Ruthenium porphyrin encapsulated in modified mesoporous molecular sieve MCM-41 for alkene oxidation

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Ruthenium(II) *meso*-tetrakis(4-chlorophenyl)porphyrin encapsulated in MCM-41 modified with 3-aminopropyltriethoxysilane is a stable catalyst for alkene oxidation by *tert*-butyl hydroperoxide with high product turnovers.

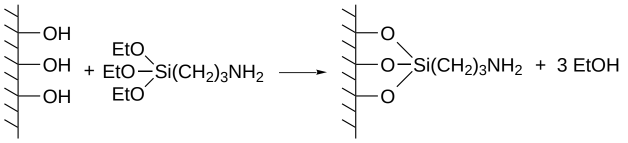
A useful means to improve the stability and selectivity of metalloporphyrin catalysts is by encapsulation in microporous materials such as zeolites.[1–5] However, the commonly employed zeolite Y has a small pore size and encapsulation of metalloporphyrins of second- and third-row transition metals is difficult. In this context, the large pore size of the MCM-41 mesoporous materials[6] is advantageous. Herein is described the encapsulation of a ruthenium porphyrin in modified MCM-41, and its catalytic properties.

MCM-41 was synthesized by a literature method[6] and was characterized by its XRD pattern, which shows a very strong peak at d = 39.74 Å. [RuL(CO)(EtOH)] [H_2L = *meso*-tetrakis(4-chlorophenyl)porphyrin] was prepared according to the literature method.[7]

Direct encapsulation of [RuL(CO)(EtOH)] in MCM-41 was unsuccessful, presumably due to the interaction of the neutral ruthenium(II) porphyrin and the channel surface of MCM-41 being weak. To resolve this problem, the surface of MCM-41 was modified by using 3-aminopropyltriethoxysilane (APTES) as shown in Scheme 1. The modified MCM-41 characterized by IR (stretching and bending of the NH_2 group at 3470 and 1634 cm^{-1}), elemental analysis (found: C, 6.96; N, 2.49%) and XRD is designated as MCM-41(m).

In a typical experiment, MCM-41 (0.1 g) was mixed with a chloroform solution of APTES (10 ml, 0.1 m) and stirred at room temp. for 8–12 h. The MCM-41(m) was filtered and washed with chloroform and dichloromethane. As shown in Fig. 1, its XRD pattern is essentially the same as that of MCM-41.

MCM-41(m) exhibits a powerful encapsulation ability. Stirring a mixture of MCM-41(m) (0.1 g) and [RuL(CO)(EtOH)] (10 mg) in CH_2Cl_2 (10 ml) at room temp. for 1 h gave the encapsulated product containing 8.3 mass% of [RuL(CO)], designated 8.3 mass% Ru/M-41(m) (IR, $\nu_{C\equiv O}$ 1952.4 cm^{-1}; UV–VIS λ_{max} 411, 528 nm). Products with different mass% [RuL(CO)] were obtained by varying the amount of [RuL(CO)(EtOH)] used in the reaction. The amount of [RuL(CO)] in Ru/M-41(m) was determined by dissolving the latter in an aqueous solution of HF (3 mass%) followed by extraction with dichloromethane. The UV–VIS absorption spectrum of the CH_2Cl_2 extract was essentially the same as that of [RuL(CO)(EtOH)] in CH_2Cl_2 (λ_{max} 411.2, 528.8 nm). The solid diffuse-reflectance UV–VIS† and FT Raman spectra‡ of Ru/M-41(m) are very similar to those of [RuL(CO)], indicating that the molecule remains intact during the process of encapsulation.



Scheme 1

As shown in Fig. 1, the XRD pattern of 8.3 mass% Ru/M-41(m) exhibits the characteristic peaks of MCM-41 but no peaks due to [RuL(CO)]. This indicates that the MCM-41 structure is retained and that the [RuL(CO)] molecules should be dispersed in the channels.

The immobilization of [RuL(CO)] onto the channel surface of MCM-41 is attributed to a ligand exchange reaction as shown in Scheme 2.

