MCM-41-supported *cis*-diaquabis(6,6′-dichloro-2,2′-bipyridine) ruthenium(II) complex. Immobilisation, characterisation and catalytic activities

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Received (in Montpellier, France) 5th January 1999, Accepted 22nd April 1999

cis-$[Ru^{II}(6,6'\text{-}Cl_2bpy)_2(OH_2)_2](CF_3SO_3)_2$ (6,6′-Cl_2bpy = 6,6′-dichloro-2,2′-bipyridine) was immobilised into the mesoporous molecular sieve MCM-41 by a simple and direct method and the highest loading of *cis*-$[Ru^{II}(6,6'\text{-}Cl_2bpy)_2(OH_2)_2](CF_3SO_3)_2$ achieved was 8.4 wt%. The supported ruthenium complex, designated as Ru/MCM-41, has been characterised by elemental analyses, N_2 adsorption isotherm, X-ray diffraction (XRD), thermogravimetric and differential thermal analyses (TG-DTA), UV-visible and FT-Raman spectroscopies. XRD spectra showed that the immobilised *cis*-$[Ru^{II}(6,6'\text{-}Cl_2bpy)_2(OH_2)_2](CF_3SO_3)_2$ was not in a crystalline form and the MCM-41 structure was retained. Preliminary studies revealed that the Ru/MCM-41 materials catalysed the oxidation of alkanes by *tert*-butylhydroperoxide (TBHP) with high turnover. High catalytic activity has been obtained with low ruthenium loading catalysts.

Inorganic molecular sieves are excellent solid supports that are widely used as heterogeneous catalysts and sorption media because of their narrow pore size distribution and large internal surface area.[1] The effective site isolation of a metal complex within the channels/cages of these supports enhances its catalytic activity and oxidative stability.[2] Other advantages of these supported catalysts offered are ease of recovery and recycling.

In early studies, microporous molecular sieves with pore sizes of 4–13 Å were used as solid support materials.[3] However, their small pore sizes limit their applications; for example, it is difficult to encapsulate metal-organic compounds in microporous molecular sieves. Much attention has recently been directed to large pore size molecular sieves,[1d] such as the mesoporous molecular sieves designated as M41S. We were particularly interested in one member of this family, denoted as MCM-41, which exhibits a regular pore system consisting of a hexagonal arrangement of unidimensional pores (15–100 Å) with a narrow pore size distribution and high surface area (up to 1000 $m^2\ g^{-1}$).[1b,4] Its enormous pore size offers more opportunities for immobilisation of large catalytic species and catalytic conversion of large and bulky substrates. The immobilisation of transition metal catalysts on the channel walls of MCM-41 has received much attention in recent years.[5–7] Burch *et al.* reported the surface grafting of manganese-oxo species on the internal walls of MCM-41 channels, which are active for hydrocarbon oxidations.[6] Recently, Che and co-workers reported that immobilisation of $[Ru^{II}(Por)(CO)(EtOH)]$ (Por = porphyrin dianion) on the internal walls of MCM-41(m) channels greatly enhanced its catalytic activity and stability towards alkene oxidations.[7]

The oxidation chemistry of ruthenium complexes containing polypyridine ligands has been extensively studied.[8–11] Previous studies by Che and co-workers showed that *cis*-$[Ru^{II}(6,6'\text{-}Cl_2bpy)_2(OH_2)_2](CF_3SO_3)_2$(6,6′-$Cl_2$bpy = 6,6′-dichloro-2,2′-bipyridine) is a robust catalyst for organic oxidations by TBHP.[8a,b] We envisaged that immobilisation of this complex into MCM-41 channels would improve the catalytic activity and recyclability of the catalyst. Herein we describe the immobilisation of *cis*-$[Ru^{II}(6,6'\text{-}Cl_2bpy)_2(OH_2)_2](CF_3SO_3)_2$ into MCM-41, together with a thorough characterisation by means of elemental analyses, N_2 adsorption isotherm, X-ray powder diffraction, differential thermal and thermogravimetric analyses, UV-visible and FT-Raman spectroscopies.

