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Formylation with supercritical carbon dioxide over Ru/Al_2O_3 modified by phosphines: heterogeneous or homogeneous catalysis?

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Abstract

The formylation of 3-methoxypropylamine with hydrogen and "supercritical" carbon dioxide over Ru-based catalysts was studied. In this solventless process, carbon dioxide acts as both reactant and solvent. Interestingly, Ru/Al_2O_3 modified by the phosphine 1,2-bis(diphenylphosphino)ethane (dppe) showed a high formylation activity at 100% selectivity, comparable to those of the homogeneous catalysts $RuCl_2(dppe)_2$ and $RuCl_2(PPh_3)_3$. Analysis of the reaction mixture by ICP-OES and structural studies by in situ X-ray absorption spectroscopy discovered that the presence of the phosphine modifier led to the formation of a homogeneous ruthenium catalyst.

Keywords: Formylation of amines; 3-Methoxypropylamine; Supercritical carbon dioxide; Ru/Al_2O_3; Phosphines; X-ray absorption spectroscopy; EXAFS; In situ spectroscopy

1. Introduction

A step toward "green" formylation of amines is the use of carbon dioxide and hydrogen as formylation agents instead of toxic compounds such as carbon monoxide and phosgene [1–5]. This approach provides the opportunity to use supercritical carbon dioxide acting as both C1-building block and solvent (solvent-free process) [6–9]. A variety of ruthenium complexes have been reported [10,11] to be active and selective for such formylation reactions, including $RuCl_2(PMe_3)_4$ in the formylation of hydrogen with carbon dioxide to formic acid [7], and $RuCl_2(PPh_3)_3$, $Ru_3(CO)_{12}$ [12], and $RuCl_2(dppe)_2$ [13] in the formylation of dimethylamine, propylamine [14], and morpholine [15]. Among these ruthenium-based complexes, $RuCl_2(dppe)_2$ was found to be superior with respect to activity and stability [13,14,16].

A further step toward a "green process" is the application of heterogeneous catalysts because of their intrinsic advantages concerning catalyst separation, reuse, and handling. An interesting approach is the immobilization of the corresponding homogeneous complexes functionalized by silyl ether groups in an inert silica matrix, as shown previously for $RuCl_2X_3$ ($X = Ph_2P(CH_2)_2Si(OEt)_3$, $Me_2P(CH_2)_2Si(OEt)_3$) [8,17], and $RuCl_2(dppp)_2$ ($dppp = Ph_2P(CH_2)_3PPh_2$) [18]. However, the preparation of these Ru-silica hybrid gels is rather demanding, and more easily accessible heterogeneous catalysts would be desirable. A simpler approach could be the modification of a supported Ru catalyst with a suitable phosphine, which is the focus of this study. The modification of metal catalysts by adsorbed auxiliaries (modifiers) has been successfully applied to improve the catalytic properties of a variety of metals, as covered in a recent review [19]. A related example is the use of phosphine modifiers in partial oxidation reactions on Pt/alumina catalysts [20]. This prompted us to apply this strategy for formylation with a 5 wt% Ru/Al_2O_3 catalyst modified with a phosphine (dppe or PPh_3). We show that these catalysts exhibit good activity in the formylation of 3-methoxypropylamine at 100% selectivity. Extensive in situ

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EXAFS studies using a specially designed high-pressure cell revealed that the observed catalytic behavior has to be attributed to a highly active homogeneous Ru complex formed from the Ru/alumina catalyst during reaction.

2. Experimental

2.1. Catalyst materials

The 5 wt% Ru/Al_2O_3 catalyst (9001, escat 44, powder, prereduced) was used as received from Engelhard. Note that the ruthenium catalyst was partially oxidized, but we denote it as Ru/Al_2O_3. The 5 wt% Ru/Al_2O_3 catalyst was modified with dppe in two different ways. On the one hand, dppe was added before the reaction by reflux in THF for 2 h and dried under high vacuum; on the other hand, it was simply added during the reaction (Section 2.2).

The homogeneous $RuCl_2(dppe)_2$ catalyst was synthesized according to the method of Mason et al. [21]. A suspension of 1.00 g $RuCl_2(PPh_3)_3$ in 20 ml of acetone was mixed with 0.85 g dppe under an Ar atmosphere and fast stirring. A yellow precipitate was observed after 2 min and separated with a suction filter after 10 min of stirring at room temperature. The yellow powder produced was washed with acetone and methanol and dried in vacuum, and its structure was confirmed with ^{1}H- and ^{31}P-NMR and elemental analysis [calculated (%) for $C_{52}H_{48}Cl_2P_4Ru$ (968.8 g/mol): C 64.47, H 4.99, P 12.79, Cl 7.32, Ru 10.43; found: C 64.30, H 5.19, P 12.94]. $RuCl_2(PPh_3)_3$ (tris(triphenylphosphine)ruthenium(II)dichloride; Fluka, purum) was used as received after structural analysis by ^{1}H- and ^{31}P-NMR and elemental analysis [calculated (%) for $C_{54}H_{45}Cl_2P_3Ru$ (958.8 g/mol): C 67.64, H 4.73, P 9.69, Cl 7.39, Ru 10.54; found: C 67.36, H 4.84, P 9.72, Cl 7.56].

2.2. Catalytic formylation of 3-methoxypropylamine

The catalytic studies were performed in a 500-ml high-pressure stainless-steel autoclave (Medimex No. 128) with temperature control, a rupture disk, and a dosing system for gases [22]. The chemicals 3-methoxypropylamine (mpa) (Fluka, $>99\%$) and 1,2-bis(diphenylphosphino)ethane (dppe) (Fluka, 98%) were used as received; liquid carbon dioxide (4.5) and hydrogen gas (5.0) were supplied by Pangas.

In a typical procedure, mpa, dppe, and Ru/Al_2O_3 were poured into the reactor before it was closed and flushed with hydrogen. The reactor was filled with hydrogen ($p \sim 60$ bar). After the reactor was heated to 100 °C, the hydrogen pressure was adjusted to 80 bar, and 100 g of carbon dioxide was added. This resulted in a total pressure of about 200 bar. The stirring rate was fixed at 300 min^{-1}. After a certain reaction time, the reactor was cooled down and depressurized through the outlet valve. The reaction mixture was analyzed with a gas chromatograph (HP-6890) equipped with a HP-5 capillary column (30 m × 0.32 mm × 0.25 µm) and a flame ionization detector (FID). Product identification was achieved with a gas chromatograph (HP-6890) coupled to a mass spectrometer (HP-5973) after separation of the components from the reaction mixture by vacuum distillation. In a parametric study the temperature and the amounts of catalyst, mpa, hydrogen, and carbon dioxide were varied to find the optimal reaction conditions.

