

Silica hybrid gel catalysts containing ruthenium complexes: influence of reaction parameters on the catalytic behaviour in the synthesis of *N,N*-dimethylformamide from carbon dioxide

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Abstract

The synthesis of *N,N*-dimethylformamide from carbon dioxide, hydrogen and dimethylamine has been studied in an autoclave using a sol-gel derived heterogeneous catalyst made of $\text{RuCl}_2\{\text{PPh}_2(\text{CH}_2)_2\text{Si}(\text{OEt})_3\}_3$ and $\text{Si}(\text{OEt})_4$ in a ratio of 1:50. The effect of the reaction variables on the activity and selectivity of the hybrid gel was examined by varying the initial concentrations of the catalyst and dimethylamine, the partial pressures of hydrogen and carbon dioxide, the temperature and the stirring frequency. Parametric investigations revealed that the measured reaction rates are not disguised by mass transfer phenomena under the conditions applied. The suitable temperature range of the reaction is between 370 and 400 K, with the upper temperature limit given by the thermal stability of the catalyst. Hydrogen appeared to be the limiting reactant since it significantly influenced the reaction rate. In contrast, the carbon dioxide partial pressure in the range 3–18 MPa and the dimethylamine concentration had only a negligible effect on the turnover frequency, indicating a zeroth order dependence. High concentrations of hydrogen and carbon dioxide in the liquid dimethylamine phase afford high concentrations of all reactants at the catalytic centres in an ideal reaction design. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Hybrid gel catalyst; Sol-gel; Ruthenium; *N,N*-Dimethylformamide; Carbon dioxide; Supercritical fluid

1. Introduction

An increasing number of studies has been concerned with the use of carbon dioxide as a C_1 feedstock for the manufacture of valuable chemicals and fuels, alternative to the current predominant use of carbon monoxide [1–6]. In the presence of amines the hydrogenation of

CO_2 can lead to formamides under suitable reaction conditions. It has been shown that the synthesis of *N,N*-dimethylformamide (dmf) from CO_2 , H_2 and dimethylamine using transition metal catalysts in the presence [5–13] or absence [7] of solvents represents an interesting alternative route for producing this base chemical.

Recently, Jessop et al. [5,14,15] reported a highly efficient reaction design for the homogeneous catalytic synthesis of dmf, where super-

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critical carbon dioxide (scCO₂) was used as both a reaction medium and a reactant. The utilization of a [RuCl₂(P(Me)₃)₄] catalyst dissolved in a supercritical phase of CO₂ and H₂ resulted in markedly higher turnover numbers (TON) compared to similar reactions in organic solvents. The high reaction rate was attributed to a number of factors, including the high miscibility of H₂ with scCO₂, a weaker coordination sphere around the catalyst, rapid diffusion in the supercritical phase, and elimination of mass transfer between the gaseous and liquid phases [5,15]. The application of complexes soluble in scCO₂ was reported to be crucial for achieving high activities [14].

To overcome technical difficulties associated with the separation and recovery of soluble homogeneous catalysts from the products, considerable effort has been made in the past decades by anchoring active transition metal complexes to organic or inorganic solid supports [18–21]. The resulting materials combine the advantages of both homogeneous and heterogeneous catalysts but also suffer from inherent problems, namely limited surface loading and leaching of the metal complex into the solution of the reactants [20,21]. An alternative approach for the heterogenization of homogeneous catalysts offers the simultaneous co-condensation of transition metal silylether complexes with tetraalkoxysilanes by a sol-gel process [20–25]. Compared to surface-attached complexes, the sol-gel method yields stable hybrid gel materials with preferable structural and chemical properties. Moreover, sol-gel processing allows the flexible control of the metal loading in a wide range. In a preliminary study we have shown that sol-gel processed, silica matrix stabilized, transition metal complexes with silylether ligands are highly active heterogeneous catalysts for the synthesis of *N,N*-dimethylformamide from carbon dioxide, hydrogen and dimethylamine [16,17,25]. Among the catalysts tested, ruthenium containing silica gels exhibited highest activities. The immobilized complexes were more stable towards oxygen

compared to their free analogues and showed negligible leaching.