Results and discussion

Immobilisation

The immobilisation of *cis*-$[Ru^{II}(6,6'\text{-}Cl_2bpy)_2(OH_2)_2]$-$(CF_3SO_3)_2$ into MCM-41 was undertaken by stirring a mixture of *cis*-$[Ru^{II}(6,6'\text{-}Cl_2bpy)_2(OH_2)_2](CF_3SO_3)_2$ and MCM-41 in deionised water at 25 °C for 4–6 h. The Ru/MCM-41 materials with different wt% of *cis*-$[Ru^{II}(6,6'\text{-}Cl_2bpy)_2(OH_2)_2](CF_3SO_3)_2$ (0.02–8.4 wt%) were obtained by varying the amount of complex used in the reaction. As shown in Fig. 1, the amount (wt%) of the immobilised ruthenium complex increased with the concentration of *cis*-$[Ru^{II}(6,6'\text{-}Cl_2bpy)_2(OH_2)_2](CF_3SO_3)_2$ (mM) used in the reaction but the relationship was not linear. When the concentration was below 5 mM, R/R_0 [ratio of *cis*-$[Ru^{II}(6,6'\text{-}Cl_2bpy)_2(OH_2)_2](CF_3SO_3)_2$ immobilised in MCM-41 (R) to amount of *cis*-$[Ru^{II}(6,6'\text{-}Cl_2bpy)_2(OH_2)_2](CF_3SO_3)_2$ used in reaction (R_0)] was less than 50%. This ratio increased with higher concentrations up to 15 mM and then remained constant up to 18 mM. Above this value this ratio dropped below 70%. The highest loading of immobilised *cis*-$[Ru^{II}(6,6'\text{-}Cl_2bpy)_2(OH_2)_2](CF_3SO_3)_2$ was 8.4 wt%. No leaching of the ruthenium complex from Ru/MCM-41 was measured even upon suspending a 8.4 wt% Ru/MCM-41 sample (50 mg) in water (10 ml) at 25 °C for a week, as evidenced by measuring the absorbance of the aqueous solution at 495 nm, which corresponds to the $d_\pi(Ru) \rightarrow \pi^*(6,6'\text{-}Cl_2bpy)$ transition. Our detection limit of *cis*-$[Ru^{II}(6,6'\text{-}Cl_2bpy)_2(OH_2)_2](CF_3SO_3)_2$ in water was 0.4 ppm by UV-visible spectrophotometry.

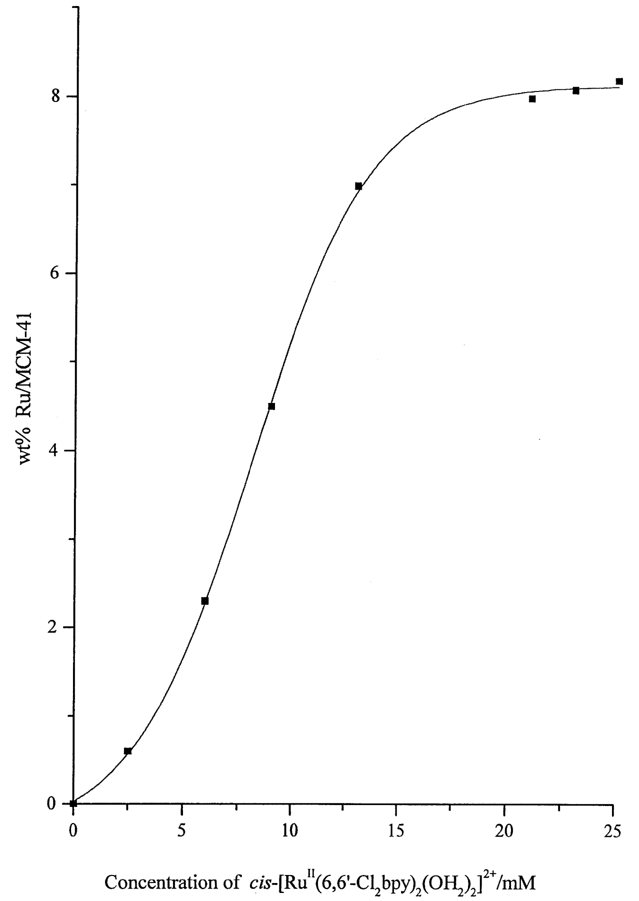


Fig. 1 Relation between the amount of the immobilised cis-[Ru^{II}-(6,6′-Cl$_2$bpy)$_2$(OH$_2$)$_2$](CF$_3$SO$_3$)$_2$ complex and its concentration used for the immobilisation reaction.

