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Highly productive CO₂ hydrogenation to methanol – a tandem catalytic approach via amide intermediates†

M. Everett  and D. F. Wass  *

A new system for CO₂ 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 [RuCl₂(Ph₂PCH₂CH₂NHMe)₂] catalyst with a diisopropylamine 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 C₁ feedstock source. The controlled reduction of carbon dioxide to methanol is an especially interesting goal.¹

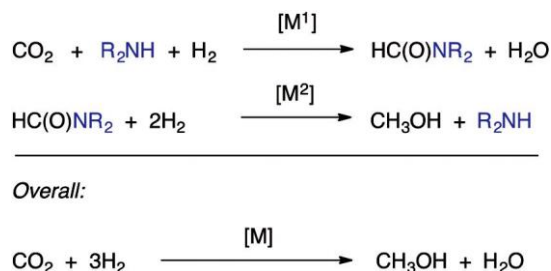
Heterogeneous catalysts for CO₂ reduction to methanol are well known and indeed CO₂ is implicated as an intermediate in commercial methanol production.² Homogeneous catalysts for this transformation are more unusual. The first reported example was by Tominaga and co-workers in 1993, using a Ru₃(CO)₁₂-KI 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. Nevertheless, we were inspired by this intriguing approach and reasoned that if an amine was used as an auxiliary instead of an alcohol (which is necessarily limited to methanol) we could investigate a much wider range of intermediate amides. This should allow us to fine tune the reactions to both form and hydrogenate this intermediate, giving us greater scope to make the various catalytic steps compatible (Scheme 1).

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 CO₂ 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.

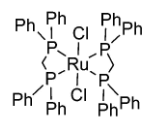
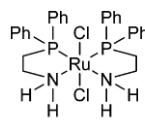
Studying the two parts of our proposed tandem catalytic system in turn, we initially examined the reaction of different



Scheme 1 Tandem catalytic approach to carbon dioxide hydrogenation to methanol using an amine auxiliary.

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Table 1 Catalysis results

<div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;"> $[\text{RuCl}_2(\text{PMe}_3)_4]$ 1 </div> <div style="text-align: center;">  2 </div> <div style="text-align: center;">  3 </div> </div>				
$\text{CO}_2 + n\text{H}_2 \xrightarrow[\text{NaOEt, toluene}]{[\text{M}], \text{R}_2\text{NH}} \text{HC(O)NR}_2 + \text{CH}_3\text{OH} + \text{H}_2\text{O}$				
Run	Precat.	Amine	Amide, mmol (TON) ^c [TOF h ⁻¹]	MeOH, mmol (TON) ^c [TOF h ⁻¹]
1 ^a	1	Me ₂ NH	72 (14 000) [700]	0.0 (0) [0]
2 ^a	2	Me ₂ NH	6.5 (1300) [65]	0.0 (0) [0]
3 ^b	2	Me ₂ NH	52 (10 000) [500]	0.0 (0) [0]
4 ^a	2	Et ₂ NH	3.8 (760) [38]	0.0 (0) [0]
5 ^a	2	¹ Pr ₂ NH	0.038 (7.5) [0.38]	0.0 (0) [0]
6 ^a	2	ⁿ Pr ₂ NH	0.071 (14) [0.70]	0.0 (0) [0]
7 ^a	2	Pyrrolidine	0.75 (150) [7.5]	0.0 (0) [0]
8 ^a	2	Et ₃ N	0.0 (0) [0]	0.0 (0) [0]
9 ^a	3	Me ₂ NH	0.62 (120) [6]	0.55 (110) [5.5]
10 ^b	3	Me ₂ NH	2.8 (550) [28]	1.9 (370) [18]
11 ^b	3	Et ₂ NH	1.3 (260) [13]	1.0 (200) [10]
12 ^b	3	Pr ₂ NH	0.0 (0) [0]	1.1 (220) [11]
13 ^b	3	¹ Pr ₂ NH	0.0 (0) [0]	12 (2300) [120]
14 ^b	3	Pyrrolidine	0.0 (0) [0]	3.0 (590) [30]
15 ^b	2/3	Me ₂ NH	3.7 (730) [37]	0.23 (46) [2.3]