The aim of the present work was to study the influence of different reaction parameters on the catalytic behaviour of a silica matrix stabilized ruthenium complex in the synthesis of *N,N*-dimethylformamide from carbon dioxide, hydrogen and dimethylamine. The effect of stirring frequency, temperature, CO₂ and H₂ partial pressure, amount of dimethylamine and amount of catalyst on activity and selectivity is investigated.

2. Experimental

2.1. Catalyst preparation

All preparations were carried out under dry, oxygen-free argon using Schlenk techniques. Solvents were used in spectrophotometric purity, dried over molecular sieve, degassed and stored under argon. Vinyltriethoxysilane was supplied from Alfa and diphenylphosphine from Strem Chemicals. All other compounds were supplied from Fluka.

(Trisethoxysilyl)ethyldiphenylphosphine (**1**) was obtained by the photochemical reaction of vinyltriethoxysilane (20.2 g, 106 mmol) and diphenylphosphine (19.8 g, 106 mmol) for 4 days and purified by distillation (1 Torr, 174°C) to give a colourless liquid [26]. (**1**, 38.7 g, 97%): ¹H NMR (CDCl₃) δ 7.2–7.7 (m, 10H, ArH), 3.80 [q, *J* = 7.0 Hz, 6H, OCH₂CH₃], 2.13 (m, 2H, CH₂P), 1.21 [t, 9H, *J* = 7.0 Hz, OCH₂CH₃], 0.72 (m, 2H, SiCH₂); ³¹P{¹H} NMR (CDCl₃) δ – 8.4.

The synthesis of the silylether complex RuCl₂{PPh₂(CH₂)₂Si(OEt)₃}₃ (**2**) was carried out according to the literature [27]. RuCl₃·H₂O (0.60 g, 2.30 mmol) was dissolved in methanol (75 ml) in a Schlenk tube and **1** (5.18 g, 13.8 mmol) was added under stirring. Sodium borohydride was added in small portions until the colour changed to brown. After further stirring for 15 h the methanol was evaporated (15 h,

60°C, 0.5 Torr). The solid residue was shaken 30 min with CH₂Cl₂ (50 ml) and the insoluble salts subsequently filtered off over Celite. Finally the CH₂Cl₂ was evaporated at 50°C (15 h, 0.5 Torr) and the oily residue extracted two times with pentane. (**2**, 5.93 g, 89%): Anal. Calc. for C₆₀H₈₇O₉Cl₂P₃RuSi₃: C, 55.37; H, 6.74. Found: C, 55.08; H, 6.46.

The hybrid gel catalyst was prepared by the acid catalysed co-condensation of **2** with Si(OEt)₄. The silylether complex and tetraethoxysilane (TEOS) in the molar ratio 1:50 were dissolved in acetone under argon and a seven-fold excess of 2.8 N orthophosphoric acid, based on the stoichiometric equivalent of water required for complete hydrolysis, was added. After moderately stirring the solution for 24 h, the acetone was evaporated off by passing a continuous flow of argon through the flask for 3 days. The resulting glassy coloured lumps, which had the same colour as the precursor complex were kept for further 4 days in an open beaker. The lumps were crushed, washed three times with water (20 ml) and three times with acetone (20 ml), and finally dried for 6 h at room temperature under vacuum (0.1 Torr).

