Internal/External Use of Dendrimer in Catalysis

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Abstract−Dendrimers, well-defined hyper-branched macromolecules with characteristic globular structures, have inspired chemists and chemical engineers to develop new materials and several applications have been explored. The dendritic molecule has emerged as an attractive material in the field of catalysis and various dendrimer catalysts have been applied not only to catalytic reactions but also to non-catalytic ones such as nanoscale reactor systems. This article presents a review of research work on the dendrimer-based catalysis involving the rational design of homogeneous or heterogeneous chiral dendrimer catalysts for enantioselective reactions and the synthesis of catalytically active bimetallic nanoparticles in the presence of dendrimer as a template.

Key words: Dendrimer, Immobilization, Asymmetric Synthesis, Chiral Auxiliary, Encapsulation, Nanoreactor, Nanoparticle, Bimetal, Organic-Inorganic Hybrid, Catalysis

INTRODUCTION

What potential would precise macromolecular fractals, constructed by geometrically progressive structural branching, possibly offer to the scientific and industrial community? This is a question that has been asked many times over the past decade, since the discovery of the new class of polymeric architecture called "dendrimers." Would these tree-like molecules initiate new fields of application or would they merely be remembered as esoteric objects of symmetrical beauty?

Undoubtedly, the chemistry of dendritic molecules has become more and more interesting and the developments in this field show the efforts of many research groups to design new dendritic molecules focusing on novel properties, functions, and potential applications. The development of a number of dendritic systems (Polyamidoamines (PAMAMs), carbosilane dendrimers and others) in the early years of dendrimer chemistry has made dendritic skeletons available that can be used for further functionalization. Building up from, *e.g.*, dendritic polyamine cores or from dendritic polyarylether "wedges" multiple functional groups can be introduced and thus functional dendrimers can be obtained. Many functions have been reported up to now targeting future applications and including supramolecular recognition/assembly processes, ion transport, guest enclosure, adhesion, catalysis, microstructuring, coating, and diagnostics.

In the field of catalysis, the hope is that dendrimer catalysts will retain the benefits of homogeneous catalysts (high activity, high selectivity, good reproducibility, accessibility of the metal site and so on), and unlike most other polymeric species they will be readily recoverable after reaction. In principle, dendrimer is one of the most promising candidates which can meet the needs for an ideal cata-

lyst: persistent and controllable nanoscale dimensions, chemically reactive surface, favorable configurations in which all the active sites would always be exposed towards the reaction mixture so that they are easily accessible to migrating reactants, and soluble but can be easily recovered by filtration. These properties, or some combination of them, are what makes dendrimers so useful not only in catalytic applications but also in non-catalytic ones such as nanoscale reactor systems [Turro et al., 1991; Tomalia and Durst, 1993].

The aim of this article is therefore to discuss the interesting features of dendrimer-based catalytic systems with an expectation that an efficient catalyst can be realized by virtue of the unique features of dendrimer. Section 2 covers the important characteristics and some examples of chiral dendrimer catalysis using internal and external surface of a dendrimer. In section 3, we describe the design of silica supported dendritic chiral auxiliaries to overcome the drawbacks of the conventional supports associated with the irregular texture and heterogeneous chemical nature of silica gel. Section 4 is related to dendrimer nanoreactors. In particular, we demonstrate the preparation of various bimetallic nanoparticles in the presence of dendrimers.

Since Knapen and coworkers opened a new avenue by introducing the first dendrimer-supported catalysts [Knapen et al., 1994], with the possibility of combining catalysis with other unique features of dendrimers, expectations are running high in this area [Tomalia and Dvornic, 1994]. Only time and more experimentation will determine whether dendrimer catalysts will live up to their generous promises.

CHIRAL DENDRIMER IN CATALYSIS

Homogeneous reaction systems have advantages over their respective heterogeneous counterparts in attaining high activity and selectivity by virtue of the concentrating and intimate-contacting between the catalyst and reactant(s); however, some significant shortcomings are experienced in the homogeneous reaction systems such as the recovery of catalyst and the separation of substrate and product.

The problematic separation of homogeneous catalysts from reaction products in solution has hampered the commercialization of a number of excellent homogeneous catalysts. Furthermore, complex ligands and homogeneous metal catalysts have become increasingly expensive.

Therefore, it is natural that besides the efforts to design effective catalysts, bridging the gap between homogeneous and heterogeneous catalyses by the variation of the application phase, *i.e.*, "heterogenized," "immobilized" or "anchored" catalysis, has been another subject of intensive research on homogeneous catalysis ever since its beginning [Panster et al., 1996; Copéret et al., 2003].

Unfortunately, particularly in asymmetric reactions which will be discussed in this article, the efficiency of the heterogenized catalysts generally depends on the nature of the support and is less than satisfactory compared with their homogeneous counterparts [Jannes et al., 1993; De Vos et al., 2000]. With organic polymer supports, enantiomeric excesses are high but rates are generally low due to the intrinsic nature of polymer that reactions taking place on the interior surface of a porous catalyst particle encounter resistance to mass transport through the pores. On the other hand, inorganic materials such as silica are particularly suited for heterogeneous support because of their high physical strength and chemical inertness. In the case of inorganic supports, however, lower rates, selectivities, and enantioselectivities are obtained.

Dendrimers are highly branched macromolecules and they are generally described to have a structure of spherical shape with a high degree of symmetry [Newkome, 1994; Newkome et al., 1996; Fischer and Vögtle, 1999; Archut and Vögtle, 2000]. Since the discovery of this highly ordered material, the elegance often expressed in dendritic molecules, beyond their aesthetic appeal, has inspired many research groups and consequently a large number of dendrimer-related reports have exploded targeting future applications during the past decade.

In line with the prospect of dendrimer catalysts, an overwhelming number of dendrimer-based catalysts have been designed and applied to various reactions [Seebach et al., 1998; Bosman et al., 1999; van Koten et al., 1999; Hechet and Fréchet, 2001; Oosterom et al., 2001; Kreiter et al., 2001; Astruc and Chardac, 2001; van Heebeek et al., 2002; Twyman et al., 2002; King and Twyman, 2002]. In particular, chiral dendrimers have drawn much attention because the highly ordered structures of dendrimers are considered to be suitable for realizing approximately the same chiral environments. Dendrimers make themselves attractive in the design of asymmetric catalysts by combining chirality or asymmetry with their highly symmetrical nature.

While dendritic chiral catalysts have been applied to several reactions, the major portion of this and next sections is mainly concerned with the enantioselective addition of dialkylzincs to aldehydes as shown in Fig. 1 because this reaction is generally accepted as being an ideal test reaction for the induction of asymmetry [Soai
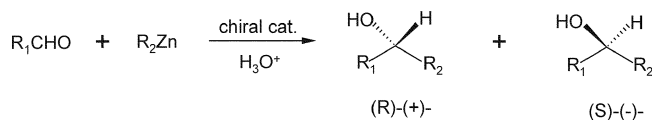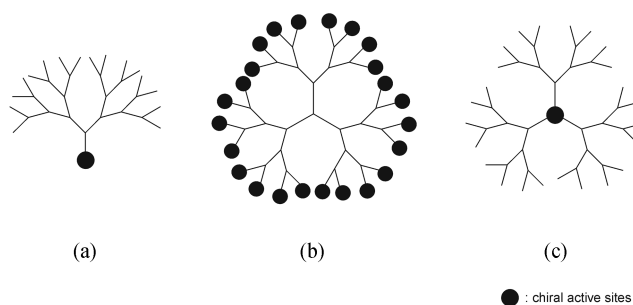

Fig. 2. Chiral active sites incorporated at the focal point (a), periphery (b), and core (c), respectively.

and Niwa, 1992] and is one of the most widely studied reactions catalyzed by chiral dendrimers. As described in Fig. 2, there have been three types of catalyst design in which chiral active sites are incorporated at the focal point, periphery, and core, respectively.

1. Focal Point-functionalized Chiral Dendrimers

Bolm et al. carried out enantioselective addition of diethylzinc to aldehyde with pyridyl alcohol and found that the enantioselectivity was significantly influenced by the aggregation behavior of the various zinc-containing species involved in this reaction [Bolm et al., 1990]. They also prepared dendritic macromolecules using the Fréchet convergent approach to investigate the influence of the catalyst periphery on the reaction performance [Bolm et al., 1996]. The chiral dendrimers were synthesized by attachment of Fréchet-type branches up to the 3rd generation to a chiral pyridyl alcohol at the focal point. However, practically no changes in enantiomeric excess (ee) were observed regardless of the dendrimer catalysts used (about 85% ee). This suggests that the size of catalyst periphery has little influence on the chiral environment.

2. Periphery-functionalized Chiral Dendrimers

In 1995, Meijer and coworkers synthesized poly(propylene imine) dendrimers modified with chiral secondary alcohols to investigate the conformational effect of dendrimer on the enantioselective addition of diethylzinc to aldehyde [Sanders-Hovens et al., 1995]. R-styrene oxide was introduced at the periphery of dendrimer (by ring opening) and used as asymmetric controllers. It was found that increasing dendrimer generation results in a dramatic drop in enantiomeric excess and the catalyst obtained from the 5th generation dendrimer showed almost no preference for one enantiomer over the other. This phenomenon results from a distribution of different conformations caused by the multiple interactions between end groups. The subtle differences between chiral active sites may influence the stereochemical course of the reaction and result in a poor enantiomeric excess. They explained this negative dendritic effect in conjunction with the peculiar chiroptical properties of dendritic boxes (poly(propylene imine) dendrimers modified with N-tert-Boc-L-phenyl alanine) [Peerlings et al., 1995; Jansen et al., 1995; Peerlings and Meijer, 1997]. The vanishing optical rotation of these dendritic boxes agrees with the poor enantiomeric excess attained from the reaction catalyzed by the 5th generation dendrimer.

Soai and coworkers reported the preparation of chiral imino and amino dendrimers possessing ephedrine derivatives at their terminal positions [Suzuki et al., 1997]. The resulting chiral dendrimers were used as chiral inducers in the enantioselective addition of di-

Fig. 1. Enantioselective addition of dialkylzinc to aldehyde.

ethylzinc to N-diphenylphosphinylimines. Compared to the chiral imine and amine ligands (~92% ee), chiral dendrimer ligands afforded a moderate enantioselectivity (30-43% ee) regardless of the ligand type (imino or amino). Moreover, increasing dendrimer generations resulted in a decrease in the enantioselectivity. Similarly to the case of Meijer group's poly(propylene imine) dendrimers, the decrease in the enantioselectivity may be ascribed to the unfavorable intramolecular interactions between chiral functionalities caused by flexible backbones.

