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Formylation with ‘‘supercritical’’ CO_2: efficient ruthenium-catalyzed synthesis of *N*-formylmorpholine

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Formylation of morpholine with ‘‘supercritical’’ CO_2 using the bidentate ruthenium catalyst $RuCl_2(dppe)_2$ affords high *N*-formylmorpholine production rate at almost 100% selectivity. The solventless reaction could be an interesting alternative to the present *N*-formylmorpholine synthesis routes, which are based on environmentally harmful formylation agents. Video monitoring of the reaction mixture during reaction revealed a complex phase behavior, including the formation of solid carbamate, which was most prominent at low conversion and gradually disappeared with higher conversion, *i.e*., with the formation of *N*-formylmorpholine and water as a by-product. Addition of water as an additive suppressed solid carbamate formation and enhanced the reaction rate. Infrared spectroscopy was applied to follow the changes in the liquid and dense gas phase. The ruthenium catalyst was confined to the liquid phase, containing morpholine, *N*-formylmorpholine, water, dissolved carbon dioxide and hydrogen. Although the solubility of the ruthenium catalyst in the liquid phase decreased with increasing conversion, good performance in the synthesis of *N*-formylmorpholine could be achieved.

KEY WORDS: carbon dioxide; supercritical; $RuCl_2(dppe)_2$; formylation; morpholine; *N*-formylmorpholine; carbamate; phase behavior; IR spectroscopy; video monitoring.

1. Introduction

Carbon dioxide fixation has gained considerable attention due to environmental considerations and its large-scale availability at low cost [1–4]. Replacement of environmentally harmful C_1-building units used in chemical synthesis by nontoxic and easy-to-handle CO_2 represents an interesting challenge for green chemistry. ‘‘Supercritical’’[1] or dense CO_2 is gaining growing attention as an environmentally benign solvent, which has several distinct advantages over conventional liquid solvents. The beneficial features include tunable density, easy separation, relatively high solubility of gases and improved mass- and heat-transfer properties [5–12]. Particularly challenging is the use of ‘‘supercritical’’ CO_2 ($scCO_2$) in syntheses where it acts simultaneously as a reactant as well as a solvent. This powerful approach has been applied successfully to various reactions, such as copolymerization of CO_2 and cyclohexene oxide [13], olefin epoxidation [14], vinylcarbamate synthesis [15] and dimethyl carbonate synthesis [16]. Another intensively studied reaction is the synthesis of formic acid derivatives, including *N,N*-dimethylformamide (dmf) from dimethylamine and $scCO_2$ with hydrogen using homogeneous monodentate ruthenium complexes like $RuH_2[P(CH_3)_3]_4$ or $RuCl_2[P(CH_3)_3]_4$ as catalysts [17–19]. Exchanging the monodentate ruthenium complexes by bidentate ruthenium complexes of the type $RuCl_2L_2$ ($L = Ph_2P(CH_2)_nPPh_2, n = 1–3$), the stability of the catalysts and the production rate of dmf could be greatly improved [20,21]. Immobilization of the active ruthenium complex in a porous silica matrix afforded a heterogeneous variant of this catalytic system with inherent technical advantages concerning catalyst separation [22–25].

The excellent catalytic properties of the bidentate ruthenium complexes in the formylation of alkylamines with dense CO_2 prompted us to explore the synthesis of *N*-formylmorpholine using a similar strategy (scheme 1). *N*-formylmorpholine is technically produced in large quantities mainly owing to its application in process gas cleaning and in the isolation of BTX aromatics from crude oil [26,27]. It is industrially synthesized by a two-step process: either morpholine is reacted with methyl formate or a transamidation is performed, typically involving formamide [28].

The catalytic synthesis described here affords *N*-formylmorpholine by formylation of morpholine with $scCO_2$ and hydrogen, but in contrast to the hitherto

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[1] For convenience, the term ‘‘supercritical’’ is used here between quotation marks for the CO_2-containing dense phase at temperatures exceeding its mixture critical point (irrespective of further liquid or solid phases present). Note that the term supercritical is generally used in chemistry for two- or multicomponent systems being beyond the critical parameters of the solvent or the mixture. In fluid theory, however, the expression is well defined only for single-component systems and has no meaning concerning the phase behavior of multicomponent systems since immiscibility phenomena can still occur beyond the mixture’s critical point.

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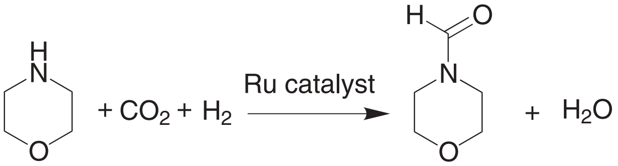


Scheme 1. Formylation of morpholine with hydrogen and carbon dioxide.

reported synthesis [29], without any additional solvent, *i.e.*, in a solventless process. It is shown that this solvent-free catalytic synthesis affords much higher turnover numbers (ton) and turnover frequencies (tof) than that achieved before [29] at nearly 100% selectivity (> 99.9%). Special attention has been given to unravel the complex phase behavior inherent in this reaction, using video imaging combined with infrared spectroscopy.

2. Experimental

2.1. Materials and catalytic studies

The bidentate ruthenium catalyst $RuCl_2(dppe)_2$ (dppe = $Ph_2P(CH_2)_2PPh_2$) was prepared according to the procedure described in the literature [30]. Morpholine (mp) and *N*-formylmorpholine (fmp) were purchased from Fluka. Carbon dioxide (purity 3.0) and hydrogen (purity 4.8) were supplied by Pangas. Catalytic tests were carried out in a temperature-controlled high-pressure apparatus consisting essentially of a 500-ml stainless steel autoclave, and a dosing system for the various gases. The apparatus has been described in detail in a previous study [24].

