Preparation of Noble-metal Nanoparticles by Microwave-assisted Chemical Reduction and Evaluation as Catalysts for Nitrile Hydrogenation under Ambient Conditions

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Herein, we report a protocol for rapid preparation of uniformly sized Ru, Rh, Pd, Ir, and Pt nanoparticles stabilized by poly(N-vinyl-2-pyrrolidone) via microwave-assisted chemical reduction with ethanol. Although the boiling point of ethanol, which has high reduction ability, is much lower than the temperature required for metal cation reduction, this solvent could be used as a reductant because the preparation was carried out in a sealed vessel. All metal nanoparticles showed similar sizes and amounts of poly(N-vinyl-2-pyrrolidone). The crystallite size of the Pd and Pt nanoparticles could be controlled by changing the ethanol concentration. The catalytic performance of the prepared metal nanoparticles was evaluated for the hydrogenation of benzonitrile under ambient conditions (25 °C, 1 bar H2). Rh nanoparticles showed the highest benzonitrile conversion and highest selectivity for secondary imine product. Interestingly, the particle-size dependence of the catalytic activity of the Rh nanoparticles showed volcano-type behavior; that is, the second smallest Rh nanoparticles (3.3 nm) showed the highest activity, which was attributed to high metal surface area and high turnover frequency. Notably, this is the first report of nitrile hydrogenation to afford a secondary imine under ambient conditions.

Keywords
Metal nanoparticle, Catalyst preparation, Chemical reduction, Microwave heating, Nitrile hydrogenation

1. Introduction

Metal nanoparticles have different properties from the corresponding bulk metals1). For instance, Rh nanoparticles have hydrogen-storage properties, whereas bulk Rh does not absorb hydrogen at all2). Metal nanoparticles are widely used as catalysts because they are not only highly active but also reusable. The catalytic performance of metal nanoparticles often depends on the particle size and the identity of the metal. For example, in catalytic CO oxidation over small Rh nanoparticles, turnover frequency (TOF) increases with decreasing particle size, whereas the opposite relationships were observed over small Ru nanoparticles3)−6). These observations suggest that controlling the size of metal nanoparticles is a promising approach to improve their catalytic performance. Chemical reduction with alcohol and heat is a well-known technique for preparing metal nanoparticles, but has two drawbacks. First, obtaining well-grown and uniform metal nanoparticles takes a long time (2-3 h) because heating with a conventional electric heater is slow and produces heterogeneous temperatures7)−9). Second, careful control of other preparation parameters is necessary for controlling particle size. For example, Rh particle size depends on the precursor, the preparation temperature, and the preparation time10). Clearly, catalyst research must investigate these phenomena to make progress.

Recently, we reported a method for simple, rapid preparation of Rh nanoparticles with controlled size via microwave-assisted chemical reduction with alcohol11). The alcohol acts as both reductant and solvent, and is very important in modifying the Rh particle size. In particular, we found that the use of ethanol, which has high reduction ability, leads to the formation of small Rh particles with high catalytic activity for CO oxidation. In addition, we reported briefly that small Rh...
nanoparticle catalyst showed high activity and reusability in nitrile hydrogenation (30 °C, 3 bar H₂, 1 bar = 10⁵ Pa)²¹. In particular, aromatic and heterocyclic nitriles were selectively transformed to the corresponding secondary amines whereas aliphatic nitrile was converted to primary amine, secondary imine, and secondary amine.

Motivated by this previous research, we have now applied our method to the preparation of nanoparticles of other noble metals (Ru, Pd, Ir, and Pt). The catalytic activities of the resulting poly(N-vinyl-2-pyrrolidone) (PVP)-stabilized nanoparticles were evaluated for nitrile hydrogenation under ambient conditions (25 °C, 1 bar H₂). Rh nanoparticles showed the highest activity and selectivity among the prepared nanoparticles, so we evaluated the effect of their particle size on the reaction rate.

