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Chemoselective hydrogenation of heteroarenes and arenes by Pd–Ru–PVP under mild conditions†

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Monometallic (Pd, Ru or Rh) and bimetallic (Pd_{0.5}–Ru_{0.5}) alloy NPs catalysts were examined for the hydrogenation of quinoline. Pd–Ru alloy catalyst showed superior catalytic activity to the traditional Rh catalyst. The characterization of Pd_{0.5}–Ru_{0.5} catalysts, HAADF-EDX mapping and XPS analysis suggested that the alloy state of PdRu catalysts remained unchanged in the recovered catalyst. Furthermore, the catalyst was highly selective for the hydrogenation of different arenes.

1,2,3,4-Tetrahydroquinolines are important building blocks for the synthesis of fine chemicals, pharmaceuticals and petrochemicals.^{1–3} Traditionally, 1,2,3,4-tetrahydroquinolines have been synthesized by catalytic cyclization or the Beckman rearrangement method.^{3–6} Direct hydrogenation of readily available quinoline by molecular hydrogen is a simple and atom-economical route for the hydrogenated quinoline compounds. Nevertheless, the hydrogenation of quinolines reaction suffers from catalyst deactivation caused by the strong interaction between the nitrogen atom of quinoline and active sites of the catalyst. Recently, several heterogeneous (Co, Au, Ru, Pt, Pd and Rh) catalysts have been developed to overcome the catalyst deactivation problem (Table S1†).^{7–24} Specifically, Rh catalysts exhibits remarkably excellent activity in comparison with other noble metal catalysts but some of them require high temperature (>80 °C)^{13,21} and/or high pressure (>10 bar).^{14–21} Later, Rh/AlOOH and Rh nanoparticles (NPs) catalysts have been reported for efficient hydrogenation of quinolines under ambient conditions (1 bar H₂ and 25 °C).^{22–24} Although high selectivity

and activity of Rh catalysts, the high cost of Rh make it unfavourable for the industrial purposes. From the economical and environmental point of view, the cost-effective catalyst is necessary for the hydrogenation of quinolines under mild condition.

Solid-solution alloy method is a promising way for the synthesis of alloy NPs which offers an opportunity to control the electronic state of alloy by changing the composition ratio and/or different combinations of alloy in this method. In search of a cheap alternative for Rh catalyst, Pd and Ru are important metals because both metals are relatively cheaper than Rh metal and their well-known activity for hydrogenation reactions. We believe that Pd_{0.5}–Ru_{0.5} solid solution alloy NPs could be alternative for the traditional Rh catalyst. However, a solid-solution alloy of Pd and Ru is a challenging task due to the immiscibility of Pd and Ru in bulk state.^{25,26} Recently, our research group led by H. Kitagawa has reported the first successful example of Pd_{0.5}–Ru_{0.5} NPs *via* a chemical reduction method using a nano-size effect which showed almost similar catalytic activity than those of Rh for CO oxidation and automobile exhaust purification.^{27,28} As part of our continuing interest in the applications of Pd–Ru as pseudo Rh catalyst, we herein report that chemo-selective hydrogenation of heteroarenes and arenes under mild condition.

In preliminary experiments, we carried out the hydrogenation of quinoline to 1,2,3,4-tetrahydroquinoline as model reaction (Table 1). Monometallic Pd and Ru catalysts were inactive for hydrogenation of quinoline (entries 1 and 2). In previous reports, our group has shown that the electronic state and consequently, catalytic activity of monometallic Pd and Ru could be modified by making Pd_{0.5}–Ru_{0.5} alloy catalyst.^{27,28} We found the similar trend using Pd_{0.5}Ru_{0.5} catalyst and it showed full conversion with 95% yield of 1,2,3,4-tetrahydroquinolines (entry 3). The effect of the solvent showed that the reactivity of

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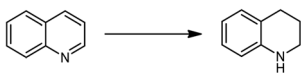
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Table 1 Optimization of reaction conditions for hydrogenation of quinoline^a