Characterisation

The average pore size of MCM-41 is 30.7 Å based on the N_2 adsorption isotherm. The XRD pattern of cis-[Ru^{II}(6,6′-Cl$_2$bpy)$_2$(OH$_2$)$_2$](CF$_3$SO$_3$)$_2$ (Fig. 2, trace a) exhibits characteristic peaks at $2\theta > 6°$. As shown by trace c, the XRD pattern of 8.4 wt% Ru/MCM-41 is typical of MCM-41 with an intense diffraction peak at $2\theta = 2.785°$ ($d_{100} = 31.7$ Å) and three weak peaks. The absence of peaks above $2\theta = 6°$ indicates that this sample is free from crystalline cis-[Ru^{II}(6,6′-Cl$_2$bpy)$_2$(OH$_2$)$_2$](CF$_3$SO$_3$)$_2$. For comparison, a 8 : 92 wt/wt physical mixture of cis-[Ru^{II}(6,6′-Cl$_2$bpy)$_2$(OH$_2$)$_2$](CF$_3$SO$_3$)$_2$ and MCM-41 was prepared, the XRD pattern (trace b) of which showed the peaks arising from the crystalline cis-[Ru^{II}(6,6′-Cl$_2$bpy)$_2$(OH$_2$)$_2$](CF$_3$SO$_3$)$_2$. This suggests that the ruthenium complex in MCM-41 is not in a crystalline form and that the structure of MCM-41 is retained.

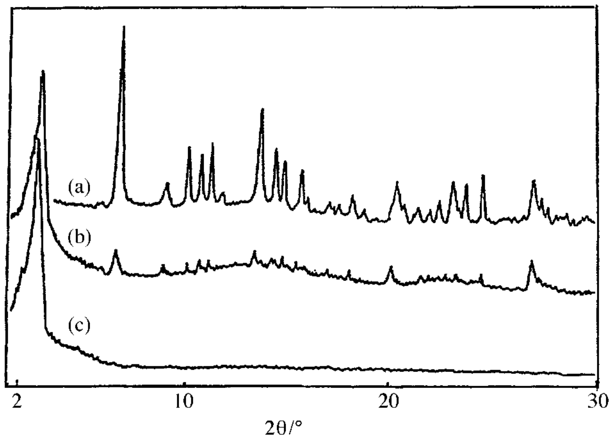


Fig. 2 XRD patterns of (a) cis-[Ru^{II}(6,6′-Cl$_2$bpy)$_2$(OH$_2$)$_2$](CF$_3$SO$_3$)$_2$, (b) a 8:92 wt/wt physical mixture of cis-[Ru^{II}(6,6′-Cl$_2$bpy)$_2$(OH$_2$)$_2$](CF$_3$SO$_3$)$_2$ and MCM-41 and (c) 8.4 wt% Ru/MCM-41.

The TG and DTA thermograms of 8.4 wt% Ru/MCM-41 are depicted in Fig. 3 (traces a and b, respectively). From these results, an endotherm at 100 °C with a weight loss of 3.7 wt% and an exotherm at 401 °C with a weight loss of 6.5 wt% were observed. The weight loss at 100 °C is attributed to the desorption of water whereas that at 401 °C arises from the oxidative decomposition of the immobilised ruthenium complex.

The immobilised ruthenium complex could be recovered after digesting the Ru/MCM-41 materials in a 3 wt% HF solution. The UV-visible spectrum obtained after digesting a 8.4 wt% Ru/MCM-41 material (Fig. 4, trace b) showed an absorption band at 495 nm attributed to the $d_\pi(Ru) \rightarrow \pi^*$(6,6′-

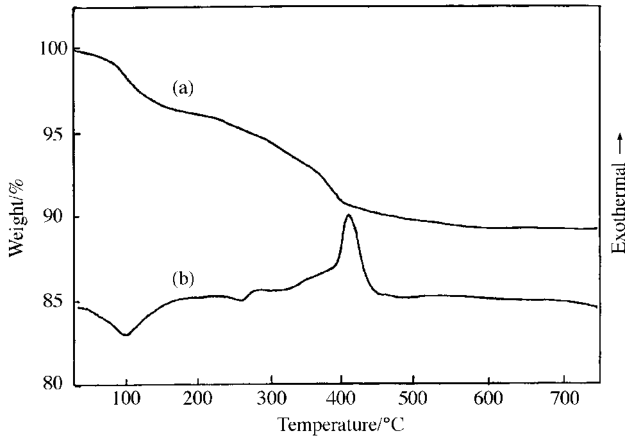


Fig. 3 (a) TG and (b) DTA of 8.4 wt% Ru/MCM-41.