In a typical experiment, mp was poured into the reactor and the catalyst was added. If additives were used, they were also added before closing the autoclave. The reactor was flushed with hydrogen several times, and heated to 100 °C. The hydrogen pressure was set to 8.7 MPa. Subsequently, CO_2 was dosed to the autoclave until a total pressure of 21 MPa was reached (*ca.* 100 g CO_2) and the stirrer was switched on (rpm $\sim 300\,\mathrm{min}^{-1}$). After 3 h, the reaction was stopped by cooling and venting and the reaction mixture was removed from the autoclave and analyzed using a Hewlett-Packard HP-6890 gas chromatograph equipped with an HP-1 capillary column (methyl siloxane; $30\,\mathrm{m} \times 0.32\,\mathrm{mm} \times 0.25\,\mu\mathrm{m}$) and a TCD detector. The product was identified by GC-MS, and after separation from the reaction mixture by vacuum distillation by ^{1}H-NMR, ^{13}C-NMR and IR spectroscopy. Blanc tests, without catalyst, did not show any conversion to fmp, but a slightly yellow solid was formed. Analysis of this powder indicated morpholinium 4-morpholinecarboxylate (carbamate).

N-Formylmorpholine (fmp): δ_H(500 MHz; $CDCl_3$) 8.06 (1, s, CHO), 3.39–3.71 (8 H, m, 4 CH_2); δ_C(125MHz; $CDCl_3$) 160.83 (CHO), 66.41–67.22 (NCH_2 CH_2O), 40.58–45.77 (NCH_2CH_2O); IR (CH_2Cl_2) $\nu = 2968$, 2917, 2859, 1665 cm^{-1}; MS, *m/z* 115, 100, 86, 72, 56, 42.

Morpholinium 4-morpholinecarboxylate: δ_C(100 MHz; solid CP-MAS rot. 4K) 164.52 ($NCOO^-$), 41,03–64.69 (CH_2); IR (KBr) $\nu = 3441, 3284, 2853$, 1559, 1460, 1437, 1275, 1105 cm^{-1}; $C_9H_{18}N_2O_4$ requires C, 49.53; N, 12.84; Found: C, 49.75; N, 12.67.

2.2. Phase behavior studies—video monitoring

We followed a two-step approach to investigate the phase behavior. First, some experiments were carried out in a computer-controlled half-liter autoclave equipped with a glass window (described in detail in [31]), where geometry and stirring effects are of the same kind as in the standard autoclave used for the catalytic tests. The experiments were performed in the same way as the catalytic standard experiment.

Second, a more detailed analysis was done in a more flexible high-pressure view-cell of variable volume (22–62 ml), which has been described in detail elsewhere [32]. A sapphire window covered the whole diameter of the horizontal stainless steel cylinder, thus allowing the observation of even minor gaseous or liquid phases by video imaging. The phases were equilibrated by means of a magnetic stirrer. Various mixtures of the components involved in the reaction were investigated to gain information on the phase behavior of the reaction mixture corresponding to particular states of conversion. No catalyst was added to those mixtures. The influence of the catalyst on the phase behavior could be neglected because its concentration was in the range of the impurities contained in the various components of the reaction mixture. The phase behavior experiments were performed in the same way as the catalytic experiments. Initially the volume of the reactor was set to 50 ml. The particular liquid mixture (corresponding to a specific conversion calculated with a starting amount of morpholine of 0.012 mol) was filled into the view-cell. The cell was flushed three times with hydrogen, and then the pressure was set to 70 bar, which after heating to 100 °C resulted in a pressure of 85 bar. After addition of 10 g CO_2, the pressure increased to *ca.* 190 bar; stirring for 30 min led to equilibration of the system.

2.3. Infrared spectroscopy

Infrared spectroscopic investigations were carried out in a view-cell of the same type as used for the phase behavior studies with the addition of two cylindrical ZnSe windows, on each side in the upper half, and a trapezoidal ZnSe crystal at the bottom of the reactor.

The latter allows measurements with the attenuated total reflection (ATR) technique [33], where the liquid phase is probed at the interface to the crystal. By placing the front end of the view-cell in a Bruker IFS-66 spectrometer, spectra of the gas phase by transmission measurements through the windows and that of the liquid phase by ATR measurements through the crystal could be recorded. Spectra were obtained with an MCT detector by accumulating 100 scans at 4 cm^{-1} at an angle of incidence of 60°. No polarizer was used. Details of the experimental setup will be reported elsewhere [34]. The tests were performed in the same way as the phase behavior measurements using a mixture corresponding to a conversion of 50%. Additionally, a tenfold catalyst–substrate ratio compared to the catalytic experiments was used, to be able to detect the catalyst bands despite the extremely low concentration. Infrared studies had to be limited to a pressure range up to 100 bar (but the $H_2:CO_2$ ratio was kept the same) because mechanical stress due to high pressure and temperature led to the rupture of the ZnSe crystal at more rigorous conditions.

Safety note: the experiments described in this paper involve the use of high pressure and require equipment with the appropriate pressure rating.

