Pt–Pd bimetallic nanoparticles encapsulated in dendrimer nanoreactor

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This article reports the first effort for the preparation of dendrimer-templated Pt–Pd bimetallic nanoparticles and their application to catalysis. The resulting monodispersed bimetallic nanoparticles show a promising catalytic activity in the partial hydrogenation of 1,3-cyclooctadiene.

KEY WORDS: dendrimer; nanoreactor; nanoparticle; bimetal; organic–inorganic composite; hydrogenation.

1. Introduction

The preparation of narrowly distributed metal nanoparticles has been the subject of intense investigation, and research is in progress from various points of view [1,2]. Metal nanoparticles have also provided new opportunities for catalysis and consequently research in this area has paved the way to new solid catalysts over the past decade.

From the catalytic point of view, bimetallic nanoparticles, composed of two different metal elements, have drawn a greater interest than monometallic ones because bimetallization makes it possible not only to obtain an improved catalytic activity but also to create new properties, which may not be achieved by monometallic catalysts [3].

Dendrimers are highly branched macromolecules and they are generally described as having a structure of spherical shape with a high degree of symmetry [4,5]. By virtue of their three-dimensional structure having interior void spaces, dendrimers have been considered as new types of host for the accommodation of guest molecules [6,7].

In line with the prospect of dendrimers as templates for the formation of inorganic nanoparticles, various metal nanoparticles have been successfully prepared [8–17]. However, it is worth noting that most previous studies have been confined to "monometallic" nanoparticles, and "bimetallic" nanoparticles have not been exploited yet, although there has been a preliminary attempt to prepare a dendrimer/bimetal nanocomposite using two different metal precursors [15,16].

In this regard, we aim here to demonstrate the preparation of Pt–Pd bimetallic nanoparticles in the presence of poly(amidoamine) dendrimers with surface hydroxyl groups (fourth generation, PAMAM-OH) and the application of these bimetallic nanoparticles as catalysts for the partial hydrogenation of 1,3-cyclooctadiene. To our knowledge, this is the first effort for the preparation of dendrimer-encapsulated bimetallic nanoparticles which exhibit a promising catalytic activity.

2. Experimental

2.1. Chemicals

Hydroxy- or amine-terminated fourth-generation starburst poly(amidoamine) (PAMAM) dendrimers having an ethylenediamine core were obtained as 10 wt% methanol solutions (Aldrich). Prior to use, the methanol was removed by rotary evaporation at room temperature. K_2PtCl_4 (98%), K_2PdCl_4 (98%), $NaBH_4$ (99%), 1,3-cyclooctadiene (98%), and cyclooctene (95%) were supplied from Aldrich and used as received without further purification. All solutions, used for the preparation of samples for TEM, XPS, and UV–vis spectroscopy and for test reactions, were dialyzed against water for 24 h. Cellulose membranes (Pierce) having a molecular weight cutoff of 10 000 were soaked in water for 1 h and rinsed with deionized water thoroughly before dialysis.

2.2. Synthesis of dendrimer-encapsulated Pt–Pd bimetallic nanoparticles

Dendrimer-encapsulated Pt–Pd bimetallic nanoparticles were prepared by simultaneous co-complexation of two different metal ions, followed by a single reduction step. Complexation of metal ions with dendrimers was carried out by the addition of desired amounts of Pt^{2+} and Pd^{2+} (total metal concentration = 55 mM) to 1 mM

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PAMAM-OH dendrimer solution (fourth generation) under vigorous stirring. After 1 h, 0.55 M sodium borohydride was slowly added under vigorous stirring.

2.3. Characterization

Absorption spectra were recorded using a Perkin-Elmer Lambda 35 UV–vis spectrometer using deionized water as a reference for all measurements.

Samples for XPS (X-ray photoelectron spectroscopy) analysis were prepared by soaking Si wafers in aqueous solutions of dendrimers containing metal nanoparticles for 20 h, followed by careful rinsing and drying. Before use, Si wafers were rinsed with ethanol, and dried in a nitrogen atmosphere. XPS data were acquired using a Perkin-Elmer PHI 558 spectrometer and employing a pass energy of 40 eV, a step increment of 0.1 eV, and an Al anode. XPS peak positions were referenced to the carbon (1s) peak at 284.6 eV.

