Asymmetric epoxidation of alkenes catalysed by chromium binaphthyl Schiff base complex supported on MCM-41

Xiang-Ge Zhou,[a] Xiao-Qi Yu,[a] Jie-Sheng Huang,[a] Shou-Gui Li,[b] Lian-Sheng Li[b] and Chi-Ming Che*[a]

[a] *Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong.*
E-mail: cmche@hkucc.kku.hk
[b] *Department of Chemistry, Jilin University, Changchun 130023, P.R. China*

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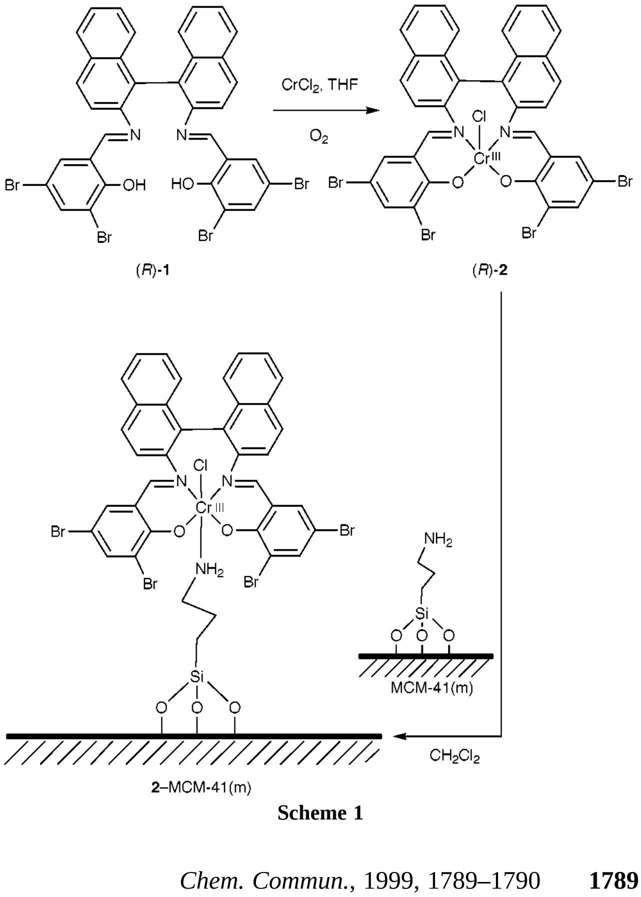
A chromium(III) binaphthyl Schiff base complex immobilised on modified MCM-41 is an effective catalyst for asymmetric epoxidation of unfunctionalised alkenes and gave significantly higher ee than the free complex.

The heterogenisation of homogeneous catalysts, which endows the homogeneous systems with attractive features such as easy product separation and catalyst recovery, constitutes a rapidly expanding research area.[1–5] Chief among various types of heterogenised catalysts are the metal complexes immobilised onto solid supports such as molecular sieves,[2,3] ion-exchange resins[4] and polymer membrance.[5] Although such immobilisation can sometimes enhance the activity of homogeneous catalysts, a common problem encountered in asymmetric catalysis is a decrease of enantioselectivity upon heterogenisation.[6] Indeed, all the heterogenised catalysts developed very recently for epoxidation of unfunctionalised alkenes exhibit considerably lower[7–10] or no higher[5,11] enantioseletivity than their homogeneous counterparts. Herein we report the alkene epoxidation with PhIO catalysed by a chromium binaphthyl Schiff base complex immobilised on MCM-41,[2] which demonstrates that the heterogenisation of a homogeneous catalyst can result in an increase of enantioselectivity for epoxidation of unfunctionalised alkenes.

The preparation of the heterogenised chromium Schiff base complex is depicted in Scheme 1.† Species **2** was characterised by IR and FAB mass spectroscopy as well as elemental analysis.‡ Based on the structures of the iron and manganese complexes,[12] the size of **2** is estimated to be 14 Å. Treatment of **2** with MCM-41(m),[13] a modified MCM-41 having a pore size of 36 Å, in CH_2Cl_2 readily led to immobilisation of **2** on the support.§ The catalyst thus obtained is designated as **2**–MCM-41(m), as indicated in Scheme 1. By varying the amount of **2** used in the immobilisation reaction, **2**–MCM-41(m) having four different contents of **2**, namely, 0.5, 0.8, 1.8 and 3.6 wt% determined on a POEMS ICP spectrometer, was obtained. The X-ray diffraction patterns of these catalysts all resemble that of MCM-41 as well as that of MCM-41(m), indicating that, after the above immobilisation treatments, the mesoporous structure of this support remains undisrupted and the molecules of **2** should be dispersed on the surface of the support. On the other hand, the FT-Raman spectrum of **2**–MCM-41(m) is similar to that of **2** if the bands belonging to MCM-41(m) are excluded. This suggests that **2** remains intact in the heterogenised catalysts.

