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Synthesis and Characterization of Branched *fcc/hcp* Ruthenium Nanostructures and their Catalytic Activity in Ammonia Borane Hydrolysis

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ABSTRACT. Several systems have shown the ability to stabilize uncommon crystal structures during the synthesis of metallic nanoparticles. By tailoring the nanoparticle crystal structure, the physical and chemical properties of the particles can also be controlled. Herein, we first synthesized branched nanoparticles of mixed *hcp/fcc* ruthenium, which were formed using tungsten carbonyl [W(CO)₆] as both a reducing agent and a source of carbon monoxide. The branched particles were formed from multiple particulates off a central core. High-resolution transmission electron microscopy (HRTEM) clearly showed that the branched structures consisted of aligned *hcp* crystal domains, a mixture of *fcc* and *hcp* crystal domains with several defects and misalignments, and particles that contained multiple cores and branches. Branched particles were also formed with molybdenum carbonyl [Mo(CO)₆], and faceted particles of *hcp* and *fcc* particles were formed with rhenium carbonyl [Re₂(CO)₁₀] as a carbon monoxide source. Without metal carbonyls, small particles of spherical *hcp* ruthenium were produced, and their size could be controlled by the selection of the precursor. The

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5 ruthenium nanoparticles were tested for ammonia borane hydrolysis; the branched
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7 nanoparticles were more reactive for catalytic hydrogen evolution than the faceted
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9 *hcp/fcc* nanoparticles or the spherical *hcp* nanoparticles. This work showcases the
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11 potential of crystal phase engineering of transition metal nanoparticles by different
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13 carbon monoxide precursors for tailoring their catalytic reactivity.
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20 Physical and chemical properties, such as magnetism and catalytic activity, are
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22 intrinsically related to the crystal structure of nanomaterials.¹⁻³ Over the past two
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24 decades, a variety of noble metals have been produced in uncommon or previously
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26 unknown crystal structures, including Au, Ag, Pd, Rh and Ru.⁴ For example, face-
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28 centered cubic (*fcc*) Ru nanoparticles were synthesized by Kitagawa *et al.*, showing
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30 increased catalytic activity toward CO oxidation at larger particle sizes over
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32 nanoparticles made of the common crystal structure for Ru, *i.e.*, hexagonal close packed
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34 (*hcp*).⁵ Further work with *fcc* Ru and *fcc* Ru@Pt demonstrated enhanced catalytic
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36 properties over *hcp* Ru in the hydrogen evolution reaction,⁶⁻⁷ hydrogen oxidation
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38 reaction,⁸ and oxygen evolution reaction.⁹ Nanoframes of *fcc* Ru were also reported to
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40 exhibit increased activity in the ammonium hydrolysis reaction compared to nanowires
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42 of *hcp* Ru.⁶ These results indicate that *fcc* Ru is a promising system for increasing the
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44 activity of Ru catalysts. Shape-controlled *fcc* Ru nanoparticles have been synthesized as
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46 cages, frames and cubes, using a core of a second metal as a template.^{6, 9-10}
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51 Branched or hierarchical nanoparticles have shown great promise in the stabilization
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53 of uncommon crystal structures because the reactions generally have multiple growth
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stages giving rise to complex morphologies.¹¹⁻¹⁴ Another common method to make branched or hierarchical nanomaterials is to use a controlled seed to act as a core or template to control the growth of a branched or flower-like shell.¹⁵⁻²¹ Branched and hierarchical nanoparticles give rise to less common crystal structures due to conditions of high strain or templating, which causes *fcc* metals to adopt *hcp* crystal structures.^{14, 22} With judicious reaction design, this form of polymorphism, which is uncommon in the bulk, can be induced on the nanoscale. It has also been shown that this unique polymorphism can be tailored to yield materials with more complicated shapes.^{14, 22-23}

