

Particle Size Control in Dendrimer-Derived Supported Ruthenium Catalysts

Gwendoline Lafaye,[‡] Attilio Siani,[†] Patrice Marécot,[‡] Michael D. Amiridis,^{*,†} and Christopher T. Williams^{*,†}

Department of Chemical Engineering, Swearingen Engineering Center, University of South Carolina, Columbia, South Carolina 29208, and Laboratoire Associé de Catalyse en Chimie Organique, UMR CNRS, Université de Poitiers, 40 Avenue du Recteur Pineau, F-86022 Poitiers Cedex, France

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A high-resolution transmission electron microscopy (HRTEM) investigation of a family of supported Ru catalysts prepared from Ru hydroxyl-terminated poly(amidoamine) dendrimer–metal nanocomposite (DMN) precursors has been conducted. Ru particle sizes observed following deposition of DMNs on a HRTEM grid can be controlled within a 0.9–1.4 nm range depending on the metal-to-dendrimer molar ratio. The average particle size in this case correlates well with the theoretically predicted particle size from the molar loading of Ru in the dendrimer. Upon impregnation of Ru-DMNs on Al₂O₃ and subsequent thermal removal of the dendrimer via reduction at 300 °C, significant sintering of the Ru particles was observed. Nevertheless, the resulting supported Ru particles maintained a narrow particle size distribution and average particle size below 2.5 nm. These particle sizes no longer correlate with the metal-to-dendrimer molar ratio but do correlate with the metal-to-dendrimer weight ratio, suggesting that the dendrimer may be acting as a “sintering-control” agent on the catalyst surface. This process is not affected by the surface area of the support, since almost identical particle size distributions were obtained on three different commercial supports.

Introduction

The metal particle size of supported metal catalysts is an important parameter affecting catalytic behavior. Supported metal catalysts are usually prepared by impregnation of salt precursors onto the surface of a solid support, followed by calcination and/or reduction treatment at elevated temperatures. Such “activation” treatments offer limited control of the particle size and distribution and result in an uneven dispersion of particles across the support surface (i.e., monodispersion versus aggregation). One of the most challenging goals in catalyst synthesis is to achieve control of these particle properties while maintaining a constant metal loading on the support. When different support materials (i.e., various oxides, carbon) are involved, the situation becomes even more complicated, since the surface structures and properties of these materials vary significantly. For example, the adsorption strength of a given metal precursor on the support surface as well as the metal atom diffusion rate across the surface during catalyst treatment strongly affect the final particle properties. These factors hinder studies of support effects independently of particle size, distribution, and monodispersity.

The use of dendrimer–metal nanocomposites (DMNs) as precursors for supported metal catalysts has been proposed and demonstrated in recent years.^{1–13} Dendrimers are a special class of hyperbranched polymers that emanate from a central core with repetitive branching units, thus having a specific molecular structure and controllable size.^{14–16} While exhibiting a very dense exterior, they contain a hollow interior that can be ideal

for the formation and stabilization of metal nanoparticles. For example, hydroxyl-terminated poly(amidoamine) (PAMAM-OH) dendrimers contain interior tertiary amine and secondary amide groups that can effectively chelate metal ions. Such metal ions may be subsequently reduced to form encapsulated metal nanoparticles that can be highly stable. Since the same number of chelating sites is present in all dendrimer molecules of the same generation, this process should in principle yield metal nanoparticles with a narrow size distribution.

Dendrimers have been very successfully used to template and stabilize metal nanoparticles in solution,^{6,17–21} and more recently such DMNs have been employed as precursors for supported metal catalysts on high-surface-area^{2–10} and flat^{11,12} oxide supports. For example, Pt–PAMAM-OH DMNs have been used as precursors for Pt/SiO₂ catalysts,^{2,4} producing a narrow distribution of Pt nanoparticles on the SiO₂ support after dendrimer removal. We have previously reported the use of Ru–PAMAM-OH DMNs for the synthesis of Ru/Al₂O₃ catalysts.⁶ This approach produced Ru nanoparticles with a narrow particle size distribution and an average size that was similar to that predicted by an equal distribution of the initial Ru³⁺ cations to the dendrimer molecules in the original solution. After delivery to the support and subsequent thermal removal of the dendrimer in hydrogen, the resulting catalyst exhibited a mean Ru particle size that was approximately 50% larger than what was observed in the unsupported DMNs, suggesting some degree of sintering during the dendrimer removal process. However, the DMN-derived catalyst exhibited a much narrower particle size distribution than a corresponding catalyst prepared through a conventional wet impregnation procedure using the same Ru salt precursor.⁶

In this paper we present a high-resolution transmission electron microscopy (HRTEM) investigation of a family of

* Authors to whom correspondence should be addressed. Fax: (803) 777-8265. E-mail: willia84@engr.sc.edu; amiridis@engr.sc.edu.

