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High-activity heterogeneous catalysts prepared in one step from the mesophases of metallosurfactants

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Surfactant Ru(II) complexes have been used to template mesoporous silicates using the true liquid crystal templating method, giving evenly dispersed, nanometer-sized ruthenium particles which show very high catalytic activity and selectivity in the hydrogenation of 1-hexene.

KEY WORDS: mesoporous silicate; metallosurfactant; true liquid crystal templating; ruthenium; catalysis; hydrogenation.

In 1992, Mobil scientists [1] used surfactants to template the formation of mesoporous solids possessing a framework of regular channels with large pore diameters (20–100 Å) and high surface areas ($>700\,m^2\,g^{-1}$). These inorganic structures mimicked the morphology of lyotropic liquid crystal mesophases and the pore sizes could be tuned by altering the surfactant chain length or by addition of an auxiliary organic molecule. Although the syntheses of these siliceous materials were reproducible once established, their initial outcome was not easily predictable; and while the templating surfactant was present above its critical micelle concentration, it was well below that required for liquid crystal phase formation. Attard *et al.* [2] addressed this problem and developed the true liquid crystal templating (TLCT) route where the silicate was formed by a sol-gel condensation of tetramethoxysilane (TMOS) around the pre-formed lyotropic mesophase, making the synthesis predictable as well as reproducible. A range of porous structures was attainable by the choice of templating mesophase (which was determined by the surfactant concentration). The method also offered the advantage of being able to use both cationic and neutral surfactants. The various approaches to liquid crystal templating have been extensively reviewed [3].

Such materials have been found extremely useful in applications such as catalysis [4], and the potential for carrying out reactions of large molecules inside the uniform pores of a material is substantial. Mesoporous silica is itself a poor catalyst, but framework substitution of Si(IV) with, for example, Al(III) generates Brønsted acid sites that can be utilized in acid catalysis [5]. The incorporation of transition metals into a mesoporous environment can lead to the use of heterogeneous catalysts in traditionally homogeneously catalysed reactions [4]. One approach to the introduction of transition metals is *via* the addition of metal precursors into the synthesis mixture, where the metals will then be dispersed within the framework [6], but where they are also often inaccessible for catalysis. Other useful routes are to tether transition metal complexes to the mesopore and carry out catalytic reactions in a confined environment [7] or to deposit metal particles onto the pore walls by thermolysis [8,9]. These last two approaches require prior preparation of the mesoporous support, although recently it has been shown that a metal species can be introduced during gel formation [10].

For some time, some of us have been interested in the synthesis of surfactant metal complexes and their lyotropic liquid crystal behaviour [11]. In particular, we have studied surfactant tris(bipyridine)ruthenium(II) complexes of the type shown in figure 1 [12]. We have described the use of these complexes to generate mesoporous silicates *via* the TLCT method and shown a successful, one-step route to a mesoporous material with RuO_2 particles deposited on the pore walls [13]. The surfactant complex acted both to determine the hexagonal structure of the silicate and as a source of material to generate a catalytic site. Thus, in the hydrogenation of 1-hexene, the material was shown to be an active catalyst [877 mol hexane$(\mathrm{mol\,Ru\,h})^{-1}$] and to give only a single product, namely *n*-hexane. These results compared well with those obtained for the same reaction catalyzed by AgRu [8] and CuRu [9] nanoparticles deposited onto mesoporous silicates from metal carbonyl precursors, where rates of 690 mol hexane$(\mathrm{mol\,metal\,h})^{-1}$ and

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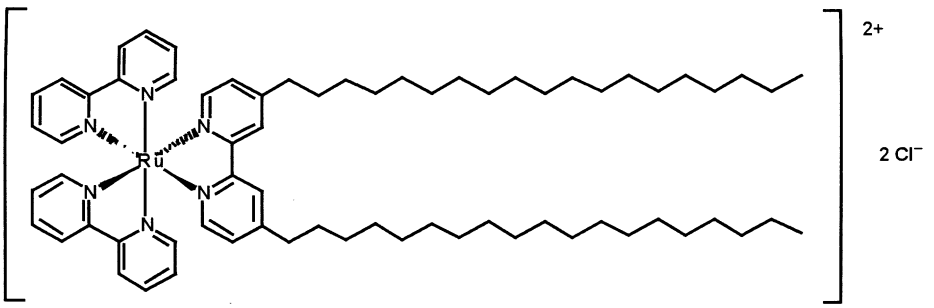


Figure 1. Structure of the surfactant ruthenium(II) complex.

1560 mol hexane(mol metal h)$^{-1}$ were found, respectively. To explore the catalytic activity of our system further, we varied the calcination protocols and we report some of these results here.

