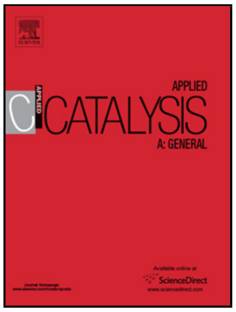

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Synthesis of *N,N*-dimethylformamide from carbon dioxide in aqueous biphasic solvent systems

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Graphical Abstract

<InlineImage1>

Highlights

- CO_2 is hydrogenated to formate and condensed with an amine to yield formamides
- The immobilization of a homogeneous catalyst in nonpolar solvents is investigated
- Catalyst complex formation and product separation are performed in-situ
- Several recycling runs demonstrate the concept and the catalyst stability towards air

Abstract

This paper presents the homogeneous catalyzed hydrogenation of carbon dioxide to *N,N*-dimethylformamide (DMF) with an in-situ generated ruthenium catalyst based on $RuCl_3 \times H_2O$ and the phosphine ligand 2,2’-bis(diphenylphosphinomethyl)-1,1’-biphenyl (BISBI). Investigations showed that the complex formation of an active species requires the presence of an amine. The catalyst was recycled by immobilization in a nonpolar alcoholic solvent while the formed product was extracted in-situ into the aqueous phase. The self-assembling reaction system showed stability for 10 recycling runs without a significant loss of activity resulting in an average yield of 31% DMF at 40 bar and 140 °C without the occurrence of any byproducts. Furthermore, a combination of the developed reaction system with ternary amines enables the application of wash amine solutions as carbon dioxide carrier.

Keywords: Carbon dioxide; hydrogenation; formamide; homogeneous catalysis; catalyst recycling

1. Introduction

The utilization of carbon dioxide as universal C_1-building block is of high ecological and economical interest and investigated for several decades [1–6]. Especially the hydrogenation of carbon dioxide was researched in detail since it allows to broaden the product diversity due to the possible change of the carbon atom's oxidation state [7–10]. Interesting hydrogenation products are formic acid or formic acid derivatives like formamides. Especially *N,N*-dimethylformamide (DMF) can be used as intermediate, e.g. for the synthesis of isocyanates, or directly as excellent solvent [11–14]. The first synthesis of *N,N*-dimethylformamide by carbon dioxide hydrogenation was performed in 1970 by Haynes et al. with different metal complexes [15]. The hydrogenation is reported to accompany with a formate salt as intermediate (Figure 1) [16,17]. Especially, the condensation of formic acid salts requires higher pressures or temperatures to yield formamides with better turnover numbers [18]. Nevertheless, recent developments of complex tailor-made catalysts lead to high activities at milder reaction conditions and show that even non precious metals like iron and cobalt can be applied [19,20].

The industrial formamide synthesis consists of the alcoholate catalyzed carbonylation of amines with carbon monoxide. In order to establish a competitive carbon dioxide based process, a high recycling efficiency of the more expensive hydrogenation catalyst is indispensable for a technical application. However, the long-time stability of most developed homogeneous catalyst systems has not been proven yet. Only Ding et al. recently reported a recycling concept for a homogeneous catalyst where the product DMF is vacuum distilled out of the ruthenium catalyst solution resulting in 12 batch recycling runs without a significant loss in activity but limiting this concept to low boiling products [21]. The separation of catalyst and synthesized formamide is at all a difficult task because formamides are generally excellent solvents for a broad variation of components [11].

An attractive method for a homogeneous catalyst recycling is the immobilization of the dissolved catalyst in a liquid solvent since the catalyst stays in an active environment [22]. For an efficient immobilization, the catalyst should be insoluble in the product phase while the catalyst-solvent is not soluble in the product phase. A general approach to this problem is the application of a catalyst and solvent that have a maximum polarity difference to the formed product so that a second phase is automatically formed. However, an insolubility of the substrate inside the catalytic liquid phase leads to mass transfer problems so that a compromise between reactivity and recyclability has to be made in a liquid liquid two phase system. Nevertheless, due to its efficiency this recycling concept has already found applications in industrial processes like the Ruhrchemie-Rhône-Poulenc process and the SHOP-process where the products form a separate phase [23,24]. In these applications the catalysts are immobilized in polar solvents, since products like aldehydes or α-olefins are rather nonpolar.

Based on this idea we developed a liquid-liquid biphasic reaction system for the synthesis of *N,N*-dimethylformamide as model formamide product. Unlike in the industrial examples, the catalyst has to be immobilized in a nonpolar solvent as many formamides are polar aprotic solvents [11]. In order to guarantee a sufficient catalyst separation, water is used as product extraction agent since it is formed as byproduct in the condensation step anyway and has to be removed. The general application of this concept should be verified by the utilization of an in-situ generated catalyst system consisting of the polar precursor ruthenium(III)chloride hydrate and 2,2'-bis(diphenylphosphinomethyl)-1,1'-biphenyl (BISBI) as commercial nonpolar phosphine ligand. Desired is the formation of a catalyst complex [Ru] that stays in the organic solvent phase (step I in Figure 2) and catalyzes the hydrogenation reaction selectively (step II, Figure *2*).

2. Experimental

2.1. Materials

All applied solvents and the dimethylamine solution (40 wt.% in water) were purchased from Acros Organics in standard purity. Ruthenium(III)chloride monohydrate (99.9% on metal basis, 38-40 wt.% ruthenium) and BISBI (99%) were purchased from ABCR. All chemicals were used as delivered without any further purification.

