Ru catalyzed formylation of diethylamine
with CO$_2$ and H$_2$ under moderate
pressure condition

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Ru catalyzed formylation of diethylamine (bulky secondary
amine) with CO$_2$ and H$_2$ has been investigated using a series of
phosphine ligands. Significant influence on the catalyst activity
and selectivity is observed with bidentate phosphine ligands. The
Ru catalyst with the ligand, 1,2-bis(diphenylphosphino)benzene
exhibits the highest catalyst performance (TON up to 2475). The
high conversion (99%) and high selectivity to the corresponding
formamide (up to 90-98%) is achieved at 150 °C and moderate
pressure conditions. The effects of temperature, concentration of
diethylamine and partial pressure of CO$_2$ on the
formylation of diethyl amine catalyzed have been examined in
order to improve the catalytic activity and selectivity.

Keywords: Catalysis, Formylation, Diethyl amine, Carbon dioxide,
Ruthenium, Bidentate phosphines

C$_1$ chemistry based on synthesis gas (CO/H$_2$),
methane (CH$_4$) and carbon dioxide (CO$_2$) offers many
routes to synthesized industrially useful chemicals.
Considering the environmental effects of CO$_2$ and
economical concerns, the utilization of CO$_2$ as a C$_1$
feedstock to synthesizes value-added chemicals has
received growing impetus since CO$_2$ is available in
abundance and is cheap, non-toxic, non-flammable and
renewable$^{1-7}$. Catalytic hydrogenation of CO$_2$ is
one of the most promising approaches to convert CO$_2$
to various valuable products such as methanol, ethers,
esters, formamides and formic acid$^{8-12}$. The
formamides such as dimethylformamide (DMF),
diethylformamide are commonly used as a solvent in
the plastics, pharmaceutical, paint industries and in
many other chemical processes$^{13}$. Conventionally,
dialkyl formamide (DAF) is produced by sodium
methoxide catalyzed carbonylation of dialkylamine
with carbon monoxide (CO) in methanol at 20–100
bar and 353–373 K$^{14}$. Thus, hydrogenation of CO$_2$ in
the presence of secondary alkylamine is an
environment friendly alternative route for the
production of formamide instead of using toxic
compounds. The synthesis of formamides from
dialkylamines, CO$_2$, and H$_2$ has been studied using
various metal based catalysts. It was observed that Ru
based catalyst exhibited high conversion and selectivity$^{15-19}$. In pioneering studies in this field,
Noyori and co-workers$^{18}$ reported formylation of
different secondary amines by hydrogenation of
supercritical CO$_2$ (pCO$_2$ + pH$_2$ = 210 bar) using
They achieved high TOF (8000 h$^{-1}$ for formylation of
dimethylamine) under supercritical CO$_2$
condition since scCO$_2$ has rapid diffusion, weak catalyst
solvation and the high miscibility with H$_2$. However,
the observed TOFs were considerably low in the case
of bulky amines (50–63 h$^{-1}$)$^{19}$. Baiker et al.$^{20}$ applied
Ru complexes with bidentate phosphine ligands,
[RuCl$_2$(L)$_2$] [L = Ph$_2$P(CH$_2$)$_3$PPh$_2$ (n = 1–3),
Me$_2$P(CH$_2$)$_3$PMe$_2$] for hydrogenation of scCO$_2$
and achieved high TOF and high selectivity for DMF and
methyl formate. Formylation of cyclic and aliphatic
amines has also been carried out using RuCl$_2$(dppe)$_2$
[dppe = 1,2-bis(diphenylphosphino)ethane] and
Ru/Al$_2$O$_3$ modified by dppe as catalysts under scCO$_2$
and H$_2$ (180 to 220 bar)$^{21-23}$. From the reported
literature, it was observed that the formylation of
bulky secondary amine using CO$_2$ usually requires
high pressure (180–220 bar) especially supercritical
state to achieve high reaction rate and yield due to the
high thermodynamic stability and low reactivity of
CO$_2$$^{15-23}$. Literature shows that the major attention is
towards formylation of dimethylamine to DMF, while
there are only a few reports wherein other derivatives
of dialkylamine have been formylated. In the case of
dimethylamine, high conversion and selectivity for
DMF can be obtained while bulky dialkylamines
such as diethylamine, diisopropylamine and
dicyclohexylamine are difficult to formylate as they
produce ammonium formate salts and the rate of
dehydration of such salts to the corresponding
formamides is strongly influenced by steric factors$^{19}$. In view of the above, we focused attention on
synthesis of formamide from bulky dialkylamine such
as diethylamine (as a model substrate) under moderate

