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Synthesis and catalytic evaluation of dendrimer-templated and reverse microemulsion Pd and Pt nanoparticles in the reduction of 4-nitrophenol: The effect of size and synthetic methodologies☆

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ABSTRACT

The objective of this study was to produce well-defined palladium and platinum nanoparticles and investigate the effect of nanoparticle size and synthetic methodologies in the catalytic activities. Two types of template, hydroxyl terminated poly(amidoamine) dendrimer template and reverse microemulsions using sodium dietylhexylsulfosuccinate (AOT) surfactant/isooctane/water system, were utilized to produce Pd and Pt nanoparticles. The average diameter (d) of Pd and Pt nanoparticles were 1.9–2.5 nm by the dendrimer-template method, 3.5–5.1 nm by the reverse microemulsions. Overall, smaller sizes with narrower size distributions were obtained by the dendrimer template method. The reduction of 4-nitrophenol (4-Nip) was selected as a model reaction to fulfill the objective of this study. The surface normalized rate constant (k_1), which takes into account the size of nanoparticle, was utilized to compare the catalytic activities of various catalytic systems in literature as well as in this study. The effect of nanoparticle size and synthetic methodologies on the catalytic activities will be discussed based on k_1. The results indicate that Pd based nanoparticles presented higher catalytic activities as compared to Pt based nanoparticles and the nanoparticle produced by the dendrimer template showed superior activities to that of the reverse microemulsions for the reduction of 4-Nip.

1. Introduction

Much attention has been given to noble metal nanoparticles in the field of catalysis due to their high surface energy and a high surface-to-volume ratio, which render higher catalytic activities. In spite of this great merit, the dramatic decrease of catalytic activities due to the agglomeration of nanoparticles has been a challenge [1]. This pitfall has been overcome by stabilizing agents adsorbed onto the surface of nanoparticles, such as ligands [2] and surfactants [3], or templating the nanoparticles, such as block copolymers [4], mesoporous sieves [5], and dendrimers [6]. Interestingly, the size of noble metal nanoparticles strongly influences the catalytic performance [7–10]. For example, Zhou et al. investigated nanoparticle size effects on oxygen reduction reaction (ORR) by synthesizing various carbon supported Pd nanoparticle sizes between 2.7 nm and 8.7 nm. The activities on ORR displayed a volcano curve with maximum activities between 5.0 and 6.0 nm particles [9]. The shape of nanoparticle is also a crucial factor on catalytic activities [11–14]. Near spherical shaped polyvinylpyrrolidone (PVP)-Pt nanoparticles were not active in Suzuki reaction between phenylboronic acid and iodobenzene however, the same reaction could be catalyzed by using tetrahedral PVP-Pt nanoparticles [12]. Because of the influence of size and shape of nanoparticles, a demand for the synthesis of well-defined metal nanoparticles as well as a model reaction to conclusively define and evaluate their catalytic action has significantly increased. The aim of present study was to synthesize well-defined Pd and Pt nanoparticles with narrow size distribution using two types of templates, dendrimer templates and reverse microemulsions.

Dendrimers are repetitively branched molecules with a well-defined structure having a perfect monodispersity, composed of core, branch and terminal groups [15]. It has been reported that two types of nanoparticles can be synthesized using dendrimers, either intra-dendrimer encapsulated nanoparticles (DENs) [16], or inter-dendrimer stabilized nanoparticles (DSNs) [17]. In the former case, dendrimers act as templates which enable metal nanoparticles to form inside the dendrimer cavities, whereas in the latter, metal nanoparticles are trapped among several dendrimers that absorb on the surface of the metal nanoparticles. The great merit

☆ Dedicated to Professor Cedric Holzapfel on the occasion of his 80th birthday.

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Nomenclature

k_{app}	apparent rate constant, s^{-1}
k_1	surface normalized rate constant, $s^{-1}\,m^{-2}\,L$
k_{bm}	bimolecular rate constant, $M^{-1}\,s^{-1}$
d	diameter of metal nanoparticle, nm
r	radius of metal nanoparticle, nm
m	mass of metal, g
N	total number of metal nanoparticles in the system
M_r	molecular mass, $g\,mol^{-1}$
v	volume of one metal nanoparticle, m^3
v_s	volume of the system, L
ρ	bulk density of metal, $kg\,m^{-3}$
c_m	concentration of metal atom, $mol\,L^{-1}$
s	surface area of one metal nanoparticle, m^2
S	surface area of total metal nanoparticles normalized to the unit volume of the system, $m^2\,L^{-1}$
β	mass transport coefficient, $m\,s^{-1}$
D	diffusion coefficient of 4-Nip, $m^2\,s^{-1}$
a	interfacial area, m^{-1}
δ	characteristic diffusion length scale, m

of DENs is the formation of nanoparticles without passivating the active sites on the surface of particles. It is likely to yield both cases in the synthesis of metal nanoparticles using dendrimers, hence, a term 'dendrimer-templated nanoparticles' is used to include both. The dendrimer-templated synthetic methodology is facile and has produced nanosized metal particles with a narrow size distribution. This has promoted dendrimers to be a popular choice for nanoparticle synthesis [16]. The commercially available hydroxyl terminated poly(amidoamine) dendrimers (PAMAM) were utilized for this study. The nomenclature used here for the hydroxyl terminated PAMAM based nanoparticles is G*x*-OH(M_n), where *x* refers to the generation of the PAMAM dendrimer, M to the type of metal and, *n* to the molar ratio of metal to dendrimer [18].

