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Chiral ruthenium porphyrin encapsulated in ordered mesoporous molecular sieves (MCM-41 and MCM-48) as catalysts for asymmetric alkene epoxidation and cyclopropanation†

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Encapsulation of chiral ruthenium porphyrin [Ru^{II}(D_4-Por*)CO] in modified mesoporous silica supports such as MCM-41 and MCM-48 achieves active catalysts for asymmetric epoxidation of alkenes by 2,6-dichloropyridine *N*-oxide and intramolecular cyclopropanation, which is the first example of chiral metalloporphyrin supported on ordered molecular sieves.

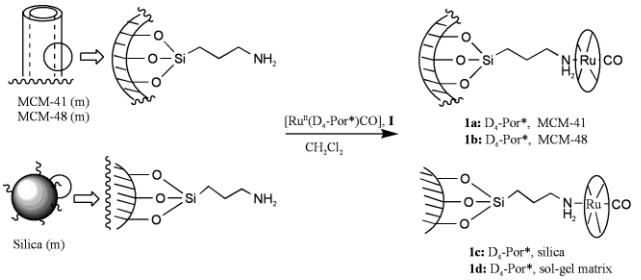
Although significant progress has been made in transition metal-catalyzed enantioselective organic reactions, the search for efficient, robust and recyclable chiral metal catalysts remains a difficult task in asymmetric catalysis.[1] Recent studies showed that the D_4-symmetric ruthenium complex of [5,10,15,20-tetrakis-(1*S*,4*R*,5*R*,8*S*)-1,2,3,4,5,6,7,8-octahydro-1,2:5,8-dimeth ano-anthracen-9-yl] porphyrin H_2(D_4-Por*) is an excellent catalyst for its reactivity, versatility, and enantioselectivity in asymmetric alkene epoxidation and cyclopropanation.[2] However, the tedious preparation and high cost of the H_2(D_4-Por*) ligand obstruct its application in organic syntheses. An approach to circumvent this problem is to immobilize [Ru^{II}(D_4-Por*)(CO)] on solid support, facilitating the product-catalyst separation and recycling of the chiral catalyst.[3] Although some progress in heterogeneous organic oxidations catalyzed by soluble and insoluble polymer supported ruthenium porphyrins have been made,[4,5] a similar strategy is not suitable to develop polymer supported chiral metalloporphyrins because of the difficulty involved in attaching chiral porphyrin ligand particularly the D_4-symmetric H_2(D_4-Por*) onto the polymer chain.

An alternative method is to attach ruthenium porphyrin to mesoporous silica material by *coordinative grafting*; this would circumvent the problem encountered in the structural modification of the porphyrin ligand.[3] We previously encapsulated chiral [Ru^{IV}(D_4-Por*)Cl_2] in a sol–gel matrix which exhibited lower reactivity by physical host–guest interaction; the obtained heterogenous catalyst exhibited lower reactivity in asymmetric epoxidation of alkenes compared to its homogenous counterpart.[6] This was ascribed to a blocking of the reactant to the active sites of amorphous silica. However, in the case of MCM-41, an ordered mesoporous silica support, attachment of ruthenium porphyrins [Ru^{II}(Por)CO] (Por = *p*-Cl-TPP and TDCPP) or chiral chromium Schiff base could achieve effective catalysts for alkene epoxidation.[7] We envision the structure of solid support could play an important role in heterogeneous organic oxidations catalyzed by chiral ruthenium porphyrins.

In contrast to the MCM-41 silica phase with a one-dimensional straight channel system, MCM-48 contains a three-dimensional network, which provides a large surface area for high accessibility of reactant(s) to active sites within the porous network structure.[8] These features make MCM-48 a good solid support for heterogenous catalysis. Herein, we report the preparation and reactivities of chiral metalloporphyrin catalysts encapsulated in ordered mesoporous molecular sieves **1a–b** (Scheme 1). To compare the effect of different silica supports, we also anchored [Ru^{II}(D_4-Por*)(CO)] on silica surface **1c**.