[†] University of South Carolina.

[‡] Université de Poitiers.

supported catalysts prepared from Ru–PAMAM-OH DMN precursors. It is demonstrated that these precursors afford control over the average particle size, particle size distribution, and monodispersity of Ru on an Al₂O₃ support. The differences in particle sizes observed prior to and after dendrimer removal are addressed and appear to be the result of sintering that occurs during the thermal activation process. In addition, it is shown that Ru-DMNs can be used to achieve very similar nanoparticle average sizes and distributions on three different support materials.

2. Experimental Section

Materials. Hydroxyl-terminated third- (G3OH), fourth- (G4OH), and fifth-generation (G5OH) poly(amidoamine) (PAMAM) dendrimers were obtained as methanol solutions (Aldrich). Prior to use, the methanol was removed under N₂ flow at room temperature. RuCl₃ (99.9% PGM-based) was purchased from Alfa Aesar and used as received. Three different supports were used: low-surface-area γ -Al₂O₃ (Alfa Aesar, 45 m² g⁻¹), high-surface-area γ -Al₂O₃ (BASF, 160 m² g⁻¹), and SiO₂ (Grace Davison, 292 m² g⁻¹). The supports were calcined in air for 4 h at 500 °C prior to their use. Water purified to 18 M Ω cm (Milli-Q) was used to prepare all of the aqueous solutions.

DMN Synthesis. The procedure for the preparation of dendrimer–Ru nanocomposites (DMNs) has been reported previously.⁶ In brief, an appropriate amount of aqueous RuCl₃ solution was added, under inert atmosphere, to a dilute aqueous solution of the hydroxyl-terminated PAMAM dendrimer (1.75 \times 10⁻⁴ M) to obtain the desired Ru-to-dendrimer ratio. The final total volume has been fixed to 40 mL. After 3 days of Ru–dendrimer complexation, a reduction of the Ru ions was performed by bubbling hydrogen through the solution for 1 h at room temperature. We use the designation Ru_XG_YOH to classify the various DMNs, where *X* is the molar ratio of Ru metal ions to the dendrimer and *Y* is the dendrimer generation. For the present study we have varied *X* between 20 and 100 and *Y* between 3 and 5.

Catalyst Synthesis. The Ru_XG_YOH DMNs were deposited onto various supports via standard wet impregnation at room temperature. In all cases, the metal loading was kept constant at 1 wt % Ru. To expose the Ru nanoparticles, the dendrimer “shell” was subsequently removed by thermal treatment. It has been shown in the literature that oxidation followed by reduction with H₂ results in enhanced sintering of conventionally prepared supported Ru catalysts.^{22–27} Since our previous study⁶ of a Ru₄₀G₄OH-derived 1 wt % Ru/Al₂O₃ catalyst further suggested that a H₂ treatment at 300 °C for 2 h was sufficient for dendrimer removal, such direct reduction treatments were also used for all catalysts prepared for the current study as well.

Electron Microscopy. HRTEM studies were performed with two different instruments: a Philips CM 120 microscope (Poitiers) operating at 120 kV and a Hitachi HF-2000 microscope (Oak Ridge National Laboratory) operating at 200 kV. In preparation for the HRTEM imaging a Ru–dendrimer solution was dried onto a copper grid covered by a carbon support film. The supported Ru catalysts were ultrasonically dispersed in ethanol prior to their deposition onto the copper grid. Histograms of particle size distributions were obtained through measurement of at least 150 randomly selected particles from at least three images of any given sample. The experimental volume–surface mean diameters of the particles in

different samples were calculated by the following equation

$$\bar{D} = \frac{\sum_i^N N_i D_{p,i}^3}{\sum_i^N N_i D_{p,i}^2}$$

where *N_i* is the number of particles with a diameter *D_{p,i}*.