A water-in-oil (w/o) microemulsion, also called reverse microemulsion, has presented an attractive synthetic methodology to produce ultrafine metal nanoparticles since the first metal nanoparticles synthesis using this method has been published in 1982 [19]. These reverse microemulsions consist of water droplets, dispersed in a continuous oil phase, stabilized by added surfactants at the water/oil interface [20]. Metal nanoparticles formed within this reverse micelle, which acts as a nanoreactor where a nucleation and particle growth occurred by collisions of reverse micelles followed by exchanging of the water phase. The frequently applied composition has been the AOT/isooctane/water system, since the structure of isooctane is similar to the structure of the AOT tail, which results in isooctane having a good miscibility with the AOT tails [21]. The Huang group conducted the systematic investigation including the kinetics of Pd and Pt nanoparticles using the AOT/isooctane/water system with hydrazine as the reducing agent [22]. They concluded from their experimental data that the metal nanoparticle sizes are mainly controlled by water to surfactant ratio (ω_0) and the concentration of metal salt in the aqueous phase, while the influence of temperature and AOT concentration as well as the concentration of reducing agent (hydrazine) on the size of nanoparticles was negligible. Chen et al. employed a capping agent such as dodecanethiol, thiolated poly(ethylene glycol) and tiopronin to further stabilize the synthesized Pd nanoparticles by adding the capping agents in the purification step after synthesizing Pd nanoparticles by reverse microemulsions to prevent nanoparticles from further agglomeration [23]. Only a few papers presented the catalytic application of Pd and Pt nanoparticles synthesized by reverse microemulsions using AOT/isooctane/water systems. Semagina et al. reported the application of Pd nanoparticles in the solvent-free selective hydrogenation of 2-methyl-3-butyn-2-ol [24] and 1-hexyne selective hydrogenation [25] and we published the catalytic application of Pd nanoparticles in the Heck C-C coupling reaction between iodobenzene and butylacrylate which was carried out relatively high temperature above 75 °C [26]. Here, the catalytic application of Pd and Pt nanoparticles by reverse microemulsions using AOT/isooctane/water system is reported in the reduction of 4-nitrophenol (4-Nip) at room temperature.

Recently, the catalytic reduction of 4-Nip by borohydride has been a popular choice as a model reaction to evaluate the catalytic performance of metal nanoparticles of various systems. Since the unique properties of metal nanoparticles are a direct result of their size, a model reaction has to be chosen to conclusively define and evaluate their catalytic action. As such, the reduction of 4-Nip by borohydride to 4-aminophenol (4-Amp) represents a satisfactory model since it is easy to observe the reduction process by color change as well as a simple technique, UV–vis spectroscopy, monitoring the decrease in the absorbance peak attributed to the 4-nitrophenolate anion at λ 400 nm, leading directly to the rate constant [27]. Since the Pal group first published this reaction catalyzed by Au, Ag, and Cu nanoparticles using borohydride as a reducing agent in 2001 [28], the number of papers dramatically increased to verify various catalytic systems, which reflects the suitability of this reaction as a model reaction.

The main objective of this study was to produce well-defined Pd and Pt nanoparticles and evaluate the effect of size and synthetic methodologies in catalytic activities. Two templates, dendrimer and reverse microemulsions, were selected in the synthetic protocols, and the reduction of 4-Nip as a model reaction to achieve this goal. The surface normalized rate constant (k_1) was employed to take the size of nanoparticle into account and a direct comparison of catalytic activities from various catalytic systems in literature as well as in this study was performed using these values. This study will provide the effect of nanoparticle size and synthetic methodologies in the catalytic activities of 4-Nip reduction based on k_1 values. Several papers have reported the metal nanoparticle synthesis from each template on its own, however, it is rare to find the direct comparison of these two synthetic methodologies as well as the size effect on the catalytic activities. This study, therefore, will provide an important insight regarding the feasibility of the synthetic methodology, the efficiency of the catalytic system as well as the performance of two different metal nanoparticles (Pd and Pt) in the reduction of 4-Nip. Moreover, the comparison of our results with the various Pd and Pt catalytic systems in recent papers will be provided.

2. Materials and methods

2.1. Materials and instrumentation

Fourth-, fifth-, and sixth generation hydroxyl terminated polyamidoamine (PAMAM) dendrimers (G4-OH, G5-OH, and G6-OH) having an ethylenediamine core were purchased as 10% w/w, 5% w/w, and 5% w/w methanol solutions respectively from Sigma–Aldrich. Sodium dietylhexylsulfosuccinate (AOT), anhydrous isooctane (99.8%), dodecanethiol, potassium tetrachloropalladate (K_2PdCl_4, 98%), potassium tetrachloroplatinate (K_2PtCl_4, 98%) were obtained from Sigma-Aldrich, sodium borohydride from Fluka. All chemicals used were of analytical grade and used as received without further purification. Milli-Q deionized water (18 MΩ cm) was utilized in all experiments.

A Shimadzu UV 1800 UV–Visible spectrophotometer was used for both characterization of Pd and Pt nanocatalysts at room temperature and kinetic runs at various temperatures using a 10 mm