Three years later, they synthesized ephedrine-functionalized poly (phenylacetylene) dendrimers with a hope that the rigid hydrocarbon backbone may be effective to resolve the unfavorable multiple interaction problems observed in the case of chiral PAMAM (poly (amidoamine)) dendrimers [Sato et al., 2000a]. They prepared three types of chiral dendrimers (the first generation dendrimers bearing chiral sites at *para*- and *meta*-positions and the second generation dendrimer having six chiral β-amino alcohols on the phenylacetylene chain-end) and used the resulting chiral dendritic ligands in the enantioselective addition of diethylzinc to N-(diphenylphosphinyl)imines. It was found that these chiral poly(phenylacetylene) dendrimers were effective to obtain high enantioselectivities and that the *para*-substituted chiral dendrimer (89-94%) showed a slightly higher enantioselectivity than the *meta*-substituted one (73-85%). It is believed that the *para* position has a larger space than the *meta* position and therefore almost the same chiral environment can be established in the *para* position. The second generation chiral dendritic ligand was also used in the reaction and high enantioselectivities (87-90%) were obtained. The chiral dendritic ligands could also be reused without a significant loss of enantioselectivity.

The same chiral dendritic ligands were applied in the enantioselective addition of dialkylzincs (ethyl and isopropyl) to aldehydes (phenyl, 2-naphtyl, p-tolyl) and 77-86% enantioselectivities were observed [Sato et al., 2000b]. This indicates that the use of a rigid dendritic branch is effective in weakening the multiple interactions between end groups; thus almost the same chiral environment of respective active sites can be formed.

Recently, they also expanded their strategy to carbosilane dendrimers and reported that chiral dendrimers possessing four or twelve chiral amino alcohol groups at the flexible carbosilane chain-ends were successfully used as catalyst in the enantioselective addition of dialkylzinc to N-(diphenylphosphinyl)imines [Sato et al., 2002a] or aldehyde [Sato et al., 2002b]. The carbosilane-based chiral dendrimers afforded the enantiomerically enriched secondary alcohols (74-93% ee) or N-(diphenylphosphinyl)imines (82-92% ee). The enantiomeric excesses were as high as those of monomeric chiral dimers. In both cases, however, little change in enantioselectivities was observed as the dendrimer generations increased.

Hu et al. synthesized optically active ephedrine bearing dendronized polymers with poly(phenylene) backbones [Hu et al., 2002]. They applied the macromolecular chiral catalysts to the enantioselective addition of diethylzinc to benzaldehyde and compared their catalytic performance with those of their corresponding linear polymeric and dendritic chiral catalysts. The macromolecular chiral catalyst effectively promoted the reaction and afforded (R)-1-phenyl-1-propanol with 75% enantioselectivity. The enantioselectivity was as high as that of polymer (76% ee) or dendrimer (78% ee). The dendronized polymer was readily recovered by filtration and reused

without a loss of activity.

Seebach et al. synthesized dendrimer-bound TADDOLates in which triol was used as a starting material for the preparation of dendritic molecules and then TADDOLs (α,α,α′,α′-tetraaryl-1,3-dioxolane-4,5-dimethanols) were attached at the periphery of dendrimers [Seebach et al., 1996, 1998]. The TADDOL moieties were accessible to form Ti complexes and dendrimer-bound Ti-TADDOLates efficiently promoted the enantioselective addition of diethylzinc to benzaldehyde. The enantioselectivities obtained with the chiral metallodendrimers (97 and 98% enantioselectivity with the zero and first generations, respectively) were comparable to that observed with monomeric chiral catalyst (~98% ee). The dendrimer catalyst was separated by column chromatography.

3. Core-functionalized Chiral Dendrimers

Pu and coworkers prepared rigid and optically active dendrimers containing cross-conjugated units from the coupling of phenylacetylene-based dendrons with an optically active pure diacetate of 4,4′,6,6′-tetrabromo-1,1′-bi-2-naphthol [Hu et al., 1999]. The convergent method pioneered by Fréchet and coworkers was adopted in the synthesis of the binaphthyl-based dendrimers [Hawker and Fréchet, 1990]. The resulting dendrimers were found effective in conducting the energy migration from the periphery to the core. This suggests their potential use for developing an enantioselective fluorescence sensor.

In addition, the binaphthyl-based dendrimer was also used as a chiral inducer in the enantioselective addition of diethylzinc to benzaldehyde, and the catalytic performance was compared with that of the (S)-BINOL molecule. It was revealed that the binaphthyl-based dendrimer showed a much higher catalytic activity (98.6% conversion at room temperature in 24 h) than the parent BINOL (37% conversion). The enhanced catalytic activity was explained by the different Lewis acidity of the zinc complexes; the zinc complex generated between dendrimer and diethylzinc may have a much higher Lewis acidity than that formed from the reaction of BINOL with diethylzinc.

Concerning the enantioselectivity, it is interesting to note that the use of binaphthyl-based dendrimer provided the opposite enantiomeric product compared to BINOL, although enantioselectivities of the dendrimer and BINOL remained very low. The zinc complex generated from BINOL exists as aggregates or oligomers in solution through intermolecular Zn-O-Zn bonds which greatly reduces the Lewis acidity of the zinc center. In the case of dendrimer, however, bulky and rigid dendritic arms prevent the formation of oligomers through Zn-O-Zn bonds, and yet there is enough space allowing the substrate approaching the active sites.

In the presence of Ti(O-*i*-Pr)$_4$, the same enantiomeric product with high enantioselectivities (90% ee for dendrimer and 89% ee for BINOL, respectively) was obtained when either dendrimer or BINOL was used. This indicates that structurally similar chiral active sites were formed if dendrimer or BINOL was used in the presence of titanium complex. Moreover, because the titanium-dendrimer complex is considered to form the monomeric structure, the complex formed between Ti(O-*i*-Pr)$_4$ and BINOL may also be monomeric. The binaphthyl-based dendrimer was easily recovered from the reaction mixture by precipitation with methanol.

Development of dendrimer-bound Ti-TADDOLAates was pioneered by Seebach and coworkers [Seebach et al., 1998, 2001; Sell-

ner et al., 2002]. In 1996, they synthesized dendritic Ti-TADDOLates built in a polystyrene matrix. For this, TADDOLs were attached to Fréchet-type branches with 8 or 16 peripheral styryl double bonds, and then these compounds were incorporated into polystyrene matrix through a suspension copolymerization [Seebach et al., 1997; Rheiner and Seebach, 1999]. The dendrimer-bound Ti-TADDOLates were prepared by the reaction of the resulting beads with $Ti(O\text{-}i\text{-}Pr)_4$. Compared to the conventional polymer attached one, the novel polymer-incorporated dendritic Ti-TADDOLates showed a high enantioselectivity (98%), as high as that of their homogeneous analogue (99%). However, the dendrimer generation had little impact on the enantioselectivity and little change was observed as the generation of dendrimers increased. The high enantioselectivity was ascribed to the dendritic structure preventing the blocking of active sites in the polymer matrix. It is worth noting that the enantioselectivity was dependent upon the degree of crosslinking and a lower content of Ti-TADDOLates was favorable to obtain a higher enantioselectivity.

They also investigated the effects of chain length and flexibility of dendrimer on the reaction performance [Sellner and Seebach, 1999]. From a more detailed study, it was found that enantioselectivities were largely dependent upon the properties of dendrimers. First, while ~90% enantioselectivity was obtained with all the polymers of low loading, dendrimer-bound Ti-TADDOLates in polymer matrix gave rise to a high enantioselectivity up to 98% in 20 sequential applications. Second, a longer chain length of linkers between the TADDOL core and polymer backbone resulted in a dramatic drop in the catalytic performances. Furthermore, the low-loaded dendritic beads with a short chain length were advantageous in maintaining their swelling properties even after repetitive uses. Third, the rate of reaction was the same with and without stirring using the dendritic beads bearing the shortest spacer. This indicates that active sites are readily accessible for the reactants.

Sellner et al. also applied their strategies to the preparation of a dendrimer-bound BINOL ligand in polymer matrix [Sellner et al., 2000]. Several dendritic BINOL derivatives bearing at least two polymerizable styryl groups were prepared and subsequently treated with $Ti(O\text{-}i\text{-}Pr)_4$. The resulting polymer-incorporated dendritic Ti-BINOLates were employed as catalysts for the enantioselective addition of diethylzinc to benzaldehyde and high enantioselectivities up to 93% were obtained over 20 cycles.

SILICA-SUPPORTED DENDRITIC CHIRAL AUXILIARIES

For the purpose of immobilization, inorganic supports are considered appropriate because of their high physical strength and chemical inertness. However, while a variety of metal complexes and ligands have been immobilized on silica supports, the catalytic performances of the heterogenized catalysts were not always successful [de Vos et al., 2000]. Concerning the enantioselective addition of dialkylzinc reagents to aldehydes, the irregular pore structure and reactive surface of silica give rise to some serious problems. The former restricts the accessibility of reactant to the active sites, which results in a decrease of not only the reaction rate but also the selectivity. In addition, the participation of the latter in the unfavorable racemic reaction is clearly responsible for the decrease in the

enantioselectivity [Soai et al., 1990].

In an attempt to overcome these intrinsic problems of amorphous silica, highly ordered mesoporous materials have emerged as an alternative and there have been investigations involving changes in the pore size and the composition of the support, end-capping of the surface, and dilution of the catalytic sites to improve the activity, selectivity, and enantioselectivity [Brunel, 1999; Bellocq et al., 1999; Abramson et al., 2000; Bae et al., 2000]. It is claimed that two factors, the suppression of the activity of the naked surface towards the formation of racemic alcohols and the accessibility of reactants to the catalytic sites, are of prime importance.

In this regard, this section is focused on the design of catalyst systems satisfying these two crucial conditions by employing dendritic systems [Chung and Rhee, 2002a, b, 2003d]. It is worth noting that little attention has been directed to heterogeneous dendritic chiral catalysts, and thus the examples for the catalytic achievement through these systems have been extremely limited.