The gel was prepared as described previously [13] by templating on the lyotropic hexagonal H_1 phase of the surfactant, using HCl as the source of acid. The as-synthesized gel, which retained the optical texture of the liquid crystal phase, was then calcined under nitrogen up to the desired temperature and then for a further hour before being heated for a further 5 h in air. Calcination temperatures of 400 and 500 °C were employed. There was no significant difference in weight loss between each run, with each of the silicates losing between 56 and 63% in weight on calcination. Thermogravimetric analysis showed that on heating in the N_2 atmosphere, there was a gradual weight loss, with loss of water and the initial decomposition of organic species. When the atmosphere was switched to oxygen, there was a sharp loss in weight, probably due to the burning of volatile organic species, followed by an increase in weight on continued heating which can be attributed to the oxidation of the ruthenium particles to RuO_2. Powder X-ray diffraction (figure 2) of each of the calcined samples gave a *d*(10) spacing of ~46 Å (corresponding to a hole centre–hole centre separation, $a_0 = 53$ Å) corresponding to a small contraction in the lattice parameter compared to the as-synthesized gel for which *d*(10) appeared at 48 Å. Each of the calcined samples also displayed a second, broad reflection, the spacings of which would correspond to the *d*(11) and *d*(20) reflections of a two-dimensional hexagonal lattice. BET surface area analysis by N_2 adsorption–desorption at 77 K gave Type IV isotherms with little hysteresis, indicating mesoporosity and a rather narrow pore-size distribution. The surface areas were in the range 660–710 m^2 g^{-1}, although more recently we have realized surface areas in excess of 1500 m^2 g^{-1} [14]. The pore diameters of the samples were calculated to be 28 Å, leaving a substantial wall thickness of 25 Å. These materials would, therefore, be expected to be mechanically, thermally and hydrothermally stable. Electron-induced X-ray emission maps (figure 3) showed that the material calcined at 400 °C gave the highest spatial uniformity of all the samples, with complete homogeneity and Ru particles no larger than 10 Å. As the calcination temperature was increased, a few large Ru particles appeared due to sintering, and above 500 °C the distribution of Ru was uneven. This is consistent with the known Huttig temperature for ruthenium (484 °C), above which it is known to sinter.

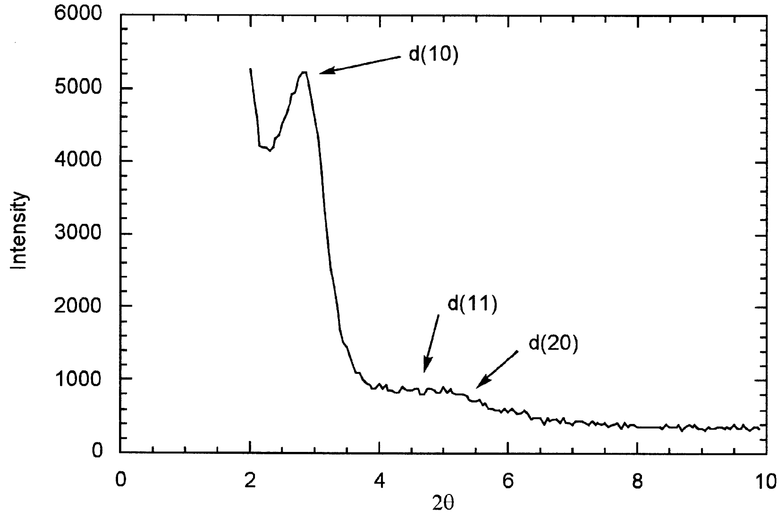
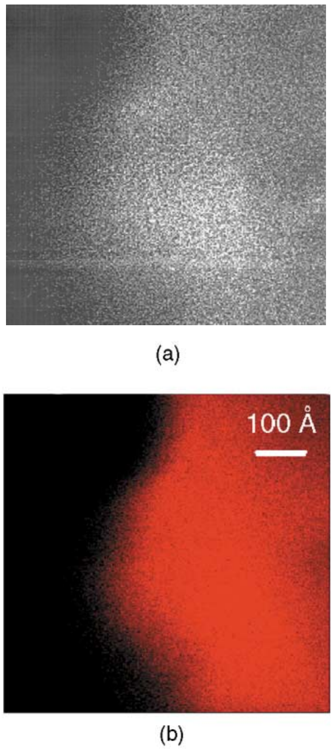


Figure 2. XRD trace of the silicate calcined at 500 °C.



(a)

(b)

Figure 3. Electron-induced X-ray emission maps (a = Ru; b = Si) for the sample calcined at 400 °C.

Table 1
Results from hydrogenation of 1-hexene by the Ru-doped silicates

Calcination (°C)	BET surface area ($m^2 g^{-1}$)	Ru (wt%)	1-hexene converted in 1 h (%)	TON (in 1 h)
400	680	2.87(7)	79	49 375
500	660	4.59(8)	58	20 610

General conditions: 150 cm^3 Parr autoclave, 50 ml 1-hexene, activated catalyst (20 mg, heated in a vacuum at 463 K for 2 h), 20 atm H_2, 16 h. The catalysts were activated at 623 K under vacuum of 10^{-6} atm for 16 h.