3. Results and Discussion

3.1. Ru_XG_YOH. Figure 1 shows a characteristic HRTEM image and the size-distribution histograms observed following deposition of aqueous Ru-DMN solution with a Ru-to-dendrimer ratio between 20 and 100 onto the copper grid. Higher Ru-to-dendrimer ratios can also be achieved, but they would require G₆OH dendrimer to be used so as to provide a sufficient number of sites for complexation of the metal ions within the interior of the dendrimer. Given the cost of these higher-generation dendrimers and the diminishing catalytic benefits with larger Ru particles, such an approach would be of limited value in this case. Inspection of these histograms reveals a narrow particle size distribution in all four samples shown. Furthermore the HRTEM images indicate a roughly spherical shape in all cases. All of the observed particles are smaller than 2.5 nm, in stark contrast with control experiments involving the reduction of a nondendrimer containing an aqueous solution of RuCl₃, which led to visible black precipitates of metallic Ru.

One of the primary hypotheses for the utilization of DMNs is that the size of the resulting particles can be controlled by varying the metal loading in the metal–dendrimer solution. This is based on the assumption of a “fixed” loading law model, which assumes that the metal ions are completely complexed inside the dendrimer and that upon final reduction only the metal ions in a given dendrimer molecule coalesce to form a single nanoparticle. Table 1 lists the experimentally observed mean particle diameters for these samples, revealing that the average size of the resulting Ru particles does indeed depend on the metal-to-dendrimer molar ratio. Similar results have been reported in the literature for other metals such as Pt, Pd, Cu, and Au.^{2,17,19,21,28,29} Assuming that these Ru nanoparticles have close-packed hexagonal single-crystal structures, theoretical diameters can be calculated by considering the smallest sphere circumscribing the number of atoms within the crystal lattice. A schematic of this procedure is presented in Scheme 1, along with the relevant equations for the calculation, and the results are included in Table 1. A correlation between theoretically predicted sizes for the Ru particles and the experimentally observed particle sizes is shown in Figure 2. The diagonal in Figure 2 represents the ideal case in which predicted and experimentally observed particle sizes would be equal. In general though, the observed particle sizes appear to be 10–20% greater than the theoretical predictions.

3.2. Ru_XG_YOH-Derived 1 wt % Ru/Al₂O₃ Catalysts. Ru-DMNs were deposited onto the calcined low-surface-area γ -Al₂O₃ support via wet impregnation at room temperature to obtain a 1 wt % Ru/Al₂O₃ catalyst. The dendrimer component was subsequently removed by thermal treatment in hydrogen at 300 °C (2 °C/min heating ramp) for 2 h, based on a protocol established previously.⁶ Figure 3 shows a characteristic HRTEM image and the size-distribution histograms obtained for a set of catalyst samples thus prepared. In all cases the HRTEM images reveal small and well-dispersed particles on the alumina surface,