1. Catalyst Design I: Stepwise Propagation of Dendrimers on Silica

Propagation of the dendrimer generation on silica support was carried out by repeating two steps pioneered by Tomalia and co-workers [Tomalia et al., 1985]: (1) Michael addition of methyl acrylate to surface amino groups as an initiator site (G_0), and (2) amidation of the resulting ester moieties with ethylenediamine. As shown in Fig. 3, the treatment with methyl acrylate and ethylenediamine was repeated n times to obtain the nth generation dendrimer grafted silica. It is noteworthy that the propagation of dendrimer on silica surface at a higher generation is hardly as high as that of the theoretical value [Tsubokawa et al., 1998; Yoshikawa et al., 1999; Tsubokawa and Takayama, 2000; Murota et al., 2002]. This is believed
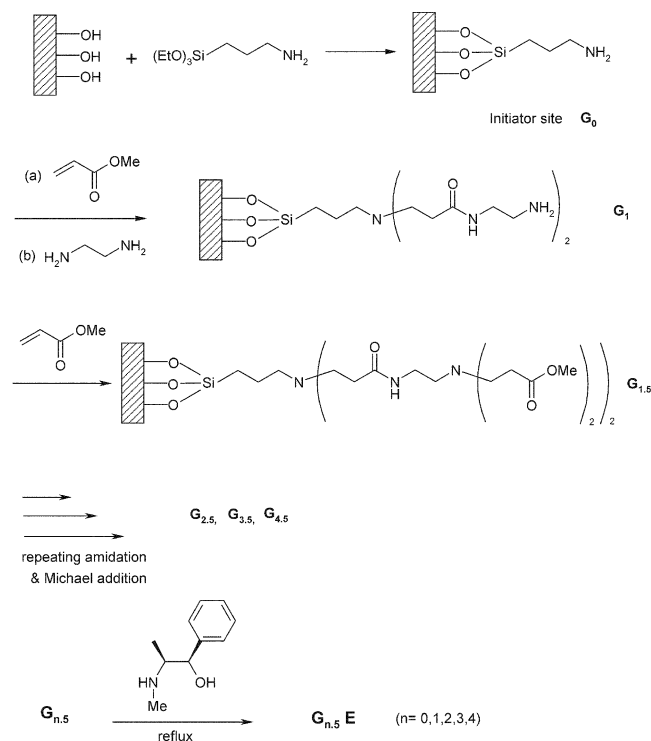

Fig. 3. Stepwise propagation of dendrimer from initiator sites on silica.

to be due to the incomplete Michael addition and amidation with surface functional groups, arising from steric crowding and ultimately resulting in the threshold of dendrimer growth being reached [Bourque et al., 1999, 2000].

In view of the catalyst support, the irregular hyper-branching is unfavorable because in such a case the dendrimer may not render the microenvironments of individual active sites approximately the same. Therefore, a well-defined structure seems more favorable for the design of an effective dendritic catalyst. In this regard, we prepared two types of aminopropylsilicas containing 0.24 (G_0L) and 0.9 mmol/g (G_0H) of amino group, respectively, as the initiator site. The amount of amino group introduced onto the silica surface was controlled by the concentration of 3-aminopropyltriethoxysilane (APES).

As shown in Figs. 4 and 5, the amount of amino groups on the resulting silica increased with the number of generations regardless of the amino group content of initiator sites. As expected, the graft-
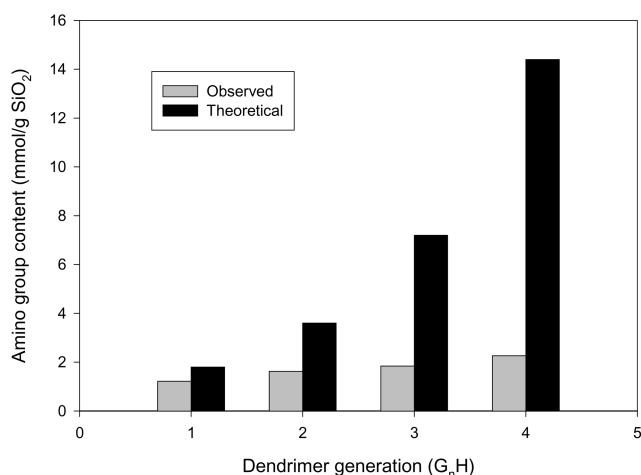

Fig. 6. Schematic diagram of silica-supported chiral dendrimer constructed by stepwise propagations.

ing at every generation was lower than the theoretical value. However, the propagation on silica surface having a low density of amino group (G_0L) was more efficient than that on silica surface having a high density of amino group (G_0H). With a high density of initiator sites, the actual amount of the grafted amino group became much less than the theoretical value as the number of generation increased. This suggests that the propagation of highly branched dendrimer on G_0H is more sterically hindered than that on G_0L.

Dendritic chiral catalysts were prepared by reactions of various dendrimers ($G_{n.5}H$, $G_{n.5}L$) with a chiral ligand such as (1R, 2S)-ephedrine. The immobilization of chiral ligands on the dendritic supports affords two series of catalysts, $G_{n.5}H$-E and $G_{n.5}L$-E. The heterogeneous dendritic system depicted in Fig. 6 is thought to be advantageous in many facets. One of the expectations is that the access of reagents to the native mineral surface may be effectively suppressed due to the crowding or globularly hyper-branched nature of dendrimers. In case of the conventional inorganic supports including mesoporous materials, treatment of mineral surface such as silylation is needed to suppress the involvement of uncovered

Fig. 4. The amino group content of dendrimer constructed silica having a high density of amino groups (G_0H, 0.9 mmol/g SiO_2).
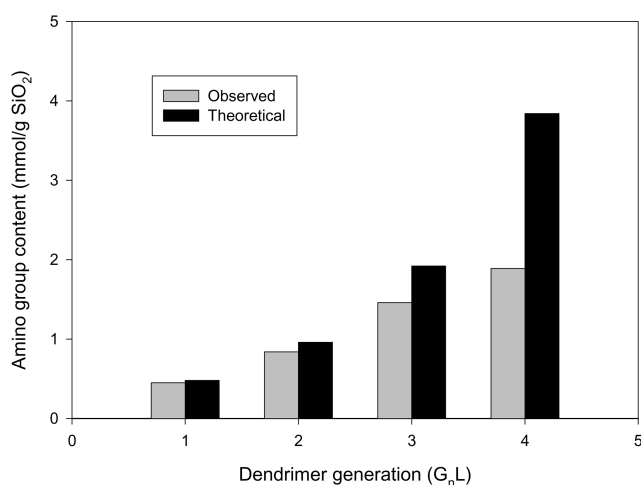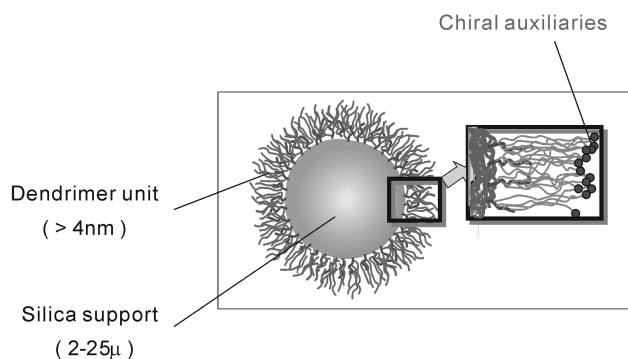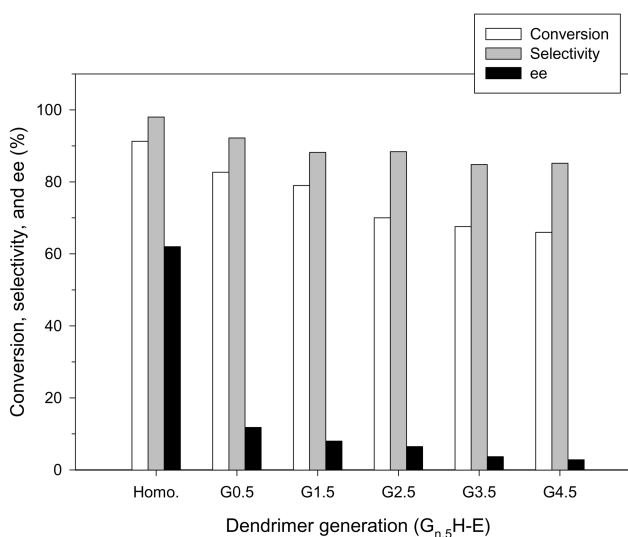

Fig. 5. The amino group content of dendrimer constructed silica having a low density of amino groups (G_0L, 0.24 mmol/g SiO_2).

Fig. 7. Enantioselective addition of diethylzinc to benzaldehyde in the presence of $G_{n.5}H$-E series.[a]
[a]All the reactions were carried out in toluene at 0 °C for 48 h using 2.2 molar equiv. of diethylzinc and 5 mol% of catalyst.

surface in the racemic reaction. By passivation of the naked surface, the enantioselectivity can be improved at the expense of a decrease in the activity [Bellocq et al., 1999]. Therefore, the use of dendritic support is considered to be an effective alternative to the conventional methods for the suppression of the unfavorable surface reaction.

The reaction performance was found to be strongly dependent on both the number of generations and the amino group content of initiator sites. In all the cases with $G_{n.5}H$-E series, the conversion, 1-phenyl-1-propanol selectivity, and enantiomeric excess decreased with an increase in the number of generations as shown in Fig. 7. Our speculation is that this might be caused by the incomplete reactions at individual propagation steps. The incomplete propagation left several branches unreacted and resulted in amputated versions of the proposed structures. An incomplete reaction at one state would propagate itself into higher generations. This indicates that digressions from ideally symmetric dendrimer growth are manifested at higher generations. In this case, the hyper-branched backbone of dendrimer becomes more densely coiled. It is evident that the more significant the irregular hyper-branching, the less accessible the catalytic sites and the less efficient the overall catalytic process. Therefore, the situation becomes similar to the case of a cross-linked or highly branched polymer support.

The chiral microenvironment cannot operate independently as the irregular hyper-branching becomes more significant. This implies that the end groups will have a number of different frozen-in conformations, which will result in the presence of different chiral environments [Jansen et al., 1995]. Moreover, the chiral ligand can also be incorporated with the end groups which have propagated from incomplete branches. It seems that a large portion of the end groups may be located not at the periphery but in the middle of the irregular branches. Therefore, one may assume that they have less degree of freedom in comparison with those of end groups existing at the periphery; thus it seems hardly achievable for a chiral catalyst to take its preferred conformation. The restricted flexibility
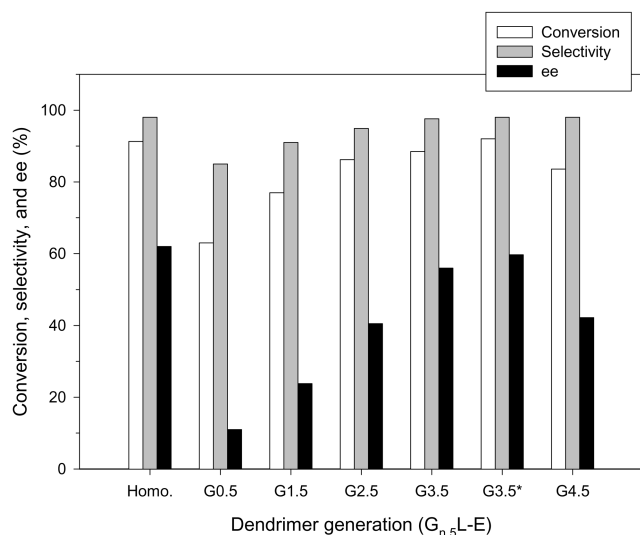
may have a significant impact on the stereochemical properties. In addition, the irregular branching seems ineffective to prevent the reactant from accessing the native support on which the unfavorable racemic alkyl transfer proceeds. These features will certainly have the effect of significantly decreasing the enantiomeric excess.