2.4. Catalyst solubility tests

The solubility tests were carried out at room temperature. Related to an initial amount of 0.1-mol mp, reaction mixtures corresponding to different conversions were prepared with mp, fmp and water. To these mixtures, $1.0 \cdot 10^{-6}$ mol $RuCl_2(dppe)_2$ was added and vigorously stirred. After centrifugation of the samples, the ruthenium content of the liquid phase was quantified with inductively coupled plasma–optical emission spectroscopy (ICP-OES).

3. Results

3.1. Catalytic tests

Results of the $RuCl_2(dppe)_2$-catalyzed formylation of morpholine affording *N*-formylmorpholine are summarized in table 1. The selectivity to *N*-formylmorpholine was always $> 99.9\%$. Reactions with 100% conversion of mp afforded a ton of up to 136 000. It had been stated previously [19,21] that basic amines show a promoting influence on formylation reactions with CO_2 due to stabilization of the formic acid intermediate. In the case of morpholine, the use of NEt_3 as additive had only a marginal effect (table 1, entries 9, 10). More significant was the influence of water, which is formed as a by-product during synthesis. This effect was studied by adding water to the reaction mixture (table 1, entries 5–8). The promoting effect of water was most prominent for reactions carried out with 2 to 3% water (relative to the amount of morpholine) as additive; a ton of 210 000 could be reached under these conditions. Higher amounts of water were not beneficial. Intimate mixing seems to be an important prerequisite for obtaining high catalytic efficiency as a comparison of experiments carried out with different stirring rates (table 1, entries 2 and 3) revealed.

3.2. Phase behavior

The catalytic reaction system showed prominent changes in its phase behavior, depending on the composition of the reaction mixture and thus conver-

Table 1
Catalytic formylation of morpholine (mp) with carbon dioxide and hydrogen using $RuCl_2(dppe)_2$ as catalyst[a]

Run	Catalyst μmol	Additive/mp[b]	ton[c]	tof/h^{-1c}	Conv. (%)
1	—	—		0	0[e]
2	1.00	—	174 000	57 000	74
3	0.99	—	142 000	46 700	60[f]
4	0.89	—	136 000	8 300	100[g]
5	0.98	0.012 (H_2O)	177 000	57 700	74
6	0.97	0.023 (H_2O)	210 000	68 400	86
7	0.96	0.024 (H_2O)	204 000	66 100	84
8	0.99	0.045 (H_2O)	175 000	56 700	73
9	1.00	0.022 (NEt_3)	185 000	60 100	79
10	1.01	0.025 (NEt_3)	184 000	60 200	79

[a] Conditions, if not otherwise stated: 100 °C, 0.24 mol mp, hydrogen pressure 8.7 MPa, 100 g CO_2, stirring rate 300 min^{-1}, reaction time 3 h, total pressure 21.5 MPa. The conversion is calculated from morpholine as limiting reactant. Differences in catalyst amount are due to small sample weights.

[b] Molar ratio.

[c] ton: turnover number.

[d] tof: turnover frequency.

[e] Blind test (without catalyst).

[f] Stirring rate 100 min^{-1}.

[g] 16 h 0.12 mol mp.

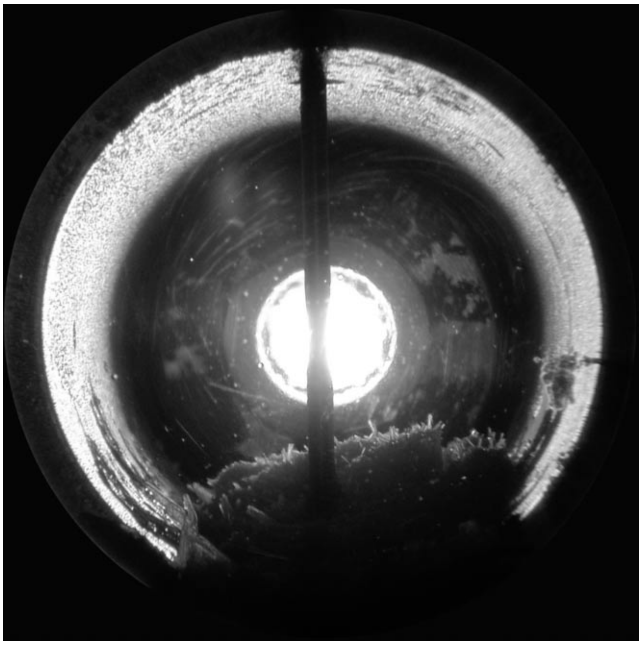
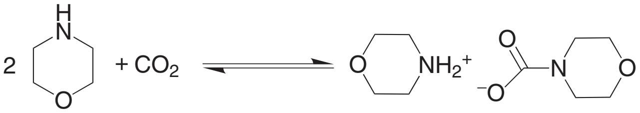


Figure 1. Solid carbamate (morpholinium 4-morpholinecarboxylate) formation observed during video monitoring of the reaction. Snapshot after the addition of 10 g CO_2 to 0.12 mol mp and 85 bar H_2 at 100 °C, total pressure was 190 bar. The vertical line is the thermocouple, the bright spot in the middle is the light source. The white carbamate needles are accumulated at the bottom of the view-cell.

sion. At the start of the reaction, *i.e.*, when CO_2 was added to morpholine and hydrogen at reaction temperature, needle-shaped crystals of solid carbamate (morpholinium 4-morpholinecarboxylate) were formed, surrounded by a dense CO_2-rich gaseous phase, as revealed by video monitoring (figure 1). Elementary analysis revealed a nitrogen to carbon ratio corresponding to a carbamate complex with an amine to CO_2 ratio of about 2 : 1 (scheme 2).