2.2. Catalytic experiments and sampling

At first, the desired amount of ruthenium precursor and ligand were weighted on a precision scale and transferred into the reaction vessel. The solvent and subsequently the aqueous amine-solution were added directly into the autoclave with a precision of 0.01 g. Afterwards, the reactor was sealed and the gas phase was flushed with argon. The reactor was pressurized with the desired hydrogen and carbon dioxide pressures and the reaction was started by heating to the desired temperature. In case of a perturbation experiment, two hours of preforming duration were performed, before the actual reaction was started with all components.

After the desired reaction time the reactor was cooled to ambient temperature and degassed, if not other stated. Subsequently, the biphasic reaction mixture was split in a tempered separating funnel and each phase was weighted and analyzed. In the case of a recycling experiment, the organic phase was returned to the reactor without any sampling of this phase.

Two different reactor types were used which were made out of stainless steel 316 L. The first reactor type contained a volume of 22 ml and is stirred via a magnetic bar while the second reactor, purchased from Parr Instrument GmbH, held a total volume of 300 ml and was stirred via a magnetically coupled stirrer motor. Both reactor types were electrically heated with a temperature deviation below 2 K.

2.3. Analysis

The amount of synthesized DMF was measured gas chromatographically (Agilent 6890) by a thermal conductivity detector. The GC was equipped with an Innowax column (30 m, 250 µm, 0.25 µm) and dimethyl sulfoxide was used as internal standard. The turn-over-number (TON_i) of carbon dioxide to a component i and the degree of extraction were calculated with the following equations (1) and (2).

$$\mathrm{TON}_i = \frac{n_i}{n_{\mathrm{ruthenium}}} \tag{1}$$

$$E_i(\%) = \frac{n_{\mathrm{i,aqueous\ phase}}}{n_{\mathrm{i,total}}} \tag{2}$$

The measurement of formic acid was performed by HPLC (Hitachi Lachrom Elite) with an UV/Vis detector at 207 nm. Acidic water (pH 2.2 adjusted by H_3PO_4) and acetonitrile at a volume ratio of 98:2 were used as mobile phase with a total flow rate of 1.5 ml/min over a Zorbax XDB-C8 stationary phase (150 mm, 4.6 mm, 5 µm) with propionic acid as internal standard. The column temperature was set to 413 K. The amount of ruthenium and phosphorous compounds were measured with ICP-AES (Iris Intrepid from Thermo Elemental) and according standard solutions as reference. The leaching of a catalyst component was calculated via equation (3).

$$\text{Ru-Loss}\ (\%) = \frac{n_{\mathrm{Ru,aqueous\ phase}}}{n_{\mathrm{Ru,applied}}} \tag{3}$$

3. Results and Discussion

3.1. Design of a biphasic solvent system

In homogeneous catalysis, the first step for the development of an efficient catalyst immobilization in a biphasic solvent system is the identification of suitable solvents. The investigated polar substrate dimethylamine (DMA) is already applied as 40 wt.% aqueous solution so that a suitable nonpolar solvent for the catalyst immobilization is necessary. In order to balance out a sufficient solubility of the substrate dimethylamine in the catalytic phase and a good recyclability of the ruthenium catalyst, several nonpolar solvents with different water solubility were investigated in the ruthenium catalyzed hydrogenation reaction (Table 1).

Table 1: Variation of the nonpolar solvent

Entry	Solvent	Water solubility (g/l)	X_{DMA} (%)	Y_{DMF} (%)	E_{DMF} (%)	Ru-Loss (wt.%)
1	Octane	0.001	5	5	98	10
2	Anisole	0.14	9	9	64	15
3	Di-*n*-butylether	0.3	9	9	94	86
4	Toluene	0.52	10	10	78	19
5	2-Ethylhexan-1-ol	0.6	22	22	55	9
6	Benzyl alcohol	39	21	21	21	3

Reaction conditions: $V_{reactor}$ = 22 ml, V_{liquid} = 5 ml, T_R = 120 °C, $c_{Ru.}$ = 2 mmol/l c_{BISBI} = 2 mmol/l, c_{DMA} = 3.9 mol/l, p_{CO_2/H_2}.= 20/20 bar, t_R = 16 h, V_{DMA/H_2O} : $V_{organic\ solvent}$ = 1:1, U = 500 1/min

The screening revealed that very water insoluble compounds, as aliphatic hydrocarbons are not suitable as catalyst solvents because they do not dissolve the substrate and additionally lead to a precipitation of ruthenium. A minimal water solubility increases the yield of DMF significantly. Especially alcohols form a stable catalytic phase with the highest activities. A reason for the higher activity might be that the alcohol acts as reducing agent for the ruthenium(III)chloride hydrate to form an active ruthenium(II) species. General procedures for ex-situ syntheses of ruthenium complexes with $RuCl_3$ x H_2O utilize alcohols like ethanol as reducing agent whereby the corresponding aldehydes are formed [25,26]. Traces of aldehydes were not observed since the ruthenium species is highly active for the aldehyde reduction to alcohols (see supporting info for details).

A higher water solubility of benzyl alcohol does not benefit the reaction anymore and leads to an unsatisfactory product distribution where 79 wt.% of the formed DMF stays in the catalytic phase. In conclusion, benzyl alcohol does not fulfill the separation between catalyst and product anymore even though the catalyst leaching is with 3 wt.% of ruthenium minimal. That is why 2-ethylhexan-1-ol delivers the best combination of reactivity, extraction efficiency and catalyst leaching.