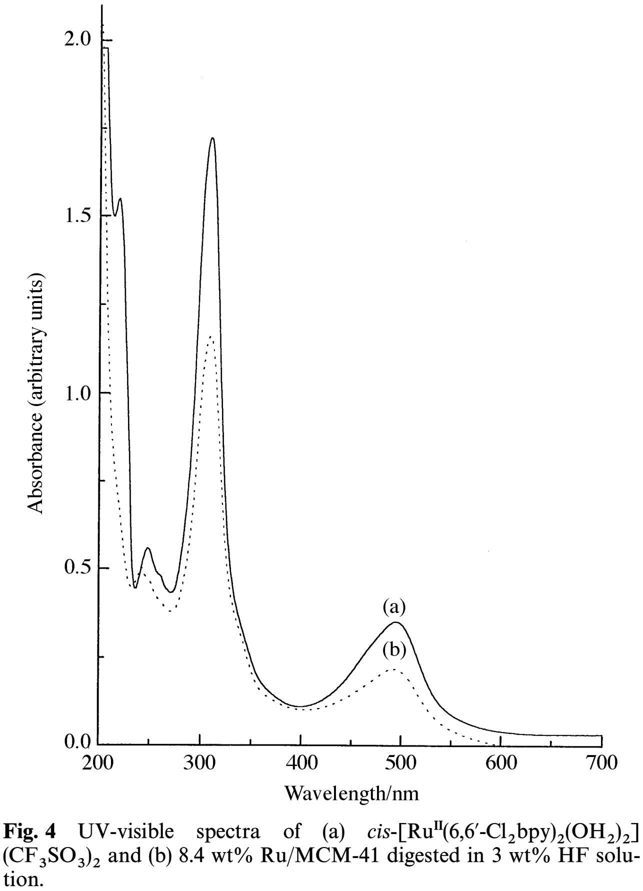


Fig. 4 UV-visible spectra of (a) cis-[Ru^{II}(6,6′-Cl$_2$bpy)$_2$(OH$_2$)$_2$](CF$_3$SO$_3$)$_2$ and (b) 8.4 wt% Ru/MCM-41 digested in 3 wt% HF solution.

Cl_2bpy) transition (MLCT). This spectrum matches well that of the free ruthenium complex recorded in aqueous solution (trace a).

The FT-Raman spectrum of Ru/MCM-41 (Fig. 5, trace a) exhibited the characteristic peaks of *cis*-[Ru^{II}(6,6′-Cl_2bpy)$_2$(OH_2)$_2$](CF_3SO_3)$_2$ (trace b) between 500–1500 cm^{-1}, which are absent in MCM-41.

Interaction between the ruthenium complex and MCM-41

It is difficult to ascertain the interaction(s) between the *cis*-[Ru^{II}(6,6′-Cl_2bpy)$_2$(OH_2)$_2$](CF_3SO_3)$_2$ complex with the channel surface of MCM-41. Previous studies from our laboratory showed that [Ru^{II}(bpy)$_3$]$^{2+}$ cations can be immobilised into MCM-41,[12] whereas neutral ruthenium(II) porphyrin complexes such as [Ru^{II}(tcpp)(CO)(EtOH)] (H_2tcpp = *meso*-tetrakis(4-chlorophenyl)porphyrin) and [Ru^{II}(tdcpp)(CO)(EtOH)] (H_2tdcpp = *meso*-tetrakis(2,6-dichlorophenyl)porphyrin) could not be immobilised.[7] We have also modified the MCM-41 surface with silylation agents such as chlorotrimethylsilane (TMS) or 3-aminopropyltriethoxysilane (APTES) as depicted in Scheme 1. The MCM-41 modified by reaction (1) is hydrophobic, whereas that by reaction (2) is hydrophilic in nature. We have found that both *cis*-[Ru^{II}(6,6′-Cl_2bpy)$_2$(OH_2)$_2$]$^{2+}$ and [Ru^{II}(bpy)$_3$]$^{2+}$ cations cannot be immobilised in the MCM-41 modified by either reaction 1 or 2. We suggest that this does not result from the decrease of the MCM-41 pore size due to silylation but to the disappearance of surface silanol groups. It has been reported that silylation of MCM-41 would lead to a decrease in the pore radius by 4.5 Å only.[1b,13] This suggests that the surface silanol groups play an important role in the immobilisation of the *cis*-[Ru^{II}(6,6′-Cl_2bpy)$_2$(OH_2)$_2$]$^{2+}$ cations. The interaction could be electrostatic and/or H-bonding in nature.

