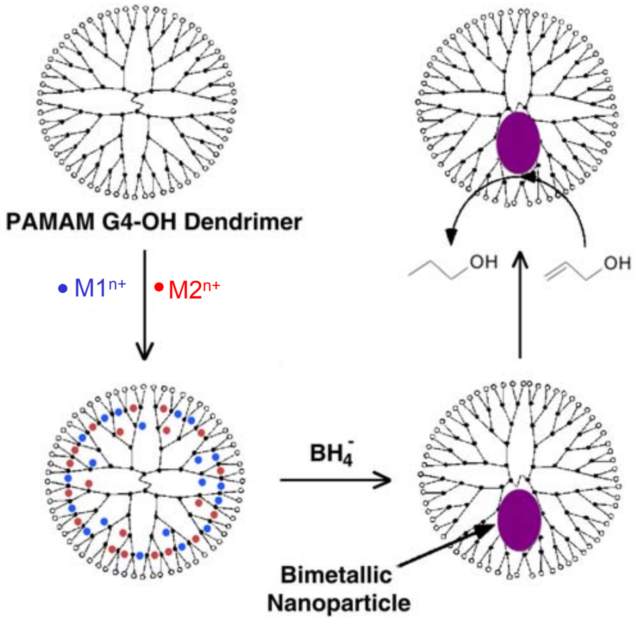
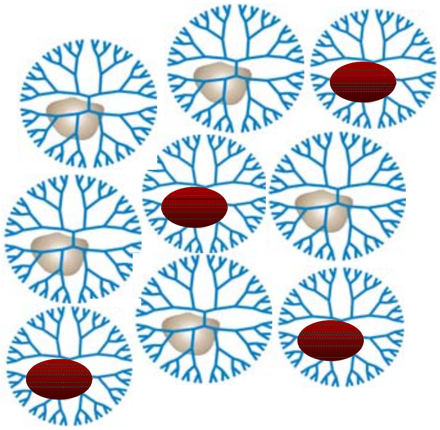
Research Proposal

An Investigation of Structure-Function Relationships Using Dendrimer-Encapsulated Bimetallic Nanoparticles





Orla Wilson

Department of Chemistry

Texas A&M University

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10:00

Room 011

Introduction and Objectives

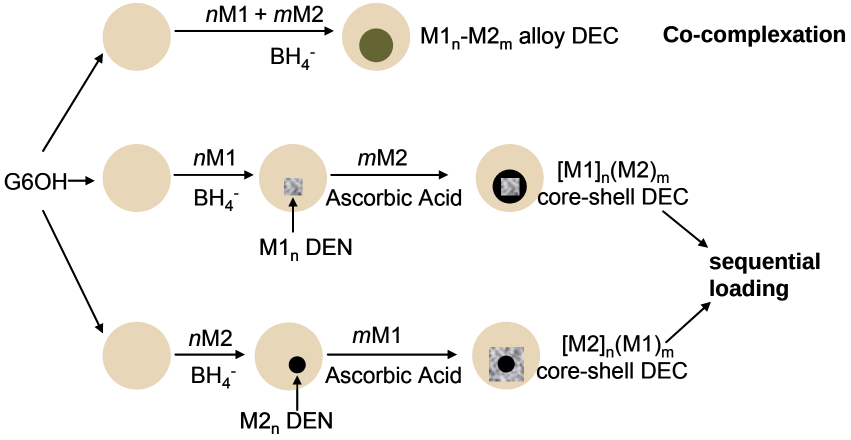
"….At this length scale, the physical, chemical and biological properties of materials differ fundamentally and often unexpectedly from those of the corresponding bulk materials. Nanotechnology R&D is directed towards understanding and creating materials, devices and systems that exploit these fundamentally new properties, phenomena and functions". This is taken from the Supplement to the President's FY 2004 Budget and is part of the National Nanotechnology Initiative. It is within this realm that we are working to try and understand and improve the design, fabrication, manipulation, and applications of dendrimer-encapsulated nanoparticles (DENs).