2.3. Characterization of in situ formed homogeneous complex by ICP-OES

After reaction, selected samples were filtrated and centrifuged to quantify the ruthenium and phosphorus content of the liquid phase with inductively coupled plasma atomic emission spectroscopy (performed at ALAB AG in Urdorf, Switzerland).

2.4. Ex situ and in situ X-ray absorption spectroscopy studies

The extended X-ray absorption fine structure (EXAFS) and X-ray absorption near-edge structure (XANES) experiments were mainly performed at the beamline X1, HASYLAB, at DESY in Hamburg, Germany. The storage ring typically operates at 4.45 GeV with a ring current between 80 and 120 mA. A Si(311) double-crystal monochromator was used, and higher harmonics were effectively removed by detuning of the crystals to 70% of the maximum intensity. Three ionization chambers filled with Ar were used to record the intensity of the incident and the transmitted X-rays. The samples were located between the first and second ionization chambers, and a reference sample ($RuCl_3$ pellet) was placed between the second and third ionization chambers. Some additional experiments were performed at the Swiss–Norwegian beamline (SNBL) at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. At SNBL, a Si(111) crystal was used as a channel-cut monochromator and a double-bounce gold-coated mirror system for rejection of higher harmonics. The three ionization chambers were filled with Ar, N_2, or Kr in different combinations (I_0 Ar, I_t 30% Kr and 70% N_2, I_{ref} 30% Kr and 70% N_2). At both beamlines (X1 and SNBL), EXAFS spectra were taken under stationary conditions in the step-scanning mode around the Ru K-edge (22.117 keV) between 21,900 and 22,800 eV, with a $RuCl_3$ pellet as a reference. Fast QEXAFS scans were recorded in the continuous scanning mode, usually between 22,065 and 22,665 eV (0.15 s/eV). The raw data were energy calibrated (Ru K-edge energy of the $RuCl_3$ pellet: 22,120 eV [23], first inflection point), background corrected, and normalized with WINXAS 3.0 software [24]. Fourier transformation for EXAFS data was applied to the k^1-weighted functions in the interval $k = 3$–$12.5\ \text{Å}^{-1}$ for the EXAFS data and were fitted in R-space. Typically deviations for the coordination number were within ±0.5, and those for the distance were within ±0.02 Å.

To identify the structure of the ruthenium complexes formed, the product solution was investigated by EXAFS on liquid samples after reaction as well. For this purpose a special stainless-steel EXAFS cell was used for transmission experiments. Because of the low concentration of Ru in the product mixture (50–100 ppm), a long path length of 4 cm was chosen, with a cross section of 6 mm × 11 mm. The volume of the cell was 2 ml, and exchangeable Kapton windows were used on both sides of the cell. The cell can be filled from the top, and a 1 mm × 10 mm beam was focused to the middle of the spectroscopic cell with an x, z, θ-table (Newport). After calibration with a sample of known absorption step $\mu \cdot d$, the concentration of the solution could also be determined independently of the ICP-OES measurements.

For spectroscopic studies under reaction conditions, in addition, an in situ batch reactor was designed that allows investigation of the volume at two locations. In this way the solid catalyst sample at the bottom and the liquid phase 10 mm above the bottom could be probed. The in situ cell can be used up to a pressure of 250 bar and a temperature of 200 °C and equipped with a burst plate (250 bar), a magnetic stirrer, a thermocouple, and an in/outlet [25]. For the experiments, 100 mg of 5%-Ru/Al_2O_3 was loaded into the batch reactor cell, 3.0 ml of mpa was added, and the reactor was closed. After cell alignment, normal EXAFS spectra of the solid catalyst and the solution were taken at room temperature, while the solution was stirred with a magnetic stirrer. Then hydrogen (purity 5.0) was added to a pressure of 70 bar, and 4 g of liquid CO_2 was introduced with the help of a CO_2 compressor (NWA PM-101) and a Rheonik mass flow controller (RHM015). While changes in the solid material were monitored by QEXAFS, the mixture was heated to 120 °C. Then the reaction mixture was cooled to room temperature. After the addition of 50 mg of dppe, the same treatment (addition of hydrogen and carbon dioxide and heating to 100 °C) was performed, but as without dppe.

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

3. Results

3.1. Modification of Ru/Al_2O_3 with dppe and its performance in the formylation of mpa

Table 1 gives an overview of the catalytic results obtained during formylation under different reaction conditions. The dppe-modified Ru/Al_2O_3 catalyst system showed good catalytic performance, whereas runs without either catalyst or dppe (runs 1–3) were unsuccessful. A highly active catalyst was thus formed by modification of the Ru/Al_2O_3 surface with dppe in a molar dppe:Ru ratio of 1:1. The addition of dppe before the catalytic reaction under reflux in THF (premodification) or its addition directly during the reaction itself led to similar catalytic performance. Therefore most of the experiments were carried out without premodification. Table 1 provides some information about the influence of parameters like temperature, the amount of carbon dioxide, the initial partial pressure of hydrogen, and the amounts of Ru/Al_2O_3 and dppe on the conversion. The increase in temperature led to a higher reaction rate (runs 4–6), as expected. The conversion was also influenced by the amount of carbon dioxide added (runs 5, 7, 8), which resulted in the best conversion of 48% with 100 g of carbon dioxide (run 8). Previous studies of the formylation of various amines [14,15] under similar conditions showed that the reaction mixture is made up of two distinguishable phases: A dense liquid-like phase containing mainly the amine, the product formamide and water, and on top a “supercritical”

Table 1
Catalytic formylation of 3-methoxypropylamine (mpa) with carbon dioxide and hydrogen using dppe-modified Ru/Al_2O_3 as catalyst[a]

Run	Amount of dppe (µmol)	Amount of CO_2 (g)	H_2 initial pressure (bar)	Temperature (°C)	Time (h)	Conversion (%)
1[b]	0	100	80	100	3	0
2	0	100	80	100	3	0
3[b]	50	100	80	100	3	0
4	50	25	80	80	3	18
5	50	25	80	100	3	24
6	50	25	80	120	3	35
7	50	50	80	100	3	23
8	50	100	80	100	3	48
9	50	25	40	100	3	15
10	50	25	140	100	3	38
11	50	25	180	100	3	39
12	14	100	80	100	20	16
13	25	100	80	100	20	47
14	37	100	80	100	20	67
15	50	100	80	100	20	82
16	100	100	80	100	20	63

[a] Conditions, if not otherwise stated: 100 mmol mpa, 50 µmol Ru.