Cyclic voltammetry

The electrochemical properties of Ru/MCM-41 were studied by cyclic voltammetry. A cyclic voltammogram obtained with an edge-pyrolytic graphite electrode at pH 1.1 (0.1 M CF_3COOH) is depicted in Fig. 6 (trace a). Two quasi-reversible couples, denoted as I and II, are observed at 0.92 and 1.17 V *vs.* SCE, respectively. Compared with previous electrochemical studies on *cis*-[Ru^{II}(6,6′-Cl_2bpy)$_2$(OH_2)$_2$](CF_3SO_3)$_2$ in 0.1 M CF_3COOH,[8a,14] couples I and II are attributed to the redox processes shown in Scheme 2.

Thus, the immobilised *cis*-[Ru^{II}(6,6′-Cl_2bpy)$_2$(OH_2)$_2$]$^{2+}$ cations retained the same chemical form as that of the free

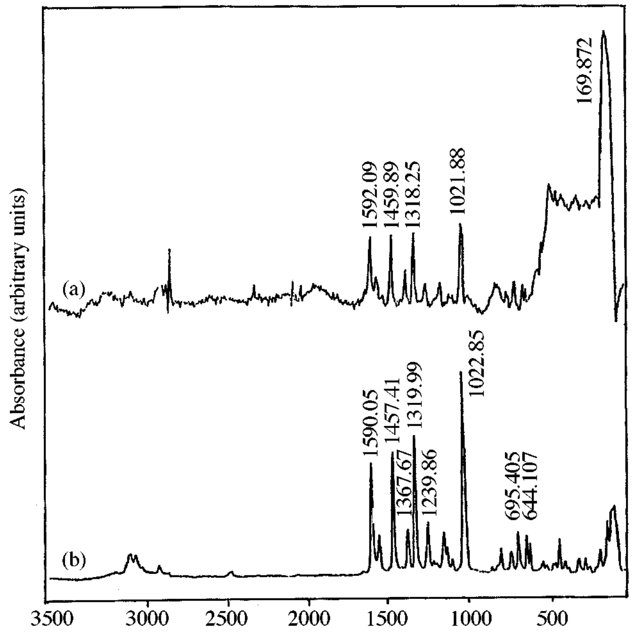
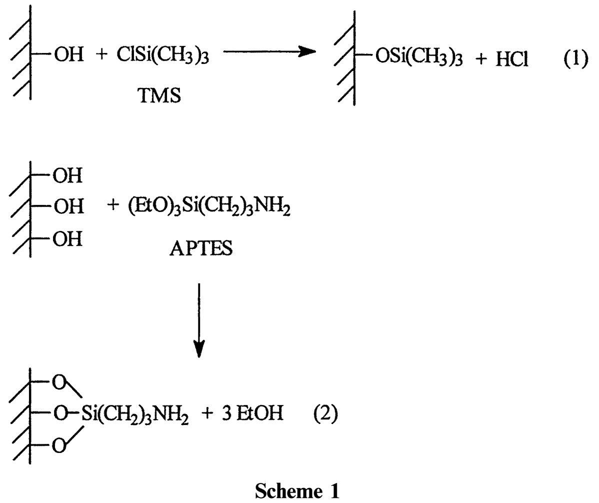


Fig. 5 FT-Raman spectra of (a) 8.4 wt% Ru/MCM-41 and (b) *cis*-[Ru^{II}(6,6′-Cl_2bpy)$_2$(OH_2)$_2$](CF_3SO_3)$_2$.



