Short communication

N-formylation of amines using phenylsilane and CO$_2$ over ZnO catalyst under mild condition

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ARTICLE INFO

ABSTRACT

Several research studies have been conducted on N-formylation of amines using phenylsilane and CO$_2$. However, most of these studies involved tedious processes of catalyst preparation or complex procedures. In the present study, we describe the use of a simple and commercially available ZnO catalyst for selective N-formylation of amines under mild condition. High-yielding N-formylation products with good recyclability and wide substrate scope were obtained, which can promote fine chemical synthesis and CO$_2$ capture.

1. Introduction

N-formylation of amines using phenylsilane (PhSiH$_3$) and CO$_2$ is a hot topic of research because of the importance of fine chemical synthesis and CO$_2$ capture [1–3], and the reaction products are widely used as solvents and key intermediates in organic synthesis and industry [4,5].

For successful N-formylation of amines to formamides, many strategies using various catalyst types and reaction conditions have been developed. For example, Jacquet et al. reported that the Zn-complex can efficiently catalyze the reductive functionalization of CO$_2$ with amines and phenylsilane at 100 °C [6]. Islam's group designed a modified graphene oxide-based Zn catalyst for CO$_2$ fixation reactions in N-formamides and organic carbamates [7]. Li's group used polymethylhydrosiloxane to achieve selective N-formylation [8]. Beller et al. reported the Ru-complex system for the N-formylation of amines and CO$_2$ under high pressure of H$_2$ (60 bar) and CO$_2$ (20 bar) and elevated temperatures (> 140 °C) [9]. However, most of these studies involved complex catalyst designs or harsh catalytic conditions.

In the present study, our group reported a facile and commercially available ZnO catalyst for selective N-formylation of amines using phenylsilane and CO$_2$ under mild condition, wherein we systematically investigated the catalyst type, co-catalyst, reductant, reaction time, and CO$_2$ pressure. By adjusting the reaction conditions, we achieved high-yielding N-formylation products with good recyclability and wide substrate scope.

2. Experimental

2.1. Materials

All the reagents and solvents were purchased from commercial sources and used without any purification unless specifically stated.

ZnO (99%), Co$_3$O$_4$ (99%), Fe$_2$O$_3$ (99%), CuO (99%), NiO (99%), Mn$_2$O$_3$ (99%), Zn(acac)$_2$ (99%), N-methylaniline (97%), phenylsilane (97%), diphenylsilane (99%), methylphenylsilane (99%), and methylbenzene (99.5%) were obtained from J&K. Zn(OAc)$_2$ (99%), Zn(SO$_4$)$_2$ (99.5%), ZnCl$_2$ (99.5%), Zn(NO$_3$)$_2$·6H$_2$O (99.99%), dimethylamine (98%), N-methylformanilide (99%), diisopropylamine (99.5%), 2,6-diisopropylaniline (96%), 1,2,3,4-tetrahydroquinoline (98%), 1,2,3,4-tetrahydroisoquinoline (97%), and diphenylamine (99%) were purchased from Aladdin. Methanol (99.8%), tetrabutylammonium bromide (TBAB, 99%), tetraethylammonium bromide (TTAB, 98%), and tetrabutylammonium iodide (TBAI, 98%) were obtained from TCI. CO$_2$ (99.99%, Guangzhou Guangqi Gas Company Limited). All other reagents were purchased from commercial sources without purification.

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2.2. Catalytic activity test

First, ZnO (5 mg), *N*-methylaniline (1 mmol), phenylsilane (1 mmol), and TBAB (1% mmol) were charged into an autoclave (10 mL). The autoclave was then sealed and flushed with CO_2 several times to maintain the reactor pressure at 1 MPa. Next, the autoclave was heated at 40 °C for 2 h under stirring. After cooling to room temperature, the solution was extracted with 1 mL methanol and filtered through a Jinteng nylon filter. The products were identified using ^{1}H and ^{13}C nuclear magnetic resonance spectrum on Bruker Avance III 500 HD (NMR, Bruker; Supplementary Figs. 1–10) or GCMS-QP2010 plus gas chromatograph-mass spectrometer (GC–MS, Shimadzu; Supplementary Figs. 11–16). The conversion and selectivities were determined using hexane as the internal standard and measured on the GC 2010 Gas Chromatograph (GC, Shimadzu; Supplementary Figs. 17–22) equipped with a flame ionization detector or the area normalization method (Supplementary Figs. 23–24, Supplementary Table 1).