[b] 0 µmol Ru.

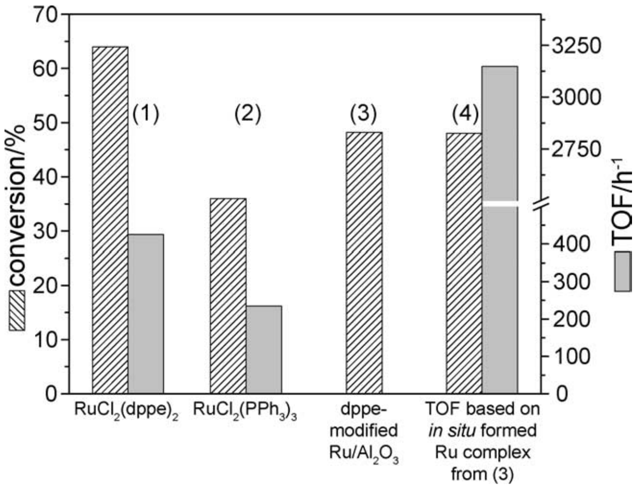


Fig. 1. Comparison of the activity in 3-methoxypropylamine formylation of the homogeneous complexes $RuCl_2(dppe)_2$, $RuCl_2(PPh_3)_3$ with dppe-modified Ru/Al_2O_3. Reaction conditions: 100 mmol mpa, 0.050 mmol Ru, 100 g CO_2, 80 bar H_2 initial partial pressure, 3 h and 100 °C.

more gas-like phase containing mainly hydrogen and the carbon dioxide (note that the term "supercritical" is exactly defined only for pure substances [26]). Increasing the hydrogen initial pressure resulted in higher conversions (Table 1, runs 5, 9–11). At a hydrogen pressure of 40 bar, 15% conversion was reached within 3 h, whereas at 180 bar, 39% conversion was achieved. The amount of dppe added influenced the reaction as well (Table 1, runs 12–16). Conversion increased with the addition of dppe up to 82%; the P:Ru ratio (mol/L Ru per mol/L P) in this optimal case was 2:1. When dppe was added in a P:Ru ratio of 4:1, the conversion decreased to 63%.

For comparison, related homogeneous ruthenium catalysts were tested in the formylation reaction; results are shown in Fig. 1. The homogeneous complexes $RuCl_2(dppe)_2$ and $RuCl_2(PPh_3)_3$ showed a turnover frequency of 425 and 235 h^{-1}, respectively, at 100% selectivity. Dppe-modified Ru/Al_2O_3 showed a conversion of 48% under the same reaction conditions. This conversion is higher than that observed with the homogeneous catalyst $RuCl_2(PPh_3)_3$ but lower than that observed with $RuCl_2(dppe)_2$. The higher activity of $RuCl_2(dppe)_2$ compared with $RuCl_2(PPh_3)_3$ is in line with earlier studies [14], where $RuCl_2(dppe)_2$ has been found to be most active.

3.2. Identification of the catalytically active species

Fig. 2 shows the ex situ X-ray absorption spectra of the solid catalyst under different conditions:

(1) Ru/Al_2O_3 untreated,
(2) Ru/Al_2O_3 treated with dppe and amine before the reaction, and
(3) dppe-modified Ru/Al_2O_3 after the reaction.

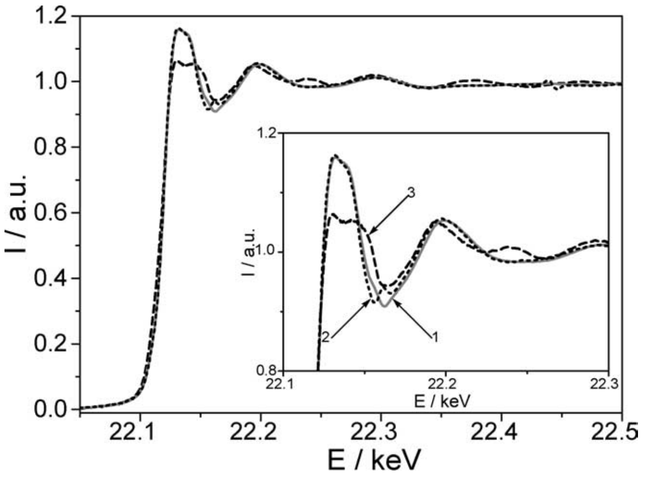


Fig. 2. XAFS spectra of (1) Ru/Al_2O_3, compared to (2) dppe-modified Ru/Al_2O_3 before reaction (pretreated with dppe and amine under reflux), and (3) dppe-modified Ru/Al_2O_3 after reaction.

Table 2
Test series of the formylation of 3-methoxypropylamine with dppe-modified Ru/Al_2O_3 to check the possibility of the formation of a homogeneous catalyst[a]

Run	Catalytic system	Time (h)	Conversion (%)
17	Dppe-modified Ru/Al_2O_3	3	48
18	Filtered reaction mixture of run 17	20[b]	78
19	Dppe-modified Ru/Al_2O_3	20	82

[a] Conditions: 100 mmol mpa, 50 µmol Ru on Al_2O_3, 50 µmol dppe, 100 g CO_2, 80 bar H_2 at 100 °C. After 3 h (run 17), the solid catalyst was removed and the reaction was continued in the filtered reaction mixture. The conversion after 20 h (run 18) was equal to the one observed with the catalyst present during 20 h (run 19).

[b] Catalyst was filtered off after 3 h.

