Rhodium nanoparticles entrapped in boehmite nanofibers: recyclable catalyst for arene hydrogenation under mild conditions†

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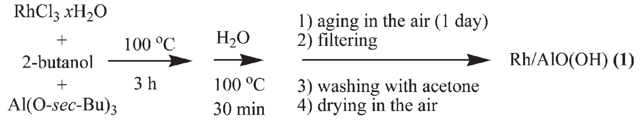
A new recyclable rhodium catalyst was synthesized by a simple procedure from readily available reagents, which showed high activities in the hydrogenation of various arenes under 1 atm H_2 at room temperature.

Metal nanoparticles are attracting much attention in organic synthesis due to their distinct catalytic activities for various transformations.[1,2] Arene hydrogenation, which is an important transformation for small scale synthesis as well as for industrial process, is a typical example in that metal nanoparticles catalyze the reaction under mild conditions.[3–7] Bare metal nanoparticles are kinetically unstable with respect to agglomeration; a wide variety of methods to stabilize metal nanoparticles have been developed.[3,4] However, they often suffer from difficult synthetic procedures, low stability and low activity. Herein we report a readily preparable rhodium nanoparticles in boehmite nanofibers for the hydrogenation of various arenes. Our catalyst is robust in recycling and highly active even at room temperature under 1 atm H_2.

The catalyst, Rh/AlO(OH) (**1**), was synthesized by a one-pot procedure similar to that for a palladium catalyst reported previously by us (Scheme 1).[8,9] Rhodium nanoparticles were generated by heating a mixture of $RhCl_3$ hydrate, 2-butanol and Al(O-*sec*-Bu)$_3$, and then entrapped in a boehmite matrix by gelation with water. Dark gray powder obtained from the gel through aging, washing with acetone, and drying was characterized by transmission electron microscopy (TEM) (Fig. 1), powder X-ray diffraction (XRD) analysis (Fig. 2), ^{27}Al magic-angle spinning NMR (Fig. 3) and BET nitrogen adsorption analysis. The low-resolution TEM image shows the boehmite nanofibers morphology,[10] while Rh nanoparticles entrapped in the boehmite nanofibers are observed in the high-resolution image.[11] The crystalline state of the rhodium nanoparticles was verified by XRD analysis.[11] The particle size of rhodium was estimated to be 2.5–3.0 nm by HRTEM and XRD analysis. The ^{27}Al NMR spectrum of **1** shows three resonances at 7, 35 and 60 ppm. The major resonance at 7 ppm is common in the spectra of boehmite



Scheme 1 Preparation of the rhodium nanoparticle catalyst.

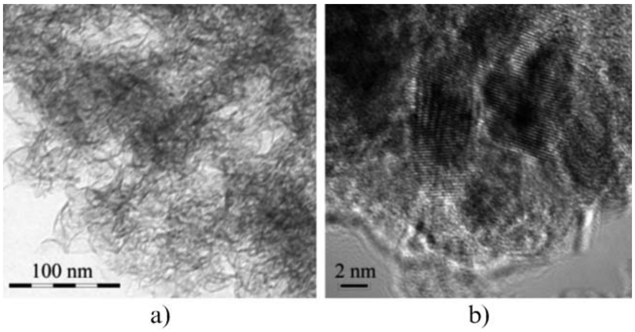


Fig. 1 TEM image: (a) low resolution, (b) high resolution

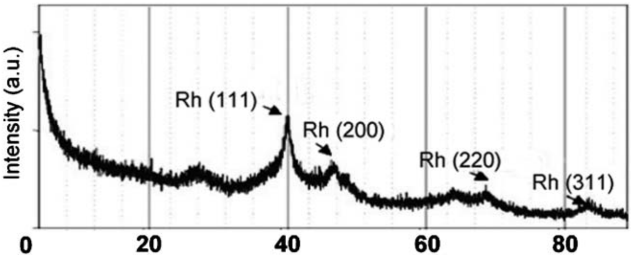


Fig. 2 XRD spectrum

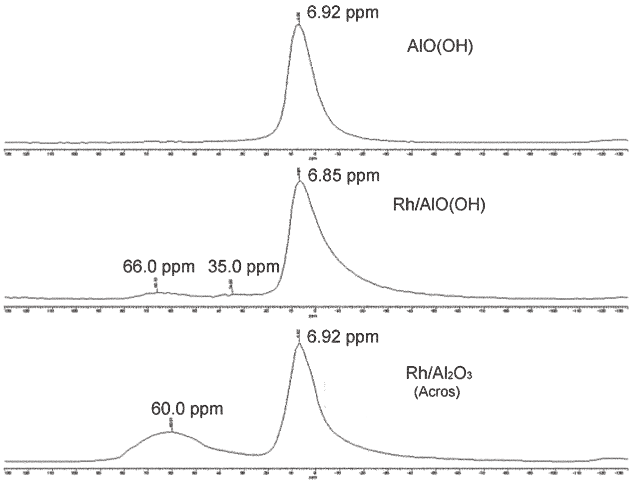


Fig. 3 ^{27}Al MAS NMR spectra

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Table 1 Hydrogenation of benzene and anisole with various catalysts

