Epoxidation of olefins catalyzed by Mn(II) salen complex anchored on PAMAM–SiO$_2$ dendrimer

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New dendritic catalysts have been prepared by the immobilization of a Mn(II) salen complex on a polyamidoamine dendrimer propagated on the surface of silica. These have been applied in the catalytic epoxidation of olefins. Although the increase of the amount of Mn loading is found to be limited on high-generation dendrimers, the Mn(II) salen complex anchored on the fourth-generation dendrimer shows much higher catalytic activity toward the epoxidation of styrene than that anchored on lower generations. These results suggest that the length of the dendritic backbone chain plays an important role in increasing the accessibility between the catalytic active sites of the immobilized Mn(II) salen complex and the reactant molecules, resulting in the enhancement of the catalytic activity of the Mn(II) salen complex anchored on the fourth-generation dendrimer.

KEY WORDS: anchored; immobilization; Mn(II) salen; dendrimer; olefin epoxidation; dendritic catalyst.

1. Introduction

Since epoxides are versatile building blocks in organic syntheses [1,2], significant attention has been given to developing efficient catalysts for epoxidation of olefins. In 1986, Srinivasan *et al.* [3] first reported that cationic manganese complexes of the salen ligand were effective catalysts for the epoxidation of various olefins. Katsuki [4] gave an extensive review of 10 years of development of the enantiomeric epoxidation with active (salen) manganese complexes. Subsequently, the immobilization of transition metal complexes on various solid supports, such as zeolite [5], MCM-41 [6–11], silica gel [12] and polymers [13], has been reported. Immobilization of catalysts on solid supports allows easy separation from the reaction mixture by simple filtration and thus greatly facilitates the handling of such catalysts. Unfortunately, heterogeneous catalysts prepared in this way are often less active than their homogeneous counterparts due to the fact that diffusion of substrates and products to and from the catalytic centers on the support is hindered [14].

In recent years, major efforts have been directed toward the development of new catalytic systems that effectively combine the advantages of both heterogeneous and homogeneous catalysis [15]. Such a catalyst would ideally be easily recoverable and potentially recyclable while maintaining high catalytic efficiency. Dendrimers are highly branched macromolecules and are of great interest as carriers of functional groups [16,17]. Consequently, dendritic catalysts have found numerous applications including metal complexation and occasional use as catalysts [18,19]. A variation on the catalyst support approach is to use a dendrimer grafted on silica that can be easily precipitated out of the reaction solution [20,21]. Recently, several groups have reported the applications of polyamidoamine (PAMAM) dendritic catalysts anchored on silica for hydroformylation [15,22] and addition of diethylzinc to benzaldehyde [23].

Although many functional ligands and some metal complexes immobilized on dendrimers have been studied [15–19,22,23], the influences of the generation number of dendrimer on the grafting of metal complexes as well as on the catalytic performance have been seldom reported [22]. This paper reports the synthesis of the PAMAM dendrimer anchored on ultrafine silica and the immobilization of a Mn(II) salen complex onto the periphery of lower- and higher-generation PAMAM–SiO$_2$ dendrimers for the preparation of dendritic catalysts for olefin epoxidation. The objective of our study is to experimentally investigate the effect of the generation number of the dendrimer on the amount of manganese loading and the catalytic activity of the resulting immobilized Mn(II) salen dendritic catalysts.

2. Experimental

2.1. *Preparation of PAMAM–SiO$_2$ dendrimer*

Dendrimer building methods pioneered by Tsubokawa and co-workers [21] were employed to propagate

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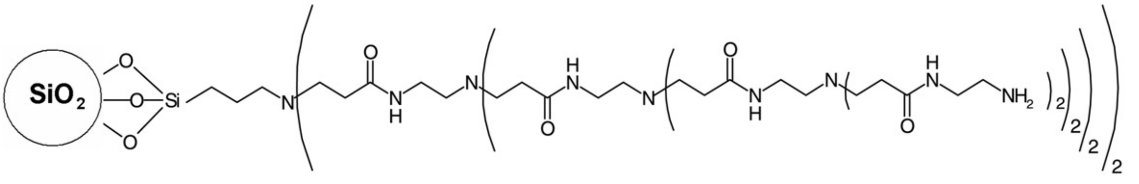


