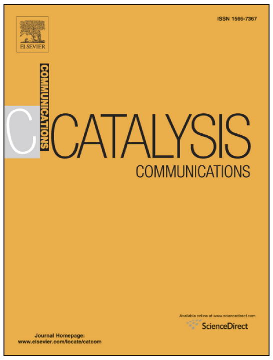

Recyclable Rh-PVP nanoparticles catalyzed hydrogenation of benzoic acid derivatives and quinolines under solvent-free conditions

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Recyclable Rh-PVP nanoparticles catalyzed hydrogenation of benzoic acid derivatives and quinolines under solvent-free conditions

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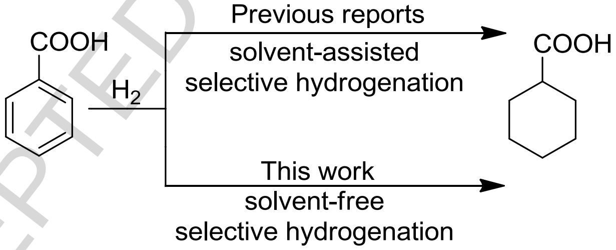
Abstract

Various transition metal nanoparticles, prepared by microwave-assisted alcohol reduction method were examined for hydrogenation of benzoic acid to cyclohexanecarboxylic acid under solvent-free conditions. Rh metal was the most effective catalyst over other metal catalyst. The catalyst showed moderate to high yield for the hydrogenation of substituted benzoic acid and substituted quinolines. Rh-PVP was recycled four times with minor loss in catalytic activity.

Keywords: Heterogeneous catalyst, Rhodium, Nanoparticles, Hydrogenation, Benzoic acid, Quinolines

1. Introduction

The chemoselective hydrogenation of benzoic acid to cyclohexanecarboxylic acid (CCA) has great significance in chemical and pharmaceutical industries. The pharmaceutical drugs such as ansatrienin can be synthesized by using cyclohexyl carboxylic acid [1]. Moreover, the formation of cyclohexanecarboxylic acid by hydrogenation of benzoic acid is a crucial step for the production of caprolactam from toluene in SNIA process (developed by SNIA S.p.A, Italy) [2]. Traditionally, the hydrogenation of benzoic acid and its derivatives was carried out with stoichiometric amount of Na-K alloys [3]. Several Supported monometallic (Pd, Ir, Rh, Ru and Ni) catalysts have been reported for hydrogenation of benzoic acid [4-18]. Bimetallic alloy based catalysts (Pd-Au, Ru-Pt, Ru-Pd, Ni-Pd-B and Ni-Zr-B) were also examined [19-24]. However, some of them suffer from use of additives [24, 25], high temperature (200 °C) [18], high pressure (>20 bar)[5-7, 12-15, 18, 19, 22-25], high catalyst loading (> 1 mol%) [4, 9, 10, 17, 20] and non-recyclable catalyst (Table S1) [7-14, 23, 24]. In addition, the solvent was necessary for selective hydrogenation of benzoic acid to cyclohexane carboxylic acid (Scheme 1) [4-25].



Scheme 1. Hydrogenation of benzoic acid

Metal nanoparticles exhibit a wide range of applications, particularly in the field of catalysis [26]. Among them, polymer or ionic liquids stabilized nanoparticles are located at the border of homogeneous and heterogeneous catalysis. The intrinsic catalytic activity of these systems is easy to understand compared to metal nanoparticles supported on metal oxides because substrate and support direct interactions can be eliminated. Rh metal demonstrated excellent activity for the hydrogenation reactions. Polyvinylpyrrolidone (PVP) stabilized Rh nanoparticles were reported for the biphasic hydrogenation of benzene but deactivation of catalyst was observed due to aggregation of

Rh nanoparticles [27]. In 2016, Philippot and co-workers studied Rh-PVP catalyzed hydrogenation of benzoic acid using water as solvent [28]. However, benzoic acid derivatives and recyclability of catalyst were not investigated. Very recently, our group synthesized PVP stabilized Rh nanoparticles by microwave-assisted alcohol as reduction method [29]. This catalyst showed good recyclability for the synthesis of secondary imines from nitriles. As part of continuing interest in the applications of the Rh nanoparticles, we report herein recyclable Rh nanoparticles catalyzed selective hydrogenation of benzoic acid with different functional groups under solvent-free conditions. In addition, the catalyst was applied to selective hydrogenation of quinolines to tetrahydroquinolines which are important bioactive compounds. Good to excellent yields of hydrogenated carboxylic acid derivatives and quinolines were obtained.

2. Experimental

2.1. Catalyst preparation

All metal precursors were purchased from Wako Pure Chemical Industries, Ltd. Japan. Ru, Rh, Pd, Ir and Pt nanoparticles were synthesized by microwave-assisted alcohol reduction method [29]. In typical procedure, 0.25 mmol of metal chloride and 1.25 mmol of polyvinylpyrrolidone (molecular weight M ≈ 40000) were dissolved in 20 ml of ethylene glycol. After purging by Argon, the vessel was sealed with cap and heated to (180 °C) with microwave irradiation (400 W) for 15 min. The obtained colloidal suspension was precipitated using diethyl ether and acetone followed by washing with water and drying under vacuum at 40 °C.