2. Experimental Section

2.1. Materials

All chemicals used for the preparation of metal nanoparticles were purchased from FUJIFILM Wako Pure Chemical Corp. Benzonitrile and dodecane (used as an internal standard) were obtained from TCI Co. and used as supplied.

2.2. Preparation of Metal Nanoparticle Catalysts

Ru, Rh, Pd, Ir, and Pt nanoparticles stabilized by PVP were prepared via microwave-assisted chemical reduction. Briefly, a sealable vessel was charged with 0.25 mmol of RuCl₃·nH₂O, RhCl₃·3H₂O, (NH₄)₂[PdCl₄], IrCl₆, or (NH₄)₂[PtCl₄] as a metal precursor and 1.25 mmol of PVP, and these reagents were then dissolved in 20 mL of ethanol as a reductant. For preparation with the Pd, Ir, and Pt precursors, the ethanol was diluted with purified water to 30, 50, and 80 %, respectively, because these precursors are barely soluble in 100 % ethanol. After Ar was bubbled through the solution for 5 min, the vessel was sealed, and the solution was heated to 165 °C in a microwave synthesizer (Initiator, Biotage) and maintained at that temperature for 15 min. The obtained colloidal suspension was concentrated with an evaporator, and the residual solid was washed three times by dispersion in water and coagulation with diethyl ether and acetone. The washed product was dried under vacuum at 50 °C. The same preparation conditions were used for experiments aimed at tuning the Rh particle size, except that the reductant was changed from ethanol to 2-propanol, ethyleneglycol, diethyleneglycol, or triethyleneglycol.

2.3. Hydrogenation of Benzonitrile

Hydrogenation reactions were performed in a glass tube reactor equipped with a Tedlar bag as follows. The reactor was charged with benzonitrile (1 mmol), catalyst (1 mol%), and methanol (0.5 mL). The reactor was depressurized and then purged several times with H₂ gas from the Tedlar bag to remove air. After the reactor was purged, the reaction was allowed to proceed at 25 °C with stirring at 800 rpm. Nitrile conversion and product yield were determined by gas chromatography with dodecane as an internal standard.

3. Results and Discussion

3.1. Comparison of the Effects of Microwave and Conventional Heating on Particle Morphology

The heating rates observed for microwave and conventional electric heating, and the morphologies of the resulting Rh nanoparticles were compared using diethyleneglycol as the reductant (Fig. 1). Under microwave heating, the desired temperature (165 °C) was reached within 1 min, and uniform Rh nanoparticles had formed after 15 min. In contrast, with conventional heating, the desired temperature was reached after 15 min, and irregular Rh nanoparticles were obtained after 15 min. These results confirmed that microwave heating is a promising technique for rapid preparation of uniform metal nanoparticles owing to homogeneous and rapid heating, as we reported previously²¹.

3.2. Particle-size Distributions of Noble-metal Nanoparticles Prepared by Microwave-assisted Reduction

The boiling point of ethanol is much lower than the temperature required for reducing metal cations other than Pd²⁺, Pt⁴⁺, and Pt⁶⁺, so a sealed vessel was used to heat the ethanol to 165 °C (Fig. S1). We obtained transmission electron microscopy images of the nanoparticles synthesized by reduction of each of the five metals (Fig. 2). As expected, the use of ethanol as a reductant led to the formation of small nanoparticles, not only for Rh, but also for the other metals. The mean particle sizes (n = 100) were 3.0 ± 0.9 nm for Ru, 3.3 ± 0.5 nm for Rh, 4.1 ± 0.5 nm for Pd, 2.1 ± 0.3 nm for Ir, and 3.9 ± 1.0 nm for Pt (Fig. S2).
Notably, microwave-assisted reduction with ethanol generated nanoparticles of similar sizes for all five metals, which is difficult by other methods because of the varying properties of the metals\(^{13,14}\). We also found that the amount of PVP, which is a crucial determinant of catalytic activity\(^9\), varied over a narrow range (74.1-84.5 wt%). As described later, particle size greatly affects catalytic performance, so consistent particle sizes are important for comparing the intrinsic catalytic activities of various metals.