2.2. Catalyst characterization

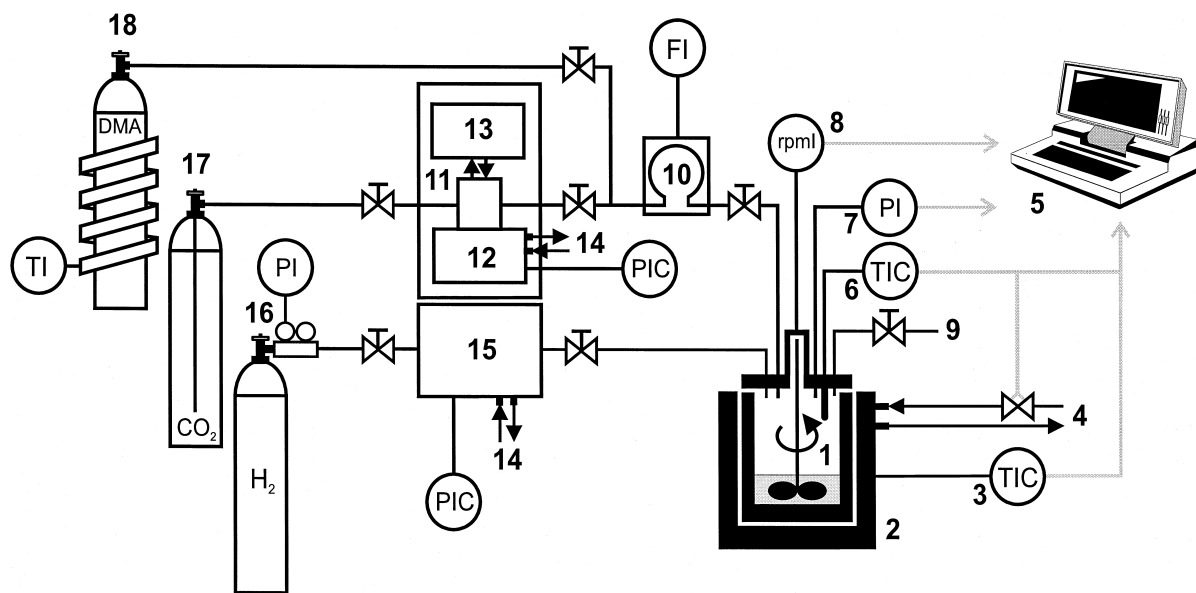
Details on the characterization of the catalyst by means of ²⁹Si NMR spectroscopy, extended X-ray absorption fine structure (EXAFS), X-ray diffraction (XRD), transmission electron microscopy (TEM) and nitrogen physisorption have been reported in Ref. [28]. The hybrid gel possessed a BET surface area of 460 m²/g and a mean pore diameter of 2.8 nm. EXAFS measurements indicated no metal–metal interactions, confirming the non-destructive incorporation of the ruthenium complex as isolated entity. TEM and XRD analysis proved the homogeneity and non-crystallinity of the material and solid state ²⁹Si NMR spectroscopy revealed significant parts of incompletely condensed silicon species, indicative of a highly disordered structure of the gel [28].

2.3. Catalytic tests

A diagram of the equipment used for the catalytic tests is shown in Scheme 1. Reactions were carried out in a 500 ml stainless-steel autoclave (Medimex W.Nr. 1.4980) with metal sealing, agitated by a straight 6-blade turbine (Medimex type SR). The autoclave was heated by a copper jacket with electric heating elements and cooled by water running through an outer aluminium jacket. Jacket and core temperature were controlled by a PID-controller, regulating the heating elements and the cooling water. The pressure was measured by a piezoelectric pressure transducer and the stirring frequency by a stirring frequency gauge. Carbon dioxide and dimethylamine were charged into the reactor using a medium independent mass flow controller measuring the Coriolis force (Rheonik RHM 01 GNT). Carbon dioxide was compressed by a fluid compressor (New Ways of Analysis, PM-101), keeping the temperature of the pumped medium below its boiling point. Hydrogen was compressed by a Maximator gas compressor. All relevant parameters were monitored by a computer system, equipped with a PCI-20000 a/d-converter card.

Hydrogen (99.999%), dimethylamine (99.5%) and carbon dioxide (99.98%) were purchased from Pangas. The reactor was carefully cleaned with ethanol prior to catalytic tests. Blank experiments were carried out regularly to confirm that no catalytically active material remained in the reactor after cleaning.

