Hydrogenation of CO₂ to Methanol with Mn-PNP-Pincer Complexes in the Presence of Lewis Acids: the Formate Resting State Unleashed

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Dedicated to Professor Christian Bruneau on the occasion of his 70th birthday.

The hydrogenation of CO₂ to methanol was achieved using a catalytic system comprising metal complexes of the form \( \text{Mn(CO)}_2 \text{[N(C}_2\text{H}_5\text{H}_P\text{Ph}_2]} \) (R = Pr, Ph, H)\( \text{[HN(C}_2\text{H}_5\text{H}_P\text{Ph}_2]} \) = MACHO–Ph) together with Lewis acid additives. Mechanistic studies suggest initial CO₂ insertion into a Mn–H bond leads to a formate complex as resting state. By systematically balancing the interaction between the acidic additive and the catalyst, the formate ligand could be removed through esterification to unleash the full catalytic potential. The reaction conditions were optimized on basis of the partial reaction order of relevant compounds. The combination of MACHO–Ph and Ti(OPr)₄ was identified as the most active system with a TON of 160 \((p(\text{CO}_2) = 5 \text{ bar}, p(\text{H}_2) = 160 \text{ bar}, T = 150 ^\circ \text{C})\). Using methanol as solvent and co-reagent allows the catalytic conversion of CO₂/ H₂ in a liquid phase process comprising only the substrates and products.

Methanol from renewable resources is a key compound to establish a sustainable energy/chemistry nexus.[1] The production of methanol from CO₂ and green hydrogen in gas phase processes over heterogeneous catalysts is pursued on pre-industrial scale already[2] and the fundamental bond breaking and bond forming processes at catalyst surfaces are widely investigated.[3] In contrast, very few molecular catalysts are known to affect this transformation in liquid phase and systematic studies to unravel the mechanistic principles and control factors have started only most recently.[4] In the present paper, we report the design of a catalytic system based on a Manganese pincer-type complex using a rational approach to unlock the potential for catalytic turnover (Scheme 1). The key factor is the application of suitable Lewis-acids as co-catalysts to avoid the blockage of the active site by a formate anion through its conversion into a formate ester intermediate. If methanol is used as the esterification reagent and solvent, the overall process corresponds to direct “breeding” of methanol from CO₂ and H₂ without any additional co-reactant. The direct hydrogenation of CO₂ and H₂ to form methanol is very challenging. Currently, only complexes bearing the triphos-

Previous work: Prakash et al.

\[
\text{CO}_2 + \text{HNR}_2 + \text{H}_2 \xrightarrow{1} \text{H}_2\text{O} \xrightarrow{1} \text{CO}_2 + \text{H}_2 \xrightarrow{1} \text{CH}_3\text{OH} + \text{HNR}_2 \\
\text{TON 36}
\]

This work:

\[
\text{CO}_2 + 3 \text{H}_2 \xrightarrow{2 \text{ or } 3 \text{ and Ti(O} \text{OPr}_4)} \text{ROH (R = Me, Et)} \xrightarrow{150 ^\circ \text{C}} \text{CH}_3\text{OH} \\
\text{TON up to 160}
\]

Scheme 1. Hydrogenation of CO₂ to methanol using manganese complexes.

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Most recently, we found that complex 1 was highly active for the hydrogenation of carbon monoxide (CO) to methanol.[13] The reaction proceeds via formate intermediate formed under the basic reaction conditions from ROH and CO. Initial attempts in our laboratories to use a similar strategy starting from CO$_2$, H$_2$ and ROH gave no or only marginal yields of MeOH, however. We systematically investigated which step of the presumed reaction sequence was responsible for the blocking of the overall catalytic cycle. While the activated complex 2 was capable to hydrogenate ethyl formate under the given conditions as expected,[13] no conversion of the ester was observed in the presence of 20 bar CO$_2$. The inhibiting effect of CO$_2$ could be associated with the formation of the pale yellow formate complex 4 that was identified after precipitation from the reaction mixture by comparison to literature data (Scheme 2).[14] Complex 4 exhibits a $^{31}$P-NMR signal at 86.5 ppm (singulet) and C–O vibrational modes at 1907 cm$^{-1}$ and 1822 cm$^{-1}$, consistent with an $\eta^1$ bonded formate ligand engaging in a H-bridge at the non-innocent ligand framework.

