Supporting Information

Dendrimer-Stabilized Metal Nanoparticles as Efficient Catalysts for Reversible Dehydrogenation/Hydrogenation of N-Heterocycles

*Christophe Deraedt, ‡,† Rong Ye, ‡,† Walter T. Ralston, ‡,† Dean, F. Toste, *, ‡,†*

Gabor A. Somorjai,‡,†*

‡Department of Chemistry, University of California, Berkeley, California 94720, United States.

†Chemical Science Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States

*E-mail: somorjai@berkeley.edu, fdtoste@berkeley.edu

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1) Syntheses of all the catalysts

1.a) Synthesis of nanoparticle stabilized by PAMAM dendrimer (Scheme 1 and Figure 1 main text)

The catalysts studied in the hydrogenation and dehydrogenation were synthesized in two steps. The first step consists in synthesizing the homogeneous MNPs (M= Pt, Pd, Rh, Au, and Cu) stabilized by the fourth generation G4OH PAMAM dendrimer in water solution by following Crooks' method.[2b,4a] The PtNPs were synthesized using a Schlenk flask containing 1.25 μmol of PAMAM G4OH (Dendritech 9.81% water solution) dissolved in 5 mL of deionized water. Subsequently, a 0.05 mmol of H_2PtCl_6 (Sigma Aldrich, 99.9%) dissolved in 5 mL of deionized water was added to the dendrimer solution in order to achieve a ratio 40/1 of Pt atoms for one dendrimer (0.0625 mmol was used for a stoichiometry 50/1 and 0.025 mmol for 20/1). The solution was degassed with argon during 30-45 min, and then allowed to stir slowly for 3 days at room temperature. This time length is necessary to ensure the complete complexation of Pt(II) by the tertiary amine of the dendrimer. A partial complexation of Pt(II) would lead to a poly-dispersed size of nanoparticle after the reduction step. After 3 days of complexation, fresh sodium borohydride $NaBH_4$ (10 equivalents per Pt) dissolved in 2 mL of 5°C deionized water, was added dropwise to the Pt(II)/PAMAM-G4OH solution with a fast stirring. This leads to an instantaneous change of color from yellow/brown to dark black. The solution was allowed to stir 6 more hours before proceeding to the purification/washing step. The PtNPs solution was transferred into a snakeskin dialysis bag, and dialysis was conducted during 1.5 days in a flask containing 2 L of deionized water, regularly changing the water (4 times). The size and the distribution of the PtNPs were checked with a FEI Tecnai TEM at an accelerating voltage of 200 kV. The average sizes measured from the TEM image were 1.6 ± 0.2 nm for Pt40G4OH. The synthesis slightly differs when the metal is changed, see the following procedure. At this stage, the catalyst is ready for homogeneous catalysis.

1.b Synthesis of support (SBA-15)

The heterogenized, i.e. supported version, of the nanoparticle stabilized by dendrimers is obtained by impregnation on mesoporous silica. As the nanoparticles are very small, and the size of PAMAM G4OH is 4.5 nm, we were able to load it inside mesoporous SBA-15 with 6-7 nm channel pores (as determined by nitrogen physisorption). For the synthesis of SBA-15, Pluronic P123 (12.0 g, BASF) was dissolved in deionized water (90 mL) and 2 M HCl (360

mL) while stirring at 40-45°C for 1 h. Tetraethylorthosilicate (25.6 g, Sigma Aldrich, 98%) was added to the solution dropwise and allowed to stir for 20 h at 35°C. The solgel was aged at 100°C in an oven for 24 h. The resulting product was filtered to give a white powder, which was further washed with ethanol and deionized water (2 times). Finally, the support was dried in air at 100°C and then calcined at 550°C for 6 h. To prevent H_2O absorption, the SBA-15 is stored in a desiccator before its use as a support.