An in-depth understanding of the structure of nanoscopic metal particles is perhaps the main hurdle to attaining complete control over the resulting function of the material. Once the structure is fully rationalized, the entire scope of functionality should become clear. The applications (potential or actual) of metal nanoparticles has provoked a lot of research interest in recent years due to their inherently interesting physical and chemical properties. Our group has been particularly concerned with the novel catalytic properties of sub-3 nm, almost-monodisperse noble metallic and, more recently bimetallic nanoparticles and the exploitation thereof.[1-12] Our well-established, dendrimer-templated synthesis leads to almost monodisperse metal nanoparticles housed within the interior of the dendrimer. Within this nanoreactor, part of the surface of the nanoparticles remains essentially unpassivated, thereby providing a novel catalytic body at which substrates can undergo reactions before exiting by diffusion through the porous dendritic structure. Our timely discovery relating to the synthesis of dendrimer-encapsulated bimetallic nanoparticles (DEBNs) opens up a plethora of new avenues to further probe the catalytic properties of DENs, as bimetallic nanoparticles are even more important than their monometallic counterparts in the field of catalysis. This is due to the fact that their activity and selectivity has been shown to exceed that of the individual components.[13] It is in the particular areas of the fabrication, characterization and applications of DEBNs that my research proposal will focus, with specific attention being paid to examining the relationship between the structure of the bimetallic nanoparticle and its concomitant function. This is an important goal, because if we can understand precisely the factors that determine the reactivity of a nanoparticle, it then becomes feasible to propose that sites with very specified functions e.g. catalytic activity can be designed. The importance of understanding the nanoparticles reactivity is exemplified by the discovery that Au, hitherto considered catalytically inactive, displays high catalytic activity, within a certain size-regime and on certain supports, for particular reactions.[14,15]

It is my intention to study the synthesis and characterization of DEBNs and to subsequently correlate the bimetallic nanoparticle structure with its properties. By utilizing the DEBNs as both heterogeneous and homogeneous catalysts, and as optical probes, a wealth of knowledge should be attainable to aid in determining the extent of architectural control we can obtain in our synthesis. I also intend to examine the assembly of DENs and DEBNs as it is well accepted that in order to use nanoparticles in functional devices it is going to be first necessary to assemble them into superstructures. This is the only way that the full technological potential of nanomaterials can be attained and as such is an important part of our research.

Background

Since this group's discovery in 1998 that the synthesis of almost monodisperse metal nanoparticles was possible within the interior of a dendrimer template, much effort has been spent on understanding the scope of this facile process and examining the applications of these DENs. What we have realized is that (a) a number of metals and even semi-conductors, can be directly synthesized within the templates, namely Cu,[1] Pt,[3] Pd,[2] Au,[9] CdS.[16] Metals with weak or no interaction with the interior amines such as Ag, can be synthesized through a displacement method;[17] (b) because the solubility and surface reactivity of the dendrimers can be tuned, the DENs can be synthesized in a variety of environments, such as $scCO_2$;[4] (c) the steric crowding on the dendrimer periphery, which increases with increasing generation, can act as a size-and-shape selective molecular filter which endows the encapsulated catalyst with selectivity;[10] (d) the almost monodisperse DENs can be extracted intact from the dendrimer template using a thiol ligand to give monodisperse monolayer-protected clusters (MPCs);[18] and (e) it is possible to synthesize dendrimer-encapsulated bimetallic nanoparticles (DEBNs) by either co-complexation or sequential loading methods, Scheme 1.[12,19] With all this valuable information it should now be possible to further probe the relationship between the structure of the DEBNs and their concomitant function.



Scheme 1

Bimetallic nanoparticles as catalysts

As mentioned in the introduction, the importance of bimetallic catalysts is due to the fact that their activity and selectivity has been shown to exceed that of the individual components.[13] It is also well established that the electronic properties of nanoparticles are strongly correlated with their catalytic efficiency. In the case of bimetallic catalysts, the "electronic effect" which describes the charge transfer that takes place, plays a big role. When an atom with a filled d-shell (eg. Cu) comes in contact with one that has an unfilled valence shell (eg. Ni), the latter gains electrons from the former.[13] One of the many examples of bimetallic catalysts that have been widely investigated is PtRu, which has an important application as a CO-tolerant anode catalyst in direct-methanol fuel cells.[20] Compared to pure Pt catalysts, incorporation of Ru enhances the catalytic oxidation of adsorbed CO to CO_2 thereby preventing CO poisoning of the catalyst – a common occurrence with Pt catalysts. More often than not, reports on the synthesis of new bimetallic clusters involve pairs of noble metals whereas noble metal/light transition metals are less frequently investigated. This is despite the fact that noble metal/light transition metal systems possibly have more potential for tailoring catalytic properties. Depending on the strength of the heteronuclear bond formed between the adjacent different metals, the strength of the adsorption of a substrate will be inversely affected. In other words, an increase in the strength of the metal1-metal2 bond compared to the pure metal will result in a proportional weakening in the strength of any chemisorbed molecule to the bimetallic surface and an increase in the catalytic rate.

