ChemPubSoc Europe

DOI: 10.1002/chem.201402136

CHEMISTRY
A European Journal
Full Paper

Heterogeneous Catalysis

Asymmetric Epoxidation of *cis*/*trans*-β-Methylstyrene Catalysed by Immobilised Mn(Salen) with Different Linkages: Heterogenisation of Homogeneous Asymmetric Catalysis

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In memory of Haidong Zhang's father

Abstract: Immobilised Mn(salen) catalysts with two different linkages were studied in the asymmetric epoxidation of *cis*/*trans*-β-methylstyrene using NaClO as oxidant. The immobilised Mn(salen) complexes inside nanopores can lead to different catalytic behaviour compared with that of homogeneous Jacobsen catalyst. The rigidity of the linkage was found to be a key factor affecting the catalytic performance of immobilised catalysts. The immobilised catalyst with a rigid linkage exhibited comparable chemical selectivity, enantioselectivity and *cis*/*trans* ratio of product formation to that obtained with homogeneous Jacobsen catalysts. In contrast, the immobilised catalyst with a flexible linkage gave remarkably lower chemical selectivity, enantioselectivity and inverted *cis*/*trans* ratio compared with the results obtained with the homogeneous Jacobsen catalyst and the immobilised catalyst with rigid linkage. Thus, for immobilised Mn(salen) catalysts, a rigid linkage connecting active centres to the support is essential to obtain activity and enantioselectivity as high as those obtained in homogeneous systems.

Introduction

The immobilisation of homogeneous asymmetric catalysts has attracted much attention over the past few decades.[1] The most usual starting point for the design of immobilised asymmetric catalysts is typically a homogeneous catalyst that shows high enantioselectivity in homogeneous reactions.[1a] Some homogeneous Mn(salen) complexes were found to be highly enantioselective in the asymmetric epoxidation of unfunctionalised olefins, particularly tri-substituted and (*Z*)-substituted alkenes.[2] Consequently, the immobilisation of homogeneous Mn(salen) complexes was especially attractive.[1,2g] One key point for the design of such immobilised catalysts is the requirement to maintain the high levels of enantioselectivity shown by homogeneous catalysts, thus, the immobilisation strategy should be carefully selected.[3] Many studies have focused on the confinement effect of the support materials on heterogeneous asymmetric epoxidation, and the results of these investigations have shown that the pore size of the support material can tune the chemical environment of immobilised Mn(salen) catalysts and thus significantly affect their catalytic behaviour.[2f,4]

Another key aspect in this field is the linkage used to connect Mn(salen) complexes to the support surface.[3a] Like the pore-size of the support, the length of the linkage was found to influence the enantioselectivity in heterogeneous asymmetric epoxidation.[2d,4c,f] Linkages (-CH_2-Ph-SO_3-, -CH_2CH_2-Ph-SO_3- and -$CH_2CH_2CH_2$-Ph-SO_3-) with different length were used by Zhang et al. in the immobilisation of Mn(salen) complexes for the heterogeneous epoxidation of styrene.[4c] They found that longer linkage can result in higher conversion of styrene, higher chemical selectivity and higher enantioselectivity towards epoxides, when Mn(salen) complexes were immobilised in the nanopores of an amorphous silica material. In contrast, an increase in linkage length had no influence on the enantioselectivity when Mn(salen) complexes were immobilised on the external surface of the support. However, Tu et al. discovered an opposite trend for immobilised Mn(salen) catalysts with different linkage length (-$C_6H_4CH_2$-, -$C_6H_4CH_2OCH_2$- and -$C_6H_4CH_2OCH_2CH_2$-), also on the outer surface of support.[4j] They found that longer linkage led to higher enantioselectivity in the heterogeneous epoxidation. The results of the studies on the linkages of immobilised Mn(salen) catalysts carried out by Zhang et al.[4c] and Tu et al.[4j] suggest further research in this field is required. All the studies described above focused

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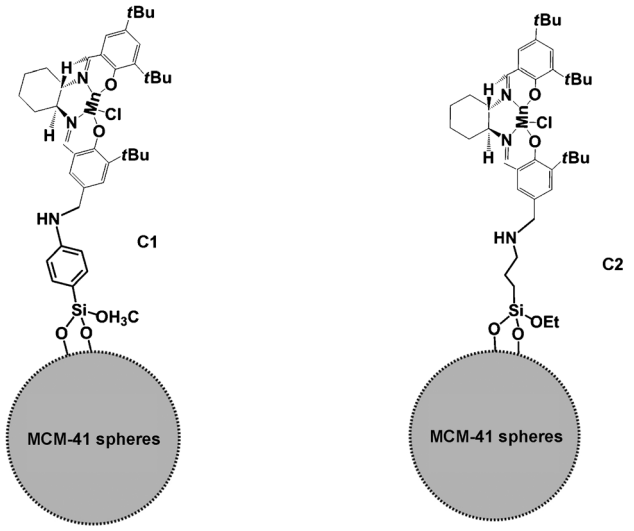
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201402136.

on the linkage length of immobilised Mn(salen) catalysts, however, to our knowledge, no investigation on other aspects of the linkages of immobilised Mn(salen) catalysts have been reported.

In this work, we also conducted a study on the effect of the linkage of immobilised Mn(salen) catalysts on their catalytic activities in heterogeneous asymmetric epoxidation, but focused on another property of the linkage, rigidity. Two linkages (see Scheme 1), with very similar length but significantly different ri-



Scheme 1. Illustration of the catalysts with anilino- (C1) and propylamino- (C2) tethers.

gidity, were used to investigate the effect of linkage flexibility on the catalytic behaviour of immobilised Mn(salen) catalysts, especially the enantiomeric excess (*ee*) and the *cis*/*trans* ratio of products. In this study, a uniform and spherical MCM-41 (MCM = mobil composition of matter) material, with a pore diameter close to the dimension of the solvated Mn(salen) complex, was used as the support for the immobilised Mn(salen) catalysts to reduce the impact of motion restriction and help the evaluation of confinement effects on the catalytic behaviour of immobilised Mn(salen) catalysts. *cis*/*trans*-β-Methylstyrene was chosen as the model substrate for the heterogeneous asymmetric epoxidation with NaClO as oxidant, because its sp^2 C=C double bond will be transformed into an sp^3 C–C single bond and *cis* epoxides will be produced through the *cis* route, whereas *trans* epoxides will be produced through the *trans* route.[4c,f] In this way, the *ee* value and *cis*/*trans* ratio of products can be tuned by adjusting the support pore size and the linkage of immobilised Mn(salen) catalysts.

Results

Figure 1a presents the N_2 adsorption–desorption isotherms of MCM-41 material. Being similar to conventional MCM-41 materials,[5] this MCM-41 material shows typical type IV adsorption–desorption isotherms without clear hysteretic loops, with high specific area of 1007 $m^2 g^{-1}$ and a large pore volume of