Scheme 1

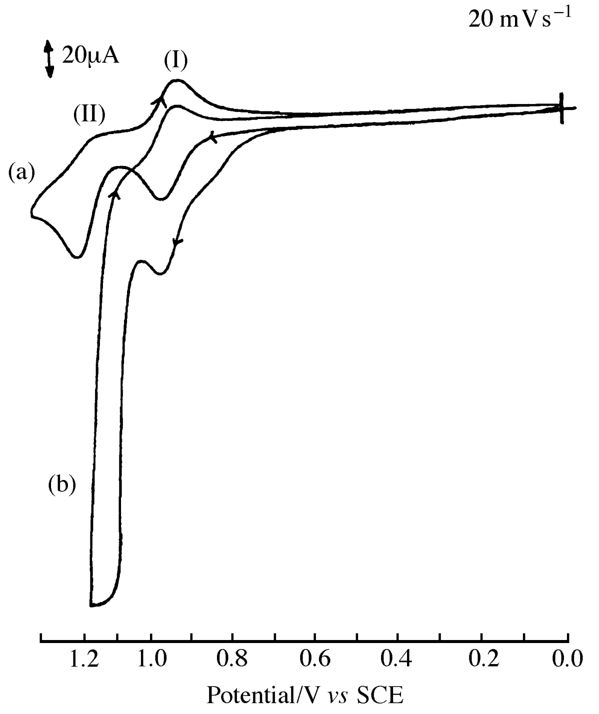


Fig. 6 Cyclic voltammogram of 8.4 wt% Ru/MCM-41 in 0.1 M CF_3COOH: (a) with no benzyl alcohol and (b) with 50 μl benzyl alcohol, using a potential sweep of 20 mV s^{-1} and an edge-plane pyrolytic graphite working electrode.

$$cis\text{-}[Ru^{IV}(6,6'\text{-}Cl_2bpy)_2(OH_2)(O)]^{2+} + 2e^- + 2H^+ \downarrow cis\text{-}[Ru^{II}(6,6'\text{-}Cl_2bpy)_2(OH_2)_2]^{2+} \quad \text{Peak I}$$

$$cis\text{-}[Ru^{VI}(6,6'\text{-}Cl_2bpy)_2O_2]^{2+} + 2e^- + 2H^+ \downarrow cis\text{-}[Ru^{IV}(6,6'\text{-}Cl_2bpy)_2(OH_2)(O)]^{2+} \quad \text{Peak II}$$

Scheme 2

ruthenium complex during the cyclic voltammetric measurements. In the presence of benzyl alcohol (Fig. 6, trace b), couple II was replaced by an irreversible wave with an enhanced anodic current. This indicates that the electrogenerated *cis*-dioxoruthenium(VI) inside the channels of MCM-41 could function as an active oxidant for the oxidation of benzyl alcohol at a rate compatible with the CV time scale.

Catalytic experiments

The Ru/MCM-41 materials are competent catalysts for the oxidation of alkanes by TBHP under mild conditions. The results for the catalytic oxidation of cyclohexane by TBHP in acetone are summarised in Table 1. Control experiments using MCM-41 as catalyst revealed no activity and the rate of TBHP addition did not affect the results. The catalytic activity was not due to leached ruthenium complex in the acetone solution. This is because the filtered solution obtained by filtering off the solid catalyst showed no catalytic activity even when fresh batches of cyclohexane (0.2 ml) and TBHP (4 mmol) were added to it. Indeed, no detectable leaching of the ruthenium complex into the acetone solution (detection limit = 0.4 ppm) was recorded as determined by UV-visible spectroscopy.

The Ru/MCM-41 materials with 0.02 to 2.4 wt% *cis*-$[Ru^{II}(6,6'\text{-}Cl_2bpy)_2(OH_2)_2](CF_3SO_3)_2$ loading showed good catalytic activity. For cyclohexane oxidation, the turnover of 7.2 wt% Ru/MCM-41 was similar to that of *cis*-$[Ru^{II}(6,6'\text{-}Cl_2bpy)_2(OH_2)_2](CF_3SO_3)_2$ whereas those of 0.02–1.0 wt% Ru/MCM-41 were about 30 to 2 times higher. The product turnovers with 0.02 and 2.4 wt% Ru/MCM-41 as catalyst were 24960 and 1130, respectively. Similar observations were also made for the oxidation of adamantane and cyclooctane (Table 2).

Table 1 Oxidation of cyclohexane by TBHP catalysed by free and MCM-41-supported *cis*-$[Ru^{II}(6,6'\text{-}Cl_2bpy)_2(OH_2)_2](CF_3SO_3)_2$

Entry	Catalyst	Yield/% (ketone + alcohol)	Turnover[a]	Ratio of ketone to alcohol
1	Free complex	46	870	0.78
2	0.02 wt%[b]	58	24960	1.40
3	0.1 wt%[b]	54	3500	1.33
4	1.0 wt%[b]	39	1580	0.86
5	2.4 wt%[b]	35	1130	0.92
6	7.2 wt%[b]	29	610	0.95

Reaction conditions: a mixture of cyclohexane (0.2 ml), *cis*-$[Ru^{II}(6,6'\text{-}Cl_2bpy)_2(OH_2)_2](CF_3SO_3)_2$ or Ru/MCM-41 (1 or 30 mg) and TBHP (4 mmol) in acetone (3 ml) was stirred at 25 °C in a water bath for 24 h. [a] Turnover is based on the ratio of moles of oxidised products to moles of metal catalyst used. [b] Ru/MCM-41.