Notes

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synthesis of formamide from bulky dialkylamine such
as diethylamine (as a model substrate) under moderate
pressure of CO₂ and H₂ (75–125 bar). Herein, we have screened a series of phosphine ligands in Ru catalyzed formylation of diethylamine and present our findings on the impact of nature of ligands on the reaction rates and selectivity. In order to improve activity and selectivity, the effect of temperature, partial pressure of CO₂ and H₂ and concentration of diethylamine on the hydrogenation of CO₂ were examined systematically in detail.

**Experimental**

RuCl₃·3H₂O, RuCl₂(PPh₃)₃, PPh₃, tri-1-naphthylphosphine (PNp₃), tricyclohexylphosphine (PCy₃), tris(4-methoxyphenyl)phosphine (p-MeO-C₆H₄)₃P, tris(4-trifluoromethylphenyl)phosphine (p-CF₃-C₆H₄)₃P, monosulfonated triphenylphosphine (TPPMS), 1,2-bis(diphenylphosphino)ethane (dppe), 1,2-bis(diphenylphosphino)benzene (dppbz), Bis(2-diphenylphosphinoethyl)phenylphosphine (tridentate phosphate, Trid P) and diethylamine were purchased from M/s Sigma-Aldrich Chemicals, USA and used as received. CO₂ and hydrogen gas (99.9%) used was from Hydro Gas India Pvt. Ltd., India.

The formylation reactions were performed in 100 mL stainless steel autoclave (Autoclave Engineers, EZE-Seal Reactor, USA). In a typical formylation experiment, the required amount of RuCl₃ or RuCl₂(PPh₃)₃, P ligand, substrate and solvent were charged into the reactor. The stirrer was adjusted to 600 rpm. The reactor was flushed three times with nitrogen followed by flushing CO₂ twice at room temperature. The reactor was brought to the desired reaction temperature within 30 min and pressurized with CO₂ and H₂. The reaction was initiated by stirring. After preset reaction time, the stirring was stopped, reactor was cooled down to room temperature, depressurized, flushed with N₂ and opened to collect final sample for a GC analysis. The reaction products were analyzed on Shimadzu GC-17A gas chromatograph equipped with a flame ionization detector having 5% diphenyl- and 95% dimethyl siloxane capillary column (60 m length, 0.25 mm diameter).

**Results and discussion**

Catalytic activities of the ruthenium based catalysts have been evaluated for the synthesis of N,N-diethylformamide (DEF) from diethylamine (Scheme 1). In the

![Scheme 1](image)

Ru catalyzed formylation of diethylamine with CO₂ and H₂
present study, the ruthenium catalysts used for formylation were generated in situ from RuCl₃ as the ruthenium source and different phosphine ligands. It is well known that ligand with different steric and electronic property dramatically influence the catalyst activity and selectivity in transition metal catalyzed reaction. The selection and designing of an appropriate ligand is one of the crucial factors in the transition metal/ligand catalyzed reaction. In view of this, various phosphine ligands were screened to study the influence of phosphine ligands on the activity and selectivity in Ru catalyzed formylation of diethylamine under the identical and moderate reaction conditions (Temperature = 100 °C, pCO₂ = 40 bar, and pH₂ = 60 bar). The results are summarized in the Table 1. Initially, some preliminary experiments were performed with RuCl₃, RuCl₃/PPh₃ and RuCl₃(PPh₃)₃ to understand the role of metal and metal-ligand complex. In the absence of ligand, RuCl₃ alone failed to convert diethylamine giving only 1% conversion. The addition of phosphine ligands considerably enhanced the conversion of diethylamine even at lower pressure of CO₂ and H₂. However, no significant different was observed with in situ prepared ruthenium-phosphine ligand complex and as-synthesized ruthenium complex. In all cases, 100% selectivity to DEF was observed under the studied reaction conditions. The ruthenium complex modified with monodentate bulky phosphine ligand PNP₃ (L₂), PCy₃ (L₃) and (p-MeO-C₆H₄)₃P (L₄) resulted in comparatively lower conversion than with PPh₃ (L₅) (Table 1, entries 3-5). However, the conversion was good compared to unmodified RuCl₃ catalyst. The ruthenium complex modified with (p-CF₃-C₆H₄)₃P (L₆) and water soluble ligand, TPPMS (L₇) displayed comparable TOF for the RuCl₃/PPh₃ system (Table 1, entries 6 and 7). The tridentate phosphine ligand (L₈) gave higher TOF than bulky phosphines (L₂ and L₅), but lower than PPh₃ and bidentate phosphine ligands. In fact, a high conversion with high TOF was attained with bidentate phosphate ligands; in particular, 1,2-bis(diphenylphosphino)-benzene (L₈) yielded the highest conversion with high TOF. The observed TOF is at least 1.4 times higher than those observed for the Ru/PPh₃ catalyst. In order to perceive whether further improvements are possible in activity using Ru/1,2-bis(diphenylphosphino)-benzene (L₈) catalyst system, the effect of temperature, concentration of diethylamine and partial pressure of CO₂/H₂ on the reaction were examined.