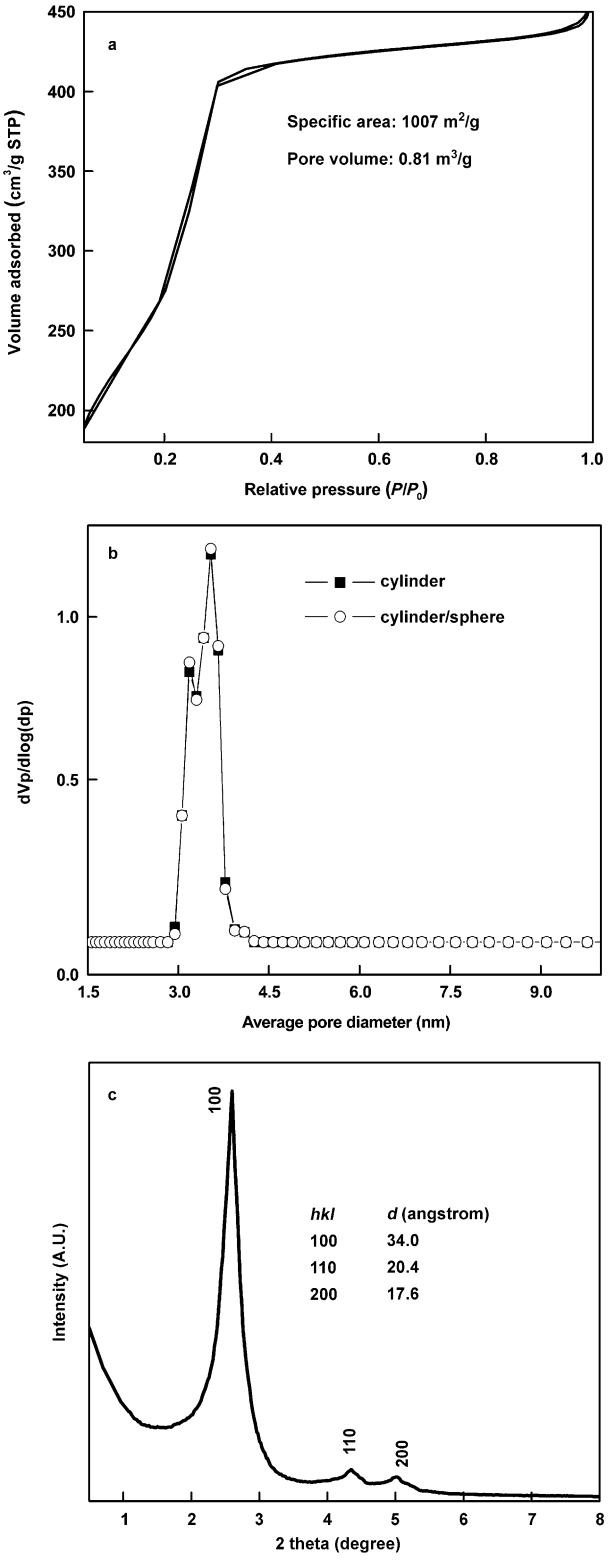


Figure 1. a) N_2 adsorption–desorption isotherms of MCM-41 material; b) Pore-size distributions measured by the adsorption branch of N_2 adsorption–desorption isotherms and by the NLDFT method; c) SXRD pattern of MCM-41 spheres.

0.81 $cm^3 g^{-1}$. As shown in Figure 1b, the pore-size distribution calculated by the nonlocal density functional theory (NLDFT) method with either a cylinder model or cylinder/sphere model

shows a main peak centred at 3.5 nm with a very small shoulder peak at 3.2 nm. In Figure 1c, the small-angle X-ray diffraction (SXRD) pattern of this MCM-41 material presents three Bragg peaks between 2.0 and 6.0°. These peaks are indexed as (100), (110) and (200) reflections, respectively.[5] The ratios of the corresponding d values of (100), (110) and (200) reflections confirm the 2-dimensional hexagonal symmetry (*p6mm*) of this material.

Scanning electron microscope (SEM) and transmission electron microscope (TEM) images of the MCM-41 material are given in Figure 2. The SEM images in Figure 2a and b show

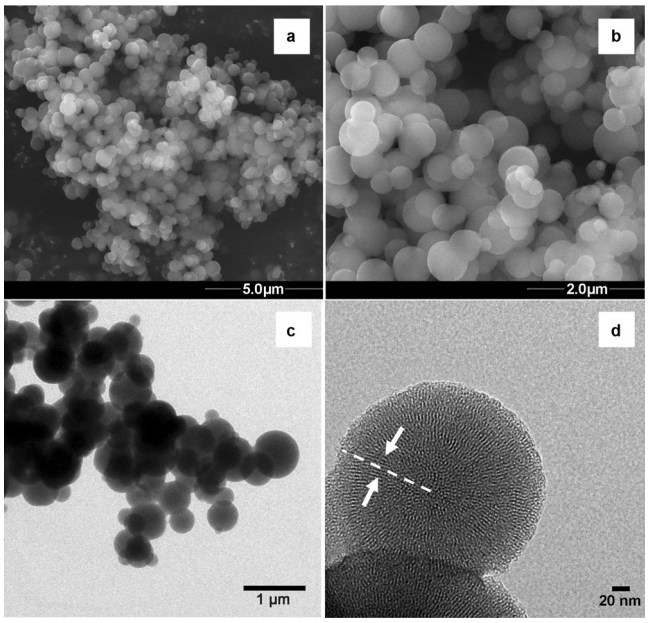


Figure 2. a, b) SEM and c, d) TEM images of MCM-41 support material. The arrows in panel d indicate the pore channels and the dashed line demonstrates the growing direction of nanochannels perpendicular to the surface of spherical particle.

that this MCM-41 material has a regular shape that is almost perfectly spherical. The particle size of these MCM-41 spheres is much less than 1 μm. According to the TEM image (Figure 2c), we can reliably evaluate the particle size distribution of these MCM-41 spheres. The dimensions of almost 90% of the particles range from 400 to 600 nm.

The TEM image in Figure 2d demonstrates the perfectly orbicular shape of these MCM-41 spheres, in which nanochannels start from the inner part of each particle and extend out to the surface.[5a,b,6] The dimension of the solvated Mn(salen) complex, which has the same structure as that of commercial Jacobsen catalyst and immobilised Mn(salen) catalysts C1 and C2, is 2.05 nm (see Scheme S1 in the Supporting Information).[4c] The dimension of solvated Mn(salen) complex is smaller than the most probable pore diameter calculated by the NLDFT method for the MCM-41 material. This suggests that the Mn(salen) complexes can be immobilised into the nanochannels of this MCM-41 material. The NLDFT pore distribution centred at 3.2–3.5 nm, which is slightly larger than the dimension of the solvated Mn(salen) complex, indicates that the immobilisation of Mn(salen) complexes onto the external surface of this MCM-41 material is also possible. For those Mn(salen) complexes immobilised into nanochannels of this MCM-41 material, the very similar pore diameter compared to the complex dimension could lead to stronger confinement effects than those in larger pores.[2e,g,4c,d,e,f,h]

Figure 3 shows the FTIR spectra of the MCM-41 material and immobilised Mn(salen) catalysts. In Figure 3a, the spectrum obtained from the MCM-41 support shows intense and large bands in the region 3200–3700 cm^{-1}. These bands are related to the surface hydroxyl groups from SiOH. The C=N groups in the immobilised Mn(salen) catalysts, which participated in coordination with manganese ions, should give a characteristic band overlapped by this O–H bending vibration band.[4e] An intense band near 1630 cm^{-1}, which is assigned to the adsorbed water on MCM-41,[7] can also be observed in the spectrum of MCM-41 material. These bands, which relate to MCM-41 support, are also identifiable in the spectra of both immobilised Mn(salen) catalysts. In the ranges of 2800–3000 and 1400–1700 cm^{-1}, the spectrum of Jacobsen catalyst presents a number of bands that cannot be observed in the spectrum of MCM-41 material but can be identified in the spectra of both immobilised catalysts.

In Figure 3b, bands at 1608, 1557, 1534, 1432, 1410, 1390 and 1360 cm^{-1} can be identified, which relate to the Mn(salen) complex of commercial Jacobsen catalyst.[4e] These bands are also identifiable in the spectra of both immobilised catalysts, with slight shifts due to immobilisation, proving the existence of immobilised Mn(salen) complexes with same structure as that of commercial Jacobsen catalyst on MCM-41. As shown in Figure 3c, the bands at 2866, 2905 and 2954 cm^{-1}, which are absent in the spectra of MCM-41 support but distinguishable in the spectrum of commercial Jacobsen catalyst, can be observed in the spectra of both immobilised Mn(salen) catalysts, confirming the successful immobilisation of Mn(salen) complex on MCM-41, although slight shifts can also be observed for those bands at 1608, 1557, 1534, 1432, 1410, 1390 and 1360 cm^{-1}.[4d,e] Furthermore, the appearance of a band at 2924 cm^{-1} in the spectra of both immobilised Mn(salen) catalysts and Jacobsen catalyst, are attributed to the presence of *tert*-butyl groups in the Mn(salen) complexes.[4e] This further indicates the immobilisation of Mn(salen) complexes with the same structure as that of commercial Jacobsen catalyst on MCM-41.