High-resolution transmission electron microscopy (HRTEM) was carried out using a JEOL JEM-3000F transmission electron microscope equipped with an EDS (energy dispersive spectroscopy) detector (Oxford Co.). The specimens of various bimetallic nanoparticles were prepared by placing a drop of dilute, aqueous dendrimer solution on a carbon-coated copper TEM grid and allowing the water to evaporate in air. The HRTEM images were recorded digitally with a charge-coupled-device (CCD) camera (Gattan MSC-794 model). Average particle sizes and the size distribution of the nanoparticles (approximately 150 particles) were measured from enlargements of TEM images using image analysis software (Scion image).

2.4. Partial hydrogenation of 1,3-cyclooctadiene

Partial hydrogenation of 1,3-cyclooctadiene was carried out in ethanol/water mixture (4/1 v/v) at 20 °C under hydrogen at atmospheric pressure. Ethanol (7 ml) and the colloidal dispersions of the dendrimer-encapsulated Pt–Pd bimetallic clusters (2 ml, total metal $= 5.5 \times 10^{-6}$ mol) were poured into a 50 ml three-necked round-bottomed flask reactor. The mixture was stirred under hydrogen atmosphere. After the initial hydrogen uptake ceased, 1 ml solution of 1,3-cyclooctadiene (1 mmol) in ethanol was added to the flask to initiate the reaction. After the reaction was initiated by starting the magnetic stirrer, maintaining the total pressure of hydrogen at 1 atm, the hydrogen uptake was monitored using a constant-pressure manometric unit which has been reported elsewhere [18]. After completion of the reaction, the reaction mixture was analyzed using a Varian CP-3380 gas chromatograph equipped with a Carbowax column. The turnover frequency (TOF) was calculated on the basis of hydrogen uptake.

3. Results and discussion

A schematic representation of the preparation of the dendrimer-encapsulated bimetallic nanoparticles is shown in figure 1. The method is similar to those for

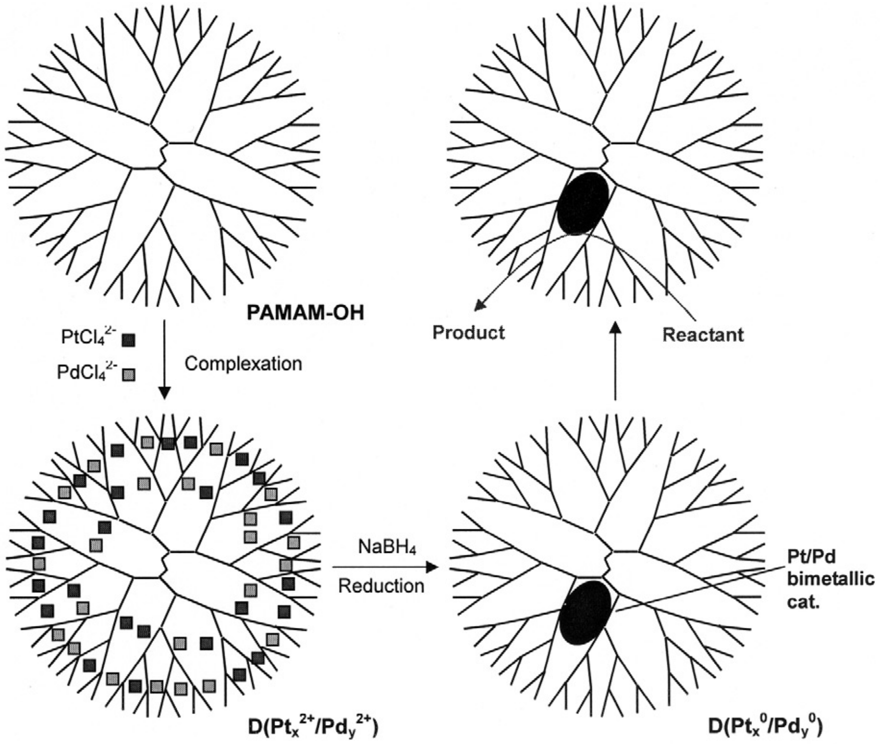


Figure 1. Schematic diagram of the preparation of dendrimer-encapsulated Pt–Pd bimetallic nanoparticles.