Scheme 1. Proposed structure of PAMAM–SiO_2 dendrimer for the fourth generation (G4).

the dendrimer generation. Polyaminoamido dendrimers, up to the fourth generation (G4), were constructed on the surface of ultrafine silica (Aerosil 200) particles (16 nm). The introduction of amino groups onto the silica surface for the preparation of an "initiator site" (G0) was achieved by the treatment of surface silanol groups with 3-aminopropyltriethoxysilane (APES). To minimize the effect of steric hindrance during the propagation of dendrimer on silica, the suggestions proposed by other research groups [21,23] were used in this study to prepare the dendrimer with low initiator sites by introducing 0.4 mmol/g of amino group onto the silica surface.

A Michael-type addition of the pre-existing amino group to methyl acrylate (MA) formed the amino propionate ester (G0.5). Subsequent amidation of the ester moieties with ethylenediamine (EDA) completed the first generation (G1). A repetition of Michael addition and the amidation reactions then produced the desired generation of the dendrimer. Vacuum filtration, extraction using a Soxhlet apparatus and drying *in vacuo* were used to remove excess reagents for the purification of the dendrimer product. The amino group contents introduced onto the surface of silica and the periphery of each generation of dendrimer were determined by titration with HCl aqueous solution [24]. The proposed structure of the resulting fourth-generation dendrimer grafted on SiO_2 is shown in scheme 1.

2.2. Anchored complexes

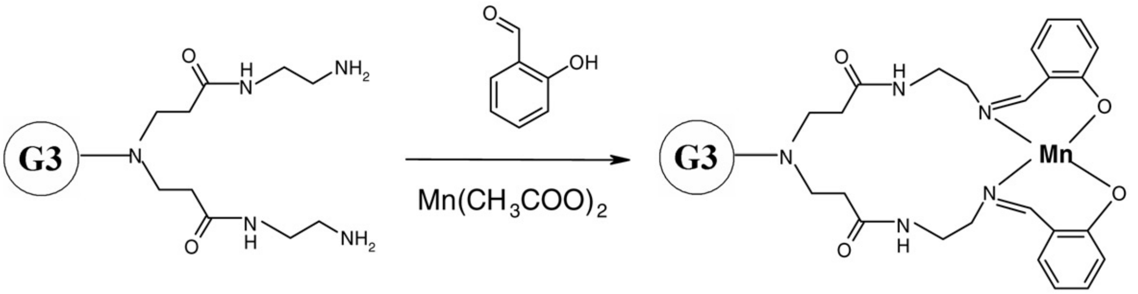
Following a procedure adopted for the preparation of MCM-41-supported Mn(II) salen complex [11], 1 g of the prepared G*n* ($n = 0, 1, 2, 3, 4$) dendrimer was refluxed with 6 mmol of salicylaldehyde in 20 ml of ethanol for 8 h to give a Schiff base. The anchored Mn(II) salen dendrimer was prepared by reacting the Schiff base anchored on solid dendrimer with $Mn(OAc)_2 \cdot 4H_2O$ in ethanol under N_2 protection for 30 min. The complexes were subjected to Soxhlet extraction in ethanol for about 8 h. Scheme 2 shows schematically the immobilization of Mn(II) salen onto the PAMAM–SiO_2 dendrimer. Based on this synthesis method, five anchored catalysts, named here as Mn-G*n* ($n = 0, 1, 2, 3, 4$), were synthesized.

2.3. Characterization

The metal (Mn) content analysis was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES). UV–vis spectra were recorded using a Varian CARY 3E double-beam spectrometer. The amount of dendrimer grafted onto the silica surface was determined by heating the dendrimer-grafted silica from room temperature to 600 °C and the weight loss [21] was measured using a thermogravimetric analyzer (Perkin-Elmer TGA-7). FTIR spectra were measured using a Nicolet Impact 410 FTIR instrument, whereby powder containing 2 wt% of sample in KBr was pressed to a wafer.