Herein, we report a single and continuous synthesis for the formation of different morphologies of Ru nanoparticles with varying proportions of the *fcc* and *hcp* crystal structures. The nanoparticles were grown continuously via a millifluidic reaction system²⁴⁻²⁵ run with toluene as the solvent, oleylamine as the surfactant and metal carbonyls supplying carbon monoxide (CO) as the reducing agent.^{9, 26-28} The metal carbonyls were observed to control the proportion of the crystal structures in the nanoparticles formed, and the morphology of the particles with $\text{W}(\text{CO})_6$, or $\text{Re}_2(\text{CO})_{10}$ as the reducing agent formed branched or faceted nanoparticles respectively. Without the carbonyl spherical Ru nanoparticles were formed. These nanoparticles were tested for the hydrolysis of ammonia borane, which is a leading molecular candidate for hydrogen storage. The branched Ru nanoparticles were found to display the highest catalytic activity toward ammonia borane hydrolysis compared to the faceted and spherical ones.

Experimental Section:

Chemicals. Toluene, ammonia borane complex (97%), tungsten hexacarbonyl (97%), dirhenium decacarbonyl (99%), and dimanganese decacarbonyl (98%) were purchased from Sigma-Aldrich. Ruthenium(III) acetylacetonate (99%), ruthenium(III) chloride, and molybdenum hexacarbonyl (98%) were purchased from STREM. Oleylamine (technical grade, 70%) was purchased from Acros. Dichloromethane (99.8%) and toluene (100%) were purchased from VWR Chemicals. All chemicals were used as received without further purification.

Synthesis of Ru nanoparticles. A flow reactor device obtained from Uniqsis Ltd. (FlowSyn Multi X) was fitted with a 10 mL Teflon-coated stainless-steel coil reactor and a 30 bar inert back pressure regulator. A solution containing 22 mM of ruthenium precursor (ruthenium acetylacetonate $[\text{Ru}(\text{acac})_3]$ or ruthenium chloride $[\text{RuCl}_3]$) dissolved in oleylamine (75% by solution volume) and toluene (25% by solution volume) was streamed via the pump. Another pump was set to drive another stream of 14 mM reducing agent $[\text{W}(\text{CO})_6, \text{Mo}(\text{CO})_6, \text{Re}_2(\text{CO})_{10}]$ in toluene. For reactions without the metal carbonyl, only toluene was pumped in this stream. Both pumps were set to a flow rate of 1.0 mL/min. The residence time of the reaction was 5 minutes. The two streams entered a mixing zone and then continued through the preheated and pressurized coil reactor at 300 °C and 30 bar.⁹ A black solution was collected indicating the formation of nanoparticles. The nanoparticles were precipitated and washed with ethanol three times. After the nanoparticles were purified, they were re-dispersed in toluene for further characterization.

Preparation of the Ru/C Catalysts: The Ru nanoparticles (branched, faceted and spherical) were supported on carbon black for use as catalysts. Carbon black (0.4 g) was

dissolved in dichloromethane and toluene, while the solution was stirring 200 μL of Ru nanoparticles in toluene (0.05 g Ru in 1 mL toluene) was added drop wise. The solution was left stirring for 3 hours, and then dried under a nitrogen flow to form the Ru/C catalyst. The supported Ru/C catalyst was then heated to 300 $^{\circ}\text{C}$ under hydrogen for 2 hours to remove the ligands and prepare a bare nanoparticle surface.

Ammonia Borane Hydrolysis. The reaction was performed in an aqueous suspension, at room temperature ($\sim 23^{\circ}\text{C}$), and under one atmosphere of pressure. In a typical experiment, 4 mL of ammonia borane aqueous solution (0.062 g) and 1 mL of an aqueous suspension of the 0.01 g Ru/C nanocatalyst (branched, faceted and spherical, 2 wt% Ru element) were consecutively added into a 50 mL three-neck flask kept at room temperature ($\sim 23^{\circ}\text{C}$) under magnetic stirring, with one of the openings connected to a gas burette. The volume of hydrogen produced from the flask at different reaction times was recorded using the gas burette readings.