On the other hand, the reactions with $G_{n.5}L$-E series exhibit different characteristics compared to those with $G_{n.5}H$-E series as shown in Fig. 8. Increasing the number of generations results in an increase in the conversion, going from 63 ($G_{0.5}L$-E) to 88.5% ($G_{3.5}L$-E). This indicates that a large number of active sites exist at the periphery of dendrimers and are exposed towards the reaction mixture so that they are easily accessible. Although incomplete propagation was also observed in this case, the diffusional resistance does not seem so serious as in the case of the $G_{n.5}H$-E series. When the fourth generation is reached ($G_{4.5}L$-E), however, the steric hindrance caused by the hyper-branching appears so high that the access of reagents to the active sites is partially restricted and this may lead to a decrease in the catalytic activity.

The most conspicuous feature of the reactions with the $G_{n.5}L$-E series is the changes in enantioselectivities. Unlike in the case of the $G_{n.5}H$-E series, the enantioselectivity was enhanced as the number of generations increased. When the reaction was carried out in the presence of $G_{3.5}L$-E, the enantioselectivity was increased to 56%.
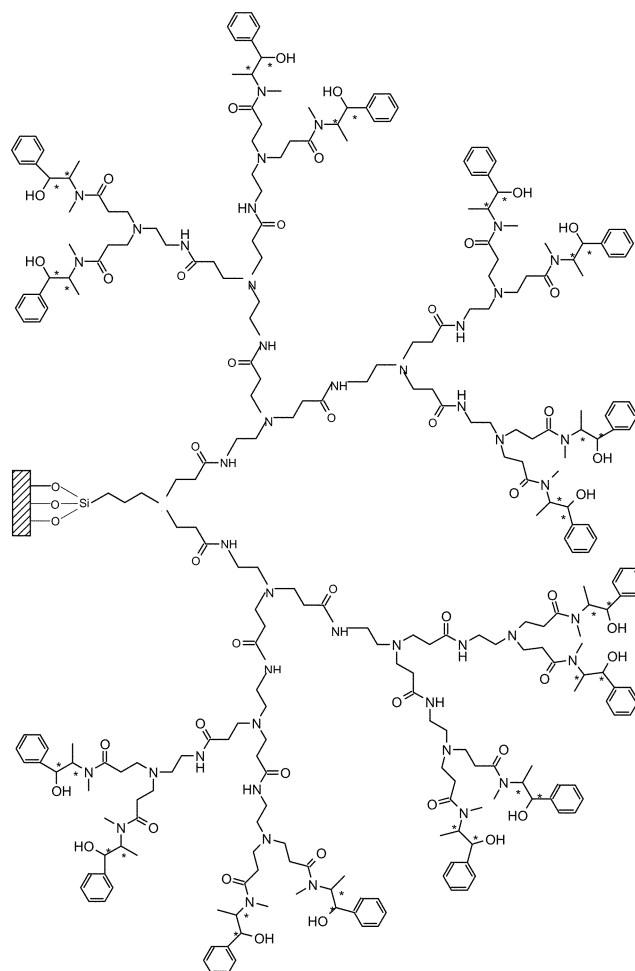

Fig. 8. Enantioselective addition of diethylzinc to benzaldehyde in the presence of $G_{n.5}L$-E series.
* Excess Et$_2$Zn

Fig. 9. Schematic representation of $G_{3.5}E$.

Moreover, increasing the diethylzinc concentration improved the reaction performance to a level almost equivalent to that of homogeneous counterpart as shown in Fig. 8 because the unfavorable racemic reaction associated with the hetero atoms was suppressed by the coordination of diethylzinc with the hetero atoms on the dendritic backbone [Sato et al., 2000a]. The high enantioselectivity demonstrates the efficiency of the dendritic chiral catalyst and suggests that the drawbacks of inorganic support can be overcome by the propagation of dendrimer on the silica support.

The high enantioselectivity may originate from the unique feature of the dendritic catalyst. Presumably, the globularly hyper-branched nature of the dendritic backbone effectively prevents reagents from gaining access to the native mineral surface which is responsible for the production of racemic alcohol. In other words, as the number of generations increases or the dendritic backbone becomes more crowded, the reagents will have less chance to meet the silanol groups of mineral support, and this leads to an increase in the enantioselectivity (cf. Fig. 9). However, the lower enantioselectivity observed in the reaction with $G_{4.5}L$-E suggests that the so-called frozen-in effect becomes so high that it may have an impact on the chiral environment. The possibility of surface reaction can be excluded because the dendritic backbone is more crowded at the fourth generation. One may recall that in the case of $G_{n.5}H$-E series which were constructed on G_0H having a high density of amino group, the enantioselectivity was decreased as the number of generations increased.

In order to confirm the feasibility of catalyst recycling, after the reaction with $G_{3.5}L$-E was completed, the catalyst was filtered, washed thoroughly, and reused three times. As shown in Table 1, it is evident that the dendritic catalyst can be reused without apparent loss of catalytic activity.

2. Catalyst Design II: Direct Immobilization of "Ready-made" Dendrimers on Silica

Table 1. Catalytic performance of recycled catalyst ($G_{3.5}L$-E)

Recycle	Conversion (%)	Selectivity (%)	e.e. (%), (R)
Fresh ($G_{3.5}L$-E)	88.5	97.6	56
1	86	97.2	53.8
2	80	97	50.4
3	71.3	93.6	39
4[a]	85.3	98	56.2

[a]Additional fresh catalyst was supplemented for the loss during recycling.

For the purpose of suppressing the racemic reaction, it may be conceivable that immobilization of a perfectly symmetric dendrimer would be more effective than the previous method, i.e., stepwise propagation of dendrimer on silica support. However, a ready-made dendrimer carries dense packing caused by multiple interactions on the dendritic surface at higher generations and this will bring about not only the diffusional resistance but also the different chiral environments [Peerlings and Meijer, 1997]. Therefore, another type of silica supported dendritic chiral catalyst was designed to achieve two goals: suppression of the unfavorable racemic reaction caused by the surface silanol groups and weakening of the multiple interactions between the chiral functionalities at the periphery of dendrimer.

As shown in Fig. 10, the preparation of silica supported dendritic chiral catalysts was carried out in four steps: (1) grafting of epoxide linker on the silica support, (2) immobilization of the nth generation dendrimer, (3) introduction of a long alkyl spacer, and (4) anchoring of chiral auxiliaries at the periphery of dendrimer.

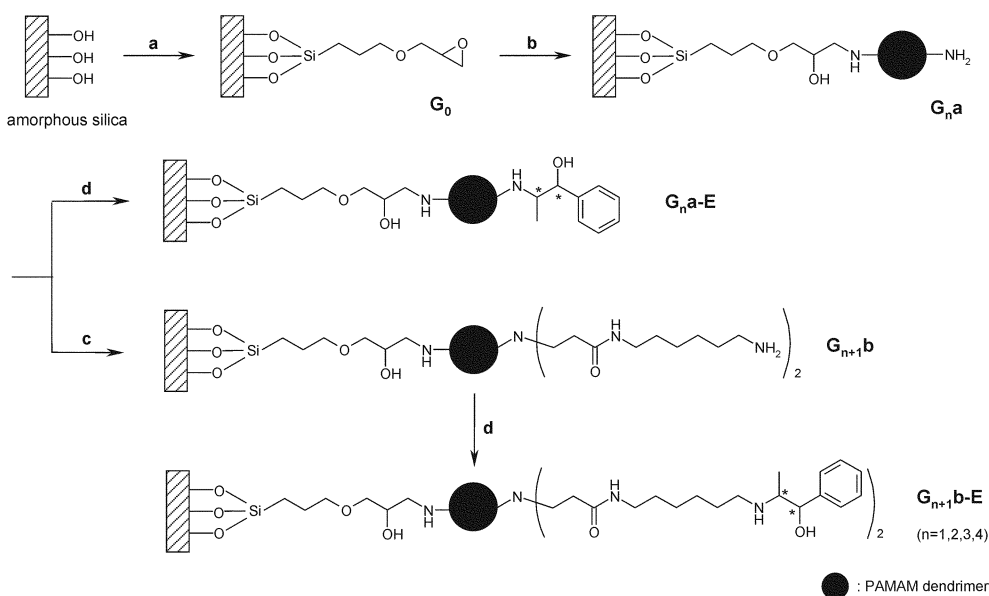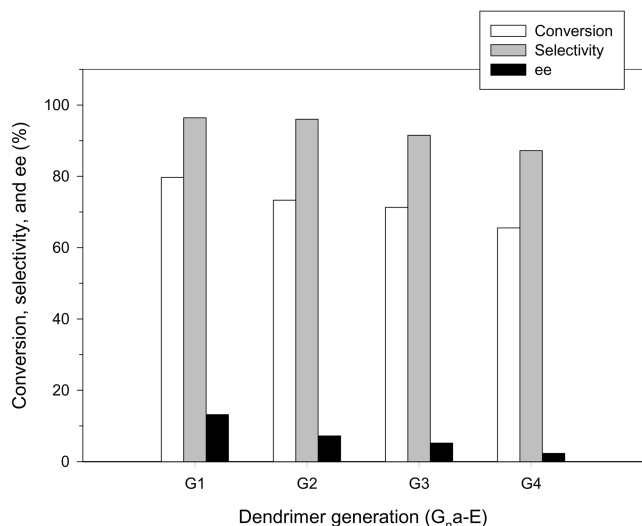The grafting of epoxide linker on the silica support (G_0) was con-

Fig. 10. Direct immobilization of ready-made dendrimers on silica.
a: (3-glycidoxypropyl)trimethoxysilane, toluene, reflux, 3 h; b: nth generation PAMAM dendrimer, methanol, reflux, 4 h; c: (i) excess of methyl acrylate, methanol, 50 °C, 3 days, (ii) excess of 1,6-diaminohexane, methanol, 50 °C, 3 days; d: (1R, 2R)-(+)-1-phenylpropylene oxide, hexane, reflux, 3 h

Fig. 11. Enantioselective addition of diethylzinc to benzaldehyde in the presence of G_na-E series.
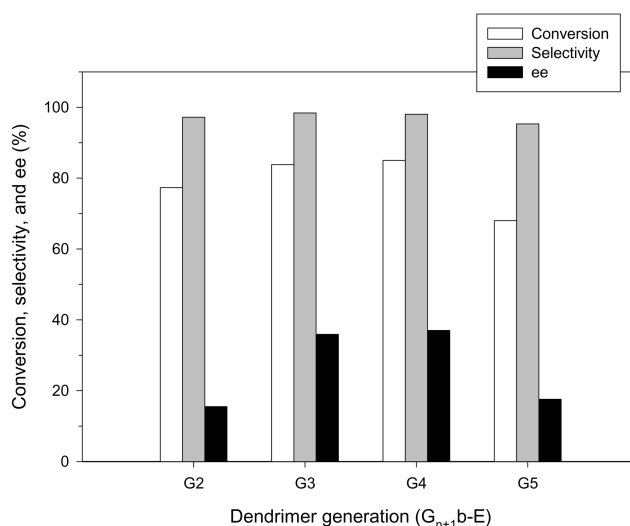

Fig. 12. Enantioselective addition of diethylzinc to benzaldehyde in the presence of G_{n+1}b-E series.

ducted by treating the surface silanol groups with 3-glycidoxypropyltrimethoxysilane (GPTMS) under reflux of toluene. Immobilization of the nth generation dendrimer on G_0 afforded the dendrimer grafted silica (G_na). To extend the chain length, the terminal ethylenediamine was substituted by 1, 6-diaminohexane. Michael addition of G_na with methyl acrylate gave rise to the formation of terminal ester groups ($G_{n.s}$a). Subsequent amidation of the resulting product with 1, 6-diaminohexane completed the reaction to yield G_{n+1}b. Introduction of chiral functionalities at the periphery of dendrimer was carried out by the reactions of various silica supported dendrimers (G_na and G_{n+1}b) with (1R, 2R)-(+)-1-phenylpropylene oxide. The reaction afforded two series of catalysts, G_na-E and G_{n+1}b-E.