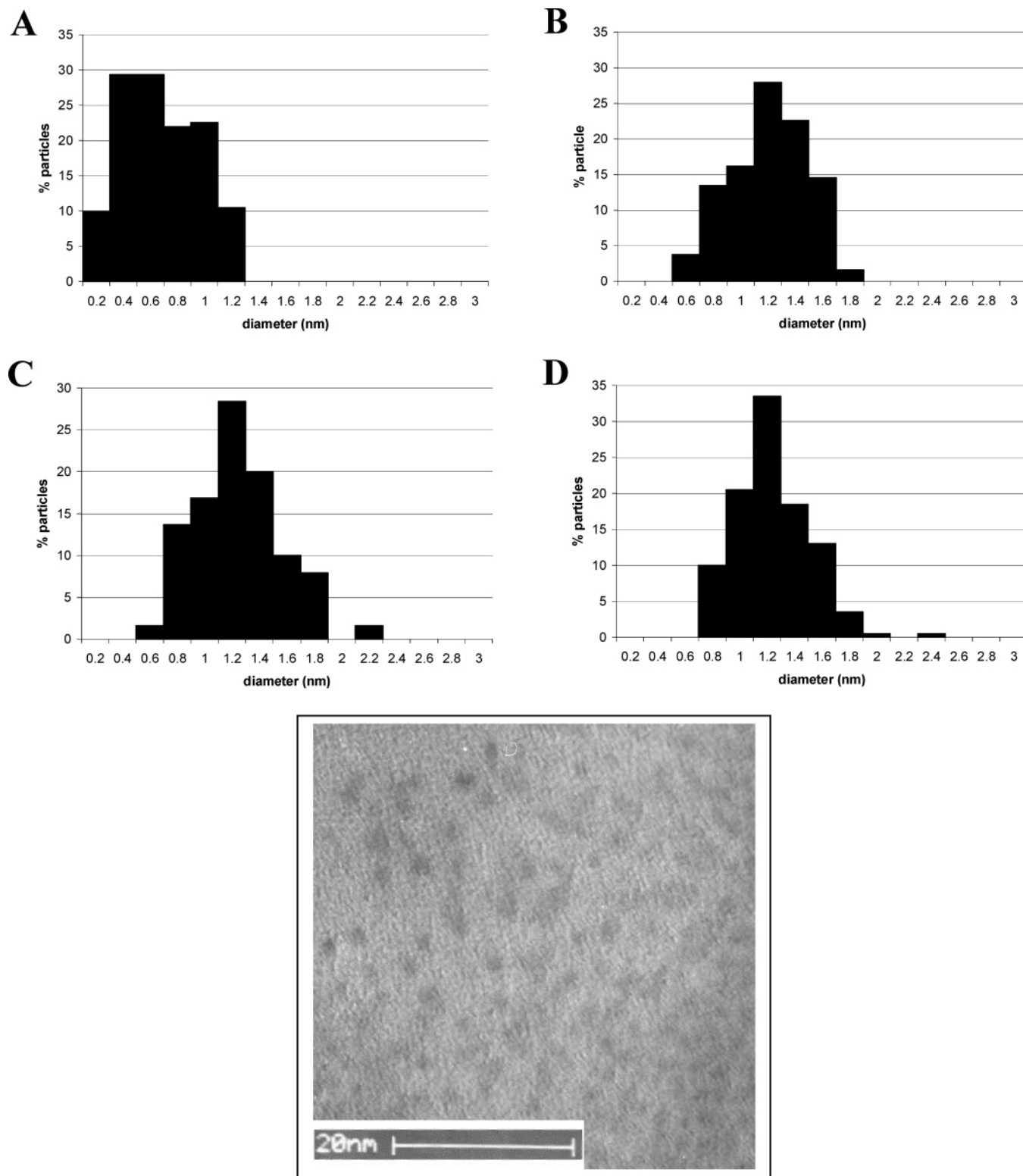


Figure 1. Metal particle size distributions obtained by HRTEM measurements of (A) $\text{Ru}_{20}\text{G}_4\text{OH}$, (B) $\text{Ru}_{40}\text{G}_4\text{OH}$, (C) $\text{Ru}_{60}\text{G}_5\text{OH}$, and (D) $\text{Ru}_{100}\text{G}_5\text{OH}$ solution deposited on a carbon-coated copper grid. The representative HRTEM image is of $\text{Ru}_{60}\text{G}_5\text{OH}$.

with the volume–surface mean diameters reported in Table 2. A comparison with the precursor data shown in Table 1 reveals that some sintering of Ru takes place during the hydrogen treatment step needed for the dendrimer removal, consistent with results reported previously.⁶ In the case of the $\text{Ru}_{20}\text{G}_4\text{OH}$ -derived catalysts, the percentage increase in the particle size is as high as 75%. Furthermore the mean diameters of the supported particles observed no longer correlate with the theoretical Ru crystallite sizes calculated on the Ru-to-dendrimer

ratio of the precursor DMNs. Figure 4A shows the observed mean particle diameters plotted versus the calculated theoretical sizes from the relevant Ru-DMN precursors and demonstrates the lack of such a correlation.

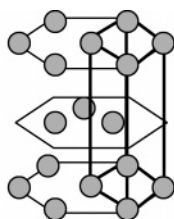
One common attribute of DMN-derived catalysts is that the Ru particles are very well dispersed across the support surface and maintain a tight particle size distribution. This suggests that there is still an attribute of the DMN precursor that can be used to predict the particle size of the resulting catalysts. Indeed, we

TABLE 1: Comparison between Calculated and Experimental Diameters of Ru Nanoparticles

Ru-DMN	experimental volume–surface mean diameter ^a (nm)	calculated theoretical diameter ^b (nm)
Ru ₂₀ G ₄ OH	0.9	0.81
Ru ₄₀ G ₄ OH	1.2	1.02
Ru ₆₀ G ₅ OH	1.4	1.17
Ru ₁₀₀ G ₅ OH	1.4	1.39

^a Obtained from the particle size distributions of Figure 1. ^b See Scheme 1 for details.