3. Results and discussion

3.1. Effect of catalyst

The catalytic activity of *N*-formylation of amines using phenylsilane and CO_2 is greatly affected by catalysts [10–12]. Hence, we first investigated the influence of different catalysts. The conditions were first investigated using *N*-methylaniline (as the model substrate), 1 equiv. of $PhSiH_3$ (as the reductant), and 1.0 mol% of TBAB (as the co-catalyst); the reaction was performed with 5 mg catalyst under 1 MPa CO_2 at 40 °C for 120 min.

In the control experiment without the catalyst, no conversion was observed (Table 1, entry 1). On the one hand, the highest *N*-methylaniline conversion (92%) and selectivity (99%) were obtained with ZnO as the catalytic system for different metal oxides (Co_3O_4, Fe_2O_3, CuO, NiO, Mn_2O_3; Table 1, entries 2–7); on the other hand, compared to various inorganic Zn salts ($Zn(acac)_2$, $Zn(OAc)_2$, $ZnSO_4$, $ZnCl_2$, and $Zn(NO_3)_2$), ZnO showed excellent catalytic performance (Table 1; entries 2 and 8–12). Therefore, ZnO was chosen as the model catalyst for further studies.

3.2. Effect of the co-catalyst and reductant

The catalytic activity of *N*-formylation of amines strongly depends on the co-catalyst and reductant. As shown in Fig. 1a, the reaction did not proceed without a co-catalyst; when TBAB was replaced with TBAI or TTAB, poor results were obtained (46% yield for TBAI, 41% yield for TTAB) because of the lack of highly efficient cations and anions [13].

Similarly, when Ph_2SiH_2 or $PhCH_3$ or $PhSiH_2CH_3$ was used instead of $PhSiH_3$ as the reductant (Fig. 1b), there was no observable *N*-formylation product in the reaction; this finding is in good agreement with Yang's report [14]. Taken together, we can conclude that these co-catalyst and reductant play important roles in the catalysis process.

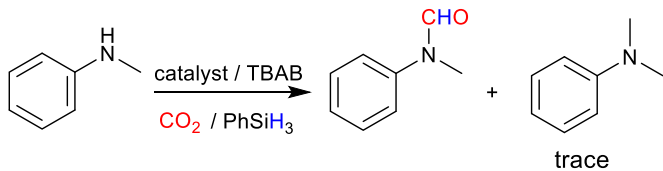### 3.3. Effect of reaction time and CO_2 pressure

The effect of reaction time and CO_2 pressure was further investigated. We examined *N*-formylation in the presence of 1.0 mmol substrate, 5 mg catalyst, 1.0 mol% TBAB, and 1.0 mmol $PhSiH_3$ at 40 °C. The reaction time curve (Fig. 2a) showed that the yield of *N*-formylation products increased with time progression and showed excellent selectivity, thus indicating that prolonging time may promote the reaction [15,16]. Furthermore, as shown in Fig. 2b, the increase in CO_2 pressure steeply enhanced the yield of *N*-formylation products and slightly increased the selectivity. It has been reported that high CO_2 pressure enables to rapidly consume $PhSiH_3$ and thus avoid further reduction [17].

3.4. Recyclability and substrate screening

The commercially available ZnO catalyst could be easily collected by filtration, washed with MeOH, and reused for the next cycle. As shown in Fig. 3a, the ZnO catalyst showed excellent recyclability in the *N*-formylation reaction. The catalytic performance of ZnO in *N*-formylation of *N*-methylaniline remained almost unchanged during 5-time recycling (yield > 95%), which indicated excellent long-term stability [18].

On the basis of the optimized conditions, different types of amines were studied for *N*-formylation of amines by using phenylsilane and CO_2 (Fig. 3b). A wide variety of amines were converted into their

Table 1
Results of *N*-formylation of *N*-methylaniline with $PhSiH_3$ and CO_2 over various catalysts [a].