Concerning the catalytic performance, there is a striking difference between the two series of dendrimer catalysts in promoting the reaction. In all the cases with G_na-E series, the conversion, selectivity, and enantiomeric excess decreased with an increase in the number of generations as shown in Fig. 11. The decrease in the catalytic activity indicates that the access of reagents to the active sites is restricted due to the steric hindrance as the packing becomes denser at higher generations. In addition, the denser packing of the end groups at higher generations brings about the presence of a number of different frozen-in conformations. Consequently, it seems hardly achievable for a chiral catalyst to adopt its preferred conformation, and this results in a poor enantiomeric excess.

On the other hand, the reactions with G_{n+1}b-E series exhibit different characteristics as may be observed in Fig. 12. Irrespective of the number of generations, the reaction performances with G_{n+1}b-E series were improved compared to those with G_na-E series. This indicates that the introduction of an alkyl spacer not only rendered
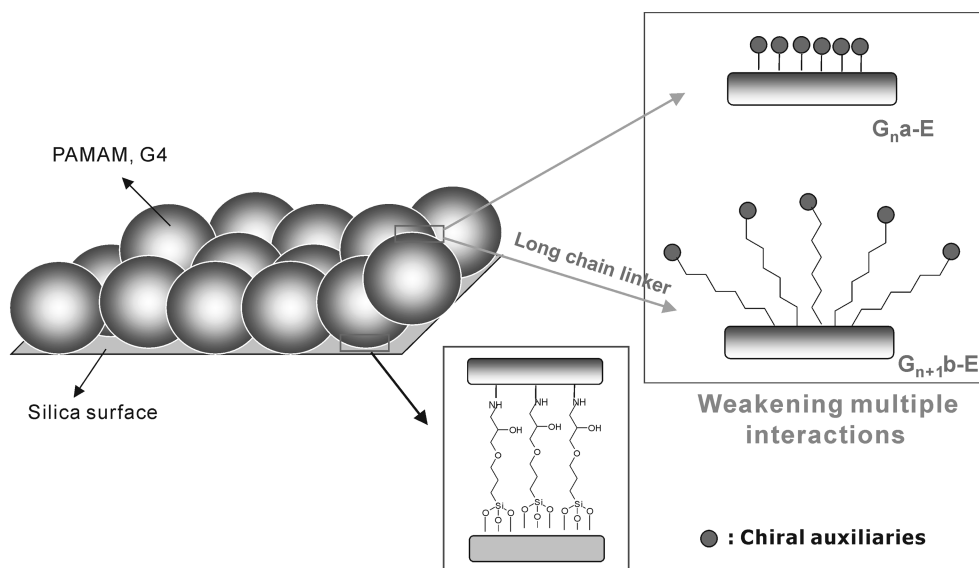

Fig. 13. Effective catalyst design for suppression of the racemic reaction on silica surface and weakening of the multiple interactions between the chiral functionalities at the periphery of dendrimer.

Table 2. Catalytic performance of recycled catalyst (G₄b-E)

Recycle	Conversion (%)	Selectivity (%)	e.e (%), (R)
Fresh (**G₄b-E**)	85	98	37
1	82	98	34
2	78	97.6	28.8
3[a]	84	98	34.2

[a]Additional fresh catalyst was supplemented for the loss during recycling.

the access of reactant to the catalytic active sites easier but also effectively relieved the unfavorable intramolecular interactions between the chiral active sites as depicted in Fig. 13. The latter feature suggests that the respective chiral ligands at the periphery of dendrimer are expected to operate independently and thus exhibit approximately the same chiral environment. In the presence of **G₅b-E**, however, the multiple interactions between the end groups become more pronounced. This may have led to the lowered reaction performance. Although the reaction performance is deteriorated at higher generations, it is evident that the use of an alkyl chain as a spacer gives rise to the enhancement of the catalytic performance. In the case of **Gₙa-E** series the increase of enantioselectivity was not observed at higher generations.

It was reported that this particular type of chiral catalyst formed by the epoxide ring-opening showed a moderate to low enantiomeric excess [Sanders-Hovens et al., 1995]; however, the chiral dendrimer catalyst has been used to investigate the viability of our strategy for the suppression of the racemic reaction taking place on the mineral surface and for the relaxation of multiple interactions between chiral active sites. It is natural that the enantioselectivity mainly depends on the nature of the chiral ligand and thus the moderate enantiomeric excess obtained in this study can be improved by using a more effective chiral ligand. The recycling experiment reveals that the silica supported dendritic chiral catalyst can also be reused with the catalytic activity maintained as shown in Table 2.

DENDRIMER NANOREACTORS

The preparation of narrowly distributed metal nanoparticles has been the subject of intense investigation and research is in progress from various points of view [Lewis, 1993; Schmid, 1994; Fendler, 2001]. Metal nanoparticles have also provided new opportunities for catalysis and thus research activities in this area have paved the way to new solid catalysts over the past decade.

Dendrimers have been considered as new types of host for the accommodation of guest molecules by virtue of their three-dimensional structure having interior void spaces and hence various metal nanoparticles have been successfully prepared by using dendrimer as a template [Zhao et al., 1998, 1999a, b; Esumi et al., 1998, 2000; Balogh and Tomalia, 1998; Zhao and Crooks, 1999; Gröhn et al., 2000; Floriano et al., 2001; Crooks et al., 2001a, b.]. The driving force for guest encapsulation within dendrimers can be based on electrostatic interactions, complexation reactions, steric confinement, various types of weaker forces (van der Waals, hydrogen bonding, hydrophobic force, etc.), and their combinations [Zeng and Zim-

merman, 1997; Matthews et al., 1998; Fischer and Vögtle, 1999; Crooks et al., 2001a, b].

The preparation of dendrimer-encapsulated metal nanoparticles is simple. First, a predetermined amount of metal ion is extracted into dendrimer. Second, the encapsulated ions are reduced with a reducing agent to yield dendrimer-encapsulated nanoparticles. The dendrimer-mediated approach is particularly well-suited for hosting metal nanoparticles for the following reasons: (1) the dendrimer templates themselves are of fairly uniform composition and structure, and therefore they yield well-defined nanoparticle replicas; (2) the nanoparticles are stabilized by encapsulation within the dendrimer, and thus they do not agglomerate; (3) the encapsulated nanoparticles are confined primarily by steric effects, and hence a substantial fraction of their surface is unpassivated and available for the participation in catalytic reactions; (4) the dendrimer branches can be used as selective gates to control the access of small molecules (substrates) to the encapsulated (catalytic) nanoparticles; (5) the terminal groups on the dendrimer periphery can be tailored to control the solubility of the hybrid nanocomposite and used to facilitate linking to surfaces and other polymers [Crooks et al., 2001b]. These five attributes take full advantage of the unique structural and chemical properties of dendrimers.

From the catalytic point of view, bimetallic nanoparticles, composed of two different metal elements, have drawn a greater interest than monometallic ones because bimetallization would make it possible not only to obtain improved catalytic activity but also to create a new property, which may not be achieved by monometallic catalysts [Sinfelt, 1987; Yoon et al., 1997]. However, it is worth noting that most of the previous studies have been confined to the "monometallic" nanoparticles, and "bimetallic" nanoparticles have not been exploited yet, although there has been a preliminary attempt to prepare dendrimer/bimetal nanocomposite by using two different metal precursors [Crooks et al., 2001a, b]. As shown in Fig. 14, dendrimer-encapsulated bimetallic clusters can be synthe-
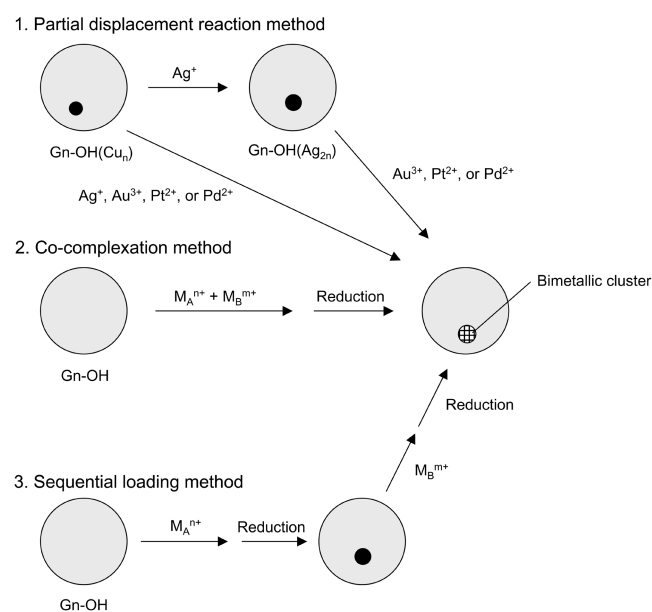

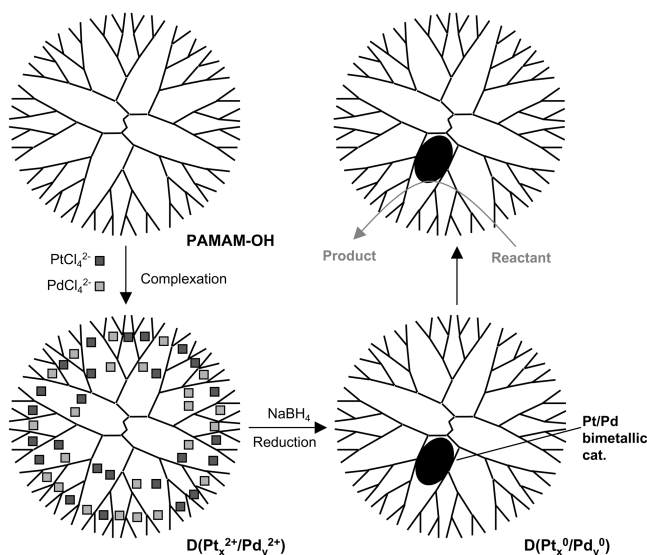**Fig. 14. Synthetic routes for the preparation of dendrimer-encapsulated bimetallic nanoparticles.**

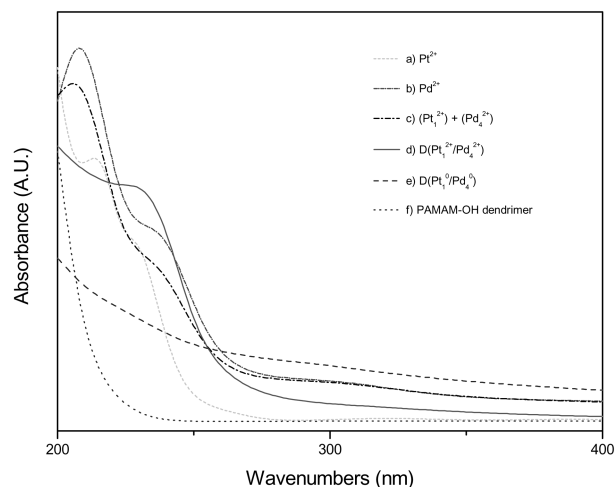Fig. 15. Schematic diagram for the preparation of dendrimer-encapsulated Pt-Pd bimetallic nanoparticles.

