa.

The H signal of the N–H bond within *N*-methylaniline clearly shifted in different deuterated solvents (DMSO- d^6 , DMF- d^7 , CD₃CN, CDCl₃) appearing at different positions, and shifted down field according to the polar order of the reaction mixture (chemical shift: DMF- d^7 > DMSO- d^6 > CD₃CN > CDCl₃). The hy-



Fig. 4. (a) *N*-Formylation reaction of amines with CO₂ in DMF with/without hydrosilane; (b) Kinetic curve of DMF-promoted *N*-formylation reaction of *N*-methylaniline with CO₂ and PhSiH₃ over ZnPc (Reaction conditions: *N*-methylaniline 1.0 mmol, PhSiH₃ 1.0 mmol, ZnPc 0.5 mol%, DMF 20 mol%, reaction temperature 25 °C, CO₂ pressure 0.5 MPa); (c) NMR spectra of *N*-methylaniline and its mixtures in different deuterated solvents; (d) NMR spectra of PhSiH₃ and its mixtures in different deuterated solvents.

dride H signal of the Si-H bond within PhSiH₃ was irregularly shifted upfield (DMSO- d^6 < DMF- d^7 < CD₃CN < CDCl₃) owing to multiple factors. We speculated that both the N-H bond of the amine and the Si-H bond of the hydrosilane could be activated by strong polar additives such as DMF and DMSO, which promoted the N-formylation reaction. On the basis of the above discussion and our previous investigations, a possible reaction mechanism is proposed in Scheme 2. First, in the absence of an amine, the hydrosilylation of CO₂ was achieved with PhSiH₃ activated by cooperative catalysis between ZnPc and DMF. The corresponding product (an active silvl format species) was determined by mass spectrometry (MS: 153.14 for [M+H]⁺). This result indicates that the nucleophilic addition of the H atom to the C=O bond of CO2 was a key step in the transformation of CO₂. Subsequently, the binary components simultaneously activated the amine to obtain the desired product. high-resolution mass spectrometry (HRMS: 137.07869) and 13C NMR spectroscopy (162.51 ppm) results of the isotopically labeled ¹³CO₂ as a C1 source demonstrated that the CO₂-reductive process occurred smoothly with N-methylaniline as a model substrate.



Scheme 2. (a) Activated models of *N*-formylation of amines with CO_2 and hydrosilanes over ZnPc/DMF and specific structure of the active Zn-H species; (b) Simulated structure of active Zn-H intermediate; (c) Proposed *N*-formylation reaction of amine with CO_2 and PhSiH₃.

4. Conclusions

In conclusion, we have developed a simple and sustainable pathway for producing formamide derivatives by *N*-formylation of amines with CO₂ and hydrosilanes under mild conditions, based on a zinc phthalocyanine (ZnPc) catalyst and a stoichiometric amount of DMF. Our experimental results and related mechanistic studies indicate that the cooperative effect between these two components promoted hydride transfer from hydrosilane to CO₂. Strong polar additives activated the Si–H bond within the hydrosilane via solvation and polarization, and simultaneously activated the N–H bond of the amine, thereby leading to the increased nucleophilicity of the active Zn-H intermediates, which promoted insertion of CO₂.

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Graphical Abstract

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Zinc phthalocyanine as an efficient catalyst for halogen-free synthesis of formamides from amines via carbon dioxide hydrosilylation under mild conditions

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Combination of zinc phthalocyanine catalyst and stoichiometric dimethyl formamide as a simple approach to produce formamides from amines, CO₂, and hydrosilanes under mild conditions.



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酞菁锌高效催化以二氧化碳、含氢硅烷和有机胺为原料合成甲酰胺类衍生物

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摘要:目前为了有效地利用好CO₂,主要策略有以下几种:(1)"水平途径"——无价态及能量变化,譬如生成尿素、环状碳酸 酯、聚碳酸酯及噁唑烷酮类衍生物等;(2)"垂直途径"——有价态及能量变化,譬如直接加氢转化成碳一产品(甲酸、甲醛、 甲醇、甲烷)等;(3)"对角线途径"——有价态及能量变化,即结合石油化工原料将CO₂还原生成醇、醚、羧酸、亚胺、酰胺、 酯等系列高附加值的精细有机化工产品.其中以二氧化碳和含氢硅烷为原料,通过有机胺的*N*-甲酰化反应合成甲酰胺类 衍生物符合绿色化学和可持续发展的要求.

基于仿生催化CO₂分子活化的基本理论, 我们借鉴强极性的有机溶剂可有效活化硅氢键的性质, 创新性地将廉价易得的酞菁锌(ZnPc)作为类酶催化剂, 并以化学计量的*N,N*·二甲基甲酰胺(DMF)为添加剂, 构成组分新颖并高效绿色的类酶协同催化体系, 实现了在温和反应条件下高效高选择性地合成甲酰胺类衍生物.研究发现:以苯硅烷作为还原剂, 当加入0.5 mol% ZnPc和2 mmol DMF, 在25 °C和0.5 MPa下仅需反应6 h, 可得到收率为99%的*N*-甲基甲酰苯胺.更值得注意的是, 当以更易得的聚甲基氢硅烷(PMHS)为还原剂时, 加入5 mol% ZnPc和1 mL DMF, 在80 °C和1 MPa下反应8 h, *N*-甲基甲酰苯胺的收率也高达99%.实验结果表明:添加剂DMF可以通过溶剂化和强极性作用高效活化含氢硅烷中的Si-H键, 然后具有亲电性的金属活性中心能够稳定氢负离子生成高活性锌氢中间体.即ZnPc/DMF之间的协同催化作用能够促进氢化物从含氢硅烷转移到CO₂分子, 进而有利于CO₂分子的高效活化.

综上所述,利用类酶催化剂反应专一性的特点,通过有机胺的N-甲酰化反应,实现了以CO₂和含氢硅烷为原料在温和条件下甲酰胺类衍生物的绿色高效合成.这对于设计和开发更加高效的催化体系具有一定的指导作用和借鉴意义. 关键词:二氧化碳;酞菁锌;协同作用;N-甲酰化;含氢硅烷

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