



Cite this: *Chem. Commun.*, 2014, 50, 12123

Received 16th June 2014,
Accepted 15th August 2014

DOI: 10.1039/c4cc04559a

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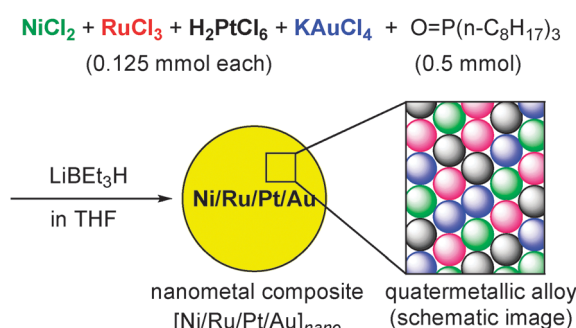
Transfer hydrogenation of alkenes using Ni/Ru/Pt/Au heteroquatermetallic nanoparticle catalysts: sequential cooperation of multiple nano-metal species†

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Quatermetallic alloy nanoparticles of Ni/Ru/Pt/Au were prepared and found to promote the catalytic transfer hydrogenation of non-activated alkenes bearing conjugating units (e.g., 4-phenyl-1-butene) with 2-propanol, where the composition metals, Ni, Ru, Pt, and Au, act cooperatively to provide significant catalytic ability.

Nanoparticles of transition metals have attracted increasing interest because of their physical and chemical properties. In particular, various transition metal nanoparticles have been found to exhibit unique catalytic activity in organic molecular transformations. Whereas the Enoki group has studied the physical properties of multiple-metallic nanoparticles,¹ the Uozumi group has concentrated on the catalytic utility of single-metallic nanoparticles.² However, during our investigations, we became intrigued by the catalytic utility of multiple-metallic nanoparticles. We thought that if the nanoparticles of a multiple-metallic alloy showed catalytic performance whereby the unique catalytic properties of the individual composition metal species were sequentially combined, then multiple-metallic nanoparticles, due to their limitless possible combinations, should find a wide range of catalytic utilities. Given the growing emphasis on green and safe chemical processes, catalytic transfer hydrogenation is emerging as a viable alternative to the conventional reduction processes that rely primarily on more hazardous molecular hydrogen or metal hydride reagents.³ Herein we report that the transfer hydrogenation of non-activated alkenes is efficiently catalyzed by Ni/Ru/Pt/Au heteroquatermetallic alloy nanoparticles, which was not promoted by uni-, bi-, or trimetallic nanoparticles of Ni, Ru, Pt, and/or Au.

Various uni-, bi-, tri-, and quatermetallic alloy nanoparticles modified with a capping agent of trioctylphosphine oxide (TOPO)



Scheme 1 Preparation of quatermetallic alloy nanoparticles.

were prepared in a parallel combinatorial manner. Thus, a mixture of NiCl₂, RuCl₃, H₂PtCl₆, and KAuCl₄ was treated with an excess amount of LiEt₃H in THF at 24 °C in the presence of TOPO for 2 h. The reaction mixture was quenched with ethanol to give agglomerates of TOPO-capped quatermetallic nanoparticles [Ni/Ru/Pt/Au]_{nano} (Scheme 1).⁴ The agglomerates were collected by filtration, rinsed with ethanol, and stored as an ethanolic suspension. A transmission electron microscopic study confirmed their nanostructures with an average diameter of 3.0 ± 0.25 nm (Fig. 1). The ratio of Ni/Ru/Pt/Au was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis to be 1.1/1.0/1.1/1.0. All combinations of uni-, bi-, and trimetallic nanoparticles were prepared under similar conditions with average diameters of ca. 3 nm.

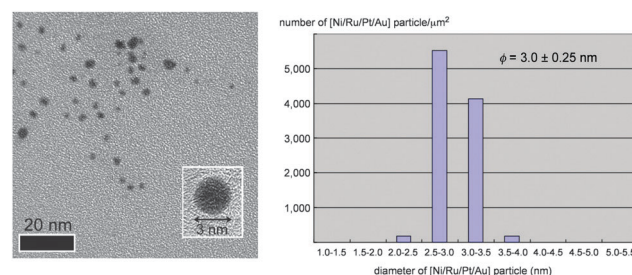


Fig. 1 A transmission electron microscopic (TEM) image and a histogram of the size distribution of [Ni/Ru/Pt/Au]_{nano}.