2.2. Catalyst characterization

The particle size of metal nanoparticles was determined by transmission electron microscopy (TEM) using a JEM-2010 transmission electron microscope (JEOL, Japan) operated at an accelerating voltage of 200 kV. The amount of PVP on metal nanoparticles was calculated by using thermogravimetric analysis (ThermoPlus; Rigaku, Japan) from room temperature to 1000 °C under air (flow rate: 200 mL/min). X-ray photoelectron spectroscopy (XPS) analysis was carried out using an ESCA-3400 (Shimadzu, Kyoto, Japan). The binding energy was calibrated using a C 1s binding energy of 284.6 eV. High-angle annular dark field scanning transmission electron microscopy images (HAADF-STEM) were obtained using JEM-ARM200F (JEOL, Japan) operated at 200 kV.

2.3. Typical procedures for catalytic hydrogenation

All organic compounds (Tokyo Chemical Industry, Japan) were used without further purification. Hydrogenation reactions were carried out in 10 ml autoclave with a glass tube inside equipped with magnetic stirrer. In a typical experiment, 1 mmol of substrate and catalyst (1 mol %) were placed in the reactor and sealed. After being sealed, hydrogen was introduced to reactor and inside of the reactor was purged for multiple times. The reactor was pressurized at 5-10 bar by hydrogen and heated to 100°C -180°C. After completion of reaction, the reactor was cooled to room temperature and depressurized. The obtained reaction crude washed with acetone several times and resultant solution was filtered by using micro filters (Sartorius RC 0.20 μm). Then, the filtrate solution was concentrated by using rotary evaporation. Conversion and yield of product were obtained by ^{1}H NMR analysis using 1, 3, 5-trimethoxybenzene as an internal standard. ^{1}H-NMR spectra were recorded using Brucker UltraShield 400 plus operating at 400 MHz.

2.4. Catalyst recycling

After the reaction, the reaction crude was washed by acetone several times. The catalyst was recovered by centrifugation and dried at 50°C for 12 h under vacuum. The dried catalyst was reused for the next run.

3. Results and Discussion

We chose hydrogenation of benzoic acid as model reaction for the optimization of reaction conditions (Table 1). First, various noble metals nanoparticles (Ru, Rh, Pd, Ir and Pt) were used for hydrogenation of benzoic acid to cyclohexanecarboxylic acid. Among the tested catalysts, Rh-PVP catalyst showed the highest yield (96 %) (entries 1-6). In previous reports, Wang [23] and Bai [25] demonstrated that highly polar solvent such as water was played a crucial role in selective hydrogenation of aromatic ring in benzoic acid. Water facilitated to aromatic ring for the adsorption on catalyst surface and avoided unwanted adsorption of carboxyl group on catalyst. Contrary to this reports, Rh-PVP catalyst showed high yield (96%) of cyclohexane carboxylic acid in the absence of solvent. Polar and non polar solvents were found to be less effective for the hydrogenation of benzoic acid.

Table 1 Hydrogenation of benzoic acid by metal catalysts[a]

Entry	Catalyst	PVP (wt %)[c]	Particle size (nm)[d]	Solvent (1 ml)	Conv. (%)	Yield (%)[b]
1	Rh-PVP	82	5.4±1.0	Neat	99	96
2[e]	Rh-PVP	82	5.4±1.0	Neat	80	80
3	Pt-PVP	72	3.9±0.4	Neat	70	70
4	Ir-PVP	78	1.9±0.5	Neat	53	53
5	Ru-PVP	83	3.8±1.1	Neat	63	34
6	Pd-PVP	84	4.8±0.7	Neat	32	21
7	Rh-PVP	82	5.4±1.0	Water	48	46
8	Rh-PVP	82	5.4±1.0	Methanol	20	13
9	Rh-PVP	82	5.4±1.0	CH_3CN	1	1
10	Rh-PVP	82	5.4±1.0	THF	66	57
11	Rh-PVP	82	5.4±1.0	Cyclohexane	47	35
12	no catalyst	--	--	Neat	0	0

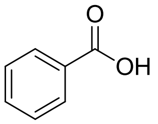
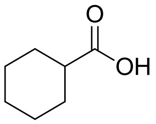
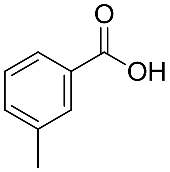
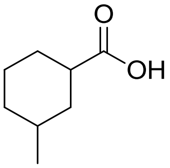
[a] Reaction conditions: substrate (1 mmol), Metal (1 mol%), 150 °C, 1 h, H_2 (10 bar). [b] NMR Yield. [c] Calculated by thermogravimetric analysis. [d] Determined by transmission electron microscopy. [e] Rh catalyst (0.5 mol%)