Both products (fmp and water) exhibited considerable solvent power. Upon addition of one or two drops of water to the mixture described above, the solid carbamate turned into a gel-like liquid phase. *N*-formylmorpholine addition had a similar but less prominent effect. As a consequence, with increasing product amounts the solid phase turned into a gel-like liquid phase (at a conversion between 5 and 10%). This behavior is illustrated in figure 2, which shows the phase changes observed by video imaging as a function of conversion. Mixtures corresponding to a conversion around *ca.* 25% consisted of a liquid phase and a dense gaseous phase only; the solid carbamate disappeared. At higher conversions, the liquid phase increased in volume and considerable amounts of carbon dioxide were dissolved, as indicated by intense degassing from the liquid phase upon venting (see figure 3). The experiments carried out in the half-liter autoclave showed the same phase behavior confirming the view-cell results.



Scheme 2. Carbamate complex formation.

Intimate mixing seems to be an important prerequisite for obtaining high catalytic efficiency as a comparison of experiments carried out with different stirring rates (table 1, entries 2 and 3) reveals. This dependence of the catalytic efficiency on the mixing properties is understandable in light of the complex phase behavior of the reaction system.

3.3. *Infrared spectroscopy*

Infrared spectroscopy was applied to gain some qualitative information on the different phases present in the reaction mixture. All mentioned frequencies are referred to either in literature or in reference measurements with pure substances (fmp and catalyst). Transmission IR spectra of the gas phase and ATR-IR spectra of the liquid phase are shown in figures 4 and 5, respectively. The spectra have been measured before (a) and after (b) addition of CO_2 to the system, and after cooling the reaction mixture to room temperature (c). Note that the intense lines of CO_2 are located at 667 and 2349 cm^{-1} and did not disturb the spectra.

The broad peak at 1093 cm^{-1} (as well as the smaller ones at 885, 1318 and 1463 cm^{-1}) in the transmission spectrum (figure 4(a)) is attributed to gaseous mp. While no signal is visible in the dense gaseous phase at 1708 cm^{-1} (amide band of fmp) in the beginning, the spectrum (figure 4(b)) indicates the solubility of fmp in CO_2. Upon cooling down, the fmp bands also mostly disappeared, leaving only the CO_2 bands in the spectrum (figure 4(c)), none of which is shown in the frequency range covered in the figure.

Figure 5 depicts the ATR-IR spectra in the 1000–1120 cm^{-1} region, where some typical bands of mp and fmp are located. The bands of mp at 1093, 1063 and 1032 cm^{-1} vanish, while the bands of fmp (1004, 1022, 1068 and 1109 cm^{-1}) all grow.

Figure 6 compares the ATR-spectrum of a reaction mixture without catalyst (a) and with catalyst (b). The vibrations at 694 and 743 cm^{-1} are the most prominent bands of the catalyst, attributed to its phenyl groups. No corresponding bands were determined in the gaseous phase by transmission IR, indicating that the catalyst was confined to the liquid phase.

Finally, it should be noted that neither characteristic bands of CO (2183 and 2115 cm^{-1}) nor the signals of formic acid (633, 1115 and 1791 cm^{-1}) were observed during the experiments.