Calculation of Moles of Hydrogen Produced and TOF. The number of moles of hydrogen (n) was calculated from the volume of hydrogen (V) according to the ideal gas law $PV = nRT$ (P : absolute gas pressure; R : ideal gas constant; T : absolute temperature). n was then used to calculate the turnover frequency [$\text{mol H}_2 \text{ min}^{-1} (\text{mol Ru})^{-1}$].

Transmission Electron Microscopy (TEM). TEM of the prepared samples was performed with a Thermo-Fisher Scientific Model Titan 80-300 ST microscope equipped with an extra-brightness field emission gun (x-FEG). The energy dispersive X-ray spectroscopy (EDS) measurements were obtained with a detector from EDAX, Inc., with a lithium-doped silicon diode, a beryllium window and a solid angle of 0.07 steradians. The sample was tilted to an optimum angle of 14 degrees before acquisition.

Aberration corrected high resolution transmission electron microscopy (HR-TEM) was carried out on a Thermo-Fisher Scientific Model Titan G² 80-300 ST microscope with an extra-brightness field emission gun (x-FEG) and equipped with an Image-Corrector to reduce the co-efficient spherical aberration (Cs) of its objective lens. The TEM analysis was carried out by operating the scope at the accelerating voltage of 300 kV, and Cs was reduced to a value of approximately negative 5 microns. All the size distributions were measured over 500 particles. The imaging was performed on a 400 square mesh copper grid with a carbon film on top (Electron Microscopy Services).

X-ray Diffraction (XRD). XRD patterns were obtained from samples dried on zero background silicon plates with a Powder XRD Bruker D8 Advance instrument with Cu K α radiation (1.5409 Å). The XRD patterns were then analyzed with TOPAS software to refine the proportions of *fcc* and *hcp* Ru phases.

Results and Discussion:

Nanoparticles were grown from ruthenium precursors dissolved in toluene and oleylamine to form a homogeneous solution. In another vial, W(CO)₆ was dissolved in toluene. The two solutions were pumped together at equal flow rates and mixed before entering a stainless-steel reactor preheated at 300 °C. The synthesis was carried out with a residence time of 5 minutes operating at 30 bar (Figure 1 A). The nanoparticles were separated directly after synthesis to avoid contamination from the carbonyl through oxidation of the W metal center. The W stayed in solution after releasing the carbon monoxide and could be separated readily with the supernatant as previously reported.^{26, 29} Branched Ru nanoparticles with dimensions of 18 ± 3 nm were formed (Figure 1 B). The size of the core and branches were measured to be 4.8 ± 0.6 nm and 5.7 ± 0.7 nm,

respectively. The branched nanoparticles were made up of a majority of polycrystalline particles (Figure 1C and FFT inset) with branches extruding from a central core (Figure 1C). Polycrystalline and faceted branches can be observed, along with twin planes (one is denoted by a white arrow) that point along the branches toward the central core of the particle (Figure 1C and FFT inset). Single crystalline branched particles were also observed aligned along the [001] direction of the *hcp* crystal structure (Figure 1D and FFT inset). Temperatures of 260 °C and above were seen to form branched nanostructures (Figure S1), below this temperature nanoparticles were not formed.

Figure 1. A) Schematic illustration of the reactor setup and conditions used. B) TEM image of the branched Ru nanoparticles. HRTEM images and insets of their fast Fourier transforms (FFT) are shown in C) for a polycrystalline particle and D) for a single

crystalline particle. The white arrow shows the direction of a twin plane, which points toward the central core.

