Selective Hydrogenation of Nitroarenes and Olefins over Rhodium Nanoparticles on Hydroxyapatite

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Abstract: We have demonstrated a highly active and selective nanocatalyst, Rh/HAP (rhodium supported on hydroxyapatite), for the reduction of nitroarenes with hydrazine and for the hydrogenation of olefins with hydrogen gas under mild conditions. Nitroarenes were hydrogenated selectively to the corresponding anilines over the Rh/HAP catalyst with hydrazine as reducing agent, and reducible groups, such as halides (fluorine, chlorine, bromine and iodine), cyano and alkene were untouched. Moreover, olefins can be hydrogenated selectively to the corresponding alkanes in good yields over the Rh/HAP catalyst in the presence of reducible nitro, carbonyl and cyano groups when H_2 was used.

Keywords: anilines; hydrogenation; nanoparticles; nitroarenes; olefins; rhodium

Hydrogenation is one of the most important chemical processes because a lot of fine chemicals are produced by hydrogenation processes.[1] The reduction of nitroarenes to anilines is applied widely in industrial processes since functional anilines are essential intermediates for the production of agrochemicals, pharmaceuticals, dyes, and pigments.[2] Traditionally, the Bechamp reduction of nitroarenes which employs iron and hydrochloric produced a large amount of waste, which is not environmentally acceptable nowadays. Green processes are highly favorable for the hydrogenation of nitroarenes, and a number of transition metal catalysts (based on Pt, Pd, Ru, Au, Rh etc.) were reported to be efficient for the transformation.[3–7] However, the selective hydrogenation of a nitro group is a challenging issue in organic synthesis, when other reducible groups are present in the

same molecules. Recently, we have reported on Pt and Rh nanocatalysts for the selective hydrogenation of nitroarenes with H_2 and hydrazine (N_2H_4), respectively.[8]

On the other hand, the selective hydrogenation of olefins in the presence of a nitro group is a demanding task, since the nitro group is one of the most easily reducible groups in transition metal-catalyzed processes. Although the selective reduction of a double bond in the presence of a nitro group with baker's yeast[9] and metal hydride[10] has been reported, very few transition metal-catalyzed processes have been described in the literature. A homogeneous Rh complex (Wilkinson's catalyst) was reported as an efficient catalyst for the selective reduction of double bonds in the presence of nitro groups,[11] but the application was limited as the homogeneous catalyst was air sensitive and separation was hardly possible. In addition, the selective hydrogenation of olefins in the presence of other functional groups (such as C=O and CN etc.) is useful in industrial applications and in the academic laboratory.[12] Thereafter, the development of heterogeneous catalysts for the selective hydrogenation of olefins in the presence of reducible groups is also highly desirable.

Hydroxyapatites have attracted considerable interest and have been widely used as biomaterials, adsorbents, and ion exchangers.[13] In addition, hydroxyapatites were also applied as catalysts or catalyst supports because of their several unique characteristics. Some kinds of transition metal cations were readily accommodated into the apatite framework based on their large cation exchange ability, and transition metal cation-exchanged hydroxyapatites were used as effective heterogeneous catalysts.[13,14] Recently, Ru nanoclusters supported on hydroxyapatite were reported as highly active catalysts for the hydrogenation of aromatics under mild conditions.[15]

Herein, hydroxyapatite-supported Rh nanoparticles are reported as a highly active and selective catalyst (Rh/HAP) for the hydrogenation of nitroarenes and olefins, respectively under mild conditions. When N_2H_4 was used as reducing agent, nitro groups were hydrogenated selectively to the corresponding anilines with the Rh/HAP nanocatalyst, and reducible groups, such as halides (F, Cl, Br and I), CN and alkene were untouched. Furthermore, olefins can be hydrogenated selectively to alkanes with the Rh/HAP nanocatalyst in the presence of reducible groups (such as NO_2, C=O and CN etc.) when H_2 is used (Scheme 1). Thus, the selectivity of the hydrogenation of nitro or alkene groups can be tunable by selecting the reducing agents with the Rh/HAP catalyst.

