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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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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.

1. Introduction

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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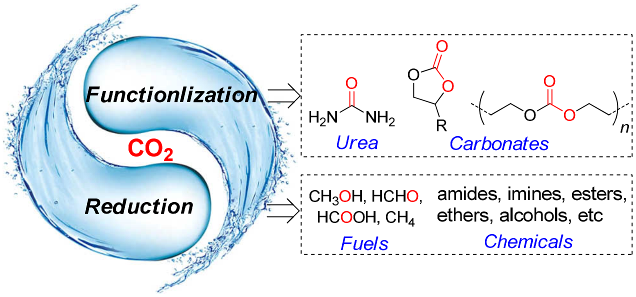
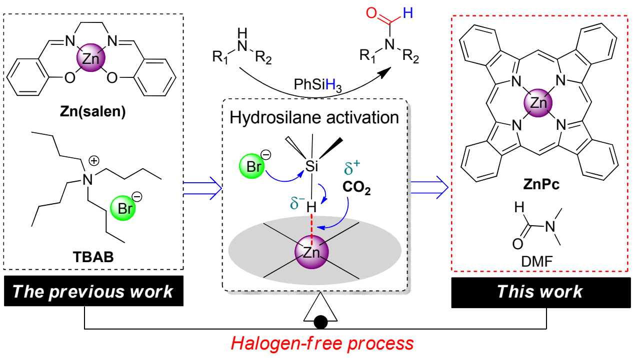


Fig. 1. Green approaches to transforming CO_2.

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 CO_2 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 CO_2, 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 CO_2. 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 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 CO_2 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 CO_2 and hydrosilanes, as an alternative to halogen- and phosphine-based approaches. This synthetic process represents a promising method for using CO_2 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.



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.

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**), morpholine (**1g**), 1,2,3,4-tetrahydroisoquinoline (**1h**), *N*-methylpiperazine (**1i**), proline (**1j**), cyclohexylamine (**1k**), aniline (**1l**), 4-aminoacetophenone (**1m**), *n*-butyl-4-aminobenzoate (**1n**), imidazole (**1o**) or 1H-indole (**1p**), *N*-methylformanilide, phenylsilane ($PhSiH_3$), diphenylsilane (Ph_2SiH_2), dimethylphenylsilane ($PhMe_2SiH$), triethylsilane (Et_3SiH), 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 $PhSiH_3$ (1.0 mmol) were added to a 10-mL stainless steel autoclave. The reactor was then charged with CO_2 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, ^{13}C 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 CO_2 and $PhSiH_3$ to produce *N*-methylformanilide and examined the influence of different amounts of DMF at 35 °C and 1.5 MPa CO_2 pressure in the presence of 2.0 eq. of $PhSiH_3$ 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