

Rhodium and Iridium Nanoparticles Entrapped in Aluminum Oxyhydroxide Nanofibers: Catalysts for Hydrogenations of Arenes and Ketones at Room Temperature with Hydrogen Balloon

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Abstract: The recyclable metal nanoparticle catalysts, rhodium in aluminum oxyhydroxide [Rh/AlO(OH)] and iridium in aluminum oxyhydroxide [Ir/AlO(OH)], were simply prepared from readily available reagents. The catalysts showed high activities in the hydrogenation of various arenes and ketones under mild conditions. Selective hydrogenation was possible for bicyclic and tricyclic arenes in high yields. The catalysts were active at room temperature even with a hydrogen balloon. Also, the catalysts showed high turnover frequency (TOF) values under solventless conditions at 75 °C under 4 atm hydrogen pressure: *ca.* 1700 h⁻¹ in the hydrogenation of benzene. Furthermore, Rh/AlO(OH) can be reused for

at least 10 times without activity loss. The catalysts were characterized by the transmission electron microscopy (TEM), powder X-ray diffraction (XRD), inductively coupled plasma (ICP), energy dispersive X-ray analysis (EDX), X-ray photoelectron spectroscopy (XPS), nitrogen adsorption and hydrogen chemisorption experiments. The sizes of rhodium and iridium particles were estimated to be 3–4 nm and 2–3 nm, respectively. Aluminum oxyhydroxide nanofibers of these catalysts have surface areas of 500–600 m² g⁻¹.

Keywords: arenes; heterogeneous catalysis; hydrogenation; iridium; ketones; rhodium

Introduction

Developing efficient catalytic systems has been intensively pursued, not only for high catalytic activity and selectivity, but also for catalyst recycling. Indeed, various homogeneous catalysts which are immobilized on heterogeneous supports such as polymers or inorganic materials, suffer from the low activity, difficult synthesis and limited stability. Recently, nanometer sized metal particles with the strictly controlled geometry and uniform size show unexpected catalytic activities as well as physical and chemical properties. Thus, the design of solid-phase metal nanoparticle catalysts is an interesting research topic for organic synthesis and for chemical and pharmaceutical processes.^[1] Due to the high tendency toward agglomeration and recycling problems, the metal nanoparticle itself is not suitable for catalytic reactions. Therefore, several mesoporous

materials including SBA-15, MCM-41 and activated carbon have been used as supports for metal nanoparticles, and extensive research efforts have been focused on their applications to catalytic reactions.^[2]

The hydrogenation of arenes to non-aromatic compounds and that of ketones to alcohols are important organic transformations. Although a large number of stoichiometric metal hydride reagents have been developed, these reagents produce a large amount of undesirable wastes and also cause problems in large scale processes. Traditionally, arene hydrogenation has been performed with heterogeneous catalysts such as Rh/Al₂O₃, Raney nickel, and metal sulfide under drastic reaction conditions.^[3] Rothwell et al. have used homogenous niobium and tantalum catalysts for the hydrogenation of arenes and arylphosphines.^[4] Finke et al. reported that metal nanoparticles act as catalysts for the hydrogenation of arenes

and ketones.^[5] As recyclable catalysts, molecular rhodium catalysts tethered to a palladium-silica support^[6] or ionic copolymer^[7] have been reported. Arene hydrogenation has been performed under various conditions such as liquid-liquid biphasic conditions,^[8] ionic liquid conditions,^[9] and supercritical CO₂ conditions.^[10]

Recently, we have reported a simple synthetic method for recyclable metal nanoparticle catalysts.^[11] Among the catalysts, rhodium nanoparticles entrapped in aluminum oxyhydroxide [Rh/AlO(OH) (**1**)] showed excellent catalytic activity for the hydrogenation of various arenes even under 1 atm H₂ at room temperature. Herein we detail the preparation of Rh/AlO(OH) (**1**) and Ir/AlO(OH) (**2**) and their catalytic activities in arene hydrogenation and in ketone hydrogenation. Also, the catalysts were characterized by TEM, powder XRD, ICP analysis, EDX, XPS, N₂ adsorption and H₂ chemisorption experiments. Notably, the catalysts are recyclable and stable in water as well as in the air. Both catalysts showed high activities in arene hydrogenation and in ketone hydrogenation under mild conditions. The turnover number (TON) was over 20,000 in the hydrogenation of anisole and benzene under solventless conditions at 75 °C under 4 atm H₂ pressure. This activity is the highest one among those observed previously under similar conditions.