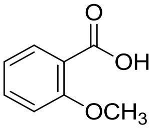
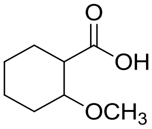
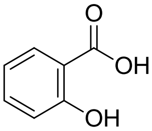
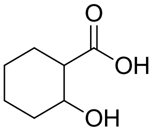
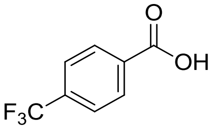
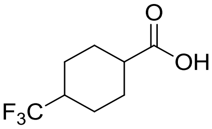
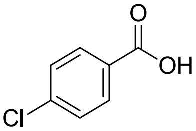
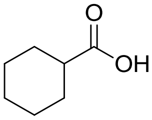
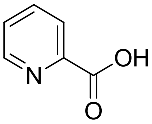
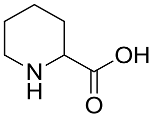
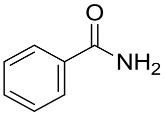
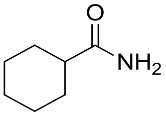
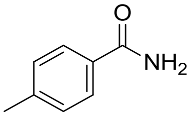
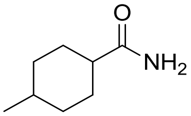
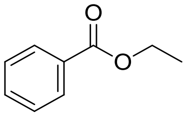
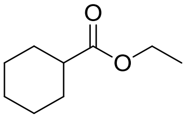
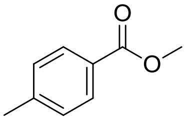
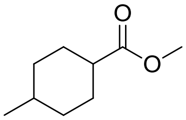
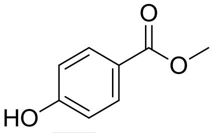
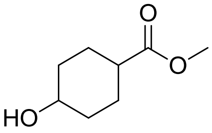
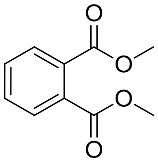
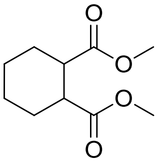
To demonstrate the general applicability of Rh nanoparticles, we carried out hydrogenation reaction of various substituted benzoic acid and derivatives under aforementioned reaction conditions (Table 2). The substituted benzoic acid bearing electron donating group such as methyl gave 99% yield, and benzoic acid bearing electron withdrawing trifluoromethyl group delivered in 60% yield (entries 2 and 3). Due to reductive dechlorination reaction, the hydrogenation of *para*-chlorobenzoic acid proceeded to cyclohexanecarboxylic acid as final product instead of *para*-chlorocyclohexanecarboxylic acid (entry 6). The catalyst was useful for hydrogenation of nitrogen-containing heterocyclic carboxylic acid (entry 7). The hydrogenation of benzamide and *para*-methylbenzamide leads to corresponding products with good yields (70-85 %) (entries 8 and 9）. Moderate to high yields (53-98 %) were obtained when hydrogenation reactions of ethyl benzoate and *para*-substituted methyl benzoate were carried out (entries 10-12). The catalyst was also applicable for the synthesis of industrially important cyclohexyldicarboxylic ester from hydrogenation of dimethyl phthalate (entry 13).

Encouraged by benzoic acid hydrogenation results, we studied the applicability of Rh-PVP catalysts for the selective hydrogenation of quinolines to 1,2,3,4-tetrahydroquinoline. Hydrogenation of quinolines has gained much attention for the synthesis of tetrahydroquinoline-derived natural products and bioactive compounds [30]. The first row transition metal (Mn, Co and Ni) nanoparticles were investigated for the hydrogenation of quinoline using lithium metal and water as hydrogen source. In compared to lithium and water system, molecular hydrogen is an atom-economical source of hydrogen. Unsupported Rh catalyst has been reported for direct hydrogenation of quinolines using molecular hydrogen [32-35]. However, these catalytic methods require high pressure (30 bar H_2) and organic solvents (Table S2).

Using our Rh nanopaticles, quinoline was easily hydrogenated to 1,2,3,4-tetrahydroquinoline under mild pressure (5 bar H_2). Electron donating ($-OCH_3$) and withdrawing (-Cl) bearing quinolines were hydrogenated to corresponding tetrahydroquinoline and decahydroquinoline (entry 2 and 3).

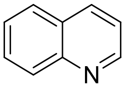
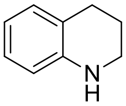
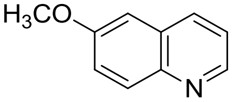
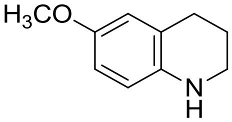
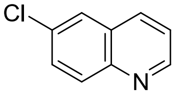
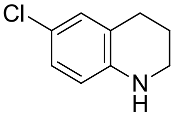
Table 2 Hydrogenation of benzoic acid derivatives using Rh-PVP^a

Entry	Substrate	Products	Temp. (ºC)	Time (h)	Conv. (%)	Yield(%)^b (cis/trans)
1			150	1	99	96
2			150	5	99	99(62:38)

3			120	2	96	96(62:38)
4[c]			160	1	85	50(59:41)
5			150	1	90	60(70:30)
6			180	24	99	99
7			150	24	78	75
8			150	24	85	85
9			180	24	88	70(65:35)
10			150	3	98	98
11			180	6	95	95(71:29)
12			180	24	61	53(83:17)
13			150	6	89	81(78:22)

[a]Reaction conditions: substrate (1 mmol), Rh (1 mol%), H_2 (10 bar). [b]NMR Yield. [c]0.5 mol % catalyst.

Table 3 Hydrogenation of quinolines by Rh-PVP.[a]

Entry	Substrate	Products	Conv. (%)	Yield[b] (%)
1			99	94
2			95	83[c]
3			92	78[c]

[a]Reaction conditions: substrate (1 mmol), Rh (1 mol%), 100 °C, 2 h, H_2 (5 bar). [b]NMR Yield. [c] Decahydroquinoline was obtained as byproduct.

We investigated reusability of Rh nanoparticles for hydrogenation of benzoic acid at optimized reaction condition. The recovered catalyst was recycled three times with slightly loss in catalytic activity from 1st to 2nd cycle (Fig.2). ICP-AES analysis showed that the Rh amount in reaction mixture was below the detection limit (10 ppb).

