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A mesoporous ruthenium silica hybrid aerogel with outstanding catalytic properties in the synthesis of *N,N*-diethylformamide from CO_2, H_2 and diethylamine

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A mesoporous ruthenium silica hybrid aerogel containing well dispersed bidentate $RuCl_2[Ph_2P(CH_2)_3PPh_2]_2$ complexes, synthesized using a sol–gel method, affords turnover frequencies up to 18 400 h^{-1} and 100% selectivity from CO_2, H_2 and diethylamine for the formation of *N,N*-diethylformamide.

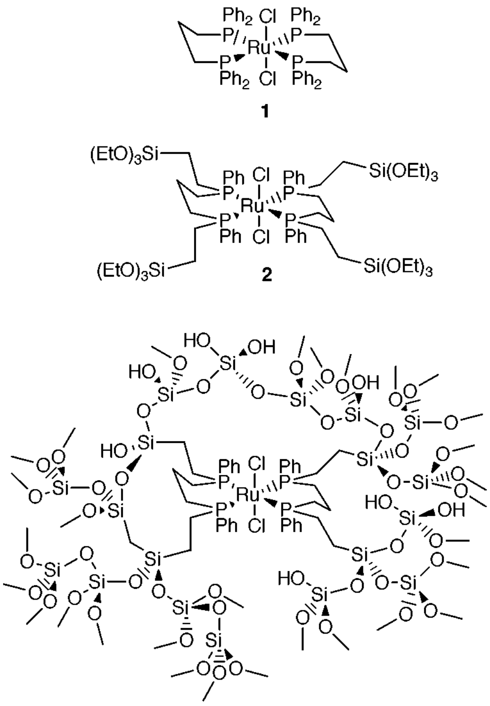
Utilization of carbon dioxide in chemical synthesis has been fostered owing to its abundance, easy handling and non-toxicity.[1] Among several other syntheses the preparation of formic acid derivatives such as methyl formate and *N,N*-dimethylformamide have received considerable attention.[2,3] The first successful catalytic syntheses were exclusively based on homogeneous catalysts.[4] The technical potential of this approach is limited by the difficulties in catalyst separation and product recovery steps. This prompted us to search for a heterogeneous catalytic variant of these syntheses.[5–8] In our previous studies the mono- and bi-dentate group VIII metal phosphine complexes were covalently incorporated into microporous silica based xerogels. A considerable improvement in the stability of the active ruthenium complex could be achieved by employing biadentate complexes.[5,8] Although all of these catalysts showed high activity at 100% selectivity to the desired dimethylformamide the intrinsic activity of the free active complexes could not be reached owing to unfavourable microporous structure of the xerogel materials. Here, we report for the first time, the successful synthesis of a mesoporous hybrid aerogel catalyst and compare its catalytic behaviour with the corresponding microporous xerogel. It is shown that the activity of the mesoporous material outperforms the intrinsic activity of the free active ruthenium complex and that of the microporous catalyst by a factor of more than six.

The bidentate ruthenium phosphine complex $RuCl_2(dppp)_2$ **1** [Fig. 1, dppp = $Ph_2P(CH_2)_3PPh_2$] was prepared according to the procedure described in the literature.[9] The synthesis of the corresponding functionalized sol–gel precursor **2** (Fig. 1) and its ligand has also been described in detail.[8]

The hybrid gel catalysts **3a** and **3b** were synthesized from the functionalized precursor **2** by immobilizing this complex within a silica matrix and applying a sol–gel process. To a mixture of 15.22 g (0.10 mol) tetramethylorthosilicate (TMOS) and 7 ml tetrahydrofuran, 1.03 g 65% HNO_3 in 8.81 g H_2O and 27 ml tetrahydrofuran was added dropwise. Subsequently, 0.727 g (5×10^{-4} mol) of **2** in 20 ml tetrahydrofuran was slowly added. After stirring the homogeneous mixture overnight, 4.05 g (0.015 mol) trihexylamine in 15 ml tetrahydrofuran was added dropwise to the solution over 10 min. Within 1 h a solid gel had formed which was aged for 7 days. During this time the tetrahydrofuran which was released from the gel was replaced by ethanol. The gel was dried either by extraction of the solvent with supercritical CO_2 at 22.0 MPa and 41 °C, affording aerogel **3a** or by slow evaporation of the solvent, producing xerogel **3b**. Finally, the gels were washed with acetone and dried in vacuum at 100 °C. All steps, including aging, crushing, washing and drying, were carried out under an argon atmosphere.

^{31}P and ^{29}Si NMR investigations were carried out as described previously.[8] Nitrogen physisorption measurements of the specific surface area and mean pore diameters of the gel catalysts were performed at 77 K using a Micromeritics ASAP 2010 instrument.[6] For catalytic tests a 500 ml stainless steel reactor was used.[7] The products were analyzed by a GC equipped with a TCD and a fused silica capillary column (Supelco SPB-1).

