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Synthesis of acetamides using CO_2, methanol, H_2 and amines†

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Herein, we report the synthesis of acetamides from CO_2, methanol, H_2 and corresponding amines, which is a new route used to synthesize acetamides. It was found that the Rh catalyst with LiI/LiCl as promoters could effectively catalyze this reaction. Interestingly, no ligand was required and amine substrates played a role in accelerating the reaction.

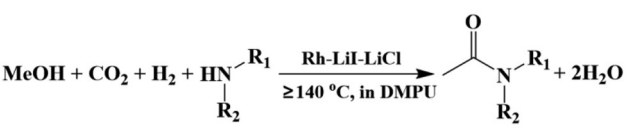
Introduction

As an abundant, non-toxic and renewable C1 resource, CO_2 has been widely used to synthesize value-added chemicals, such as alcohols, urea, carboxylic acids, esters, hydrocarbons, amides, and carbonates.[1–6] Amides are important chemicals that are widely used in human life. Over the past decades, the synthesis of formamides using CO_2 has been extensively investigated and significant progress has been made.[7–9] However, the synthesis of acetamides using CO_2 as a C1 synthon has not been reported till date. In many cases, acetamides are more useful than formamides. For example, *N*,*N*-dimethylacetamide, abbreviated as DMA, is usually utilized as a solvent in the chemical synthesis and analysis of cellulose.[10] DMA is also a promising substitute for the well-known solvent DMF because of its better stability and solubility, particularly for the synthesis of adhesives, resins and pesticides.[11] *N*-Acetylmorpholine is an important intermediate for the synthesis of fungicides, such as dimethomorph and flumorph. It also plays a key role in aromatic extraction and natural gas desulphurization.[12] Acetanilide is a precursor for manufacturing penicillin and other pharmaceuticals, and an important intermediate for the synthesis of camphor and sulfa drugs.[13] Acetanilide can also be applied to inhibit hydrogen peroxide decomposition, and was the first aniline derivative possessing antipyretic as well as analgesic properties.[14] Currently, the production of acetamides is usually based on acetic acid, acetic anhydride, and acetyl chloride or acetate as a feedstock. CO_2 is a renewable, safe and easily available carbon resource. Clearly, the synthesis of acetamides using CO_2 as a C1 synthon is highly desirable.

Recently, we reported the synthesis of acetic acid *via* methanol hydrocarboxylation with CO_2 and H_2, where an imidazole or its derivative was a necessary ligand for the catalyst.[15,16] Herein, we report a method to produce acetamides from CO_2, methanol, H_2, and amines (Scheme 1). In this method, CO_2 was converted to an acetic acid intermediate *via* methanol hydrocarboxylation to provide the acetyl source in the acetamide products. The reaction could be effectively accelerated by a Rh catalyst with LiI/LiCl as promoters in the cyclic amide solvent. Interestingly, no ligand was needed to trigger the catalysis. To the best of our knowledge, this is the first report of acetamide synthesis using CO_2 as a C1 synthon.

Results and discussion

N,*N*-Dimethylacetamide is an important and the simplest acetamide. We adopted DMA synthesis from methanol, CO_2/H_2, and dimethylamine as a model reaction to screen the basic catalytic system and reaction conditions. Dimethyl ammonium dimethylcarbamate (DIMCARB), which dissociates to dimethylamine and CO_2 above 60 °C, was widely used as a safe source



Scheme 1 Synthesis of acetamides using CO_2, methanol, H_2, and amines.

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for dimethylamine.[17] In this study, we utilized DIMCARB to release dimethylamine in the reaction. We conducted the reactions in different catalytic systems, and the results are shown in Table 1. The reaction proceeded efficiently with Rh(acac)$(CO)_2$ as the catalyst and LiI/LiCl as the promoters in 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (DMPU) solvent at 190 °C (entry 1). DMA was the major product and the yield of DMA based on dimethylamine was 65.3%. Trimethylamine, acetic acid, and trace dimethylformamide (DMF) were the by-products.