SCHEME 1: Theoretical Calculation of Ru Particle Diameter



Ru cell parameters: $a=b=0.27059$ nm, $c=0.42815$ nm
 $\alpha=\beta=90^\circ$, $\gamma=120^\circ$

$$V = \text{volume of hexagonal unit cell} = \frac{\sqrt{3}}{2} a^2 c$$

$$N = \text{Atoms per unit cell} = 2$$

$$\rho = \text{Volume of unit cell per atom} = V/N$$

$$n = \text{number of Ru atoms in particle}$$

$$D = \text{particle diameter assuming spherical shape} = 2 \cdot \sqrt[3]{\frac{\rho \cdot n \cdot 3}{4 \cdot \pi}}$$

have previously synthesized a 1% Ru/Al₂O₃ catalyst by aqueous wet impregnation of RuCl₃ onto the same low-surface-area γ -Al₂O₃ support using an identical H₂ treatment.⁶ The resulting mean Ru particle diameter was found to be 3.4 nm, and the particles exhibited a wide distribution ranging from 0.5 to 5 nm with a relatively flat profile. This contrasts with the significantly smaller mean particle sizes and tighter distributions shown in Figures 3 and 4. We therefore hypothesized that during thermal treatment the dendrimer is functioning as a “sintering-control” agent limiting the degree to which encapsulated Ru particles can agglomerate and/or coalesce on the surface of the support. Under this scenario, an increase in the amount of polymer present on the support would result in a smaller final particle size. Along this line, Figure 4B shows the mean particle diameters of the different Ru catalysts plotted versus the dendrimer-to-metal weight ratio. The least-squares fit of these data (solid line) reveals a good fit and correlation. Through the use of the statistical standard errors in the slope and intercept, the error to the predicted particle size can be estimated. The dashed line boundaries in Figure 4B indicate this estimated uncertainty in the correlation to be on the order of 10–20%. Perhaps most surprising is that very different precursor DMNs having roughly the same dendrimer-to-metal weight ratio exhibit roughly the same final average Ru particle size. For example, the data contained within the solid circle in Figure 4B represent catalysts synthesized by Ru₂₀G₃OH, Ru₄₀G₄OH, and Ru₁₀₀G₅OH DMNs.

While the weight loading of dendrimer in the catalyst sample is clearly an important design parameter, we maintain that the metal-to-dendrimer molar ratio in the DMN precursor is also important and should be considered. In the synthesis of the different Ru-DMNs, this ratio was often kept well below the number of complexation sites present within each dendrimer

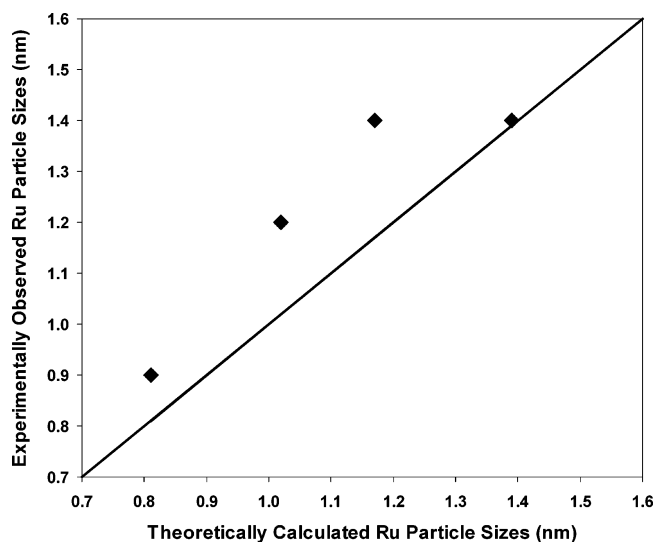


Figure 2. Comparison of the experimentally observed and theoretically calculated averaged particle sizes for the various DMN precursors.

to avoid the presence of “free” Ru in solution. We have shown that such free Ru species result in the formation of visible black precipitates upon reduction with hydrogen and therefore a very wide final particle size distribution.⁶ This in turn would likely affect the monodispersity of the final catalyst, resulting in multiple size ranges of Ru particles (although the degree of thermal sintering could still be controlled by the dendrimer content). For example, in the case of the Ru₅₅G₄OH-derived catalyst the metal loading is very close to the maximum number of complexation sites possible (i.e., 62). It is therefore likely that the somewhat inconsistent mean particle size for this catalyst (in terms of the correlation) is a result of some Ru remaining free in solution, thus leading to larger particles.