The preparation of the Rh/HAP (2.01 wt% Rh determined by ICP-OES) catalyst is presented in the Supporting Information. The Rh/HAP catalyst was characterized by TEM and the Rh particles were dispersed well on the HAP (Figure 1), and the mean diameter of the Rh particles was around 3–7 nm (Figure 1, left). The BET (Brunauer–Emmett–Teller) surface area of the Rh/HAP was found to be $62 \text{ m}^2\text{g}^{-1}$, which is similar to the parent HAP material ($65 \text{ m}^2\text{g}^{-1}$), based on the nitrogen adsorption–desorption analysis (see the Supporting Information, Figure S1 and Figure S2). The XRD patterns of Rh/

HAP were nearly identical with that of HAP (see the Supporting Information, Figure S3), which indicated that the crystal structure of the HAP remained intact when Rh nanoparticles were supported on the HAP material.

The reduction of nitrobenzene with N_2H_4 was performed as a model reaction, and the results are listed in Table S1 (Supporting Information). The Rh/HAP catalyst was highly active for the hydrogenation of nitrobenzene to aniline at room temperature in toluene. Cyclohexane, ethanol, and H_2O were also good solvents, but THF and 1,4-dioxane were less effective solvents for the transformation (see the Supproting Information, Table S1, entries 1–6). The reduction of nitrobenzene afforded aniline in good yield also without a solvent (see the Supporting Information, Table S1, entry 10). Rh catalysts with other supports, such as Rh on TiO_2, HT (hydrotalcite) and Al_2O_3, were found to be less active for the transformation (see the Supporting Information, Table S1, entries 7–9). No aniline was obtained without the catalyst under similar reaction conditions (see the Supporting Information, Table S1, entry 11).

The reusability of the Rh/HAP nanocatalyst was tested and the results are shown in Table 1. The Rh/HAP nanocatalyst was easily recycled by filtration and reused for the next reaction cycle. The Rh/HAP
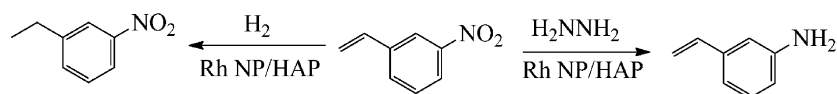
Scheme 1. Rh-catalyzed selective hydrogenation of nitro/alkene groups.
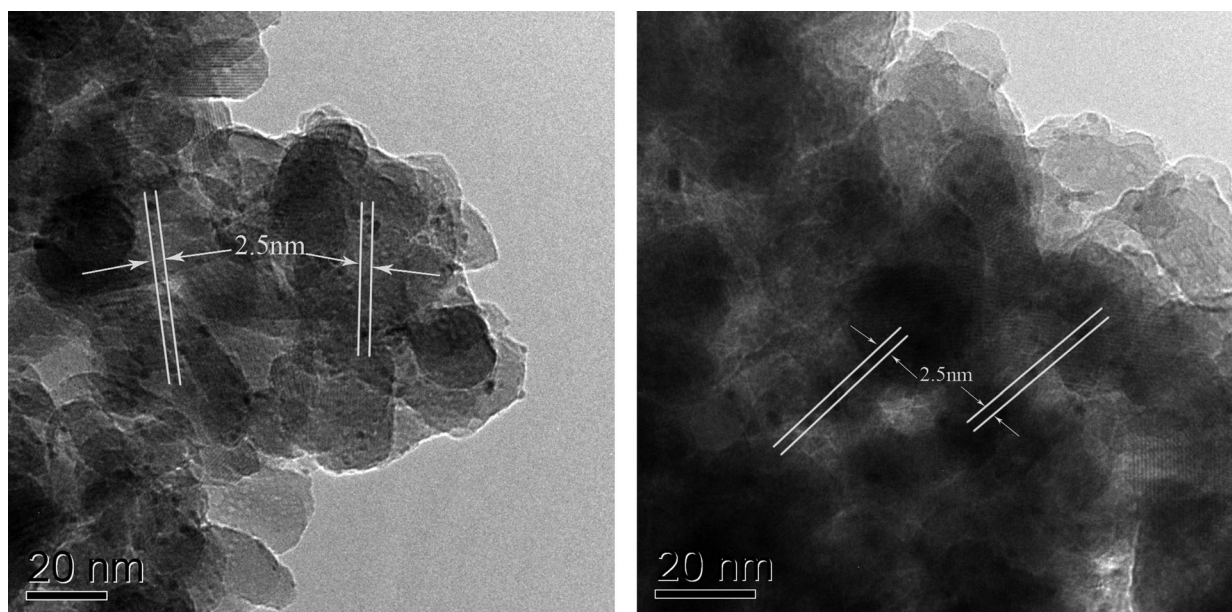
Figure 1. TEM images of the Rh/HAP nanocatalyst. The fresh Rh/HAP nanocatalyst (*left*); Rh/HAP nanocatalyst recovered for the 5th time (*right*); scale bar = 20 nm.