The effective cooperation of different catalytic components is crucial for improving the reaction rate. Without one or two of the components, the reaction activity was much lower or the reaction did not take place at all (entries 2–5). The Rh precursor was important for the good catalytic performance. When other Rh complexes, *i.e.*, Rh_2(1,5-cod)$_2Cl_2$, $Rh_2(CO)_4Cl_2$, Rh(acac)$_3$, RhCl(CO)$(PPh_3)_2$, RhI_3, $RhCl_3$, were used as catalysts, the yield of DMA was much lower or no DMA was observed in the reaction (entries 6–11). When heterogeneous Rh (Rh/C, Rh/Al_2O_3) was used as the catalyst, the reaction did not occur (entries 12 and 13). Apart from the Rh complexes, we tested other metal complexes, namely, $Ru_3(CO)_{12}$, $Ir_4(CO)_{12}$, $Ni(PPH_3)_2Br_2$, $Co_2(CO)_8$, $Re_2(CO)_{10}$. The results revealed that these metal complexes could not accelerate the reaction at all (entries 14–18). We also combined Rh(acac)$(CO)_2$ with other metal complexes ($Ru_3(CO)_{12}$, $Ir_4(CO)_{12}$, $Co_2(CO)_8$), but the catalytic performances were remarkably lower than that of a single Rh(acac)$(CO)_2$ catalyst (entries 1 and 19–21). In short, Rh(acac)$(CO)_2$ was the appropriate catalyst for the model reaction.

Table 1 Different catalytic systems of DMA synthesis from methanol, CO_2, H_2, and DIMCARB[a]

Entry	Catalyst	Promoter I	Promoter II	Solvent	Yield[b] (%)
1	Rh(acac)$(CO)_2$	LiI	LiCl	DMPU	65.3
2	Rh(acac)$(CO)_2$	—	LiCl	DMPU	0
3	Rh(acac)$(CO)_2$	LiI	—	DMPU	17
4	Rh(acac)$(CO)_2$	—	—	DMPU	0
5	—	LiI	LiCl	DMPU	0
6	Rh_2(1,5-cod)$_2Cl_2$	LiI	LiCl	DMPU	0.5
7	$Rh_2(CO)_4Cl_2$	LiI	LiCl	DMPU	40.9
8	Rh(acac)$_3$	LiI	LiCl	DMPU	3.6
9	RhI_3	LiI	LiCl	DMPU	0.2
10	$RhCl_3$	LiI	LiCl	DMPU	0.3
11	RhCl(CO)$(PPh_3)_2$	LiI	LiCl	DMPU	0
12	Rh/C	LiI	LiCl	DMPU	0
13	Rh/Al_2O_3	LiI	LiCl	DMPU	0
14	$Ru_3(CO)_{12}$	LiI	LiCl	DMPU	0
15	$Ir_4(CO)_{12}$	LiI	LiCl	DMPU	0
16	$Ni(PPH_3)_2Br_2$	LiI	LiCl	DMPU	0
17	$Co_2(CO)_8$	LiI	LiCl	DMPU	0
18	$Re_2(CO)_{10}$	LiI	LiCl	DMPU	0
19	Rh(acac)$(CO)_2$, $Ir_4(CO)_{12}$	LiI	LiCl	DMPU	0.1
20	Rh(acac)$(CO)_2$, $Ru_3(CO)_{12}$	LiI	LiCl	DMPU	1.3
21	Rh(acac)$(CO)_2$, $Co_2(CO)_8$	LiI	LiCl	DMPU	33.4
22	Rh(acac)$(CO)_2$	NaI	LiCl	DMPU	10.2
23	Rh(acac)$(CO)_2$	KI	LiCl	DMPU	0
24	Rh(acac)$(CO)_2$	LiCl	LiCl	DMPU	0
25	Rh(acac)$(CO)_2$	LiBr	LiCl	DMPU	0.8
26	Rh(acac)$(CO)_2$	I_2	LiCl	DMPU	0
27	Rh(acac)$(CO)_2$	LiI	LiBr	DMPU	31.5
28	Rh(acac)$(CO)_2$	LiI	$LiBF_4$	DMPU	21.8
29	Rh(acac)$(CO)_2$	LiI	LiF	DMPU	32.3
30	Rh(acac)$(CO)_2$	LiI	KF	DMPU	22.2
31	Rh(acac)$(CO)_2$	LiI	NaCl	DMPU	50.1
32	Rh(acac)$(CO)_2$	LiI	KCl	DMPU	43.8
33	Rh(acac)$(CO)_2$	LiI	LiCl	DMI	45.1
34	Rh(acac)$(CO)_2$	LiI	LiCl	NMP	39.3
35	Rh(acac)$(CO)_2$	LiI	LiCl	NEP	36.9
36	Rh(acac)$(CO)_2$	LiI	LiCl	NOP	35.4
37	Rh(acac)$(CO)_2$	LiI	LiCl	Tetramethylurea	0
38	Rh(acac)$(CO)_2$	LiI	LiCl	3-Methyl-2-oxazolidinone	0
39	Rh(acac)$(CO)_2$	LiI	LiCl	Squalane	0
40	Rh(acac)$(CO)_2$	LiI	LiCl	Water	0
41	Rh(acac)$(CO)_2$	LiI	LiCl	Cyclohexane	0
42	Rh(acac)$(CO)_2$	LiI	LiCl	THF	0