Some studies have reduced Pd and Pt cations in ethanol with conventional electric heaters\(^{15-18}\). For example, investigation of the effect of ethanol concentration on the size of Pd and Pt nanoparticles found that Pd particle size decreases with lower ethanol concentration; whereas Pt particle size decreases with higher ethanol concentration\(^{19,20}\). We observed similar trends for our microwave-assisted chemical reduction of Pd and Pt (Fig. 3). However, the ethanol concentration had no significant effect on the Ir crystallite size, although the uniformity of the Ir nanoparticles was better using 50 vol% ethanol than 100 % ethanol (Fig. S3).

### 3.3. Performance of Nanoparticle Catalysts for the Hydrogenation of Benzonitrile

The catalytic activities of the prepared metal nanoparticles were evaluated for the hydrogenation of benzonitrile. Nitrile hydrogenation affords three main products (primary amines, secondary imines, and secondary amines; \textbf{Scheme 1}), so the development of catalysts that can selectively produce the desired product is important. The synthesis of secondary imines is particularly difficult because over-hydrogenation occurs easily in the presence of hydrogen. For this reason, non-reusable homogeneous catalysts, which show better selectivity than heterogeneous catalysts, are widely used for the synthesis of secondary imines.

In contrast, our heterogeneous Rh nanoparticle catalyst exhibited high selectivity for the secondary imine product in benzonitrile hydrogenation, whereas the Ir and Pt nanoparticle catalysts gave mainly the secondary amine. Nitrile conversion over Rh was also excellent after 8 h (\textbf{Table 1}), probably due to the high

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**Table 1** Catalytic Performance of Metal Nanoparticles in the Hydrogenation of Benzonitrile\(^a\)

| Catalyst | Particle size [nm] | Amount of PVP\(^b\) [wt%] | Conversion [%] | 1° amine yield [%] | 2° imine yield [%] | 2° amine yield [%] | 2° imine selectivity [%] |
|----------|-------------------|---------------------------|---------------|-------------------|-------------------|-------------------|--------------------------|
| Ru-PVP   | 3.0 ± 0.9         | 84.2                      | 6             | 0                 | 4                 | 0                 | 67                       |
| Rh-PVP   | 3.3 ± 0.3         | 83.7                      | >99           | 0                 | 85                | 0                 | 86                       |
| Pd-PVP   | 4.1 ± 0.5         | 84.5                      | 77            | 62                | 0                 | 11                | 0                        |
| Ir-PVP   | 2.1 ± 0.3         | 77.7                      | 19            | 0                 | 1                 | 12                | 5                        |
| Pt-PVP   | 3.9 ± 1.0         | 74.1                      | 61            | 0                 | 1                 | 48                | 2                        |

\(a\) Reaction was performed at 25 °C under 1 bar of H\(_2\) for 8 h, with stirring at 800 rpm.

\(b\) Estimated by thermogravimetric analysis (see the supporting information).
catalyst-dispersibility induced by hydrophilic PVP. Investigation of the time course of the reaction over the Rh catalyst (Fig. 4) showed that the yield of the secondary imine gradually increased together with conversion of benzonitrile until complete consumption, at which point the secondary imine began to undergo hydrogenation to form the secondary amine. These results indicate that the observed selectivity for the secondary imine originated from competitive adsorption between the reactant and the secondary imine product. In contrast, the Pd catalyst favored production of the primary amine, as reported previously. It should be noted that this is the first report of hydrogenation of a nitrile to afford a secondary imine under ambient conditions (25 °C, 1 bar H₂); this transformation typically requires heat, pressure, or both, even in homogeneous catalyst systems.

