

# Sol-gel derived hybrid materials as heterogeneous catalysts for the synthesis of *N,N*-dimethylformamide from supercritical carbon dioxide

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Hybrid materials derived from group VIII metal-chloro complexes of the type  $MCl_2X_2$  ( $M = Pt, Pd$ ),  $MCIX_3$  ( $M = Rh, Ir$ ) and especially  $RuCl_2X_3$  [ $X = Ph_2P(CH_2)_2Si(OEt)_3$ ,  $Me_2P(CH_2)_2Si(OEt)_3$ ] by cocondensation with  $Si(OEt)_4$  via a sol-gel process are highly active heterogeneous catalysts for the synthesis of *N,N*-dimethylformamide (dmf) from  $CO_2$ ,  $H_2$  and dimethylamine under supercritical conditions, affording turnover numbers up to 110 800 at 100% selectivity.

During recent years considerable efforts have been made to use carbon dioxide as a starting material for the synthesis of valuable chemicals.<sup>1,2</sup> Recently, Jessop *et al.*<sup>3</sup> reported a reaction design, where supercritical carbon dioxide ( $scCO_2$ ) was used as both reaction medium and reactant in the homogeneous catalytic synthesis of formic acid and its derivatives, methyl formate and *N,N*-dimethylformamide (dmf). They demonstrated that high yields of dmf can be obtained by performing the reaction in  $scCO_2$  in the presence of a homogeneous ruthenium catalyst.<sup>4</sup> The utilization of a supercritical phase, in which hydrogen is highly soluble, resulted in markedly higher turnover numbers (TON) compared to similar reactions using organic solvents. However, application of the homogeneous catalytic process on an industrial scale is limited due to the difficulties in separating the homogeneous catalyst from the products.

Anchoring of catalytically active metal complexes via organic groups within oxide networks offers the possibility to overcome this problem and to combine the advantages of both homogeneous and heterogeneous catalysts.<sup>5,6</sup> Silica gel-like metal-containing materials with highly active tailored metal centres can be produced by simultaneous cocondensation of

transition-metal silylether complexes with tetraalkoxysilanes by a sol-gel process.<sup>5,6</sup> The immobilized complexes are generally more stable towards oxygen and water compared to their free analogues and show negligible leaching.

In this study we report the solvent-free synthesis of *N,N*-dimethylformamide from carbon dioxide, hydrogen and dimethylamine [eqn. (1)] under supercritical conditions, employing sol-gel derived silica matrix stabilized transition-metal complexes as catalysts.



The silylether complexes *cis/trans*- $[PdCl_2\{PPh_2(CH_2)_2Si(OEt)_3\}_2]$ , *cis*- $[PtCl_2\{PPh_2(CH_2)_2Si(OEt)_3\}_2]$ ,  $[RhCl\{PPh_2(CH_2)_2Si(OEt)_3\}_3]$  and  $[IrCl\{PPh_2(CH_2)_2Si(OEt)_3\}_3]$  were obtained in good yields from the cycloocta-1,5-diene complexes  $[PdCl_2(cod)]$ ,  $[PtCl_2(cod)]$ ,  $[RhCl(cod)]_2$  and  $[IrCl(cod)]_2$  by ligand-exchange reaction with  $PPh_2(CH_2)_2Si(OEt)_3$ . The ruthenium complexes (see Table 1) were synthesized from  $RuCl_3 \cdot xH_2O$  by adding, in excess, the silylether ligands  $PPh_2(CH_2)_2Si(OEt)_3$  and  $PMe_2(CH_2)_2Si(OEt)_3$ , respectively, and using sodium borohydride as a reductant. The structures of the ruthenium complexes could not be unequivocally assured due to several reasons: (i) similar reaction conditions led to a variety of possible products, which differed in the number of ligands or in the degree of dimerization, (ii) fluxional behaviour of the ligands, (iii) cleavage of ligands in solution and (iv) rearrangement reactions.<sup>7</sup>

Cocondensation of the silylether complexes with  $Si(OEt)_4$  was achieved following a method of Schubert *et al.*<sup>8</sup> using modified gelation conditions adjusted to the precursors used. Acetic acid or orthophosphoric acid was added to an acetonic solution containing tetraethoxysilane (teos) and the silylether