2.4. Epoxidation of olefins

The activity of the prepared dendritic catalysts was tested for the epoxidation reaction of styrene and cyclic olefins with MCPBA-NMO in CH_2Cl_2 at 0 °C [11]. All the reactions were performed in the presence of 0.01 mmol of the Mn catalysts. The sample was analyzed by a gas chromatograph (HP 5890 Series II) equipped with an FID and an HP-5 capillary column.



Scheme 2. Immobilization of Mn(II) salen onto PAMAM–SiO_2 dendrimer.

3. Results and discussion

3.1. Characterization of dendrimer and catalyst

Table 1 shows the amino group content of the *n*th generation of dendrimer after the grafting reaction. The result shows that the initiator sites containing 0.4 mmol/g of amino group on the silica support have been successfully prepared and the amount of amino groups on the silica support increased with increasing number of generations. Table 1 also gives the percentage of the dendritic polymer grafted onto the silica surface at every generation, whereby the percentage of grafting increased with increasing number of generations. However, table 1 shows that the propagation of dendrimer on the silica surface at higher generations is not as high as the theoretical value; this may be due to the incomplete propagation caused by the steric crowding [21,22].

Figure 1 presents the FTIR spectra of dendrimer grafted on the silica surface at each step. In the IR spectrum of APES-treated silica (G0), a new band at ~1640 cm^{-1}, which is characteristic of the amino group ($-NH_2$), is observed. The presence of this new band suggests that amino groups have been successfully introduced onto the silica surface. The IR spectrum of sample G0.5, which was obtained by Michael addition with the amine group of G0, exhibits a new band at ~1730 cm^{-1}; this new band is attributed to the formation of ester (–COOR) as all IR spectra of samples G*n*.5 ($n = 0, 1, 2, 3$), which were obtained by Michael addition, show this ester band.

As mentioned in section 2, in a process called amidation, EDA could react with the ester group on G0.5, producing combined branches of amides (–CONH–) and amino groups to form sample G1. The two new IR bands at 1655 and 1550 cm^{-1} observed for G1 are characteristic of these amide groups. Each subsequent step of amidation results in the increase of the intensity of the amide IR band and the disappearance of the ester group on samples G*n* ($n = 2, 3, 4$). At the same time, as the dendrimer grows, the amount of amino groups on the terminal ends of the dendrimers increases with increasing number of generations. This result is summarized in table 1. It is worth noting that a small ester band at 1730 cm^{-1} also appeared for G1 and G2, indicating the incomplete amidation with EDA [21]. The proposed structure of the resulting PAMAM–SiO_2 dendrimer is shown in scheme 1.

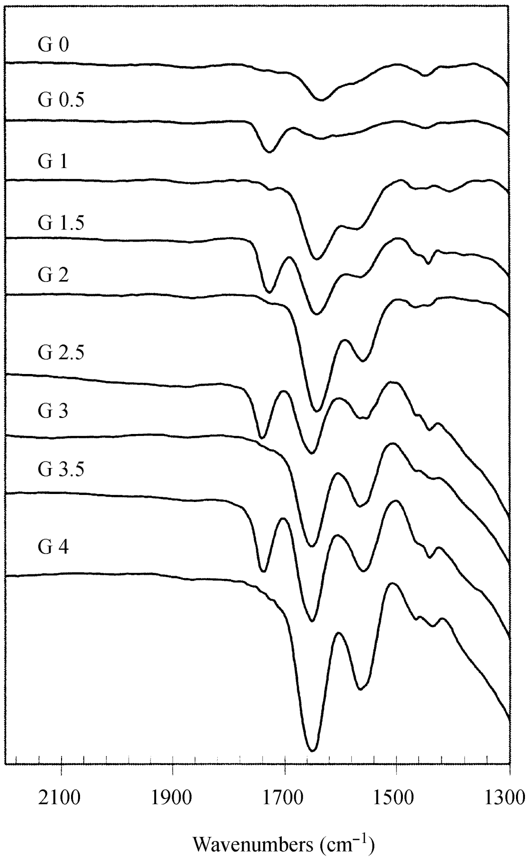


Figure 1. IR spectra characterizing the silica-grafted dendrimers of increasing generation number from G0 to G4.