A clear decrease in the whiteline at 22.12 eV is apparent after step (3), which reveals that ruthenium was reduced during the reaction. No change in the EXAFS spectra was observed during modification of the Ru/Al_2O_3 catalysts by treatment with amine and dppe beforehand. In the EXAFS region (Fourier-transformed data, not shown) a clear change in the Ru–O and the Ru–Ru backscattering was found. However, ruthenium was not completely reduced.

To elucidate the role of possible corrosion of the Ru constituent and the formation of active ruthenium complexes in solution under reaction conditions in the presence of dppe, we performed suitable tests that allowed us to distinguish between heterogeneous and homogeneous catalysis [27]. The reaction was stopped after a certain time, the solid catalyst was filtered off, and we checked it to determine whether the reaction could be continued in the filtered reaction mixture (Table 2). Note that almost the same conversion was observed irrespective of whether the Ru/Al_2O_3 catalyst was filtered off after 3 h or was present during the whole reaction time. This implies that during the first 3 h of the reaction, a highly active Ru-based homogeneous catalyst must have been formed.

Table 3
Solubility of the in situ formed catalyst from Ru/Al_2O_3 and dppe in the liquid phase, compared to $RuCl_2(PPh_3)_3$ and $RuCl_2(dppe)_2$

Run	Catalyst	Reaction data[a]			Dissolved in reaction mixture		
		Time (h)	Conversion (%)	TOF[b] (h^{-1})	Ru (ppm)	P (ppm)	P/Ru (mol/mol)
20	dppe-modified Ru/Al_2O_3	3	48	3147	50.5	251	16.2
21	dppe-modified Ru/Al_2O_3	20	82	559	66.4	256	12.6
22	dppe-modified Ru/Al_2O_3	20	78	585	60.6	294	15.8
23[c]	Blank test	3	0	0	0.60	21.8	118
24[d]	dppe	3	0	0	1.89	268	463
25	$RuCl_2(PPh_3)_3$	3	36	315	385	375	3
26	$RuCl_2(dppe)_2$	3	64	425	133	173	4.2
27	$RuCl_2(dppe)_2$	20	91	91	252	319	4.1

[a] Conditions: 50 µmol Ru, 100 mmol mpa, 100 g CO_2, 80 bar H_2 partial pressure, 100 °C.
[b] TOF based on Ru dissolved in reaction mixture.
[c] 0 mol Ru, 0 mol dppe.
[d] 0 mol Ru, 50 µmol dppe.

In addition, the ruthenium and phosphorus contents in the liquid phase of the samples were measured by ICP-OES; Table 3 gives an overview. The ruthenium concentration in the liquid reaction mixture was about 50 ppm (50 mg/kg, mass based) after 3 h (run 20) under standard reaction conditions, as described above. The results show that after 20 h, 66 ppm (0.689 mmol/L) ruthenium was dissolved in the liquid phase (run 21), compared with 60 ppm (0.631 mmol/L) if the catalyst was filtered off after 3 h (run 22). The ruthenium concentrations were corroborated by X-ray absorption spectroscopy (edge jump at the Ru K-edge). Application of UV–vis spectroscopy was biased by the very low Ru concentration, which was at the detection limit of the technique. Note that the Ru concentration in the liquid phase was very similar, irrespective of whether the reaction was stopped after 3 h, and whether the Ru/Al_2O_3 catalyst was removed or was present in the reactor for 20 h. The background concentrations of ruthenium and phosphorus were significantly lower during blank runs (Table 3, runs 23, 24), and no conversion was observed. If we relate TOF to the amount of ruthenium dissolved in the liquid phase, a very high rate of 3148 h^{-1} is estimated based on a ruthenium concentration of 51 ppm in the reaction mixture. For comparison, the Ru concentration of the homogeneous catalyst $RuCl_2(dppe)_2$ was also determined. After a reaction time of 3 h, 133 ppm Ru (corresponding to 1.386 mmol/L) (run 26) was found, which increased to 252 ppm (2.577 mmol/L in run 27) after 20 h, reflecting the time dependence of the solubility of the catalyst in the amine-rich liquid-like phase. And in case of the homogeneous catalyst $RuCl_2(PPh_3)_3$, a concentration of 385 ppm Ru and 375 ppm P (according to a P/Ru ratio of 3) was detected (run 25). Note that the concentration of Ru was very small but sufficient to catalyze the formylation of mpa.

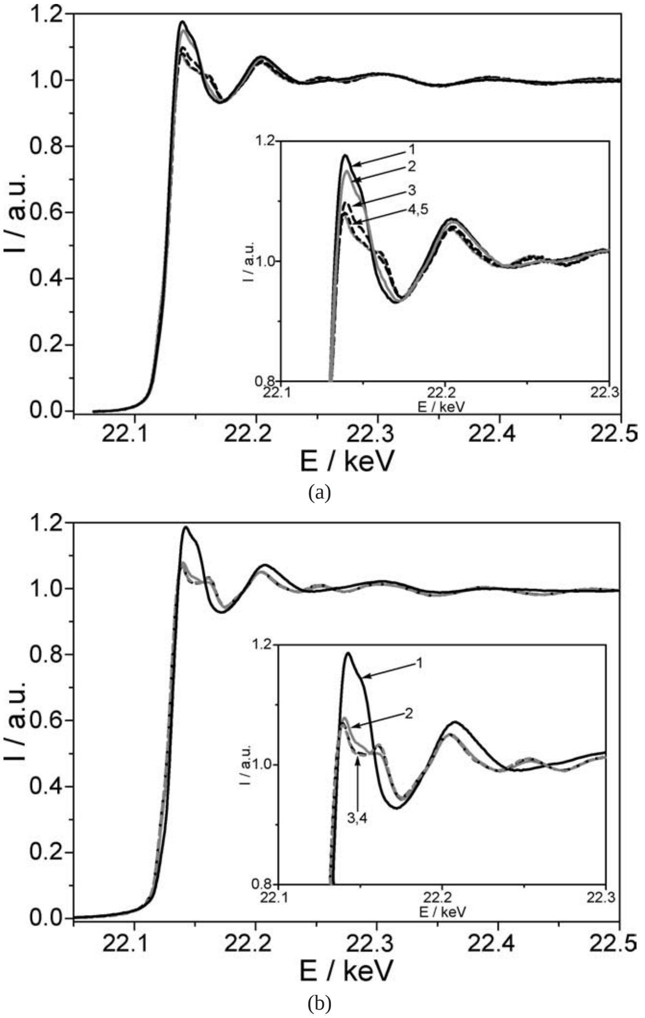
3.3. *Spectroscopic study of the in situ formation of the homogeneous Ru catalyst*

To understand the formation of the homogeneous catalyst, the changes in the solid Ru/Al_2O_3 catalyst and in the liquid phase were investigated. For this purpose, a specially designed batch reactor cell was used that allowed in situ EXAFS measurements both at the bottom (solid phase) and in the middle (liquid) of the batch reactor [25]. In the first step the catalyst in the presence of mpa, hydrogen, and carbon dioxide was investigated; the results are shown in Fig. 3. Fig. 3a shows the treatment of the catalyst in the reaction mixture without dppe; Fig. 3b depicts the spectra taken during the reaction in the presence of dppe.