1.c) Synthesis of nanoparticle stabilized by PAMAM dendrimer supported on SBA-15 (Scheme 2)

The final supported catalyst is obtained by mixing 460 mg of SBA-15 with the nanoparticle water solution (9 mL) in an ultrasonic bath for 3 hours at room temperature, leading to 1.83 wt% Pt loading. The catalyst was centifigated and then dry in an oven at 80°C during 2-3 days. The success of the impregnation was proved by ICP-OES, and TEM. ICP-OES revealed that the loading was 100% successful. TEM images, revealed that the size of the MNPs remain unchanged after the loading (1.8 ± 0.4 nm). Using this technic, we were able to produce MNPs-supported with 0.0094 mol%, of Pt, Rh (1 wt%) and Pd (1 wt%).

1.d) Synthesis of RhNP stabilized by PAMAM dendrimer and Rh/SBA-15

RhNPs were synthesized by the following: in a Schlenk flask, 1.25 μmol of PAMAM G4OH (purchased from Dendritech 9.81% water solution) was dissolved in 5 mL of deionized water, then 0.05 mmol of $RhCl_3.xH_2O$ (Sigma Aldrich, 99.9%) dissolved in 5 mL of deionized water. Subsequently, the Rh solution was added to the dendrimer solution in order to achieve a stoichiometry 40 atoms of Rh for one dendrimer (0.0625 mmol was used for a stoichiometry 50/1 and 0.025 mmol for 20/1). The solution was degassed with argon during 30-45 min, and then allowed to stir slowly overnight. This time length is necessary to ensure the complete complexation of Rh(III) to the interior tertiary amine of the dendrimer at room temperature. Then, the fresh sodium borohydride $NaBH_4$ (from 5 to 20 equivalents per Rh, 10 here) dissolved in 2 mL of 5°C deionized water, was added dropwise in the Rh(III)/PAMAM-G4OH solution, with a faster stirring, leading to the instantaneously change of color from orange to dark brown/black. The solution was allowed to stir 2-3 more hours before proceeding to the purification/washing step. The RhNP solution was transferred into a snakeskin dialysis bag, and dialysis was conducted during 1.5 days in a flask containing 2 L of deionized water, with regularly changing the water (4 times). The size and the distribution of the RhNPs were checked

with a FEI Tecnai TEM at an accelerating voltage of 200 kV, giving an average size of 1.68 ± 0.287 nm (Fig S1a). The RhNPs were then supported on SBA-15 after 3 hours of signification as for **Pt/SBA-15**, the centrifugation of the catalyst plus the drying for 2-3 days in an oven at 80°C allow to obtain **Rh/SBA-15** (see Fig S1b for TEM image, average size 1.6 ± 0.4, difficult to determined exactly).

1.e) Synthesis of PdNP stabilized by PAMAM dendrimer and Pd/SBA-15

PdNPs were synthesized by the following: in a Schlenk flask, 1.25 μmol of PAMAM G4OH (purchased from Dendritech 9.81% water solution) was dissolved in 5 mL of deionized water, then 0.05 mmol of K_2PdCl_4 (Sigma Aldrich, 99.9%) dissolved in 5 mL of deionized water. 30 mL of deionized water was added to the dendrimer solution. Subsequently, the Pd solution was added to the dendrimer solution in order to achieve a stoichiometry 40 atoms of Pd for one dendrimer (0.0625 mmol was used for a stoichiometry 50/1 and 0.025 mmol for 20/1). The solution was degassed with argon during 30-45 min. This time length is necessary to ensure the complete complexation of Pd(II) to the interior tertiary amine of the dendrimer at room temperature. Then, the fresh sodium borohydride $NaBH_4$ (from 5 to 20 equivalents per Pd, 10 here) dissolved in 2 mL of 5°C deionized water, was added dropwise in the Pd(II)/PAMAM-G4OH solution, with a faster stirring, leading to the instantaneously change of color from yellow to dark brown/black. The solution was allowed to stir 2-3 more hours before proceeding to the purification/washing step. The PdNP solution was transferred into a snakeskin dialysis bag, and dialysis was conducted during 1.5 days in a flask containing 2 L of deionized water, with regularly changing the water (4 times). The size and the distribution of the PdNPs were checked with a FEI Tecnai TEM at an accelerating voltage of 200 kV, giving an average size of 1.5 ± 0.2 nm. The PdNPs were then supported on SBA-15 after 3 hours of signification as for **Pt/SBA-15**, the centrifugation of the catalyst plus the drying for 2-3 days in an oven at 80°C allow to obtain **Pd/SBA-15** (average size 1.5 ± 0.3, difficult to determined exactly).