This suggestion is supported by the following experiments. First, [CuL] containing no axial ligands was found not to be encapsulated in MCM-41(m). Secondly, MCM-41 modified by trimethylsilation does not encapsulate [RuL(CO)(EtOH)], due to the conversion of surface –OH to –$SiMe_3$ groups which have little coordination ability.[6,8]

Ru/M-41(m) catalyses alkene oxidation by *tert*-butyl hydroperoxide (TBHP). In a typical experiment, a mixture of alkene (0.2 g), TBHP (0.1 g), Ru/M-41(m) (0.05 g, 5.84 × 10^{-5} mmol) and dichloromethane (2 ml) in a sealed vial was stirred for 24 h under a nitrogen atmosphere at room temp. Products were analysed and quantified by gas–liquid chromatography and/or

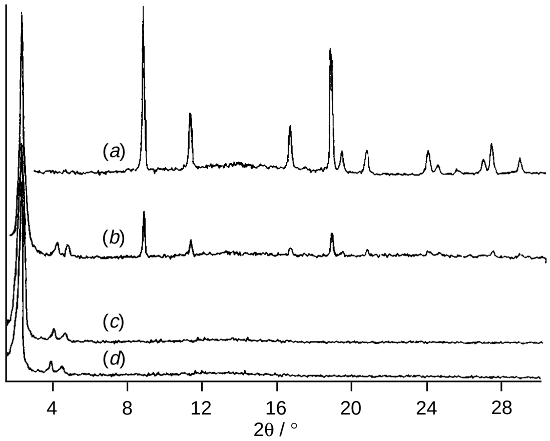
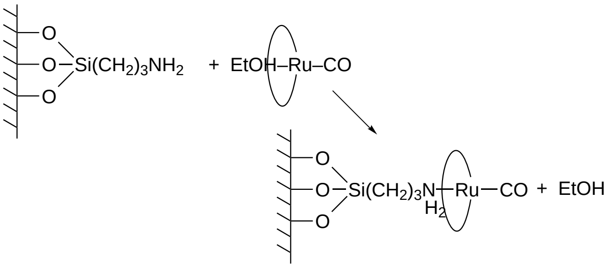


Fig. 1 XRD patterns of (*a*) [RuL(CO)(EtOH)], (*b*) a physical mixture of [RuL(CO)(EtOH)] and MCM-41(m) in a mass ratio of 8 : 92, (*c*) 8.3 mass% Ru/M-41(m) and (*d*) MCM-41 and MCM-41(m)



Scheme 2

Table 1 Oxidation of alkenes by TBHP catalysed by [RuL(CO)(EtOH)] and 0.1 mass% Ru/M-41(m)

		0.1 mass% Ru/M-41(m)		[RuL(CO)(EtOH)]	
Substrate	Product	Turnover	% Yield[a]	Turnover	% Yield
Norbornene	*exo*-Norbornene oxide	9003	52.6	230	53.8
Cyclooctene	Cyclooctene oxide	2044	11.9	69	11.9
Styrene	Styrene oxide	1878	11.0	52	12.2
	Benzaldehyde	4545	26.5	121	28.4
Cyclohexene	Cyclohexene oxide	377	2.2	20	4.6
	Cyclohex-2-en-1-ol	1219	7.1	26	6.1
	Cyclohex-2-en-1-one	2100	12.3	38	8.8
cis-Stilbene[b]	*cis*-Stilbene oxide	245	1.4	35	8.2
	trans-Stilbene oxide	1468	8.6	37	8.6
	Benzaldehyde	161	0.94	3	0.64
trans-Stilbene[b]	*cis*-Stilbene oxide	31	0.18	1	0.28
	trans-Stilbene oxide	1595	9.35	85	19.9
	Benzaldehyde	59	0.27	Trace	—

[a] Product yields were determined by GC and based on TBHP consumed. [b] The yield was determined by ^1H NMR spectroscopy with 1,1-diphenylethylene as internal standard.

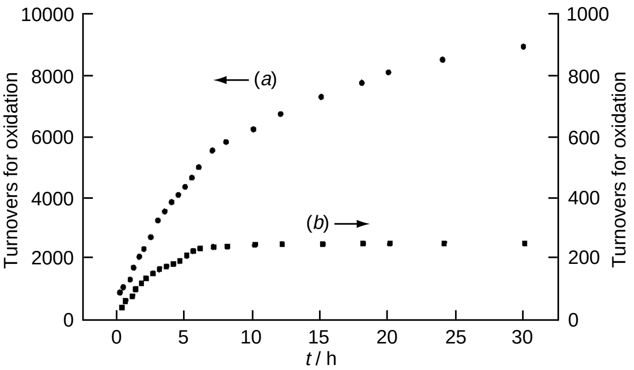


Fig. 2 Time course of oxidation for norbornene by TBHP with (*a*) 0.1 mass% Ru/M-41(m) and (*b*) [RuL(CO)(EtOH)]