With increasing temperature and in the absence of dppe (Fig. 3a), Ru was reduced, indicated by the decrease in the whiteline at 22.12 keV. The structural changes in ruthenium were limited to the solid phase, and no Ru species were observed in the liquid phase.

After a reaction time of 4.5 h (without dppe), the concentration of ruthenium in the liquid phase was still negligible. Only after an increase in the stirring rate (Fig. 4, spectrum 2) was some Ru visible in the X-ray absorption spectrum. Some part of the catalyst was probably suspended in the upper part of the cell, and thus a small edge jump was observed. Note that the XANES scans around the Ru K-edge were taken only directly around the edge (spectra 2 and 3), and the absorption step was related to the maximum intensity observed at the end of the experiment (Fig. 4, spectrum 4, absorption edge of 1.0).

Hence, during this first step no catalyst was dissolved in the liquid-like amine-rich phase. However, as soon as dppe was added, an abrupt increase in the Ru concentration and a further increase during heating were observed (Fig. 4, traces 3 and 4). During this step hardly any changes in the solid Ru catalyst (Fig. 3b) could be observed. Thus the in situ formation of the active species in the liquid-like amine-rich phase could be observed as soon as dppe was added (Fig. 4) and can be related to the tendency of this ligand to corrode the ruthenium and form Ru complexes. This behavior was also supported by the observation that no catalytic activity was observed in the absence of dppe, and no significant amount of Ru was found in the liquid solution with ICP-OES (Table 3). Note, furthermore, that the in situ spectrum after the reaction (Fig. 4, spectrum 4) and the ex situ spectrum after the reaction (Fig. 4, trace 5) are similar. Dur-



(a)

(b)

Fig. 3. (a) Reduction of Ru/Al_2O_3, monitored in situ by X-ray absorption spectroscopy, solid phase (1) before reaction at 40 °C as reference and at 120 °C after (2) 0 min, (3) 30 min, (4) 60 min, (5) 150 min reaction time. (b) In situ monitoring during reaction over Ru/Al_2O_3, solid phase (1) before reaction at 40 °C as reference and with dppe at 100 °C after (2) 150 min, (3) 160 min, (4) 250 min. Conditions: 10 ml batch reactor cell, 3 ml mpa, 70 bar H_2, total pressure 120 bar, rest CO_2.

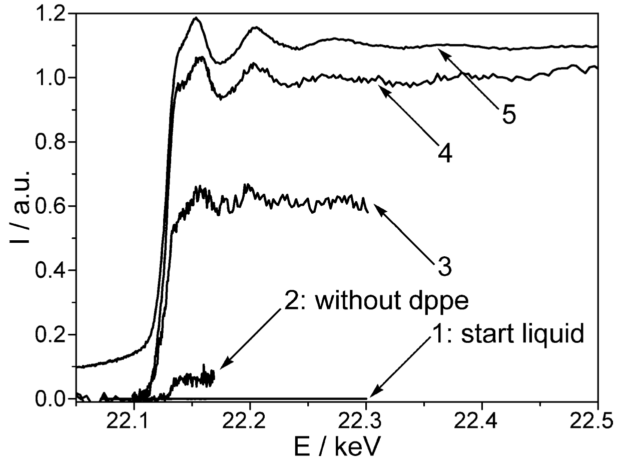


Fig. 4. Solubility and formation of the catalytic active species monitored by XANES in liquid phase during reaction. (1) at 0 min, without dppe; (2) at 4.5 h, without dppe, increased stirring rate, 120 °C; (3) at 30 min, with dppe, 120 °C; (4) after reaction, with dppe, 25 °C; (5) ex situ spectrum after reaction with dppe, 25 °C; absorption of spectra 1–4 are calibrated to the normalized spectrum 4; simultaneously recorded to Fig. 3.

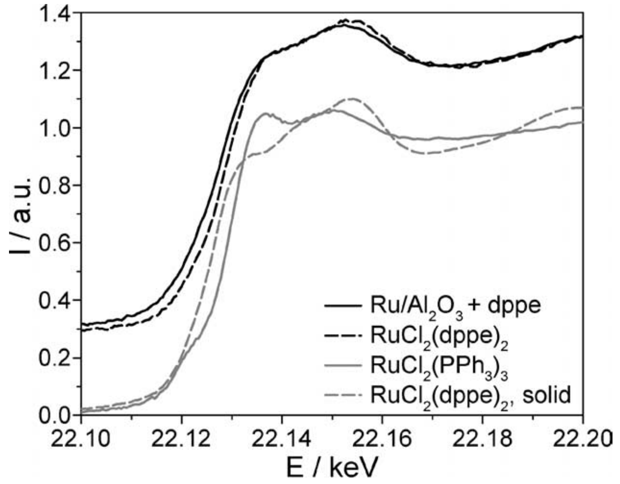


Fig. 5. X-ray absorption near-edge structure at the Ru K-edge of $RuCl_2(dppe)_2$, liquid product mixture (dotted black line), dppe-modified Ru/Al_2O_3, liquid product mixture (solid black line), $RuCl_2(dppe)_2$, solid complex (dotted gray line) and $RuCl_2(PPh_3)_3$, liquid product mixture (solid gray line). Reference spectrum: solid $RuCl_2(dppe)_2$.

ing cooling and depressurizing no remarkable change was detected.