3.2. Investigation of the in-situ catalyst complex formation

Further investigations with 2-ethylhexan-1-ol (EH) as solvent were made regarding the in-situ generated catalyst system in order to understand and optimize the catalyst formation. Literature known synthesized catalyst complexes start of a pre-coordinated ruthenium-phosphine ligand complex which can contain different ligand to precursor ratios [8,17,27]. In our case both catalyst components are initially located in different solvent phases. The applied hydrophilic ruthenium(III)-precursor $RuCl_3$ x H_2O has to be transferred into the nonpolar solvent. A ruthenium to ligand screening was performed in order to find an optimum ratio of both components (Figure 3).

Reaction conditions: Precursor: $RuCl_3 \cdot xH_2O$, Ligand: BISBI, $V_{reactor}$ = 22 ml, V_{liquid} = 5 ml, T_R = 120 °C, c_{DMA} = 3.8 mol/, p_{CO_2}/p_{H_2}.= 20/20 bar, t_R = 16 h, $V_{DMA\text{-}solution}$:V_{EH} = 1:1, U = 500 1/min

The results of these experiments show that a small excess over a 1:1 ratio of either precursor or ligand (yellow bars) leads to complexes with the highest activities. This indicates that the active species only requires about one mole bidentate phosphine ligand per mole ruthenium, which matches investigations of Li et al. [28]. The small excess of one component could be necessary to fully utilize the amount of the other component. A bigger excess of ruthenium or ligand can lead to an enhanced formation of inactive or less active catalytic species. While a higher excess of ligand might shield the metal center from the substrate, an excess of ruthenium could lead to a formation of multinuclear ruthenium complexes (Figure 4) [29]. The formation of ruthenium clusters might occur since the initially applied ruthenium trichloride hydrate usually comes as a chloro-bridged crystal [30,31] that has to be broken down into single ruthenium complexes. Thus, much higher concentrations of ruthenium could lead to an increasing probability of the formation of clusters.

The application of a ruthenium : ligand ratio of 1.25:1 does not lead to a higher leaching since more than 90 wt.% of the ruthenium are transferred into the nonpolar alcoholic phase and additionally result in highest activities.

Further investigations were made with a small ruthenium excess referring to the complex formation. Perturbation experiments were performed in which one or more components were missing for 2 h under reaction conditions (preforming conditions). After this duration, the reaction was induced by adding the remaining components. This should demonstrate which other components, except precursor and ligand, take a role in the complex formation, as the formation of unreactive catalyst complexes should be minimized.

Table 2: Results of the perturbation experiments with additional 2 h of preforming duration

Entry	Preforming conditions			X_{DMA} (%)	Y_{DMF} (%)	TON_{DMF}	$TON_{Formate}$
	Amine	CO_2	H_2				
1	no preforming			14	14	218	192
2	-	+	+	1	1	25	< 10
3	+	-	+	9	9	144	141
4	+	+	-	17	17	254	223
5	-	+	-	1	1	21	< 10

Reaction conditions: Precursor: $RuCl_3 \cdot xH_2O$, Ligand: BISBI, $c_{Kat.}$ = 2.5 mmol/L, $c_{Lig.}$ = 2.0 mmol/L, p_{CO_2}/p_{H_2} = 20/20 bar, T_R = 120 °C, c_{DMA} = 3.8 mol/L, $m_{DMA\text{-}solution}:m_{EH}$ = 1:1, $V_{reactor}$ = 300 mL, V_{liquid} = 75 mL, U = 700 1/min, $t_{preforming}$ = 2 h ,t_R = 5 h

The perturbation experiments show that the amine plays a decisive role in the formation of the catalytic species. The initial absence of amine leads to a formation of black ruthenium precipitates which are inactive for the hydrogenation reaction and could not be reconverted into a catalytic form even though amine was added after the preforming duration (Table 2, Entry 2+5). Most likely is the reduction of the ruthenium chloride with the alcohols to ruthenium nanoparticles (Figure *5*, pathway I) [32]. Since the amine can work as nitrogen-ligand, it could lead to a stabilization of ruthenium intermediates that are afterwards converted to the active species with BISBI (Figure 5, pathway II).

Moreover, carbon dioxide has a minor positive effect on the complex formation whereas the absence of hydrogen has no effect at all. Due to the negligible increase in product yield with regard to the added preforming duration, further investigations were made without an additional preforming.

3.3. Optimization of the reaction system

In order to increase the activity of the reaction system, the reaction conditions were varied. A closer look on the product composition reveals that a significant amount of the intermediate formate is still in the solution (Table 2, Entries 1+4). This indicates that the condensation step for the amide-formation is slower under the reaction conditions of 120 °C. A temperature screening confirmed that the condensation of the formate salt benefits from higher temperatures (Figure 6).