In a typical experiment, the 500 ml stainless-steel autoclave was charged with the catalyst at room temperature and then pressurized/depressurized twice with carbon dioxide to guarantee oxygen free conditions. Subsequently, liquid dimethylamine was added and the autoclave was pressurized with hydrogen (4 MPa) and heated up to the desired temperature under stirring. After temperature equilibration, hydrogen was pressed into the reactor up to the desired pressure followed by the addition of carbon dioxide, which was charged to the reactor by



Scheme 1. Schematic illustration of the apparatus used for the synthesis of dmf. **1**: 500-ml stainless steel autoclave agitated by a magnetic coupled stirrer; **2**: inner copper jacket with electric heating elements and outer aluminium jacket with water cooling; **3**: jacket temperature controller; **4**: cooling water regulated by temperature controllers; **5**: computer; **6**: core temperature controller; **7**: piezoelectric pressure transducer; **8**: stirring frequency gauge; **9**: vent; **10**: medium independent mass flow controller measuring the coriolis force; **11**: fluid compressor consisting of **12**: pump and **13**: cooler; **14**: compressed air; **15**: gas compressor; **16**: hydrogen supply with pressure reducing valve; **17**: carbon dioxide supply with plunge pipe; **18**: dimethylamine supply with heating band.

the same mass flow controller as used for dimethylamine. The start of the reaction is defined by the time of CO₂ introduction.

After the desired reaction time, the autoclave was cooled rapidly to 288 K and the gas phase vented. A sample of the gas phase was collected using a gas burette. In case of low conversions, the products were solid after opening the autoclave, but melted when warmed to room temperature. The catalyst was separated from the reaction mixture using a PTFE syringe filter (0.2 μm). The liquid products were analysed by ¹H NMR and gas chromatography. NMR analysis was applied to determine unstable formate intermediates, not detectable by GC analysis. About 50 mg of the samples were dissolved in 0.8 ml DMSO and analysed at a sweep frequency of 300 MHz with a Bruker MSL 300. Quantification of the different products was made by integration of the proton signals. For GC analysis, a Hewlett-Packard 5890 gas chromatograph equipped with a thermal conductivity

detector and with a Supelco SPB-1 fused silica capillary column (60 m, 0.53 mm i.d., 5 μm film) was used. Gaseous compounds were separated using a Porapak QS column (5 m, 1/8 in. o.d., 80–100 mesh).

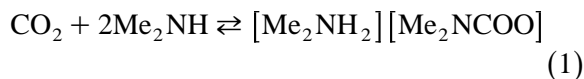
3. Results

3.1. Catalytic behaviour of the ruthenium hybrid gel in dmf synthesis

The sol-gel derived ruthenium containing hybrid gel catalyst was tested for the solvent free synthesis of *N,N*-dimethylformamide (dmf) from carbon dioxide, hydrogen and dimethylamine. Standard reaction conditions used were 5 · 10⁻⁵ mol Ru, 0.7 mol dimethylamine, 8.5 MPa H₂, 13.0 MPa CO₂, 373 K, 300 min⁻¹ stirring rate and 15 h reaction time. Catalyst separation from the liquid products could be

easily achieved by filtration. The colourless liquid product showed no catalytic activity, as evidenced by subsequent activity tests, indicating that leaching of the active ruthenium component from the silica matrix was negligible.

For low catalytic conversions a white precipitate was obtained, which melted at room temperature. GC analysis of this product revealed signals characteristic of dimethylamine and carbon dioxide, respectively, indicating that the compound could be dimethylammonium *N,N*-dimethylcarbamate [29]. The latter is formed reversibly in a temperature and pressure dependent side reaction of dimethylamine and carbon dioxide (Eq. (1)).



Under GC conditions the carbamate decomposes to dimethylamine and carbon dioxide.

GC and ^1H NMR analysis of the liquid phase indicated the production of dmf with 100% selectivity up to 403 K. Besides, no by-products could be detected in the gas phase, showing that neither CO formation by the reverse water gas shift reaction, nor methane synthesis occurred under the conditions used.