[a] Reaction conditions: 40 μmol Rh catalyst (based on the metal), 3 mmol promoter I, 1 mmol promoter II, 5 mmol MeOH, 2 mL solvent, 0.15 g DIMCARB (*i.e.* 2 mmol dimethylamine), 5 MPa CO_2, and 3 MPa H_2 (at room temperature), 190 °C, 14 h. [b] The yield of DMA was based on dimethylamine in DIMCARB (100 × moles of DMA product per mole of dimethylamine feedstock). All the yields were calculated based on gas chromatography using toluene as the internal standard.

The promoters were indispensable in the reaction. Without LiI, no DMA could be observed (entries 2 and 4). Without LiCl, the yield of DMA was markedly lower (entry 3). When other alkali metal halides (NaI, KI, LiCl, and LiBr) were used instead of LiI, the catalytic performance was either much worse or the target reaction did not proceed (entries 1 and 22–25). As can be seen from the abovementioned results, the promoting effect of the alkali metal cations followed the sequence: $Li^+ > Na^+ > K^+$, while the promoting effect of the halide anions followed the order: $Cl^- < Br^- < I^-$. No DMA was generated when iodine (I_2) was used instead of LiI, indicating that I^- was indispensable in this reaction (entry 26). Hence, LiI was a suitable promoter for the reaction. The eminent promoting effect of LiI may lie in two aspects: the stronger Lewis acidity and smaller size of Li^+ and the better nucleophilicity of I^-.[18] In addition, the very good solubility of LiI in the reaction solution was also beneficial for the reaction. We also replaced another promoter LiCl with LiBr, $LiBF_4$, LiF, KF, NaCl, or KCl, but the yields of DMA decreased (entries 1 and 27–32). This indicated that synergistic effects existed between the Rh catalyst and promoters in stabilizing the catalytic system and accelerating the reaction.

The solvent also significantly affected the catalytic performance. On the basis of Rh(acac)$(CO)_2$ and LiI/LiCl, we conducted the reaction using 1,3-dimethyl-2-imidazolidinone (DMI) as the solvent. DMI was used as the optimal solvent in the acetic acid synthesis *via* methanol hydrocarboxylation with CO_2 and H_2. However, in the model reaction of this study, the solvent effect was significantly lower than that of DMPU (entries 1 and 33). DMPU has a similar structure to DMI, but DMPU has one more carbon in the ring skeleton of the cyclic amide compared to DMI. The different solvent effects may be ascribed to their different ring strains, which may affect the state of the lone pair electrons. We also tested other cyclic amides with five-membered rings as the reaction solvent, namely, 1-methyl-2-pyrrolidone (NMP), 1-ethyl-2-pyrrolidone (NEP), and 1-*n*-octyl-2-pyrrolidone (NOP). The results demonstrated that yields of DMA were less than that obtained using DMI (entries 34–36). In addition, the larger the alkyl substituent on the N atom, the lower was the yield of DMA in the corresponding reaction. We also tried a solvent with similar structure to DMPU and DMI, but without the ring skeleton, *i.e.*, tetramethylurea. However, no DMA was detected after the reaction (entry 37). Thus, the ring structure was necessary for triggering the catalysis. The cyclic structure affected the p–π conjugation between the lone pair electrons of N atom and π-electrons of C═O group, which may account for this phenomenon. Based on the cyclic amide structure, we substituted one N atom on the ring skeleton with an O atom, but no DMA was observed (entry 38). We also used squalane, water, cyclohexane, and THF as the solvents, but the target reaction did not take place (entries 39–42). Thus, the cyclic amide structure was necessary for the solvent and DMPU was a suitable choice. In brief, the catalytic system consisting of Rh(acac)$(CO)_2$, LiI/LiCl and DMPU was fit for the model reaction.