3.4. Effect of Particle Size on Catalytic Activity in Benzonitrile Hydrogenation

We previously showed that activity per weight of catalyst increases with decreasing Rh particle size for the hydrogenation of nitrile at 30 °C under H₂ pressure of 3 bar. The present study investigated five Rh samples with different particle sizes to elucidate the effect of particle size in more detail. Rh samples with different particle sizes were obtained simply by changing the alcohol reductant. The use of stronger reductants (i.e., alcohols that are readily oxidized at low potential in linear sweep voltammetry, Fig. S4) gave Rh nanoparticles with smaller particle sizes (Fig. S5). Substrate conversion, product yield, and Rh dispersion (i.e., number of exposed Rh atoms per weight) for the Rh nanoparticles are shown in Fig. 5. Conversion and yield generally increased with smaller particle size and were highest for the 3.3 nm nanoparticles. Notably, the activity of the smallest Rh nanoparticles (2.7 nm), with the highest Rh dispersion, was lower than that of the 3.3 nm nanoparticles. Rh dispersion was calculated by assuming that the Rh nanoparticles were spherical. Then TOF was calculated from the imine yield in the low-conversion region (Fig. 6). These calculations showed that TOF more than doubled as Rh particle size decreased from 9.5 to 5.7 nm, but TOF then decreased as the particle size was decreased further to 2.7 nm. In general, smaller metal particles show higher TOF because of the larger fraction of active sites, such as step (edge) and corner sites, consisting of atoms with low coordination. However, Satsuma et al. reported that moderately sized metal nanoparticles have higher fraction of active sites and higher TOF, which is consistent with the volcano-type plot shown in Fig. 6. It has also been reported that the electronic state of metal nanoparticles is markedly affected by particle size, especially for 2-10 nm particles. We are explor...
ing the cause of the volcano-type particle-size dependence of TOF exhibited by our Rh nanoparticles using X-ray absorption fine structure analysis and will report the results in the near future.

4. Conclusion

Five types of PVP-stabilized noble-metal nanoparticles were prepared via microwave-assisted chemical reduction using ethanol as a reductant. This method afforded uniform metal nanoparticles with similar particle sizes and amounts of PVP in a short time. Ethanol could be used as the reductant even though the boiling point of ethanol is much lower than the temperature required for reduction of the metal cations because the preparation was carried out in a sealed vessel. The crystallite sizes of Pd and Pt nanoparticles could be controlled simply by changing the ethanol concentration, as described previously. Only the Rh nanoparticles exhibited excellent conversion of the substrate and selectivity for the secondary imine product in the hydrogenation of benzonitrile. Analysis of the time course of the hydrogenation reaction indicated that selectivity for the secondary imine over Rh was due to competitive adsorption between the reactant and the secondary imine product. Furthermore, catalytic activity per weight was markedly influenced by the effect of particle size on both Rh dispersion and TOF. This is the first report of nitrile hydrogenation to afford a secondary imine under ambient conditions.

Supporting Information

S1. Experimental Details

S1.1. X-ray Diffraction Measurements
Crystal structures and crystallite sizes of the metal nanoparticles were determined by X-ray diffraction analysis with a Smart Lab X-ray diffractometer (Rigaku Corp., Japan) using Cu Kα radiation.

S1.2. Transmission Electron Microscopy
Particle sizes of the metal nanoparticles were estimated by transmission electron microscopy on a JEM-2010 instrument (JEOL Ltd., Japan) operated at an accelerating voltage of 200 kV.

S1.3. High-resolution Scanning Transmission Electron Microscopy
High-resolution scanning transmission electron microscopy images were obtained with a JEM-ARM200F instrument (JEOL Ltd., Japan) operated at an accelerating voltage of 200 kV.

S1.4. Thermogravimetric Analysis
Amounts of poly(N-vinyl-2-pyrrolidone) on the metal nanoparticles were estimated by thermogravimetric analysis (ThermoPlus, Rigaku Corp., Japan) in the range from room temperature to 1000 °C under air at a flow rate of 200 mL/min.