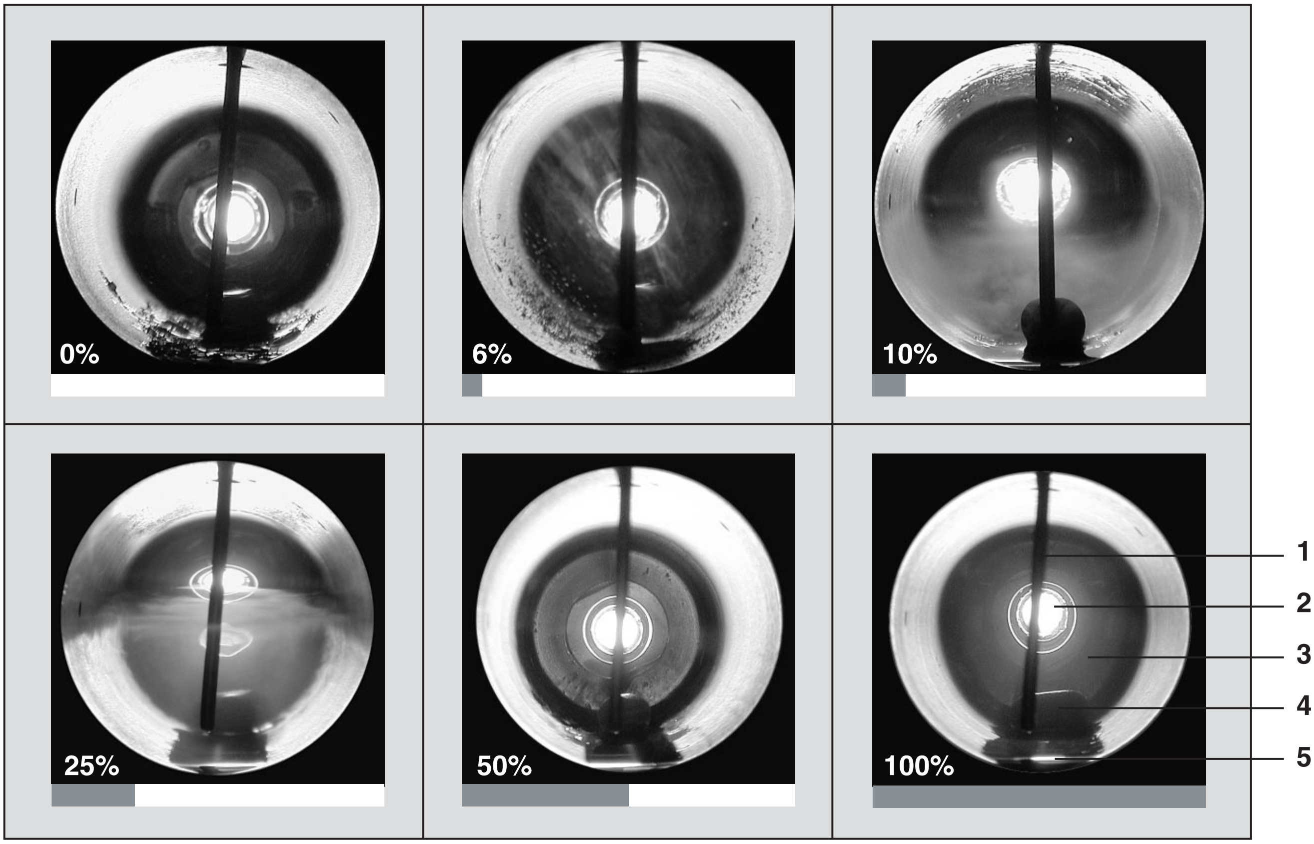


Figure 2. Relation between conversion and phase behavior. The video images show the phase behavior of reaction mixtures corresponding to different conversion levels at 100 °C and 190 bar. Note the transition of the solid (0%, 6%) via a gel (10%) to liquid (complete dissolution, > 25%). Composition: sum of reactant (mp) and product (fmp) 0.012 mol; 85 bar hydrogen and 10 g CO_2. 1: thermocouple, 2: illumination, 3: dense gas phase, 4: magnetic stirrer, 5: liquid phase. Bar and numbers indicate conversion level.

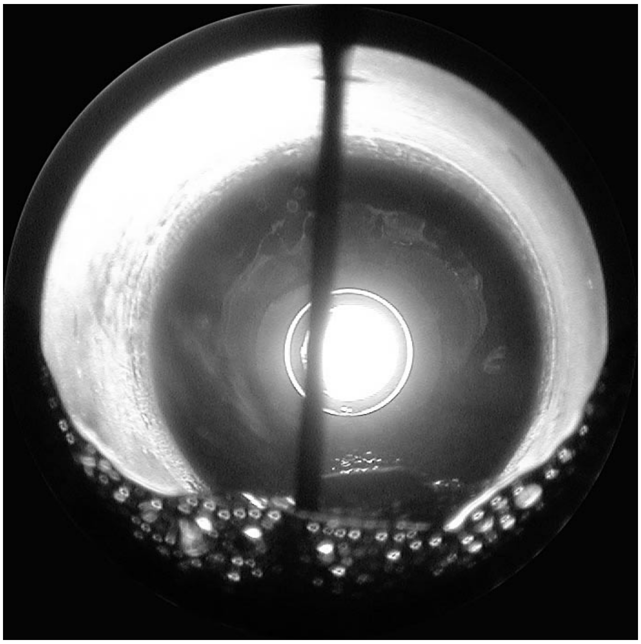


Figure 3. Strong bubble formation in the liquid phase upon decompression shows degassing of CO_2 for a reaction mixture at 100% conversion and 30 °C. The vertical line is the thermocouple, the bright spot in the middle the light source. The magnetic stirrer lies next to the thermocouple.

3.4. *Solubility of catalyst*

Water in the reaction mixture was strongly influencing the solubility of the ruthenium complex in the mp–fmp–water phase. A systematic study of the solubility of the ruthenium complex in the liquid reaction phase, mimicking reaction mixtures corresponding to 0, 50 and 100% conversion, revealed that the solubility of the catalyst in the liquid phase decreased strongly with increasing conversion (table 2). It should be noted that the solubility tests were carried out at room temperature owing to experimental difficulties connected with temperature control during centrifugation. However, the observed tendencies are assumed to hold also at the reaction temperature of 100 °C. An interesting practical consequence of this solubility behavior of the ruthenium complex in the morpholine-containing liquid phase is that the catalyst can easily be separated after reaction by filtration.

4. Discussion

Various formylation agents have been applied for the synthesis of *N*-formylmorpholine. Table 3 summarizes