Figure 4 gives the spectra obtained by ultraviolet–visible diffuse reflectance spectroscopy (UV/Vis DRS) of MCM-41 support material, commercial Jacobsen catalyst and immobilised catalysts C1 and C2. No band can be observed in the spectrum of MCM-41 support material. In the spectrum of Jacobsen catalyst, the band at 290 nm is related to $\pi \rightarrow \pi^*$ excitation whereas the band at 325 nm is related to $n \rightarrow \pi^*$ excitation of its salen ligand.[2g,4c,e,f,j] The band at 447 nm is due to charge transfer (CT) transition from the salen ligand to Mn.[8] The band at 515 nm is attributed to the d–d transition of neat Mn(salen) complex.[4e] The band at 244 nm can be detected in the spectra of Jacobsen catalyst and both immobilised catalysts, and

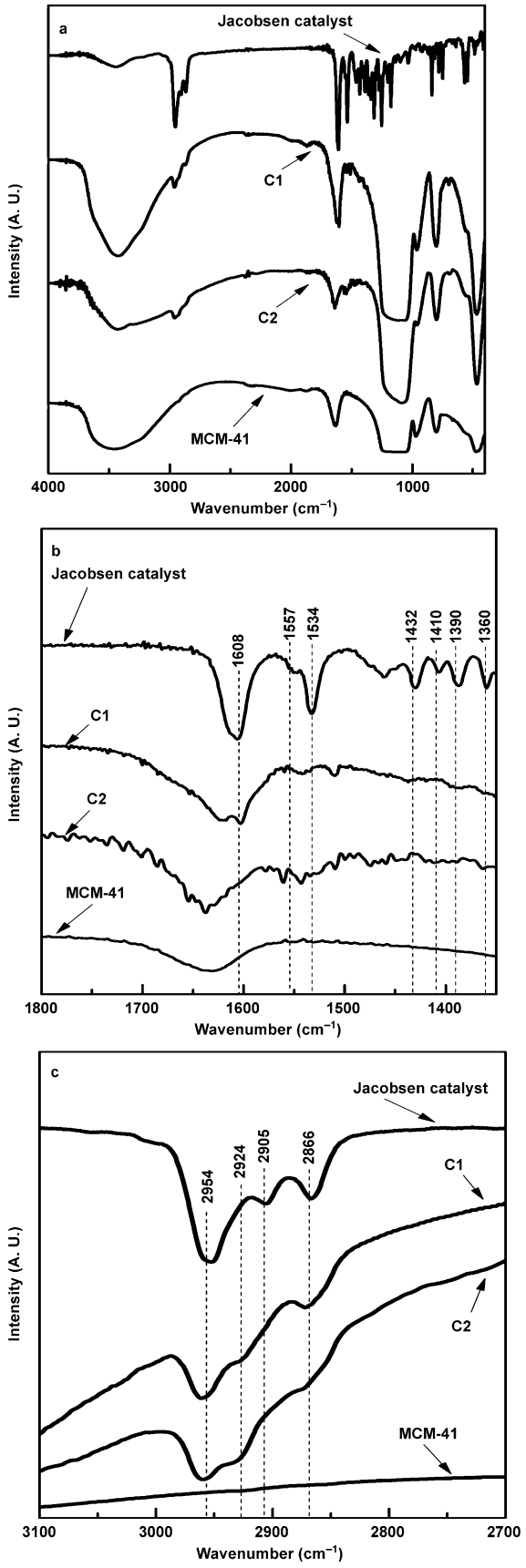


Figure 3. FTIR spectra of MCM-41 support material, Jacobsen catalyst and immobilised catalysts.

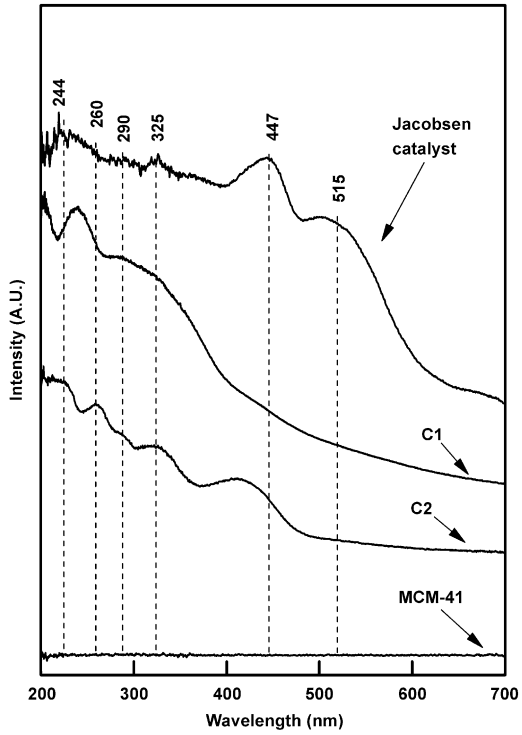


Figure 4. UV/Vis DRS spectra of MCM-41 support material, commercial Jacobsen catalyst and immobilised catalysts.

should be related to the C–N group of the Mn(salen) complex.[2g,4e,f,j]

As shown in the spectra of both immobilised catalysts, the bands centred at 244, 260, 290, 325, 447 and 515 nm can be identified with slight shifts compared with that for Jacobsen catalyst, reflecting the interaction between Mn(salen) complex and the MCM-41 support and thus the immobilisation of Mn(salen) complexes on MCM-41 support material. The minor difference between the spectra of the free Mn(salen) complex in commercial Jacobsen catalyst and the immobilised Mn(salen) complex comes from the effect of different immobilisation methods.[2g,4c,d,e,f,j] Similar shift of UV/Vis DRS bands can also be observed for the immobilised Mn(salen) catalysts on other support materials.[2g,4c,d,e,f]

It was found that the length of linkage can affect the catalytic behaviour of immobilised Mn(salen) catalysts.[2g] To maximally reduce the influence of differences in linkage length, two linkages (-$CH_2CH_2CH_2NH$- and -C_6H_4NH-) with similar length were used in this study. Calculations using Gaussian 09[9] on the models shown in Figure 5 were conducted to determine the length of these two linkages. The results indicate that the distances from the N atom to the Si atom of each model are 5.4 Å for -$CH_2CH_2CH_2NH$- and 6.1 Å for -C_6H_4NH-. This suggests that the effect of the length of these different linkages on the catalytic behaviour of immobilised Mn(salen) catalysts C1 and C2 should be minimal.

Figure 6 presents the catalytic behaviour of commercial Jacobsen catalyst and immobilised catalysts in the asymmetric epoxidation of *cis*-β-methylstyrene with NaClO as oxidant. Table 1 gives more details of the data presented in Figure 6.

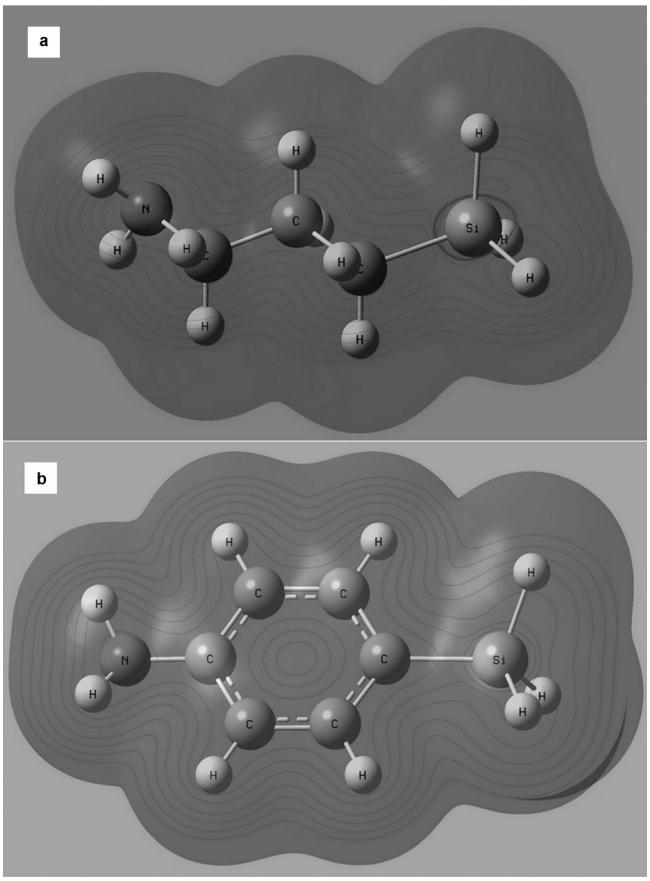


Figure 5. a) $H_3SiCH_2CH_2CH_2NH_2$ and b) $H_3Si\text{-}C_6H_4NH_2$ models optimised by using Gaussian 09.