Effect of temperature was studied and varied in the range of 100–160 °C at constant CO₂ and H₂ total pressure (100 bar). The investigation of the effect of temperature revealed that the temperature had a significant effect on both conversion and selectivity (Fig. 1). It can be seen that with an increase of temperature, the reaction proceeds faster by a factor of ~2.4 but lowers the selectivity to DEF by forming side products, such as N,N-diethylmethylamine (by over reduction of N,N-diethylformamide)²⁴,²⁵. At lower reaction temperatures, the conversion of diethylamine was low but high selectivity toward DEF was observed. With an increase in temperature from 100 to 160 °C, the conversion of diethylamine was increased from 31% to 77% ensuing TOF 481 with DEF selectivity decreased to 83%. The conversion of diethylamine was increased significantly above 140 °C whereas high selectivity to DEF (~90%) was maintained up to 150 °C. The selectivity to DEF was decreased drastically above 150 °C. Therefore, the optimum reaction temperature was kept as 150 °C, where a good balance between conversion and selectivity was achieved.

The effect of diethylamine concentration on Ru catalyzed formylation was investigated at 150 °C, 40 bar CO₂ and 60 bar H₂ pressure (Fig. 2) by varying the substrate concentration from 19.2–57.6 mmol (19.2, 28.8, 38.4, 48, 57.6 mmol). The results indicate that the conversion (70%) and selectivity to N,N-diethylformamide (94%) were high at lower diethylamine concentration of 19.2 mmol which were gradually decreased to 48% and 86% respectively at substrate concentration of 57.6 mmol. On other hand, the reverse trend was observed for TOF when substrate concentrations were varied. At substrate concentration of 19.2 mmol, the TOF was low (175 h⁻¹) which increased considerably up to 362 h⁻¹ at

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**Table 1—Ru catalyzed formylation of diethylamine using distinct phosphine ligands.** (React. cond.: diethylamine = 48 mmol, RuCl₃·3H₂O = 0.0192 mmol, Temp. = 100 °C, pCO₂ = 40 bar, pH₂ = 60 bar, methanol = 20 mL, reaction time = 4 h)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Ligand</th>
<th>L/Ru ratio</th>
<th>Conv. (%)</th>
<th>TOF (h⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>--</td>
<td>-</td>
<td>1</td>
<td>6</td>
</tr>
<tr>
<td>2</td>
<td>L₁</td>
<td>6</td>
<td>22</td>
<td>137</td>
</tr>
<tr>
<td>3</td>
<td>L₂</td>
<td>6</td>
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<td>87</td>
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<tr>
<td>4</td>
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<tr>
<td>5</td>
<td>L₄</td>
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<tr>
<td>6</td>
<td>L₅</td>
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<td>7</td>
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<td>10</td>
<td>L₉</td>
<td>2</td>
<td>15</td>
<td>93</td>
</tr>
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diethylamine concentration of 48 mmol. However, there was no significant change in TOF with further increase in substrate concentration from 48–57.6 mmol.

