Hydrogenation

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A Uniform Bimetallic Rhodium/Iron Nanoparticle Catalyst for the Hydrogenation of Olefins and Nitroarenes**

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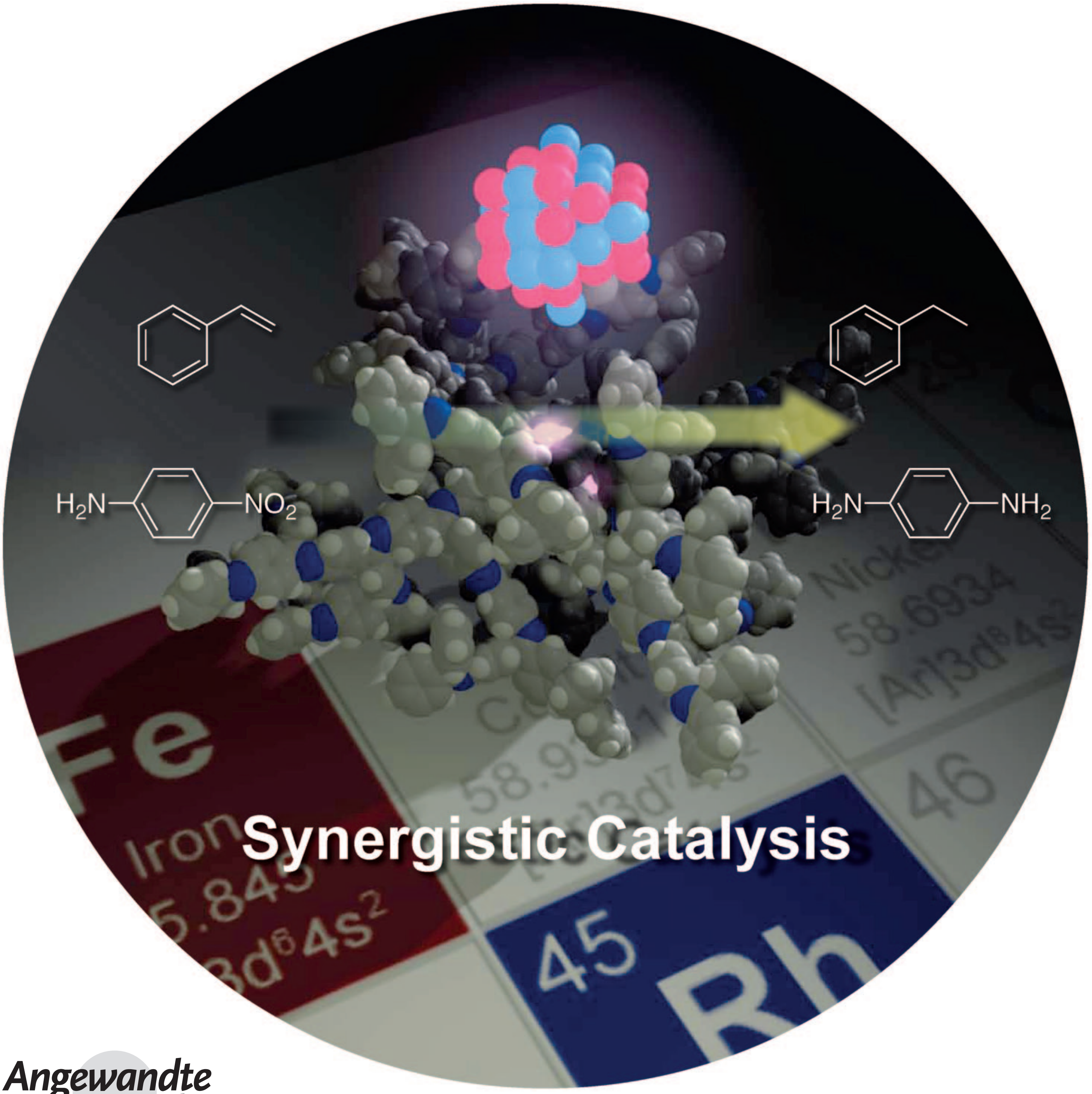

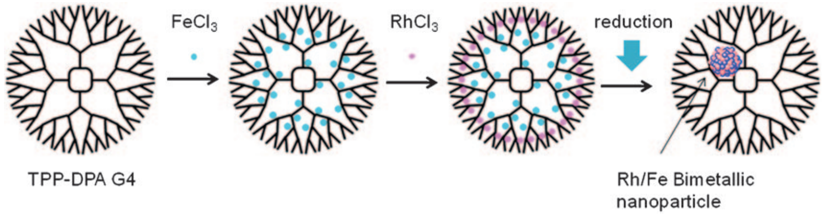

Scheme 1. The preparation of $Rh_{32}Fe_{28}$@TPP-DPA G4.