High-resolution images of the nanoparticles showed that the majority of the branched nanoparticles were polycrystalline and made of multiple domains. To further analyze the complicated multi-domain nature of the branched nanoparticles, high-resolution analysis was carried out. Figure 2 shows the HRTEM image of a branched Ru nanoparticle and the FFT's taken from specific areas surrounded by the blue, red and white boxes. The blue and red color represent the *fcc* and *hcp* crystal structures, respectively. The FFT of the main area of the particle (white box, Figure 3 A) shows that the branched Ru nanoparticle has a mixed phase of *hcp* and *fcc*. The nanoparticle was viewed down the $[110]_f$ and $[001]_h$ zone axes of the *fcc* and *hcp* crystal structures, respectively. The large area in Figure 2 A was divided into four small ones to identify the packing of the atoms (*i.e.*, either *hcp* and/or *fcc*), as shown in Figure 2 B, C, D and E. Figure 2 B, C and E illustrate that the atoms were arranged and packed in a *fcc* crystal structure. The FFT's were indexed to the $(111)_f$ and $(100)_f$ spacings of a *fcc* crystal structure. The nanoparticle was enclosed predominantly by the $(111)_f$ facets (Figure 2, inset of B). The *fcc* domains of the particle were viewed down the $[110]_f$ zone axis. In Figure 2 D, the particle showed an *hcp* crystal structure packing for the FFT indexed to the $[001]_h$ zone axis of the *hcp* crystal structure. The packing of atoms shows the typical atomic arrangements of the *hcp* structure (Figure 2, inset of D). The analysis shows that the nanoparticle contained both phases in a single particle. The center and several branches were shown to be *fcc* Ru, whereas another branch was *hcp*.

Figure 2. Aberration-corrected HRTEM image of a branched Ru nanoparticle. A-E) FFT's taken from the areas enclosed by the boxes in the HRTEM image. The insets are the enlarged areas of B and D. Defect planes in the *fcc* lattice are denoted by dashed blue lines, and the defect planes in the *hcp* lattice are denoted by dashed red lines. The $\{111\}$ *fcc* facets are shown with solid blue lines in the inset of B. The diffraction spots and zone axes of *hcp* Ru are shown in red, and those of *fcc* Ru are shown in blue.

A high-resolution image of another particle was analyzed. This particle also fell into the multi-domain profile, except that it did not have a distinct central particle (Figure 3). There were two main central points in the particle, instead of the single core structure seen in the other particles. From these central points, there were multiple twinned branches that could be readily imaged. One of these branches showed triangular domains separated by defects (Figure 3 B, blue notations). These triangular domains exhibited a *fcc* crystal structure, were imaged down the $[110]_f$ zone axis of each of the triangular domains, and had an icosahedral or decahedral profile. The surfaces that were exposed from this branch were a mixture of $\{111\}_f$ and $\{100\}_f$ facets (Figure 3 B). Another twinned branch had a single twin down its center, and the domains were also *fcc* viewed down the $[110]_f$ zone axis (Figure 3 C). The domain in Figure 3 D shows a single branch down the $[110]_f$ direction with a twin plane facing toward the center of the particle. The final branch in Figure 3 E showed an *hcp* packing of atoms when viewed down the $[001]_h$ zone axis. The particle contained multiple defects near the particle surface (white arrows in Figure 3 E).

Figure 3. A) Aberration-corrected HRTEM image of the branched Ru nanoparticle. B-E) Magnifications of the boxes labeled in A. Defect planes in the *fcc* lattice are noted by dashed blue lines. The $\{111\}$ *fcc* facets are shown with solid blue lines, and the $\{100\}$ *fcc* facets are shown by solid purple lines. Point defects are noted with the white arrows.

Nanoparticles with different degrees of branching were studied to understand how the particles were formed. Of the particles observed without branching some were icosahedral Ru nanoparticles with the *fcc* crystal structure, as shown in Figure 4 A. Other particles observed have a single defect plane present. Figure 4 B shows a particle that is viewed down the $[110]_f$ zone axis of the *fcc* domain, with a mixture of the $\{111\}_f$ and $\{100\}_f$ low index facets observable on its surface and a single defect plane down its center. A particle with a single branch shows that the defect planes of a particle with a single defect area aligns with the defect planes facing toward the icosahedral particle and forms a branched particle, as shown in Figure 4 C. The branch does not show any relationship between the twinned area and the central core particle; however, the $(111)_f$ spacings are pointed toward the $\{111\}_f$ facet of the icosahedra, with a degree of lattice mismatching observed between the arm and the core (Figure 3 C). A two-branched structure shows a similar morphology to the single branched particle, with two branches from an icosahedral core (Figure 4 D).