Based on the above catalytic system, we studied the impact of the reaction temperature, as shown in Fig. 1a. DMA emerged at 130 °C and the yield increased remarkably with the elevation of reaction temperature. At 190 °C, the yield of DMA reached 65.3%, and then gradually increased with the increase in temperature. Hence, 190 °C was a suitable reaction temperature. At 190 °C, we investigated the impact of dosages of Rh catalyst, LiI and LiCl. The yield of DMA increased with an increase in Rh dosage and it reached 65.3% at 40 μmol Rh catalyst; however, the yield decreased when the Rh dosage was further enhanced (Fig. 1b). The impact of LiI and LiCl dosages followed a similar trend and their suitable dosages were 3 mmol and 1 mmol, respectively (Fig. 1c and d). It can be deduced that excess I^- and/or Cl^- may occupy the active sites of the Rh catalyst and thus inhibit the reaction.

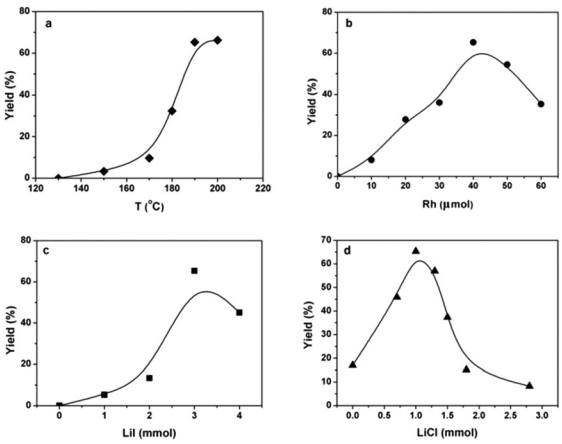


Fig. 1 Effect of reaction conditions (a–d) over 5 mmol MeOH, 0.15 g DIMCARB (*i.e.* 2 mmol dimethylamine), 2 mL DMPU, 5 MPa CO_2, and 3 MPa H_2 (at room temperature) and 14 h. (a) Effect of reaction temperature, 40 μmol Rh(acac)$(CO)_2$ catalyst, 3 mmol LiI, and 1 mmol LiCl; (b) effect of Rh catalyst dosage, 190 °C, 3 mmol LiI, and 1 mmol LiCl; (c) effect of LiI dosage, 190 °C, 40 μmol Rh(acac)$(CO)_2$ catalyst, and 1 mmol LiCl; (d) effect of LiCl dosage, 190 °C, 40 μmol Rh(acac)$(CO)_2$ catalyst, and 3 mmol LiI.

The pressure of CO_2 and H_2 also remarkably influenced the catalytic performance (Table 2). No product was detected when the total pressure was 2 MPa (entry 1). With the enhancement of the pressure, the yield of DMA increased markedly and 65.3% of DMA could be obtained when the CO_2/H_2 pressure reached 5/3 MPa (entries 2–4). The effect of pressure became minor when the pressure was further increased (entry 5). The ratio of CO_2/H_2 was also important for the catalytic performance. We fixed the total pressure at 8 MPa and altered the ratio of CO_2/H_2. It was found that 5 MPa CO_2 and 3 MPa H_2 gave the best result (entries 4 and 6–9). The presence of CO_2 and H_2 was necessary for the reaction. Without CO_2 and/or H_2, no DMA was observed after reaction (entries 10–12). The substrates were also indispensable in the target reaction because the reaction did not proceed without methanol or DIMCARB (entries 13 and 14).

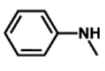
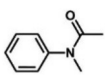
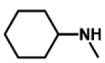
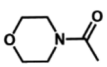
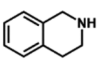
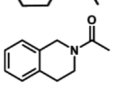
Based on the Rh-LiI/LiCl catalytic system, more complex amine substrates could also be used as a substrate to produce the corresponding acetamides (Table 3). The amine with

Table 2 Impact of gas pressure on the yield of DMA after the reaction[a]

Entry	CO_2/MPa	H_2/MPa	Yield (%)
1	1.25	0.75	0
2	2.5	1.5	1.7
3	3.75	2.25	22.6
4	5	3	65.3
5	6.25	3.75	66.2
6	2	6	0
7	3	5	6.2
8	4	4	24.9
9	6	2	45.5
10	0	3	0
11	0	0	0
12	5	0	0
13[b]	5	3	0
14[c]	5	3	0
15[d]	5	3	49.0

[a] Reaction conditions: 40 μmol $Rh(acac)(CO)_2$ (based on the metal), 3 mmol LiI, 1 mmol LiCl, 5 mmol MeOH, 0.15 g DIMCARB (*i.e.*, 2 mmol dimethylamine), 2 mL DMPU, 190 °C, and 14 h. [b] No MeOH was added before the reaction. [c] No DIMCARB was added before the reaction and trace acetic acid was observed after the reaction. [d] 0.5 mmol 4-methylimidazole was added before the reaction.