3.4. Structural identification of the homogeneous Ru complex

To gain information about the structure of the active species formed in situ, ex situ XANES and EXAFS spectra were recorded. Because of the low concentration of 50–100 ppm in the reaction mixture, a liquid cell with a 4-cm path length was constructed. The cell was open on top to eliminate possible gas bubbles in the highly viscous product mixture, and Kapton foils were used as X-ray transparent windows on both sides of the liquid cell to keep the liquid in the beam.

Fig. 5 shows the XANES region of the dppe-modified Ru/Al_2O_3 catalyst in the liquid product mixture in comparison, with the homogeneous catalyst $RuCl_2(dppe)_2$ in liquid phase and as a solid (see corresponding catalytic results in Table 1). For structural identification $RuCl_2(PPh_3)_3$ in the liquid reaction mixture was also investigated. The analytical results indicate that the structure of the catalyst formed in situ from Ru/Al_2O_3 and dppe is similar to the structure of $RuCl_2(dppe)_2$ under reaction conditions, whereas the structure of the solid $RuCl_2(dppe)_2$ seems to be different, probably as a consequence of the replacement of the chloride by hydrogen and by the amine under reaction conditions. Note that a change in the XANES region is also due to the change in multiple scattering paths that also influence the near-edge structure [28,29]. From the variation of the XANES region of $RuCl_2(PPh_3)_3$ it can also be inferred that the structure

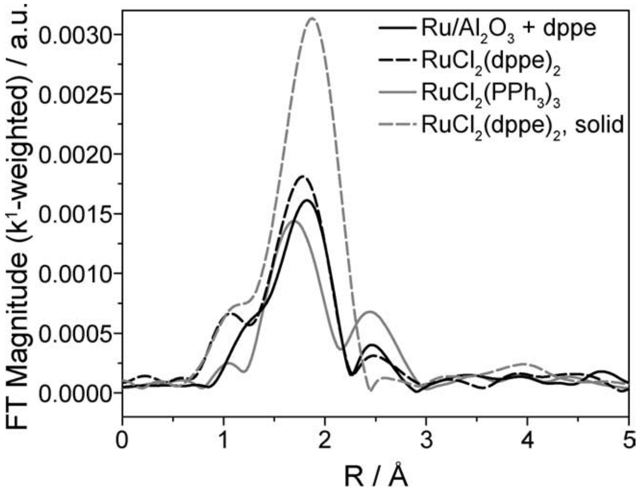
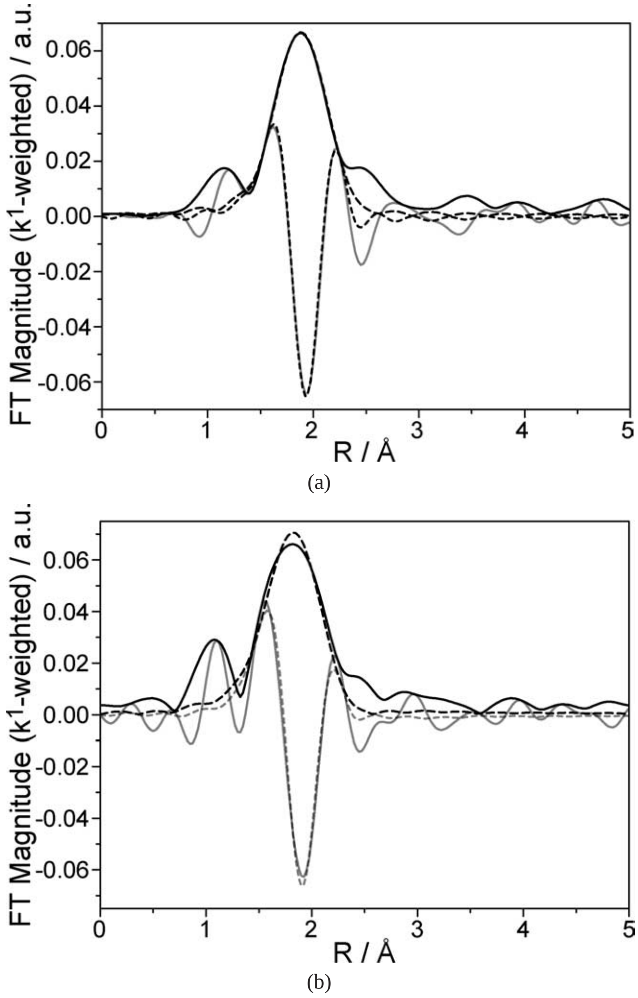


Fig. 6. Comparison of the Fourier transformed EXAFS spectra (k^1 weighted) at the Ru K-edge of $RuCl_2(dppe)_2$ in reaction mixture from reaction with mpa (dotted black line), dppe-modified Ru/Al_2O_3 in reaction mixture (solid black line), $RuCl_2(dppe)_2$, solid phase (dotted gray line) and $RuCl_2(PPh_3)_3$, in reaction mixture (solid gray line).



(a)

(b)

Fig. 7. Fourier-transformed and k^1-weighted Ru K-edge EXAFS spectra ($k^1 \cdot \chi(k)$) of (a) dppe-modified Ru/Al_2O_3 (20 h) and (b) $RuCl_2(dppe)_2$ after reaction: radial distribution function together with the imaginary part—measured data (solid line), fitted data (dotted line).

of the catalyst formed in situ from Ru/Al_2O_3 and dppe is more similar to the structure of $RuCl_2(dppe)_2$ than to that of $RuCl_2(PPh_3)_3$. Only a slight shift in the Ru K-edge is found, indicating that the oxidation states of the two complexes are similar [23].

Fig. 6 shows the corresponding Fourier transformed k^1-weighted extended X-ray absorption fine structure (EXAFS) spectra. Similar to the near-edge spectra, significant differences of the as-prepared solid catalysts $RuCl_2(PPh_3)_3$ and $RuCl_2(dppe)_2$ and the corresponding Ru complexes after reaction (liquid product mixture) are evident. The backscattering is lower for both Ru–Cl and Ru–P, and the peak is shifted to lower R values (spectra not corrected for the phase shift). The spectra of the catalysts exhibit backscattering peaks at 1.8 and 2.5 Å for all catalysts. Whereas $RuCl_2(dppe)_2$ in reaction mixture and dppe-modified Ru/Al_2O_3 show similar backscattering from the nearest-neighbor atoms, the solid $RuCl_2(dppe)_2$ exhibits a large peak at 1.8 Å and only a very small one at 2.5 Å. The corresponding spectrum of $RuCl_2(PPh_3)_3$ is quite different (Fig. 6).