As previously reported, treatment of [Ru^{II}(D_4-Por*)(CO)] (**I**) with surface modified (by 3-aminopropyltriethoxysilane) mesoporous silica in CH_2Cl_2 led to immobilization of **I** on the support through a ligand exchange reaction (Scheme 1).[7] The catalysts (**1a–d**) were characterized by FT-IR, powder-XRD (for **1a** and **1b**) and solid diffuse-reflectance UV–VIS spectra. And the loading amount of ruthenium porphyrin was determined by a published method.[7] IR spectra of the catalysts show stretching vibrations at 1940, 1942, 1938 and 1939 cm^{-1} ($\nu_{C=O}$), respectively. Solid diffuse-reflectance UV–VIS spectra show the absorption bands at *ca.* 418 and 528 nm. These spectroscopic data are close to that of [Ru^{II}(D_4-Por*)(CO)], indicating that the molecular structure of [Ru^{II}(D_4-Por*)(CO)] remains intact during the process of encapsulation. The XRD patterns of **1a–b** exhibit the characteristic peaks of MCM-41 and MCM-48, without the peaks due to free ruthenium porphyrin, which demonstrates that the ordered structure of MCM-41 and MCM-48 was retained and [Ru^{II}(D_4-Por*)(CO)] molecules should be dispersed in the channels. For **1c**, [Ru^{II}(D_4-Por*)(CO)] was anchored on the surface of silica gel. Using sol–gel method, we encapsulated [Ru^{II}(D_4-Por*)(CO)] into the matrix of silica gel (**1d**).

The asymmetric epoxidation of styrene with 2,6-Cl_2pyNO catalyzed by **1a–1d** were carried out in benzene for 24 h at room temperature. The results are summarized in Table 1. From entries 1–3, the reactivity and enantioselectivity of styrene epoxide are the best when the loading amount of [Ru^{II}(D_4-Por*)(CO)] of **1a** reaches 1.6 wt%; a further increase in loading amount results in decrease of product yield (entry 3). Therefore, the loading amount of [Ru^{II}(D_4-Por*)(CO)] in **1b**, **1c** and **1d** are 1.7, 1.6 and 1.7 wt%, respectively, for the studies. In this work, the reaction performed in benzene gave a better ee than that in CH_2Cl_2 (Table S1†). Entries 4–6 of Table 1 show the results of styrene epoxidation by 2,6-Cl_2pyNO with catalysts **1b–d** and free ruthenium porphyrin as catalysts. Notably, **1b**, with modified MCM-48 as solid support, gave the highest ee and yield, while **1a** exhibited similar reactivity and enantioselectiv-



Scheme 1

† Electronic supplementary information (ESI) available: experimental section. See http://www.rsc.org/suppdata/cc/b2/b209276j/

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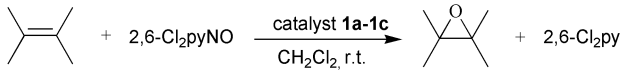
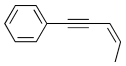
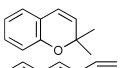
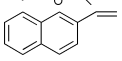
ity to the homogenous counterpart. But **1c**, with [$Ru^{II}(D_4$-$Por^*)(CO)$] anchored on the silica gel surface, could not efficiently catalyze the reaction and most of ruthenium complex leached from the surface of silica gel after the reaction. Complex **1d** exhibited stability in this reaction and little free ruthenium porphyrin released from the solid catalyst was observed after 24 h. However, its reactivity was low (conversion 10%). From entries 7 and 8, we found that, in the presence of HCl, **1a** and **1b** could give high turnover numbers (up to 1.0×10^4, Table S2† and entries 7–9 in Table 1). For **1b**, when total turnovers reached 2.6×10^4 after two recycles, reactivity remained almost unchanged and ee decreased to 66%. Compared to the previously reported [$Ru^{IV}(D_4$-$Por^*)Cl_2$]/sol–gel catalyst, the reactivity and stability of **1b** exhibited in epoxidation of styrene are better (entry 8).[3] Extension of the epoxidation of styrene to other alkene substrates also gave high reactivity and comparable selectivity (entries 10–16) than those obtained using free [$Ru^{II}(D_4$-$Por^*)(CO)$] catalyst. Similar to free [$Ru^{II}(D_4$-$Por^*)(CO)$] catalyst, **1b** gave better enantioselectivity and reactivity towards *cis*-alkenes than *trans*-counterparts (Table S3†). This shows that, upon immobilization on the inside surface of channels of MCM-48, [$Ru^{II}(D_4$-$Por^*)(CO)$] performed like the homogenous condition and the unique environment constituted by [$Ru^{II}(D_4$-$Por^*)(CO)$] and the channels of MCM-48 leads to maintain the chiral introduction, enhance its reactivity and stabilize the catalyst in asymmetric epoxidation of alkenes.