As shown in table 1, the mole ratios of Mn/SiO_2 for each catalyst are in the range 0.3–1.3%, which corresponds to 0.05–0.15 mmol Mn/g loading on the dendrimers. The UV–vis spectra of samples Mn-G0 to Mn-G4 show bands at 240, 280, 320 and 390 nm; these bands are slightly different from the absorption spectra of the corresponding pure Mn(II) salen complex whose bands appear at 236, 280, 309 and 416 nm [11]. This result suggests a slight distortion of the Mn(II) complex immobilized on the surface (scheme 2).

3.2. Catalytic reaction

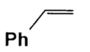
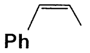
All the dendritic catalysts prepared were employed in the epoxidation of unfunctionalized olefins and the results are reported in table 2. In each reaction, the same amount of Mn was used and the reaction was carried out under identical conditions. The Mn-G4

Table 1
Characterization of dendrimer and dendritic catalyst

Generation	Amino group content (mmol/g SiO_2)		Grafting [b] (wt%)	Mn/SiO_2 [c] (mol%)
	Theoretical	Observed [a]		
0	0.4	0.4	3.2	0.33
1	0.8	0.58	9.9	0.61
2	1.6	0.88	19.9	0.95
3	3.2	1.43	36.4	1.2
4	6.4	2.16	60.8	1.3

[a] Determined by titration with HCl aqueous solution [24].
[b] Based on the weight loss (wt%) measured by TGA [21].
[c] Determined by ICP and TGA measurements.

Table 2
Epoxidation of olefins over Mn(II) salen anchored on PAMAM–SiO_2 dendritic catalyst[a]

Reaction run	Substrate	Catalyst	Time (h)	Yield (%)[b]
1		Mn-G0	1	20.2
2		Mn-G1	1	25.6
3		Mn-G2	1	36
4		Mn-G3	1	53.4
5		Mn-G4	1	75
6		Mn-G4[c]	1	71
7		Mn-G4[d]	1	68
8		Mn-G4	2	69
9		Mn-G4	3	63

[a] Reaction temperature: 0 °C; 0.01 mmol of Mn catalyst; 2 mmol of olefin; 10 mmol of *N*-methylmorpholine *N*-oxide; 4 mmol of *m*-CPBA; and 5 ml of CH_2Cl_2 used as solvent.

[b] Based on olefin.

[c] The catalyst was reused after the first recycle.

[d] The catalyst was reused after the fourth recycle.

dendritic catalyst exhibits the highest activity for the epoxidation of styrene or cyclic olefins during a relatively short time of reaction (1–3 h). Furthermore, the experimental results clearly show that with Mn-G*n* series, the yield increases with an increase in the number of generations.

Figure 2 shows the effects of the generation number of dendrimer on the catalytic activity of the resulting Mn salen immobilized dendritic catalysts for epoxidation of styrene. The activity of Mn-G*n* series catalysts increased with an increase in the generation number of dendrimer. This result is not surprising because the dendrimer has a hyper-branched structure, where the long and hyper-branches make the dendritic backbone more flexible (scheme 1). In other words, the interactions between the terminal group of the dendrimer and the solid support are weakened because the dendritic branches are propagated far away from the rigid solid surface. Therefore, the active sites linked on the periphery of the dendrimer with higher generations are more easily accessible to the reactants than those with lower generations.