Results and Discussion

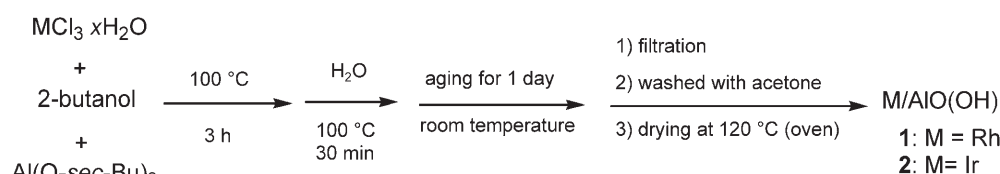
Rh/AlO(OH) (**1**) and Ir/AlO(OH) (**2**) were prepared by a one-pot procedure from RhCl₃ hydrates and IrCl₃ hydrates similar to that reported for the corresponding palladium catalyst.^[11] The metal nanoparticles were generated by heating a mixture of the metal chloride, 2-butanol and Al(O-*sec*-Bu)₃ at 100 °C (Scheme 1). When the reaction mixture turned to black suspension after 3 h, excess water was added to make gel. Heating the reaction mixture above 120 °C or prolonging the reaction time caused agglomeration of the metal nanoparticles.

A bluish-gray powder was obtained after aging the gel for 1 day, washing it with acetone, and drying at 120 °C. The TEM images of **1** and **2** show nanofiber morphologies which are characteristic for the aluminum oxyhydroxide matrix (Figure 1 and Figure 2).^[12]

From the high-resolution TEM images, the sizes of the rhodium nanoparticles are 3–4 nm. The powder XRD pattern for **1** shows the existence of metallic rhodium. The particle size is calculated to be 3.3 nm from the half-width of the diffraction line (111) (Figure 3). In the case of the iridium catalyst **2**, the particle size is 2–3 nm from the high-resolution TEM image, but the XRD pattern shows the presence of not only metallic iridium but also iridium dioxide.^[13] The XPS analysis for **2** reveals that iridium particles are covered with iridium dioxide (Figure 4). The binding energy from the XPS spectrum shows two peaks at 61.1 eV and 64.4 eV that were assigned to the 4f_{7/2} and 4f_{5/2} peaks of metallic iridium, respectively. Also, two peaks at 62.3 eV and 65.7 eV were assigned to the 4f_{7/2} and 4f_{5/2} peaks of iridium dioxide, respectively. Compared to previously reported iridium XPS data,^[13,14] our data certainly confirm the formation of iridium dioxide on the surface of iridium nanoparticles in aluminum oxyhydroxide.

The nitrogen adsorption experiments conducted for **1** and **2** have shown their specific surface areas, pore volumes and the pore sizes (Table 1). Also, the metallic surface areas, active particle diameters and metal dispersions were estimated by the H₂ chemisorption experiments. Zeng et al. had already reported high surface-area alumina using the sol-gel method with aluminum tri-*sec*-butoxide.^[12b] When compared to the results obtained by the Zeng group, the surface areas of **1** and **2** possess similar values. Recently, the fibrous structure of aluminum oxyhydroxide was fully characterized by the Seal group.^[12a] We confirmed the existence of Rh or Ir by EDX, and the metal contents were controlled at between 0.1 and 8 wt%, which could be analyzed by ICP. It is notable that the metal entrapment in our synthetic method was almost quantitative on the basis of the ICP data.

We tested the catalytic activity of **1** in the hydrogenation of benzene and anisole and compared the activity with those reported previously (Table 2). Anisole was selected as the standard substrate for arene hydrogenation.^[5] Anisole hydrogenation using **1** (1.0 mol% Rh) gave methoxycyclohexane in 100% conversion within 1 h at room temperature under 1 atm H₂. Even with 0.010 mol% of Rh, 20 mmol of neat anisole were hydrogenated completely (TON: 10,000) in 26 h at 75 °C under 4 atm H₂. Importantly, this activity is the highest one among those observed previ-



Scheme 1. Preparation of Rh/AlO(OH) and Ir/AlO(OH).