3.2. Effect of reaction parameters on catalyst performance in dmf synthesis

3.2.1. Influence of reaction time

For optimization of the reaction conditions several parameters were varied. Fig. 1 depicts the typical dependence of the total pressure in the autoclave on reaction time. Note the almost linear dependence of the total pressure as a function of time, indicating a nearly constant reaction rate as long as enough dimethylamine was available in the reactor (conversion < 80%). Although higher yields might have been achievable with prolonged reaction times, a comparison of the catalyst activity under these conditions was not reasonable, due to possible rate

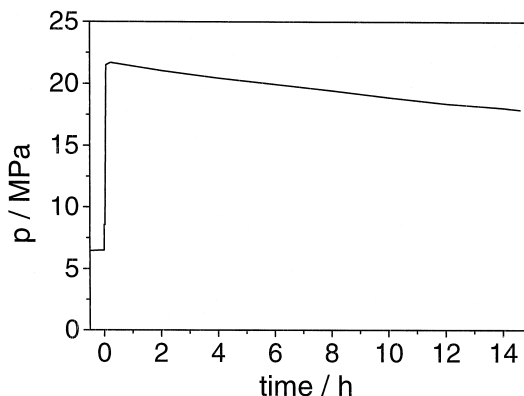


Fig. 1. Change of total pressure as a function of time. Thermal equilibration of the autoclave was achieved after pressurizing it with hydrogen and preheating to 373 K for 2 h. After this equilibration period, further hydrogen was added until a pressure of 8.5 MPa was reached. The reaction was started by the addition of carbon dioxide ($t = 0$).

limitation caused by too low dimethylamine concentration.

3.2.2. Mass transfer influences

A series of preliminary tests were performed to investigate possible influences caused by mass transfer phenomena. Fig. 2 depicts the influence of the stirring frequency on the reaction rate expressed as turnover frequency (TOF). Below 100 min^{-1} , TOF increased with the stirring frequency. Between 100 and 300 min^{-1} , the stirring frequency had no influence on TOF, corroborating that external diffusion did not influence the reaction rate in this region.

In order to get further information concerning possible mass transfer influences the reaction rate was measured in dependence of the amount of catalyst charged to the slurry reactor. Fig. 3 shows that a linear dependence was obtained when the reciprocal reaction rate, $1/r_A$, was plotted versus $1/c_{\text{cat}}$, corroborating that mass transfer from the supercritical phase to the liquid dimethylamine phase containing the catalyst was not significantly influencing the global reaction rate [30]. A possible effect of intraparticle diffusion could not be completely ruled out. This became evident from the influence of catalyst particle size on the reaction rate. Uncrushed

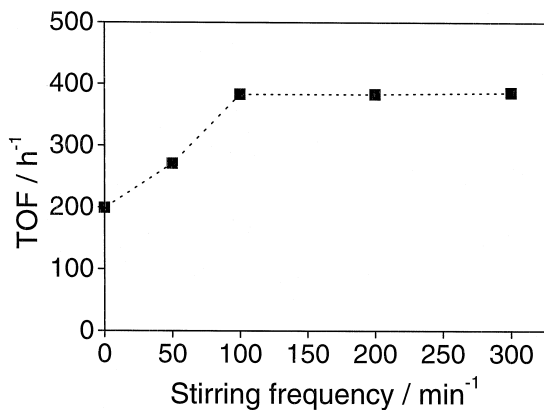


Fig. 2. Influence of stirring frequency on TOF. Conditions: $n[\text{Me}_2\text{NH}] = 0.7$ mol, $p[\text{H}_2] = 8.5$ MPa, $p[\text{CO}_2] = 13.0$ MPa, $p_{\text{tot}} = 21.5$ MPa, $T = 373$ K, $t = 15$ h, $n[\text{catalyst}] = 5 \cdot 10^{-5}$ mol.

or poorly crushed lumps of 1–5 mm mean diameter showed a much lower TOF (50 h^{-1}) compared to the TOF (220 h^{-1}) achieved with a carefully powdered catalyst ($< 50 \mu\text{m}$).

As a consequence of the investigations concerning mass transfer, in all further experiments finely crushed catalyst samples ($< 50 \mu\text{m}$) were used.