Reaction conditions: Precursor: $RuCl_3{\cdot}xH_2O$, Ligand: BISBI, c_{Ru} = 2.5 mmol/L, c_{BISBI} = 2.0 mmol/L, $p_{CO_2}/p_{H_2.}$= 20/20 bar, c_{DMA} = 3.8 mol/L, $m_{DMA\text{-}solution}$:m_{EH} = 1:1, $V_{reactor}$ = 300 mL, V_{liquid} = 75 mL, U = 700 1/min, t_R = 5 h

Especially an increase of the temperature to 140 °C leads to a much faster formation of DMF whereas a lower temperature primary results in the intermediate. The ruthenium leaching was with 3 wt.% lower than in previous investigations. Higher reaction temperatures might convert more of the ruthenium trichloride into a nonpolar catalytic species. Noteworthy is, that the catalyst is stable up to 160 °C for at least one reaction sequence. Only at 180 °C, a white precipitate was observed which indicates a ligand decomposition. The yield time plots in Fig. 6 show that a maximum yield of 30 – 35% can be achieved under these conditions before the reaction rate turns towards zero. A high initial consumption of reaction gas could be observed since the pressure decreased to 30 bar in the first hour. Several pressure variations show a linear dependency between applied pressure and product yield so that a pressure reduction is not reasonable (see supporting information for details).

3.4. Recycling of the homogeneous catalyst

After we gained a better understanding of the self-assembling catalyst system and optimized reaction conditions resulting in a yield of 32% after 5 h, recycling experiments were performed with a reaction temperature of 140 °C. After each batch reaction, the nonpolar alcoholic phase was separated from the aqueous product phase and reused without any further addition of precursor, ligand or solvent. Only aqueous amine solution was added after each batch run.

Reaction conditions: Precursor: $RuCl_3{\cdot}xH_2O$, Ligand: BISBI, c_{Ru} = 2.5 mmol/L, c_{BISBI} = 2.0 mmol/L, $p_{CO_2}/p_{H_2.}$= 20/20 bar, c_{DMA} = 3.8 mol/L, $m_{DMA\text{-}solution}$:$m_{2\text{-}Ethylhexan\text{-}1\text{-}ol}$ = 1:1, $V_{reactor}$ = 300 mL, V_{liquid} = 75 mL, U = 700 1/min, T_R = 140 °C, t_R = 5 h, $t_{separation}$ = 1 h, $T_{separation}$ = 10 °C *) $T_{separation}$ = 25 °C

An analysis of the aqueous liquid revealed a stability of the reaction system of at least 10 runs with an average yield of 31% DMF (Figure 7). An optimized separation temperature of 10 °C lead to an enhanced product extraction degree of 65%. The loss of catalyst could be reduced to about 1.5 wt.% in the 3rd-5th run. However, an increased separation temperature of 25 °C in the last 5 runs shows that especially the ruthenium leaching is temperature dependent so that a low separation temperature should be favored. Noteworthy, the evolved catalyst system is stable towards oxygen since no extra precautions towards air were made during the separation steps. The amount of lost alcohol is with less than 0.3 wt.% insignificantly low. After ten runs only 1.6 wt.% of 2-ethylhexan-1-ol were lost while a total turnover number of 4942 could be achieved.

3.5. Application of ternary amines as carbon capture components

The developed biphasic reaction system allows further process intensification. In industry, the added gaseous carbon dioxide is usually captured by an absorption process in a gas scrubber [33]. By applying aqueous wash amine solutions, e.g. in coal-fired power plants, CO_2 can be absorbed out of flue gas in sufficient purities [34,35]. A combination of carbon dioxide capture and reaction would save the energy, which is usually required for the wash amine regeneration. Since primary and secondary amines can be converted into formamides as well, some ternary amines with different solubility and functionality were investigated for compatibility.

Table 3: Reaction results with an addition of a ternary amine

Entry	Added ternary Amine	Water solubility (g/l)	Y_{DMF} (%)	Ru-Loss (wt.%)	P-Loss (wt.%)
1	none	-	32	3	3
2	2-Dibutylaminoethanol	11.6	31	5	5
3	*N*,*N*-Dimethylbutylamine	37	34	4	7
4	2-Dimethylaminoethanol	limitless	36	5	6

Reaction conditions: Precursor: $RuCl_3·xH_2O$, Ligand: BISBI, c_{Ru} = 2.5 mmol/L, c_{BISBI} = 2.0 mmol/L, p_{CO_2}/p_{H_2} = 20/20 bar, c_{DMA} = 3.8 mol/L, $c_{ternary\ amine}$ = 2 mol/L, $m_{DMA\text{-}Solution}:m_{EH}$ = 1:1, $V_{reactor}$ = 300 mL, V_{liquid} = 75 mL, U = 700 1/min, T_R = 140 °C, t_R = 5 h

All three added amines result in a comparable reactivity with a yield of DMF between 31 - 36% and no byproducts were observed in the reaction with the additional amines. The catalyst leaching did not increase significantly, no matter which polarity the amine has. Thus, a general applicability of wash amine solutions could be demonstrated.

4. Conclusions

An efficient catalyst recycling concept for the homogeneous catalyzed hydrogenation of carbon dioxide to *N,N*-dimethylformamide with an in-situ generated catalyst system consisting of commercial available components like ruthenium(III)chloride hydrate has been developed. By applying a liquid-liquid biphasic reaction system comprising 2-ethylhexan-1-ol as catalyst solvent and water as product extraction agent over 97 wt.% of the catalyst could be recycled.

The reaction system showed a stable activity for at least ten runs resulting in an average yield of 31% DMF and a total turnover number of 4942. Investigations on the in-situ formation of the catalyst complex revealed that the amine has a significant influence on the catalyst formation and that a small excess of ligand or precursor over a 1:1 ratio leads to higher activities. Furthermore, a higher reaction temperature of 140 °C results in a faster condensation of the formate intermediate. The developed reaction setup allows further process intensification since the aqueous solution could be combined with wash amines. This enables the possibility for a combination of a gas scrubber and a reactor so that carbon dioxide can be converted out of flue gas without further purification steps.