We previously reported that the size of the Ru particles is not affected by simple immobilization on the support itself.⁶ As observed in the current study, however, the changes in the average particle size occur during the heat treatment required to remove the dendrimer from the catalyst surface. The present study is limited to only one set of treatment conditions for thermal removal of the dendrimer. However, several parameters may be adjusted to limit the degree of sintering observed, including the heating ramp speed, the reduction temperature, and the reduction time. For example, a longer (e.g., >10 h) treatment of the catalyst at a considerably lower temperature⁴ might result in particle sizes that correlate better with the initial size of the DMN precursors. Nevertheless, the present results suggest that for a chosen treatment condition that induces substantial sintering it should be still possible to partially control and predict the final Ru particle size through control of the metal-to-dendrimer weight and molecular ratios.

3.3. Ru₄₀G₄OH-Derived 1 wt % Ru on Various Supports.

The particle size of conventionally prepared supported metal catalysts often depends on the nature and the surface area of the support (e.g., Al₂O₃, SiO₂, TiO₂, etc.). For example, two catalysts made via the same synthetic procedure (i.e., identical metal precursor, activation procedure, etc.) on Al₂O₃ supports having different surface areas would likely exhibit different average metal particle sizes and distributions. Furthermore, optimal synthetic protocols are often not transferable between various oxide supports of similar surface area. Another of the hypotheses of the DMN approach to catalyst synthesis is the opportunity for “cross platform” delivery of very similar nanoparticles. In principle, the support in these cases should