S1.5. Electrochemical Analysis
To evaluate the oxidative behavior of the alcohols, linear sweep voltammetry (LSV) was performed. The LSV profiles were obtained with an HZ-7000 electrochemical analyzer (Hokuto Denko Corp., Japan) equipped with a constant rotation system (RRDE-3A, ALS Co.) and a conventional three-electrode system consisting of a glassy carbon working electrode (ϕ 5 mm), a Ag/AgCl reference electrode (3 M NaCl), and a coiled Pt wire (23 cm in length) counter electrode. Prior to the measurements, the working electrode was cleaned by sequential polishing with diamond and Al₂O₃ powder and subsequent washing with ethanol-acetone mixture (ALS Co.). The suspension of commercial Pt/C (containing 10 µg of metal) was then dropped on the working electrode to act as the electrocatalyst. Before the alcohols were added to the electrolyte, cyclic voltammetry measurements from −0.2 to 0.8 V were conducted in Ar-saturated 0.1 M HClO₄ solution at a sweep rate of 300 mV/s for 250 cycles to clean the electrode surface. Then LSV measurements of Pt/C were carried out in alcohol-containing electrolyte at a sweep rate of 10 mV/s at 1600 rpm. All the experiments were conducted at room temperature.

S2. Microwave-assisted Heating for Catalyst Preparation

For Pd, Ir, and Pt, the ethanol was diluted to 30, 50, and 80 vol%, respectively, with water.

Fig. S1 Time Course of Temperature during Catalyst Preparation
S3. Particle Size Distribution

For Pd, Ir, and Pt, the ethanol was diluted to 30, 50, and 80 vol%, respectively, with water.

Fig. S2 Particle-size Distributions for the Five Types of Metal Nanoparticles

S4. Effect of Dilution on Ir Nanoparticle Morphology

Fig. S3 Transmission Electron Microscopy Images of Ir Nanoparticles Reduced with 100% and 50% vol% Ethanol

S5. LSV Profiles

Fig. S4 LSV Profiles for Various Alcohols (0.25 M) in the Presence of 0.1 M HClO₄
S6. High-angle Annular Dark-field Scanning Transmission Electron Microscopy Images of Size-controlled Rh Nanoparticles

Acknowledgment
This work was partly supported by the ACCEL, Japan Science and Technology Agency (grant number JPMJAC1501). K. Sato thanks the Program for Elements Strategy Initiative for Catalysts & Batteries commissioned by MEXT. The authors thank Mr. T. Toriyama, Mr. T. Yamamoto, and Prof. S. Matsumura (Kyushu University, Japan) for assistance with High-angle annular dark-field scanning transmission electron microscopy, and Mr. K. Matsutori (Oita University, Japan) for assistance with the electrochemical analysis.

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要 旨
マイクロ波加熱を利用した化学的還元法による貴金属ナノ粒子の調製と常温常圧におけるニトリルの水素化反応活性

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マイクロ波加熱を利用した化学的還元法により、ポリビニルビロリドにて装填された貴金属ナノ粒子を適便に調製した。通常、エタノールは非粘性が低すぎるため、還元剤として適さないが、本研究では密閉調製容器を用いることでエタノールを還元剤として使用することを試みた。その結果、エタノールの優れた還元力により、3 nm 前後の粒径を有する Ru, Rh, Pd, Ir, Pt ナノ粒子が形成することが分かった。Pd と Pt ナノ粒子についても、それらの結晶相分が還元剤であるエタノールの濃度に依存していた。さらに、調製した各金属ナノ粒子のニトリル水素化活性を評価したところ、Rh のみが優れたニトリルの転化率及び目的生成物（第二級イミン）の収率を示すことが分かった。

Rh の触媒活性は、その粒径によって大きく変化し、平均粒径 3.3 nm の Rh ナノ粒子が最も優れた触媒活性を示した。このような粒径の最適化により、我々は世界で初めてニトリルを常温常圧で第二級イミンへと変換することに成功した。