Figure 4. TEM images of multiple particles: A) an icosahedral particle, B) a particle with a defect plane running through it, C) a single branch with defect planes attached to an icosahedral particle, and D) two branches from a central icosahedral particle. Defect planes in the *fcc* lattice are noted by dashed blue lines. The $\{111\}$ *fcc* facets are shown with solid blue lines, and the $\{100\}$ *fcc* facets are shown by solid purple lines.

When the nanoparticle growth stages were studied at different times, the branched particles appeared after 20 seconds in low yields. By 2.5 minutes, the branched particles were the majority of the product. Before 2.5 minutes, branched nanoparticles of the same size and type could be seen, but the majority of the sample was small spherical particles (Figure S2).

The study of the dendritic Ru nanoparticles demonstrates that there are several initial particles, including *fcc* icosahedral Ru particles, defected particles, and presumably

single crystalline *hcp* particles. These particles can aggregate together into multiple growth modes, creating single crystalline *hcp* branched structures, polycrystalline branched structures with defected particles attached to a central icosahedral core, defected particles attached to a central single crystalline core, and multiple core particles where particles are attached in a more random pattern, with icosahedral branches and cores. This complicated mixture of particles in solution indicates that the initial nucleation process of the particles is relatively uncontrolled, leading to a mixture of *fcc* and *hcp* particles with differing levels of faceting and a mixture of structures. In the second stage of growth, the aggregation of the particles is relatively well-controlled, as the aggregates are all similar in size.

The particles growth is similar to aggregation-based growth, which has been shown in other noble metals where the particles are formed via slow nucleation and fast growth.³⁰⁻³¹ The self-aggregation occurs due to the small size of the particles and the high surface to volume ratios; the aggregation occurs to reduce the surface energy³⁰⁻³¹ and has been shown to occur in the presence of intermediate or weakly bound ligands.³²⁻³³

In previous studies of branched particles, the growth of branches occurs from a well-defined core. This is often evident by crystallographic relationships between the arms and the core,¹³⁻¹⁴ such as defects in the arms originating from defects in the core of the particle.³⁴⁻³⁵ In this study, we observed that defects in the branches perpendicular to the core of the particle do not appear to have a relationship to any defects that are observed in the core particle (Figure S3). In this case, it appears that the defects pointing toward other defects of the core occur by facet alignment of particulates during aggregation. The particles would collide in solution and try to minimize their surface area during

aggregation, causing a degree of alignment between the cores and the branches. The core continues to aggregate with branches until there is no empty space at the surface of the particle. Further branching could occur by additional collisions onto another branch, making a multiple core structure. Some of the branches that are icosahedral, or decahedral in nature would attach in a different formation, and give rise to multiple defect points at where aggregation could occur. This in turn could create a new center during the formation of branched nanoparticles. This aggregation, however, was well-controlled with a reasonably narrow particle size distribution of the final branched nanostructures.

Previous studies of branched or urchin-like ruthenium nanostructures were carried out with $\text{Ru}_3(\text{CO})_{12}$ as a precursor at $290\text{ }^\circ\text{C}$,³⁴⁻³⁵ indicating that the carbonyl introduced with $\text{W}(\text{CO})_6$ is important for the formation of the branched structures. However, in the previous studies, the branched and urchin-like Ru nanostructures were seen to be pure *hcp*,³⁴⁻³⁵ whereas the conditions in the current work favor the *fcc* phase, with mostly mixed *hcp/fcc* particles formed. There are two key synthetic differences in this work. The first is that it is carried out at elevated pressures, and the second is the oxidation state of the precursor used. Previous work has shown that high pressures favor the *fcc* polymorph of polymorphic materials.³⁶ Although we use moderate pressures during nanoparticle growth, it could play a role in forming the denser polymorph of Ru. With regards to the precursor, the previous studies started with Ru^0 metal without the need for reduction, whereas the current study reduced the Ru^{3+} to Ru^0 . It has been previously reported that the reduction of $\text{Ru}(\text{acac})_3$ gives rise to *fcc* Ru, under certain conditions.⁵

This reduction step is considered to be what favors the formation of the *fcc* Ru, but the pressure could also play a role in the reaction.