2) Characterization

a) Transmission Electron Microscopy TEM

Three to four drops of the nanoparticles solution were deposed on a TEM copper grid, after 1 night of drying (air) the samples were analyzed and the TEM images were obtained using a FEI Tecnai TEM an accelerating voltage of 200 kV. The average diameter size of the nanoparticles was determined by measuring hundred nanoparticles per sample.

b) Physical surface area measurement

BET measurements were performed on a ASAP 2020 from Micromeritrics using nitrogen as a probe at a temperature of -196°C. BET model was used for surface and BHJ model used for porous distribution.

c) X-ray Spectroscopy EXAFS

Performed at beamline 10.3.2 at ALS (Advance Light Source) Berkeley Lawrence National Laboratory. The data were collected in the fluorescence mode at an angle of 45° to the beam. Data were analyzed, (deadtime, pre-edge, normalization) using beamline software and the open source Athena program.

d) Inductively Coupled Plasma Optical Emission Spectroscopy ICP-OES

15mg of the heterogeneous catalysts were digested with 1.2 mL of Aqua Regia at 40°C during 6 hours. 12.8 mL of deionized water were added, and the resulting solution was centrifugated before ICP-OES analysis. The analyses were performed by an Optima 7000 DV Inductively Coupled Plasma Optical Emission Spectroscopy.

e) Nuclear magnetic resonance spectroscopy

Products of the catalytic reactions were analyzed either by ^{1}H NMR or by GC-MS. The ^{1}H NMR spectra were recorded on three different NMR machines.

VB-400

This instrument is set up with a computer-tuned (ATMA) 5 mm Z-gradient broad band (109Ag to 31P) probe. In addition the commonly measured ^{1}H ^{13}C, ^{31}P, etc., spectra, a large number of nuclei can be observed.

Equipment Description

- Avance electronics console installed on the magnet previously part of a (1987) Bruker AM-400.
- BOSS 20 gradient shim system and sample transport, ^{2}H lock. 2-Channel rf system. 150 kHz maximum sweep width.
- Linux based data system.

In service since 2003, this instrument was funded in part by NSF grant CHE-0130862. The original AM-400 was partially funded by NIH grant S10 RR 03353-01 and NSF grant CHE 8703048.

AVQ-400

This instrument is set up with a Z-gradient 5 mm QNP (Quad Nucleus) probe for measuring proton, carbon, phosphorus and fluorine spectra without having to tune the probe. The probe is optimized for observing nuclei other than protons.

Equipment Description

- Avance electronics console installed on the magnet previously part of a (1989) Bruker AMX-400.
- BOSS 20 gradient shim system and sample transport, ^{2}H lock. 2-Channel rf system. 1 MHz maximum sweep width.
- Linux based data system.

In service since 2003, this instrument was funded in part by NSF grant CHE-0130862. The original AMX-400 magnet was partially funded by NSF grant HE79-26291-A02.

AV-300

This instrument is set up with a 5 mm Z-gradient dual ^{1}H/^{13}C probe, optimized for direct carbon observation. It is also possible to observe ^{2}H and ^{19}F. A non-gradient inverse broad-band observe probe is also available.

Equipment Description

- Avance electronics console installed on the magnet previously part of a (1992) Bruker AMX-300.
- BOSS 20 gradient shim system and sample transport, ^{2}H lock. 2-Channel rf system. 150 kHz maximum sweep width.
- Linux based data system.