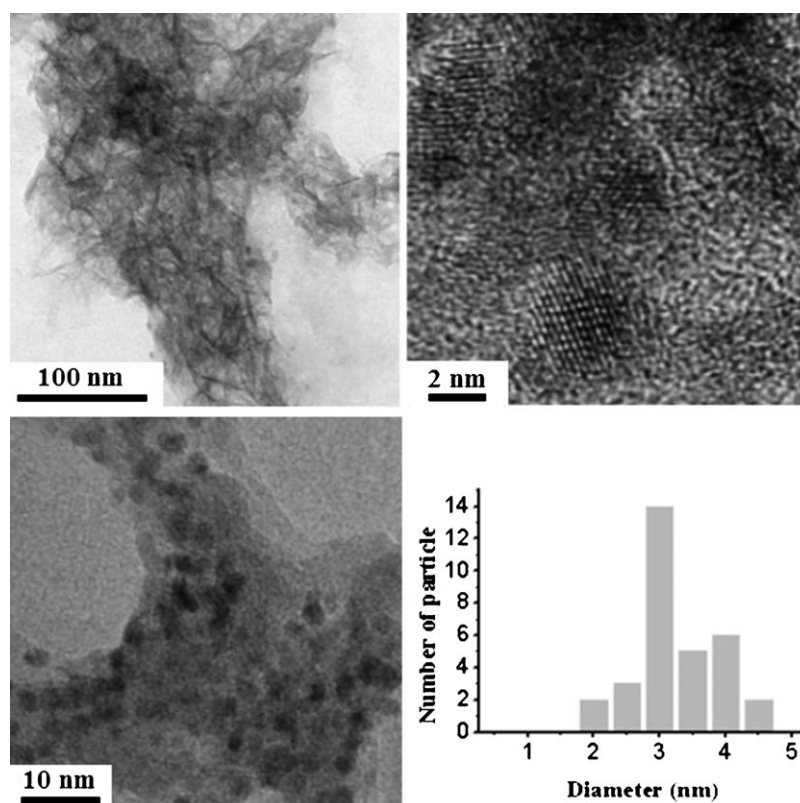


Figure 1. TEM images of Rh/AIO(OH) (**1**) and size distribution of particles.

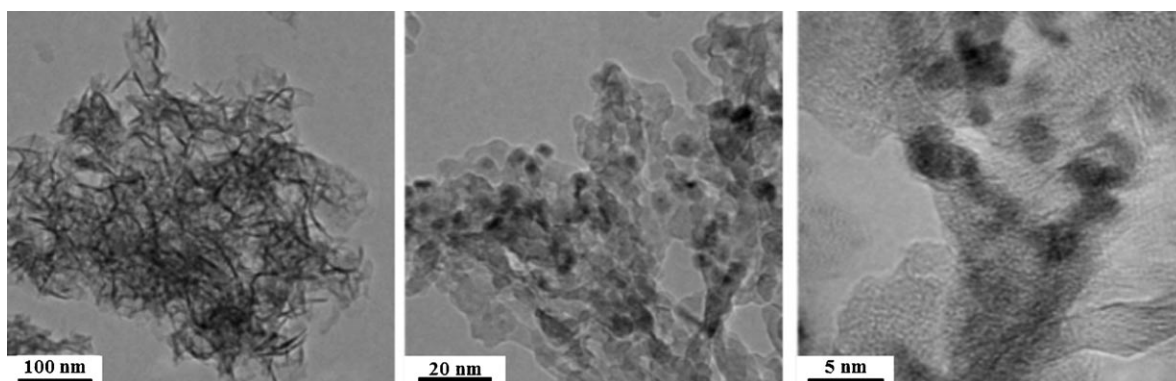


Figure 2. TEM images of Ir/AIO(OH) (**2**).

ously under similar conditions. A commercial rhodium catalyst (Rh/Al₂O₃) showed only about 4 % of the activity of **1** under similar conditions. Schulz et al. have reported that rhodium nanoparticles stabilized by surfactants act as hydrogenation catalysts in aqueous medium.^[6e] Although a high activity in arene hydrogenation under biphasic conditions was observed, it was very difficult to recover the catalyst from the reaction mixture and the recovered catalyst showed lowered activity. Angelici et al. have used a hybrid catalyst consisting of a homogeneous rhodium catalyst tethered to a silica-supported palladium catalyst and observed a synergy effect on arene hydrogenation.^[8]

The catalyst was active at 40 °C under 1 atm H₂, but ten times more palladium than rhodium were required. Recently, rhodium nanoparticles immobilized on carbon nanotubes^[15] and entrapped in ionic liquid copolymers^[10] have been employed as arene hydrogenation catalysts. The former was tested in anthracene hydrogenation under 10 atm H₂, and the latter in benzene hydrogenation under 40 atm H₂.

The scope of arene hydrogenation with **1** was investigated at room temperature with a hydrogen balloon (Table 3). Mono- and disubstituted benzene derivatives were hydrogenated to their corresponding cyclohexane derivatives in 1–5 h with 1.0 mol % of Rh. An

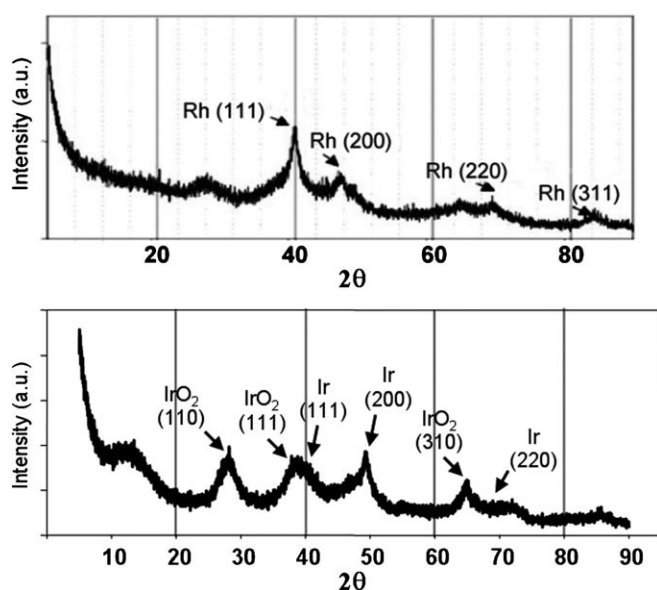


Figure 3. XRD spectra of **1** and **2**.