Fig. 16. Variations in the UV-vis spectra of Pt and Pd metals in the course of the complexation and the subsequent reduction (Pt/Pd ratio=1/4).
a) 55 mM K_2PtCl_4, b) 55 mM K_2PdCl_4, c) mixture of 11 mM K_2PtCl_4 and 44 mM K_2PdCl_4, d) complexation of metal mixture with 1 mM dendrimer, e) reduction with 0.55 M $NaBH_4$, and f) PAMAM-OH dendrimer (generation 4)
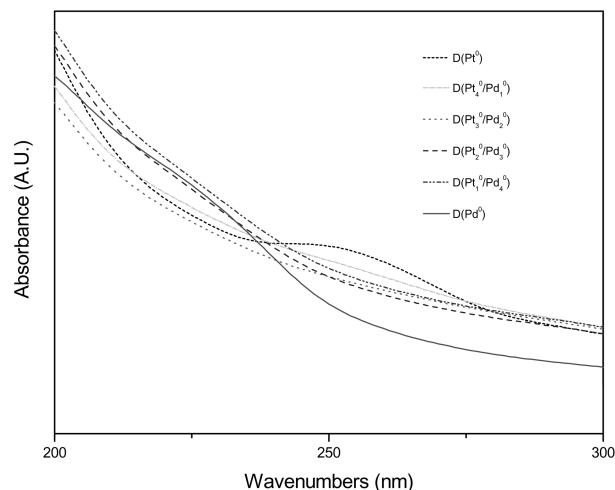

Fig. 17. UV-vis spectra of dendrimer-encapsulated Pt-Pd bimetallic nanoparticles with various Pt/Pd ratios.

sized by any of three methods: (1) partial displacement of the dendrimer-encapsulated cluster, (2) simultaneous co-complexation of two different metal ions followed by reduction, or (3) sequential loading and reduction of two different metal ions. However, detailed experimental results have been limited.

In this regard, we will describe here the preparation of dendrimer-templated bimetallic nanoparticles and the application of these bimetallic nanoparticles as catalysts [Chung and Rhee, 2003a, b, c].

1. Pt-Pd Bimetallic Nanoparticles

A schematic illustration for the preparation of dendrimer-encapsulated bimetallic nanoparticles is presented in Fig. 15 [Chung and Rhee, 2003a]. The method is similar to that for monometallic nanoparticles [Zhao and Crooks, 1999] except for the simultaneous use of two metal precursors, K_2PtCl_4 and K_2PdCl_4. Recently, Scott et al. applied the same approach to the preparation of dendrimer-encapsulated Pt-Pd bimetallic nanoparticles and used the resulting nanoparticles in the hydrogenation of ally alcohol [Scott et al., 2003]. Dilute aqueous solution of PAMAM-OH dendrimer was mixed with the aqueous solution of two metal ions at controlled stoichiometries. After stirring the solution for 1 h, aqueous solution of $NaBH_4$ was slowly added and subsequently the two metal ions ($PtCl_4^{2-}$ and $PdCl_4^{2-}$) were simultaneously reduced to yield zero-valent metal particles. The light yellow dendrimer/($PtCl_4^{2+}+PdCl_4^{2-}$) solution immediately turned dark brown indicating the formation of colloidal nanoparticles. The resulting nanoparticles were very stable and there was no precipitation up to six months.

Fig. 16 shows the changes in the absorption spectra of Pt and Pd metals (Pt/Pd ratio=1/4) in the course of the complexation with dendrimer and the subsequent reduction. Concerning the monometal ions, the characteristic absorption peaks at 214 and 208 nm arising from a ligand-to-metal charge-transfer (LMCT) are observed for $PtCl_4^{2-}$ and $PdCl_4^{2-}$, respectively [Gerloch and Constable, 1994]. In the absence of dendrimer, the mixture of $PtCl_4^{2-}$ and $PdCl_4^{2-}$ also exhibits the mixed absorption peaks of two metal ions. After the addition of PAMAM-OH to the solution of the $PtCl_4^{2-}$ and $PdCl_4^{2-}$,

however, a new band at 230 nm appears at the expense of the decrease in the strong absorption peak at 205 nm. This indicates that two metal ions are complexed with the internal functional groups of the dendrimer and are encapsulated in the dendrimer host. After reduction, the band observed in the former case completely disappears and a new broad absorption band appears over a wide wavelength region.

A series of UV-vis spectra of the Pt-Pd bimetallic nanoparticles with various Pt/Pd ratios ($D(Pt_x^0/Pd_y^0)$, where x/y=Pt/Pd mol ratio) are presented in Fig. 17. Regardless of the Pt/Pd ratios, the absorption bands are of nearly exponential shape and this indicates the complete reduction of metal ions. Moreover, it should be noted that the spectra of the resulting nanoparticles are different not only from those of the monometallic Pt or Pd nanoparticles but also from those
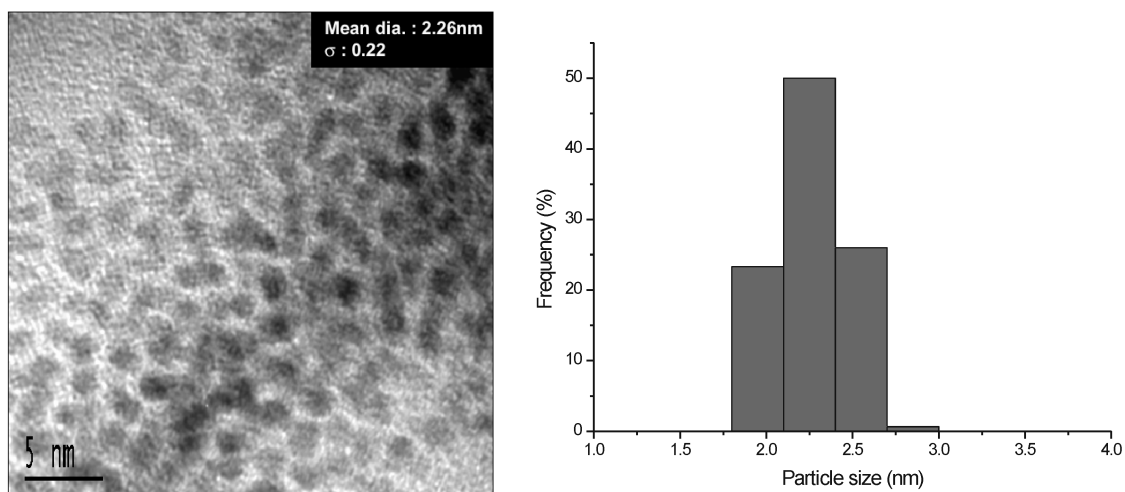
Fig. 18. HRTEM image and particle size distribution of Pt-Pd bimetallic nanoparticles with a Pt/Pd ratio of 1/4.

of their physical mixtures.

The result of X-Ray photospectroscopy (XPS) analysis also supports that all the metal ions are completely reduced irrespective of the Pt/Pd ratios. In the case of Pt, the peaks corresponding to platinum $4f_{7/2}$ and $4f_{5/2}$ levels are observed at 72.5 and 75.7 eV binding energies, respectively, and these peaks are assigned to Pt^{2+}. Upon reduction, the peaks are shifted to 71.3 and 74.4 eV, respectively, which are assigned to Pt^0. Similarly, it is observed that the $Pd(3d_{5/2})$ peak is shifted from 337.6 to 334.9 eV and $Pd(3d_{3/2})$ peak from 342.7 to 340.5 eV upon reduction.

The representative HRTEM image of $D(Pt_1^0/Pd_4^0)$ is shown in Fig. 18. The microscopy demonstrates that the particle size is uniform and the shape is nearly spherical. The formation of quite monodispersed nanoparticles suggests the effectiveness of dendrimers acting as both nanoreactors for the preparation of nanoparticles and nanoporous stabilizers for the prevention of aggregation. Regardless of the metal composition, bimetallic nanoparticles with a diameter of ~2.3 nm were observed.

To confirm whether the nanoparticles are a mixture of Pt and Pd nanoparticles or bimetallic ones, EDS analysis was carried out and both Pt and Pd elements were detected. However, it was rather difficult to acquire the elements of one particle because the spatial resolution (ca. 5 nm) was not high enough to detect the X-rays generated from a single particle. At this stage, therefore, only their average compositions are discussed. Since precipitation was expected due to the metal-induced crosslinking of amine terminated dendrimers (PAMAM-NH_2), we prepared another type of Pt-Pd bimetal/dendrimer nanocomposite using PAMAM-NH_2 to obtain nanoparticles large enough to detect the X-ray generated from a single particle. For these alternative samples, the two elements were detected
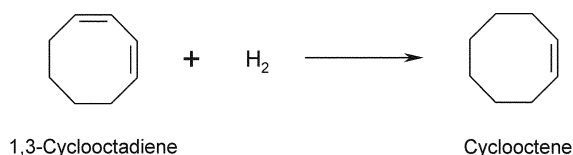
in all the particles analyzed and this clearly indicates that they are bimetallic ones.

The dendrimer-encapsulated Pt-Pd bimetallic nanoparticles were applied as catalyst to the partial hydrogenation of 1, 3-cyclooctadiene (see Fig. 19) in ethanol/water mixture (v/v=4/1). As shown in Fig. 20, the dendrimer-encapsulated Pt-Pd bimetallic nanoparticles were found to be effective in the partial hydrogenation of 1, 3-cyclooctadiene. This result indicates that, being different from the conventional polymer-stabilized nanoparticles, the catalytic nanoparticles which are sterically confined by dendrimer branches are available for reactants to access in catalytic reactions. In addition, it is worth noting that in the case of the 4th generation dendrimer, the compactness of dendrimer branching is not severe and thus would not restrict the accessibility of reactant to the active sites [Niu et al., 2001]. These unique features of the dendrimer nanoreactor make it possible to obtain the high catalytic activity.