^1H NMR spectroscopy. Control experiments using [RuL(CO)(EtOH)] or MCM-41(m) as catalyst and under identical reaction conditions were also performed. TBHP in the absence of catalyst and/or MCM-41(m) showed very little catalytic activity compared with Ru/M-41(m).[9]

Ru/M-41(m) with a ruthenium content ranging from 0.1 to 8.3 mass% showed good catalytic activity. In norbornene oxidation, turnovers of *exo*-norbornene oxide with 0.1, 5 and 8.3 mass% Ru/M-41(m) as catalyst are 9003, 303 and 216, respectively, suggesting that the catalytic activity is high at low ruthenium content. Presumably this is due to efficient site isolation and diffusion pathways during the reaction. Owing to its better catalytic activity, the 0.1 mass% Ru/M-41(m) catalyst was used for further oxidation experiments. Table 1 compares the results obtained for the oxidation of norbornene (bicyclo[2.2.1]hept-2-ene), cyclooctene, cyclohexene, styrene, *cis*- and *trans*-stilbenes catalysed by 0.1 mass% Ru/M-41(m) and free [RuL(CO)(EtOH)]. In general the product turnovers are 20–40 times higher with the former.

A typical time course for norbornene oxidation is shown in Fig. 2. With 0.1 mass% Ru/M-41(m), norbornene was oxidized to the *exo*-norbornene oxide at a rate of 300 turnovers h^{-1} *cf*. 38 turnovers h^{-1} with [RuL(CO)(EtOH)]. Also [RuL(CO)(EtOH)] was unstable and was completely deactivated after 6 h. By contrast, the 0.1 mass% Ru/M-41(m) catalyst appeared to be very stable and its catalytic activity did not change appreciably even after 48 h of reaction. Embedding of [RuL(CO)] molecules and their isolation from each other in the channels of MCM-41(m) precludes formation of stable inactive μ-oxo dimers. This may partly explain the stability of Ru/M-41(m) in the TBHP oxidation reaction. It is of note that the 0.1 mass% Ru/M-41(m) catalyst could be easily recovered by filtration and washing with CH_2Cl_2.

From Table 1, *trans*-stilbene oxide was the major product of *trans*-stilbene oxidation. However, oxidation of *cis*-stilbene catalysed by 0.1 mass% Ru/M-41(m) gave *trans*-stilbene oxide as the major product, in contrast to [RuL(CO)(EtOH)] for which an essentially 1 : 1 mixture of *cis*- and *trans*-stilbene oxides was obtained. This could be a consequence of the steric constraints imposed by the straight channels of MCM-41(m) which would favour the formation of linear *trans*-stilbene oxide.

We acknowledge supports from the Hong Kong Research Council and the University of Hong Kong.

Footnotes

† Solid diffuse-reflectance UV–VIS spectrum of 0.1 mass% Ru/M-41(m) (λ_{max}/nm): 414, 535, 570.

‡ FT Raman spectrum of 8.3 mass% Ru/M-41(m) ($\tilde{\nu}$/cm^{-1}): 1591.7, 1545.0, 1488.3, 1462.9, 1363.9, 1235.4, 1206.5, 1088.5, 1036.4, 1012.9, 884.0, 848.3, 807.1, 708.7, 471.9, 397.3, 357.3, 337.9, 285.4, 159.7.

References

1 M. Nakamura, T. Tatsumi and H. Tominaga, *Bull. Chem. Soc. Jpn.*, 1990, **63**, 3334.
2 F. Bedioui, *Coord. Chem. Rev.*, 1995, **144**, 39.
3 P. Battioni, R. Iwanejko, D. Mansuy, T. Mlodnicka, J. Poltowicz and F. Sanchez, *J. Mol. Catal.*, 1996, **109**, 91.
4 R. C. Sosa, R. F. Parton, P. E. Neys, O. Lardinois, P. A. Jacobs and P. G. Rouxhet, *J. Mol. Catal.*, 1996, **110**, 141.
5 B. Meunier, *Chem. Rev.*, 1992, **92**, 1441.
6 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.*, 1992, **114**, 10 834.
7 D. P. Rillema, J. K. Nagle, L. F. Barringer Jr. and T. J. Meyer, *J. Am. Chem. Soc.*, 1981, **103**, 56.
8 G. A. Ozin and S. Özkar, *Chem. Mater.*, 1992, **4**, 511.
9 E. M. Gaigneaux, R. Maggi, P. Ruiz and B. Delmon, *J. Mol. Catal.*, 1996, **109**, 67.

Received, 16th August 1996; Com. 6/05721G