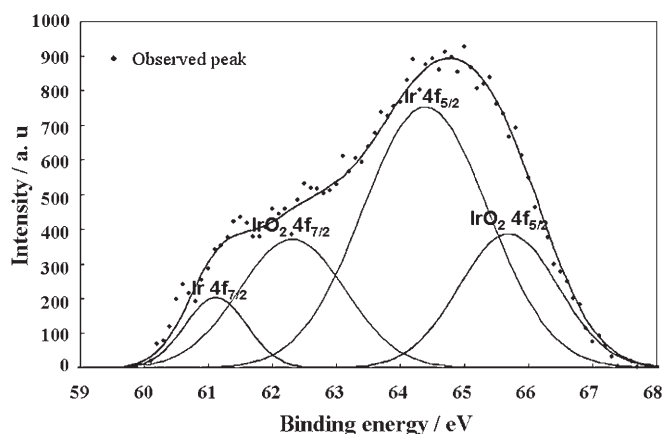


Figure 4. XPS spectra of **2**.

Table 1. Properties calculated from N₂ adsorption and H₂ chemisorption of **1**, **2**.

Property	Rh/AlO(OH) (1)	Ir/AlO(OH) (2)
BET surface area (m ² g ⁻¹)	616	516
Pore volume (cm ³ g ⁻¹)	0.85	1.1
Pore size (nm)	2.9	3.7
Dispersion (%)	28.7	36.2
Metallic surface area (m ² g ⁻¹)	126	124
Active particle diameter (nm)	3.8	2.1

interesting observation was that the hydrogenation of acetophenone resulted in a 65:35 mixture of 1-cyclohexylethanol and cyclohexyl methyl ketone, respec-

tively. However, in a separate experiment, cyclohexyl methyl ketone was not hydrogenated to 1-cyclohexylethanol under the same conditions. Generally, the hydrogenation of electron-rich arenes is faster than that of electron-poor ones. Particularly, the hydrogenation of dimethyl terephthalate took 46 h. Selective hydrogenation was possible for bicyclic arenes. Tetrahydronaphthalene was obtained in 97% yield after 3 h, while decalin was produced in 99% yield after 10 h. From 2-methoxynaphthalene, 1,2,3,4-tetrahydro-6-methoxynaphthalene was obtained in 96% yield after 5 h, while 2-methoxydecalin was produced in 99% yield after 30 h. Quinoline was hydrogenated selectively to 1,2,3,4-tetrahydroquinoline in 94% after 6 h. These results from the hydrogenation of bicyclic arenes are worthy of note, compared to those obtained by using a polymer-incarcerated palladium (PI-Pd) catalyst.^[16] For example, only a 7:3 mixture of 5,6,7,8-tetrahydro-2-methoxynaphthalene and 1,2,3,4-tetrahydro-2-methoxynaphthalene was obtained in the hydrogenation of 2-methoxynaphthalene with PI-Pd (5.0 mol% Pd) under 70 atm H₂ at 50 °C. In the hydrogenation of disubstituted benzenes and bicyclic arenes, about 9:1 *cis/trans* selectivities were observed except in the case of *o*-cresol, where a 1:1 *cis/trans* mixture was obtained. Selective hydrogenation is also possible for anthracene: 9,10-dihydroanthracene was obtained in 97% yield. Dehalogenation accompanied the hydrogenation of 4-chloroanisole to give methoxycyclohexane. The use of triethylamine facilitated the dehalogenation by quenching the hydrochloride formed during the reaction. The activity that **1** shows in the dehalogenation is much higher than the recent one that requires high hydrogen pressure (40 atm) and high reaction temperature (75 °C).^[17]

To show the effectiveness of **1** in large-scale reactions, we performed the hydrogenation of liquid arenes without solvent under 4 atm H₂ at 75 °C (Table 4). Benzene was hydrogenated to cyclohexane completely after 1.5 h by using 0.10 mol% of Rh. The hydrogenation proceeded also smoothly with 0.010 mol% of Rh to result in a TOF of 1700 h⁻¹. Even with 0.0050 mol% of Rh, the hydrogenation was completed in 15 h (TOF = 1300 h⁻¹). Anisole was converted completely to methoxycyclohexane with 0.10 mol% of Rh, although the reaction was about four times slower than that of benzene. In the reaction with 0.0050 mol% of Rh, a mixture of anisole and hydrogenation products (57% of methoxycyclohexane and 11% of 1-methoxycyclohexene) was found after 24 h, but the mixture was converted to methoxycyclohexane completely after 42 h (TOF = 480 h⁻¹). The hydrogenation of toluene was slightly slower than that of benzene, while that of *o*-xylene was about two times slower than that of benzene. Heteroatom-containing substrates such as ethyl benzoate, *o*-cresol, and pyridine were hydrogenated in comparable rates

Table 2. Arene hydrogenation for various catalysts.