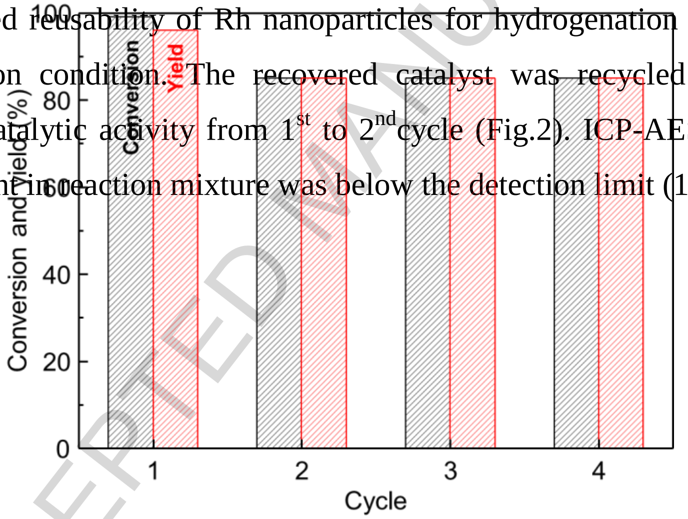


Fig. 2. Recycle study for hydrogenation of benzoic acid by Rh catalyst.

In previous reports, deactivation of unsupported Rh nanoparticles which was synthesized by conventional alcohol reduction method was observed for hydrogenation of arene reactions [35]. In that case, morphological changes such as aggregation headed to catalyst deactivation. To study morphological changes, HAADF-STEM images of fresh and recovered Rh catalyst after first reaction were taken (Fig. 3). Although Rh nanoparticles were partially aggregated, the catalytic activity was not changed significantly. Probably, reaction solvent has some role in catalyst deactivation. During reaction, PVP could be dissolve in water and resultant Rh nanoparticles with less amount of PVP are easily aggregated. By contrast, the removal of PVP was suppressed in our solvent-free conditions, which provides the recyclability of our Rh catalyst. More detailed exploration about the rate of aggregation is necessary and it will be objective of future works.

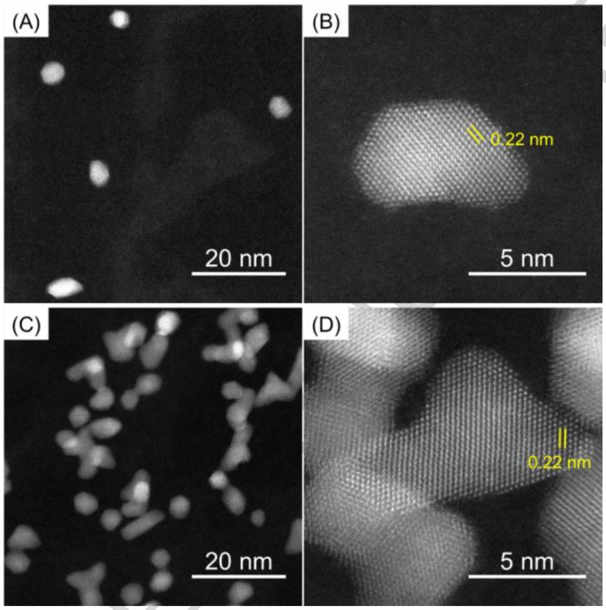


Fig.3.HAADF-STEM images of fresh (A,B) and used (C,D) Rh catalyst.

Moreover, electronic states of fresh and aggregated Rh nanoparticles were examined by XPS analysis (Fig. 4).The binding energy of fresh Rh catalyst was slightly shifted to lower binding energy than that of Rh bulk, indicating charge transfer from PVP to Rh occurs. The binding energy of recovered Rh catalyst was identical to that of fresh Rh nanoparticles, indicating that during the reaction electronic state of Rh nanoparticles remained unchanged. Therefore, we concluded slight loss of activity after 1st cycle was due to aggregation of Rh particles.

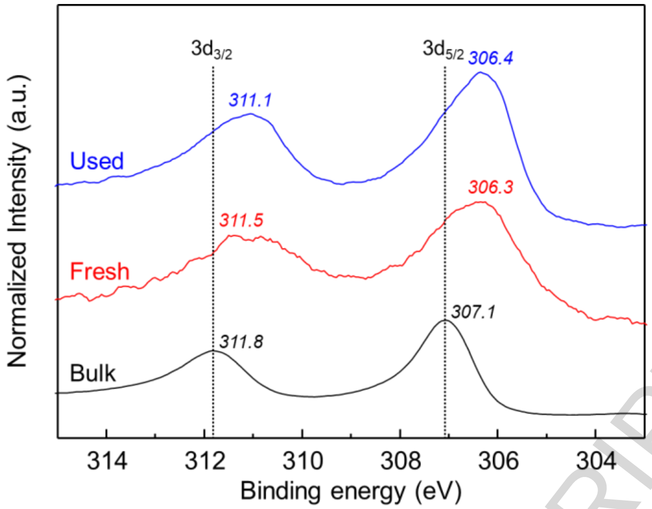


Fig. 4.XPS spectra of fresh and used Rh catalyst.