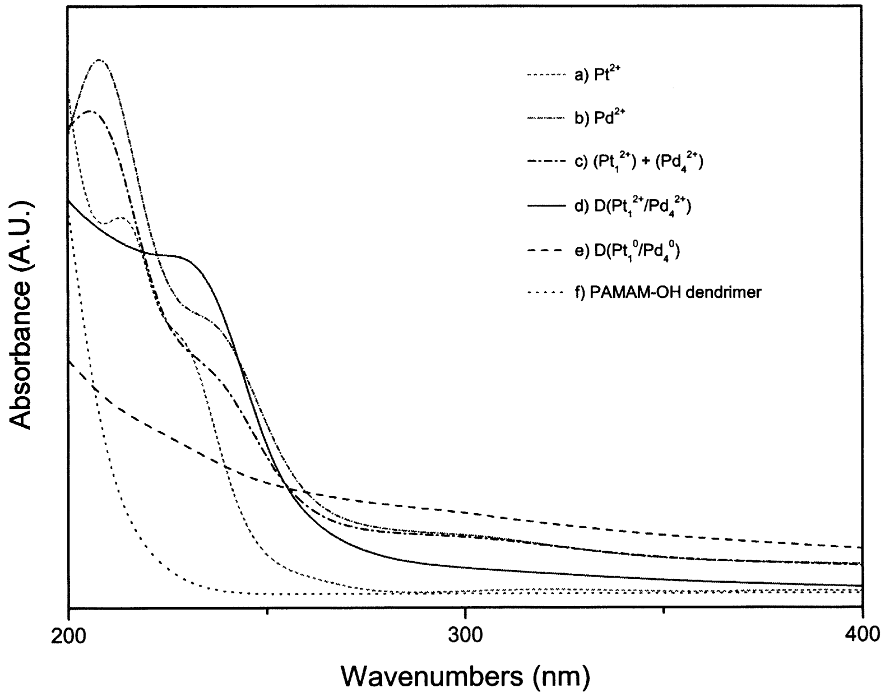


Figure 2. Variations in the UV–vis spectra of Pt and Pd metals in the course of the complexation and the subsequent reduction (Pt/Pd ratio = 1/4): (a) 55 mM K_2PtCl_4; (b) 55 mM K_2PdCl_4; (c) mixture of 11 mM K_2PtCl_4 and 44 mM K_2PdCl_4; (d) complexation of metal mixture with 1 mM dendrimer; (e) reduction with 0.55 M $NaBH_4$; (f) PAMAM-OH dendrimer (fourth generation).

monometallic nanoparticles [17] except for the simultaneous use of two metal precursors, K_2PtCl_4 and K_2PdCl_4. A 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, an 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 for up to three months.

Figure 2 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 following 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 [19]. 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 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.

Figure 3 presents 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 mole ratio). 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 of their physical mixtures. The change in the absorption spectra of the bimetallic nanoparticles from those of individual ones can be primarily attributed to the change in dielectric function caused by mixing the two different metal atoms [20]. Therefore, the characteristic monotonic absorption spectra strongly suggest that bimetallic nanoparticles are formed in the cavity of the dendrimer.

The result of XPS analysis also supports the fact 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 [21]. Similarly, it is observed that the $Pd(3d_{5/2})$ peak is shifted from 337.6 to 334.9 eV and the $Pd(3d_{3/2})$ peak from 342.7 to 340.5 eV upon reduction.

A representative HRTEM image of $D(Pt_1^0/Pd_4^0)$ is shown figure 4. The microscopy demonstrates that the particle size is uniform and the shape is nearly spherical. The formation of quite monodispersed nanoparticles