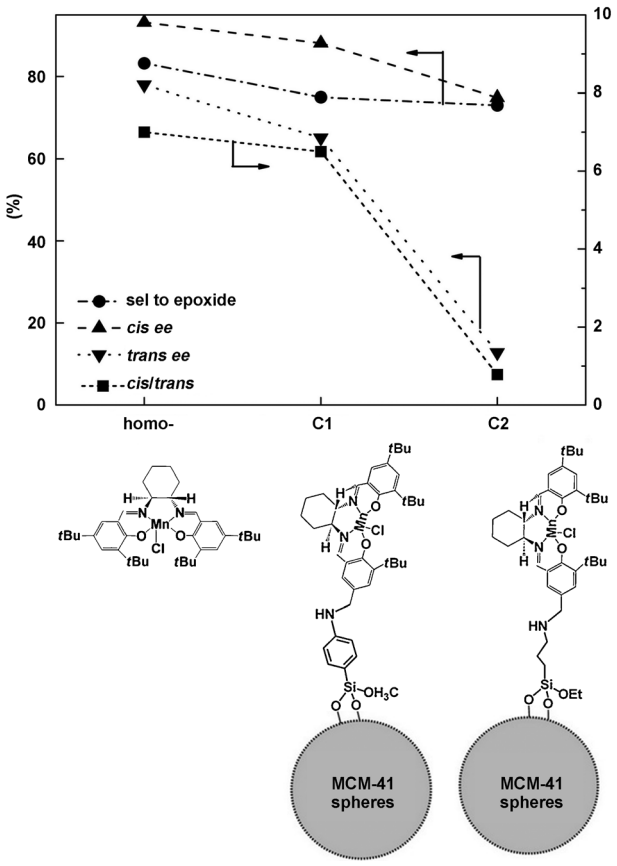


Figure 6. Heterogeneous asymmetric epoxidation of *cis*-β-methylstyrene catalysed by commercial Jacobsen catalyst, C1 and C2 catalysts. Sel to epoxide: the molecular proportion of all epoxides in the products. *cis ee*: the *ee* value for *cis* epoxides. *trans ee*: the *ee* value for *trans* epoxides. *cis*/*trans* ratio: (molecular proportion of *cis* epoxides in the products)/(molecular proportion of *trans* epoxides in the products). homo-: Jacobsen catalyst from Acros under homogeneous catalysis conditions.

Commercial Jacobsen catalyst presents almost the same conversion, *cis*/*trans* ratio and *ee* value with either *cis* or *trans* epoxides to those reported by Zhang, Lee and Jacobsen also with NaClO as oxidant.[10] Each immobilised Mn(salen) catalyst exhibits significantly lower conversion than homogeneous Jacobsen catalyst. This is a common phenomenon in heterogeneous asymmetric epoxidation due to the significantly lower Mn content in heterogeneous reactions compared with those in homogeneous reactions.[1b] Additionally, the diminished accessibility of the heterogeneous active sites to substrates also can result in lower conversion and facial TOF value in heterogeneous reactions than in homogeneous reactions.[2f,4] In the heterogeneous epoxidation of *cis*-β-methylstyrene, C1 catalyst with $\text{-}C_6H_4NH\text{-}$ linkage demonstrates higher epoxide selectivity, *ee* value of *cis*/*trans* epoxides and *cis*/*trans* ratio than those obtained with C2 catalyst with $\text{-}CH_2CH_2CH_2NH\text{-}$ linkage.

Similar trends for epoxide selectivity and for the *ee* value of *trans* epoxides can also be identified as shown in Figure 7 and Table 2, which demonstrate the catalytic performance of commercial Jacobsen catalyst and immobilised catalysts in the asymmetric epoxidation of *trans*-β-methylstyrene with NaClO as oxidant. In either homogeneous or heterogeneous reactions, only *trans* epoxides can be detected. This is consistent with the fact that only *trans* epoxides with relatively poor enantioselectivities can be obtained when *trans* olefins are used as substrates, according to side-on approach mechanism[11] and theoretical analysis.[12] Notably, C1 catalyst with $\text{-}C_6H_4NH\text{-}$ linkage also demonstrates higher chemical selectivity to epoxides and *ee* value of *trans* epoxides than C2 catalyst with $\text{-}CH_2CH_2CH_2NH\text{-}$ linkage.

Table 1. Asymmetric epoxidation of *cis*-β-methylstyrene catalysed by commercial Jacobsen catalyst and immobilised Mn(salen) catalysts.

Cat.	Mn [mg g^{-1}]	*t* [h]	Conv. [%]	Epoxide sel. [%]			*ee* [%]		Epoxide config.		Facial TOF [$\times 10^{-3}$ s^{-1}][d]
				total[a]	*trans*[b]	*cis*[b]	*trans*	*cis*	*trans*	*cis*	
homo[c]	–	6	99.8	83.2	12.5	87.5	78.0	93.2	1*S*,2*S*	1*R*,2*S*	3.4
C1	1.2	48	53.9	75.0	13.4	86.6	65.1	88.1	1*S*,2*S*	1*R*,2*S*	2.4
C2	0.9	48	32.4	73.0	56.1	43.9	12.8	74.9	1*S*,2*S*	1*R*,2*S*	1.8

[a] The molecular proportion of all epoxides in the products. [b] The molecular proportion of *cis* or *trans* epoxide in the sum of all epoxides. [c] Jacobsen catalyst from Acros. [d] Facial turnover frequency (TOF) was calculated by the expression [converted substrate]/([catalyst]×time) and according to the reaction data at 3 h.

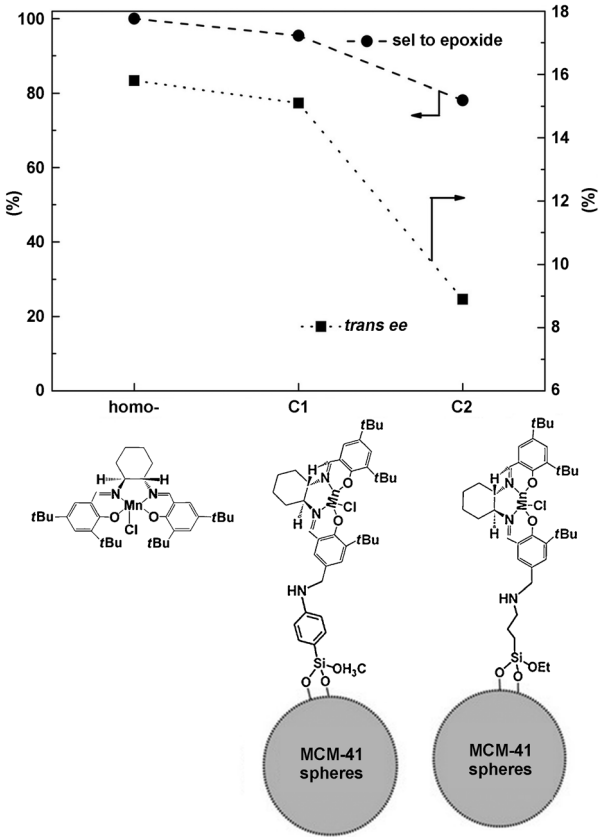


Figure 7. Heterogeneous asymmetric epoxidation of *trans*-β-methylstyrene catalysed by commercial Jacobsen catalyst, C1 and C2 catalysts. Sel to epoxide: the molecular proportion of all epoxides in the products. *trans ee*: the *ee* values for *trans* epoxides. homo-: Jacobsen catalyst from Acros under homogeneous catalysis conditions.

Table 2. Asymmetric epoxidation of *trans*-β-methylstyrene catalysed by commercial Jacobsen catalyst and immobilised Mn(salen) catalysts.

Cat.	Mn [mg g^{-1}]	*t* [h]	Conv. [%]	Epoxide sel. [%]			*ee* [%]		Epoxide config.		Facial TOF [$\times 10^{-3}$ s^{-1}][d]
				total[a]	*trans*[b]	*cis*[b]	*trans*	*cis*	*trans*	*cis*	
homo[c]	–	6	100	100	100	n.d.	15.8	n.d.	1*R*,2*R*	n.d.	3.4
C1	1.2	48	89.8	98.4	100	n.d.	15.1	n.d.	1*R*,2*R*	n.d.	2.4
C2	0.9	48	39.3	78.1	100	n.d.	8.9	n.d.	1*R*,2*R*	n.d.	1.8

[a] The molecular proportion of all epoxides in the products. [b] The molecular proportion of *cis* or *trans* epoxide in the sum of all epoxides. [c] Jacobsen catalyst from Acros. [d] Facial turnover frequency (TOF) was calculated by the expression [converted substrate]/([catalyst]×time) and according to the reaction data at 3 h. n.d. = not detected.