There have been numerous reviews concerning the physical, chemical and electronic properties of bimetallic clusters in the recent literature, however an in-depth discussion of this area is beyond the scope of this proposal.[13,21-23] We have previously demonstrated a range of reactions in which DENs function efficiently as catalysts due to their large surface-to-volume ratio and partly unpassivated surface.[7] However, the main reaction that has been used to probe the catalytic activity of DE(B)Ns, and which I will continue to use for further analogous investigations of DEBNs, is the simple hydrogenation of unsaturated organic compounds such as allyl alcohol.[2,6,10,12,19] In addition I will use other simple catalytic reactions, namely the hydration of acrylonitrile and the reduction of nitrophenol, and a more involved "Wacker" oxidation of an olefin to investigate structure-function relationships. As these reactions have been widely investigated and documented[12,19,24-26] they are ideal candidates for examining the catalytic efficiency of new DEBNs.

Extraction of DENs from template to yield MPCs

We have recently demonstrated that Pd nanoparticles can be extracted from a dendrimer template and transferred to an organic phase using an alkanethiol surfactant, while leaving the dendrimer intact.[18] That this process is feasible clearly demonstrates that complicated chemistry, such as the formation of a covalent bond on the nanoparticle surface, can take place within the dendrimer template. Other events such as electron-transfer, molecular transport, self-assembly and transport of the nanoparticle are also clearly possible within the dendrimer nanoreactor. In addition, this appears to be an useful and facile route to obtaining more monodisperse monolayer-protected clusters (MPCs)[27] than has previously been possible. In general multi-step purification processes are necessary before a metal nanoparticle MPC sample is considered monodisperse. Methods that have been used to increase monodispersity include size-selective precipitation,[28,29] chromatography,[30] and annealing.[31] Here, we have shown that by using the dendrimer template to initially form a monodisperse nanoparticle, the resultant MPC sample needs no further purification. FT-IR spectroscopy was used to ascertain the whereabouts of the dendrimer after extraction – the amide bands, characteristic of PAMAM dendrimers were only present in the aqueous phase. Additionally, a fresh batch of DENs could be synthesized in the aqueous phase isolated from the first extraction, which also demonstrates that the template can be recycled. Extraction of Au,[32] Ag[33] and AuAg alloy[33] DENs is also possible using an alkanethiol surfactant. While alkanethiol molecules were the obvious choice for initial experiments due to their well-known strong interaction with metal surfaces (in particular Au), we speculated that it might be possible to extract different metals using selective ligands; the initial results of a study designed to test the feasibility of this idea will be discussed later. This process would be somewhat analogous to the concept of "Orthogonal Assembly" first described in 1989 by the Wrighton and Whitesides groups, Fig. 1.[34] The authors demonstrated that two different surfactants could selectively interact with a surface composed of two different materials, thus forming two chemically distinct self-assembled monolayers on a single substrate.

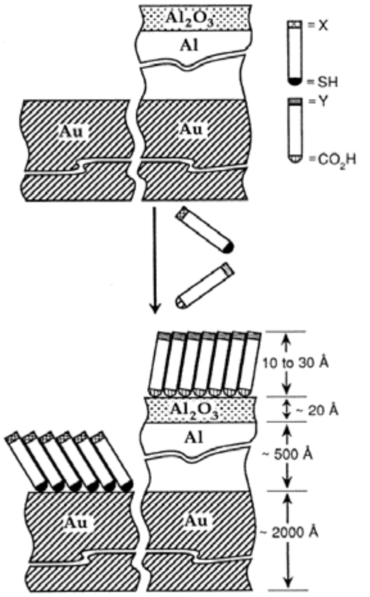


Figure 1. Illustration of the formation of orthogonal SAMs[34]

Assembly of Nanoparticles

There has been a lot of recent interest in the area of nanoparticle assembly due to the realization that in order to construct useful devices from the almost monodisperse nanoparticles that now abound, robust methods of assembly are required. Late last year for example, a Faraday Discussion took place entitled "Nanoparticle Assemblies", which covered many aspects of producing structures from nanoparticles. Some of the earliest reports of large-scale ordering of nanocrystals upon solvent evaporation involved thiol-passivated Au and Ag MPCs.[27,29,35-38] Slow solvent evaporation and monodisperse particles are the driving forces for the organization, and the smaller than expected distance between adjacent particles is explained by the interdigitation of the alkane chains protruding from neighboring nanoparticles.[35] Of these reports, the most recent describes the ordered assembly of different-sized thiol-functionalized Au and Ag superlattices into a colloidal alloy superstructure. The assembly described in this report by Kiely *et al.* relies on the ratio between (a) the radii of the Au and Ag nanoparticles, and (b) the concentration of the nanoparticles, and it is only within a very tight range that perfect structures can be formed. Other routes to the assembly of metal nanoparticles that have been investigated include the use of complementary strands of DNA,[39,40] and a 'brick and mortar' approach in which gold MPCs were functionalized with molecular-recognition elements in the ligand shell.[41] Controllable assembly was shown to occur in the latter case when a diaminotriazine-thymine hydrogen bonding interaction was initiated.