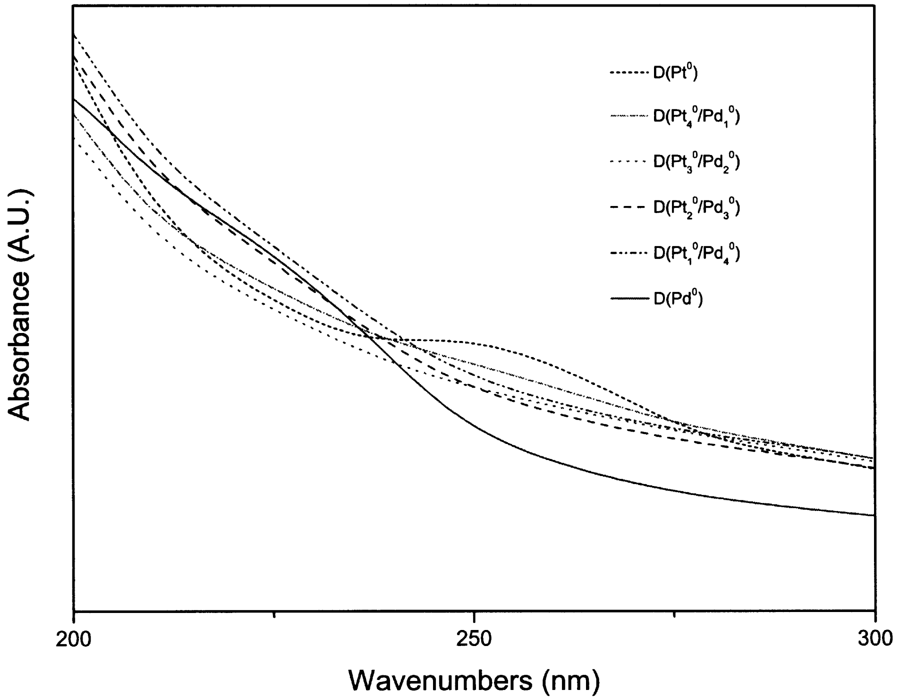


Figure 3. UV–vis spectra of dendrimer-encapsulated Pt–Pd bimetallic nanoparticles with various Pt/Pd ratios.

suggests the effectiveness of the 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 (~5 nm) was not high enough to detect the X-rays generated from a single particle. In the present study, therefore, only their average compositions are discussed. Since precipitation was expected due to the metal-induced crosslinking of amine-terminated dendrimers (PAMAM-NH$_2$) [22], we prepared another type of Pt–Pd bimetal/dendrimer nanocomposite using PAMAM-NH$_2$ to obtain nanoparticles large enough to detect the X-rays 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.

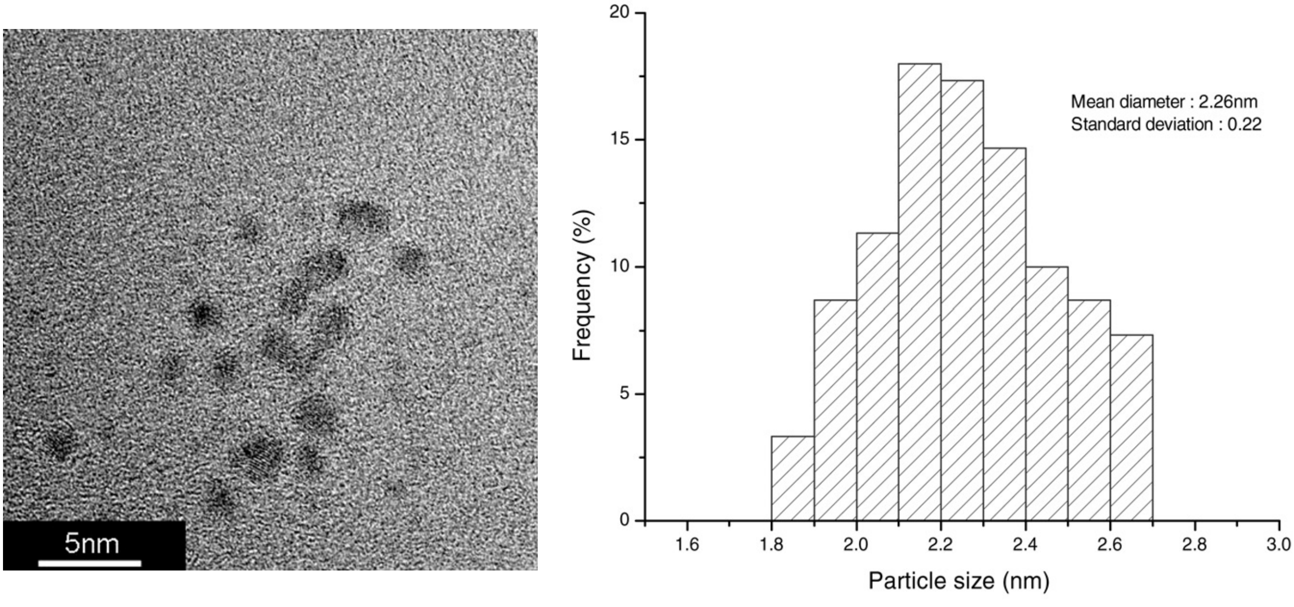
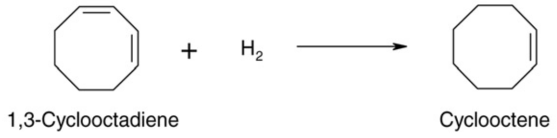


Figure 4. HRTEM image and particle size distribution of Pt–Pd bimetallic nanoparticles with a Pt/Pd ratio of 1/4.