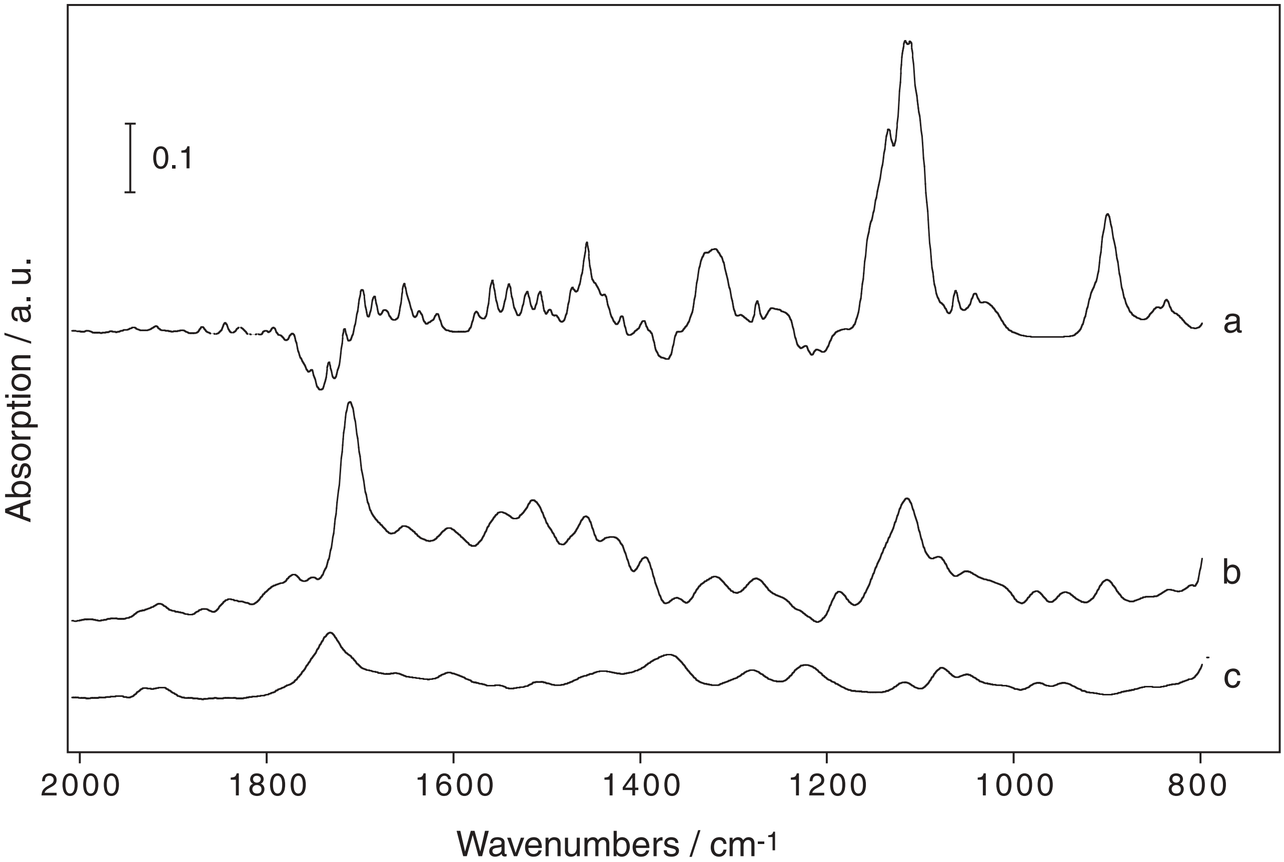


Figure 4. FTIR spectra of the gaseous phase, measured in transmission mode. The reaction mixture contained mp, fmp, and water corresponding to a conversion of 50% at 80 °C, hydrogen pressure was 50 bar, total pressure 100 bar. The different spectra were measured (a) before addition of CO_2, (b) after addition of CO_2, (c) after cooling down to room temperature.