Preliminary Results

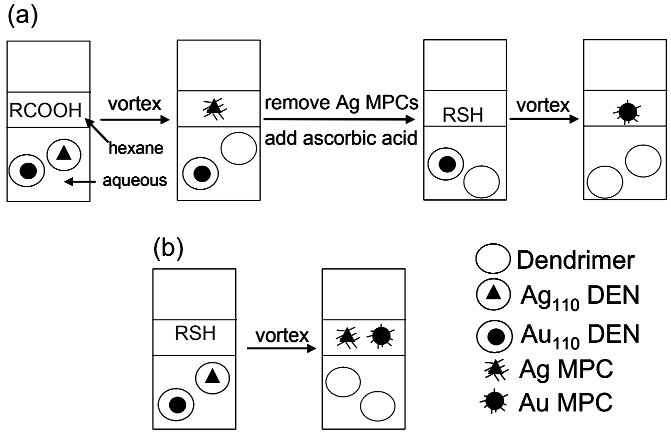
Synthesis of Dendrimer-Encapsulated Bimetallic Nanoparticles

Recently our group reported the synthesis of PtPd DEBNs using a co-complexation route. The bimetallic nature of individual particles was confirmed using single-particle x-ray energy dispersive spectroscopy (EDS). The nanoparticle size and composition could be controlled by the stoichometric loading of metal ions into the dendrimer. The catalytic activity of these DEBNs for the hydrogenation of allyl alcohol was monitored and found to be enhanced for Pd-rich DEBNs compared to either of the corresponding monometallic DENs. Chung and Rhee have reported similar results for PdPt[42] and PdRh[43] DEBNs, but there is no other literature pertaining to DEBNs. We will soon publish a report in which the synthesis and catalytic activity of structurally well-defined bimetallic PdAu dendrimer-encapsulated catalysts is described.[19] In this case, we have shown that some control over the structure of the bimetallic nanoparticle seems to be possible through the sequential loading method whereby a DEN of one of the metal is used as a seed for the deposition of the second shell metal, Scheme 1. While it is likely that some surface alloying occurs initially, it is also likely that as the shell thickness increases, the surface becomes enriched in the shell metal. UV-vis absorption spectroscopy of the DEBNs differed considerably depending on whether the co-complexation or sequential loading method was used for the synthesis. We have demonstrated that (a) as the shell metal is reduced onto the seed, the size of the resulting particles increases with a dependence that tracks the metal loading; and (b) the catalytic rate for the hydrogenation of allyl alcohol is enhanced for PdAu dendrimer-encapsulated catalysts compared to the monometallic equivalents.

A New Chemical Method for the Characterization of Metal Nanoparticles

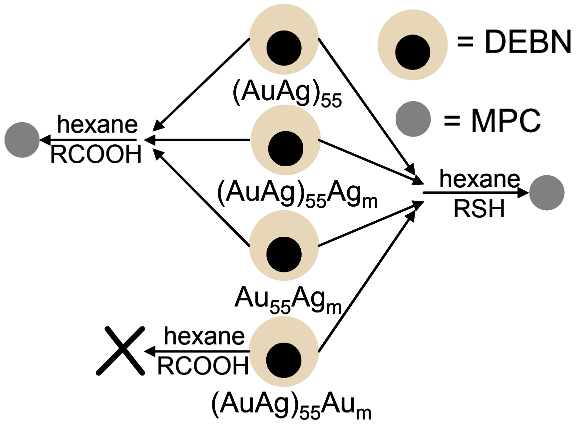
Separation of Dendrimer-Encapsulated Au and Ag nanoparticles by Selective Extraction

We have applied the concept of Orthogonal Assembly, Figure 1,[34] to a mixture of DENs and will soon report the separation of individual metals from an aqueous mixture of Au and Ag DENs using a selective extraction approach, Scheme 2(a).[44] In this method, a carboxylic acid surfactant with enhanced selectivity for Ag over Au is added to the aqueous mixture of DENs in an immiscible solvent. Through a strong ligand-nanoparticle interaction, the Ag nanoparticles can be extracted from the mixture into the organic phase resulting in a solution of Ag MPCs. Subsequent addition of a thiol surfactant can lead to extraction of the remaining Au into a new organic phase. By careful choice of the surfactants, simultaneous extraction of the two metals can be avoided. It is also possible, by judicious choice of the surfactant and conditions, to extract both metals at the same time, Scheme 2(b). These experiments are of great importance because they demonstrate unambiguous selectivity of a surfactant for nanoparticles of one metal over the other, allowing chemical separation of nanoparticles based solely on their composition. In addition, it potentially provides a facile chemical means of identifying the surface metal in a bimetallic ensemble. While we have focused on the separation of Au and Ag nanoparticles in this work, this methodology should prove to be easily adaptable to the separation and consequent identification of other metal and semiconducting nanoparticles. In addition to structure elucidation this chemical technique will also be useful in the purification of samples containing a mixture of bimetallic nanoparticles. For example, it is envisioned that under certain conditions AuAg alloy nanoparticles could be separated from core-shell particles or from monometallic nanoparticles that may have formed during the reduction step.