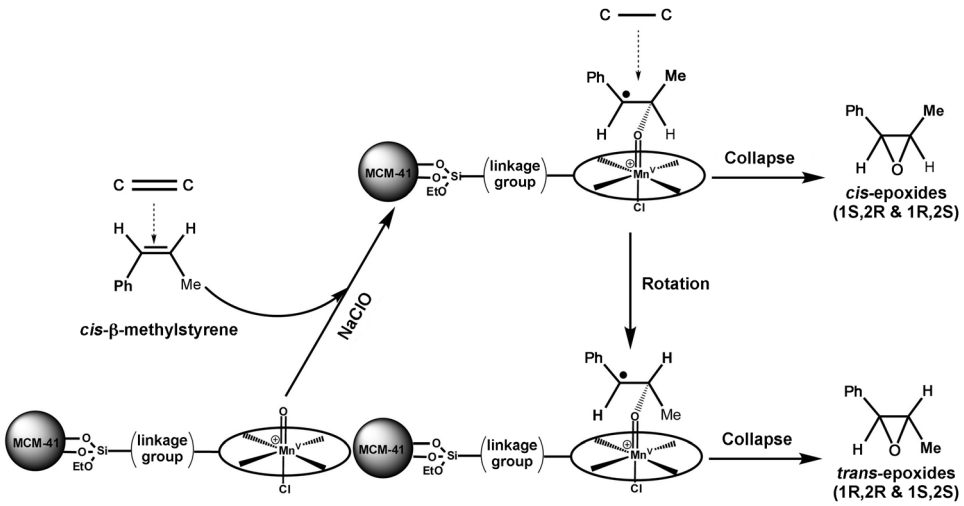
The results presented in Figure 6 and Figure 7, and in Table 1 and Table 2 support the conclusion that C1 catalyst with -C_6H_4NH- linkage can lead to higher chemical selectivity to epoxides, *cis*/*trans* ratio and *ee* value of *cis*/*trans* epoxides in the asymmetric epoxidation of *cis*/*trans*-β-methylstyrene than C2 catalyst with -$CH_2CH_2CH_2NH$- linkage. In other words, catalyst C1 demonstrates a catalytic performance much more comparable to that of homogeneous Jacobsen catalyst than catalyst C2.

Discussion

According to the average pore-size values calculated by the NLDFT method, the immobilisation of Mn(salen) complexes into the nanopores of MCM-41 support is possible. Its pore-size distribution (3.2–3.5 nm) is very close to the size of immobilised Mn(salen) complexes, suggesting that the confinement effect from nanopores on heterogeneous epoxidation could be strong because the nanopores of support materials can lead to remarkable confinement effects on the catalytic performance of immobilised Mn(salen) catalysts.[2f,g,4] Zhang et al. immobilised Mn(salen) into the nanopores of amorphous silica (average pore size 9.7 nm), SBA-15 (average pore size 7.6 nm) and MCM-41 (average pore size 2.7 nm) and found that the *ee* value increases with decreasing pore size.[4c] However, it should be noted that this tendency was observed in the 2.7–9.7 nm pore size range, which is much bigger than the pore size of the MCM-41 spheres used in the current work. In the pore size range of 1.7–3.1 nm, which is very similar to the pore size in the current work, Yu et al.[2g] and Lou et al.[4g] found larger pore size lead to higher activity and higher *ee* values. Nevertheless, these trends[2g,4c,g] can explain the different catalytic performance between homogeneous Jacobsen catalyst and the immobilised catalysts used in current study but cannot adequately explain the different catalytic performance between these two immobilised catalysts C1 and C2. In other words, the confinement effect inside the nanopores of MCM-41 spheres can affect the catalytic performance of these two immobilised catalysts and thus lead to their different catalytic performance from that for homogeneous Jacobsen catalyst, but some other possible factors affecting the heterogeneous asymmetric epoxidation of *cis*/*trans*-β-methylstyrene should be considered to explain the different catalytic performance between these immobilised catalysts themselves.

The linkage of phenylamine has greater steric hindrance in heterogeneous epoxidation than the linkage of propylamine, which may result in negative effect on the *ee* value and chemical selectivity to epoxides.[2h,4c,10] Smith et al. immobilised Mn(salen) complexes with the linkage connected to the 6-position in the salen ligand, which is far from the active Mn atoms, and then achieved a high *ee* value.[4k] In catalysts C1 and C2, the linkages are also connected to the 6-position in the salen ligand, which is likewise far from the Mn atoms, thus this is unlikely to result in the different chemical selectivity to epoxides, *cis*/*trans* ratio and *ee* value, as shown in Table 1 and Table 2.[13,14]

In the heterogeneous epoxidation of *cis*-β-methylstyrene, *cis* epoxides and *trans* epoxides result from the *cis* and *trans* route, respectively (as illustrated in Scheme 2).[4c,f,14,15] The nanopores inside which Mn(salen) complexes can be immobilised can benefit the rotation of the C–C bond in radical intermediates and thus result in a decrease in the *cis*/*trans* ratio.[4f] Smaller pore and longer channels, in which Mn(salen) complexes can be immobilised, have also been found to produce a lower *ee* value for *trans* epoxides, but show little apparent



Scheme 2. Illustration of the mechanism for the asymmetric epoxidation of *cis*-β-methylstyrene catalysed by immobilised Mn(salen) catalysts.

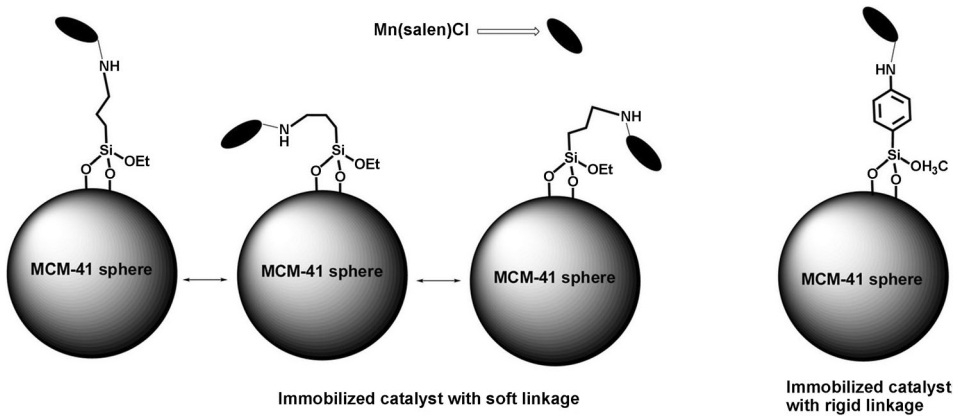
effect on the *ee* value for *cis* epoxides.[4f] However, in the current work, the trends of pore size[2g,4c,g] do not explain the different catalytic performance between two immobilised catalysts C1 and C2 as shown in Figure 1 and Figure 2, and Table 1 and Table 2. The confinement effect inside nanochannels would not be the only intrinsic driving force tuning the product distribution like that in Figure 6 and Figure 7. Considering the perfectly spherical morphology and regular particle size of this MCM-41 material, the effect of the morphology of support material on the epoxidation is also negligible. This can benefit an evaluation of the intrinsic driving force that determines product distribution in the heterogeneous epoxidation of *cis*/*trans*-β-methylstyrene catalysed by immobilised Mn(salen) catalysts.

Zhang et al.[4c] and Tu et al.[4j] obtained opposite results in their studies on the effect of linkage of immobilised Mn(salen) on heterogeneous epoxidation. A detailed analysis of their immobilisation strategies is very helpful for understanding the results of the current study. Zhang et al. immobilised Mn(salen) complexes using linkages (-CH_2-Ph-SO_3-, -CH_2CH_2-Ph-SO_3- and -$CH_2CH_2CH_2$-Ph-SO_3-) with different length.[4c] The linkage length was found to affect activity, the *ee* value and chemical selectivity to epoxides when the Mn(salen) complexes were immobilised in the nanopores of support material. However, the linkage length does not show any effect on the activity, *ee* value and chemical selectivity when the complexes were immobilised on the external surface of support material. In their immobilisation strategy, Mn(salen) complexes were connected to the rigid part (-Ph-SO_3-) of linkages, with the flexible ends (-CH_2-, -CH_2CH_2- and -$CH_2CH_2CH_2$-) of those linkages being anchored to support surface. Thus, in the restricted space inside the nanopores, the difference in the space between the immobilised Mn(salen) complexes and the bending surface of nanopores is not negligible due to different linkage length, and thus these immobilised Mn(salen) catalysts with different linkage length inside nanochannels can exhibit different catalytic performance.