3.2.3. Influences of reactant concentrations

Regarding the effect of dimethylamine (dma) on the reaction rate, for amounts below 0.4 mol

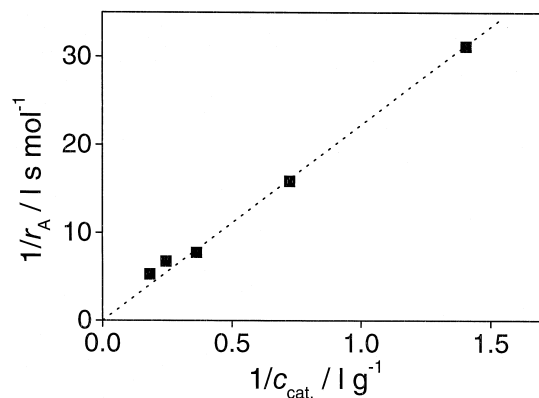


Fig. 3. Influence of the amount of catalyst charged to the autoclave on the reaction rate. Conditions: $n[\text{Me}_2\text{NH}] = 0.7$ mol, $p[\text{H}_2] = 8.5$ MPa, $p[\text{CO}_2] = 13.0$ MPa, $p_{\text{tot}} = 21.5$ MPa, $T = 373$ K, $t = 15$ h, stirring rate = 300 min^{-1} .

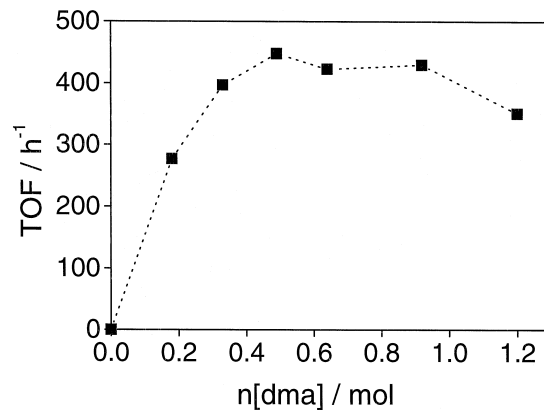


Fig. 4. Dependence of turnover frequency on the amount of dma charged. Conditions: $p[\text{H}_2] = 8.5$ MPa, $p[\text{CO}_2] = 13.0$ MPa, $p_{\text{tot}} = 21.5$ MPa, $T = 373$ K, $t = 15$ h, stirring rate = 300 min^{-1} , $n[\text{catalyst}] = 5 \cdot 10^{-5}$ mol.

TOF increased with the dma concentration, whereas for higher dma amounts TOFs remained nearly constant (Fig. 4). With respect to dimethylamine, the reaction rate appeared to be first order at lower concentrations and 0th order at higher concentrations.

As evidenced by Fig. 5, the influence of the carbon dioxide partial pressure seemed to be negligible in the range investigated. Note that the total pressure varied simultaneously with the carbon dioxide partial pressure. At a total pres-

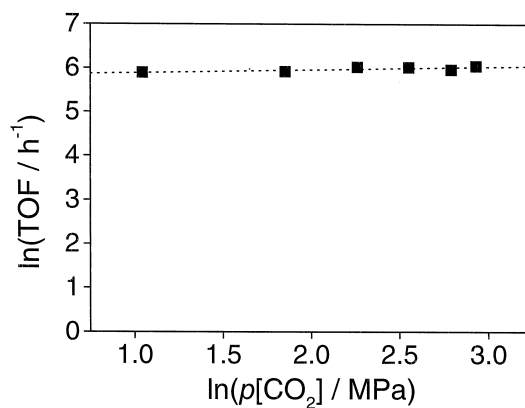


Fig. 5. Effect of carbon dioxide partial pressure on turnover frequency. Conditions: $n[\text{Me}_2\text{NH}] = 0.7$ mol, $p[\text{H}_2] = 8.5$ MPa, $p_{\text{tot}} = 11.3\text{--}28.8$ MPa, $t = 15$ h, stirring rate = 300 min^{-1} , $n[\text{catalyst}] = 5 \cdot 10^{-5}$ mol.

sure of 11.2 MPa and a carbon dioxide partial pressure of only 2.8 MPa the reaction was nearly as efficient as at a total pressure of 21.5 MPa, the normally applied conditions.

Fig. 6 depicts the influence of the hydrogen partial pressure on the turnover frequency. An increase of the reaction rate with increasing hydrogen partial pressure was observed. The kinetic data indicate approximately 0.6th order dependence of the rate on hydrogen partial pressure.