Scheme 2

Synthesis, Characterization and Structure-Dependent Extraction of AuAg Bimetallic DENs



Scheme 3

We have demonstrated the synthesis and characterization of bimetallic AuAg dendrimer-encapsulated nanoparticles (DENs) having differing structures. We have further shown that depending on the surface metal and its oxidation state, these nanoparticles can be extracted from the dendrimer into an organic phase using very different surfactants, Scheme 3. The significance of this work lies in the fact that, after utilizing the templating ability of the dendrimer in the synthesis step, we employ our new chemical strategy of selective extraction to identify the surface metal. Overall, four different bimetallic systems were examined – AuAg alloys synthesized by our previously described co-complexation route,[12,19] and core-shell ((C)S) structures where the core and the shell are (a) Au and Ag; (b) AuAg alloy and Au; and (c) AuAg alloy and Ag respectively. All four types of bimetallic DENs can be extracted from their host using alkanethiol molecules when the particles are in a reduced state. Conversely, only those with an oxidized Ag surface can be extracted using alkanoic acids. This important finding adds a valuable and accessible chemical characterization tool to the expensive, time-consuming, and highly-specialized tools available for routine characterization of sub -3 nm bimetallic nanoparticles.

Single-particle x-ray EDS carried out on AuAg alloys before and after extraction with decanoic acid indicates that all individual particles are bimetallic with percentage compositions of 37 ± 6% Ag and 63 ± 6% Au before extraction and 39 ± 12% Ag and 61 ± 12% Au after extraction. This is convincing evidence that after the extraction the particles are indeed the same as they were before. This conclusion is supported by HRTEM results, which indicate that the particle size distribution is not significantly altered by the extraction process. Taken together, this work demonstrates that we can use selective extraction as a valuable aid in identifying the surface composition in a bimetallic nanoparticle. It is also a fine example of a structure-function relationship, in that the extraction step depends on the structure of the DEBN.

Fabrication of heterogeneous catalysts

The objective of this work was to deposit near-monodisperse metallic and bimetallic DENs onto metal oxide surfaces and to examine the resulting heterogeneous materials for catalytic activity for the oxidation of CO. Attempts were made to fabricate size-monodisperse heterogeneous Au catalysts on a TiO_2 support starting from Au DENs. The process involved the synthesis of 1 mL of 1 wt% Au DENs, their incorporation onto a high surface area TiO_2 support via wetness impregnation, followed by attempted removal of the dendrimer by calcination or oxygen plasma treatment. UV-vis and TEM was carried out at each stage of the manipulation and revealed good size retention after each step. Thermogravimetric analysis (TGA) was carried out after the wet impregnation step to determine the decomposition temperature of the dendrimer. The final Au/TiO_2 nanocomposite did not show any catalytic activity for the oxidation of CO and it was concluded that this was due to either (a) the particle size of the Au

DENs being too small to show activity or (b) incomplete removal of the dendrimer resulting in a layer of carbon surrounding the Au nanoparticle rendering it catalytically inactive. The size-dependence of the melting point of Au nanoparticles is a well-known phenomenon, with the melting point dramatically lowering as the particle diameter becomes less than 3 nm.[45,46] For this reason, attempts to remove the dendrimer by high-temperature calcination resulted in large aggregates of particles due to the Au melting and agglomerating. We have also examined the synthesis of heterogeneous catalysts by incorporation of DENs into an amorphous titania network and found that this route leads to active Pd and AuPd heterogeneous catalysts.[47]

Proposed research

My preliminary results indicate that it is possible to (1) synthesize DEBNs and characterize the resulting particles using both physical and chemical techniques, and (2) attain some control over the resulting structure of the DEBN. Next, I will propose my future research based on these preliminary findings.