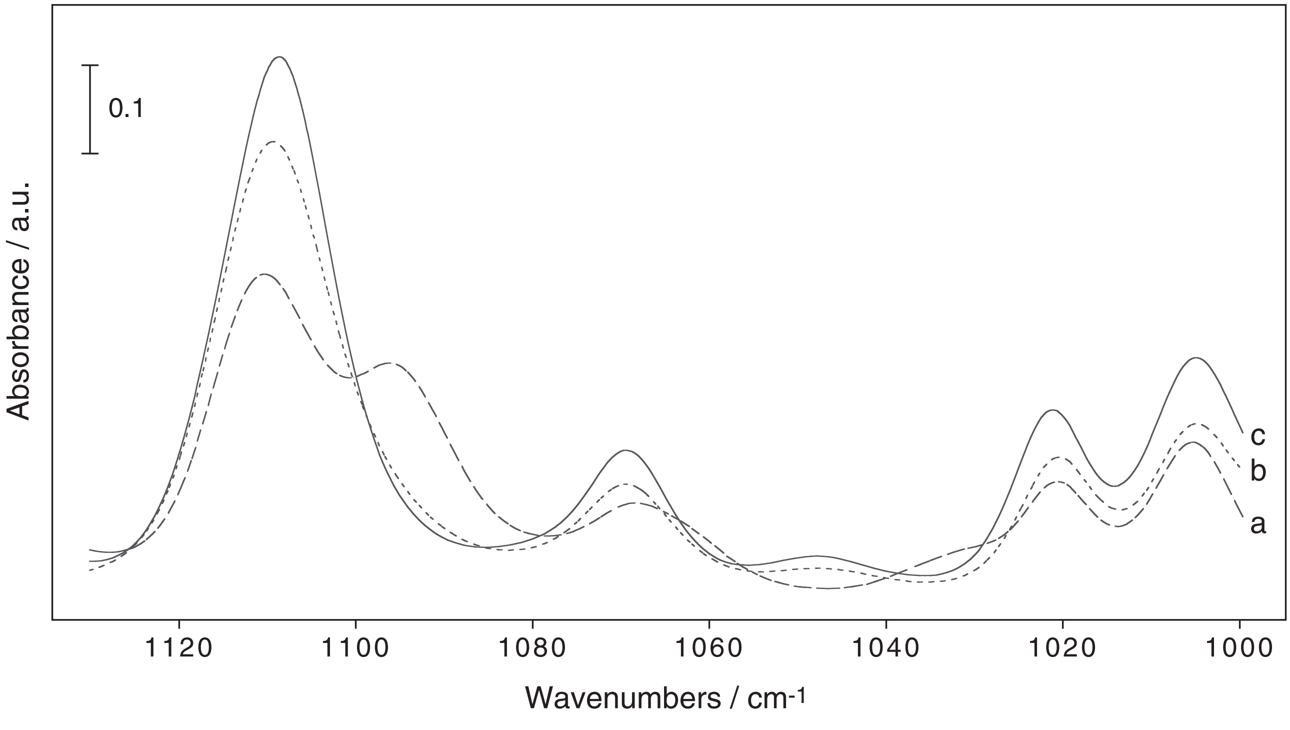


Figure 5. FTIR spectra of the liquid phase, measured in ATR mode. The reaction mixture contained mp, fmp, and water corresponding to a conversion of 50% at 80 °C, hydrogen pressure was 50 bar, total pressure 100 bar. The different spectra were measured (a) before addition of CO_2, (b) after addition of CO_2, (c) after cooling down to room temperature.

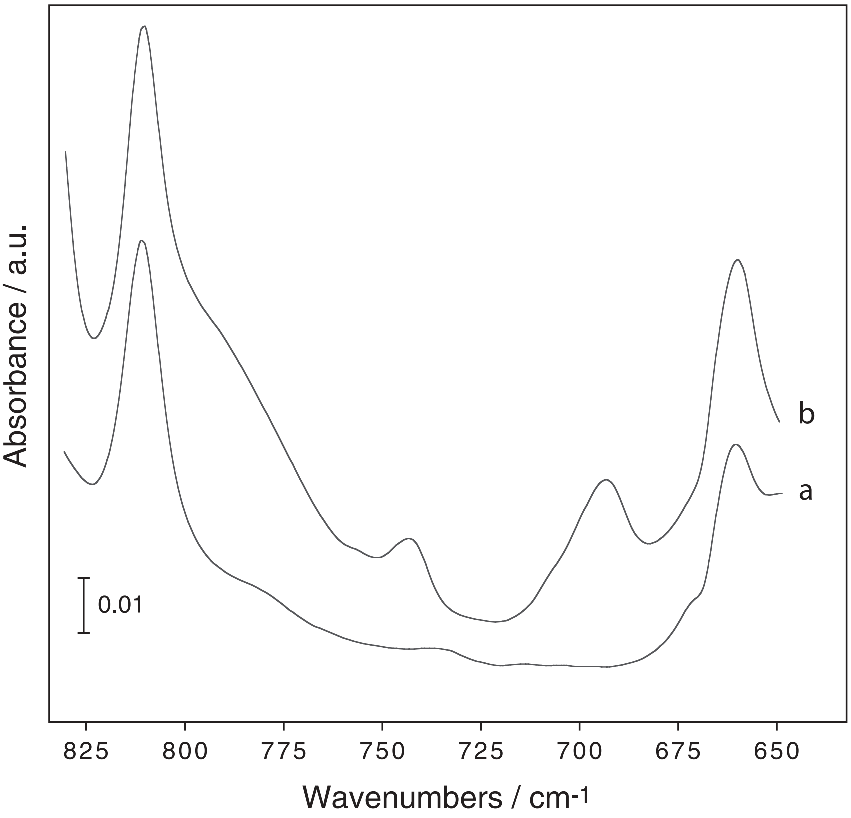


Figure 6. FTIR ATR-spectrum of the liquid phase of the reaction mixture containing mp, fmp and water corresponding to a conversion of 50% at 80 °C, hydrogen pressure was 50 bar, (a) without catalyst, (b) with catalyst.

some characteristic features of known formylation processes. The present work clearly demonstrates that the synthesis of *N*-formylmorpholine can be efficiently performed using nontoxic, nonflammable, cheap and easy to handle CO_2 as formylation agent. The solventless reaction design combined with the highly active ruthenium catalyst brought a great improvement of the earlier reported CO_2 based formylation of morpholine [29]. With the bidentate ruthenium catalyst, which exhibits high activity in the synthesis of dmf from dense carbon dioxide, hydrogen and dimethylamine [20,21], morpholine could be formylated with $scCO_2$ and hydrogen at almost 100% selectivity. Turnover numbers and turnover frequencies achieved are more than three orders of magnitude higher than those reported previously for the same reaction (see table 3) [29], confirming the outstanding catalytic properties of $RuCl_2(dppe)_2$ and the favorable solventless reaction design. Compared to the formylation of dimethylamine, a strongly different situation is observed in the formylation of morpholine. The immediately occurring dimethylammonium dimethylcarbamate formed from dimethylamine and carbon dioxide is liquid at the reaction temperature [42], whereas morpholinium 4-morpholinecarboxylate built from morpholine and carbon dioxide is solid. This leads to a complex phase behavior, which changes with conversion, *i.e.*, with composition of the reaction mixture.

At the beginning, a solid carbamate phase is formed instantly, rendering solid–liquid mass transfer probably a decisive step in the global reaction behavior. At low conversions, relatively small amounts of product and water are present in the reaction mixture, which can only partially dissolve the solid carbamate. With

Table 2
Solubility of $RuCl_2(dppe)_2$ in different compositions of reaction mixtures[a]

Composition (mp/water/fmp)	Conversion (%)	Ru content, ppm[b]
0.1 mol/0 mol/0 mol	0	32.8
0.05 mol/0.05 mol/0.05 mol	50	13.5
0 mol/0.1 mol/0.1 mol	100	2.5

[a] A catalyst amount of $1.0 \cdot 10^{-6}$ mol was added to the samples and well stirred before centrifugation. Tests were made at room temperatures.