Figure 2 also shows that the generation number of dendrimer affects the Mn loading. Based on the total weight of dendritic catalyst, with the exception of Mn-G4, the amount of Mn loading increases with an increase in the number of generations. As shown in scheme 2, two step reactions are needed to form Mn salen anchored on the dendrimer: the first step involves the reaction of salicylaldehyde with the amino groups on the periphery of the dendrimers to give a Schiff base (reductive coupling), and the second step involves the coordination of manganese cations with the Schiff base to form the Mn(II) salen complex anchored onto the dendrimers. The observed amounts of Mn loading are not as high as the desired values, and the amount of Mn loading of Mn-G4 is a little lower than that of Mn-G3. These results indicate that the amount of Mn loading is influenced not only by the concentrations of amino groups on the periphery of each generation of dendrimer, but also by the formation of the slightly distorted structure of the Mn salen complex. However, it is interesting to observe that Mn-G4 exhibits much higher catalytic activity for the epoxidation of styrene than Mn-G2 and Mn-G3

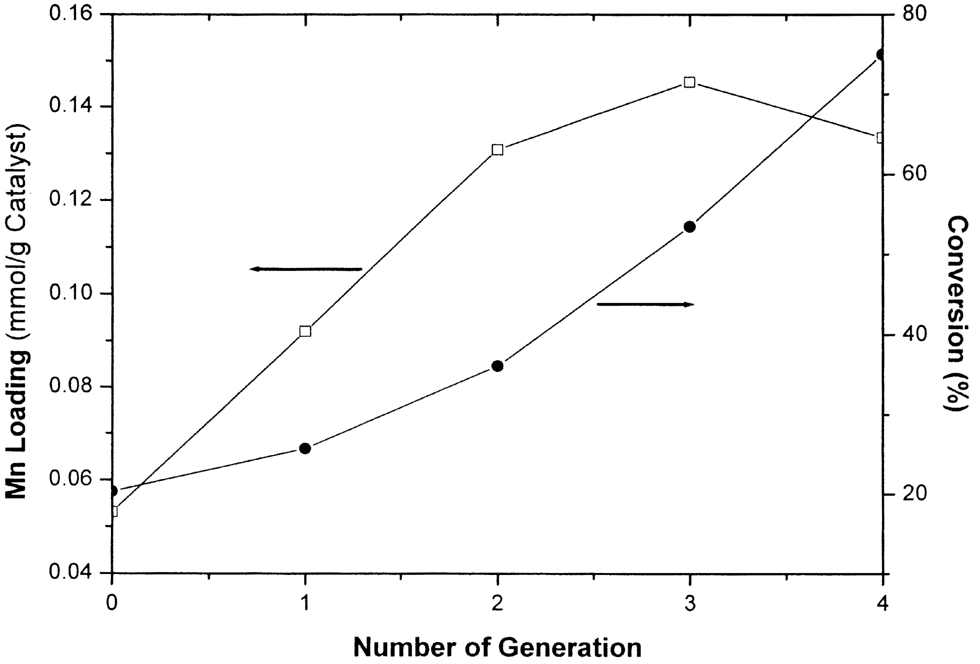


Figure 2. Effects of the generation number of dendrimer on the Mn loading and the catalytic activity of the dendritic catalyst for the epoxidation of styrene.

although these three samples do not have significant differences in the Mn loading. These results strongly suggest that the length of the dendritic backbone chain plays a more important role in the catalytic activity than the amount of active sites, with the catalytic sites having a longer backbone chain being more active than those having a shorter backbone chain.

Furthermore, table 2 shows that the solid dendritic catalyst can also be recycled and reused without a significant loss of the catalytic activity. For all reactions, the catalyst employed in the reaction was filtered and the residue of the reaction mixture was analyzed by ICP; no manganese was found in the residue, indicating that there was no leaching of Mn salen complex from the dendritic catalyst. The slight loss of catalytic activity observed for the reused dendritic catalyst may be attributed to the degradation of the salen complex during the reaction [25].

4. Conclusions

The new PAMAM dendrimer-supported Mn(II) salen complex catalysts have been successfully synthesized and applied in the catalytic epoxidation of a variety of olefins. The activity of the dendritic catalyst was found to increase remarkably with an increase in the number of dendrimer generations for styrene epoxidation. Experimental observations indicate that not only the concentrations of amino groups on the periphery of each generation of dendrimer, but also the properties of the Mn salen complex influence the Mn loading amount. However, the length of the dendritic backbone chain plays an important role in improving the accessibility between the active sites and the reactant molecules resulting in the enhancement of catalytic activity.

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