3.2.4. Effect of temperature

The reaction became significant at about 333 K and the rate of dmf formation increased rapidly at higher temperatures. At 413 K small amounts of *N*-methylformamide could be observed (0.28%) in addition to dmf. At higher temperatures of 433 K decomposition of the catalyst began, perceptible in a bad phosphine smell after opening the reactor and grey deposits on the reactor wall. In accordance with this observation, a sharp bend is apparent in the Arrhenius type plot shown in Fig. 7, which illustrates the temperature dependence of dmf production. Based on activity data in the temperature range 333–413 K an activation energy

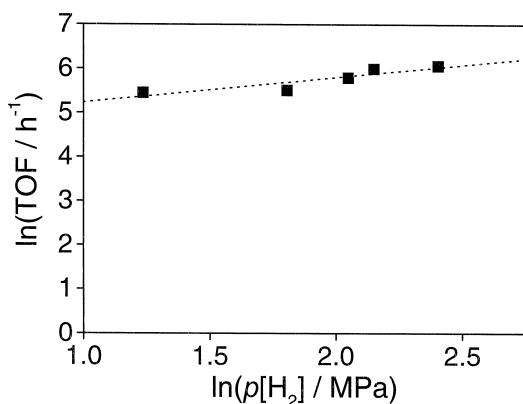


Fig. 6. Influence of hydrogen partial pressure on TOF in the synthesis of dmf. Conditions: $n[\text{Me}_2\text{NH}] = 0.71$ mol, $p[\text{CO}_2] = 10.4\text{--}18.0$ MPa, $p_{\text{tot}} = 21.5$ MPa, $T = 373$ K, $t = 15$ h, stirring rate = 300 min^{-1} , $n[\text{catalyst}] = 5 \cdot 10^{-5}$ mol.

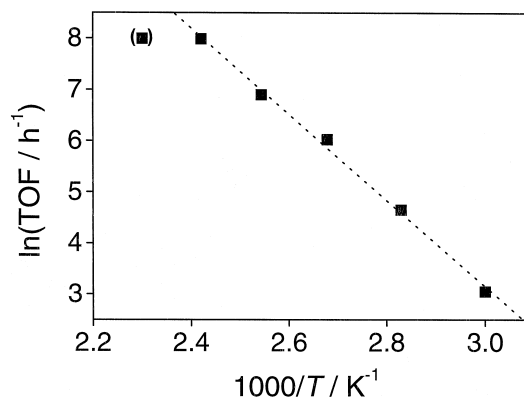


Fig. 7. Arrhenius type plot of dmf production. dmf-turnover frequency is plotted versus reciprocal temperature. The value in parentheses has to be taken with caution because catalyst decomposition occurred. Conditions: $n[\text{Me}_2\text{NH}] = 0.7$ mol, $p[\text{H}_2] = 8.5$ MPa, $p[\text{CO}_2] = 13.0$ MPa, $p_{\text{tot}} = 21.5$ MPa, $t = 15$ h, stirring rate = 300 min^{-1} , $n[\text{catalyst}] = 5 \cdot 10^{-5}$ mol.

of 69.8 ± 2.4 kJ/mol was calculated for the dmf synthesis reaction.

4. Discussion

4.1. Catalytic properties of hybrid gel catalysts in the synthesis of *N,N*-dimethylformamide

To explain the observed high activity of the ruthenium hybrid gel catalyst in the synthesis of dmf, elucidation of the phase behaviour inside the autoclave is of crucial importance. The white solid observed at low conversions after cooling of the autoclave was identified as dimethylammonium *N,N*-dimethylcarbamate. The carbamate forms reversibly from CO_2 and dimethylamine and is preparatively used as an easy to handle carrier for the volatile dimethylamine [13,29]. Under reaction conditions a dimethylamine-carbon dioxide complex of variable stoichiometry, which at higher temperature rather resembles a solution of carbon dioxide in dimethylamine [29] is expected to form a liquid phase at the bottom of the autoclave. By investigating the phase behaviour of a triethylamine/ CO_2/H_2 mixture, high swelling of the liquid $\text{N}(\text{Et})_3$ phase by dissolved gases has been ob-

served for supercritical [15] and subcritical [31] conditions of the gas phase. Thus, high concentrations of CO₂, dimethylamine and possibly H₂ can be assumed in the liquid phase, affording high concentrations of all reactants at the catalytic centres in an ideal reaction design.