The cyclohexane oxidation catalysed by the Ru/MCM-41 materials with low ruthenium loadings (entries 2 and 3 in Table 1) have a higher ketone-to-alcohol ratio compared to that obtained by the free *cis*-$[Ru^{II}(6,6'\text{-}Cl_2bpy)_2(OH_2)_2](CF_3SO_3)_2$ complex. We attribute this to the sorption property of MCM-41. Since MCM-41 is hydrophilic in nature,[2c] there is a preference for interaction with the alcohol products rather than with the alkane substrates. Thus the alcohol molecule would be subsequently oxidised once it was formed and retained inside the MCM-41 channels.[2a,c] It is noteworthy that the Ru/MCM-41 catalyst could be easily recovered by filtration after the reaction and reused successively three times under the typical reaction conditions: cyclohexane (0.2 ml), 0.1 wt% Ru/MCM-41 (30 mg) and TBHP (4 mmol) in acetone (3 ml) at 25 °C in a water bath for 24 h. The recovered and dried catalyst was found to exhibit a similar catalytic activity: first run, turnover = 3500; second run, turnover = 3495 and third run, turnover = 3492.

Conclusions

Ru/MCM-41 samples with a wide range of ruthenium complex loadings can be readily prepared by a simple and direct method. The highest loading of *cis*-$[Ru^{II}(6,6'\text{-}Cl_2bpy)_2(OH_2)_2](CF_3SO_3)_2$ immobilised on the internal walls of MCM-41 was 8.4 wt%. Preliminary studies showed that the Ru/MCM-41 samples are capable of catalysing oxidation of alkanes by TBHP, with very high product turnovers. This system has the combined features of both homogeneous and heterogeneous catalytic systems, in the context of stability, ease of handling, ease of product separation, recoverability and recyclability of the supported catalysts and mild reaction conditions.

Experimental

General

Tetraethyl orthosilicate $[Si(OC_2H_5)_4]$, hexadecyltrimethylammonium bromide $[C_{16}H_{33}(CH_3)_3NBr]$, trimethylsilyl chloride $[(CH_3)_3SiCl]$, hexamethyldisiloxane $\{[(CH_3)_3Si]_2O\}$ and 3-aminopropyltriethoxysilane (APTES) were purchased from Aldrich. Acetone (GR, Merck) was used as received. Cyclohexane was first washed with concentrated H_2SO_4, then distilled over calcium hydride. Adamantane (Aldrich) was recrystallised from acetone followed by sublimation. Cyclooctane (99 + %) was obtained from Aldrich. *tert*-Butylhydroperoxide (80% in di-*tert*-butylperoxide) was purchased from Merck and standardised by iodometric titration before used. *cis*-$[Ru^{II}(6,6'\text{-}Cl_2bpy)_2(OH_2)_2](CF_3SO_3)_2$ was prepared by the literature method.[14] The loading of ruthenium complex (wt%) in Ru/MCM-41 was analysed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) using a Carl Zeiss Plasmaquent ICP spectrometer 110. The pore size distribution curve of MCM-41 was

Table 2 Oxidation of alkanes by TBHP catalysed by free and MCM-41-supported *cis*-$[Ru^{II}(6,6'\text{-}Cl_2bpy)_2(OH_2)_2](CF_3SO_3)_2$

		Total turnover[a]		
Substrate	Products	0.1 wt%[b]	1.0 wt%[b]	Free complex
Adamantane[c]	Adamantan-1-ol Adamantan-(2-ol + 2-one)	720	110	180
Cyclooctane	Cyclooctanol Cyclooctanone	3540	290	410
Cyclohexane	Cyclohexanol Cyclohexanone	3500	1580	870

Reaction conditions: a mixture of substrate (0.2 ml), *cis*-$[Ru^{II}(6,6'\text{-}Cl_2bpy)_2(OH_2)_2](CF_3SO_3)_2$ or Ru/MCM-41 (1 or 30 mg) and TBHP (4 mmol) in acetone (3 ml) was stirred at 25 °C in a water bath for 24 h. [a] Turnover is based on the ratio of moles of oxidised products to moles of metal catalyst used. [b] Ru/MCM-41. [c] Adamantane (1 mmol) and TBHP (4 mmol) were used in the reaction.