In contrast, in the open space on the external surface of support material, the difference in the space between the immobilised Mn(salen) complexes and the support surface is minimised due to the swaying of the flexible chains of linkages, and thus these immobilised Mn(salen) catalysts on the outer surface of support material exhibit similar catalytic performance with significantly lower *ee* values resulting from the more mobile Mn(salen) complexes. It should be noticed that the heterogeneous activity, chemical selectivity and *ee* value in heterogeneous epoxidation are all lower than those in homogeneous systems,[4c] reflecting the fact that the heterogeneity arising from the support surface can have a negative effect on catalytic performance in some cases.

An opposite immobilisation strategy was taken by Tu et al.[4j] They immobilised Mn(salen) complexes with different linkages (-Ph-CH_2-, -Ph-CH_2OCH_2- and -Ph-$CH_2OCH_2CH_2$-), which also contained a rigid end and flexible chains with different length. In contrast to the immobilisation strategy taken by Zhang et al,[4c] Tu et al. used the rigid end (phenyl) of each linkage as the tethering group anchoring to the support surface and three chains with different length (-CH_2-, -CH_2OCH_2- and -$CH_2OCH_2CH_2$-) as bridges to connect the Mn(salen) complexes to the phenyl anchor. The rigid phenyl group used to connect Mn(salen) complexes to the support surface was found to be very helpful for achieving high activity and high *ee* values. The rigid phenyl group guarantees that the combination of Mn(salen) complex and bridge is a defined distance from the support surface. Under these conditions, Tu et al. found that the linkage length does not apparently affect the catalytic performance, and all immobilised Mn(salen) catalysts gave similar *ee* values, which varied in a narrow range from 78 to 84%, in the heterogeneous epoxidation of α-methylstyrene.[4j] The studies on linkage length reported by Zhang et al.[4c] and Tu et al.[4j] provide a valuable clue to help understand the different catalytic performance between C1 and C2 in the current study.

The two linkages employed in the current study, -$CH_2CH_2CH_2NH$- and -C_6H_4NH-, present similar chain length but remarkably different rigidity. The rigid phenyl group plays a similar role to that in the study of Tu et al.[4j] As illustrated in Scheme 3, the Mn(salen) complexes immobilised with the -$CH_2CH_2CH_2NH$- linkage can sway on the support surface due to the flexible sp^3 C–C bonds of the chain. Under these circumstances, the flexible linkage in the C2 catalyst could remarkably enhance the tendency of the neighbour Mn(salen) complexes to form μ-oxo-Mn^{IV} dimers, which are inactive and will prevent the catalytic cycle continuing.[2a] Furthermore, the flexible link-



Scheme 3. Illustration of the different rigidity of the linkage groups (-$CH_2CH_2CH_2NH$- and -C_6H_4NH-) in the immobilised Mn(salen) catalysts.

age makes the immobilised Mn(salen) complexes sway on the surface and thus the substrates cannot perfectively approach the catalyst according to either a "side-on" or a "top-on" approach,[11,14,15] which are the most accepted mechanisms leading to high *ee* values. A flexible linkage can result in random space between swaying Mn(salen) complexes and the support surface as well as low chemical selectivity to epoxides, inverted *cis*/*trans* ratio and low *ee* values in the heterogeneous epoxidation reaction. This can imply that the random space between swaying Mn(salen) complexes and the support surface may lead to an unpredictable negative effect on the catalytic performance and then to low chemical selectivity to epoxides, inverted *cis*/*trans* ratio and low *ee* values in the heterogeneous epoxidation reaction. Such an "unpredictable negative effect" will be apparent not only for immobilisation inside nanopores but also for immobilisation on the external surface of the support.

In contrast, immobilised Mn(salen) complexes with -C_6H_4NH- linkage cannot sway because of the rigid framework of the phenyl group. This catalyst can provide a more homogeneous-like environment, being similar to that in homogeneous epoxidation catalysed by Jacobsen catalyst, allowing the achievement of higher selectivity to epoxides, higher *ee* values of either *cis* or *trans* epoxides and enhanced production of *cis* epoxides.

The usual starting point for the design of immobilised catalysts is typically a homogeneous catalyst that gives high enantioselectivity. Homogeneous Mn(salen) complexes display a broad substrate scope but some olefins still fail to be converted with a high *ee* value. Some reports declared that, for those homogeneous Mn(salen) catalysts that exhibit high *ee* values in homogeneous asymmetric epoxidation of specific substrates, their corresponding immobilised catalysts can show comparable *ee* values in heterogeneous asymmetric epoxidation of the same substrates.[4c,d,e,h]

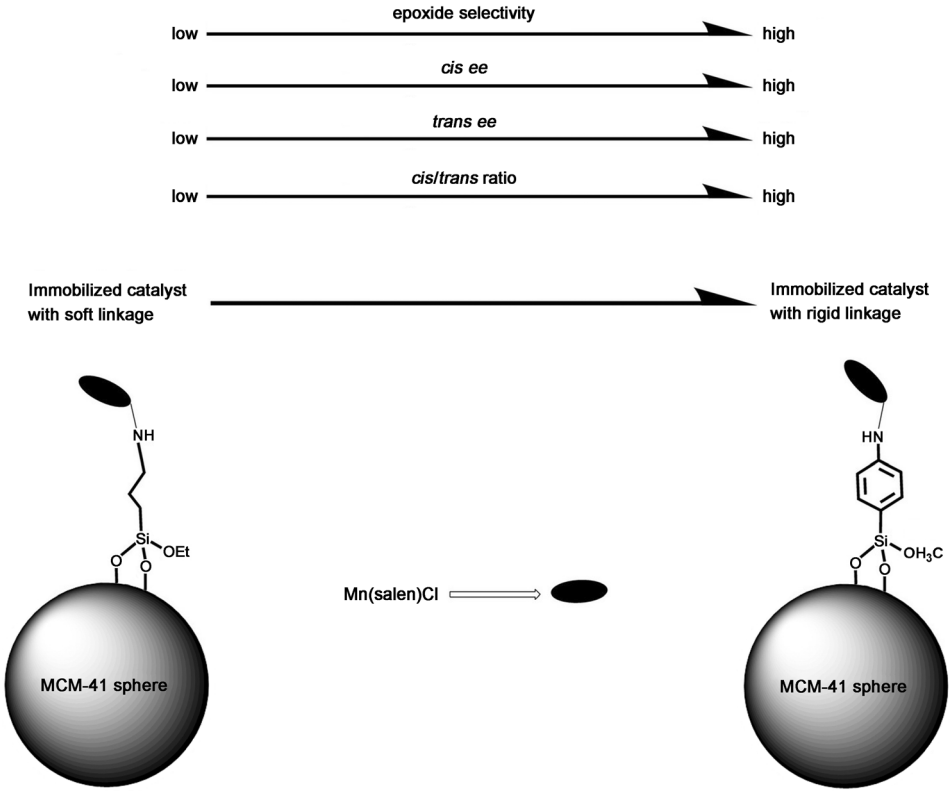
The immobilised Mn(salen) complexes of C1 and C2 catalysts contain exactly the same structure as that of commercial Jacobsen catalyst, which is highly active and enantioselective in the homogeneous epoxidation of *cis*/*trans*-β-methylstyrene. The different catalytic performance of C1 and C2 catalysts can be explained by their different linkage rigidity. This suggests that, in the heterogenisation of those highly enantioselective homogeneous catalysts, a rigid linkage is very helpful for achieving activity and enantioselectivity as high as that of the homogeneous catalyst. According to the pore size of the MCM-41 support material, Mn(salen) complex can be immobilised either into nanopores or on the external surface of these MCM-41 spheres. The balance between pore-bound and externally bound Mn-salen may be different for the two types of tether. However, one very important consideration is that the different locations of the immobilised Mn(salen) complexes cannot lead to the different heterogeneous catalytic performances between these immobilised catalysts themselves.