Entry	Catalyst	Particle size ^b (nm)	Conv. (%)	GC yield (%)
1	Ru-PVP	8.4 ± 2.4	13	13
2	Pd-PVP	4.8 ± 0.8	41	32
3	Pd _{0.5} Ru _{0.5} -PVP	5.6 ± 1.6	99	95
4 ^c	Pd _{0.5} Ru _{0.5} -PVP	5.6 ± 1.6	63	60
5 ^d	Pd _{0.5} Ru _{0.5} -PVP	5.6 ± 1.6	45	40
6 ^e	Pd _{0.5} Ru _{0.5} -PVP	5.6 ± 1.6	21	13
7	Rh-PVP	5.4 ± 1.0 ^f	66	66

^a Reaction conditions: quinoline (1 mmol), catalyst (2 mol%), CH₃OH (1 mL), 5 bar H₂, 25 °C, 6 h, CH₃OH. ^b Determined by STEM analysis. ^c THF. ^d Toluene. ^e 1,4-Dioxane. ^f Ref. 38.

Pd_{0.5}Ru_{0.5} was improved using methanol as solvent. Probably, methanol provides the better dispersion of Pd_{0.5}-Ru_{0.5} NPs in the reactions and/or high solubility of hydrogen gas in methanol. Next, we examined the activity of previously reported Rh catalyst. Although, the particle size of Rh and Pd_{0.5}-Ru_{0.5} was similar, the moderate yield of tetrahydroquinoline was obtained in the presence of Rh-PVP (entry 7). Due to the high amount of PVP, the catalytic activity of Rh was slightly declined *via* less interaction between quinoline and metal sites.²⁹

The substrate scope of Pd_{0.5}-Ru_{0.5}PVP catalyst was explored under mild reaction conditions (5 bar H₂ and 25 °C). As summarized in Table 2, quinolines with different functional groups converted to corresponding tetrahydroquinolines. The catalyst showed reduction of the heteroarene ring only. Pd_{0.5}-Ru_{0.5} was also active for the hydrogenation of biologically important heterocyclic compounds such as 1,8-naphthyridine and quinazoline. O-Containing heterocycle, benzofuran was also transformed to 1,2-dihydrobenzofuran with high yield (80%).

Hydrogenation of arenes to saturated compounds is an important transformation for petrochemical and pharmaceutical industries. For instance, hydrogenation of benzoic acid to cyclohexanecarboxylic acid, it is used for the synthesis of pharmaceutical drugs such as ansatrienin.³⁰ Hydrogenation of benzoic acid has been reported by using supported and polymer stabilized metal nanoparticles.³¹⁻³⁸ Among them, Rh catalyst demonstrated the excellent activity for the hydrogenation of benzoic acid. The scope of Pd_{0.5}-Ru_{0.5} catalyst was examined for different arene hydrogenation for the hydrogenation of benzoic acid. The scope of Pd_{0.5}-Ru_{0.5} catalyst was examined for different arene hydrogenation under solvent-free condition (Table 3). Pd_{0.5}-Ru_{0.5}-PVP catalyst was able to hydrogenate benzoic acid with high yield. In previous reports, the role of solvent was explained for the selective hydrogenation of benzoic acid. The selectivity for cyclohexanecarboxylic acid was controlled using polar solvent (water). The byproduct (benzyl alcohol) was obtained using less polar solvent (cyclohexane). On the other

Table 2 Hydrogenation of heteroarenes by Pd_{0.5}Ru_{0.5}PVP catalyst^a

Entry	Heteroarene	Product	Conv. (%)	GC yield (%)
1			99	96
2			98	90
3			99	92
4			64	60
5			99	76
6			99	99
7			94	45 ^b
8			99	80

^a Reaction conditions: substrate (1 mmol), catalyst (2 mol%), 5 bar H₂, 25 °C, 24 h. ^b 3,4-Dihydroquinazoline was obtained.

hand, Pd_{0.5}-Ru_{0.5}-PVP catalyst showed the high activity in solvent-free conditions. Hydrogenation of benzene and its derivative were also studied under optimized conditions. The high yields of the corresponding hydrogenated products was obtained in the presence of the Pd_{0.5}-Ru_{0.5} catalyst.