**Table 1.** Reusability of the Rh/HAP for the hydrogenation of nitrobenzene.[a]

Recycled	1	2	3	4	5
Conv./Yield [%]	100/99	100/99	100/99	100/99	100/99

[a] *Reaction conditions:* nitrobenzene, 1.0 mmol; Rh/HAP (0.5 mol%); $N_2H_4 \cdot H_2O$ (2.0 mmol); toluene (2.0 mL); at room temperature; in 3 h; the conversions and yields were determined by GC ($C_{16}H_{34}$ used as internal standard).

can be reused at least 5 times without loss of activity (Table 1). The Rh/HAP recovered for the 5th time was analyzed by TEM also and the mean diameter of the recovered Rh nanoparticles had not increased evidently (Figure 1, *right*). The filtrate was detected by ICP-OES (inductively coupled plasma optical emission spectroscopy with detection limitation 7 ppb) after removal of the Rh/HAP catalyst by filtration. No Rh was detected in the filtrate, and the filtrate was not active anymore for the hydrogenation of nitrobenzene, which indicated that no Rh was leached into the reaction mixture and the Rh/HAP catalyst is a heterogeneous catalyst.

Using hydrazine as reducing agent, the nitro group was reduced selectively with the Rh/HAP nanocatalyst. Several nitrobenzenes were hydrogenated to the corresponding anilines, and the results are shown in Table 2. The Rh/HAP was highly active and selective for the hydrogenation of nitro groups, and halides (F, Cl, Br and I), CN, OH and NH_2 groups were tolerated during the hydrogenation of NO_2. The corresponding anilines were obtained in good to excellent yields (Table 2, entry 1–12). The hindered nitrobenzene, 2,6-dimethylnitrobenzene was hydrogenated to 2,6-dimethylaniline in good yield also (Table 2, entry 13). Interestingly, the hydrogenation of 3-nitrostyrene gave 3-aminostyrene quantitatively (Table 2, entry 14).

Using H_2 gas, the Rh/HAP-catalyzed hydrogenation of olefins was tested and the results are listed in Table 3. With H_2 gas, the hydrogenation of 3-nitrostyrene gave 3-nitroethylbenzene quantitatively (Table 3, entry 1). The Rh/HAP catalyzed hydrogenation of a mixture of styrene and nitrobenzene was tested with H_2 gas, and the styrene was hydrogenated completely into ethylbenzene without any aniline formed (Table 3, entry 2). Similarly, phenylacetylene was also selectively hydrogenated with H_2 gas to ethylbenzene without any aniline formed, when nitrobenzene was present in the reaction system (Table 3, entry 3). The C≡C and C=C groups were reduced at the same time, and styrene was detected as an intermediate and the final product was only ethylbenzene. The Rh/HAP-catalyzed hydrogenation of cyclohexene gave cyclohexane quantitively without hydrogenation of nitrobenzene (Table 3, entry 4). The hydrogenation of (*E*)-

Table 2. Rh/HAP-catalyzed hydrogenation of nitroarenes with hydrazine.[a]
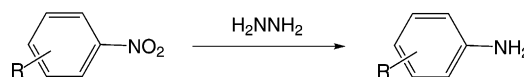
Entry	R	Time [h]	Conv./Yield [%]
1	2-F	3	100/98
2	4-F	3	100/95[b]
3	2-Cl	3	100/99
4	3-Cl	3	100/99
5	4-Cl	3	100/95[b]
6	2-Br	3	100/97[b]
7	3-I	10	100/90[b,c]
8	4-NH_2	3	100/97
9	2-NH_2	3	100/96
10	3-OH	3	100/95[d]
11	4-OH	3	100/99[d]
12	4-CN	10	100/94[d]
13	2,6-CH_3	10	100/92[d]
14	3-C=C	3	100/99[d,e]

