



Palladium nanoparticles encapsulated in a dendrimer networks as catalysts for the hydrogenation of unsaturated hydrocarbons



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ARTICLE INFO

Article history:

Received 24 July 2014

Received in revised form 14 October 2014

Accepted 15 October 2014

Available online 24 October 2014

Keyword:

Pd catalysts

Nanoparticles

PAMAM dendrimer

Selective hydrogenation

ABSTRACT

A novel method has been proposed for encapsulating palladium nanoparticles up to 5 nm in the matrix of polymeric support networks based on polyamidoamine dendrimers. The shape of the particle size distribution and the catalytic activity of the materials obtained during the hydrogenation of unsaturated compounds depend strongly on the support structure. High activity (TOF up to 86,000 h⁻¹) has been observed during the hydrogenation of styrene.

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1. Introduction

Catalysts utilising metal nanoparticles as active components deposited on dendrimer matrices have recently found numerous applications in petrochemical and organic syntheses. These materials are used during the hydrogenation of double bonds [1], hydroformylation [2,3], amination [4], carbonylation [5] and cross-coupling reactions (the Suzuki [6], Heck [7] and the Sonogashira reaction [8]). The main problem with metal nanoparticles as catalysis is their aggregation, which leads to the decrease in the total specific surface of the catalyst and, as a consequence, to the activity loss. In a number of cases, the selectivity of the reaction also depends on the particle size. Metal nanoparticles can be stabilized by the interactions with either the donor atoms of various organic ligands following the coordination mechanism, or the internal surface of pores in such systems as zeolite and mesoporous aluminosilicates.

One of the most interesting approaches toward synthesising catalysts based on metal nanoparticles is the use of the dendrimers to bind metal ions, which are nanoparticle precursors, and to stabilise the resultant particles [9–12]. The dendrimer encapsulated

nanoparticles have the advantage over other types of metal dendrite catalysts: the poly(propyleneimine) (PPI) and PAMAM dendrimers commonly used as a matrix can be relatively readily synthesized in laboratory from commercially available precursor [13–18]. We have proposed a method for synthesising a heterogeneous support based on polyamidoamine dendrimers, binding them to one another with special cross-linking agents, such as diisocyanates. It includes a preliminary cross-linking PPI- dendrimers with various bifunctional agents (diepoxides, diisocyanates) with subsequent deposition of a required metal salt and its reduction to the zerovalent state. The driving force for the preparation of the catalyst is the formation of the complex between the ions of the deposited metal and the amino groups of dendrimers. In this case, the final properties of the material (nanoparticle size distribution, catalytic activity and selectivity) are determined by the dendrimer generation, the size, rigidity, and polarity of the cross linking agent. Thus synthesized system structurally resembles metalorganic frameworks, in which the dendrimers, rather than metal ions, serve as the matrix nodes, whose rigidity increases with the increase in the generation and decrease in the length of the branches. Therefore, we prepared effective hydrogenation catalysts based on cross-linked dendrimers and palladium nanoparticles with particle sizes ranging from 1.8 to 2.8 nm based on generation of the PPI dendrimer [19]. The corresponding material exhibits a high activity when hydrogenating olefin and phenylacetylene [19–22]. In this paper,

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we report the design of catalysts based on palladium nanoparticles and PAMAM dendrimers using the same approach.

2. Experimental

2.1. Analysis

The first-, second- and third-generation polyamidoamine dendrimers, specifically PAMAM-G1 (PAMAM (NH₂)₈), PAMAM-G2 (PAMAM (NH₂)₁₆), and PAMAM-G3 (PAMAM (NH₂)₃₂), were synthesised according to the procedure described in [23]; these materials were used as starting materials. The cross-linking agents, which were obtained from Aldrich, included the following: 1,4-butylene diisocyanate (BDI), 1,6-hexamethylene diisocyanate (HMDI), 1,8-octamethylene diisocyanate (OMDI), p-phenylene diisocyanate (PDI), and 3,3'-dimethoxy-4,4'-biphenylene diisocyanate (DMPDI).

The IR spectra were obtained with a Nicolet IR2000 (Thermo Scientific) using a method involving multiple distortions in the total internal reflection with Multi-reflection HATR accessories; these accessories contained a ZnSe crystal (45°) for use at different wavelengths and a resolution of 4 cm⁻¹.

