Highly productive CO$_2$ hydrogenation to methanol – a tandem catalytic approach via amide intermediates†

M. Everett and D. F. Wass

A new system for CO$_2$ reduction to methanol has been demonstrated using homogeneous ruthenium catalysts with a range of amine auxiliaries. Modification of this amine has a profound effect on the yield and selectivity of the reaction. A TON of 8900 and TOF of 4500 h$^{-1}$ is achieved using a [RuCl$_2$(Ph$_2$PCH$_2$CH$_2$NHMe)$_2$] catalyst with a disopropylamine auxiliary.

The upgrading of carbon dioxide to commodity petrochemicals is an important objective, both in terms of sequestering atmospheric carbon dioxide to alleviate rising atmospheric levels and using this as an alternate C$_1$ feedstock source. The controlled reduction of carbon dioxide to methanol is an especially interesting goal.

Heterogeneous catalysts for CO$_2$ reduction to methanol are well known and indeed CO$_2$ is implicated as an intermediate in commercial methanol production.$^2$ Homogeneous catalysts for this transformation are more unusual. The first reported example was by Tominaga and co-workers in 1993, using a Ru$_3$(CO)$_{12}$-KI system, producing 32 catalytic turnovers of methanol in a mixture of products.$^3$ Other systems have emerged more recently;$^4$–$^6$ for example, Leitner and co-workers have reported ruthenium catalysts supported by tripodal phosphine ligands that achieve up to 442 catalytic turnovers in a single run, with a turnover frequency of 18 h$^{-1}$ in a system that has added much to mechanistic understanding of this chemistry.$^7$–$^{12}$

Sanford and co-workers have reported an alternative indirect or tandem catalytic approach to this transformation;$^{13}$ carbon dioxide first undergoes a ruthenium-catalysed reaction with hydrogen to produce formic acid, Lewis acid-catalysed esterification with methanol to yield methyl formate follows, and finally further hydrogenation to give two molecules of methanol. Overall one turnover of carbon dioxide hydrogenation to methanol is achieved with a further methanol involved as an auxiliary.

Unfortunately, in practice this suffers from very low turnover numbers (2.5) and frequencies (0.16 h$^{-1}$) unless the various steps are separated into a series of reactors because of catalyst compatibility issues.

Very recent results from Sanford and co-workers,$^{14}$ using a dimethylamine co-catalyst to achieve TON of up to 550, and TOF of 10 h$^{-1}$, gave us further grounds for optimism. Olah et al. have also demonstrated a related stepwise capture of CO$_2$ with pentaethylenehexamine (PEHA) and subsequent hydrogenation to methanol using the same conditions.$^{15}$ However, these reports have not exploited the aforementioned opportunity of selecting other amines to control catalysis. Here we report a highly productive one-pot tandem catalyst approach for carbon dioxide hydrogenation to methanol in which the nature of this amine ‘auxiliary’ plays the critical role in achieving superior performance.

Studying the two parts of our proposed tandem catalytic system in turn, we initially examined the reaction of different

$$\text{CO}_2 + R_2NH + H_2 \xrightarrow{[M]^1} \text{HC(O)NR}_2 + H_2O$$

$$\text{HC(O)NR}_2 + 2H_2 \xrightarrow{[M]^2} \text{CH}_3\text{OH} + R_2NH$$

Overall:

$$\text{CO}_2 + 3H_2 \xrightarrow{[M]} \text{CH}_3\text{OH} + H_2O$$

Scheme 1  Tandem catalytic approach to carbon dioxide hydrogenation to methanol using an amine auxiliary.
amines with CO₂ and H₂ to form the desired amide intermediate. 
Noyori and Baiker successfully carried out this conversion in supercritical CO₂, reaching turnover numbers of 740 000, and 
turnover frequencies of 360 000 h⁻¹.¹⁶,¹⁷ We started by employing 
milder pressures with the same catalysts (Table 1). The catalysts 
are still active under these conditions, achieving up to 14 000 catalytic 
turnovers, at 700 h⁻¹. The amine used influences the performance, in 
general increasing the steric bulk of the amine leading to lower 
turnover numbers further but now gives methanol as the only product detected 
by GC (run 12). The power of this approach is realised when bulk is 
increased even further to di-isopropylamine (run 13), yielding 
methanol as the only product with excellent turnover numbers. The 
value of having a single catalyst that can proficiently enable both 
steps of the tandem catalytic pathway is exemplified by run 15, 
where a mixture of 2 and 3 gives a result disappointing in terms of 
overall turnover compared to 2 alone and disappointing in terms of 
methanol selectivity compared to 3 alone; the complexity of 
expecting two catalysts to perform independently in the same vessel 
leads to a deterioration in performance for both catalysts. It should 
be noted that comparative runs with an absence of ruthenium 
catalyst, base or amine are unsuccessful under otherwise identical 
conditions.

Our working hypothesis is that whilst bulkier amines lead to more 
sluggish formation of the corresponding amides for a given catalyst 
(first reaction in Scheme 1: compare runs 3–6), the release of steric 
strain by hydrogenation of these bulkier amides leads to more facile 
reactivity in the second step (second reaction in Scheme 1) 
producing methanol and regenerating the amine auxiliary. The 
improved performance for catalyst 3 with bulkier amines suggests 
this second amide hydrogenation is rate limiting so that a 
compromise between more difficult amide formation and more facile 
hydrogenation leads to improved performance with reagents that 
favour the latter, i.e. bulkier amines. With this in mind, the 
hydrogenation of various pre-formed amides was attempted (Table 
2). As predicted, the rate of conversion of di-isopropylformamide is 
significantly higher than that for less bulky DMF, with 
diethylformamide as an intermediate case. The reduced propensity of 
bulkier amines to bind to the catalytically active metal centre 
competitively with substrate could also be a factor in their improved 
performance.

Our attention then turned to the ruthenium catalyst itself. We 
have previously reported 2 and 3 for ethanol to butanol Guerbet-type 
catalysis,²¹ the catalysts giving similar performance. By contrast, 
here there is a marked difference in selectivity, 2 favouring DMF 
formation and 3 methanol under identical conditions. One 
potentially significant difference is the ability for the amine groups 
of 3 to act as internal bases in a ligand assisted, cooperative, outer-
sphere type mechanism. With this in mind, we synthesised the 
complexes 4 and 5 in which the bound amine is mono- or 
dimethylated. Complex 6 provides another dialkylated example. 
Catalytic results are presented in Table 3.

The difference in performance between ligands having primary 
or secondary amine groups, and tertiary amines is clear. Whilst 3 and 
4 produce both DMF and methanol with dimethylamine (runs 19 and 
20), 5 and 6 produce the amide

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### Table 1 Catalysis results

<table>
<thead>
<tr>
<th>Run</th>
<th>Precat. Amine</th>
<th>Amide, mmol (TON)</th>
<th>MeOH, mmol (TON)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>Me₂NH</td>
<td>72 (14 000) [700]</td>
<td>0.0 (0) [0]</td>
</tr>
<tr>
<td>2a</td>
<td>Me₂NH</td>
<td>6.5 (1300) [65]</td>
<td>0.0 (0) [0]</td>
</tr>
<tr>
<td>3a</td>
<td>Me₂NH</td>
<td>52 (10 000) [500]</td>
<td>0.0 (0) [0]</td>
</tr>
<tr>
<td>4a</td>
<td>Et₂NH</td>
<td>3.8 (760) [38]</td>
<td>0.0 (0) [0]</td>
</tr>
<tr>
<td>5a</td>
<td>iPr₂NH</td>
<td>0.038 (7.5) [0.38]</td>
<td>0.0 (0) [0]</td>
</tr>
<tr>
<td>6a</td>
<td>Et₂P₂NH</td>
<td>0.071 (14) [0.70]</td>
<td>0.0 (0) [0]</td>
</tr>
<tr>
<td>7a</td>
<td>Pyrrolidine</td>
<td>0.75 (150) [7.5]</td>
<td>0.0 (0) [0]</td>
</tr>
<tr>
<td>8a</td>
<td>Et₂N</td>
<td>0.0 (0) [0]</td>
<td>0.0 (0) [0]</td>
</tr>
<tr>
<td>9a</td>
<td>Me₂NH</td>
<td>0.62 (120) [6]</td>
<td>0.55 (110) [5.5]</td>
</tr>
<tr>
<td>10a</td>
<td>Me₂NH</td>
<td>2.8 (550) [28]</td>
<td>1.9 (370) [18]</td>
</tr>
<tr>
<td>11a</td>
<td>Et₂NH</td>
<td>1.3 (260) [13]</td>
<td>1.0 (200) [10]</td>
</tr>
<tr>
<td>12a</td>
<td>Pr₂NH</td>
<td>0.0 (0) [0]</td>
<td>1.1 (220) [11]</td>
</tr>
<tr>
<td>13a</td>
<td>iPr₂NH</td>
<td>0.0 (0) [0]</td>
<td>12 (2300) [120]</td>
</tr>
<tr>
<td>14a</td>
<td>Pyrrolidine</td>
<td>0.0 (0) [0]</td>
<td>3.0 (590) [30]</td>
</tr>
<tr>
<td>15a</td>
<td>2/3 Me₂NH</td>
<td>3.7 (730) [37]</td>
<td>0.23 (46) [2.3]</td>
</tr>
</tbody>
</table>