Catalyst	Substrate	S/C ^[a]	Conditions	Product (Yield [%] ^[b])	TOF ^[c] [h ⁻¹]
Rh/AlO(OH) (1)	anisole	100	r.t., 1 atm H ₂ , <i>n</i> -hexane	methoxycyclohexane (100)	100 (340)
Rh/AlO(OH) (1)	benzene	100	r.t., 1 atm H ₂ , <i>n</i> -hexane	cyclohexane (100)	200 (690)
Rh/AlO(OH) (1)	anisole	10000	75 °C, 4 atm H ₂ , solventless	methoxycyclohexane (100)	380 (1320)
Rh/AlO(OH) (1)	benzene	10000	75 °C, 4 atm H ₂ , solventless	cyclohexane (100)	1700 (5920)
Ir/AlO(OH) (2)	anisole	1000	75 °C, 4 atm H ₂ , solventless	methoxycyclohexane (39)	16
Rh/PVP [BMI][BF ₄] ^[d]	benzene	4000	75 °C, 40 atm H ₂ , [BMI][BF ₄]	cyclohexane (100)	250
Ru/MMT ^[e]	benzene	10000	110 °C, 80 atm H ₂ , solventless	cyclohexane (100)	4000
Rh/CNT ^[f]	methyl benzoate	38	55 °C, 10 atm H ₂ , MeOH	methyl cyclohexanoate (100)	10
Rh/PVP ^[g]	benzene	2000	30 °C, 7 atm H ₂ , biphasic	cyclohexane (100)	250
Rh-CNC/ Pd-SiO ₂ ^[h]	anisole	2810	40 °C, 1 atm H ₂ , <i>n</i> -heptane	methoxycyclohexane (42)	130
Rh-HEA16X ^[i]	anisole	100	20 °C, 1 atm H ₂ , biphasic	methoxycyclohexane (100)	28
Rh-polyoxoanion ^[j]	anisole	2600	22 °C, 3 atm H ₂ , propylene carbonate	methoxycyclohexane (91) ^[l]	18
Ir [BMI][PF ₆] ^[k]	anisole	250	75 °C, 4 atm H ₂ , solventless	methoxycyclohexane (62); cyclohexane (12)	10 (18)
Ir [BMI][PF ₆] ^[k]	benzene	250	75 °C, 4 atm H ₂ , solventless	cyclohexane (100)	125 (219)
Rh/Al ₂ O ₃ Aldrich	anisole	100	r.t., 1 atm H ₂ , <i>n</i> -hexane	methoxycyclohexane (4.1)	4.1

^[a] Substrate/catalyst (moles/moles).^[b] Determined by GC.^[c] TOF is defined as moles of product by moles of total metal per hour, and the value in parenthesis is corrected for the exposed metal which is estimated by the H₂ chemisorption.^[d] Ref.^[7]^[e] Ref.^[9i]^[f] Ref.^[15]^[g] Ref.^[8c]^[h] Ref.^[6a]^[i] Ref.^[8e]^[j] Ref.^[5b]^[k] Ref.^[9d]^[l] 1-Methoxycyclohexene was also formed in 8%.

(TOF *ca.* 100 h⁻¹). However, the TOF of phenol hydrogenation was only 38. The hydrogenation of quinoline was much slower (TOF = 16 h⁻¹), but gave 1,2,3,4-tetrahydroquinoline selectively in 94% yield. Anthracene was hydrogenated after dissolving in cyclohexane. In contrast to the production of 9,10-dihydroanthracene in the hydrogenation at room temperature under 1 atm H₂, 1,2,3,4,5,6,7,8-octahydroanthracene was the major product in the reaction with 5 mol% of Rh at 75 °C under 4 atm H₂. Furthermore, perhydroanthracenes (*cis/trans* mixture) were produced quantitatively after 5 h when the amount of **1** was increased to 10 mol% of Rh. These results are remarkable, compared with previous results reported by the Wai group^[15] and by the Kobayashi group.^[16] Wai et al. have used carbon nanotube-supported metal nanoparticles (M/CNT) as the catalyst for the hydrogenation of anthracene. When they employed a rhodium catalyst (Rh/CNT) at room temperature under 10 atm H₂, 1,2,3,4-tetrahydroanthracene was the major product in 62% yield with a low selectivity. A bimetallic catalyst (Pd-Rh/CNT) improved the hy-

drogenation, but gave only a 7:93 mixture of 9,10-dihydroanthracene and 1,2,3,4,5,6,7,8-octahydroanthracene.