The X-ray photoelectron spectroscopy (XPS) studies were performed with a Kratos Axis Ultra DLD electronic device equipped with a photoelectron analyser and an OPX-150 slowing potential. The photoelectrons were excited using X-rays from an aluminium anode (Al K α = 1486.6 eV) at 12 kV and 20 mA. The photoelectron peaks were calibrated using the C 1s carbon line at 284.8 eV.

The palladium in the samples was quantified using inductively coupled plasma atomic emission spectroscopy (ICP-AES) with an IRIS Interpid II XPL instrument (Thermo Electron Corp., USA) through the radial and axial detection at 310 and 95.5 nm.

The transmission electron microscopy (TEM) studies of the samples were performed on a LEO912 AB OMEGA transmission electron microscope.

2.2. Synthesis of dendrimer compounds and characterization

Synthesis of PAMAM-G1-BDI. A 1.1-g portion of PAMAM(NH₂)₈ (0.773 mmol) and 50 mL of absolute THF were placed in a 100-mL single-neck flask equipped with a magnetic stirrer and a reflux condenser. Under these conditions, the dendrimer swelled but did not dissolve. Afterwards, 0.13 mL (1.031 mmol) of 1,4-butylene diisocyanate was added with stirring. The reaction proceeded for 12 h at 70 °C before the product mixture was evaporated in a rotary evaporator at 50 °C. The product was obtained as loose yellow lumps (1.357 mg).

Synthesis of PAMAM-G1-HMDI. The synthesis was carried out according to the procedure described above. The reactants included PAMAM(NH₂)₈ (1.088 g, 0.761 mmol) and 1,6-hexamethylene diisocyanate (0.16 mL, 1.014 mmol) in 50 mL of absolute THF. The reaction product was obtained as loose yellow lumps (1.259 g).

IR (sm⁻¹): 3302 (N-H_{st} in NH-C(=O)); 2933 (C-H_{st}); 2858 (C-H_{st}, CH₂-N_{st}); 1658 (C=O_{st} in NH-C(=O)); 1552 (N-H₈, CH₂₈, C-N-H₈); 1477, 1433, 1387 (CH₂₈); 1263, 1157, 1120, 1036 (C-N_{st} in NH-C(=O)).

Synthesis of PAMAM-G1-OMDI. The synthesis was carried out according to the procedure described above. The reactants included PAMAM(NH₂)₈ (0.568 g, 0.397 mmol) and 1,8-octamethylene diisocyanate (0.15 mL, 0.77 mmol) in 50 mL of absolute THF. The reaction product was obtained as yellow loose lumps (0.738 g).

Synthesis of PAMAM-G1-PDI. The synthesis was carried out according to the procedure described above. The reactants included PAMAM(NH₂)₈ (1.088 g, 0.761 mmol) and p-phenylene

diisocyanate (0.65 g, 1.014 mmol) in 50 mL of absolute THF. The reaction product was obtained as a white powder (2.124 g).

IR (sm⁻¹): 3298 (N-H_{st} in NH-C(=O)); 2954 (C-H_{st}); 2843 (C-H_{st}, CH₂-N_{st}); 1633 (C=O_{st} in NH-C(=O)); 1558, 1510 (N-H₈, CH₂₈, C-N-H₈); 1404, 1300 (CH₂₈); 1219, 1126, 1072, 1016 (C-N_{st} in NH-C(=O)); 823 (aromatic C-H₈); 761, 687, 652 (aromatic C=C₈).

XPS (eV): 284.5 (32%), 285.7 (46%), 287.1 (8%), 288.5 (14%) (C 1s, 64.9%); 399.3 (N 1s, 22.1%); 530.8 (O 1s, 12.5%).

Synthesis of PAMAM-G1-DMPDI. The synthesis was carried out according to the procedure described above. The reactants included PAMAM(NH₂)₈ (1.871 g, 1.309 mmol) and 3,3'-dimethoxy-4,4'-diphenylene diisocyanate (0.518 g, 1.748 mmol) in 50 mL of absolute THF. The reaction product was obtained as loose white lumps (2.389 g).