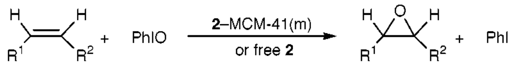
Since the chromium centre in **2** is either five-coordinate or six-coordinate with a substitutionally labile water molecule, immobilisation of **2** onto MCM-41(m) could be readily achieved through coordination of the chromium ion to a terminal NH_2 group of the surface-bound tether *via* simple addition or ligand substitution reactions, as in the case of our recent immobilisation of ruthenium porphyrins onto the same support.[13] As might be expected, attempts to immobilise **2** onto the unmodified MCM-41, which lacks the above mentioned NH_2 groups, have failed.

The epoxidation of a series of unfunctionalised alkenes with PhIO catalysed by **2**–MCM-41(m) was carried out in toluene for 12–36 h by using 20 mg of the catalyst, 0.1 ml of substrate and 16 mg of PhIO. The reactions were monitored by GC until completion. The results are summarised in Table 1. Besides epoxides, some minor side products such as benzaldehyde or its derivatives were also detected by GC. Efforts were first directed to optimise the content of **2** in the catalysis with *p*-chlorostyrene as substrate. As is obvious from entries 1–3 and 9 in Table 1, both the yield and ee of the corresponding epoxide increase with the content of **2** until it reaches 1.8%. However, a further increase of the content of **2** results in a decrease of the yield and ee. Therefore, we used **2**–MCM-41(m) containing 1.8% of **2** for all further studies. The effect of temperature was investigated. Interestingly, a temperature decease of 20 °C led to very little change in either the yield or ee (entries 3 and 8), in contrast to the catalysis involving free **2**, in which the ee markedly increased with a decrease in temperature (entries 10 and 11). The reusability of **2**–MCM-41(m) was also examined. After the epoxidation reaction was complete, the catalyst could be recovered simply by filtration followed by washing with CH_2Cl_2. Entries 4–7 give the results obtained for reusing



Scheme 1

Table 1 Asymmetric epoxidation of alkenes with PhIO catalysed by **2**–MCM-41(m).[a] The results obtained by using free **2**[b] (entries 10, 11, 17, 18) with *p*-chlorostyrene and *cis* β-methylstyrene are also listed



Entry	Substrate R¹	R²	Content of **2**/wt%[c]	Yield (%)[d]	Ee (%)[e]	TON	*T*/°C
1	4-ClC_6H_4	H	0.5	36	57 (*R*)	254	20
2	4-ClC_6H_4	H	0.8	42	60 (*R*)	162	20
3	4-ClC_6H_4	H	1.8	59	65 (*R*)	104	20
4[f]	4-ClC_6H_4	H		62	66 (*R*)	109	20
5[g]	4-ClC_6H_4	H		62	68 (*R*)	109	20
6[h]	4-ClC_6H_4	H		23	49 (*R*)	40	20
7[i]	4-ClC_6H_4	H		21	20 (*R*)	37	20
8	4-ClC_6H_4	H	1.8	61	67 (*R*)	110	0
9	4-ClC_6H_4	H	3.6	55	58 (*R*)	52	20
10[j]	4-ClC_6H_4	H		30	48 (*R*)	30	20
11[j]	4-ClC_6H_4	H		48	63 (*R*)	48	0
12	Ph	H	1.8	38	55 (*R*)	67	20
13	4-$CF_3C_6H_4$	H	1.8	31	63 (*R*)	55	20
14	4-FC_6H_4	H	1.8	32	56 (*R*)	56	20
15	–CH_2CH_2-1,2-C_6H_4–		1.8	26	42 (1*R*,2*S*)	46	20
16	Ph	Me	1.8	32[k]	73[l] (1*R*,2*S*)	56	20
17[j]	Ph	Me		43[k]	54[l] (1*R*,2*S*)	43	20
18[j]	Ph	Me		52[m]	62[l] (1*R*,2*S*)	52	0