[a] *Reaction conditions:* nitrobenzene (1.0 mmol); Rh/HAP (0.5 mol%); $N_2H_4 \cdot H_2O$ (2.0 mmol); toluene (2.0 mL); at room temperature; in 3 hours; the conversions and yields were determined by GC ($C_{16}H_{34}$ used as internal standard).
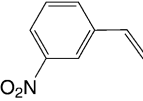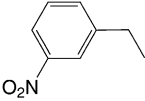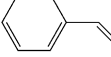[b] The by-product is aniline.
[c] 1 mol% metal used; at 100 °C; $N_2H_4 \cdot H_2O$ (5.0 mmol).
[d] At 50 °C;
[e] $N_2H_4 \cdot H_2O$ (1.6 mmol); 2.0 mL ethanol used instead of toluene as solvent; 3-vinylaniline yield.
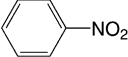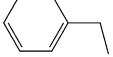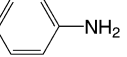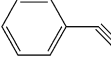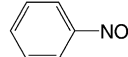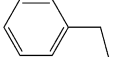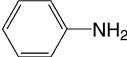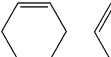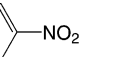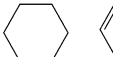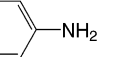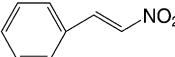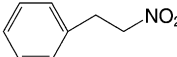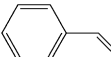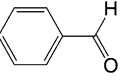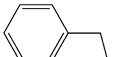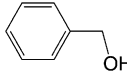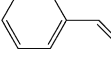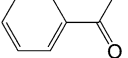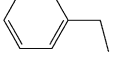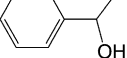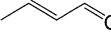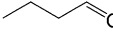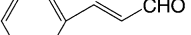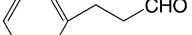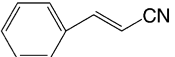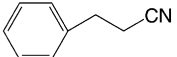
(2-nitrovinyl)benzene gave (2-nitroethyl)benzene in 81% yield (Table 3, entry 5). To examine the olefin selectivity of the Rh/HAP over the C=O group, benzaldehyde and acetophenone were added in the hydrogenation of styrene, respectively. Ethylbenzene was obtained quantitively without hydrogenation of the C=O group when benzaldehyde and acetophenone were present in the reaction system (Table 3, entries 6 and 7). Moreover, the Rh/HAP-catalyzed hydrogenation of crotonaldehyde and cinnamaldehyde gave butyraldehyde and phenylpropylaldehyde, respectively, in good yield (Table 3, entries 8 and 9). The hydrogenation of cinnamonitrile was also performed, and 3-phenylpropanenitrile was obtained in good yield. The Rh/HAP catalyst was highly selective for the hydrogenation of olefins with H_2 gas, and other groups, such as NO_2, C=O and C≡N groups were tolerated during the hydrogenation process.

In addition, the hydrogenation processes for reducing the mixture of styrene and nitrobenzene with N_2H_4 and H_2 gas were investigated, respectively, and the results are shown in Figure 2 and Figure 3. When N_2H_4 was used as reducing agent, nitrobenzene was reduced selectively to aniline quickly (within 30 min), and only a trace of styrene was reduced into ethylbenzene (Figure 2). When H_2 gas was used as reducing

Table 3. Rh/HAP-catalyzed selective hydrogenation of olefins with H_2.[a]

Entry	Substrate/mixture	Time [h]	Product	Yield [%]
1	(vinyl-nitrobenzene, O_2N)	20	(ethyl-nitrobenzene, O_2N)	99
2	(styrene) + (nitrobenzene, NO_2)	10	(ethylbenzene) + (aniline, NH_2)	99, 0
3	(phenylacetylene) + (nitrobenzene, NO_2)	20	(ethylbenzene) + (aniline, NH_2)	99, 0
4	(cyclohexene) + (nitrobenzene, NO_2)	12	(cyclohexane) + (aniline, NH_2)	99, 0
5	(β-nitrostyrene, NO_2)	24	(2-nitroethylbenzene, NO_2)	81[b]
6	(styrene) + (benzaldehyde, CHO/H)	10	(ethylbenzene) + (benzyl alcohol, OH)	99, 0
7	(styrene) + (acetophenone)	10	(ethylbenzene) + (1-phenylethanol, OH)	99, 0
8	(crotonaldehyde)	12	(butyraldehyde)	99
9	(cinnamaldehyde, CHO)	60	(3-phenylpropanal, CHO)	86[c]
10	(cinnamonitrile, CN)	20	(3-phenylpropanenitrile, CN)	91[d]

[a] *Reaction conditions:* substrate (1.0 mmol); Rh/HAP (0.5 mol%); with an H_2 balloon; room temperature; 1,4-dioxane (2.0 mL); the conversions and yields were determined by GC ($C_{16}H_{34}$ used as internal standard).
[b] Isolated yield.
[c] Rh/HAP (2.0 mol%); at 100 °C.
[d] Rh/HAP (1 mol%); at 60 °C.