IR (sm⁻¹): 3325 (N-H_{st} in NH-C(=O)); 2929 (C-H_{st}); 2856 (C-H_{st}, CH₂-N_{st}); 1628 (C=O_{st} in NH-C(=O)); 1547 (N-H₈, CH₂₈, C-N-H₈); 1462, 1431 (CH₂₈); 1261, 1119, 1038 (C-N_{st} in NH-C(=O)); 820 (aromatic C-H₈); 768, 652 (aromatic C=C₈).

Synthesis of PAMAM-G2-HMDI. The synthesis was carried out according to the procedure described above. The reactants included PAMAM(NH₂)₁₆ (2 g, 0.615 mmol) and 1,6-hexamethylene diisocyanate (0.26 mL, 1.64 mmol) in 50 mL of absolute THF. The reaction product was obtained as a yellowish sticky mass (2.011 g).

Synthesis of PAMAM-G2-PDI. The synthesis was carried out according to the procedure described above. The reactants included PAMAM(NH₂)₁₆ (2 g, 0.615 mmol) and p-phenylene diisocyanate (PDI) (0.262 g, 1.64 mmol) in 50 mL of absolute THF. The reaction product was obtained as a yellowish sticky mass (2.215 g).

Synthesis of PAMAM-G2-DMPDI. The synthesis was carried out according to the procedure described above. The reactants included PAMAM(NH₂)₁₆ (768 mg, 0.236 mmol) and 3,3'-dimethoxy-4,4'-diphenylene diisocyanate (711 mg, 2.4 mmol) in 50 mL of anhydrous methanol. The reaction product was obtained as a white powder (892 mg).

IR (sm⁻¹): 3325 (N-H_{st} in NH-C(=O)); 2929 (C-H_{st}); 2856 (C-H_{st}, CH₂-N_{st}); 1627, (C=O_{st} in NH-C(=O)); 1547 (N-H₈, CH₂₈, C-N-H₈); 1462, 1431 (CH₂₈); 1261, 1157, 1113, 1038 (C-N_{st} in NH-C(=O)); 874, 820 (aromatic C-H₈); 768, 729, 710, 658 (aromatic C=C₈).

Synthesis of PAMAM-G3-HMDI. The synthesis was carried out according to the procedure described above. The reactants included PAMAM(NH₂)₃₂ (2 g, 0.29 mmol) and 1,6-hexamethylene diisocyanate (0.25 mL, 1.547 mmol) in 50 mL of absolute THF. The reaction product was obtained as a white powder (2.124 g).

IR (sm⁻¹): 3327 (N-H_{st} in NH-C(=O)); 2929 (C-H_{st}); 2854 (C-H_{st}, CH₂-N_{st}); 1628 (C=O_{st} in NH-C(=O)); 1556 (N-H₈, CH₂₈, C-N-H₈); 1469, 1431, 1358 (CH₂₈); 1261, 1153, 1037 (C-N_{st} in NH-C(=O)).

Synthesis of PAMAM-G3-PDI material. The synthesis was carried out according to the procedure described above. The reactants included PAMAM(NH₂)₃₂ (2 g, 0.29 mmol) and p-phenylene diisocyanate (PDI) (0.248 g, 1.57 mmol) in 50 mL of absolute THF. The reaction product was obtained as a white powder (2.549 g).

IR (sm⁻¹): 3327 (N-H_{st} in NH-C(=O)); 2916 (C-H_{st}); 2862 (C-H_{st}, CH₂-N_{st}); 1631 (C=O_{st} in NH-C(=O)); 1566 (N-H₈, CH₂₈, C-N-H₈); 1477, 1433, 1335 (CH₂₈); 1265, 1153, 1047 (C-N_{st} in NH-C(=O)); 904, 862, 827 (aromatic C-H₈); 766, 669 (aromatic C=C₈).

2.3. Preparation of Pd-dendrimer compounds and characterization

Synthesis of G1-BDI-Pd. To a 50-ml flask equipped with a magnetic stirrer and a reflux condenser was added 1.1 g of PAMAM-G1-BDI in 40 mL of absolute chloroform. Afterwards, 787 mg (3.51 mmol) of Pd(OAc)₂ was added to the resulting suspension with stirring. The reaction proceeded for 12 h at 70 °C.

After the reaction, the suspension was evaporated to dryness in a rotary evaporator. The intermediate product was a dark brown

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