Nevertheless, for some other Mn(salen) catalysts exhibiting poor *ee* values in the homogeneous asymmetric epoxidation of certain substrates, some reports claimed that the corresponding immobilised catalysts can give higher *ee* values than their homogeneous counterparts due to confinement effect resulting from nanopores.[4a,a,d,e] For the immobilisation of those homogeneous catalysts, which are mostly nonselective in homogeneous reactions with certain substrates, the confinement effect arising from interaction with nanopores presents a major opportunity to design more effective asymmetric heterogeneous catalysts than their homogeneous counterparts.

Conclusion

In this study, Mn(salen) complex has been immobilised by using a MCM-41 support material with spherical morphology and uniform particle size. The linkages employed to anchor the Mn(salen) complex have similar length but different rigidity. In the heterogeneous asymmetric epoxidation of *cis*/*trans*-β-methylstyrene catalysed by these immobilised Mn(salen) catalysts with NaClO as oxidant, the effect of linkage rigidity and a confinement effect arising from the interaction with nanopores, on the catalytic performance of immobilised Mn(salen) catalysts were discussed in detail. The immobilised Mn(salen) complexes inside nanopores can lead to different catalytic performance from that of homogeneous Jacobsen catalyst but the confinement effect in nanopores cannot explain the differences in catalytic performance between the immobilised Mn(salen) catalysts themselves.

As illustrated in Scheme 4, it was found that linkages with different rigidity can greatly affect the final product distribution. The flexible linkage (-$CH_2CH_2CH_2NH$-) results in lower *ee* values and activity along with inverted *cis*/*trans* ratio compared with the catalyst complex attached through a rigid linker. The rigid linkage (-C_6H_4NH-) leads to chemical selectivity,



Scheme 4. Illustration of the effect of linkage rigidity of immobilised Mn(salen) catalyst on heterogeneous asymmetric epoxidation.

ee values and a *cis*/*trans* ratio that is comparable to that obtained in the homogeneous epoxidation catalysed by homogeneous Jacobsen catalysts. The reason seems to be that the rigid linkage forces the immobilised Mn(salen) complexes be sited a certain distance from the support matrix and, thus, the heterogeneous epoxidation takes place in a homogeneous-like environment. In contrast, the flexible linkage results in inevitable swaying of the immobilised Mn(salen) complexes on the support matrix.

This study suggests that the use of a rigid linkage to connect Mn(salen) complexes to the support matrix could be essential to obtain highly active and enantioselective immobilised catalysts, which can demonstrate activity and enantioselectivity as high as homogeneous level. Nevertheless, for some other homogeneous Mn(salen) complexes, which are mostly nonselective in homogeneous reactions with some substrates, the confinement effect arising through interaction with the nanochannels of support materials should present a possibility to design immobilised catalysts that are even more effective than their homogeneous counterparts.

Experimental Section

The chemical materials used in this study are described in Supporting Information.

Characterisation, methods and theoretical calculation models

SEM images were obtained with a FEI QUANTA 200F instrument, and TEM images were obtained with a FEI Tecnai 20 Twin instrument. The N_2 adsorption–desorption tests were performed at 77 K with a Tristar 3000 instrument. Samples were degassed at 300 °C for 4 h prior to measurements. The average pore size was calculated according to the NLDFT method. SXRD patterns were recorded with a Bruker D8 Advance powder diffractometer with Cu-K radiation ($\lambda = 1.54184$). Fourier transform infrared spectroscopy (FTIR) spectra were recorded with a Shimadzu IR Prestige-21 spectrometer with a DTGS detector, using KBr pellet method and a resolution of 4 cm^{-1}. UV/Vis DRS spectra were recorded with a Shimadzu UV-2550 instrument. The Mn content of immobilised catalysts were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES) with a Varian Vista spectrometer and used to calculate TOF values. ^{1}H NMR spectra were recorded with a Bruker Mercury 400 instrument (400 MHz, $CDCl_3$, 25 °C).

$H_3SiCH_2CH_2CH_2NH_2$ and $H_3SiC_6H_4NH_2$ models (as shown in Figure 5) were optimised on the B3LYP/6–31g(d,p) level by using Gaussian 09.[9] The distance between the Si atom and the N atom of each model was determined according to the optimised models.

Preparation of 3-*tert*-butyl-5-(chloromethyl)-2-hydroxybenzaldehyde (TBCMHB)

The synthesis of TBCMHB was carried out according to the procedure reported by Minutolo.[16] 3-*tert*-Butyl-2-hydroxybenzaldehyde (30.0 g) and paraformaldehyde (11.16 g) were added to concentrated HCl (112.2 mL). The mixture was stirred at 25 °C for 48 h and then repeatedly extracted with diethyl ether. The organic layer was repeatedly washed with saturated aqueous $NaHCO_3$ and brine, and then dried over Mg_2SO_4. A yellow crystalline solid was obtained after evaporation of the solvent in vacuum, and recrystallization with the aid of liquid nitrogen. ^{1}H NMR spectra were recorded with a Bruker Mercury 400 instrument at 25 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 1.43$ (s, 9H), 4.58 (s, 2H), 7.42 (d, $J = 2.4$ Hz, 1H), 7.52 (d, $J = 2.4$ Hz, 1H), 9.87 (s, 1H), 11.86 ppm (s, 1H); FTIR (KBr): 2967, 2910, 2862, 1650, 1611, 1436, 1268, 1235, 1209, 1162, 979, 772, 697 cm^{-1}.