The Fourier-transformed spectra were fitted with Ru–Cl and Ru–P shells calculated with FEFF 6.0 [30]; the results are listed in Table 4. Some of the experimental and fitted data are compared in Fig. 7. The structural data obtained for the solid $RuCl_2(PPh_3)_3$ (entry 1 of Table 4) are in good accordance with the literature [31]. For the solid homogeneous catalyst, three different Ru–P bond lengths, 2.23, 2.37, and 2.41 Å, were reported. Only two Ru–P distances (2.23 and 2.38 Å, Table 4) could be distinguished with EXAFS. Only one Ru–Cl bond length was detected at 2.44 Å by EXAFS, which shows the limitation of our method. While the typical uncertainty is estimated to be ±0.02 Å for the distance and about ±0.5 for the coordination number, the superposition of two shells of the same backscatterer with similar distances in particular could not be resolved sufficiently. The results from the EXAFS spectra of solid $RuCl_2(dppe)_2$ show that the different structure is appropriately reflected. Both Ru–P and Ru–Cl distances are found. The bond length of Ru–Cl (2.42 Å) in the solid $RuCl_2(dppe)_2$ calculated from the EXAFS fit is in the same range (2.436 Å) as that published in the literature [32]. Furthermore, we found only one averaged Ru–P bond, instead of the two different Ru–P bonds (2.389 and 2.369 Å) reported.

Significant structural changes were detected for the complexes formed during the formylation reaction of mpa. After the use of $RuCl_2(PPh_3)_3$ in the reaction, a Ru–P bond length of 2.22 Å and an additional contribution that could be fitted with a Ru–Ru distance at 2.93 Å were found, corresponding to the two peaks observed in Fig. 6. This shows that there are only slight changes in the Ru–P neighbors in the liquid (after reaction) or solid phase, but the Ru–Cl coordination changes. All bond lengths of the complexes $RuCl_2(dppm)_2$ [33], $RuCl_2(dppe)_2$ [32], $RuCl_2(dppp)_2$ [34],

Table 4
Structural data extracted from EXAFS spectra of different ruthenium phosphine complexes as solid and in liquid phase. Ru-concentration in the liquid phase ∼ 50–100 ppm, N: coordination number, R: distance of the corresponding neighbor, $\Delta\sigma^2$: Debye–Waller factor

Catalyst	Ru–P			Ru–Cl			Residual[d]
	N	R (Å)	$\Delta\sigma^2$ (Å^2)	N	R (Å)	$\Delta\sigma^2$ (Å^2)	
$RuCl_2(PPh_3)_3$[a]	1.0	2.23	0.0025	2.3	2.44	0.0027	1.4
	2.0	2.38	0.0025				
$RuCl_2(dppe)_2$[a]	4	2.29	0.0013	2	2.42	0.0006	2.0
$RuCl_2(PPh_3)_3$[b]	4.1	2.22	0.0044	2	2.93	0.0060	7.2
$RuCl_2(dppe)_2$[b]	3.6	2.32	0.0063	–	–	–	9.4
Dppe-modified Ru/Al_2O_3[b,c]	3.3	2.35	0.0060	–	–	–	3.2

[a] Solid catalyst.
[b] Liquid solution measured after reaction with mpa.
[c] Additional shell: Ru–N or Ru–O: $N = 0.8$, $R = 2.07$ Å, $\Delta\sigma^2 = 0.006$.
[d] Quality of the fit according to Ref. [24].

$RuBrCl(dppe)_2$ [35], and $RuClH_2(dppp)_2PF_6$ [36] reported in the literature are between 2.340 and 2.441 Å; depending on the ligand used, the Ru–Cl bond length changes from 2.407 to 2.436 Å. In the liquid phase the bond length of Ru–P in $RuCl_2(dppe)_2$, 2.32 Å, is in the expected range (the decrease may result from additional oxygen/nitrogen neighbors in the complex), but no Ru–Cl bond is indicated in the spectra. Thus a change in the structure of $RuCl_2(dppe)_2$ in the liquid phase is observed during the reaction. There are two feasible explanations for this observation: The Cl atoms could have been replaced by hydrogen to form a hydrido complex [37–39], or a partial amino (or hydroxo-) complex was formed with hydrogen and mpa present in the liquid phase. Moreover, this may be due to similar Ru–P and Ru–Cl distances in the complexes formed. However, the Ru–P distance is usually shorter than the Ru–Cl distance (see references above and [40,41]). Note also that the catalyst was investigated after air exposure. Moreover, the EXAFS analysis is limited because several species may be present, and EXAFS averages over these species.

The reaction mixture containing dppe-modified Ru/Al_2O_3 exhibited a Ru–P bond length of 2.35 Å. This shows that—as already concluded from the near-edge region and the Fourier-transformed EXAFS spectra—a homogeneous Ru-dppe-based catalyst forms. No Ru–Cl is observed, as expected. The structure of this catalyst formed in situ seems to resemble that of the observed $RuCl_2(dppe)_2$ in the liquid phase, but amino and oxygen neighbors were also found in the first shell of the dppe-modified Ru/Al_2O_3 system. The EXAFS fit of the spectrum improved significantly when nitrogen/oxygen neighbors (the two atoms have similar backscattering amplitudes, inasmuch as they are neighbors in the periodic table) were also used. The formation of such a complex is reasonable because the catalyst is dissolved in the amine-rich phase during the reaction.

4. Discussion

Ru/Al_2O_3 modified by dppe was found to be highly active for the formylation of 3-methoxypropylamine (mpa), with carbon dioxide and hydrogen. The catalyst shows good activity and 100% selectivity comparable to the performance of the homogeneous ruthenium-based phosphine complexes $RuCl_2((PCH_3)_3)_4$ and $RuCl_2(dppe)_2$. The study indicates that the formylation of amines with hydrogen and carbon dioxide can be extended to amines containing an ether group.

The reaction rates for mpa in terms of the TOF are comparable to or better than those achieved with other primary amines, such as propylamine in the presence of $RuCl_2((PCH_3)_3)_4$ with 52 h^{-1} [11]. Turnover frequencies of secondary amines like diethylamine are between 440 h^{-1} [3] and 360,000 h^{-1} [13], depending on the catalyst used and the experimental conditions.