Table 3 Rh-Catalyzed *N*-acetylation of various amines *via* reductive CO_2 hydrogenation with methanol[a]

Entry	Substrate	Product	Yield[b] (%)
1			54.2
2			41.7
3			37.2
4			40.4
5			60.5
6			48.8

[a] Reaction conditions: 40 μmol $Rh_2(CO)_4Cl_2$ catalyst (based on the metal), 3 mmol LiI, 1 mmol LiCl, 5 mmol MeOH, 2 mL DMI, 1.5 mmol amines, 5 MPa CO_2, and 3 MPa H_2 (at room temperature), 190 °C and 14 h. [b] The yield of acetamides was based on the corresponding amines.

benzene or cyclohexane as the substituent was successfully converted to the corresponding acetamide (entries 1 and 2). The cyclic amines of various structures were also suitable for the reaction. For example, cyclic amines with different ring sizes (five-, six- and seven-membered rings) could be used as substrates to obtain the corresponding acetamides (entries 3–5). Notably, the cyclic amines with a heteroatom (O) or combined with a benzene group could also be converted to the corresponding acetamides and even with higher yields (entries 5 and 6). When heteroaromatic compounds such as indole, pyrrole, imidazole or purine were used as a substrate, no acetamide was observed in the products. A further study revealed that no *N*-acetylation took place even when acetic acid was directly used in the reaction with these heteroaromatic compounds under similar conditions. This may be due to the weak basicity of the N atoms in these compounds. Thus, heteroaromatic compounds were unfit substrates for this reaction.

As a byproduct, trace acetic acid was detected after the reaction. Amines are well-known bases and acetic acid is a common organic acid. The experiment indicated that acetamide can be formed easily *via* the neutralization of an amine with acetic acid at reaction conditions. Thus, the reaction should be considered a cascade reaction consisting of methanol hydrocarboxylation and subsequent *N*-acetylation of the amines. To verify this deduction, we conducted several control experiments. The GC-MS spectra of a tracer experiment using $^{13}CH_3OH$ demonstrated that the CH_3 group of the methanol substrate was transferred to acetamide (Fig. S1†). We further conducted a tracer test with $CH_3{}^{18}OH$. Results indicated that the bond to the OH group in the methanol substrate cleaved during the reaction and the O atom in the acetamide product was from CO_2 (Fig. S2†). These facts support the above deduction. In our previous report, an imidazole-like ligand was essential to the acetic acid synthesis *via* an Rh-catalyzed methanol hydrocarboxylation.[16] Interestingly, no such ligand was needed in the DMA synthesis and an additional 4-methylimidazole ligand evidently inhibited the reaction (entry 15 of Table 2). Although remarkable amounts of DMA could be produced in the target reaction, only trace acetic acid was observed when the reaction was conducted without the amine substrate (entry 14 of Table 2). A further experiment revealed that DMA had no promoting effect on the methanol hydrocarboxylation. These phenomena suggest that the consumption of the acetic acid intermediate by the neutralization reaction with the amine could accelerate the methanol hydrocarboxylation. In our previous reports, we had suggested that acetic acid synthesis *via* methanol hydrocarboxylation with CO_2 and H_2 was not *via* CO.[15,16] To clarify the reaction path of this study, we performed experiments using CO at different pressures (0.5 MPa, 1 MPa, 3 MPa) instead of CO_2. However, no DMA was detected after these reactions. Therefore, the target reaction also did not occur *via* the CO route. The reaction contained four reactants and three catalytic components and proceeded at a relatively high temperature. Thus, acquiring a very high yield of the corresponding acetamide in such a complex reaction system is still a challenge at the present stage.

Conclusions

In summary, we developed a route for producing acetamides from CO_2, methanol, H_2 and corresponding amine substrates. The reaction can be effectively accelerated using Rh-LiI/LiCl as a catalyst at 190 °C. Evident synergy exists between the Rh catalyst and the promoters in catalyzing the reaction. The yield of DMA can reach 65.3% using DIMCARB as the feedstock. This

method also applies for various amine substrates, such as cyclic amines and amines with benzene or cycloalkane substituents. We believe that this report will trigger more investigation into the synthesis of acetamides using CO_2 as the feedstock.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

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