In line with previous observations,[8a,10a,6] the formate complex 4 can be presumed as the limiting resting state where the strong coordination of the carboxylate prevents activation of H$_2$ for further catalytic turnover. A possible way to unlock this hindrance would be to remove the formate ligand by esterification with an alcohol co-reagent in presence of a Bronsted or Lewis acidic additive. The counterion introduced by the additive must show a balanced binding affinity to stabilize the complex and yet allow for the H$_2$ activation. We therefore studied the interaction of different additives with the in situ generated active species 2 and their influence on the catalytic performance of the Mn–Pr-MACHO framework (Scheme 3).

The analogous carboxylate complex 5 was obtained from 2 and adamantylcarbonic acid and proved equally inactive. Treatment of 2 with the Lewis acid Sc(OTf)$_3$ resulted in complex 6. While the OTf anion is generally presumed as weakly coordinating, the $^{19}$F shift of 6 indicates a similar coordination as in the Br-complex 1. Consequently, the presence of OTf also shuts down the hydrogenation reaction. Finally, Ti(OPr)$_3$ was employed, which left around 63% of the activated complex 2 in solution and formed 35% of the alcoholate complex 7. As both complexes have previously been reported as intermediates in hydrogenation reactions,[11d] Lewis acids with alcoholate counterions should not interfere strongly with the catalytically active species 2.

Preliminary experiments using manganese catalyst 2 combined with Ti(OPr)$_3$ for the hydrogenation of CO$_2$ in a 1:1 mixture of EtOH and 1,4-dioxane confirmed this assumption (Table 1). Methanol and small amounts of ethyl formate were detected and quantified by $^1$H-NMR analysis of the reaction mixture. A TON of 19 towards methanol was observed at temperatures above 150°C. Control experiments showed that the Mn-catalyst is essential for the reaction (Table 1, Entry 4) as the activation. Ti(OPr)$_3$ was employed, which left around 63% of the activated complex 2 in solution and formed 35% of the alcoholate complex 7. As both complexes have previously been reported as intermediates in the reaction mixture by comparison to literature data (Scheme 2).[14] Complex 4 exhibits a $^{31}$P-NMR signal at 86.5 ppm (singulet) and C–O vibrational modes at 1907 cm$^{-1}$ and 1822 cm$^{-1}$, consistent with an $\eta^1$ bonded formate ligand engaging in a H-bridge at the non-innocent ligand framework.

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from 4 to restore the catalytic activity. The reaction rate for the formate ester hydrogenation increased only by a factor of 1.5 upon addition of Ti(OPr)$_3$ (see SI for further details), supporting further the cleavage of the formate species from the Mn catalyst as the dominant contribution of the Lewis acid.

The mechanistic picture is further supported by the reaction kinetics as determined by the initial rates method (see SI for further details). The partial reaction order for hydrogen is unity as well as for Ti(OPr)$_3$ and EtOH as alcohol and negative unity for CO$_2$. The latter supports the inhibiting role of the formic acid as a turnover limiting intermediate formed by the (reversible) insertion of CO into the Mn–H bond. For the forward reaction, the additive Ti(OPr)$_3$ needs to remove the formate ligand from the metal center through esterification. The presence of the alcohol is required to enable the esterification and therefore enhances the rate at low concentrations before reaching pseudo-zero-order behavior at higher amounts. This originates from hydrogenation-dehydrogenation equilibria that are well studied for these kind of manganese complexes.$^{[11]}$

Another alcoholate based Lewis acid, Sc(OPr)$_3$, was also tested in the reaction (Table 2, Entry 1). This improved the initial reaction rate slightly but led to less methanol compared to Ti(OPr)$_3$ (Table 2, Entry 2). Presumably, the maximum yield is limited by hydrolysis of the Lewis acid due to the stoichiometric amounts of water formed from CO$_2$ hydrogenation. The TON stayed nearly constant at 30–40 as the catalyst concentration was stepwise decreased to 5 μmol/L (Table 2, Entry 5–6).

The substituents at the phosphorous in the ligand structure also showed a pronounced effect on the catalyst's performance (Table 2, Entry 2–4). The phenyl derivative 3 resulted in an improved activity compared to 2 with a 22% increase in the methanol yield (Table 2, Entry 2–3). In contrast, the very bulky tert-butyl substituted complex 8 gave no conversion to methanol (Table 2, Entry 4), probably due to a lack of activity in the hydrogenation of the formate ester intermediate.