Dendrimer-stabilized metal nanoparticles have attracted much attention recently as a new research direction in the field of catalysis.[1] Dendrimer matrices serve as supporting materials to prevent nanoparticles from aggregating and to provide a desired chemical interface between the nanoparticles and the reaction media. We recently reported that fourth-generation (G4) phenylazomethine dendrimers (TPP-DPA G4) are useful for synthesizing and stabilizing monometallic rhodium-nanoparticles with a very narrow size distribution.[2–4] The catalyst was prepared by $NaBH_4$ reduction of $RhCl_3$ in a mixture of toluene and methanol with dendrimer as stabilizer. Bimetallic nanoparticle catalysts are widely applicable to heterogeneous transformations because the properties of these materials overcome several disadvantages of single-component nanoparticles.[5,6] Increasingly, the shape, size, composition, and architecture of a nanoparticle are being recognized as important control parameters for tailoring new bimetallic nanoparticle systems. Few reports have described the preparation of almost completely uniform (standard variation: $\leq \pm 0.2$ nm) bimetallic nanoparticles. Herein, we describe the preparation of uniform bimetallic nanoparticles in a phenylazomethine dendrimer, which provides improved catalytic reactivity compared with monometallic Rh nanoparticles in a dendrimer cage.

Iron drew our attention for its low cost, nontoxicity, and environmentally benign properties. $FeCl_3$ can quantitatively complex with the imine groups of phenylazomethine dendrimers.[7] The synthesis of bimetallic Rh/Fe nanoparticles shown in Scheme 1 was conducted using a slightly modified version of the procedure previously reported for the synthesis of monometallic Rh nanoparticles.[2] These materials were prepared by the stepwise complexation of $RhCl_3$ and $FeCl_3$ with TPP-DPA G4 in a controlled stoichiometry, and subsequent reduction with $NaBH_4$. The resulting bimetallic nanoparticles were stable in solution under Ar, and no precipitation or color changes occurred over several weeks.

The formation of Rh/Fe bimetallic nanoparticle was confirmed by TEM, X-ray fluorescence (XRF), and X-ray photoelectron spectroscopy (XPS). TEM images revealed small uniform nanoparticles with an average particle size of (1.1 ± 0.2) nm (Figure 1 a,b). Figure 1 c shows the XRF spectrum taken from the sample shown in Figure 1 a, which indicated that the nanoparticles were composed of Rh and Fe in a ratio of 32:28. These values agreed well with the mol % of $RhCl_3$ and $FeCl_3$ used in the synthetic mixture. The XPS result revealed information about the surfaces of the nanoparticles. Medium intensity Rh $3d_{5/2}$ and Rh $3d_{3/2}$ signals with binding energies of 307.5 eV and 312.4 eV, characteristic of metallic Rh, were observed.[8] A weak Fe $2p_{3/2}$ signal with a binding energy of 709.4 eV was detected. This peak corresponded to a low-valent Fe species ($FeCl_3$: 711.3 eV, $FeCl_2$: 710.7 eV).[9] No oxidized Rh or Fe was detected in this sample.

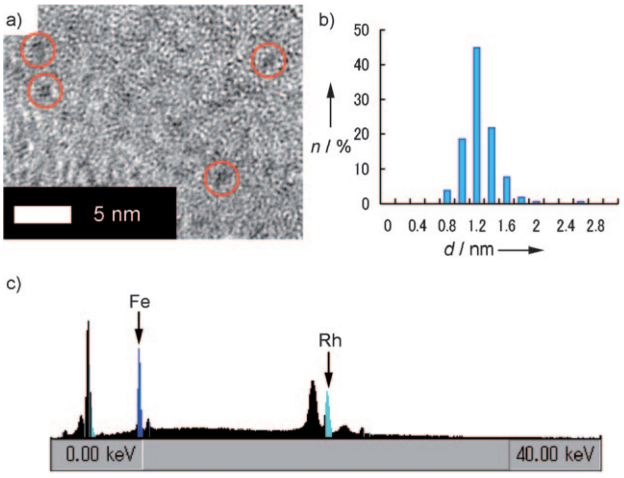

Figure 1. Characterization of $Rh_{32}Fe_{28}$@TPP-DPA G4. a) TEM image of Rh/Fe nanoparticles on a carbon-coated copper grid. A few of the nanoparticles are circled. b) Size distribution (n: frequency, d: particle size). c) XRF spectrum.