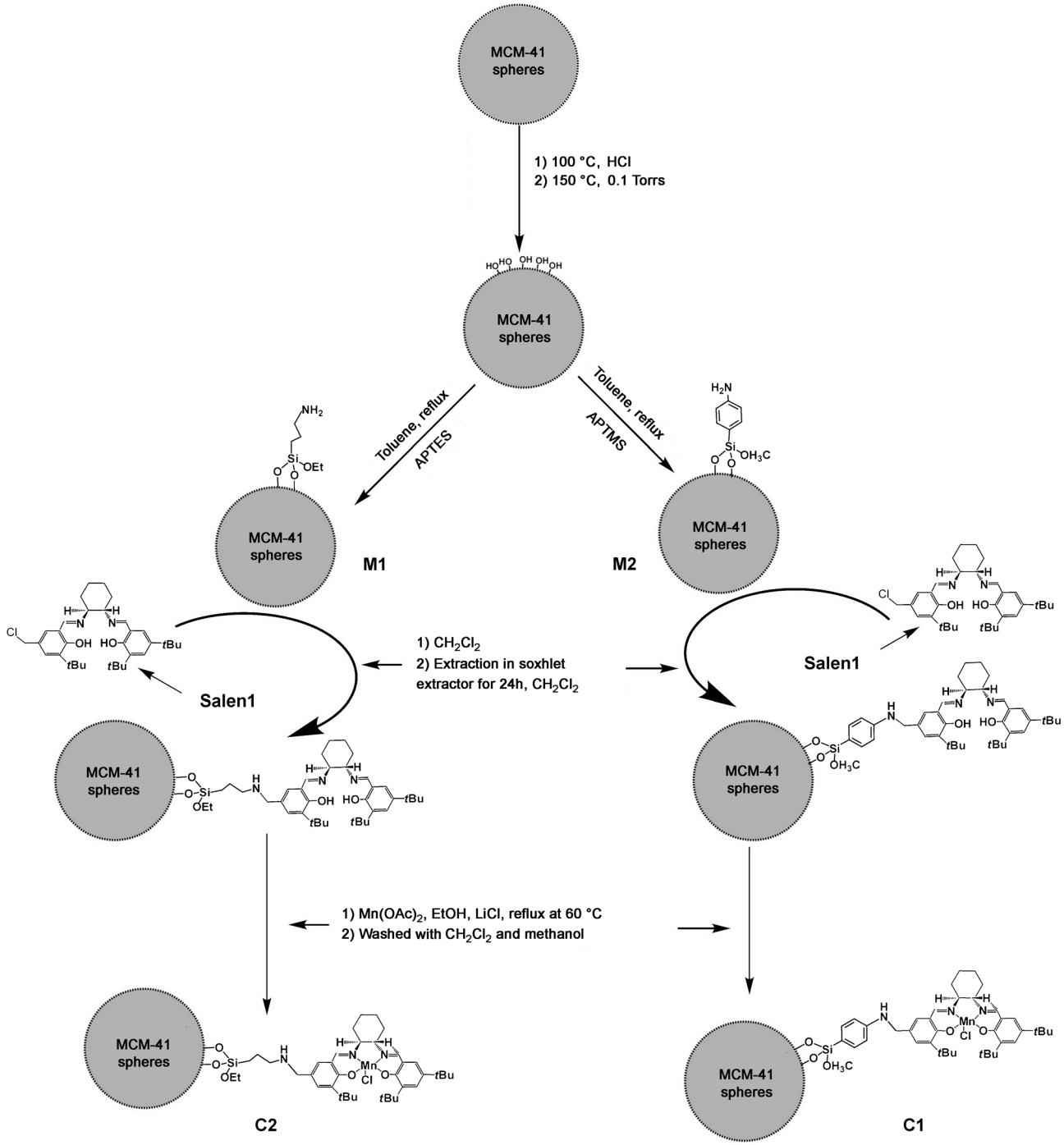
Preparation of MCM-41 spheres

To prepare the MCM-41 support, cetyltrimethyl ammonium bromide ($C_{19}H_{42}BrN$; 30.0 g) was dissolved in deionized H_2O (600 g), and aqueous ammonia (15.8 g) followed by absolute ethanol (60.0 g) were added. The solution was then stirred for 15 min at 25 °C, and TEOS (56.4 g) was added into the solution in one por-

tion. The resulting mixture was stirred at 25 °C for 2 h and then filtered to obtain a white precipitate. This precipitate was washed with a mixture of H_2O and ethanol and then dried at RT for 72 h to obtain a white power. This powder was calcined at 550 °C for 4 h in a Muffle furnace (ramping rate 5 °C min^{-1} from RT to 550 °C) with a supply of air to obtain MCM-41 material.

Preparation of immobilised Mn(salen) catalysts

The preparation of immobilised Mn(salen) catalysts is illustrated in Scheme 5. In a typical synthesis of MCM-41 material modified with 3-aminopropyl-triethoxysilane (APTES)/4-aminophenyl-trimethoxysilane(APTMS), MCM-41 (2.0 g) was treated with HCl (2 M, 200 mL) at 100 °C for 4 h. The MCM-41 material was then filtered and washed with copious amounts of water until the water became neutral, and dried overnight at 40 °C in vacuum. The dried MCM-41 material was dehydrated at 150 °C at 0.1 Torr for 4 h followed by the addition of anhydrous toluene (50 mL) and APTES (6.9 mL) or APTMS (5.9 mL). The mixture was heated to reflux at 110 °C under argon for 18 h and then filtered. The solid product was washed successively with toluene, acetone and methanol. The



Scheme 5. Preparation of immobilised Mn(salen) catalysts.

washed solid product was then dried at RT in vacuum for 4 h to obtain the APTES-modified MCM-41 materials denoted as M1 or the APTMS-modified MCM-41 material denoted as M2.

Preparation of immobilised catalysts C1 and C2

TBCMHB (0.2127 g), 3,5-di-*tert*-butyl-2-hydroxy benzaldehyde (0.7030 g) and (1*R*,2*R*)-(−)-1,2-diaminocyclohexane (0.2284 g) were added to CH_2Cl_2 (10 mL) [TBCMHB: (1*R*,2*R*)-(−)-1,2-diaminocyclohexane/3,5-di-*tert*-butyl-2-hydroxy benzaldehyde = 1:2:3]. The mixture was stirred at 25 °C for 48 h to achieve Salen1.[17] Then either M1 or M2 (2.0 g) was added to the mixture with CH_2Cl_2 (20 mL) and stirring was continued at 25 °C for 18 h. The solid product was filtered and extracted by CH_2Cl_2 in a Soxhlet extractor for 24 h.[4f,17] The immobilisation of Mn(salen) complexes was then accomplished by heating to reflux an ethanolic solution of $Mn(OAc)_4H_2O$ (0.3637 g) at 90 °C for 1 h, followed, after the addition of LiCl (0.09538 g) by 30 min heating at 90 °C . The solid products were washed with CH_2Cl_2 and methanol to obtain light-brown catalysts denoted as C1 or C2.

Asymmetric epoxidation reaction tests

The NaClO solution (pH 11.3) for epoxidation tests was prepared according to the procedure reported by Jacobsen et al.[14] The heterogeneous epoxidation reaction tests were conducted according to the procedure described elsewhere.[4f] In a typical run, a reaction mixture of *cis*/*trans*-β-methylstyrene (0.118 g), 4-phenylpyridine *N*-oxide (PPNO; 0.0175 g), *n*-decane (60 μL), CH_2Cl_2 (5 mL) and Jacobsen catalyst (0.0125 g) for homogeneous runs or immobilised Mn(salen) catalysts (0.2 g) for heterogeneous runs were mixed at 20 °C. Then 0.55 M NaClO[14] (5.5 mL) was added and the reaction mixture was stirred at 20 °C until the conversion of *cis*/*trans*-β-methylstyrene became stable.

The progress of the reaction was monitored with a Shimadzu GC 2010 gas chromatograph equipped with a FID detector and Lipodex E capillary column. In all epoxidation reaction tests and calibration runs, the conversions of *cis*/*trans*-β-methylstyrene, chemical selectivities of the epoxides and the *ee* values of both *cis* and *trans* epoxides were calculated according the FID signals obtained by using an internal standard method with *n*-decane as internal standard. In the calibration runs, (1*S*,2*S*)-*trans*-β-methylstyrene oxide, (1*R*,2*R*)-*trans*-β-methylstyrene oxide and racemic *cis*-β-methylstyrene oxides were used to set up calibration curves. The racemic *cis*-β-methylstyrene oxides (1*S*,2*R* and 1*R*,2*S*) used to established the calibration curves were prepared by epoxidation of *cis*-β-methylstyrene (1 equiv.) with *m*-chloroperoxybenzoic acid (*m*-CPBA; 1.1 equiv.) in CH_2Cl_2 at 0 °C for 24 h.[18] An Angilent 5975C GC-MS instrument was employed to analyse the products of asymmetric epoxidation and the results indicated that the by-product was mainly benzaldehyde. The control runs with mixtures of *cis*/*trans*-methylstyrene, MCM-41 support, CH_2Cl_2, *n*-decane and 0.55 M NaClO confirmed that the physical adsorption of *cis*/*trans*-β-methylstyrene by MCM-41 material is negligible.

Acknowledgements

The authors are grateful to the National Natural Science Foundation of China (U1362105, 20890124), the Chongqing Science Research Project (KJ130729, KJ130702), the Chongqing Science and Technology Foundation (cstc2013jcyjA50007, jcsf121–2012–02–1), Chongqing 100 leading scientists promotion project and the Fundamental Research Funds for the Central University. The authors appreciate valuable discussions with Dr. S. Xiang and Dr. K. J. Sun. Professor Wang also thanks the Program for New Century Excellent Talents in University (NCET-11–0145), Ministry of Education of China.

Keywords: asymmetric catalysis · epoxidation · heterogeneous catalysis · immobilization · supported catalysis · surface chemistry

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Received: February 12, 2014
Revised: March 25, 2014
Published online on ■■ ■■, 0000

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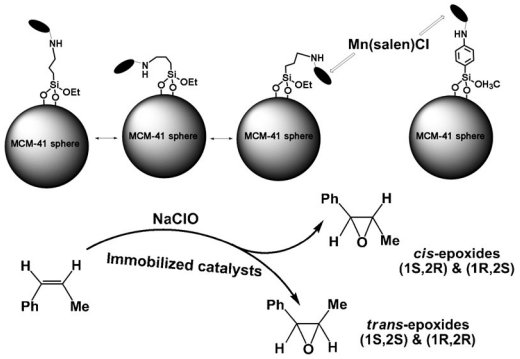

Getting it fixed: For immobilised Mn(salen) catalysts, a rigid linkage connecting active centres to a support surface is essential to obtain activity and enantioselectivity as high as those obtained in homogeneous systems (see scheme).

Heterogeneous Catalysis

H. Zhang, Y. Zou, Y.-M. Wang,* Y. Shen, X. Zheng*

■■ – ■■

Asymmetric Epoxidation of *cis*/*trans*-β-Methylstyrene Catalysed by Immobilised Mn(Salen) with Different Linkages: Heterogenisation of Homogeneous Asymmetric Catalysis