The formylation of diethylamine catalyzed by Rh/(L₈) was studied at 150 °C under varying total pressure (CO₂+H₂) and ratio of H₂/CO₂. Initially, the effect of H₂/CO₂ ratio on reaction was investigated by varying H₂/CO₂ ratio from 1.0–1.75. The experimental results indicate that the H₂/CO₂ ratio has a more prominent effect on the conversion and selectivity than total pressure of H₂ and CO₂ (Table 2). The conversion and selectivity increased with an increase in the H₂/CO₂ ratio. At H₂/CO₂ ratio of 1 with 120 bar total pressure of CO₂ and H₂, the formylation of diethyl amine proceeded slowly yielding 39% conversion and 87% selectivity to DEF. The increase in H₂/CO₂ ratio from 1 to 1.5 led to increase in conversion and selectivity to 58% and 90% respectively. On further increase in H₂/CO₂ ratio, the conversion and selectivity were less affected. Next, the effect of the total pressure of CO₂ and H₂ on reaction was investigated by varying total pressure from 75 bar to 125 bar keeping H₂/CO₂ ratio of 1.5. The conversion and TON increased considerably with increase in total pressure, whereas selectivity was found to decrease. The reaction was carried out at optimum reaction conditions of total pressure of 100 bar with H₂/CO₂ ratio of 1.5 at 150 °C. On extending the reaction time from 4 h to 12 h, the conversion increased from 58% to 99% with increase in TON from 1450 to 2475, without altering the formamide selectivity (90%). It is worthwhile to note that the catalyst system, Ru/1,2-bis(diphenylphosphino)benzene (L₈) exhibited higher activity in the case of bulky amine (diethyl amine) at comparative

Table 2—Effect of partial pressure of CO₂ and H₂ on Ru catalyzed formylation of diethyl amine. [React. cond: diethylamine = 48 mmol, RuCl₃·3H₂O = 0.0192 mmol, ligand L₈/Ru = 3, Temp. = 150 °C, methanol = 20 mL, reaction time = 4 h]

<table>
<thead>
<tr>
<th>Entry</th>
<th>pCO₂ (bar)</th>
<th>pH₂ (bar)</th>
<th>pH₂/pCO₂</th>
<th>pCO₂+pH₂ (bar)</th>
<th>Conv. (%)</th>
<th>(%) Selec. (DEF)</th>
<th>TON</th>
</tr>
</thead>
<tbody>
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<td>1.5</td>
<td>100</td>
<td>58</td>
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<td>2</td>
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<td>80</td>
<td></td>
<td>210</td>
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</tr>
</tbody>
</table>

aReaction time = 12 h.
bRef. 19; catalyst RuCl₂[P(CH₃)₃]₆, reaction time = 13 h.
moderate pressure conditions \((p\text{CO}_2 + p\text{H}_2 = 100 \text{ bar})\) than the earlier reported homogeneous catalyst, RuCl\(_3\)\([\text{P(CH}_3]_3\)\(_4\)) \((p\text{CO}_2 + p\text{H}_2 = 210 \text{ bar};\) Table 2, entries 6 & 7\)\(^{19}\). Also, the TON achieved is \(~3\) times higher, indicating the efficiency of the present catalyst system and impact of the ligand 1,2-bis(diphenylphosphino)benzene. In most previous studies, triphenyl phosphine (PPh\(_3\)) and 1,2-bis (diphenylphosphino)ethane (dppe) ligand were used to modify the Ru based catalyst and design heterogeneous catalyst systems for the formylation of amine\(^{21-23}\). In the present investigation, we have highlighted the importance of ligand in enhancement of catalyst performance. From this study, it can be seen that dppbz (L\(_8\)) is more efficient than PPh\(_3\) and dppe ligands (Table 1).

**Conclusions**

Ru catalyzed formylation of diethylamine (a bulky secondary amine) with CO\(_2\) and H\(_2\) has been developed first time by screening various phosphine ligands under moderate CO\(_2\) pressure conditions. In the case of monodentate P ligands, the catalyst activity was influenced by basicity of ligand whereas bulky P ligands lowered the reaction rate. Compare to monodentate P ligands, ruthenium complex modified with bidentate P ligands afforded high activity, particularly 1,2-bis(diphenylphosphino)benzene was found to be a promising ligand. High TON (up to 2475) and formamide selectivity (90-98%) were achieved by Ru/1,2-bis(diphosphino)benzene catalyst. The present results are promising for developing efficient heterogeneous catalyst systems for the purpose of CO\(_2\) utilization. Further investigations to utilize CO\(_2\) and mechanistic studies using dppbz ligand are currently underway in our laboratory.

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**References**