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

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 (runs 2–7). As expected, no catalysis is observed with the tertiary amine Et₃N (run 8). It is noteworthy that no methanol, or other further hydrogenation product, is observed with catalyst 2; even at higher pressure of hydrogen (run 3) the amide is the final product. By contrast, catalyst 3 supported by P–N donor ligands, although more sluggish for the formation of DMF when dimethylamine is used as auxiliary (run 9), produces some methanol via the further hydrogenation of this amide even with 20 bar hydrogen pressure; increasing pressure to 30 bar produces significant quantities of methanol (run 10). The increase in the amount of amide formed from run 9 to run 10 can be attributed to the low solubility of H₂ in toluene relative to CO₂, meaning an increase in the partial

pressure of H₂ helps to increase the rate of H₂ transport to the active site.^{18–20}

As we hypothesised, the nature of the amine profoundly affects selectivity and performance, so that increasing the steric bulk to diethylamine gives a modest decrease in overall turn-over number but a further shift to towards methanol in terms of selectivity (run 11). Di-*n*-propylamine decreases turnover

number 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-*iso*-propylamine (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-*iso*-propylformamide 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

Table 2 Amide hydrogenation study

Run	Amide	MeOH, mmol (TON) [TOF h ⁻¹]
16	DMF	0.12 (23) [1.2]
17	DEF	0.75 (150) [7.5]
18	DIPF	1.1 (210) [11]

Conditions: 3 (5 mmol), NaOEt (0.15 mmol), amide (2 mL), toluene (10 mL), H₂ (30 bar), 180 °C, 20 h.

Table 3 Catalysis results comparing complexes 3–6

4 5 6

$$\text{CO}_2 + \text{nH}_2 \xrightarrow[\text{NaOEt, toluene}]{[\text{M}], \text{R}_2\text{NH}} \text{HC(O)NR}_2 + \text{CH}_3\text{OH} + \text{H}_2\text{O}$$

Run	Precat.	Amine	Amide, mmol (TON) ^c [TOF h ⁻¹]	MeOH, mmol (TON) ^c [TOF h ⁻¹]
19	3	Me ₂ NH	1.6 (320) [16]	1.2 (240) [22]
20	4	Me ₂ NH	1.7 (330) [17]	9.1 (1800) [90]
21	5	Me ₂ NH	2.2 (430) [22]	0.0 (0) [0]
22	6	Me ₂ NH	0.39 (77) [3.9]	0.0 (0) [0]
23	3	ⁱ Pr ₂ NH	0.0 (0) [0]	12 (2300) [120]
24 ^a	4	ⁱ Pr ₂ NH	0.0 (0) [0]	21 (4000) [2000]
25	5	ⁱ Pr ₂ NH	0.0 (0) [0]	0.0 (0) [0]
26	6	ⁱ Pr ₂ NH	0.0 (0) [0]	0.0 (0) [0]
27 ^b	3	ⁱ Pr ₂ NH	0.0 (0) [0]	0.25 (5100) [260]
28 ^{a,b}	4	ⁱ Pr ₂ NH	0.0 (0) [0]	0.44 (8900) [4500]

Conditions: precatalyst (5 mmol), NaOEt (0.15 mmol), amine (2 mL), toluene (10 mL), CO₂ (10 bar), H₂ (30 bar), 100 °C, 20 h. ^a 2 h. ^b 50 nmol precatalyst used. ^c Turnover number with respect to catalyst.

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-iso-propylamine, 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 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-iso-propylamine auxiliary led us to speculate that we might now be in the regime where catalytic 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 H₂, meaning that a reduction in catalyst loading equates to a higher relative concentration of H₂, 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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