Entry [a]	Catalyst	Yield (%) [b]	Select. (%) [b]
1	–	< 1	–
2	ZnO	98	99
3	Co_3O_4	72	99
4	Fe_2O_3	71	99
5	CuO	31	99
6	NiO	22	99
7	Mn_2O_3	< 1	–
8	$Zn(acac)_2$	68	98
9	$Zn(OAc)_2$	62	97
10	$ZnSO_4$	2	–
11	$ZnCl_2$	< 1	–
12	$Zn(NO_3)_2$	< 1	–

[a] *N*-methylaniline (1.0 mmol), $PhSiH_3$ (1.0 mmol), catalyst (5 mg), TBAB (1.0 mol%), CO_2 pressure (1 MPa), 40 °C, 120 min
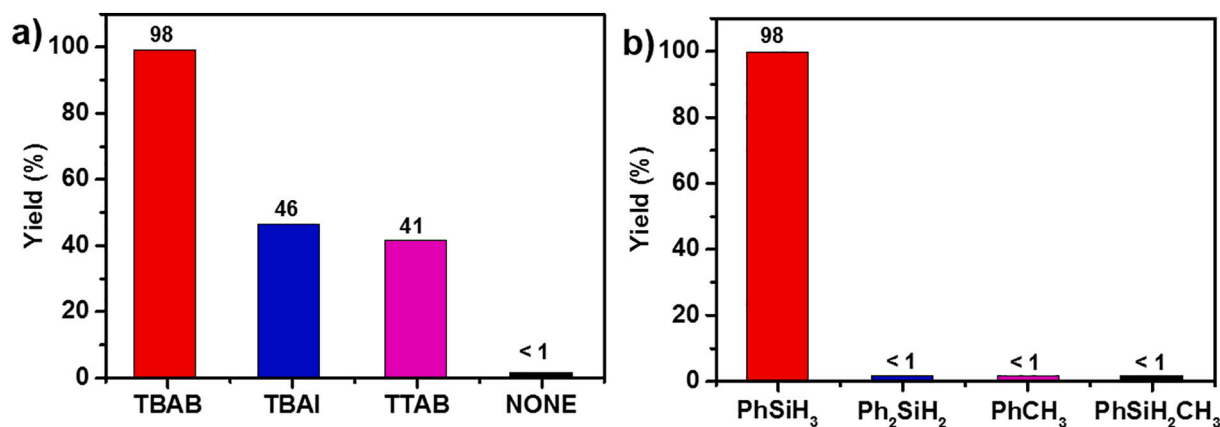
Fig. 1. (a) Effect of the co-catalyst on *N*-formylation of *N*-methylaniline. Reaction conditions: 10 mL stainless-steel autoclave, substrate (1.0 mmol), catalyst (5 mg); TBAB (1.0 mol%), 40 °C, 120 min. (b) Effect of reductant type on *N*-formylation of *N*-methylaniline. Reaction conditions: 10 mL stainless-steel autoclave, substrate (1.0 mmol), catalyst (5 mg); PhSiH$_3$ (1.0 mmol), 40 °C, 120 min.
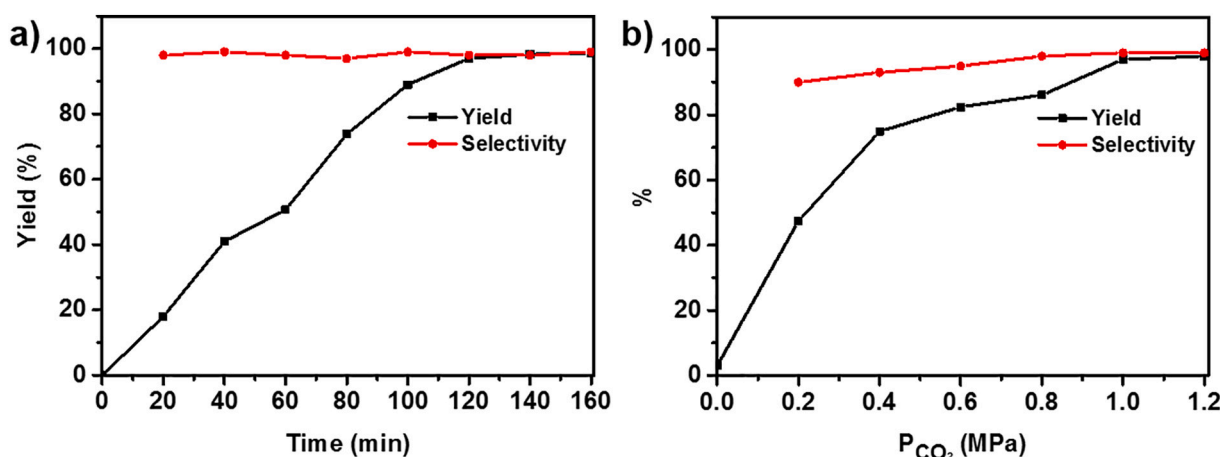