Table 3 Hydrogenation of arenes by Pd_{0.5}Ru_{0.5}PVP catalyst^a

Entry	Arene	Product	Conv. (%)	GC yield (%)
1			99	94
2			99	92
3			99	99
4			95	95
5			99	92
6			80	60

^a Reaction conditions: substrate (1 mmol), catalyst (2 mol%), 10 bar H₂, 150 °C, 24 h.

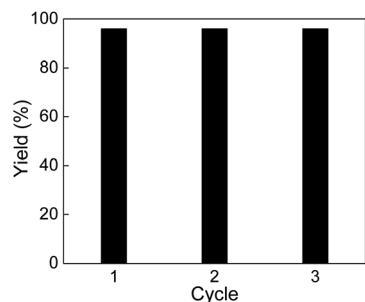


Fig. 1 Recycle experiment for the hydrogenation of quinoline over Pd_{0.5}Ru_{0.5}-PVP catalyst.

The reusability of Pd_{0.5}-Ru_{0.5} catalyst was investigated using optimized condition (5 bar H₂ and 25 °C) for the hydrogenation of quinoline. The catalyst was washed by acetone multiple times after completion of reaction and separated by centrifugation. The recovered catalyst was dried under vacuum at 40 °C for 12 h and reused without further purification. The catalyst was reused three times without loss in activity (Fig. 1).

To study morphological changes, the fresh and recovered catalyst after the 1st cycle was analysed by high-angle annular dark field. The reconstructed overlaying image of fresh Pd_{0.5}-Ru_{0.5} catalyst revealed that Pd and Ru atom was distributed equally in the particle which indicated the formation of Pd_{0.5}Ru_{0.5} alloy *via* homogeneous mixing at atomic-level. Dealloying and/or aggregation were not observed in Pd_{0.5}-Ru_{0.5} (Fig. 2). Next, the electronic state of fresh and used Pd_{0.5}-Ru_{0.5} catalyst was examined by XPS (Fig. 3). In our previous reports, the binding energy of Pd_{0.5}-Ru_{0.5} was shifted positively in 3d_{5/2} (334.5 eV) from 3d_{5/2} (334.30 eV) of monometallic Pd and negatively in 3p_{3/2} (460.6 eV) from 3p_{3/2} (461.4 eV) of monometallic Ru.³⁹ Such shifting was also observed in fresh and used Pd_{0.5}-Ru_{0.5} catalyst. From these results, we concluded that the electronic state of used catalysts was not changed significantly after 1st cycle.

The superiority of Pd_{0.5}-Ru_{0.5} alloy over Pd and Ru can be explained by unique electronic state. Our group has used first-principles methods to study the electronic states of Pd, Ru, Rh, and the Pd_{0.5}-Ru_{0.5} alloy. Interestingly, we have found that the electronic state of the Pd-Ru alloy differs from those of the

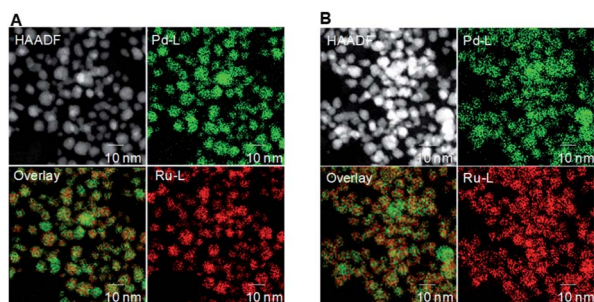


Fig. 2 HAADF-STEM images Pd-L and Ru-L STEM-EDX maps and reconstructed overlay images of fresh (A) and recovered (B) Pd_{0.5}-Ru_{0.5}-PVP catalyst.