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References

[1] A. Behr, S. Neuberg, Erdöl Erdgas Kohle 125 (2009) 367–374.

[2] M. Aresta, A. Dibenedetto, A. Angelini, Chem. Rev. 114 (2014) 1709–1742.

[3] M. Cokoja, C. Bruckmeier, B. Rieger, W.A. Herrmann, F.E. Kühn, Angew. Chem. 123 (2011) 8662–8690.

[4] A. Dibenedetto, A. Angelini, P. Stufano, J. Chem. Technol. Biotechnol. 89 (2014) 334–353.

[5] M. Hölscher, C. Gürtler, W. Keim, T.E. Müller, M. Peters, W. Leitner, Z. Naturforsch. B 67b (2012) 961–975.

[6] A. Behr, Angew. Chem. 100 (1988) 681–698.

[7] J. Klankermayer, S. Wesselbaum, K. Beydoun, W. Leitner, Angew. Chem. 128 (2016) 7416–7467.

[8] J.L. Drake, C.M. Manna, J.A. Byers, Organometallics 32 (2013) 6891–6894.

[9] P.G. Jessop, F. Joó, C.-C. Tai, Coord. Chem. Rev. 248 (2004) 2425–2442.

[10] C.A. Huff, M.S. Sanford, ACS Catal. 3 (2013) 2412–2416.

[11] H. Bipp, H. Kieczka, (2011), Formamides in: Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH, Weinheim.

[12] S. Ding, N. Jiao, Angew. Chem. 124 (2012) 9360–9371.

[13] T. Mattke, E. Ströfer, J. Leschinski, R. Abdallah, A. Franzke, M. Bock, WO2011067369 A1 (2009), BASF SE.

[14] K. Halbritter, M. Eggersdorfer, K. Brenner, EP0106038 B1 (1982), BASF Aktiengesellschaft.

[15] P. Haynes, L.H. Slaugh, J.F. Kohnle, Tetrahedron Lett. 11 (1970) 365–368.

[16] P.G. Jessop, Y. Hsiao, T. Ikariya, R. Noyori, J. Am. Chem. Soc. 116 (1994) 8851–8852.

[17] A. Behr, P. Ebbinghaus, F. Naendrup, Chem. Eng. Technol. 27 (2004) 495–501.

[18] P.G. Jessop, T. Ikariya, R. Noyori, Chem. Rev. 95 (1995) 259–272.

[19] C. Ziebart, C. Federsel, P. Anbarasan, R. Jackstell, W. Baumann, A. Spannenberg, M. Beller, J. Am. Chem. Soc. 134 (2012) 20701–20704.

[20] C. Federsel, C. Ziebart, R. Jackstell, W. Baumann, M. Beller, Chem. Eur. J. 18 (2012) 72–75.

[21] L. Zhang, Z. Han, X. Zhao, Z. Wang, K. Ding, Angew. Chem. 127 (2015) 6284–6287.

[22] A. Behr, P. Neubert, Applied homogeneous catalysis, Wiley-VCH, Weinheim, 2012.

[23] C.W. Kohlpaintner, R.W. Fischer, B. Cornils, Appl. Catal., A 221 (2001) 219–225.

[24] W. Keim, Angew. Chem. Int. Ed. 52 (2013) 12492–12496.

[25] M. Bressan, P. Rigo, Inorg. Chem. 14 (1975) 2286–2288.

[26] J. Chatt, R.G. Hayter, J. Chem. Soc. (1961) 896–904.

[27] C. Federsel, R. Jackstell, M. Beller, Angew. Chem. 122 (2010) 6392–6395.

[28] R.-X. Li, K.-C. Tin, N.-B. Wong, T.C. Mak, Z.-Y. Zhang, X.-J. Li, J. Organomet. Chem. 557 (1998) 207–212.

[29] K. Mauthner, D. Kalt, C. Slugovc, K. Mereiter, R. Schmid, K. Kirchner, Monatsh. Chem. 128 (1997) 533–540.

[30] J.M. Fletcher, W.E. Gardner, A.C. Fox, G. Topping, J. Chem. Soc. A 0 (1967) 1038–1045.

[31] R.D. Johnson, S.C. Williams, A.A. Haghighirad, J. Singleton, V. Zapf, P. Manuel, I.I. Mazin, Y. Li, H.O. Jeschke, R. Valentí, R. Coldea, Phys. Rev. B 92 (2015).

[32] X. Yan, H. Liu, K.Y. Liew, J. Mater. Chem. 11 (2001) 3387–3391.

[33] G.T. Rochelle, Science 325 (2009) 1652–1654.

[34] B.P. Spigarelli, S.K. Kawatra, J. CO2 Util. 1 (2013) 69–87.

[35] H. Yang, Z. Xu, M. Fan, R. Gupta, R.B. Slimane, A.E. Bland, I. Wright, J. Environ. Sci. 20 (2008) 14–27.