Figure 5. TEM images of Ru nanoparticles synthesized using A) Ru(acac)₃ and W(CO)₆, C) Ru(acac)₃ and Re₂(CO)₁₀, E) Ru(acac)₃ without a metal carbonyl and G) RuCl₃ without metal carbonyl. B), D), F) and H) High-resolution images from A), C), E) and G), respectively.

To test the effect of the carbon monoxide and the reduction of the ruthenium precursor, the reaction was carried out with additional carbonyls and without the carbonyl. Replacing $\text{W}(\text{CO})_6$ with $\text{Mo}(\text{CO})_6$ gave rise to branched nanoparticles with dimensions of 8 ± 2 nm, with arm widths of 3.4 ± 0.7 nm, as depicted in Figure 1 A and B. When $\text{Re}_2(\text{CO})_{10}$ was used, the branched nanocrystals were not formed. Instead, faceted Ru nanoparticles with dimensions of 4.5 ± 0.4 nm were formed (Figure 4 C and D). The absence of metal carbonyls was found to produce spherical nanoparticles with dimensions of 2.9 ± 0.5 nm (Figure 4 E and F). Larger spherical particles 4.8 ± 0.5 nm in size with some level of aggregation were formed with RuCl_3 as the precursor instead of $\text{Ru}(\text{acac})_3$ (Figure 4 G and E).

For the spherical nanoparticles, the oleylamine at 300 °C would act as a reducing agent since amines can act as electron donors at elevated temperatures.³⁷ When carbon monoxide was present, in the case of the branched and faceted particles, the carbon monoxide could act as the reducing agent directly via its CO/CO₂ couple ($\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 2\text{H}^+ + 2\text{e}^-$, or $2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2 + 4\text{e}^-$). The CO could also act as a reducing agent in conjunction with the amine by binding to the metal center.³⁷⁻³⁹ The amine can act as a coordinating ligand and alter the reduction potential of the metal center,³⁸ while also participating in the redox reactions that occur during reduction. For example, oxidative carbonylation could occur with the amine leading to reduction of the metal center.⁴⁰⁻⁴¹

The increased size of the particles using a chloride precursor instead of an acetylacetonate has been reported previously with platinum alloys.²⁷ The particles

formed without the carbonyl are generally spherical, lacking a distinct shape, which is indicative of only having a single surfactant in solution which is not interacting strongly with any particular surface facet of the particles. The work with metal carbonyls demonstrated that the carbonyl had a distinct effect on the particle size, and the occurrence of the branched particles. The $\text{Mo}(\text{CO})_6$ gave similar structures to the $\text{W}(\text{CO})_6$ but with smaller sizes. The $\text{Re}_2(\text{CO})_{10}$ formed faceted particles instead of branched particles. When $\text{Mn}_2(\text{CO})_{10}$ was tested, it also gave rise to faceted particles similar to the $\text{Re}_2(\text{CO})_{10}$ but with a large proportion of contamination from the $\text{Mn}_2(\text{CO})_{10}$ (Figure S4). These results suggest that the carbonyl used played a critical role in defining the final shape. As the nanoparticles grow, the CO could compete with the oleylamine coating layer, allowing aggregation and attachment to occur. The difference between the $\text{W}(\text{CO})_6$ and $\text{Mo}(\text{CO})_6$ to $\text{Re}_2(\text{CO})_{10}$ and $\text{Mn}_2(\text{CO})_{10}$ could be that the $\text{Re}_2(\text{CO})_{10}$ and $\text{Mn}_2(\text{CO})_{10}$ bind to the CO molecules more strongly (do not completely dissociate)⁴² and thus the CO does not destabilize the surfactant shell around the Ru particles to the same extent. It has been reported previously with Pt nanoparticles that the stability of zerovalent metals is varied and follows the order: $\text{Co}, \text{Fe} > \text{Mn} > \text{Re} > \text{Cr} > \text{W}, \text{Mo}$. This suggests that Re and Mn can re-associate with CO again, while W and Mo would form ions and free CO in solution.⁴²