Moreover, the catalytic activity of the bimetallic nanoparticles increased as the Pt/Pd ratio decreased and the catalytic activities of

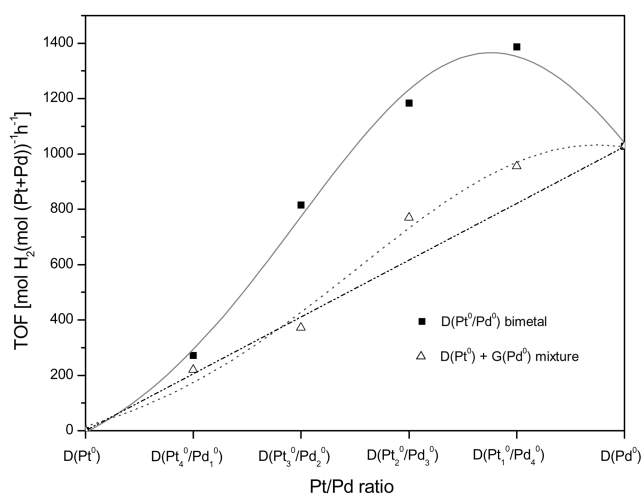**Fig. 19. Partial hydrogenation of 1,3-cyclooctadiene.**

Fig. 20. The dependence of the catalytic activity of the dendrimer-encapsulated Pt-Pd bimetallic nanoparticles on its composition in partial hydrogenation of 1, 3-cyclooctadiene.

$D(Pt_2^0/Pd_3^0)$ and $D(Pt_1^0/Pd_4^0)$ were higher than that of the palladium nanoparticles prepared by the same method. It should be noted that the enhanced catalytic activity of the bimetallic catalyst, which can be explained in terms of an ensemble and/or a ligand effect in catalysis, is hardly achievable in the case of physical mixtures of palladium and platinum nanoparticles. Similar results have also been reported for the case when Pt-Pd bimetallic nanoparticles were protected by polymer [Toshima et al., 1989, 1993].

The cyclooctene selectivity at the complete conversion of 1, 3-cyclooctadiene was higher than 99%, which is as high as that of the palladium nanoparticle catalyst.

2. Pd-Rh Bimetallic Nanoparticles

The preparation of Pd-Rh bimetallic nanoparticles within dendrimer nanoreactor was carried out by the method similar to the Pt-Pd ones except for the simultaneous use of two metal precursors, K_2PdCl_4 and $RhCl_3$ [Chung and Rhee, 2003c]. By preloading a dendrimer "nanoreactor" with suitable metal ions and then chemically reducing this composite in-situ, a dendrimer-encapsulated metal cluster was prepared. After reduction, the UV-vis spectra of the nanoparticles are different not only from those of the monometallic Pd or Rh nanoparticles but also from those of their physical mixtures regardless of the Pd/Rh ratios.

The HRTEM image of $D(Pd_1^0/Rh_2^0)$ shown Fig. 21 demonstrates that the particle size is uniform and the shape is nearly spherical. Similarly to the Pt-Pd case, bimetallic nanoparticles with a diameter of ~2.3 nm were prepared.

As presented in Fig. 22, the dendrimer-encapsulated Pd-Rh bimetallic nanoparticles were also applied as catalyst to the partial hydrogenation of 1, 3-cyclooctadiene and were found to be effective. In this case, however, the highest activity was achieved with a Pd/Rh ratio of 1/2. It should be noted that the activity is higher than that of the palladium or rhodium monometallic nanoparticles prepared by the same method.

3. Ag-Pd Bimetallic Nanoparticles

The preparation of bimetallic nanoparticles containing Ag and noble metals is more difficult than that of our previous Pt-Pd or Pd-Rh system because of the following reasons [Torigoe and Esumi, 1993]. First, there are few noble metal complexes soluble in water
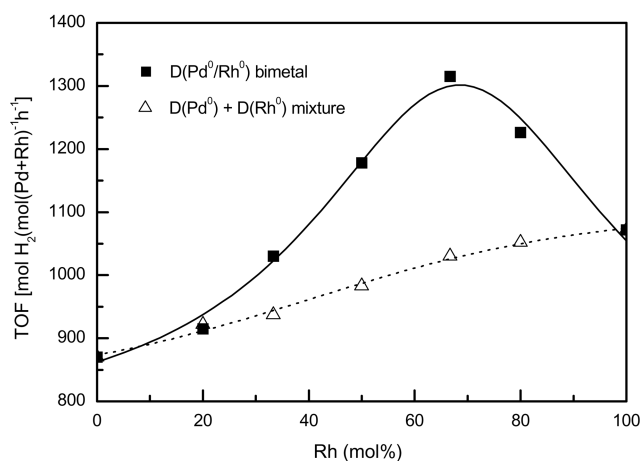

Fig. 22. The dependence of the catalytic activity of the dendrimer-encapsulated Pd-Rh bimetallic nanoparticles on its composition in partial hydrogenation of 1, 3-cyclooctadiene.

except for their halides. Unfortunately, however, Ag^+ ion readily reacts with halogen ions to provide water-insoluble silver halides. Hence, the choice of noble metal candidate to be mixed with a silver salt is restricted. In the case of other water-soluble noble metal compounds such as cyanides and ammine complexes, their strong binding with metal ions may give rise to another serious problem. They are less active than halides for elimination or substitution reactions of ligands, which is prerequisite before the reduction of metal ions [Cotton and Wilkinson, 1988]. Second, the standard electrode potential of Ag^+/Ag^0 is relatively high, so it often occurs that Ag^+ is reduced much more rapidly than other metal ions and hence bimetallic particles are hardly formed.

In addition, there are some intrinsic problems in the dendrimer templating systems. With PAMAM-OH dendrimer, cumbersome pH controls are required for the formation of Ag particles in the dendrimer cavity because Ag^+ ion cannot be spontaneously extracted into dendrimer [Zheng et al., 2002]. With PAMAM dendrimer, precipitation may occur because of the noble metal-induced crosslinking [Watanabe and Regen, 1994]. Only at low metal to dendrimer
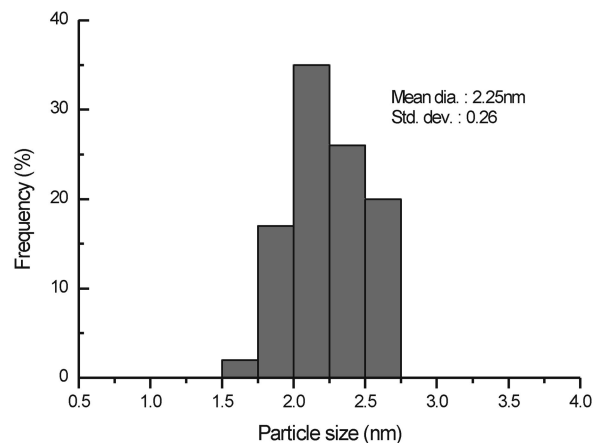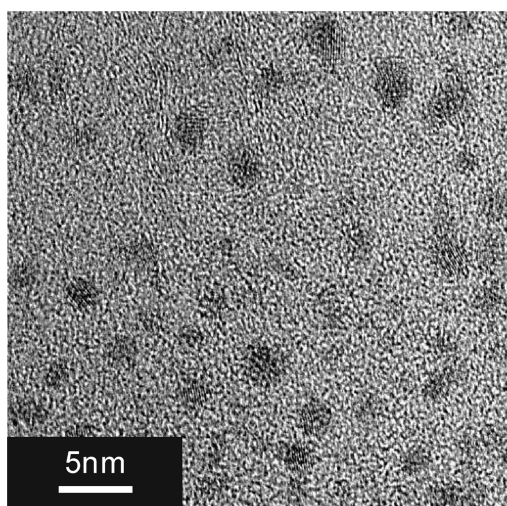

Fig. 21. HRTEM image and particle size distribution of Pd-Rh bimetallic nanoparticles with a Pd/Rh ratio of 1/2.
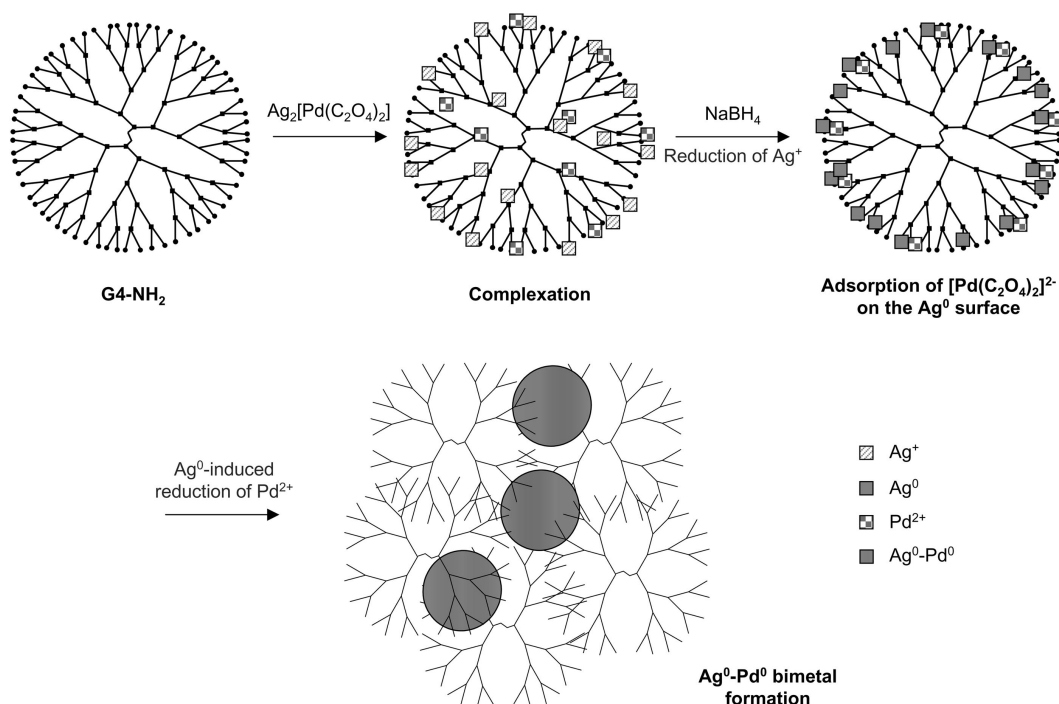
Fig. 23. Schematic diagram for the preparation of dendrimer-templated Ag-Pd bimetallic nanoparticles.

ratio can the unfavorable precipitation be prevented. Therefore, it is difficult to prepare Ag-Pd bimetallic nanoparticles with conventional metal precursors such as K_2PdCl_4 and $AgNO_3$ in dendrimer templating systems.