Conclusions

In summary, we have demonstrated a successful example of Rh catalyzed hydrogenation of benzoic acid and quinolines under solvent-free conditions. Compared to previous reports, this catalyst does not require solvent to control selectivity for cyclohexanecarboxylic acid from benzoic acid. The catalyst was tolerant to different functional group of benzoic acid. With a minor loss in catalytic activity, Rh-PVP catalyst was recycled successfully.

Acknowledgment

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Recyclable Rh-PVP nanoparticles catalyzed hydrogenation of benzoic acid derivatives and quinolines under solvent-free conditions

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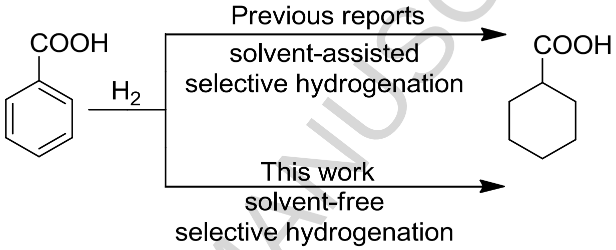
Abstract

Various transition metal nanoparticles, prepared by microwave-assisted alcohol reduction method were examined for hydrogenation of benzoic acid to cyclohexanecarboxylic acid under solvent-free conditions. Rh metal was the most effective catalyst over other metal catalyst. The catalyst showed moderate to high yield for the hydrogenation of substituted benzoic acid and substituted quinolines. Rh-PVP was recycled four times with minor loss in catalytic activity.

Keywords: Heterogeneous catalyst, Rhodium, Nanoparticles, Hydrogenation, Benzoic acid, Quinolines

1. Introduction

The chemoselective hydrogenation of benzoic acid to cyclohexanecarboxylic acid (CCA) has great significance in chemical and pharmaceutical industries. The pharmaceutical drugs such as ansatrienin can be synthesized by using cyclohexyl carboxylic acid [1]. Moreover, the formation of cyclohexanecarboxylic acid by hydrogenation of benzoic acid is a crucial step for the production of caprolactam from toluene in SNIA process (developed by SNIA S.p.A, Italy) [2]. Traditionally, the hydrogenation of benzoic acid and its derivatives was carried out with stoichiometric amount of Na-K alloys [3]. Several Supported monometallic (Pd, Ir, Rh, Ru and Ni) catalysts have been reported for hydrogenation of benzoic acid [4-18]. Bimetallic alloy based catalysts (Pd-Au, Ru-Pt, Ru-Pd, Ni-Pd-B and Ni-Zr-B) were also examined [19-24]. However, some of them suffer from use of additives [24, 25], high temperature (200 °C) [18], high pressure (>20 bar)[5-7, 12-15, 18, 19, 22-25], high catalyst loading (> 1 mol%) [4, 9, 10, 17, 20] and non-recyclable catalyst (Table S1) [7-14, 23, 24]. In addition, the solvent was necessary for selective hydrogenation of benzoic acid to cyclohexane carboxylic acid (Scheme 1) [4-25].



Scheme 1. Hydrogenation of benzoic acid

Metal nanoparticles exhibit a wide range of applications, particularly in the field of catalysis [26]. Among them, polymer or ionic liquids stabilized nanoparticles are located at the border of homogeneous and heterogeneous catalysis. The intrinsic catalytic activity of these systems is easy to understand compared to metal nanoparticles supported on metal oxides because substrate and support direct interactions can be eliminated. Rh metal demonstrated excellent activity for the hydrogenation reactions. Polyvinylpyrrolidone (PVP) stabilized Rh nanoparticles were reported for the biphasic hydrogenation of benzene but deactivation of catalyst was observed due to aggregation of Rh nanoparticles [27]. In 2016, Philippot and co-workers studied Rh-PVP catalyzed hydrogenation of benzoic acid using water as solvent [28]. However, benzoic acid derivatives and recyclability of catalyst were not investigated. Very recently, our group synthesized PVP stabilized Rh nanoparticles by microwave-assisted alcohol as reduction method [29]. This catalyst showed good recyclability for the synthesis of secondary imines from nitriles. As part of continuing interest in the applications of the Rh nanoparticles, we report herein recyclable Rh nanoparticles catalyzed selective hydrogenation of benzoic acid with different functional groups under solvent-free conditions. In addition, the catalyst was applied to selective hydrogenation of quinolines to tetrahydroquinolines which are important bioactive compounds. Good to excellent yields of hydrogenated carboxylic acid derivatives and quinolines were obtained.

2. Experimental

2.1. Catalyst preparation

All metal precursors were purchased from Wako Pure Chemical Industries, Ltd. Japan. Ru, Rh, Pd, Ir and Pt nanoparticles were synthesized by microwave-assisted alcohol reduction method [29]. In typical procedure, 0.25 mmol of metal chloride and 1.25 mmol of polyvinylpyrrolidone (molecular weight M ≈ 40000) were dissolved in 20 ml of ethylene glycol. After purging by Argon, the vessel was sealed with cap and heated to (180 °C) with microwave irradiation (400 W) for 15 min. The obtained colloidal suspension was precipitated using diethyl ether and acetone followed by washing with water and drying under vacuum at 40 °C.

