Templating mesoporous silicates on surfactant ruthenium complexes: a direct approach to heterogeneous catalysts

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Mesoporous silicas have been obtained by the true liquid crystal templating (TLCT) method, using a surfactant Ru^{II} complex as the template; on calcination, ruthenium-containing particles are deposited into the pores; the materials show high catalytic selectivity for the hydrogenation of hex-1-ene.

Since the discovery of the utility of surfactants as templates for mesoporous solids by Mobil,[1] there has been an explosion of interest in these mainly siliceous solids, particularly as pore sizes from, for example, 20–100 Å are now routinely available. For much of the time since these initial developments, the situation has been rather unsatisfactory as there was little pre-emptive control which could be employed to direct the structure of the materials to be synthesised. Thus, while a given set of conditions could reproducibly lead to a given material with given dimensions, some of the structural parameters (pore size, wall thickness, degree of crystallinity) of the solid were largely unpredictable prior to the first experiment. The exact mechanism of the templating attracted much speculation and debate. This was partly due to the fact that the surfactant was present above the critical micelle concentration (cmc), but at concentrations below those necessary for mesophase formation. More recently, this situation changed rather dramatically with the development of the true liquid crystal templating (TLCT) synthesis by Attard *et al.*[2] In this approach, a lyotropic liquid crystal phase was first formed and templating took place around the pre-formed mesophase in a sol–gel hydrolysis of tetramethoxysilane (TMOS). In forming these solids, both neutral and cationic surfactants could be employed. The various approaches to liquid crystal templating have been reviewed recently.[3]

Because of the pore sizes available in mesoporous solids, one of the great attractions is the possibility to carry out reactions therein, using molecules which would not have been able to get inside the pores of microporous materials. This reactivity can take a number of forms. First, it is possible simply to use the acidity of the mesopore surface to facilitate reactions. This is particularly attractive when doping aluminium into the silica, so as to generate Brønsted acid sites. On these sites, ion exchange can take place and the acidity or basicity of the material can be controlled. It is also possible to introduce molecular catalytic species, which may be tethered to the mesopore, to carry out reactions in confined environments. Another avenue for catalytic functionalisation is the deposition of metal particles within the pores and to use the materials as heterogeneous catalysts.[4] In the latter two approaches, it is necessary to pre-form the mesoporous solid and then to introduce the catalyst, or as has recently been shown, to introduce an extra metal-based species during gel formation.[5] What we describe here is the production of a mesoporous solid containing deposited metal particles in one step from the surfactant, exploiting the dual functionality of the surfactant ruthenium complex as, both, structure directing and catalytic site generation agent.

Some of us have been interested in the synthesis and mesomorphism of surfactant metal complexes,[6] and in particular the study of the lyotropic mesomorphism of surfactant derivatives of tris(bipyridine)ruthenium(II) (Fig. 1).[7] As part of this work, we were interested to see whether these complexes could be used to template mesoporous silicates, and in particular whether the TLCT approach could be adopted. To this end, we employed the dinonadecyl-substituted complex **1**, which we know to form a hexagonal H_1 phase in water at elevated temperatures.

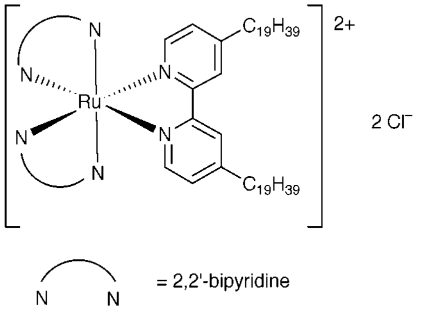

Fig. 1 Structure of the ruthenium complex used for templating.