We tested the activities of **1** and **2** for the hydrogenation of cyclohexanone under conditions **A** (0.50 mmol of a substrate dissolved in 1.0 mL of *n*-hexane at room temperature with a hydrogen balloon) or under conditions **B** (20 mmol of a neat substrate at 75 °C under 4 atm H₂). The iridium catalyst **2** showed a lower activity than the rhodium catalyst **1** under conditions **A**. However, under conditions **B**, the activity of **1** decreased considerably, while that of **2** rather increased. Thus, the activity of **2** was about ten times higher than that of **1** under condition **B** (Table 5).

Then we carried out the hydrogenation of various ketones under conditions **A** with **1** (1.0 mol% of Rh) and under conditions **B** with **2** (0.10 mol% of Ir) (Table 6). As expected, the reactions under conditions **B** with **2** showed much higher TOF than those under conditions **A** with **1**. Particularly, the TOF of 2-heptanone hydrogenation increased about 70 times. Cyclo-

Table 3. Hydrogenation of various arenes at room temperature with a hydrogen balloon.^[a]

Entry	Substrate	Time [h]	Product (Yield [%] ^[b])
1	toluene	1	methylcyclohexane (100)
2	anisole	1	methoxycyclohexane (100)
3	phenol	1	cyclohexanol (100)
4	ethyl benzoate	4.5	ethyl cyclohexanoate (100)
5	acetophenone	4.5	1-cyclohexylethanol (65), cyclohexyl methyl ketone (35)
6	1-phenylethanol	4	1-cyclohexylethanol (100)
7	<i>o</i> -xylene	2.5	1,2-dimethylcyclohexane (100) <i>cis/trans</i> = 94/6
8	<i>o</i> -cresol	3	2-methylcyclohexanol (100) <i>cis/trans</i> = 52/48
9	naphthalene	3	tetralin (97), decalin (3)
10	naphthalene	10	decaline (100) <i>cis/trans</i> = 88/12
11 ^[c]	2-methoxynaphthalene	5	1,2,3,4-tetrahydro-6-methoxynaphthalene (96), 2-methoxy-1,2,3,4-tetrahydronaphthalene (4)
12 ^[c]	2-methoxynaphthalene	30	2-methoxydecalin (99) <i>cis/trans</i> = 85/15
13 ^[d]	quinoline	6	1,2,3,4-tetrahydroquinoline (94)
14 ^[e]	anthracene	3	9,10-dihydroanthracene (97), 1,2,3,4,5,6,7,8-octahydroanthracene (3)
15 ^[f]	dimethyl terephthalate	46	dimethyl cyclohexanedicarboxylate (100) <i>cis/trans</i> = 85/15
16 ^[g]	4-chloroanisole	3	methoxycyclohexane (99)

^[a] At room temperature, 0.50 mmol substrate in *n*-hexane (1.0 mL) was reacted with **1** (1.0 mol % Rh).

^[b] Determined by GC.

^[c] 3.0 mol % of Rh was used.

^[d] 5.0 mol % of Rh was used.

^[e] 0.10 mmol anthracene, 5.0 mol % of Rh, and 5.0 mL cyclohexane were used at 70 °C.

^[f] 5.0 mol % of Rh and 3.0 mL ethyl acetate were used.

^[g] 3.0 mol % of Rh and 1.0 equiv triethylamine were used

Table 4. Hydrogenation of various arenes at 75 °C under 4 atm H₂ pressure without solvent.^[a]

Entry	Substrate	Mol % Rh	TON	Time [h]	Product (Yield [%] ^[b])	TOF ^[c]
1	benzene	0.10	1000	1.5	cyclohexane (100)	670
2	benzene	0.010	10000	6.0	cyclohexane (100)	1700
3	benzene	0.0050	20000	15	cyclohexane (100)	1300
4	anisole	0.10	1000	6.0	methoxycyclohexane (100)	170
5	anisole	0.010	10000	26	methoxycyclohexane (100)	390
6	anisole	0.0050	20000	24	anisole (32), 1-methoxycyclohexene (11), methoxycyclohexane (57)	475
				42	methoxycyclohexane (100)	480
7	toluene	0.10	1000	2.0	methylcyclohexane (100)	500
8	<i>o</i> -xylene	0.10	1000	2.5	1,2-dimethylcyclohexane (100) <i>cis/trans</i> = 92/8	330
9	ethyl benzoate	0.10	1000	12	ethyl cyclohexanoate (100)	83
10	<i>o</i> -cresol	0.10	1000	12	2-methylcyclohexanol (100) <i>cis/trans</i> = 54/48	83
11	pyridine	0.10	1000	10	piperidine (100)	100
12	phenol	0.10	1000	26	cyclohexanol (100)	38
13	quinoline	0.20	500	30	1,2,3,4-tetrahydroquinoline (94)	16
14 ^[d]	anthracene	5.0	20	3	1,2,3,4,5,6,7,8-octahydroanthracene(86)	6
15 ^[d]	anthracene	10	10	5	perhydroanthracenes (100)	2

^[a] Neat substrate (20 mmol) was reacted with **1** at 75 °C under 4 atm H₂.

^[b] Determined by GC.