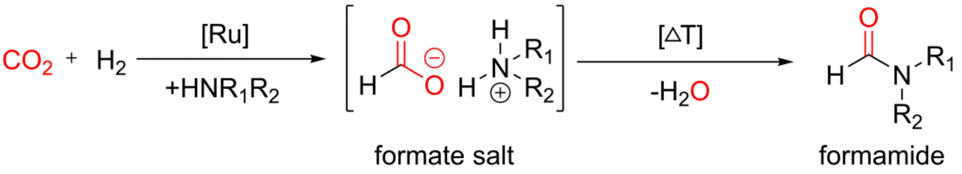

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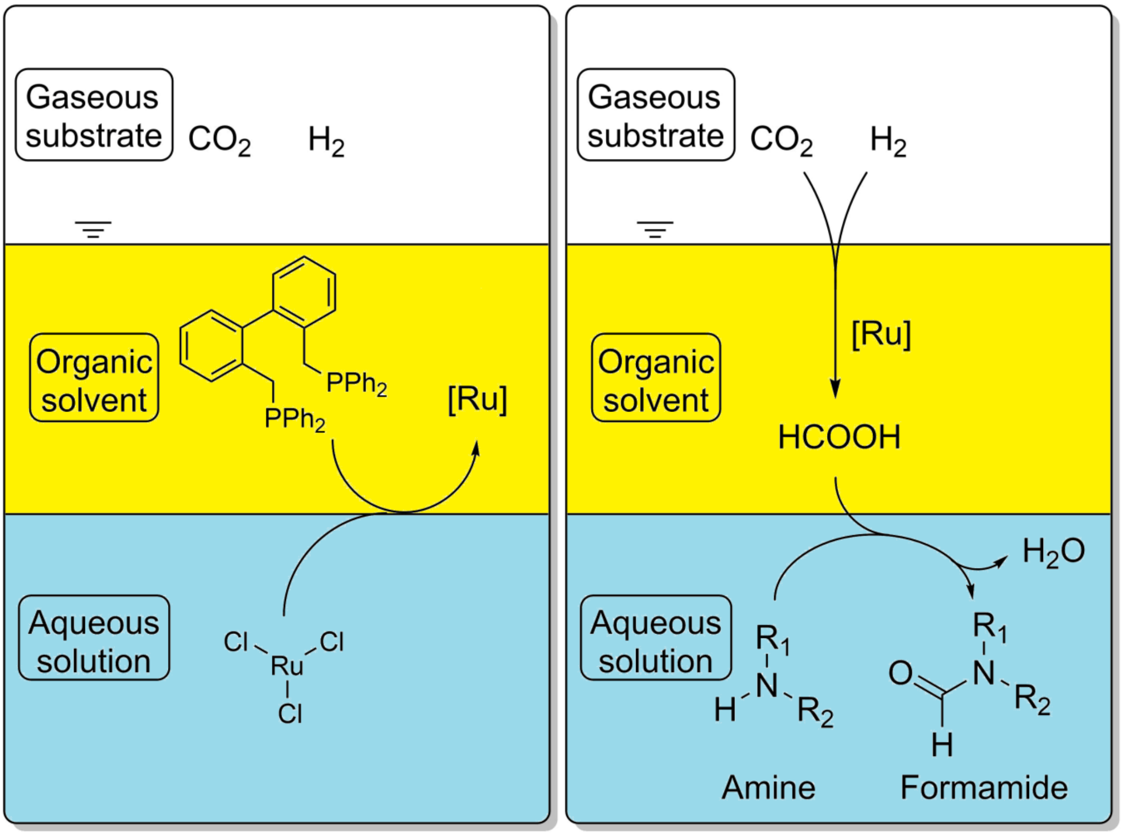
Figure 1: Hydrogenation of carbon dioxide to formamides