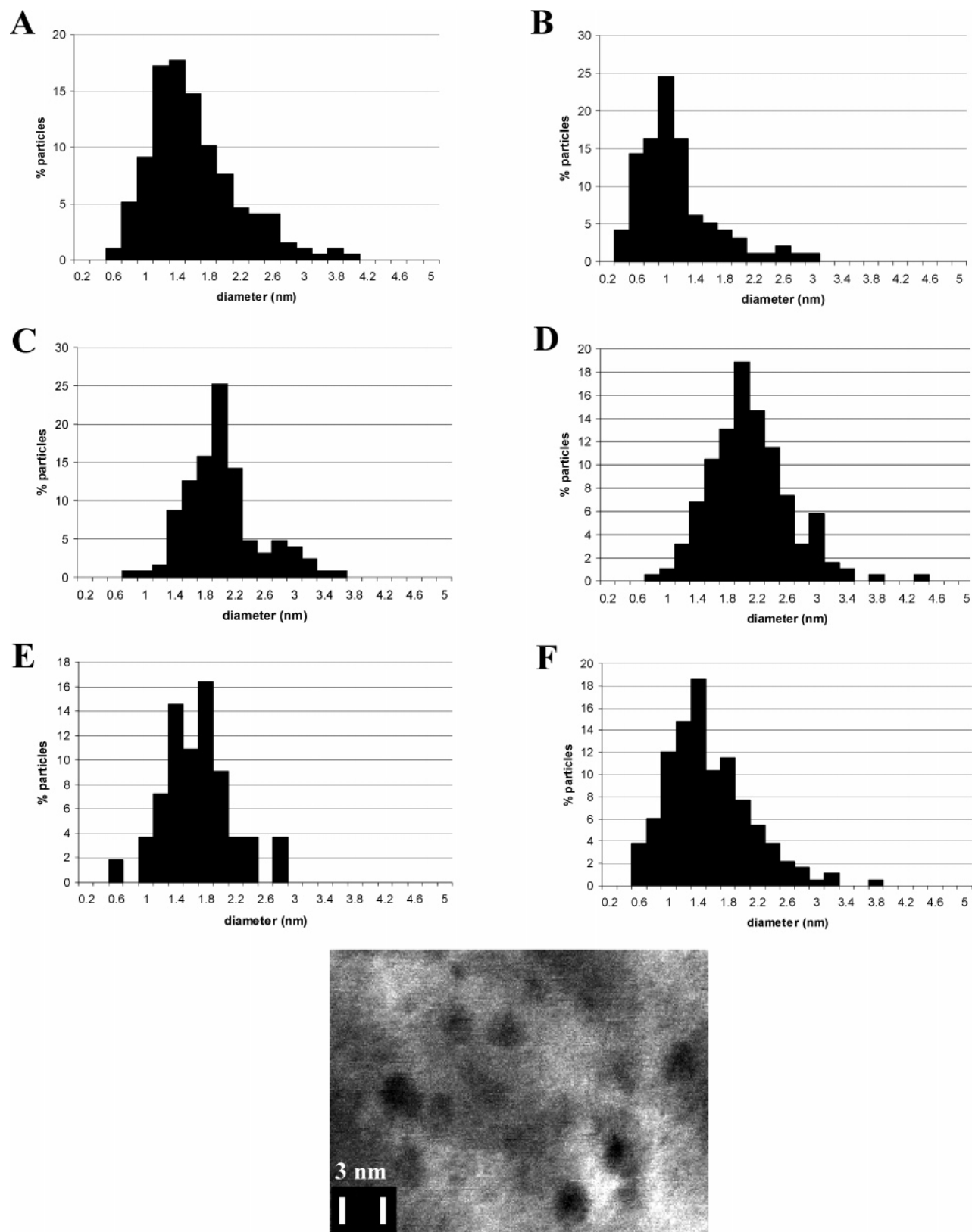


Figure 3. Metal particle size distributions obtained by HRTEM measurements of 1 wt % Ru/Al₂O₃ (LSA) catalysts prepared from (A) Ru₂₀G₃OH, (B) Ru₂₀G₄OH, (C) Ru₄₀G₄OH, (D) Ru₅₅G₄OH, (E) Ru₆₀G₅OH, and (F) Ru₁₀₀G₅OH. The representative HRTEM image is of the Ru₄₀G₄OH-derived catalyst.

play a lesser role in the final particle size distribution. To test this hypothesis, three 1 wt % Ru catalysts were prepared from the same Ru₄₀G₄OH DMN on three different commercial supports: lower-surface-area γ -Al₂O₃, higher-surface-area γ -Al₂O₃, and SiO₂. These supports were chosen because they cover a wide range of surface areas. The catalysts were

synthesized under the exact same conditions described above, using thermal activation treatment in hydrogen at 300 °C (2 °C/min heating ramp) for 2 h to remove the dendrimer. Figure 5 shows the size-distribution histograms obtained for the higher-surface-area γ -Al₂O₃ (A) and the SiO₂ (B), while the size-distribution histogram for the low-surface-area Al₂O₃ is shown

TABLE 2: Experimentally Observed Ru Particle Sizes for Ru-DMN-Derived 1 wt % Ru/Al₂O₃ Catalysts, along with the Precursor Ru_x/G_yOH Weight Ratios

sample	volume–surface mean diameter (nm)	G _y OH/ Ru _x (wt/wt)
Ru ₂₀ G ₃ OH/Al ₂ O ₃	2.0	3.4
Ru ₂₀ G ₄ OH/Al ₂ O ₃	1.6	7.0
Ru ₄₀ G ₄ OH/Al ₂ O ₃	2.0	3.5
Ru ₅₅ G ₄ OH/Al ₂ O ₃	2.3	2.5
Ru ₆₀ G ₅ OH/Al ₂ O ₃	1.9	4.7
Ru ₁₀₀ G ₅ OH/Al ₂ O ₃	2.0	2.8
1% Ru/Al ₂ O ₃ (WI) ^a	3.4	0.0

^a Conventional catalyst synthesized by wet impregnation as described in the text and in ref 6.

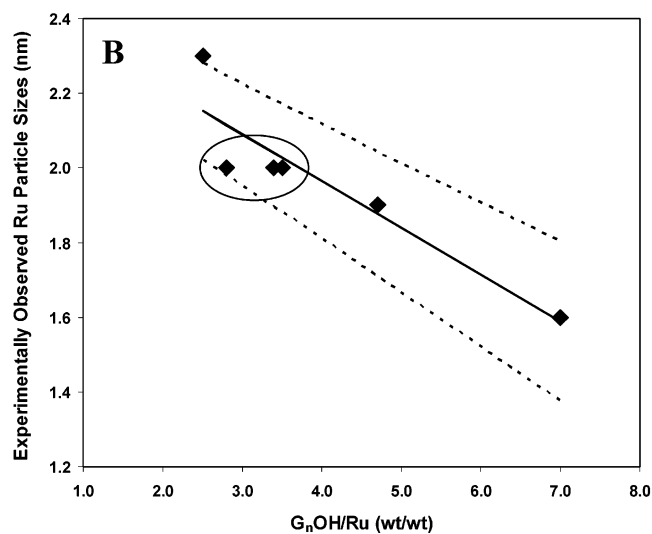
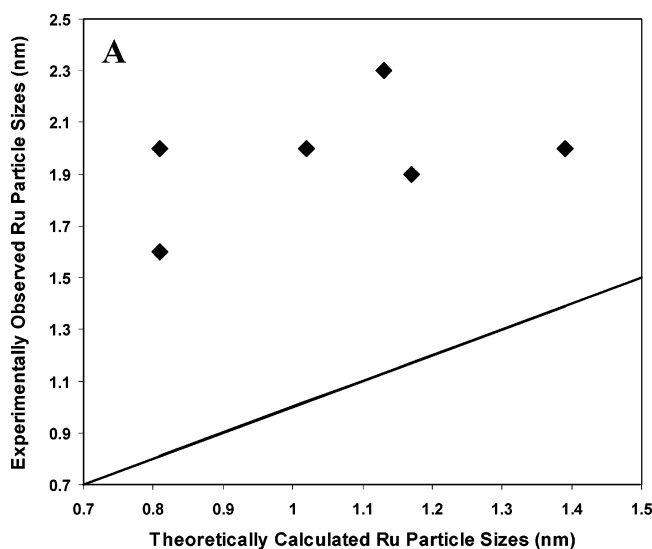