Thus, a 50 wt% mixture of **1** in water acidified to pH 2 with H_2SO_4 was prepared and maintained at 60 °C, and was shown by polarised optical microscopy to have a non-geometric texture typical of the hexagonal H_1 phase at this temperature. A small amount of methanol was added to the mesophase preparation, in order to aid mixing of the reagents, and was removed under a dynamic vacuum immediately after addition of the TMOS. Hydrolysis of the TMOS starts immediately and the methanol so produced was removed under gentle, dynamic vacuum as it was generated. After 2 h, the gel formation was complete and a strongly red-coloured gel remained, coloured due to the ruthenium complex contained therein. Interestingly, this gel still retains the texture of the hexagonal H_1 phase when viewed in the polarising microscope. The gel was then calcined in air at 600 °C for 6 h leading to a blackened silicate which we calculate to have 6 wt% Ru.

Investigation of this mesoporous silicate by transmission electron microscopy shows a material which retains the hexagonal symmetry of the mesophase on which it was templated and which contains relatively evenly distributed particles of RuO_2 (Fig. 2). Evaluation of the surface area by N_2 adsorption isotherm measurements gave a type IV absorption–desorption isotherm, confirming that the material is mesoporous and led to values in the range 870–980 m^2 g^{-1} being established

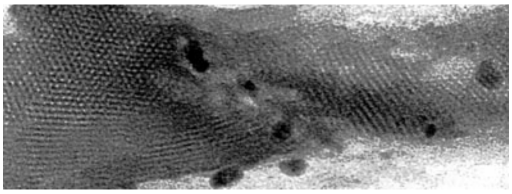

Fig. 2 TEM of the as-obtained silicate (×240 000).

for the BET surface area (depending on the sample). The same measurements also showed a very narrow pore size dispersity (half peak height values of 20–40 Å). In addition, evaluation of the surface-area-to-bulk ratio suggested rather high surface area particles with a CO dispersion of 15%. This compares with a value of 7.5% for MCM-41 impregnated with ruthenium nitrosyl nitrate [$Ru(NO)(NO_3)_3$] which was then converted to RuO_2.[8]

The materials were then tested as catalysts in the hydrogenation of hex-1-ene without prior reduction in hydrogen as a simple model system.[9] Thus, at 373 K and under 22 bar of H_2, hexene was hydrogenated *only* to *n*-hexane[10] at a turnover frequency of 877 mol hexane(mol Ru h)$^{-1}$. This exceeds turnover rates for hydrogenation on AgRu nanoparticles on MCM41 [690 mol hexane(mol metal h)$^{-1}$] under the same conditions,[11] although in its unoptimised state, it falls short of the rates[12] obtained for CuRu nanoparticles on the same support [1560 mol hexane(mol metal h)$^{-1}$].[4]

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8 We thank Johnson Matthey for letting us have sight of these results.

9 The catalytic reactions were performed in a PEEK-lined high pressure reactor (Cambridge Reactor Design) equipped with a stirrer and liquid sampling valve (for withdrawing samples under pressure to evaluate kinetics). In a typical reaction the autoclave was charged with *ca.* 50 g of hex-1-ene and the activated catalyst (*ca.* 20 mg, heated in vacuum at 463 K for 4 h) was directly introduced into the reactor without exposing it to air. The reactor was then pressurised with H_2 to 20 bar and heated to 373 K. Samples were periodically withdrawn without perturbing the pressure in the reactor and analysed by GC using 1,2-dichlorobenzene as the internal standard; a typical mass-balance showed minimal sample loss.

10 Apart from *n*-hexane, isomerised products, namely *cis*-and *trans*-hex-2-ene and small amounts *trans*-hex-3-ene were obtained when Cu_4Ru_{12}, Ag_4Ru_{12} or Pd_6Ru_6 were employed as catalysts for the hydrogenation of hex-1-ene (see ref. 4). There is no detectable thermocracking.

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12 The catalytic performance of the Ag_4Ru_{12} and Cu_4Ru_{12} catalysts was also evaluated under identical conditions, hence meaningful comparisons of TOF may be made.

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