The materials were screened for catalytic activity by looking at the hydrogenation of 1-hexene. Initially, the catalyst was tested under exactly the same conditions as used previously [13] but, under these conditions, all of the hydrogen was consumed in less than 0.5 h. Therefore, the experiment was modified to guarantee a continuous delivery of hydrogen at continuous pressure and the reaction was slowed down by reducing the temperature by 20 K to 353 K. Each of the catalysts exhibited an induction period of ~0.5 h, probably due to reduction of RuO_2 to Ru(0). Under these conditions 1-hexene was converted selectively to *n*-hexane, and while some internal hexene isomers were initially formed, they were consumed completely in the reaction to give clean product (figure 4). This was not the case for hydrogenations based on AgRu and CuRu nanoparticles [8,9]. The turnover rates obtained are shown in table 1 and the Ru loadings reported therein were obtained by X-ray fluorescence analysis. The values for the catalyst prepared at 400 °C are some eighty times better (even under milder reaction conditions) than those we observed previously [13] and well in excess of an order of magnitude greater than those reported elsewhere [8,9]. Furthermore, the figures refer to the first hour of the reaction and, as there is a 0.5 h induction period, the true rates are probably double these numbers.

We believe that the main reason for the greatly enhanced catalytic activity is due to the Ru particle size mentioned above and shown in figure 3. The catalytic runs were reproducible, indicating that there was no sintering or leaching during the reactions using these milder conditions. Furthermore, the catalysts maintained their activity despite being exposed to air between the pre-activation (cf. table footnote a) and the catalytic test runs which include an *in-situ* activation step, indicating that these pre-activated catalysts are not air-sensitive.

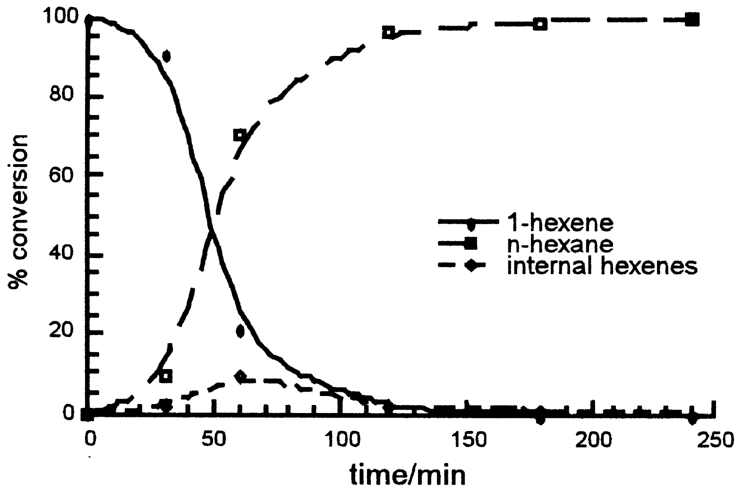


Figure 4. Reaction profile showing conversion of 1-hexene to hexane.

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References

[1] C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli and J.S. Beck, Nature 359 (1992) 710; J.S. Beck, J.C. Vartuli, W.J. Roth, M.E. Leonowicz, C.T. Kresge, K.D. Schmitt, C.T-W. Chu, D.H. Olson, E.W. Sheppard, S.B. McCullen, J.B. Higgins and J.L. Schlenker, J. Am. Chem. Soc. 114 (1992) 10834.
[2] G.S. Attard, J.C. Glyde and C.G. Göltner, Nature 378 (1995) 366.
[3] M.E. Raimondi and J.M. Seddon, Liq. Cryst. 26 (1999) 305.
[4] T. Maschmeyer, Curr. Opin. Solid State Mater. Sci. 3 (1998) 71.
[5] R. Mokaya and W. Jones, Chem. Commun. (1996) 983.
[6] A. Corma, M.T. Navarro and J. Pérez Pariente, J. Chem. Soc., Chem. Commun. (1994) 147.
[7] T. Maschmeyer, F. Rey, G. Sankar and J.M. Thomas, Nature 378 (1995) 159.
[8] D.S. Shepherd, T. Maschmeyer, B.F.G. Johnson, J.M. Thomas, G. Sankar, D. Ozkaya, W. Zhou, R.D. Oldroyd and R.G. Bell, Angew. Chem. Int. Engl. 36 (1997) 2242.
[9] D.S. Shepherd, T. Maschmeyer, G. Sankar, J.M. Thomas, D. Ozkaya, B.F.G. Johnson, R. Raja, R.D. Oldroyd and R.G. Bell, Chem. Eur. J. 4 (1998) 1214.
[10] M.E. Raimondi, L. Marchese, E Gianotti, T. Maschmeyer, J.M. Seddon and S. Coluccia, Chem. Commun. (1999) 87.
[11] D.W. Bruce, I.R. Denby, G.J.T. Tiddy and J.M. Watkins, J. Mater. Chem. 3 (1993) 911; J.D. Holbrey, D.W. Bruce and G.J.T. Tiddy, J. Chem. Soc., Dalton Trans. (1995) 1769.
[12] D.W. Bruce, J.D. Holbrey, A.R. Tajbakhsh and G.J.T. Tiddy, J. Mater. Chem. 3 (1993) 905.
[13] H.B. Jervis, M.E. Raimondi, R. Raja, T. Maschmeyer, J.M. Seddon and D.W. Bruce, Chem. Commun. (1999) 2031.
[14] K.E. Amos, M.J. Danks and D.W. Bruce, unpublished observations.