Conditions: precatalyst (5 mmol), NaOEt (0.15 mmol), amine (2 mL), toluene (10 mL), 180 1C, 20 h. ³ CO₂ (20 bar), H₂ (20 bar). ⁴ CO₂ (10 bar) H₂ (30 bar). ⁵ Turnover number and frequency with respect to catalyst.

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### Table 2 Amide hydrogenation study

<table>
<thead>
<tr>
<th>Run</th>
<th>Amide</th>
<th>MeOH, mmol (TON) [TOF h⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>DMF</td>
<td>0.12 (23) [1.2]</td>
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<tr>
<td>17</td>
<td>DEF</td>
<td>0.75 (150) [7.5]</td>
</tr>
<tr>
<td>18</td>
<td>DIPF</td>
<td>1.1 (210) [11]</td>
</tr>
</tbody>
</table>

Conditions: 3 (5 mmol), NaOEt (0.15 mmol), amide (2 mL), toluene (10 mL), H₂ (30 bar), 180 1C, 20 h.
only (runs 21 and 22). The mono-N-methylated ligand complex 4 demonstrates advantages in terms of higher overall turnover numbers and selectivity to methanol (run 24). This trend is continued with di-isopropylamine, 5 and 6 being inactive in this case but complex 4 giving the best performance seen to date, highly selective and with a turnover number of 4000. This corresponds to a TOF of 2000 h$^{-1}$.

These data are strong evidence for an outer sphere type mechanism, in which amine ligand deprotonation leads to an intermediate metal amide complex.22,23 Intriguingly, the significant-cant increase in activity from 3 to 4 is also consistent with the very recent mechanism suggested by Gordon et al., with the amine acting as a "cooperative and chemically innocent ligand".24

The excellent performance of 4 with the di-isopropylamine auxiliary led us to speculate that we might now be in the regime of catalyst performance is limited by mass transport effects. Indeed, a catalyst run with lower catalyst loading (50 nmol) over 2 h, and otherwise identical conditions, gives an unprecedented TON of 8900 with an impressive TOF of 4500 h$^{-1}$. The increase in reaction rate is attributed to the rate limiting low solubility of the H$_2$, meaning that a reduction in catalyst loading equates to a higher relative concentration of H$_2$, and therefore a higher activity.

In conclusion, we have developed a new homogeneous catalytic approach to carbon dioxide hydrogenation to methanol using ruthenium catalysts and amine auxiliaries, the nature of both the catalyst but crucially the amine being essential for good performance. The figures of merit for this system are unprecedented, surpassing previous homogeneous catalysts for this transformation in terms of turnover number and frequency by at least an order of magnitude. Further mechanistic study and a wider screen of catalysts are underway.

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Notes and references