(a) Synthesis, characterization and catalytic studies with PdCu DEBNs

It is my intention to take what we have learned thus far regarding the synthesis of DEBNs and apply it to a new bimetallic system – that of PdCu catalysts. Both of these metals are known to complex with the interior amines of PAMAM dendrimers (this complexation can be followed by UV-vis absorption spectroscopy) and have been shown to form monometallic DENs by our group.[1,2] PdCu bimetallic nanoalloys have been recognized as important selective catalysts for a number of years[48] both for the hydration of acrylonitrile and the hydrogenation of cyclooctadiene. They have also found wide usage in the removal of nitrates from aqueous solutions.[49]

PdCu DEBNs will be synthesized by both the co-complexation and sequential addition approaches that we have used to produce PdPt,[12] AuPd[19] and AuAg[33] DEBNs. In the case of co-complexation, the coordination of metal salts to the interior amines of the dendrimer will be followed using UV-vis absorption spectroscopy prior to reduction. For the sequential addition synthesis, a range of weak reducing agents will be investigated for the second reduction step. We already know that H_2 gas only reduces Pd^{2+} to Pd metal in the presence of preformed seeds,[19] that ascorbic acid reduces Pd, Au and Ag only in the presence of a preformed seed,[19,33,50] and that hydroxlyamine reduction of Ag^{+} in the presence of Au seeds leads exclusively to Au-Ag core-shell structures.[51,52] Secondary nucleation of monometallic nanoparticles has not been observed in any of these cases. These reducing agents will be examined to determine which, if any, are suitable for the reduction of Pd^{2+} and Cu^{2+} salts in the presence of preformed seeds. Initial characterization will be carried out by UV-vis absorption spectroscopy. While neither Cu nor Pd nanoparticles have very strong surface plasmon bands, Cu does have an identifiable broad shoulder at 555 nm[53] which may aid in the UV-vis studies. These particles will be analyzed here by HRTEM in order to determine their size and dispersity. Depending on the length of time before the new TEM is available for use at TAMU, single particle elemental analysis will be carried out either here or at ORNL. This will confirm the bimetallic nature of the individual nanoparticles.

One of the catalytic reactions that will be used to examine the structure-function relationship of these materials is the selective hydration of acrylonitrile to acrylamide, Figure 2, which is catalyzed by Cu nanoparticles.[24,48] This reaction is an example of the "ensemble" effect in catalysis as the seven-fold catalytic enhancement in the presence of Pd is due to the proximity of the two metals on the surface of the nanoparticle. As can be seen from the figure, the C=C bond of the substrate coordinates with the Pd site on the particle surface resulting in the C≡N bond being much closer to the Cu active site where it readily undergoes hydration. This reaction is almost 100% selective for the amide, and the product analysis will be carried out using gas chromatography (GC). It is hypothesized that by changing the metal composition of the bimetallic particles, a large variation in the yield of acrylamide will be observed. Not only will the initial Cu:Pd metal ratio be varied for the co-complexation synthesis, resulting in different surface properties of the particle, but the method of synthesis will also be varied. Using the previously described sequential addition method it may be possible to completely block one or other of the metals from the surface. This may result in "turning off" the catalyst when Pd is added as the shell metal. If such an event occurs these results can be used to provide insight into the DEBN structure. In particular, if the catalytic activity disappears when Pd is theoretically present as the shell metal and there are certain conditions whereby selective extraction can be used to differentiate between Cu and Pd surfaces, these experiments will proove to be powerful in elucidating structure-function relationships.

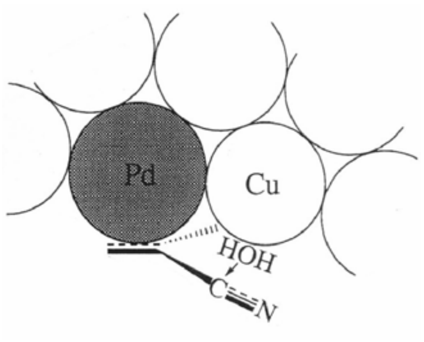


Figure 2. Schematic of the acceleration effect of Pd on the hydration of acrylonitrile.[54]

The same PdCu DEBNs will also be used as catalysts for the hydrogenation of 1,3-cyclooctadiene,[48] which is a reaction routinely catalyzed by Pd nanoparticles.[48] Cu nanoparticles on the other hand are ineffective as catalysts for this reaction. A maximum in the catalytic activity has been observed for PdCu=1, while the selectivity is highest at a PdCu ratio of 2:1. Because catalytic reactions can only occur at the surface of the particles, deposition of a thick shell of Cu onto Pd DENs may again result in the catalysis being turned off. Figure 3 shows that the rates for the hydration and hydrogenation reactions are inverted as a function of the PdCu ratio. While acknowledging the likely initial formation of a surface alloy, it is proposed that at least 3 shells of Cu be deposited onto the seed (or 3 shells of Pd deposited onto a Cu seed), at which point surface-enrichment with the shell metal would be anticipated. This will entail using dendrimers with generations as high as 8 to provide enough room for the thick shell or, in the case of co-complexation, enough interior amine groups to complex all the metal ions needed.