Figure 2. Rh/HAP -catalyzed selective hydrogenation of the mixture of styrene and nitrobenzene with $N_2H_4 \cdot H_2O$. *Reaction conditions:* nitrobenzene (1 mmol); styrene (1 mmol); $N_2H_4 \cdot H_2O$ (5 mmol); toluene (2.0 mL); Rh/HAP (0.5 mol%); at room temperature.

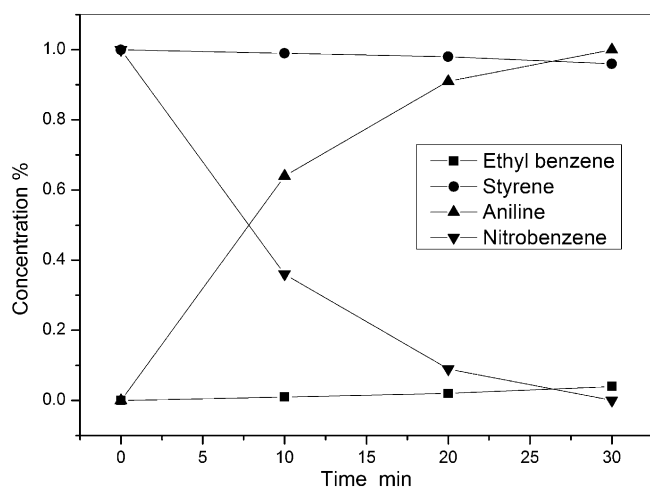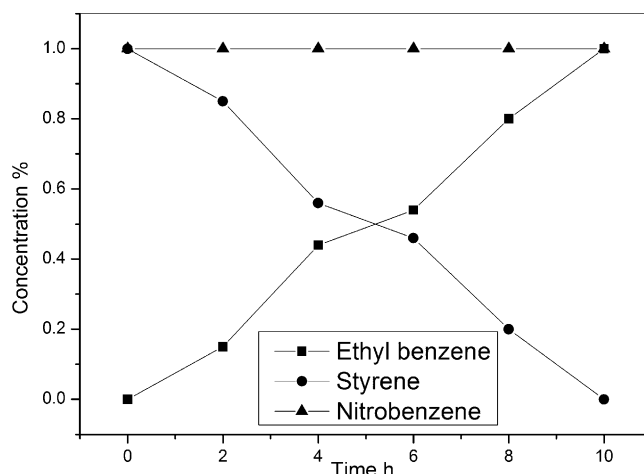**Figure 3.** Rh/HAP-catalyzed selective hydrogenation of the mixture of styrene and nitrobenzene with H_2. *Reaction conditions:* nitrobenzene (1 mmol); styrene (1 mmol); with an H_2 balloon; 1,4-dioxane (2.0 mL); Rh/HAP (0.5 mol%); at room temperature.

agent, styrene was hydrogenated slowly into ethylbenzene (within 10 h), and no aniline was detected until the hydrogenation of styrene was completed (Figure 3).
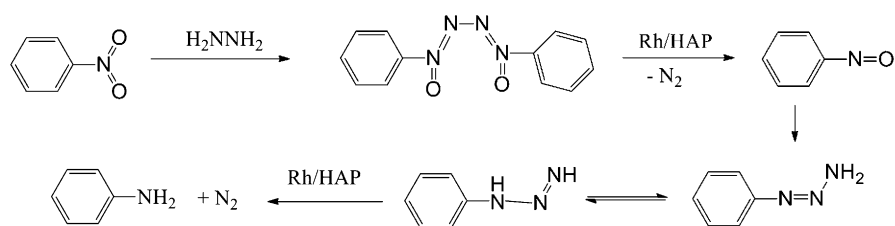
Scheme 2. A possible pathway for the reduction of nitrobenzene with H_2NNH_2.