2.2. Catalyst characterization

The particle size of metal nanoparticles was determined by transmission electron microscopy (TEM) using a JEM-2010 transmission electron microscope (JEOL, Japan) operated at an accelerating voltage of 200 kV. The amount of PVP on metal nanoparticles was calculated by using thermogravimetric analysis (ThermoPlus; Rigaku, Japan) from room temperature to 1000 °C under air (flow rate: 200 mL/min). X-ray photoelectron spectroscopy (XPS) analysis was carried out using an ESCA-3400 (Shimadzu, Kyoto, Japan). The binding energy was calibrated using a C 1s binding energy of 284.6 eV. High-angle annular dark field scanning transmission electron microscopy images (HAADF-STEM) were obtained using JEM-ARM200F (JEOL, Japan) operated at 200 kV.

2.3. Typical procedures for catalytic hydrogenation

All organic compounds (Tokyo Chemical Industry, Japan) were used without further purification. Hydrogenation reactions were carried out in 10 ml autoclave with a glass tube inside equipped with magnetic stirrer. In a typical experiment, 1 mmol of substrate and catalyst (1 mol %) were placed in the reactor and sealed. After being sealed, hydrogen was introduced to reactor and inside of the reactor was purged for multiple times. The reactor was pressurized at 5-10 bar by hydrogen and heated to 100°C -180°C. After completion of reaction, the reactor was cooled to room temperature and depressurized. The obtained reaction crude washed with acetone several times and resultant solution was filtered by using micro filters (Sartorius RC 0.20 μm). Then, the filtrate solution was concentrated by using rotary evaporation. Conversion and yield of product were obtained by ^{1}H NMR analysis using 1, 3, 5-trimethoxybenzene as an internal standard. ^{1}H-NMR spectra were recorded using Brucker UltraShield 400 plus operating at 400 MHz.

2.4. Catalyst recycling

After the reaction, the reaction crude was washed by acetone several times. The catalyst was recovered by centrifugation and dried at 50°C for 12 h under vacuum. The dried catalyst was reused for the next run.

4. Results and Discussion

We chose hydrogenation of benzoic acid as model reaction for the optimization of reaction conditions (Table 1). First, various noble metals nanoparticles (Ru, Rh, Pd, Ir and Pt) were used for hydrogenation of benzoic acid to cyclohexanecarboxylic acid. Among the tested catalysts, Rh-PVP catalyst showed the highest yield (96 %) (entries 1-6). In previous reports, Wang [23] and Bai [25] demonstrated that highly polar solvent such as water was played a crucial role in selective hydrogenation of aromatic ring in benzoic acid. Water facilitated to aromatic ring for the adsorption on catalyst surface and avoided unwanted adsorption of carboxyl group on catalyst. Contrary to this reports, Rh-PVP catalyst showed high yield (96%) of cyclohexane carboxylic acid in the absence of solvent. Polar and non polar solvents were found to be less effective for the hydrogenation of benzoic acid.

Table 1 Hydrogenation of benzoic acid by metal catalysts[a]

Entry	Catalyst	PVP (wt %)[c]	Particle size (nm)[d]	Solvent (1 ml)	Conv. (%)	Yield (%)[b]
1	Rh-PVP	82	5.4±1.0	Neat	99	96
2[e]	Rh-PVP	82	5.4±1.0	Neat	80	80
3	Pt-PVP	72	3.9±0.4	Neat	70	70
4	Ir-PVP	78	1.9±0.5	Neat	53	53
5	Ru-PVP	83	3.8±1.1	Neat	63	34
6	Pd-PVP	84	4.8±0.7	Neat	32	21
7	Rh-PVP	82	5.4±1.0	Water	48	46
8	Rh-PVP	82	5.4±1.0	Methanol	20	13
9	Rh-PVP	82	5.4±1.0	CH_3CN	1	1
10	Rh-PVP	82	5.4±1.0	THF	66	57
11	Rh-PVP	82	5.4±1.0	Cyclohexane	47	35
12	no catalyst	--	--	Neat	0	0

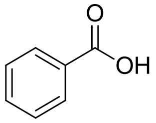
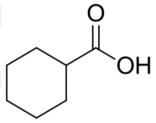
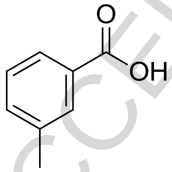
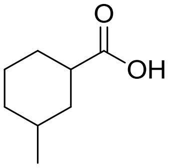
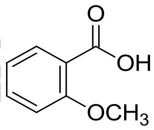
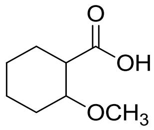
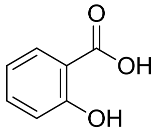
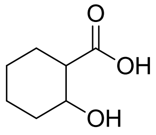
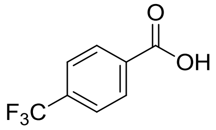
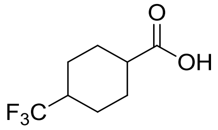
[a] Reaction conditions: substrate (1 mmol), Metal (1 mol%), 150 °C, 1 h, H_2 (10 bar). [b] NMR Yield. [c] Calculated by thermogravimetric analysis. [d] Determined by transmission electron microscopy. [e] Rh catalyst (0.5 mol%)