^[c] TOF is defined as the moles of hydrogenated products per the moles of total Rh per hour.

^[d] Anthracene (0.10 mmol) was dissolved in cyclohexane (5.0 mL).

pentanone was hydrogenated selectively to cyclopentanol in quantitative yield under conditions **A** with **1**, but was transformed into a mixture of cyclopentanol and dicyclopentyl ether in a 92:8 ratio under conditions **B** with **2**. A keto ester, ethyl pyruvate, was hy-

drogenated quantitatively to ethyl 2-hydroxypropionate under both conditions. The hydrogenation of acetone was more than 20 times faster than that of 2,6-dimethyl-4-heptanone under conditions **B**, indicating the steric effect on the metal nanoparticle-cata-

Table 5. Hydrogenation of cyclohexanone to cyclohexanol with **1** or **2**.

Entry	Catalyst	Conditions ^[a]	Time [h]	Yield [%] ^[b]	TOF ^[c] [h ⁻¹]
1	1 (0.10 mol% Rh)	A	10 15	87 99	87 66
2	1 (1.0 mol% Rh)	A	0.33 0.50	79 99	240 200
3	1 (0.10 mol% Rh)	B	3.0 6.0	5.2 9.8	17 16
4	2 (0.10 mol% Ir)	A	10 20	63 99	63 50
5	2 (1.0 mol% Ir)	A	0.50 1.0	75 99	150 100
6	2 (0.10 mol% Ir)	B	3.0 6.0	59 99	200 170

^[a] Conditions **A**: cyclohexanone (0.50 mmol) dissolved in 1.0 mL of *n*-hexane was reacted at room temperature with hydrogen balloon. Conditions **B**: neat cyclohexanone (20 mmol) was reacted at 75 °C under 4 atm H₂.

^[b] The yield of cyclohexanol was determined by GC.

^[c] TOF is defined as the moles of cyclohexanol produced per the moles of total metal per hour

lyzed hydrogenation. It is noticeable that the activity of **2** shown in the hydrogenation of acetone is five times higher than that of the previous iridium nanoparticle catalyst prepared in ionic liquid.^[7i]

Recyclability is an essential advantage of heterogeneous catalysts over homogeneous ones. Hence, we tested the recyclability of **1** in the hydrogenation of anisole under conditions **A** and under conditions **B** (Table 7). The catalyst **1** was recovered simply by filtration or by careful decantation after sedimentation. The recovered catalyst retained its original activity even in the 10th cycle under conditions **A** and at least in the 5th cycle under conditions **B**. The reaction mixtures in the recycling tests were analyzed after 30 min

as well as after 1 h under conditions **A** to show no activity loss; 50–60 % conversions and complete conversions were observed after 30 min and after 1 h, respectively. We analyzed the metal contents in the recovered catalysts also by ICP to confirm no metal leaching in the recycling tests. The observed high activity and recyclability of **1** would result from the fibrous aluminum oxyhydroxide matrix that provides a highly porous structure and stabilizes metal nanoparticles. There is a previous report that also emphasizes the fibrous morphology and hydroxy groups of alumina for high catalytic activities.^[18]

Conclusions

In summary, we have developed a simple synthetic method for recyclable Rh and Ir catalysts and demonstrated their high activities in arene hydrogenation and ketone hydrogenation. The catalysts are active for a wide range of substrates at room temperature even with a hydrogen balloon. They are also active under solventless conditions, and show high TOF values (up to 1700 h⁻¹). Highly selective hydrogenations are possible for bicyclic and tricyclic aromatic compounds in high yields by controlling the reaction conditions. Easy separation and robustness in recycling are practical advantages in addition to the easy catalyst synthesis.

Experimental Section

General

Commercial chemicals except anthracene were used without further purification. Anthracene was purified by recrystallization from cyclohexane at room temperature. The wide-angle XRD spectrums were obtained on a diffractometer (M18XHF, MAC Science Co.) with Cu K α radiation. The

Table 6. Hydrogenation of various ketones with **1** and **2**.

Entry	Substrate	Catalyst ^[a]	Conditions	Time [h]	Product (Yield [%] ^[b])	TOF ^[c] [h ⁻¹]
1	cyclopentanone	1	A	6.0	cyclopentanol (99)	17
		2	B	7.0	cyclopentanol (92) ^[d]	130
2	2-heptanone	1	A	20	2-heptanol (97)	5
		2	B	3.0	2-heptanol (99)	330
3	ethyl pyruvate	1	A	1.0	ethyl 2-hydroxypropanoate (99)	99
		2	B	4.0	ethyl 2-hydroxypropanoate (99)	250
4	acetone	2	B	1.5	isopropyl alcohol (99)	660
5	2,6-dimethyl-4-heptanone	2	B	36	2,6-dimethyl-4-heptanol (99)	28

^[a] Conditions **A**: substrate (0.50 mmol) dissolved in 1.0 mL of *n*-hexane was reacted at room temperature with hydrogen balloon. Conditions **B**: neat substrate (20 mmol) was reacted at 75 °C under 4 atm H₂. 1.0 mol % of Rh or 0.10 mol % of Ir was used respectively.