The catalytic performance of Rh/Fe bimetallic nanoparticles was initially tested for the reduction of olefinic substrates under a hydrogen atmosphere (1 atm). The progress of the reaction was monitored by conversion of the starting material as a function of time. The initial activities of Rh_{60}@TPP-DPA G4 and $Rh_{32}Fe_{28}$@TPP-DPA G4 in MeOH (represented as the turnover frequency (TOF), the number of conversions within 30 min) toward olefin hydrogenation, and of Wilkinson complex ($[RhCl(PPh_3)_3]$) were measured. As shown in Table 1 (entries 1–3), the Rh/Fe nanoparticles

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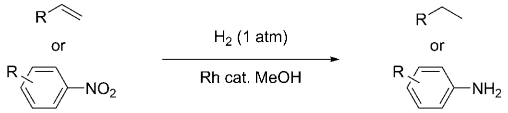
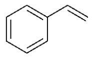
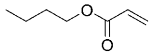
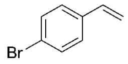
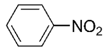
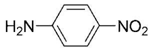
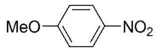
Table 1: Turnover frequencies (TOFs [h^{-1}]) of the hydrogenation of olefins and nitroarenes in the presence of various Rh catalysts.



Entry	Substrate	Wilkinson	Rh_{60}@TPP-DPA[c]	**$Rh_{32}Fe_{28}$@TPP-DPA[c]**
1[a]		8	173 (10380)	**510 (30600)**
2[a]		12	292 (17520)	**500 (30000)**
3[a]		57	78 (4680)	**139 (8340)**
4[b]		0	2 (120)	**11 (660)**
5[b]		0	2 (120)	**17 (1020)**
6[b]		0	5 (300)	**11 (660)**

[a] 1.75 mmol olefinic substrate, 0.3 mol% catalyst (based on metal), 5 mL MeOH under H_2 (1 atm). [b] 0.7 mmol aromatic nitro compound, 0.3 mol% catalyst, 5 mL MeOH under H_2 (1 atm). [c] The TOF in parentheses is corrected for the total metal content (calculated as 60 atoms/cluster). Highest values highlighted in bold.

showed enhanced catalytic activity over the Rh nanoparticles or Rh complex. The scope of the reaction was extended by examining the hydrogenation of various nitroarenes under similar conditions. Although hydrogenation of nitroarenes has been recognized as an important chemical transformation for obtaining aniline derivatives, Wilkinson catalyst showed essentially no reactivity for this transformation. Hydrogenation of the nitroarenes was observed using nanoparticles as catalyst.[10] As shown in Table 1 (entries 4–6), the TOF measured using a bimetallic catalyst was up to 8.5-times higher than that measured using the Rh nanoparticle catalyst. Comparison of hydrogenation activities of the different Rh catalysts clearly indicated that the catalysis environment played the dominant role in determining the activity of the catalyst (Figure 2).

TEM studies of both fresh and used catalysts were conducted to understand the shape and size of the particles. No obvious aggregation of nanoparticles was observed by TEM during the reaction. To determine if the nanoparticles were just a physical mixture of Rh and Fe nanoparticles or are bimetallic, we also prepared Fe_{60}@TPP-DPA G4 (1.3 ± 0.4 nm) and examined the catalytic activity.[11] Fe_{60}@TPP-DPA G4 did not show catalytic activity at all and the physical mixture of Rh and Fe nanoparticles in a ratio of 53:47 (ca. 32:28) showed lower reactivity than the bimetallic nanoparticles. The higher TOFs observed for Rh/Fe bimetallic nanoparticles were thought to arise from synergistic electronic effect.

In conclusion, we developed an efficient nanoparticle catalyst system for the hydrogenation of olefins and nitroarenes under relatively mild conditions. In a comparison with previously reported hydrogenation reactions using Rh nanoparticle catalysts in dendrimer cages, we found that the bimetallic Rh/Fe nanoparticles showed improved catalytic ability toward these hydrogenation reactions. These results also provide a means for preparing almost completely uniform bimetallic metal catalysts under easily controlled conditions. This observation provides new critical experimental parameters for the design and optimization of durable nanoparticle catalysts. Forthcoming reports will describe bimetallic nanoparticles prepared from different metal combinations.