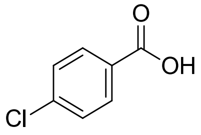
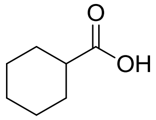
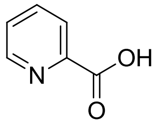
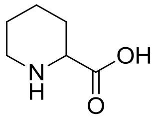
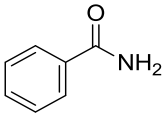
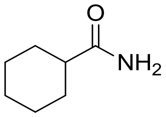
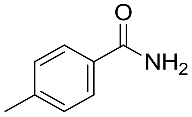
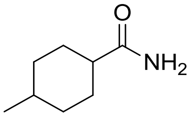
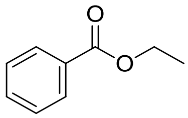
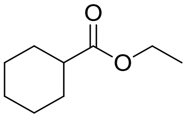
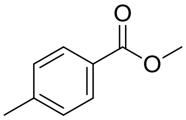
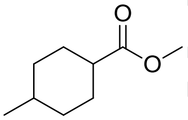
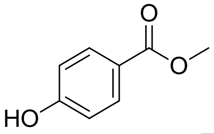
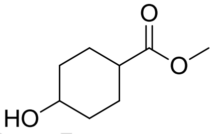
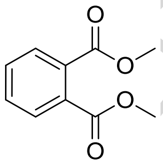
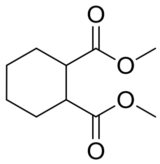
To demonstrate the general applicability of Rh nanoparticles, we carried out hydrogenation reaction of various substituted benzoic acid and derivatives under aforementioned reaction conditions (Table 2). The substituted benzoic acid bearing electron donating group such as methyl gave 99% yield, and benzoic acid bearing electron withdrawing trifluoromethyl group delivered in 60% yield (entries 2 and 3). Due to reductive dechlorination reaction, the hydrogenation of *para*-chlorobenzoic acid proceeded to cyclohexanecarboxylic acid as final product instead of *para*-chlorocyclohexanecarboxylic acid (entry 6). The catalyst was useful for hydrogenation of nitrogen-containing heterocyclic carboxylic acid (entry 7). The hydrogenation of benzamide and *para*-methylbenzamide leads to corresponding products with good yields (70-85 %) (entries 8 and 9）. Moderate to high yields (53-98 %) were obtained when hydrogenation reactions of ethyl benzoate and *para*-substituted methyl benzoate were carried out (entries 10-12). The catalyst was also applicable for the synthesis of industrially important cyclohexyldicarboxylic ester from hydrogenation of dimethyl phthalate (entry 13).

Encouraged by benzoic acid hydrogenation results, we studied the applicability of Rh-PVP catalysts for the selective hydrogenation of quinolines to 1,2,3,4-tetrahydroquinoline. Hydrogenation of quinolines has gained much attention for the synthesis of tetrahydroquinoline-derived natural products and bioactive compounds [30]. The first row transition metal (Mn, Co and Ni) nanoparticles were investigated for the hydrogenation of quinoline using lithium metal and water as hydrogen source. In compared to lithium and water system, molecular hydrogen is an atom-economical source of hydrogen. Unsupported Rh catalyst has been reported for direct hydrogenation of quinolines using molecular hydrogen [32-35]. However, these catalytic methods require high pressure (30 bar H_2) and organic solvents (Table S2).

Using our Rh nanopaticles, quinoline was easily hydrogenated to 1,2,3,4-tetrahydroquinoline under mild pressure (5 bar H_2). Electron donating (-OCH_3) and withdrawing (-Cl) bearing quinolines were hydrogenated to corresponding tetrahydroquinoline and decahydroquinoline (entry 2 and 3).

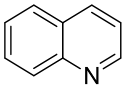
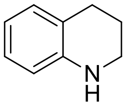
Table 2 Hydrogenation of benzoic acid derivatives using Rh-PVP[a]

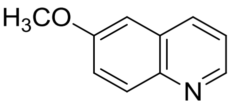
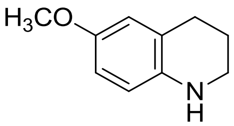
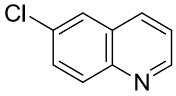
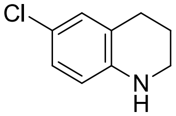
Entry	Substrate	Products	Temp. (ºC)	Time (h)	Conv. (%)	Yield(%)[b] (cis/trans)
1			150	1	99	96
2			150	5	99	99(62:38)
3			120	2	96	96(62:38)
4[c]			160	1	85	50(59:41)
5			150	1	90	60(70:30)

6			180	24	99	99
7			150	24	78	75
8			150	24	85	85
9			180	24	88	70(65:35)
10			150	3	98	98
11			180	6	95	95(71:29)
12			180	24	61	53(83:17)
13			150	6	89	81(78:22)

[a]Reaction conditions: substrate (1 mmol), Rh (1 mol%), H_2 (10 bar). [b]NMR Yield. [c]0.5 mol % catalyst.

Table 3 Hydrogenation of quinolines by Rh-PVP.[a]

Entry	Substrate	Products	Conv. (%)	Yield[b] (%)
1			99	94

2			95	83[c]
3			92	78[c]

[a]Reaction conditions: substrate (1 mmol), Rh (1 mol%), 100 °C, 2 h, H_2 (5 bar). [b]NMR Yield. [c] Decahydroquinoline was obtained as byproduct.

We investigated reusability of Rh nanoparticles for hydrogenation of benzoic acid at optimized reaction condition. The recovered catalyst was recycled three times with slightly loss in catalytic activity from 1st to 2nd cycle (Fig.2). ICP-AES analysis showed that the Rh amount in reaction mixture was below the detection limit (10 ppb).