[a] All reactions were performed in toluene by using 20 mg of catalyst, 0.1 ml of substrate, and 16 mg of PhIO. This gives, for example, 0.56 mol% of **2** relative to PhIO for the 1.8% content of **2**. [b] Reaction conditions: identical to those for **2**–MCM-41(m) except 1 mol% of **2** (relative to PhIO) was used. [c] The content of **2** in **2**–MCM-41(m) was determined on a POEMS ICP spectrometer. [d] Determined by GC based on the PhI formed. [e] Determined by GC with chiral column. [f] First, [g] second, [h] third, and [i] fourth reuse of **2**–MCM-41(m) containing 1.8% of **2**. After these reuses, a total of 2–3% of Cr had leached into solution. [j] Free **2** was used instead of **2**–MCM-41(m). [k] The ratio of *cis*:*trans* = 66:31. [l] *cis* Isomer. [m] The ratio of *cis*:*trans* = 91:9.

2–MCM-41(m) up to four times. Notably, this catalyst could be reused at least two times with a total turnover number of 322 (entries 3–5) without a decrease in enantioselectivity. In contrast, a recently reported Mn–MCM-41–salen catalyst suffered from a loss of enantioselectivity of 40% ee when reused for the first time.[10] Extension of the above epoxidation reaction to other substrates also gave moderate to relatively high ees at room temperature (entries 12–16). The highest ee (73%) was obtained for *cis*-β-methylstyrene (entry 16).

Surprisingly, the heterogenised **2** exhibits significantly higher enantioselectivity than free **2** under identical conditions (entry 3 *vs.* 10 or 16 *vs.* 17). For example, with *cis*-β-methylstyrene as substrate, the ee increased by as much as *ca.* 20% upon immobilisation of **2** onto MCM-41(m) (entries 16 and 17). As the support MCM-41(m) showed negligible catalytic activity toward these oxidation reactions, the increase in chiral recognition could arise from the enhanced stability of the chromium complex upon immobilisation. Alternatively, it could also result from the unique spatial environment constituted by both the chiral binaphthyl Schiff base ligand and the surface of the support. To make clear which environment, inside or outside the channels, is responsible for the enhancement of chiral induction, we immobilised **2** on another modified MCM-41 designated as MCM-41(m-in), whose external surface was passivated with Ph_2SiCl_2, thus placing the same surface-bound tether containing the terminal NH_2 groups as in MCM-41(m) inside the channels only.[14] Under the same conditions with *p*-chlorostyrene as substrate, both **2**–MCM-41(m-in) and **2**–MCM-41(m), having similar content of **2**, afforded the corresponding epoxide in almost the same yield and ee. This shows that the environment inside the channels of the support leads to the enhancement in the chiral induction.

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Notes and references

† *Preparation* of **2**: A mixture of anhydrous chromium(II) chloride (1 mmol) and **1** (1 mmol) in THF (20 ml) was stirred under argon at room temperature for 3 h, leading to a color change from brown to green. The mixture was then left open to the air for 3 h to allow full oxidation of chromium(II) to chromium(III). After removal of the solvent, the residual solid was recrystallised from CH_2Cl_2–hexane to give the desired product as a green solid. Yield: 70%.

‡ *Spectral data* for **2**: ν_{max}(KBr)/cm^{-1}) 3443, 1603, 1507, 1430, 1302, 1207, 1160, 1072, 820, 751, 715, 688, 539; *m/z* (FAB MS) 893 (M^+), 858 ([M − Cl]$^+$) (Calc. for $C_{34}H_{18}N_2O_2Br_4CrCl{\cdot}2H_2O$: C, 43.89; H, 2.37; N, 3.01. Found: C, 43.71; H, 2.58; N, 3.21%). The ^1H NMR spectrum of **2** is featureless due to its paramagnetism.

§ *Preparation* of **2**–*MCM-41(m)*: A mixture of **2** and MCM-41(m) (100 mg) in CH_2Cl_2 (10 ml) was stirred at room temperature for 2 h. The solid product was then collected by filtration, thoroughly washed with CH_2Cl_2, and dried under vacuum.

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