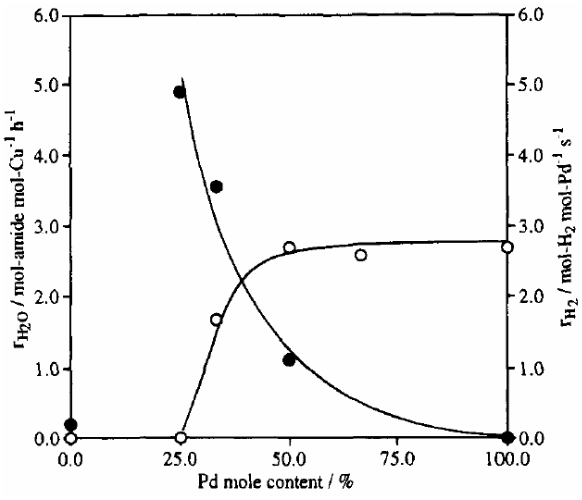


Figure 3. Plots of initial rates of hydration (●) and hydrogenation reactions (○) vs. the Cu/Pd ratio.[48]

(b) The Wacker Reaction

The earliest catalytic use of palladium was in the Wacker reaction, which, in its most important industrial form, involves the oxidation of ethylene with water to form acetaldehyde, Equation 1. This oxidation typically involves a $PdCl_2/CuCl_2$ catalyst-cocatalyst system, acidic media (usually HCl) and the presence of molecular oxygen. The HCl aids the copper co-catalyst in the reoxidation of Pd^0 to Pd^{2+}, and molecular oxygen reoxidizes Cu^+ to Cu^{2+}, thus keeping the catalytic cycle in motion.[25] By carrying out the reaction in the presence of alcohols, an acetal or ketal will be the final product.[56] There has been a lot of recent interest in attempts to develop HCl-free Wacker systems to circumvent both corrosion of reactors and the formation of chlorinated side-products. Last year, a Japanese group reported the preparation of a heterogeneous catalyst composed of a Pd cluster immobilized on a TiO_2 matrix, which demonstrated efficient catalytic activity for the Wacker oxidation of 1-decene to 2-decanone in acid-free conditions, Figure 4.[55] The best selectivity and yields of reaction product were obtained in the presence of $CuCl_2.H_2O$, H_2O and O_2. The oxidations of other terminal olefins were shown to be catalyzed equally well with the Pd/TiO_2 immobilized cluster, while that of internal olefins such as cis-2-decene, resulted in low yields of 2- and 3-decanone.

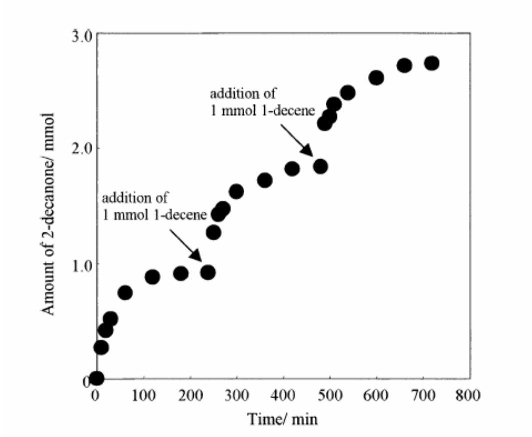


Figure 4. Wacker oxidation of 1-decene to 2-decanone[55]

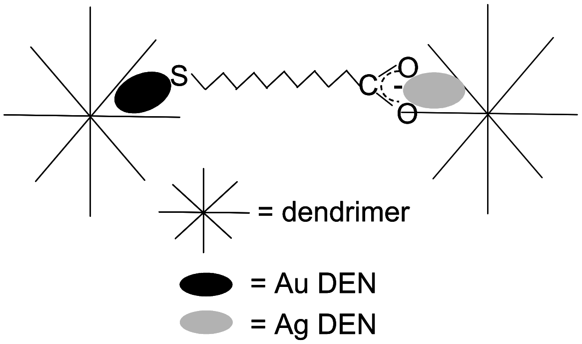
$$\begin{array}{rcl} H_2C{=}CH_2 + H_2O + PdCl_2 & \rightarrow & H_3C\text{-}CH{=}O + Pd(0) + 2HCl \\ Pd(0) + 2CuCl_2 & \rightarrow & PdCl_2 + 2CuCl \\ 2CuCl + 2HCl + 0.5O_2 & \rightarrow & 2CuCl_2 + H_2O \\ \hline H_2C{=}CH_2 + 0.5O_2 & \rightarrow & H_3C\text{-}CH{=}O \end{array} \qquad (1)$$