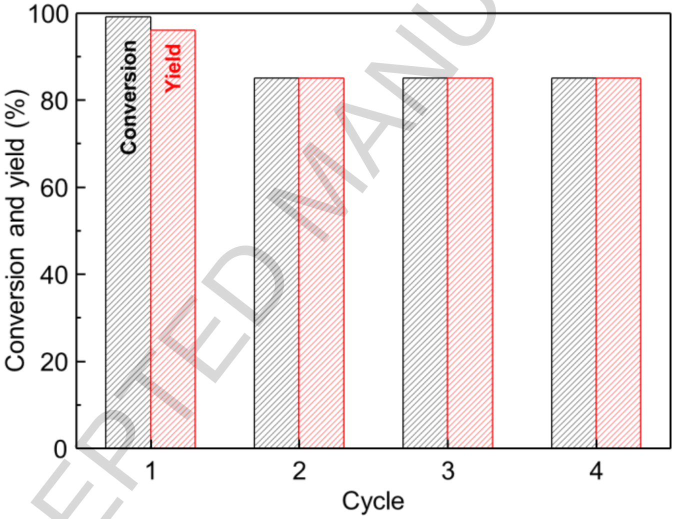


Fig. 2. Recycle study for hydrogenation of benzoic acid by Rh catalyst.

In previous reports, deactivation of unsupported Rh nanoparticles which was synthesized by conventional alcohol reduction method was observed for hydrogenation of arene reactions [35]. In that case, morphological changes such as aggregation headed to catalyst deactivation. To study morphological changes, HAADF-STEM images of fresh and recovered Rh catalyst after first reaction were taken (Fig. 3). Although Rh nanoparticles were partially aggregated, the catalytic activity was not changed significantly. Probably, reaction solvent has some role in catalyst deactivation. During reaction, PVP could be dissolve in water and resultant Rh nanoparticles with less amount of PVP are easily aggregated. By contrast, the removal of PVP was suppressed in our solvent-free conditions, which provides the recyclability of our Rh catalyst. More detailed exploration about the rate of aggregation is necessary and it will be objective of future works.

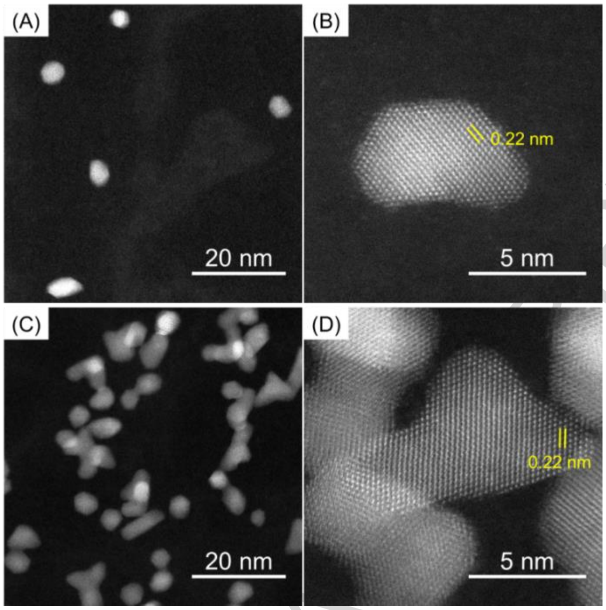


Fig.3.HAADF-STEM images of fresh (A,B) and used (C,D) Rh catalyst.

Moreover, electronic states of fresh and aggregated Rh nanoparticles were examined by XPS analysis (Fig. 4).The binding energy of fresh Rh catalyst was slightly shifted to lower binding energy than that of Rh bulk, indicating charge transfer from PVP to Rh occurs. The binding energy of recovered Rh catalyst was identical to that of fresh Rh nanoparticles, indicating that during the reaction electronic state of Rh nanoparticles remained unchanged. Therefore, we concluded slight loss of activity after 1st cycle was due to aggregation of Rh particles.

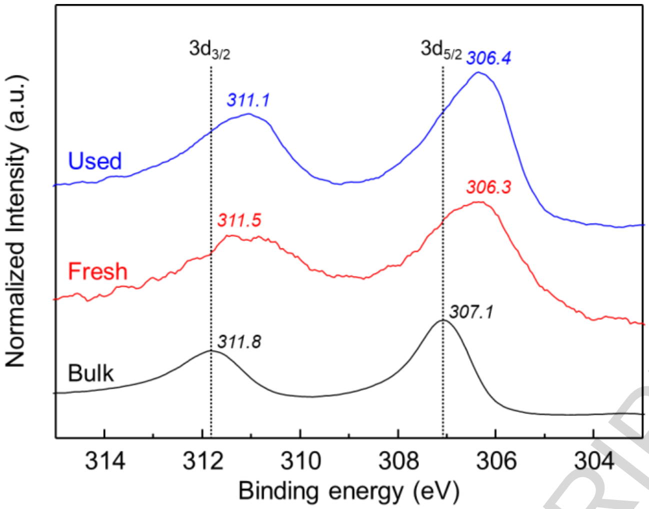


Fig. 4.XPS spectra of fresh and used Rh catalyst.

Conclusions

In summary, we have demonstrated a successful example of Rh catalyzed hydrogenation of benzoic acid and quinolines under solvent-free conditions. Compared to previous reports, this catalyst does not require solvent to control selectivity for cyclohexanecarboxylic acid from benzoic acid. The catalyst was tolerant to different functional group of benzoic acid. With a minor loss in catalytic activity, Rh-PVP catalyst was recycled successfully.

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Graphical abstract