step I: in-situ catalyst formation

step II: product synthesis

<InlineImage3>

Figure 2: Conceptual design of the reaction system

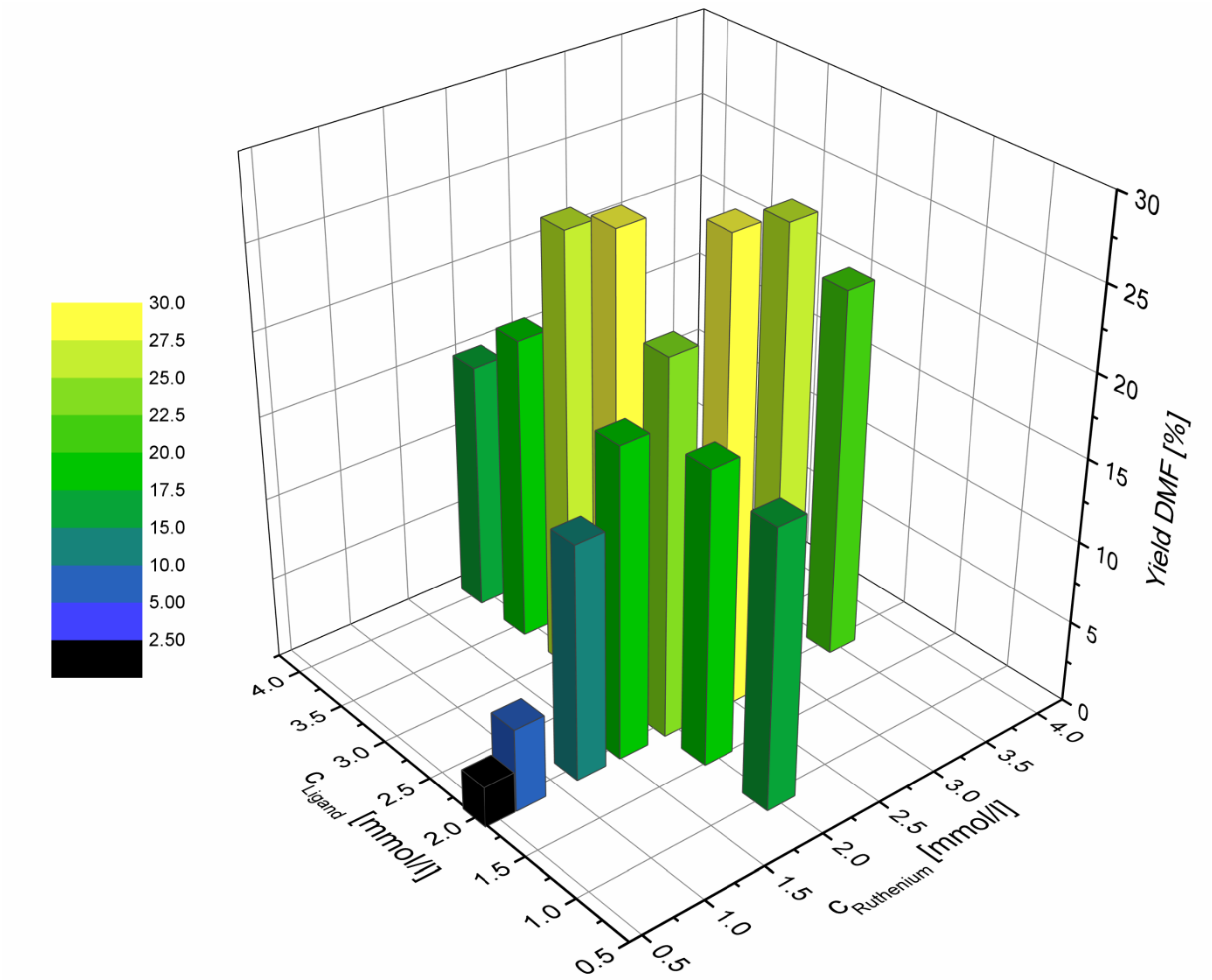


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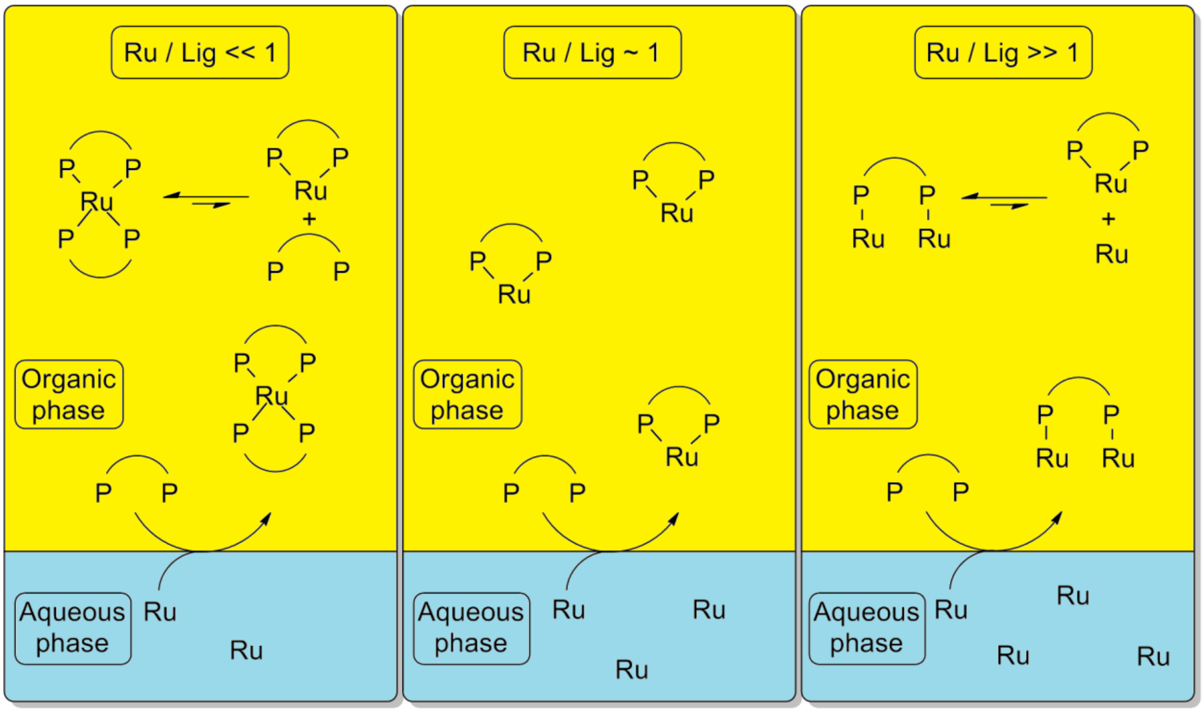
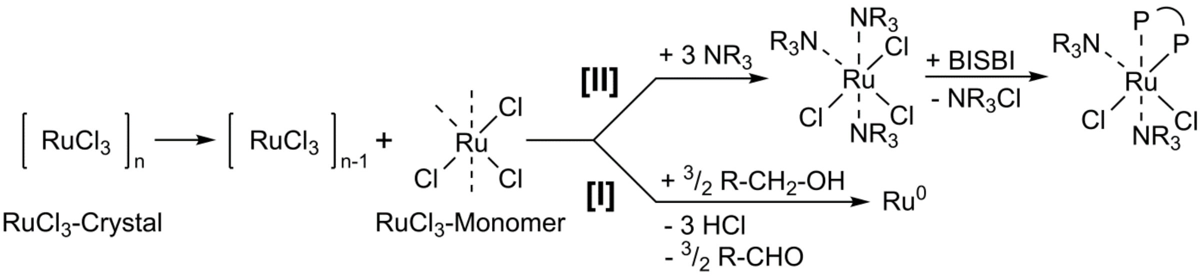
Figure 3: Variation of precursor and ligand concentration