[b] Ru content of liquid phase, measured by ICP-OES.

Table 3
Formylation of morpholine affording *N*-formylmorpholine based on different formylation agents

Formylation agent	Reaction time (h)	T (°C)	Yield (%)	ton	Reference
Formic acid	2	130–150	> 59	n.s.[a]	[35,36]
Chloral	>1	25	92	n.s.	[37,38]
Ammonium formate	10	95	95	n.s.	[39]
Hex-1-en-2-yl-formate	1	25	90	n.s.	[40]
$CO_2/HC(OR)_3$[b]	45	120	100	n.s.	[41]
CO	24	185	95	76	[29]
CO_2/H_2	24	140	62	50	[29]
CO_2/H_2	16	100	100	136 000	This work

[a] n.s.: not specified.
[b] R: methyl, ethyl.

increasing conversion, the solid phase is transferred more and more into the liquid phase. This contrasts the behavior of dimethylamine, where complete miscibility of the amine with CO_2 was reported for the same conditions [19]. Water, fmp or a mixture thereof (present at higher conversion) prevents the formation of the solid phase and a favorable phase behavior is achieved, which may explain the promoting effect of water on the reaction rate (table 1).

A positive influence of water and methanol was also observed in formic acid synthesis from CO_2 and H_2, and it was speculated that mechanistic aspects, especially interaction of the additive with the catalyst, are the reasons for an improvement in activity [19]. The same authors report a strong promoting effect of bases like NEt_3, stabilizing the intermediate formic acid. In the formylation of morpholine reported here, the influence of water on the phase behavior seems to be crucial. However, a beneficial interaction of water with the catalyst cannot be excluded. The use of NEt_3 ($pK_a = 10.75$) as additive resulted only in slightly higher turnover numbers. It seems that the basicity of mp ($pK_a = 8.50$) is sufficient to be favorable for the reaction. The fact that no solvent is necessary in the formylation of morpholine with carbon dioxide is a clear advantage compared to systems working in solution [29]. A solvent, which prevents formation of the solid carbamate phase, is not needed, because the products water and fmp suppress the buildup of the solid phase. The absence of a solvent means that concentrations are higher, which in turn enhances the reaction rate and no separation of the product from the solvent is necessary.

Solubility tests in different reaction mixtures and infrared spectroscopy of the liquid phase and the compressed CO_2-rich phase during the reaction indicated that the catalyst was dissolved predominantly in the liquid phase. This was also corroborated by the fact that the dense gas phase remained colorless, while the dissolved catalyst tints fluids yellow. Increasing product amounts enhance the solubility of carbon dioxide in the liquid phase, whereas the catalyst's solubility is lowered (table 2). Interestingly, the lowering of the solubility of the catalyst with the progress of the reaction did not greatly affect the efficiency of the synthesis. Further indication that the reaction occurs in the liquid phase is given by the quickly vanishing mp bands in the ATR-spectra (figure 5). Because only a few micrometers of solution are probed, it is hardly conceivable that the increasing bands stem from the fmp formed in the gas phase.

A noteworthy detail is that the mp bands in the dense gaseous phase are still visible at a hydrogen pressure of more than 30 bar. Thus, the concentration of mp in the gas phase seems to be much higher than that expected from ideal thermodynamic behavior, since the boiling point of mp is 130 °C. No characteristic bands of water or fmp could be measured at the same conditions.

In the synthesis of dmf from CO_2, H_2 and dimethylamine, Jessop *et al.* [19] observed the formation of formic acid, which was proposed to be involved in the catalytic cycle as an intermediate. In our investigations, the presence of free HCOOH in the reaction mixture could not be confirmed by IR spectroscopy or ^{1}H-NMR measurements. However, this does not rule out a similar mechanism for the formylation of morpholine. Investigations aimed at elucidation of the reaction mechanism are presently undertaken in our laboratories.

Finally, the present study clearly illustrates that a supposed "homogeneous" catalytic reaction can show rather complex phase behavior, which is affecting the overall behavior of the reaction. Consideration of the phase behavior by means of video monitoring and suitable spectroscopic methods [43] seems to be a necessary prerequisite for understanding this type of reaction involving carbon dioxide and amines.

5. Conclusions

Catalytic tests revealed that the bidentate Ru complex $RuCl_2(dppe)_2$ is a highly active and selective catalyst for the synthesis of *N*-formylmorpholine from morpholine, "supercritical" carbon dioxide and hydrogen. The formylation with $scCO_2$ does not require a solvent. A striking feature of the reaction is the initial formation of solid carbamate (morpholinium 4-morpholinecarboxylate). This solid carbamate formation not only has an impact on the reaction rate but also on the process itself. By means of video imaging, important insight into the phase behavior and its influence on the reaction performance could be gained. Solid carbamate formation can be suppressed by the addition of water to the reaction mixture, which has a promoting effect. Infrared spectroscopy of the liquid and dense gas phase indicated that the reaction was confined to the liquid phase, containing morpholine, *N*-formylmorpholine, water, dissolved CO_2 and H_2, and the catalyst. The solubility of the $RuCl_2(dppe)_2$ catalyst in the reaction mixture strongly decreases with conversion, affording the possibility of easy catalyst separation.

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