In line with the catalytic activity of Mn–MACHO complexes for CO hydrogenation,$^{[12,13]}$ 3 shows a high tolerance towards the presence of CO (Table 2, Entry 7). Even with additional 5 bar of CO, a high yield of methanol was obtained. This is a clear benefit as compared to the cobalt$^{[6b]}$ and ruthenium-triphos$^{[8g,17]}$ systems, where only small amounts of CO even below 0.25 bar partial pressure lead to deactivation of the catalysts due to formation of carbonyl complexes. In contrast, 3 is already a dicarbonyl complex and seems to have a low affinity for the coordination of any additional CO ligands.$^{[15]}$

The inverse dependence of the reaction rate on the initial CO$_2$ pressure could be exploited by further decreasing the CO$_2$/H$_2$ ratio and total pressure (Table 2, Entry 8). This led to a TON of 81 after 68 h. A further increase in hydrogen pressure led to a TON of 87 at 5 bar CO$_2$ pressure (Table 2, Entry 9). No further increase of the TON was reached, when the reactor was re-pressurized and the reaction continued (see SI for further details). If fresh Lewis Acid was added in between two runs the TON was increased to 110, which supports the hypothesis of Lewis acid hydrolyzation as major source of deactivation.

| #  | T [°C] | n(MeOH)$^{[a]}$ [mmol] | n(HCOOEt)$^{[a]}$ [mmol] | TON(MeOH) |
|----|--------|------------------------|--------------------------|-----------|
| 1  | 140    | 0.40                   | 0.31                     | 10        |
| 2  | 150    | 0.76                   | 0.23                     | 19        |
| 3  | 160    | 0.00                   | 0.10                     | 19        |
| 4$^{[b]}$ | 150    | 0.00                   | 0.00                     | –         |
| 5$^{[c]}$ | 150    | 0.00                   | 0.00                     | –         |
| 6$^{[d]}$ | 150    | 0.13                   | 0.11                     | 3         |

[a] Reaction conditions: 2 (0.04 mmol), Ti(OPr)$_3$ (0.16 mmol), 10 bar CO$_2$, 90 bar H$_2$, 1:1 mixture of 1,4-dioxane/EtOH (2 mL) for 68 h. (b) yield determined by $^1$H-NMR in CDCl$_3$ with mesitylene as internal standard. [c] no manganese complex was used. [d] pure 1,4-dioxane (2 mL) was used as solvent without EtOH.

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Having established the catalytic system Mn-complex/Lewis acid with ethanol as the esterification reagent, we turned to other alcohols (see SI for further details), of which methanol as co-reagent resulted in the highest activity. In order to quantify the methanol generated from CO\textsubscript{2} hydrogenation, 5 bar of CO\textsubscript{2} was used as feed gas. A TON of 160 was obtained using a mixture of methanol and 1,4-dioxane as solvent, which is even higher than with EtOH under identical conditions (Scheme 5, I, Table 2, Entry 9). Using solely methanol as the co-reagent and solvent led still to a TON of 120 (Scheme 5, II).

In conclusion, this study presents a catalytic system for direct “breeding” of methanol from CO\textsubscript{2} and H\textsubscript{2} using a molecular complex of earth-abundant and cheap manganese. The possibility to use the product alcohol as solvent eliminates the necessity for any additional co-reagent in the reaction mixture. The obtained TONs compare favorably with those obtained for indirect or direct CO\textsubscript{2} hydrogenation to methanol with other 3d metals.\textsuperscript{[10b]} The catalytic system was developed from mechanistic studies involving spectroscopic identification of potential intermediates, kinetic studies, and labelling experiments. The results confirm that the catalytic turnover is blocked at the formate stage through formation of a carboxylate complex as limiting resting state. The synergistic interplay of the Mn-PNP-complex and an alcoholate based Lewis acid was identified as crucial element to unlock the catalytic potential by transferring the formate ligand into an ester intermediate. Further studies should therefore focus on a systematic approach to improve the cooperativity within the catalytic system with the goal to establish an efficient liquid phase process for CO\textsubscript{2} hydrogenation to methanol or products on the methanol reduction level.

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Conflict of Interest

The authors declare no conflict of interest.

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