Figure 4. (A) Comparison of experimentally observed (for 1 wt % Ru/Al₂O₃ catalysts) and theoretically calculated average Ru particle sizes based on the Ru-to-dendrimer ratio for the Ru-DMN precursor used during synthesis. (B) Volume–surface mean diameter of different DMN-derived 1 wt % Ru/Al₂O₃ catalysts versus the G_nOH/Ru_x (wt/wt) ratio present in the associated Ru-DMN precursors used during synthesis.

in Figure 3C. All three catalysts contain well-dispersed Ru particles with a narrow particle size distribution, although once again some sintering has apparently taken place during dendrimer removal. Surprisingly the sintering process proceeded similarly on all three supports, as indicated by the mean particle diameter observed in all three catalysts.

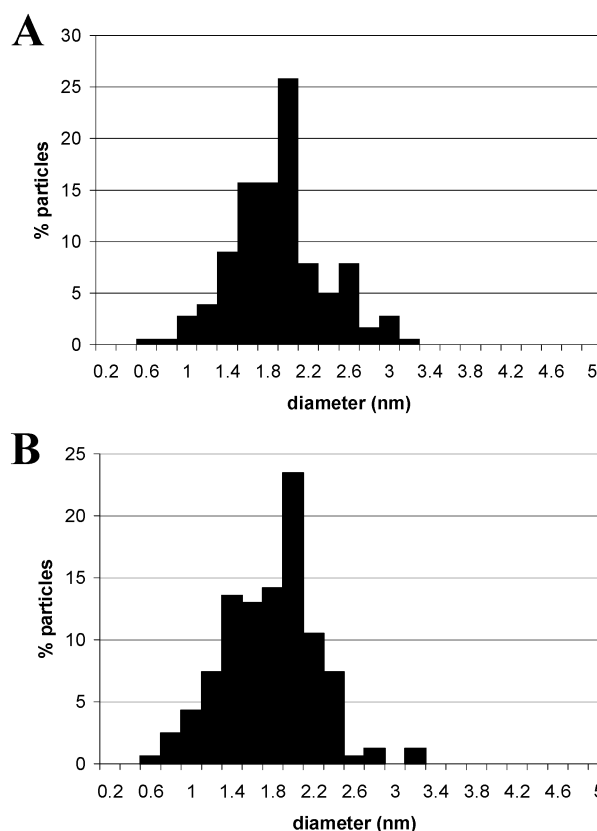


Figure 5. Metal particle size distributions obtained by HRTEM measurements of (A) Ru₄₀G₄OH/SiO₂ and (B) Ru₄₀G₄OH/Al₂O₃ (HSA).

4. Conclusions

In this paper we have presented a HRTEM investigation of a family of supported Ru catalysts prepared from Ru–PAMAM–OH DMN precursors. The average particle size of the Ru-DMN precursors on the HRTEM grid was found to correlate well with the theoretical particle size predicted from the molar loading of metal in the dendrimer. Furthermore it was demonstrated that the use of these precursors affords control over the particle size, distribution, and monodispersity of 1 wt % Ru/Al₂O₃ catalysts. However, the observed mean Ru particle sizes in these catalysts were increased by as much as 75% compared to the associated DMN precursor, suggesting that sintering was taking place during the thermal removal of the dendrimer. The mean particle diameter of the Ru particles was found to correlate well with the metal-to-dendrimer weight ratio, suggesting that the dendrimer is behaving as a sintering-control agent. Finally, it was shown that Ru-DMNs can provide a method to achieve near identical nanoparticle average sizes and distributions across different support materials.

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