In the different systems, using $\text{Ru}(\text{acac})_3$ with CO released from $\text{W}(\text{CO})_6$ or $\text{Re}_2(\text{CO})_{10}$ or using RuCl_3 without CO produced three distinct structures with comparable domain sizes. The catalytic properties of these three structures were compared. To determine their catalytic properties, first we used XRD to determine the proportion of *fcc* and *hcp* crystal structures in the sample. To determine the crystal

structure and the concentration of each phase of the Ru nanoparticles, XRD and Rietveld refinement using TOPAS software were conducted accordingly (Figure 6). The lattice parameters were $a = 2.71 \text{ \AA}$ and $c = 4.28 \text{ \AA}$ for *hcp* Ru and $a = 3.83 \text{ \AA}$ for *fcc* Ru. The lattice parameter for *fcc* Ru is within the range of other literature reports of *fcc* Ru.^{6, 10, 43} XRD patterns indicate that the nanocrystals exhibit different crystal structures, as shown in Figure 6. The maximum intensity peaks of the particles shift from being aligned with the $(002)_h$ peak of the *hcp* structure for the spherical particles to being aligned with the $(111)_f$ peak of the *fcc* structure for the branched structure. For the faceted nanoparticles, the peak maximum is between the two peaks, indicating that the main peak is made up of contributions from both phases. By applying the Rietveld refinement using the TOPAS software, we found that the percentages of *fcc* are ~89% for branched Ru nanoparticles and ~39% for faceted Ru nanoparticles. The spherical Ru nanoparticles were observed to exhibit a pure *hcp* crystal structure. The XRD patterns also reveal information regarding the average crystallite size, which was calculated using Scherrer's equation. The average crystal sizes were calculated to be 9.5, 5.5 and 3.2 nm for branched, faceted and spherical Ru nanoparticles, respectively. The average size of the faceted Ru nanoparticles was bigger than that of the average size measured from the TEM image, which is attributed to the continuous domains through the nanoparticles, giving rise to larger average domain sizes. The samples were studied with EDS to investigate if the metal carbonyl was alloying with the Ru or doping it. Only trace amounts of the W or Re were seen in the EDS patterns (Figure S5).

Figure 6. XRD patterns for branched, faceted and spherical Ru nanoparticles. The blue dashed lines correspond to the Bragg reflections of the *fcc* crystal structure. The red dashed lines represent the diffraction peaks of the *hcp* crystal structure. Insets of a TEM image of each sample is shown above each XRD pattern.

We evaluated the catalytic performance of branched, faceted and spherical Ru nanoparticles in the ammonia borane hydrolysis. Ammonia borane is an attractive hydrogen storage material because of its high hydrogen content (19.6 wt %) and good stability in solid form at room temperature.^{6, 44-50} Hydrogen can be conveniently

generated from ammonia borane through hydrolysis in the presence of a suitable catalyst: $\text{NH}_3\text{BH}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{BO}_2^- + 3\text{H}_2$.

Ru nanoparticles have been recognized to be an effective type of catalyst for this reaction.^{6, 44-46, 51-54} In our experiments, the catalytic reaction was started by adding an aqueous suspension of branched, faceted or spherical Ru nanoparticles to an aqueous solution of ammonia borane held in a flask. The volume of generated H_2 gas was measured by a gas burette. As indicated by the plots of H_2 production versus time (Figure 7), branched Ru nanoparticles showed higher catalytic activity in terms of turnover frequency compared to the faceted Ru nanoparticles [89.3 versus 33.5 $\text{mol H}_2 \text{ min}^{-1} (\text{mol Ru})^{-1}$]. The spherical Ru nanoparticles showed negligible activity [4.2 $\text{mol H}_2 \text{ min}^{-1} (\text{mol Ru})^{-1}$]. The branched Ru nanocatalyst produced almost three moles of hydrogen while the faceted catalyst produced less than one mole of H_2 gas.