Carbon dioxide acts as both reactant and solvent. CO_2 is not present as a single “supercritical” phase, but exists in two phases, an amine-rich CO_2 phase with H_2 dissolved and a CO_2/H_2 phase [14]. The volume of the amine-rich CO_2 phase with dissolved H_2 increases with increasing carbon dioxide in the system. Higher partial pressure of hydrogen affects the dissolved amount of H_2 in the amine-rich CO_2 phase and results, combined with the higher density, in a better mixing of reactants in the amine-rich CO_2 phase and thus finally in better conversion and TOF.

Interestingly, it was found that dppe-modified Ru/Al_2O_3 showed good catalytic performance in the formation of 3-methoxypropylformamide, similar to those of the homogeneous catalysts $RuCl_2(dppe)_2$ and $RuCl_2(PPh_3)_3$. This behavior could be traced to the formation of active free Ru complexes as a result of the interaction of the supported Ru particles with the strongly complexing phosphine (dppe). This interaction leads to some corrosion of the Ru particles.

The formation of a soluble complex during reaction could be proved in different ways. On the one hand, X-ray absorption spectroscopy and ICP-OES showed the presence of dissolved Ru in the product mixture. On the other hand, the reaction could be continued if the solid material was filtered off after a certain reaction time (Table 2). Only a small fraction of the ruthenium is dissolved, resulting in a concentration of 50–100 ppm in the product mixture. This shows that the homogeneous Ru-based catalyst formed is highly active (TOF based on the amount of dissolved Ru is about 3100 h^{-1}, Table 3, run 20).

The formation of the ruthenium complex, which is acting as homogeneous catalyst, could be monitored in situ by X-ray absorption spectroscopy. In principle, there are only a few techniques, such as EXAFS spectroscopy, UV–vis spectroscopy, NMR spectroscopy, and infrared spectroscopy, that make such studies possible [42–46]. Because of the low concentration of the homogeneous catalyst, structural studies using UV–vis were not successful. The concentration of the target species was also too low for NMR and IR spectroscopy. Because of the good penetration of X-rays at 20 keV, EXAFS studies in the transmission mode were possible. X-ray absorption spectroscopy has the advantage that the concentration and the structure of the Ru species can be determined element-specifically and under reaction conditions. Such studies are rare under such rigorous conditions (150 bar, 120 °C) as applied here and have only recently been reported for solid [47] and homogeneous catalysts [48,49]. Here we found that the X-ray absorption technique, combined with an appropriate high pressure cell, allowed monitoring of the solid catalyst at the bottom and identification of the in situ formed complex in the liquid phase in the upper part of the reactor at the same time.

During reaction, the ruthenium constituent in the solid catalyst is reduced. However, ruthenium can only be found in the liquid phase if dppe is added to the system. This indicates corrosion of the ruthenium particles in the presence of hydrogen and dppe. It is probably the structure of the dppe ligand and thus the possibility of forming a highly stable chelate complex that ameliorate the corrosion of the Ru and thus the in situ formation of the Ru complex I.

Such an in situ formation of a homogeneous catalyst from a supported metal catalyst has rarely been reported. Köhler et al. recently reported on the in situ formation of a Pd catalyst in Heck reactions [50]. Moreover, in this case ligands/reactants in the solution led to the formation of an active homogeneous catalyst. This example underlines the necessity for appropriate in situ spectroscopic tools to judge between homogeneous complexes and surface modification on metal particles as active species for catalysis.

The amount of dissolved ruthenium in the liquid phase was quantified by ICP-OES and corroborated by XAS. The concentration of ruthenium was very low, in the range of 50–100 ppm, and no redeposition like that in Ref. [50] was observed. The TOF (3147 h^{-1}) related to the dissolved ruthenium species turns out to be significantly higher than the TOF (324 h^{-1}) based on the total amount of ruthenium present in the reactor. We can conclude that the ruthenium species formed in situ has a higher intrinsic activity than the homogeneous catalyst $RuCl_2(dppe)_2$. The reason for the better activity may be found in the different structures of dissolved $RuCl_2(dppe)_2$ and the species formed in situ from Ru/Al_2O_3 and dppe. Furthermore, the solubility of $RuCl_2(dppe)_2$ in the reaction mixture may affect its catalytic performance.

Structural analysis of the Ru complex formed by EXAFS spectroscopy indicates that a $Ru(dppe)_2X_2$ catalyst is formed that may contain either additional hydrido- or amino/hydroxo-ligands. The formation of a hydrido complex was previously indicated in other studies [37–39,51], and the mechanism for the Ru-catalyzed formylation of amines proposed by Jessop et al. [11] can be further confirmed. Based on this, we can assume that a hydrido complex is probably formed from Ru/Al_2O_3 and dppe in the liquid phase under reaction conditions. CO_2 is activated by insertion into the metal–hydrogen bonding of the hydrido complex. In the presence of mpa, the complex reacts further to form the product 3-methoxypropylformamide, and water is formed as a by-product.

The present study shows that modification of supported transition–metal catalysts with a phosphine may corrode the metal and result in free metal phosphine complexes, which may disguise the intrinsic catalytic properties of the modified supported metal catalyst. Similar behavior has been observed when another phosphine, triphenylphosphine, was applied. Thus it seems to be of paramount importance to test for this possibility when supported metal catalysts are applied together with phosphines.

5. Conclusions

Modification of Ru/Al_2O_3 by the addition of a phosphine (dppe) has been shown to result in homogeneous Ru catalysts that are highly active in the formylation of methoxypropylamine with carbon dioxide and hydrogen. The catalytically active species were not the phosphine-modified ruthenium particles, but a homogeneous chlorine-free Ru-dppe complex that formed under reaction conditions. The presence of dppe led to dissolution (corrosion) of ruthenium and probably to the formation of a highly active homogeneous $Ru(dppe)_2X_2$ complex, which was even sufficiently active to achieve high conversion at very small concentrations (50 ppm Ru in the reaction mixture).

X-ray absorption spectroscopy proved to be a valuable technique for identifying the role of solid and liquid Ru species in the catalytic reaction. The formation of the homogeneous catalyst could be monitored under reaction conditions, and the structural identification of the homogeneous Ru-dppe complex could be achieved, even down to a concentration of less than 100 ppm in the product mixture.

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