^[b] Determined by GC.

^[c] TOF is defined as moles of hydrogenated products by moles of total metal per hour.

^[d] Dicyclopentyl ether was formed in 8 %.

Table 7. Recycling experiment of anisole hydrogenation with **1**^[a]

Conditions A	Cycle	1	2	3	4	5	6	7	8	9	10
	% yield ^[b]	51.5	56.8	57.7	50.6	65.1	58.7	51.3	51.3	52.6	50.5
	% yield ^[c]	100	100	100	100	100	100	100	100	100	100
Conditions B	Cycle	1	2	3	4	5					
	% yield ^[d]	99.9	99.9	99.9	99.9	99.9					

^[a] Conditions **A**: anisole (0.50 mmol) dissolved in 1.0 mL of *n*-hexane was reacted at room temperature with hydrogen balloon. Conditions **B**: neat anisole (20 mmol) was reacted at 75 °C under 4 atm H₂.

^[b] After 30 min, determined by GC (1.0 mol % of Rh).

^[c] After 60 min, determined by GC (1.0 mol % of Rh).

^[d] After 6 h, determined by GC (0.10 mol % of Rh).

TEM images were taken on a field emission electron microscope (JEM 2010F, JEOL) operated at 200 kV. X-ray photoelectron spectra (XPS) were acquired with a VG-Scientific ESCALAB 220iXL spectrometer equipped with a hemispherical electron analyzer and an Mg K α (1253.6 eV) X-ray source. The binding energy calibration was performed using the C1s peak at 284.6 eV as the reference energy. H₂ chemisorption experiments were performed using an Autochem II 2920 V 3.02 instrument. After a pre-treatment procedure under argon flowing at 100 °C for 2 h, H₂ chemisorption was conducted with 5 % H₂/Ar at 70 °C. Dispersion and exposed metal were estimated by the well accepted 1:1 surface hydrogen metal atom stoichiometry.

Synthesis of **1**

RhCl₃·xH₂O (Rh content: 38 wt. %) (200 mg, 0.73 mmol of Rh), 2-butanol (1.6 g, 22 mmol), Al(*O*-*sec*-Bu)₃ (4.3 g, 18 mmol) were added into 25-mL round flask equipped with a condenser. After being stirred at 100 °C for 3 h to give a black suspension, water (1.5 mL) was added. The reaction mixture was further stirred for 30 min at 100 °C, then kept at room temperature for 24 h. The black solid was filtered, washed with acetone and dried at 120 °C for 1 h to give **1** as a bluish-gray powder; yield: 1.5 g (5.0 wt. % of Rh). The rhodium content was estimated by ICP analysis.

Synthesis of **2**

IrCl₃·xH₂O (Ir content: 55 wt. %) (140 mg, 0.39 mmol of Ir), 2-butanol (1.6 g, 22 mmol), Al(*O*-*sec*-Bu)₃ (5.6 g, 23 mmol) were added into 25-mL round flask equipped with a condenser. After being stirred at 100 °C for 3 h to give a black suspension, water (1.5 mL) was added. The reaction mixture was further stirred for 30 min at 100 °C, then kept at room temperature for 24 h. The black solid was filtered, washed with acetone and dried at 120 °C for 1 h to give **2** as a bluish-gray powder; yield: 1.9 g (4.1 wt. % of Ir). The iridium content was estimated by ICP analysis.

Hydrogenation of Anisole at Room Temperature under 1 atm H₂

To a solution of anisole (54 μ L, 0.50 mmol) in hexane (1.0 mL) in a 10-mL round flask **1** (10 mg, 1.0 mol % Rh) was added, and the reaction mixture was stirred at room temperature for 1 h under an H₂ balloon. The speed of stirring was 800–900 min^{−1}. The catalyst was filtered then dried

in the air for reuse. The filtrate was analyzed by gas chromatography.

Hydrogenation of Anisole at 75 °C under 4 atm H₂

Anisole (2.2 mL, 20 mmol) and **1** (4.1 mg, 0.010 mol % Rh) were added in a 15-mL pressure vessel, and the reaction mixture was stirred at 75 °C for 26 h under 4 atm H₂. The stirring speed was 800–900 min^{−1}. The catalyst was filtered, then dried in the air for reuse. The filtrate was analyzed by gas chromatography.

Hydrogenation of Cyclohexanone at Room Temperature under 1 atm H₂

To a solution of cyclohexanone (52 μ L, 0.50 mmol) in hexane (1.0 mL) in a 10-mL round flask **2** (24 mg, 1.0 mol % Ir) was added, and the reaction mixture was stirred at room temperature for 1 h under an H₂ balloon. The speed of stirring was 800–900 min^{−1}. The reaction mixture was analyzed by gas chromatography.

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