Using the Rh/HAP as catalyst, Rh is coordinated more strongly with the C=C bond than with NO_2, C=O and C≡N groups, which allowed the preferential hydrogenation of the C=C bond with H_2 gas. Thereafter, the reduction of nitrobenzene with N_2H_4 does not go through the traditional Rh/H_2 way over the Rh/HAP catalyst. A possible pathway was proposed (Scheme 2). An intermediate is formed firstly through the condensation of the nitro group with N_2H_4, and then the decomposition of the intermediate by Rh/HAP gives nitrosobenzene and N_2. The condensation of nitrosobenzene with N_2H_4 is followed by H-transformation, and then the decomposition leads to aniline with N_2 gas (Scheme 2). A trace of nitrosobenzene was founded by GC-MS before the completion of the hydrogenation of nitrobenzene with N_2H_4. No other intermediates were found by GC-MS, which may be due to the instability of the intermediates. Although few intermediates were identified, the pathway was supported by the following reaction results. Firstly, Rh is coordinated more strongly with the C=C bond than with NO_2 group, which allowed the preferential hydrogenation of C=C bond with H_2 gas. So the reaction of the NO_2 group with H_4N_2 should have occurred before Rh is involved, otherwise the C=C bond should be reduced preferentially. Secondly, the NO_2 was reduced preferentially over the C=C bond with N_2H_4, thus the condensation of the nitro group with N_2H_4 should have occurred before the decomposition of hydrazine to N_2/H_2. Figure S4 (Supporting Information) shows that styrene can be hydrogenated slowly to ethylbenzene after the transformation of nitrobenzene to aniline with more hydrazine being added (Figure S4 in Supporting Information), since Rh can catalyze the decomposition of hydrazine to N_2/H_2.[16] Thirdly, nearly all the N_2H_4 was used for the reduction of the NO_2 group (no N_2H_4 for C=C bond). Only 1.6 mmol of N_2H_4 (1.5 mmol of N_2H_4 needed theoretically) was needed for the hydrogenation of 3-nitrostyrene to 3-aminostyrene quantitatively (as shown in Table 2 entry 14).

The reduction of nitrobenzene with N_2H_4 was completely different to the hydrogenation of styrene with H_2 gas, thus the selectivity was tuneable for the hydrogenation of nitro and olefin groups over Rh/HAP nanocatalyst. In addition, the hydroxyapatite was ap-plied as a good support for the Rh nanoparticles. The selective hydrogenation of olefins to alkanes was realized with the Rh/HAP nanocatalyst in the presence of reducible NO_2, C=O and CN groups when H_2 was used, and the selectivity of the Rh/HAP was even higher than that of homogeneous catalysts.[11,12] Moreover, these results confirmed that the Rh/HAP-catalyzed reduction of nitrobenzene with N_2H_4 did not go through the traditional Rh/H_2 pathway, thus a reasonable condensation/decomposition pathway was proposed.

In conclusion, we demonstrated an active and selective nanocatalyst Rh/HAP for the reduction of nitroarenes with N_2H_4 and for the hydrogenation of olefins with H_2 gas under mild conditions. Nitroarenes were hydrogenated selectively to the corresponding anilines over the Rh/HAP catalyst with N_2H_4 as reducing agent, and reducible groups, such as halides (F, Cl, Br and I), CN and alkene were untouched. Moreover, olefins can also be hydrogenated selectively to the corresponding alkanes over the Rh/HAP catalyst in the presence of reducible NO_2, C=O and CN groups when H_2 was used. Thus the selectivity is tuneable for the hydrogenation of nitro and olefin groups over Rh/HAP nanocatalyst. The possible condensation/decomposition pathway was proposed for the reduction of nitroarenes with N_2H_4, and we believe that the pathway will be useful for the selective reduction of the nitrobenzenes in industrial applications and in academic research.

Experimental Section

Typical Procedure for the Reduction of Nitroarenes

A nitroarene (1.0 mmol), hydrazine monohydrate (2.0 mmol) and toluene (2.0 mL) were added to a Schlenk tube which contained Rh/HAP (Rh: 0.5 mol%) catalyst and a stir bar under argon. The Schlenk tube was kept at room temperature with stirring for 3 hours. After the reaction was completed, the Rh/HAP was separated by filtration, and the products (in the filtrate mixture) were analyzed by GC/MS and GC.

Typical Procedure for the Selective Reduction of Olefins

An olefin (1.0 mmol) and 1,4-dioxane (2.0 mL) were added to a Schlenk tube which contained Rh/HAP (Rh: 0.5 mol%) catalyst and a stir bar under argon. Then argon was removed by H_2, and a balloon of H_2 was connected to the Schlenk tube. The reaction mixture was stirred at room temperature for 10 h. After the reaction was completed, the Rh/HAP was separated by filtration, and the products (in the filtrate mixture) were analyzed by GC/MS and GC.

Acknowledgements

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