	Catalyst	Substrate	Solvent	T/°C	$p\mathrm{H_2}$/atm	t/h	Yield[a] (%)	S/C[b]	TOF[c]
1	**1**	Benzene	Hexane	22	1	0.5	100	100	600
2	**1**	Benzene	Solventless	75	4	6	100	10000	5000
3	Ir[d]	Benzene	Solventless	75	4	2	100	250	375(657)
4	Rh/PVP[e]	Benzene	H_2O[f]	30	7	8	100	2000	750
5	**1**	Anisole	Hexane	22	1	1	100	100	300
6	**1**	Anisole	Solventless	75	4	30	100	10000	1000
7	Ir[d]	Anisole	Solventless	75	4	18	62[g]	250	30(54)
8	Rh/Al_2O_3[h]	Anisole	Hexane	22	1	1	4	100	12
9	Rh/Al_2O_3[i]	Anisole	Hexane	22	1	1	0	100	0
10	$Rh/HEAC_{16}Br$[j]	Anisole	H_2O[f]	20	1	3.6	100	100	84
11	Rh-Pd /SiO_2[k]	Anisole	Heptane	40	1	9	42	2810	393
12	Rh/TBA-POA[l]	Anisole	PC[m]	22	3	144	91	2600	54

[a] Determined by GC. [b] Substrate/catalyst. [c] Turnover frequency defined as mol of H_2 consumed per mol of total metal per hour. [d] In parenthesis TOF corrected for the exposed atoms of iridium nanoparticles. Iridium nanoparticles.[4] [e] PVP = poly(N-vinyl-2-pyrrolidone).[14] [f] Biphasic system. [g] Cyclohexane was also produced in 16% yield at 74% conversion. [h] Dugussa type purchased from Aldrich. [i] Purchased from Acros. [j] $HEAC_{16}Br$ = N,N-dimethyl-N-(2-hydroxyethyl)ammonium bromide.[3] [k] Ref. 5. [l] TBA-POA = tetrabutylammonium polyoxoaninon.[7] [m] PC = propylene carbonate.

and a commercial Rh/Al_2O_3, which is corresponding to the aluminum nuclei surrounded by oxygens in octahedral structure.[11] The resonance at 60 ppm is also observed in the spectrum of Rh/Al_2O_3, which reflects a tetrahedral structure.[12] A trigonal-bipyramidal structure or Al–O–Rh bonds would be responsible for the unique resonance at 35 ppm.[13] BET nitrogen adsorption analysis reveals that the BET surface area, the pore volume and the pore size of **1** are 616 $m^2\ g^{-1}$, 0.85 $cm^3\ g^{-1}$ and 2.9 nm, respectively.

We tested the activity of **1** in the hydrogenation of benzene and anisole and compared the activity with those of commercially available rhodium catalysts and also with those reported previously (Table 1). Benzene was hydrogenated to cyclohexane completely within 30 min at 22 °C under 1 atm H_2 by using **1** (1 mol% Rh). This activity is similar to that of a polymer-stabilized rhodium catalyst (Rh/PVP) under the conditions of 7 atm H_2 and 30 °C.[14] The activity of **1** was much higher than that of an iridium catalyst known for solventless hydrogenation;[4] the turnover frequency (TOF) reached 5000 under 4 atm H_2 at 75 °C and was 13 times higher than that given by the iridium catalyst. The high activity of **1** was also shown in the hydrogenation of anisole **1**; it is the highest among the commercially available Rh catalysts and the reported ones. Notably, **1** can be recovered simply by filtration and reused ten times without activity loss.

Table 2 Hydrogenations of arenes at room temperature under 1 atm H_2[a]

Entry	Substrate	t/h	Yield[b] (%)	*cis*:*trans*	TOF[c]
1	Toluene	1	100		300
2	Phenol	1	100		300
3	Ethyl benzoate	4.5	100		67
4	1-Phenylethanol	4	100		75
5	Acetophenone	4.5	35		67[d]
6	*p*-Xylene	1.5	100	72:28	200
7	*m*-Xylene	2.3	100	82:18	130
8	*o*-Xylene	2.5	100	94:6	120
9	*p*-Cresol	3	100	60:40	100
10	*m*-Cresol	3.5	100	52:48	86
11	*o*-Cresol	3	100	52:48	100
12	Dimethyl terephthalate[e]	46	100	85:15	1.3[f]
13	Naphthalene	3	97[g]		65
14	Naphthalene	10	100[h]	88:12	50
15	Quinoline	6	94		9[f]

[a] At 22 °C, 0.50 mmol of substrate in hexane (1.0 mL) was reacted with **1** (1 mol% Rh). [b] Determined by GC. [c] Turnover frequency defined as mol of H_2 consumed per mol of total metal per hour. [d] Based on the yields of cyclohexylmethyl ketone and 1-cyclohexylethanol. [e] Ethyl acetate (2 mL) was used. [f] 5 mol% of Rh was used. [g] Tetralin was the major product and decalin was produced in 3%. [h] Decalin was produced exclusively.

The scope of arene hydrogenation with **1** was investigated with various arenes at room temperature under 1 atm H_2 (Table 2). Our catalyst **1** was active for monosubstituted arenes such as toluene, phenol, ethyl benzoate and 1-phenylethanol. Interestingly, the hydrogenation of acetophenone produced 1-cyclohexylethanol as the major product in 65% yield while cyclohexylmethyl ketone was intact under the same conditions. Disubstituted arenes were also hydrogenated successfully with stereoselectivities between 94:6 to 52:48. Naphthalene was hydrogenated selectively to tetralin or decalin by controlling reaction time. Likewise, quinoline was hydrogenated selectively to give tetrahydroquinoline in high yield.

In conclusion, we have developed a simple synthetic method for a new rhodium catalyst that is recyclable and highly active in the hydrogenation of various arenes under mild conditions. The highly porous and fibrous matrix and the proper size of rhodium particles in our catalyst should be factors for the observed high activity. We are investigating the detailed effect of metal particle size and the role of hydroxy groups of the matrix on catalytic activity.

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