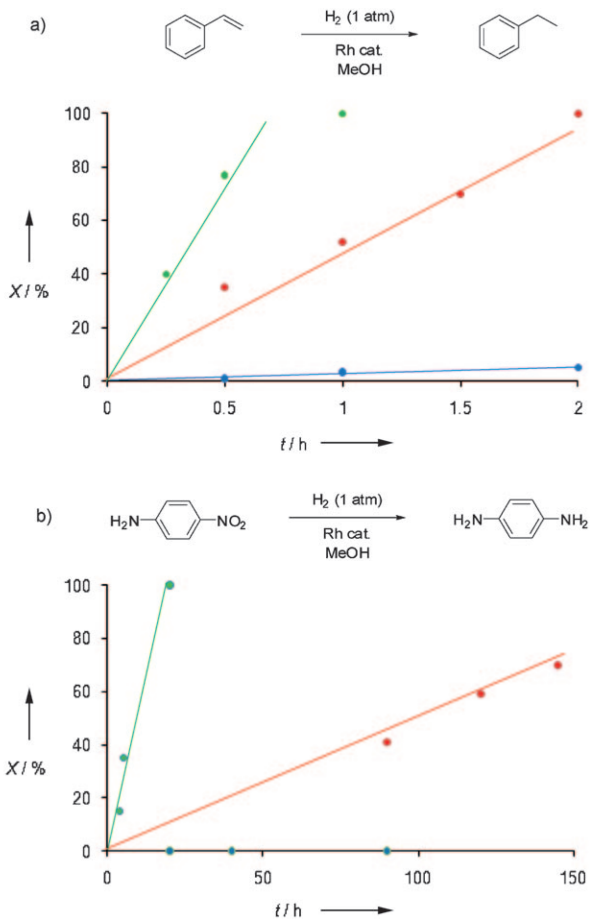


Figure 2. Dependence of conversion (*X*) on the reaction time (*t*) in the rhodium-catalyzed hydrogenation of a) styrene and b) 4-nitroaniline. Wilkinson catalyst (blue), Rh_{60}@TPP-DPA G4 (red), and $Rh_{32}Fe_{28}$@TPP-DPA G4 (green).

Experimental Section

Fe_{60}@TPP-DPA G4: All processes were conducted under a dry nitrogen atmosphere in the dark. Iron(III) chloride (0.90 mg, 5.3 μmol, 60 equiv relative to the dendrimer) in *N*,*N*-dimethylformamide (DMF, 1.5 mL) was added to the TPP-DPA G4 (1.0 mg, 0.088 μmol) solution in toluene (3 mL). After stirring for 30 min, sodium borohydride (1.0 mg, 26 μmol, 5 equiv relative to the iron) in methanol (0.5 mL) was added dropwise to the solution. This solution was stirred overnight to afford a dispersion of dendrimer-stabilized Fe nanoparticles.

$Rh_{32}Fe_{28}$@TPP-DPA G4: All processes were conducted under a dry nitrogen atmosphere in the dark. Iron(III) chloride (0.40 mg, 2.5 μmol, 28 equiv relative to dendrimer) in DMF (0.5 mL) was added to the TPP-DPA G4 (1.0 mg, 0.088 μmol) solution in toluene (3 mL). After stirring this mixture for 30 min, rhodium(III) chloride trihydrate (0.80 mg, 2.8 μmol, 32 equiv relative to dendrimer) in DMF (1 mL) was added and stirred for another 30 min. Then, sodium borohydride (1.0 mg, 26 μmol, 5 equiv relative to the sum of iron and rhodium) in methanol (0.5 mL) was added dropwise to the solution. This solution was stirred overnight to afford a dispersion of reddish black dendrimer-stabilized Rh/Fe nanoparticles.

Typical procedure for $Rh_{32}Fe_{28}$@TPP-DPA G4 catalyzed hydrogenation: All processes were conducted at room temperature under atmospheric pressure in the dark. A carefully dried Schlenk flask equipped with a magnetic stir bar was charged with dry nitrogen. Butyl acrylate (0.25 mL, 1.75 mmol) in methanol (5 mL) was then added into the flask. A solution of $Rh_{32}Fe_{28}$@TPP-DPA (0.3 mol% metal relative to the olefin) was added to this olefin solution. Hydrogen gas was supplied from a balloon. The reaction was monitored by GC-MS. The samples for GC-MS were prepared by filtering a drop of the reaction mixture in methanol through a small amount of silica gel at each time point.

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