Fig. 2. (a) Effect of reaction time and (b) CO$_2$ pressure of ZnO catalyst on *N*-formylation of *N*-methylaniline. Reaction conditions: 10 mL stainless-steel autoclave, substrate (1.0 mmol), catalyst (5 mg), TBAB (1.0 mol%); PhSiH$_3$ (1.0 mmol), 40 °C. CO$_2$ pressure (1.0 MPa) for (a) and 120 min for (b).

corresponding formamides with good yields (> 77%). Because of their small steric hindrance, amines such as diphenylamine and dimethylamine provided good yields (> 98%) [19]. However, due to the different ring and steric effect, 1,2,3,4-tetrahydroquinoline and 1,2,3,4-tetrahydroisoquinoline showed slightly lower yield (~80%) [20].

4. Conclusions

An efficient and commercially available ZnO catalyst was developed for *N*-formylation of amines using phenylsilane and CO$_2$. By varying the catalyst type, co-catalyst and reductant, reaction time, and CO$_2$ pressure, both C−N bond formation and reduction of CO$_2$ were successfully
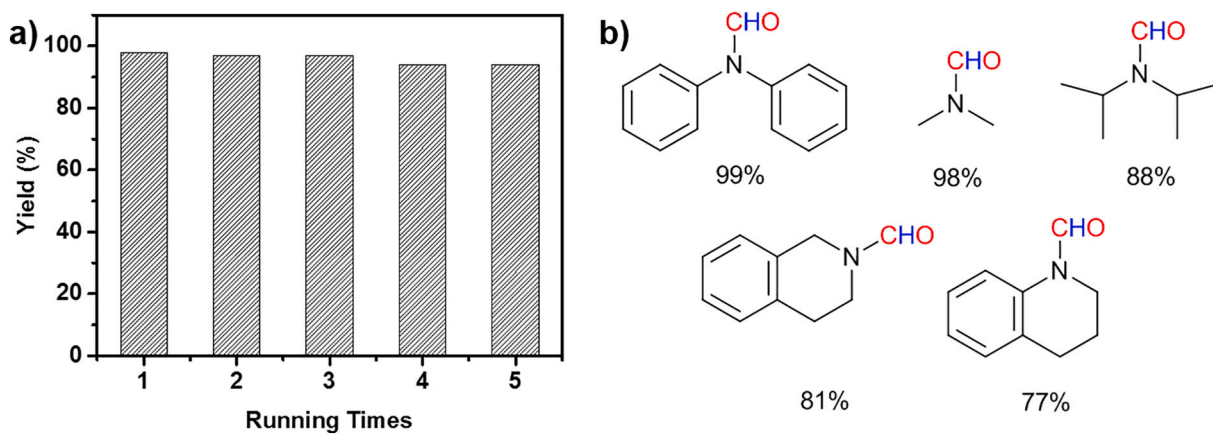

Fig. 3. (a) Recyclability of ZnO catalyst in *N*-formylation of *N*-methylaniline with PhSiH$_3$ and CO$_2$. (b) The substrate scope test of ZnO catalyst. Reaction conditions: 10 mL stainless-steel autoclave, substrate (1.0 mmol), catalyst (5 mg), TBAB (1.0 mol%); PhSiH$_3$ (1.0 mmol); CO$_2$ pressure (1.0 MPa), 40 °C, 120 min.

achieved, thus leading to fine chemical synthesis and cost-effective chemical fixation of CO_2 to value-added products.

Credit author statement

P.W., and Q.H. equally contributed to this work. X.H. developed the concept, designed these experiments, and analyzed experimental data. P.W., Q.H., H.Z., Q.S., Y.C., and T.G. contributed to catalytic experiments. Q.H., P.W., and X.H. wrote the paper. X.H. and H.J. directed the project. All authors discussed the results and commented on the manuscript.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.catcom.2020.106195.

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