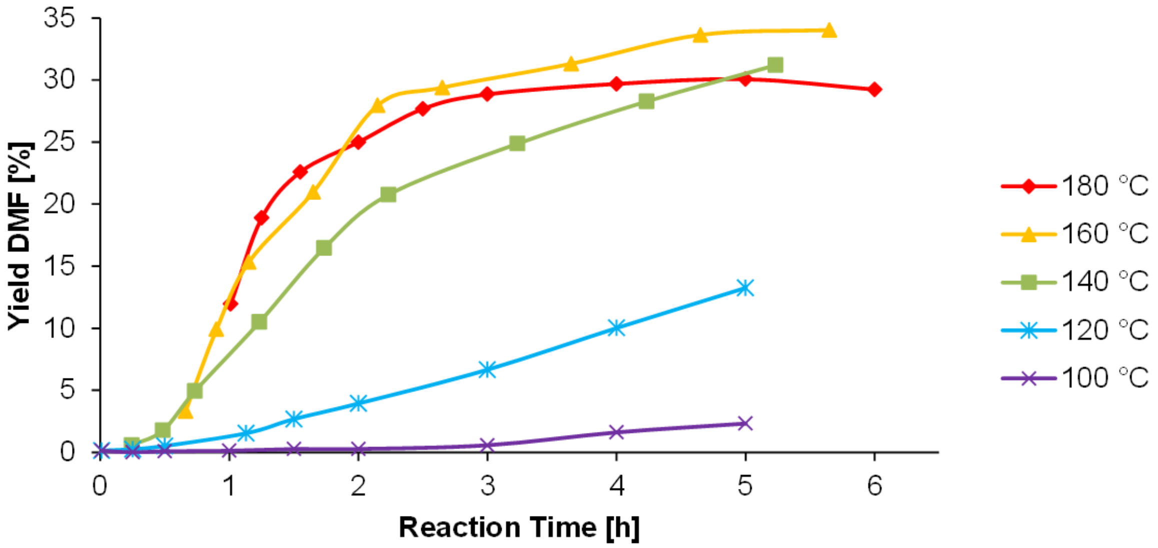
<InlineImage5>

Figure 4: Proposed influence of different precursor to ligand ratios. Chlorine and hydrogen omitted for clarity.



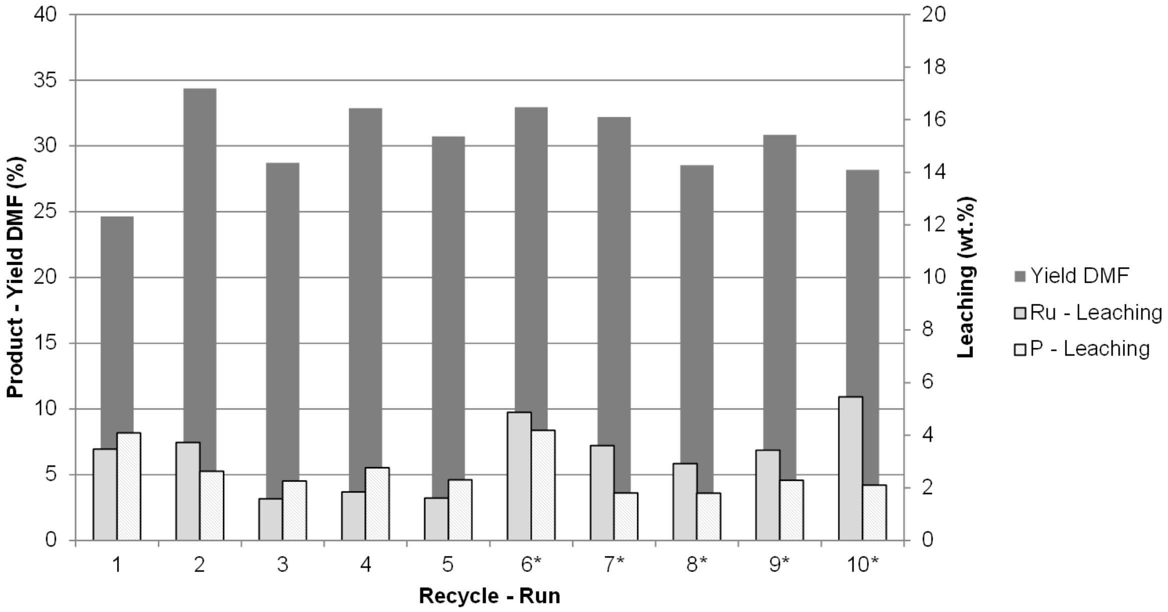
<InlineImage6>

Figure 5: Hypothesis of the ruthenium trichloride solvation and stabilization



<InlineImage7>

Figure 6: Variation of the reaction temperature



<InlineImage8>

Figure 7: Recycling of the homogeneous catalyst