**Table 1** Catalytic results of dmf production with sol-gel derived hybrid catalysts in  $scCO_2$

Complex	Complex:		Surface		dmf				
	TEOS	Acid <sup>a</sup>	$S_{BET}^b$ $m^2 g^{-1}$	$\bar{d}_p^c/nm$	TON <sup>d</sup>	TOF <sup>e</sup> / $h^{-1}$	Yield (%)	Selectivity (%)	
$[RhCl\{PPh_2(CH_2)_2Si(OEt)_3\}_3]^f$	0:100	$H_3PO_4$	880	3.2	0	0	0	0	
$[IrCl\{PPh_2(CH_2)_2Si(OEt)_3\}_3]$	1:50	$MeCO_2H$	800	2.4	530	35	4	100	
$[PtCl_2\{PPh_2(CH_2)_2Si(OEt)_3\}_2]$	1:50	$MeCO_2H$	480	2.1	2900	190	23	100	
$[PdCl_2\{PPh_2(CH_2)_2Si(OEt)_3\}_2]$	1:50	$MeCO_2H$	430	2.3	1410	90	11	100	
$[PtCl_2\{PPh_2(CH_2)_2Si(OEt)_3\}_2]$	1:50	$H_3PO_4$	770	4.1	1490	100	10	98 <sup>g</sup>	
$[RuCl_2\{PPh_2(CH_2)_2Si(OEt)_3\}_3]$	1:50	$H_3PO_4$	460	2.8	3230	220	25	100	
$[RuCl_2\{PPh_2(CH_2)_2Si(OEt)_3\}_3]$	1:20	$H_3PO_4$	200	3.4	4420	290	35	100	
$[RuCl_2\{PPh_2(CH_2)_2Si(OEt)_3\}_3]$	1:20	$MeCO_2H$	190	5.3	4140	280	30	100	
$[RuCl_2\{PMe_2(CH_2)_2Si(OEt)_3\}_3]$	1:50	$H_3PO_4$	510	2.3	13 670	900	94	100	
<sup>h</sup> $[RuCl_2\{PMe_2(CH_2)_2Si(OEt)_3\}_3]$	1:20	$MeCO_2H$	70	3.4	110 800	1860	82	100	
					11 870	800	92	100	

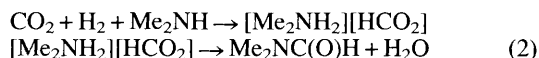
All catalytic reactions were carried out in a stirred 500 ml stainless-steel reactor. Reaction conditions:  $n[Me_2NH] = 0.7$  mol,  $p[H_2] = 8.5$  MPa,  $p[CO_2] = 13.0$  MPa,  $T = 373$  K,  $t = 15$  h, stirring rate =  $300$   $min^{-1}$ ,  $n[catalyst] = 5 \times 10^{-5}$  mol (expressed as amount of group VIII metal). Under these conditions, the  $CO_2-H_2$  mixture is in the supercritical region, whereas dmf and the products dmf and water are in the liquid state. Product analysis was achieved by GC. Gaseous compounds were analysed using a Poropak QS column. The liquid product mixture was analysed using a Supelco SPB-1 fused silica capillary column. <sup>a</sup>  $n[H^+] = 2.8$  mol. <sup>b</sup>  $S_{BET}$  = specific surface area. <sup>c</sup>  $\bar{d}_p$  = mean pore diameter. <sup>d</sup> TON = mol dmf (mol complex)<sup>-1</sup>. <sup>e</sup> TOF = TON  $h^{-1}$ . <sup>f</sup> Decomposition under the reaction conditions. <sup>g</sup> Byproduct trimethylamine. <sup>h</sup>  $n[Me_2NH] = 6.4$  mol,  $T = 406$  K,  $t = 60$  h, stirring rate =  $500$   $min^{-1}$ ,  $n[catalyst] = 1.8 \times 10^{-5}$  mol. Due to the pressure drop in the reactor, hydrogen and carbon dioxide had to be recharged regularly.

complex in different molar ratios (Table 1). The solvent was evaporated off by passing over a moderate stream of argon. High silica amounts were chosen for good fixation of the complexes within a stable matrix and to minimize interactions of neighbouring complex molecules. The platinum, palladium, rhodium and iridium complexes were incorporated without structural changes as confirmed by comparison of the  $^{31}\text{P}$  NMR spectra of the silylether complexes with  $^{31}\text{P}$  CPMAS NMR spectra of the final solid catalysts.