To solve the intrinsic problems of Ag-Pd systems, silver(I) bis (oxalato)palladate(II) complex was used [Chung and Rhee, 2003b]. The complex seems suitable for the Ag-Pd bimetal formation because two metal ions exist in one complex,, and thus the unfavorable formation of silver halides can be avoided. Moreover, the oxalate ligand rapidly decomposes by light irradiation or chemical reduction [Torigoe and Esumi, 1993]. A schematic illustration for the preparation of the dendrimer-templated Ag-Pd bimetallic nanoparticles is represented in Fig. 23.

The preparation of Ag-Pd bimetallic nanoparticles within dendrimer templates was carried out by a method similar to that for monometallic nanoparticles except for the use of silver(I) bis(oxalato) palladate(II) complex. Dilute aqueous solution of PAMAM dendrimer was mixed with the aqueous solution of oxalate complexes at controlled stoichiometries. After stirring the solution for 1 h, aqueous solution of $NaBH_4$ was slowly added and subsequently the two metal ions were simultaneously reduced to yield zero-valent metal particles. The light yellow dendrimer/(silver(I) bis(oxalato)palladate(II) complex) solution immediately turned dark brown or black indicating the formation of colloidal nanoparticles.

For the purpose of changing the Ag/Pd composition, $AgNO_3$ was mixed with $Ag_2[Pd(C_2O_4)_2]$ in the calculated ratio, and the mixed solution were reduced by $NaBH_4$ in the same manner. Monometallic Pd and Ag nanoparticles were prepared by the reduction of K_2PdCl_4 and $AgNO_3$, respectively. All of the resulting nanoparticles were very stable and there was no precipitation for up to six months.

Fig. 24 shows the changes in the absorption spectra of Ag and Pd metals (Ag/Pd ratio=2) during the course of the complexation
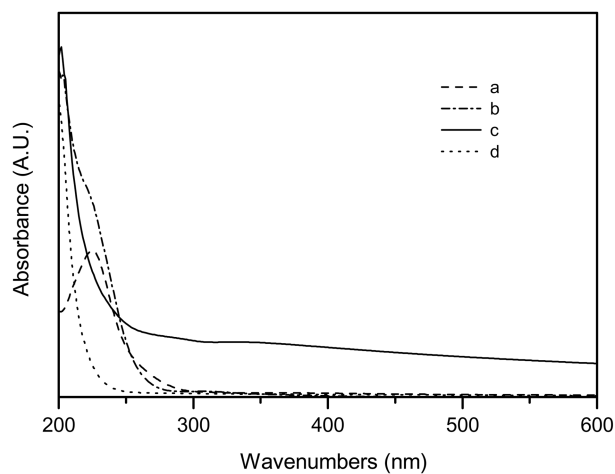

Fig. 24. Variations in the UV-vis spectra of Ag and Pd metals during the course of the complexation and the subsequent reduction.
a) 4 mM $Ag_2[Pd(C_2O_4)_2]$, b) complexation of metal ions with 40 mM dendrimer*, c) reduction with 40 mM $NaBH_4$, and d) PAMAM dendrimer (generation 4). *The concentration of dendrimer refers to the surface functional groups.

with dendrimer and the subsequent reduction. Concerning the metal ions, a mixed absorption peak of two metal ions is observed at 225 nm. After the addition of PAMAM to the solution of the $Ag_2[Pd(C_2O_4)_2]$, however, an enhanced absorption band around 230 nm appears. This indicates that the two metal ions are complexed with the dendrimer. After reduction, the band observed in the former case completely disappears and a new broad absorption band appears over a wide wavelength range.

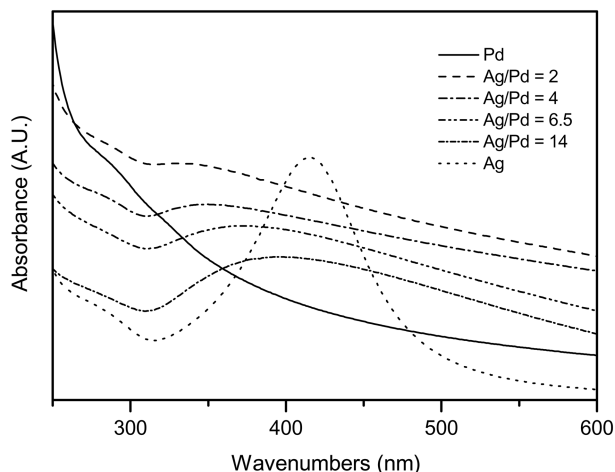Fig. 25 presents a series of UV-vis spectra of the Ag-Pd bime-

Fig. 25. UV-vis spectra of Ag-Pd bimetallic nanoparticles with various Ag/Pd ratios.

Fig. 27. Variations of particle size with the change of Ag/Pd ratio.

tallic nanoparticles with various Ag/Pd ratios. As the Ag/Pd ratio increases, the λ_{max} shifts to a shorter wavelength. Moreover, it is noted that the spectra of the resulting nanoparticles are different not only from those of the monometallic Ag or Pd nanoparticles but also from those of their physical mixtures. Therefore, the characteristic absorption spectra strongly suggest the formation of Ag-Pd bimetallic nanoparticles. The broadening of plasmon peak results from an overlap between surface plasmon band and interband transitions. According to Creighton et al., [Creighton and Eadon, 1991], silver displays approximately free-electron behavior in the visible range which gives rise to a sharp absorption band, while other metals including Pd are less free-electron metals, resulting in a broad absorption band. An intermediate bandwidth between Ag and Pd shown in Fig. 25 is consistent with the theory and may be considered as another evidence for the formation of Ag-Pd bimetallic nanoparticles.

The representative HRTEM image of G4-NH$_2$(Ag$_2^0$/Pd$_1^0$) is shown in Fig. 26. The microscopy demonstrates that the particle size is uniform and the shape is nearly spherical. Bimetallic nanoparticles
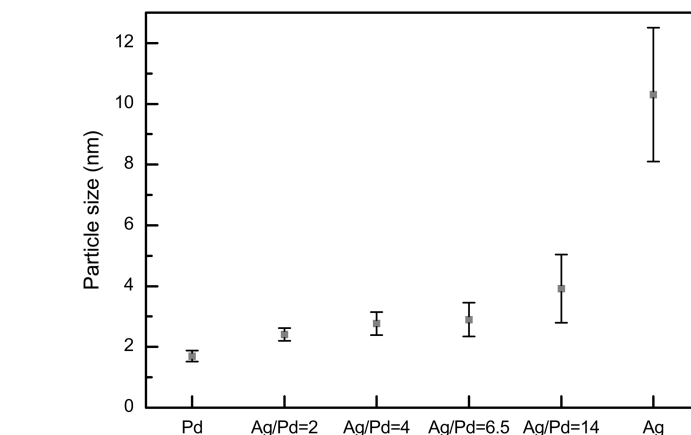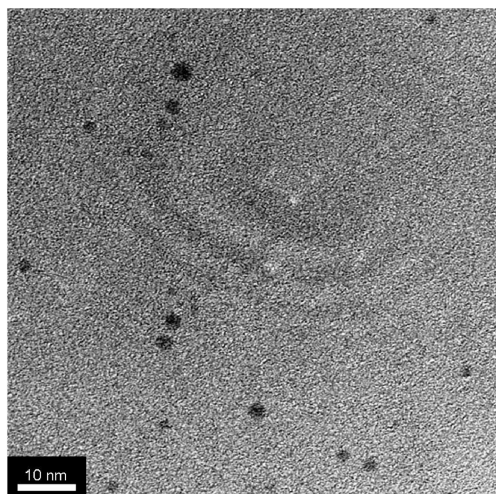
with a diameter of ~2.4±0.2 nm are observed. The variations of particle size with the change of Ag/Pd ratio are presented in Fig. 27. It is observed that the average particle size increases with the increase of Ag content. Compared with Ag nanoparticles which show broader size distributions with larger particle size, the particle size distributions of Ag/Pd bimetallic nanoparticles remain in the range of 2-5 nm regardless of the Ag/Pd ratio. The narrow particle size distributions may be another evidence of bimetal formation.

SUMMARY AND OUTLOOK

Heterogenization of homogeneous catalysts has been carried out by the immobilization of homogeneous species on polymer or silica support. Although considerable attention was paid to this technique over the past decade, the efficiency of the heterogenized catalysts is found generally lower than that of their homogeneous counterparts and remains unsatisfactory. There exist many intrinsic problems of solid support such as the diffusion resistance, the heterogeneous chemical nature, and the low concentration of active sites.

Dendrimer, a new class of well-defined macromolecules exhibiting a tree-like structure, emerges as an alternative for the achieve-
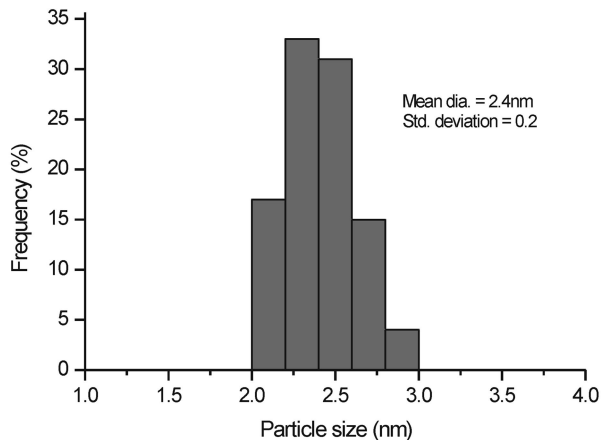

Fig. 26. HRTEM image and particle size distribution of Ag-Pd bimetallic nanoparticles with Ag/Pd ratio of 2.

ment of the elusive goal. Indeed, in the past decade the dendrimer chemistry including catalysis has been extremely popular. It is clear from the contributions of many groups that dendrimer has been considered as one of the most promising candidates accommodating the conditions for an ideal catalyst and consequently has provided new opportunities for bridging the gap between homogeneous and heterogeneous catalysts.

The approach described here for the design of dendrimer-based catalytic systems including dendritic chiral auxiliaries and dendrimer nanoreactors may be the examples of dendrimer-based catalysis taking full advantage of the unique aspects of dendrimer structure: chemistry of terminal groups, generation-dependent reaction performance, easy recovery of catalysts, and accommodation of guest molecules.

Although the research in this area still remains in its infancy, it is clear that the dendrimer-related catalytic systems will be applicable to various reaction systems and further pave the way to new catalysis. However, it is worth noting that high turnover numbers of dendrimer catalysts and development of a cheaper alternative such as hyper-branched polymer are prerequisite before these sophisticated systems become attractive for commercial applications.

ACKNOWLEDGMENT

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