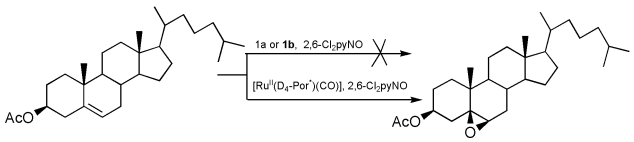
We have examined the epoxidation of cholesterol acetate (Scheme 2) using the ruthenium modified silica materials; **1a** and **1b** could not catalyze the reactions but free [$Ru^{II}(D_4$-$Por^*)(CO)$] gave high epoxide yield (> 99%) with complete β selectivity (supporting information†). The results suggest that ruthenium porphyrin is encapsulated in the channels of mesoporous molecular sieves and cannot leach off from the solid support during the reaction. The steroid molecule is unlikely to freely diffuse into the inner channels of MCM-41 or MCM-48 despite their pore sizes being *ca*. 30–50 Å.

Table 1 Asymmetric epoxidation of alkenes by 2,6-Cl_2pyNO catalysed by **1a**–**1d**[a]



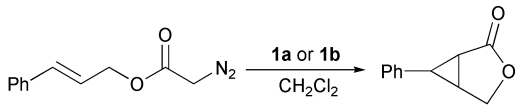
Entry	Catalyst	Substrate		Conversion%[b]	Yield(%, TON)[b]	Ee%[c]
1	**1a**		X = H	79	86(3390)	72 (*R*)
2[d]	**1a**		X = H	76	86(3260)	46 (*R*)
3[e]	**1a**		X = H	56	88(2460)	66 (*R*)
4	**1b**		X = H	84	86(3610)	75 (*R*)
5	**1c**		X = H	42	79(1650)	43 (*R*)
6	**1d**		X = H	10	68(340)	66 (*R*)
7[f]	**1a**		X = H	72	80(11520)	70 (*R*)
8[f]	**1b**		X = H	82	82(13450)	74 (*R*)
9[f]	**1b**		X = H	76	83(12620)	66 (*R*)
10	**1b**		X = 4-Cl	76	93(3530)	68 (*R*)
11	**1b**		X = 4-CF_3	62	98(3030)	70 (*R*)
12	**1b**			94	94(4420)	70 (n.d)
13	**1b**			92	99(4600)	75 (n.d.)
14	**1b**			80	92(3680)	77 (*R*)
15	**1b**			90	85(3820)	74 (1*S*, 2*R*)
16[g]	**1b**			> 99	98(4900)	76 (1*R*, 2*S*)

[a] All reactions were performed in benzene for 24 h by using 0.2 μmol catalyst, 1.0 mmol of substrate, and 1.1 mmol 2,6-Cl_2pyNO. The loading amount of [$Ru^{II}(D_4$-$Por^*)(CO)$] for catalysts **1a**–**1d** are 1.6, 1.7, 1.6 and 1.7 wt %, respectively, unless otherwise noted [b] Conversions were determined by GC using 1,4-dichlorobenzene as standard; yields were based on the amount of substrates consumed. [c] Ee% of epoxides were determined by GC equipped with chiral capillary column (J&W Scientific cyclodex-B) or ^{1}H-NMR using $Eu(hfp)_3$ as chiral shift reagent. Absolute configuration was determined by comparing with authentic chiral samples. [d] The loading amount of [$Ru^{II}(D_4$-$Por^*)(CO)$] is 0.8 wt %. [e] The loading amount of [$Ru^{II}(D_4$-$Por^*)(CO)$] is 2.4 wt %. [f] Reaction condition: 2.0 mmol alkene, 2.2 mmol 2,6-Cl_2pyNO, a catalytic amount of HCl (0.1% equiv.) and 0.1 μmol **1a** and **1b**, room temperature for 24 h. [g] *cis* Isomer.



Scheme 2

We note that there has been no report on using silica supported metal catalysts for intramolecular cyclopropanations. To demonstrate the versatility of these ruthenium porphyrin modified catalysts in organic transformation reactions, **1b** was employed as catalyst for intramolecular cyclopropanation of *trans*-cinnamyl diazoacetate. The reaction was found to proceed with high enantioselctivity (Scheme 3) (85%) and product turnover number reaches 1.5×10^3 (for homogenous counterpart: 1.5×10^2).[2] Furthermore, **1b** could be reused 4 times (support information†) and after two cycles, ee decreased to 76%. We envision that structural modification of ordered molecular sieves such as enlarging pore size and enhancing thermal stability will provide a new class of heterogeneous ruthenium catalysts for organic reactions.



Scheme 3

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