The BET surface area of the catalysts, as obtained from  $\text{N}_2$ -physorption measurements, varied over a wide range from 70 to  $800\text{ m}^2\text{ g}^{-1}$  (Table 1). The surface area was highest for pure silica and decreased significantly for higher metal loadings. The average pore diameter varied in the range 2.1–5.3 nm. No clear correlation between surface area, pore diameter and catalytic activity could be found.

Catalytic tests for the synthesis of dmf were carried out in a  $500\text{ cm}^3$  stirred stainless-steel autoclave under a total pressure of 22 MPa at 373 K for 15 h (Table 1). Under these conditions, the  $\text{CO}_2$ - $\text{H}_2$  mixture is in the supercritical region, whereas dma and the products dmf and water are in the liquid state.<sup>3</sup> High swelling of the liquid dma phase by dissolved  $\text{CO}_2$  was reported by Jessop *et al.*,<sup>3</sup> thus providing high local concentrations of educts on the surface of the catalysts. Conversion and selectivity were determined by GC analysis. Catalyst separation from the liquid products could be easily achieved by filtration. The colourless liquid product showed no catalytic activity, as evidenced by a subsequent activity test, indicating that leaching of the active component from the silica matrix was negligible. The reaction time was arbitrarily chosen and is not critical, as seen by a linear pressure drop in the reactor during reaction, indicating a nearly constant reaction rate.

All catalysts were found to be stable under reaction conditions, except for those of rhodium and iridium, whose colour changed during reaction. GC analysis of the liquid phase indicated the production of dmf with 100% selectivity except for the Pt-containing sample, which produced trace amounts of trimethylamine as a byproduct. Trimethylamine is a thermodynamically favoured disproportionation product of the dimethylamine educt. In addition, no byproducts could be detected in the gas phase, showing that neither CO formation by the reverse water gas shift reaction, nor methane synthesis took place under the conditions employed. The reaction is believed to proceed in two steps:<sup>1,3</sup>



A white precipitate, which melted at room temperature, was obtained at lower conversions. GC analysis of this product showed signals characteristic for dma and  $\text{CO}_2$ , respectively, indicating that the compound could be dimethylammonium *N,N*-dimethylcarbamate<sup>3</sup> or more precisely Dimcarb, an addition compound of dimethylamine with carbon dioxide of variable stoichiometry.<sup>9</sup> The spontaneous formation of carbamates represents a common reversible reaction between  $\text{CO}_2$  and amines:



Results of the catalytic tests are depicted in Table 1. Pure silica was tested as a reference and exhibited no catalytic activity. Comparing the different transition-metal catalysts

shows the activity, expressed as turnover frequency (TOF), to decrease in the order  $\text{Ru} > \text{Ir} > \text{Pt}, \text{Pd} > \text{Rh}$ . With a ruthenium catalyst containing methylphosphine ligands, a maximum turnover number (TON) of 110800 with a selectivity of 100% was attained under the conditions specified in Table 1. The rhodium catalyst exhibited only low activity and decomposed under the reaction conditions producing black metallic deposits on the walls of the autoclave. A change in the complex structure was observed for the iridium catalyst during reaction, indicated by a change in colour from beige to white, but in contrast to the rhodium catalyst the activity was high. Regarding the influence of the silylether ligand of the ruthenium complex, the use of methylphosphine ligands resulted in more active catalysts as compared to phenylphosphine ligands, independently of the preparation conditions. However, a different effect of metal loading on activity was observed for the two ligands. Whereas the turnover frequency (TOF) of the ruthenium catalyst increased with higher metal loading for the phenylphosphine ligand, the opposite effect was found for the methylphosphine ligand. The use of either acetic acid or orthophosphoric acid in the sol-gel process had no significant influence on catalytic activity.

Using the same ruthenium catalyst for three consecutive experiments resulted in a marked increase of catalytic activity for the second run which remained stable in the third experiment. This behaviour can probably be attributed to the formation of an active hydride intermediate by hydrogenolysis of the ruthenium-chlorine bond<sup>10</sup> or to a carbon dioxide intermediate<sup>3</sup> formed from the catalyst under reaction conditions.

In conclusion, it could be shown that silica matrix stabilized ruthenium complexes are highly active heterogeneous catalysts for the synthesis of dmf from  $\text{CO}_2$ ,  $\text{H}_2$ , and dimethylamine under supercritical conditions. The TON obtained with the ruthenium catalysts markedly exceeded previously reported values<sup>11</sup> for heterogeneous catalysts.

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