The dendrimer-encapsulated Pt–Pd bimetallic nanoparticles were applied as a catalyst in the partial hydrogenation of 1,3-cyclooctadiene in ethanol/water mixture (4/1 v/v):



As shown in figure 5, the dendrimer-encapsulated Pt–Pd bimetallic nanoparticles were found to be effective in the partial hydrogenation of 1,3-cyclooctadiene. Different from the conventional polymer-stabilized nanoparticles, the dendrimer-encapsulated nanoparticles are confined primarily by steric effects and therefore a substantial fraction of their surface is unpassivated and available for reactant to access in catalytic reactions [16]. In addition, it is worth noting that in the case of the fourth-generation dendrimer, the compactness of dendrimer branching is not severe and thus would not restrict the accessibility of reactant to the active sites [23]. These unique features of dendrimer nanoreactors make it possible to obtain high catalytic activity.

Moreover, the catalytic activity of the bimetallic nanoparticles increased as the Pt/Pd ratio decreased and the catalytic activities of $D(Pt^0_2/Pd^0_3)$ and $D(Pt^0_1/Pd^0_4)$ 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 [24,25]. 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.

4. Conclusions

Ultrafine and monodispersed dendrimer-encapsulated Pt–Pd bimetallic nanoparticles with various metal compositions have been successfully prepared. The resulting bimetallic nanoparticles effectively promote the partial hydrogenation of 1,3-cyclooctadiene and the highest activity was achieved with a Pt/Pd ratio of 1/4. This result suggests that the potential application of the dendrimer-encapsulated bimetallic nanoparticles is promising in the field of catalysis. Other types of dendrimer-encapsulated bimetallic nanoparticles will be reported in due course.

Acknowledgment

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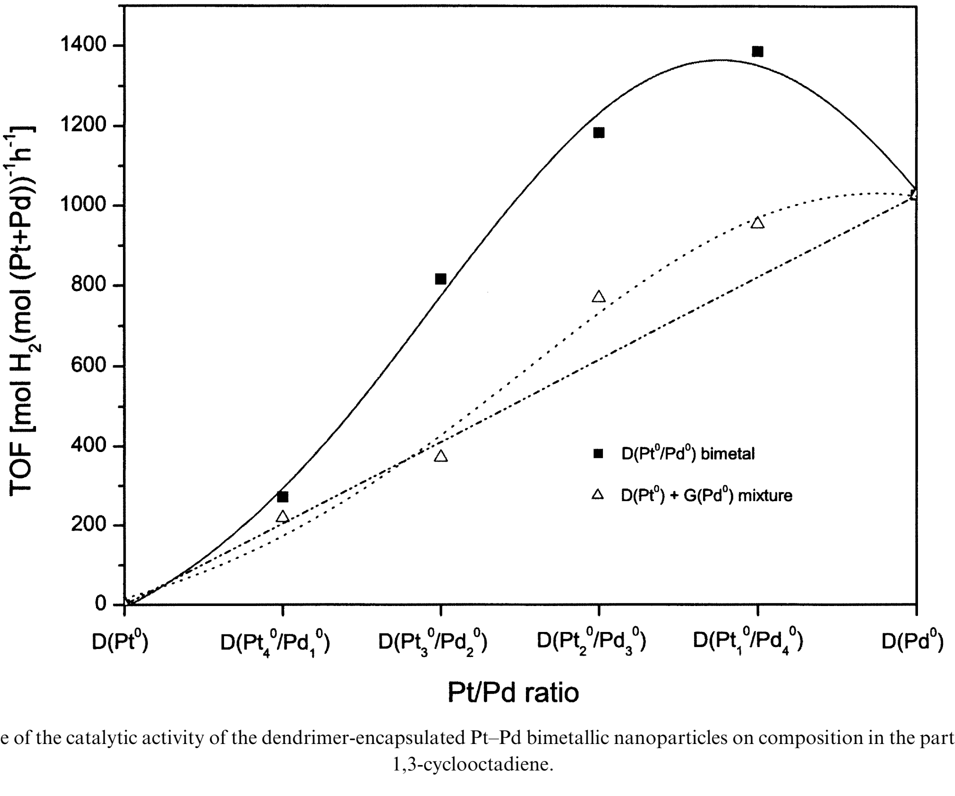

Figure 5. Dependence of the catalytic activity of the dendrimer-encapsulated Pt–Pd bimetallic nanoparticles on composition in the partial hydrogenation of 1,3-cyclooctadiene.

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