obtained from a N_2 adsorption isotherm using an ACAP 2400 automatic adsorption instrument. X-Ray powder diffractions (XRD) were obtained on a SIEMENS D5000 X-ray diffractometer using monochromatised Cu Kα radiation. Patterns were recorded over the 2θ range from 1.5 to 30° and in steps of 0.05° with a count time of 1 s at each point. Tube voltage was 40 kV with a current of 30 mA. Thermogravimetric (TG) and differential thermal (DT) analyses were carried out on a Perkin Elmer TGA-7 thermal analytic apparatus. The samples were heated in flowing air at a rate of 20 °C min^{-1}. UV-visible spectra were recorded on a Hewlett Packard model HP 845X spectrophotometer at 25 °C. FT-Raman spectra were obtained on a Bio-Rad FT-Raman spectrometer. Cyclic voltammetry was performed using a Princeton Applied Research model 175 potentiostat. Current–voltage curves were recorded on a Bipp and Zonen X–Y Recorder. Gas liquid chromatography (GLC) analyses were performed on a Hewlett Packard model HP 5890A Series II gas chromatograph equipped with a flame ionisation detector. Quantification of gas chromatographic components was performed on a Hewlett Packard HP 3393 Series II integrator. Capillary column model SPB-5 [30 m × 0.32 mm id × 0.25 μm, bonded phase: poly(5% diphenyl–95% dimethylsiloxane)] was used to identify the oxidation products.

Preparations

Preparation of purely siliceous MCM-41. To a suspension of $C_{16}H_{33}(CH_3)_3NBr$ (2.4 g) and NaOH (7 ml, 2M) in H_2O (80 ml), $Si(OC_2H_5)_4$ (10 ml) was added while stirring. The mixture was stirred at 25 °C for 2 h. The resulting solid was filtered, washed with deionised water, dried at 100 °C and finally calcinated at 550 °C under air for 5 h.

Preparation of Ru/MCM-41. A series of MCM-41-supported *cis*-$[Ru^{II}(6,6'\text{-}Cl_2bpy)_2(OH_2)_2](CF_3SO_3)_2$ samples, Ru/MCM-41 (wt% = 0.02–8.4), were prepared by stirring MCM-41 (100 mg) and *cis*-$[Ru^{II}(6,6'\text{-}Cl_2bpy)_2(OH_2)_2](CF_3SO_3)_2$ in water (10 ml, 0.04–22 mM) at 25 °C for 4–6 h. The pink solid was obtained by filtration, washed with deionised H_2O and dried in air.

Preparation of MCM-41 modified with chlorotrimethylsilane. A mixture of MCM-41 (500 mg), $(CH_3)_3SiCl$ (10 g) and $[(CH_3)_3Si]_2O$ (15 g) was refluxed for 6 h. The resulting solid was filtered, washed with acetone and dried in air.[1b]

Preparation of MCM-41 modified with 3-aminopropyltriethoxysilane. MCM-41 (500 mg) was suspended in a chloroform solution of 3-aminopropyltriethoxysilane (0.1 M, 50 ml) at 25 °C for 12 h with stirring. The resulting solid was filtered, washed with chloroform and dried in air.[7]

Determination of ruthenium complex loading in Ru/MCM-41

The amount of ruthenium complex in Ru/MCM-41 was determined by digesting the latter in a 3 wt% HF solution. The ruthenium content in the resulting solution was analysed by ICP-AES. A series of known concentrations of *cis*-$[Ru^{II}(6,6'\text{-}Cl_2bpy)_2(OH_2)_2](CF_3SO_3)_2$ in 3 wt% HF were used as standard solutions.

Catalytic oxidations

Oxidation of alkanes was performed by stirring a mixture of substrate (0.2 ml), TBHP (4 mmol) and Ru/MCM-41 catalyst (30 mg) in acetone (3 ml) at 25 °C in a water bath. A blank containing the same amount of solvent, substrate and TBHP but with MCM-41 as catalyst was simultaneously stirred under identical conditions. After the reaction, the Ru/MCM-41 catalyst was recovered by filtration and the amount of oxidation products were determined by GLC analysis.

Acknowledgements

We acknowledge support from the Hong Kong Research Grants Council, the University of Hong Kong and the National Natural Science Foundation of China (29771013) and thank Professor K. Y. Wong for electrochemical measurements.

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Paper 9/00203K