Figure 7. Plots of hydrogen evolution versus time during the hydrolysis of ammonia borane catalyzed by the branched, faceted and spherical Ru nanoparticles.

The enhanced catalytic activity for the branched Ru nanoparticles can be considered to have four major possible explanations. The first is that the branched particles will have the smallest amount of Ru interacting with the carbon support due the high surface area morphology of branched nanostructures, leaving a larger proportion of Ru available for the catalysis. The branched particles also have an increased amount of kink sites and high index facets present on the surface compared to the faceted and spherical particles, which have been attributed previously to increased catalytic activity for branched, dendritic and porous nanoparticles.^{18, 55-56} The metal carbonyls could also provide a possible dopant that could alter the catalytic properties of the particles.⁵⁷ Finally, the branched particles have the highest proportion of the *fcc* crystal structure present, which has been reported previously to result in enhanced catalytic activity.⁵⁻⁹ In our system we do not observe any obvious doping occurring, and thus we attribute the difference in catalytic activity to the morphology of the branched nanostructures and the amount of *fcc* crystal structure present.

Conclusions:

Branched structures of ~90% *fcc* Ru were formed continuously in a flow reactor. The nanoparticles were formed with W(CO)_6 , oleylamine and Ru(acac)_3 and were formed via controlled aggregation. The particles were formed as a mixture of polycrystalline and defected *fcc* nanoparticles with a small amount of *hcp* particles present, which aggregated to form branched nanostructures. The metal carbonyl was observed to affect the final shape of the Ru nanoparticles and the size of the branched aggregates. The metal carbonyls can be divided into two groups in terms of the effect on the final shape

of the Ru nanoparticles: the first group is $\text{W}(\text{CO})_6$ and $\text{Mo}(\text{CO})_6$, and the second one is $\text{Re}_2(\text{CO})_{10}$ and $\text{Mn}_2(\text{CO})_{10}$. It is believed that CO gas generated by the decomposition of the metal carbonyl acts as a reducing agent. Ru salts are also an important factor that influences the size of the particles. RuCl_3 was observed to form larger particles than those formed by $\text{Ru}(\text{acac})_3$. The catalytic activity of the branched Ru nanoparticles was seen to be much higher than that of the faceted or spherical particles, which can be ascribed to their unique morphology and increased proportion of the *fcc* crystal structure. This synthetic method was carried out at high temperature and pressure in a continuous fashion, allowing the synthesis to be readily scaled up for use in catalytic reactions. We believe that the method used in this study will pave the way for controlling the shape and crystal structure of metal nanoparticles, which will be useful for catalytic applications.

ASSOCIATED CONTENT

Supporting Information. Additional electron microscope images and experiments can be found in the supporting information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Author Contributions

N.M.A. and L.S. carried out the synthesis. N.M.A. carried out the XRD, and TEM measurements. N.M.A. and D.H.A. carried out the aberration-corrected microscopy. N.M.A., C.G., D.J.Y. and K.W.H. carried out the catalysis. X.M. carried out the TOPAS fitting. N.M.A. and A.P.L. carried out the analysis and wrote the manuscript. N.M.A., A.P.L., O.F.M. and O.M.B. designed the experiments.

[†](NMA and APL) These authors contributed equally.

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Notes

Any additional relevant notes should be placed here.

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For Table of Contents Use Only:

Synthesis and Characterization of Branched fcc/hcp Ruthenium Nanostructures and their Catalytic Activity in Ammonia Borane Hydrolysis

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Branched, faceted and spherical ruthenium nanoparticles were synthesized continuously via a millifluidic reaction system. The morphology of the particles and their crystal structure (*fcc* or *hcp*) was controlled by the presence or absence of metal carbonyls. The branched nanoparticles were found to be the most active for ammonium borane hydrolysis.