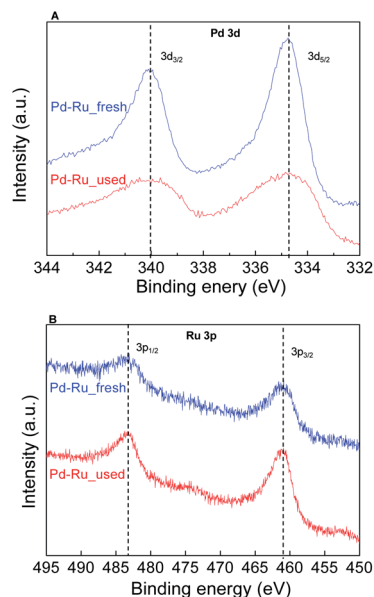
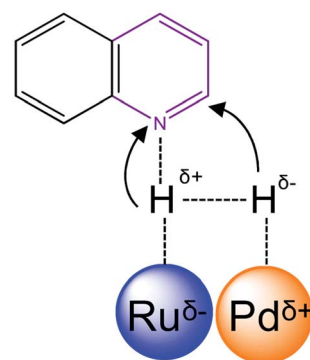


Fig. 3 XPS spectra for Pd_{0.5}-Ru_{0.5}fresh (blue) and Pd_{0.5}-Ru_{0.5}used (red) with Pd 3d (A) and Ru 3p (B).



Scheme 1 Plausible transition state for the hydrogenation of quinoline by Pd_{0.5}-Ru_{0.5}-PVP.

parental Pd or Ru metal. This result has indicated that a new electronic state is produced by alloying Pd and Ru. The density of state of the Pd_{0.5}-Ru_{0.5} alloy is similar to that of Rh.

Furthermore, Pd_{0.5}-Ru_{0.5} alloy shows the electron transfer from Pd to Ru and produced the partial positive (δ^+) charge at Pd and partial negative charge (δ^-) at Ru. This unique electronic state with bifunctional sites of Pd_{0.5}-Ru_{0.5} alloy made it favorable for chemoselective for hydrogenation of quinoline. In case of monometallic Pd or Ru catalyst, the strong adsorption of quinoline might be responsible for low conversion of quinoline.

It is well-known that the hydrogenation of organic functional group such as C=C and C=N proceeded *via* heterolytic cleavage of H₂. Such cleavage of H₂ yielded to H⁺ and H⁻ using metal and support/ligand.^{8,37} In colloidal Pd_{0.5}Ru_{0.5} catalyst, the heterolytic cleavage of hydrogen proceeded using bifunctional sites of Pd_{0.5}-Ru_{0.5} catalysis (Scheme 1). The better H₂ cleavage over bifunctional sites of Pd_{0.5}Ru_{0.5} catalyst may have been

responsible for the higher catalytic activity of the Pd_{0.5}-Ru_{0.5} catalyst for the hydrogenation of quinoline.

In summary, we have developed a successful example of Pd_{0.5}-Ru_{0.5} NPs for the hydrogenation of N-,O-heteroarenes and arenes. This catalyst exhibited the higher activity than Rh catalyst which was extensively studied for the hydrogenation of quinoline. A parametric study demonstrated that methanol was the best solvent for the hydrogenation of heteroarenes, whereas solvent-free conditions facilitated for the hydrogenation of arenes. The catalyst was recycled three times without loss in activity. It is likely that Pd_{0.5}-Ru_{0.5} NPs could be efficient catalysts for the hydrogenation of nitroarenes and synthesis of N-heterocycles. Currently, we are exploring this possibility.

Author contributions

Chandan Chaudhari: designing of research, data collection, analysis and writing-editing. Katsutoshi Sato: data curation and validation. Yoshihide Nishida: data collection. Katsutoshi Nagaoka: designing of research, data collection, analysis and writing-editing. Yasuyuki Ikeda, Kenji Terada and Naoya Abe: catalyst preparation. Tomokazu Yamamoto, Takaaki Toriyama and Syo Matsumura: HAADF-STEM analysis. Kohei Kusuda and Hiroshi Kitagawa: XPS analysis and catalyst design.

Conflicts of interest

There are no conflicts to declare.

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