Upon catalytic testing the colour of the catalyst changed from brownish to beige, presumably due to the formation of a hydrido complex. The observed marked increase of catalytic activity of the same sample used in a second and third run supports this assumption. Hydrido complexes are known to be highly active catalysts in homogeneous hydrogenations [32,33], which are easily formed from ruthenium dichloro phosphine complexes by hydrogenation in the presence of organic bases [32–34]. For similar ruthenium chloro phosphine complexes used in the homogeneous synthesis of dmf and methyl formate the mono hydrido complex could be identified as an intermediate [35]. Participation of a hydride intermediate in the dmf synthesis reaction has been occasionally discussed [5,8,11,15].

The absence of carbon monoxide in the gas phase after reaction suggests that dmf synthesis does not proceed via the intermediate formation of CO. For the ruthenium complex RuCl₂-(CO)₂{PPh₂(CH₂)₂Si(OEt)₃}₂, comparable to the complex used in this study, but containing in addition stabilizing CO ligands, an inhibiting effect of CO on the dmf synthesis reaction was reported [25]. This finding also suggests that the reverse water gas shift reaction does not occur to any significant extent.

4.2. Parametric investigations

The low impact of the stirring frequency in the range 100 to 300 min⁻¹ on the measured reaction rates in dmf synthesis indicates the absence of external diffusion limitation under the reaction conditions applied. For stirring frequencies lower than 100 min⁻¹ external mass transport has to be taken into account when interpreting kinetic data. In this range faster

stirring improved mixing of the supercritical CO₂/H₂ phase with the liquid dimethylamine phase. The negligible influence of external transport phenomena on the reaction rate under the standard conditions applied was supported by testing the activity of the catalyst in thf (50 ml) as a solvent. The same TOF as in the 'solvent free' reaction system was observed. Gas absorption could be excluded as limiting step, but absolute distinction between internal diffusion limitation and chemical reaction control was not possible (Fig. 3). However, further evidence that the catalytic behaviour reflects the intrinsic chemical reaction rate emerges from the temperature dependence of TOF shown in Fig. 7. From the Arrhenius-type plot an activation energy of 69.8 kJ/mol was calculated.

Investigating the controlling parameters of the catalytic process, hydrogen appeared to be a limiting reactant, since it was the only component having a significant influence on the reaction rate under the conditions applied (Fig. 6). In contrast, the dimethylamine concentration was not influential in the applied range of initial amine amounts (ca. 0.7 mol) (Fig. 4). Carbon dioxide was charged in excess, resulting in a negligible influence of its partial pressure on the reaction rate (Fig. 5).

The weak influence of the carbon dioxide partial pressure on the TOF gives rise to improvements of the reaction design. The reaction might be carried out under much milder conditions in the future by charging smaller amounts of carbon dioxide. Moreover, the volume of the unused supercritical gas phase could be decreased, if the gases are charged continuously, thus, enabling higher space velocities for the overall reaction. Further work towards elucidation of the reaction mechanism is presently undertaken.

5. Conclusions

A silica matrix stabilized ruthenium complex prepared by co-condensation of RuCl₂{PPh₂-

$(\text{CH}_2)_2\text{Si}(\text{OEt})_3\}_3$ with $\text{Si}(\text{OEt})_4$ in a ratio of 1:50 using a sol-gel process was tested for the solvent free synthesis of *N,N*-dimethylformamide from carbon dioxide, hydrogen and dimethylamine. Studying the controlling parameters of the catalytic process revealed that the reaction rate was limited by the chemical reaction itself and was not influenced by external mass transport processes. Carbon dioxide partial pressure and dimethylamine concentration had only negligible influence on the reaction rate, whereas kinetic data indicated approximately 0.6th order dependence of the reaction rate on hydrogen partial pressure. The temperature dependence described by the Arrhenius equation indicated an activation energy of 69.8 kJ/mol.

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