To establish the undestructive incorporation of the active sites, solid state ^{31}P CP MAS NMR measurements for the hybrid gels **3a** and **3b** were compared with liquid ^{31}P NMR investigations of the precursor **2**. The spectra corroborated that no significant change of geometry in the coordination sphere of the phosphorus atoms had taken place. In the spectra of the solid materials, side bands were observed owing to the rotational frequency of the sample during measurements, and the peaks were broader in comparison with liquid ^{31}P NMR results for precursor **2**. Based on earlier EXAFS measurements of immobilized monodentate ruthenium phosphine complexes, which showed that these precursors were incorporated as isolated single entities,[6] it was assumed that cluster formation



1

2

3a, aerogel
3b, xerogel

Fig. 1 Ruthenium phosphine complex **1**, which shows good activity and selectivity in the synthesis of formic acid derivatives, is functionalized by silyl ether groups (**2**) and immobilized within a silica matrix affording aerogel **3a** or xerogel **3b**, by different drying procedures.

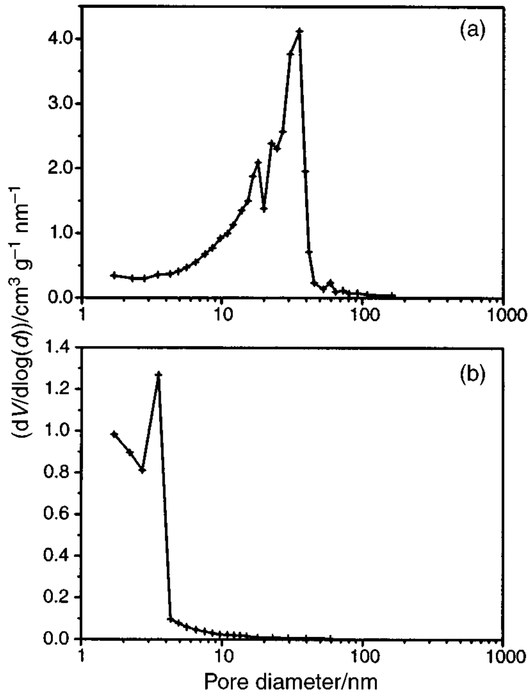
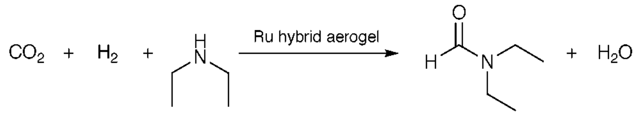


Fig. 2 Pore size distribution of aerogel **3a** (a) and xerogel **3b** (b).

could be excluded also for bidentate complexes. ^{29}Si MAS NMR with single pulse excitation indicated a similar degree of condensation (cross linkage) for aerogel **3a** and xerogel **3b**. Textural properties of the synthesized hybrid gels **3a** and **3b** were investigated by means of nitrogen physisorption and results are shown in Fig. 2. As expected, supercritical drying of the gel applied to **3a** led mainly to mesopores, whereas for xerogel **3b**, dried by thermal evaporation of the solvent, the pore size distribution shifted to much lower values [Fig. 2(b)]. Corresponding t-plots (not shown) indicated a pronounced deviation from linearity for the xerogel between thickness 0.4 to 0.8 nm, which corroborated the presence of micropores.[10] For aerogel **3a**, exhibiting a low amount of micropores, the deviation was much less pronounced. The measured BET surface areas for xerogel **3b** and aerogel **3a** were 1000 and 670 m^2 g^{-1}, respectively. Aerogel **3a** exhibited a nearly four times higher pore volume (1.74 cm^3 g^{-1}) than xerogel **3b** (0.44 cm^3 g^{-1}).

The hybrid gel catalysts **3a** and **3b** were tested in the synthesis of *N,N*-diethylformamide from CO_2, H_2 and diethylamine (Scheme 1). A fractional factorial design, including the main parameters: temperature, total pressure, amount of catalyst, amount of diethylamine, initial hydrogen pressure, and type of stirrer has been carried out with the aerogel **3a**. The most influential parameters were: amount of catalyst, temperature and total pressure. Some results of the kinetic studies are summarized in Table 1. Note, that depending on the conditions, turnover frequencies up to 18 400 h^{-1} were obtained with the mesoporous aerogel **3a**, whereas under the same conditions the microporous xerogel **3b** afforded a value of only 2210 h^{-1}. This improvement is attributed to the favourable textural properties of the aerogel eliminating intraparticle diffusion limitations. In both cases, a selectivity of 100% towards the desired product was found. Surprisingly, the measured turnover frequency, 3130 h^{-1}, for precursor **2** under similar reaction conditions was also significantly lower than that of the aerogel. The reason for this unprecedented increase in activity upon heterogenization is, as yet, not clear. Presumably electronic influences of the silica matrix may play a role. These new aerogels which combine stability with favourable textural properties should also be suitable for the synthesis of higher *N,N*-dialkylformamides from CO_2, H_2 and the corresponding dialkylamines.



Scheme 1 Synthesis of *N,N*-diethylformamide from CO_2 as a C_1-building block with heterogeneous hybrid gels as catalysts.

Table 1 Kinetic data for aerogel **3a** under different reaction conditions. Corresponding results for xerogel **3b** are quoted for comparison

	T/°C	Total pressure/ MPa	Amount of catalyst/ 10^{-7} mol	Turnover frequency/h^{-1}
3a	90	18.0	7.5	4780
3a	110	14.0	2.5	12 000
3a	110	18.0	2.5	15 300
3a	110	18.0	7.5	18 400
3b	110	18.0	7.5	2210

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