Since we can now routinely synthesize Pd DENs and potentially PdCu DEBNs, it will be of interest to examine their catalytic activity for Wacker-type oxidations as this would provide us with a deeper understanding of how DENs participate in more complicated catalytic reactions. If there is catalytic activity it would suggest that there is a mixture of oxidation states present in the bimetallic nanoparticle. It may also be possible to infer that the different metal atoms within the nanoparticle can act independently as well as cooperatively in order to catalyze the oxidation reaction. The effect of Cu will be investigated in two ways: 1) by determining the catalytic activity, if any, of PdCu DEBNs, and 2) by using Pd DENs and complexing Cu^{2+} ions with the interior amine groups of the dendrimer after reduction of the Pd^{2+}. In either case, the Cu^{2+} ions will be in close proximity to the Pd^0 atoms, the surface of the nanoparticle will be essentially free for catalysis and the molecular oxygen, whose function is to reoxidize the Cu^+ to Cu^{2+} , will be able to diffuse in and out of the dendrimer. Preliminary experiments will be carried out using the most favorable experimental conditions for the oxidation of 1-decene as determined by Choi et al.[55] According to their results the product yield in the absence of O_2, H_2O or $CuCl_2.2H_2O$ drops from 88% to less than 1% so it should be easy to determine whether or not the catalyst is active. All product identification and analysis will again be carried out by GC and the product will be confirmed by NMR.

(c) Reduction of p-nitrophenol using Ag DENs and AgX DEBNs

Ag nanoparticles are known to be active redox catalysts due to their ability to store electrons and thus act as a substrate for electron transfer between reactants in solution.[57] However, most investigations addressing the extent to which Ag nanoparticles catalyze reactions only deal with particles that are much bigger[26,58,59] than those we can prepare using a Cu displacement reaction developed previously by our group.[17] With this in mind, I propose to look at the catalytic effect of small Ag DENs for the reduction of *p*-nitrophenol, which is a reaction that can be easily monitored spectrophotometrically. Subsequently, a second metal will be added (Au or Pd) and its effect on the catalytic rate will be investigated. A recent publication by Esumi's group described the synthesis of dendrimer-*stabilized* Ag nanoparticles having a size distribution of 5.5 ± 1.9 nm. In this case the Ag nanoparticles are passivated by numerous dendrimer molecules on their surface, but there is no templating effect of the dendrimer. These particles displayed inferior catalytic activity compared to either Pt- or Pd-dendrimer nanocomposites which were also investigated. In this case the latter two metals had a much smaller size and polydispersity than their Ag counterparts. This suggests that Ag DENs and DEBNs with a small size and narrow size distribution may well be worth investigating as they could potentially provide valuable information about their size- and structure-dependent electrocatalytic ability.

(d) Assembly of mono- and bi-metallic DENs into organized structures



Scheme 4

Efforts will be made to examine the fabrication of organized assemblies of DENs and/or DEBNs in solution and their deposition onto surfaces for analysis. As a first step, I will use the selectivity already demonstrated by our selective extraction experiment to assemble similarly-sized Au and Ag DENs using mercaptoalkanoic acids. Here it is anticipated that if mercaptoundecanoic acid is added first to a solution of Au DENs the thiol will bind strongly to the Au surface. On subsequent addition of Ag DENs, the free carboxylate group of the ligand would be expected, under controlled conditions to passivate the surface of the Ag DENs, Scheme 4. While it is not clear if the particles will be extracted form the dendrimer when the ligand addition is carried out in the same phase, it will be an interesting experiment that may yield important results as it would be a purely chemical means of assembly. Other routes used to create assemblies of nanoparticles that were already discussed rely on non-chemical factors and as such are limited in their scope. A purely chemcial route may be more robust and widely applicable and is therefore worth pursuing. It is envisaged that the distance between the two particles can be altered by the length of the linker molecule. Initially, the assembly will be carried out in solution, although if it works, the expected product will sediment out due to the formation of a superstructure whose rate of sedimentation exceeds its rate of diffusion. Follow-up experiments may include incorporating different functional groups into the linker molecule in an attempt to examine electron transfer between Au and Ag nanoparticles in solution.

Summary and Conclusion

The primary goal of this proposal is to enable us to better understand the structure and concomitant function of DEBNs prepared by different routes. In particular, I hope to demonstrate that there are a number of possible chemical methods by which we can determine the surface functionality and reactivity of DEBNs. These methods include using (1) the catalytic efficiency of the constituent metals to speed up or slow down simple reactions, and (2) selective extraction and the selectivity of different ligands for specific metal surfaces to identify the surface species. As already alluded to in the introduction, the full range of applications of DENs and DEBNs can only be realized once we fully understand the relationship between the intricate structure of the particles and their role. In addition, I have proposed studying the assembly of DENs and DEBNs as this is also an important area requiring a lot of input in the attempt to develop useful devices in areas such as biological detection, drug delivery and sensors.

References

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