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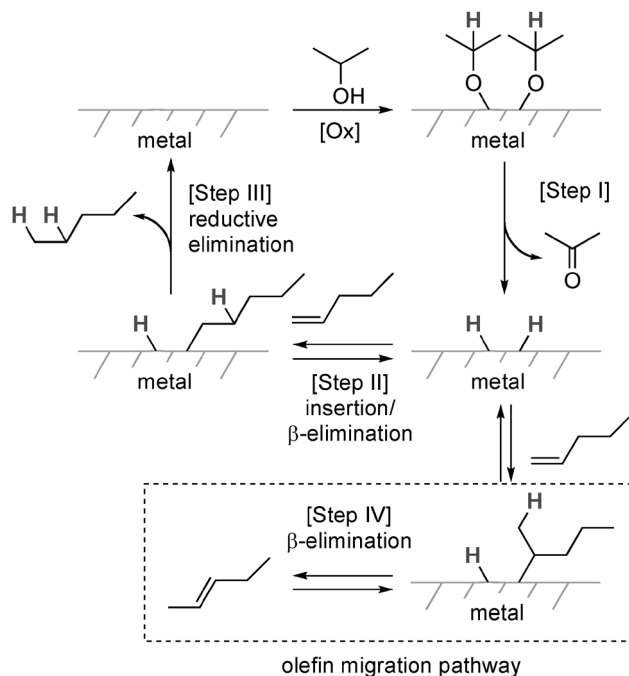
† Electronic supplementary information (ESI) available: Experimental details, TEM images of nanoparticle catalysts, GC & GC-MS charts and ¹H & ¹³C NMR spectra of the products. See DOI: 10.1039/c4cc04559a

Table 1 Transfer hydrogenation of 4-phenyl-1-butene (**1**) with various uni-, bi-, tri-, quatermetallic nanoparticles^a

Entry	Catalyst ^b	mol%	Yield of 2 ^c [%]	Yield of 3 ^c [%]
1	[Ni _{0.24} /Ru _{0.26} /Pt _{0.26} /Au _{0.24}]	0.5	98	<1
2	[Ni]	0.5	2	<1
3	[Ru]	0.5	<1	<1
4	[Pt]	0.5	<1	<1
5	[Au]	0.5	<1	<1
6	[Ni] + [Ru] + [Pt] + [Au]	0.5	<1	<1
7	[Ni _{0.54} /Ru _{0.46}]	0.5	<1	<1
8	[Ni _{0.61} /Pt _{0.39}]	0.4	5	<1
9	[Ni _{0.51} /Au _{0.49}]	0.5	2	14
10	[Ru _{0.43} /Pt _{0.57}]	0.3	1	5
11	[Ru _{0.43} /Au _{0.57}]	0.4	1	7
12	[Pt _{0.49} /Au _{0.51}]	0.7	<1	<1
13	[Ni _{0.36} /Ru _{0.35} /Pt _{0.25}]	0.7	4	16
14	[Ni _{0.36} /Ru _{0.35} /Pt _{0.25}]	2.0	16	33
15	[Ni _{0.38} /Ru _{0.27} /Au _{0.35}]	0.5	<1	22
16	[Ni _{0.34} /Pt _{0.25} /Au _{0.41}]	0.3	2	20
17	[Ru _{0.35} /Pt _{0.43} /Au _{0.22}]	0.5	<1	3

^a All reactions were carried out with 4-phenyl-1-butene (**1**, 1.0 mmol) in aqueous 2-propanol (3.3 mL, H₂O/2-propanol = 3/10) in the presence of a nanometallic catalyst at 100 °C for 24 h. ^b A ratio of composition metals is described in subscript letters. ^c GC yield.

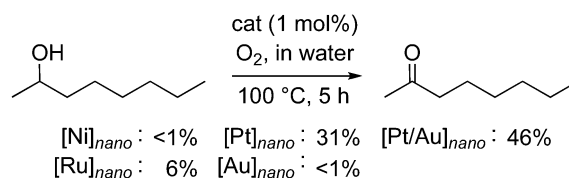
To explore the catalytic potential of the nanoparticles, we elected to study the transfer hydrogenation of alkenes, which has not been studied as extensively as that of carbonyl compounds.³ After thorough reaction screening, we were pleased to find that the quatermetallic nanoparticles [Ni/Ru/Pt/Au]_{nano} exhibited significantly higher catalytic performance for the transfer hydrogenation of 4-phenyl-1-butene (**1**)⁵ with 2-propanol than the other nanoparticles tested, and afforded a quantitative yield of butylbenzene (**2**) (Table 1). Thus, a transfer hydrogenation reaction of 4-phenyl-1-butene (**1**) was carried out in the presence of 0.5 mol% (total metal residue) of [Ni/Ru/Pt/Au]_{nano} in aqueous 2-propanol (iPrOH/H₂O = 10/3) at 100 °C for 24 h under atmospheric conditions to give butylbenzene (**2**) in 98% yield (Table 1, entry 1). Unimetallic [Ni]_{nano}, [Ru]_{nano}, [Pt]_{nano}, and [Au]_{nano} did not catalyze the transfer hydrogenation at all (entries 2–5). Furthermore, the reaction hardly proceeded even with 1 mol% each of unimetallic nanoparticles [Ni]_{nano}, [Ru]_{nano}, [Pt]_{nano}, and [Au]_{nano} (total metal residue = 4 mol%) under similar conditions (entry 6). These results indicate that the high catalytic ability of the quatermetallic [Ni/Ru/Pt/Au]_{nano} catalyst is induced in a cooperative manner by the combination of multiple metal species. In order to determine the essential metal elements for this catalysis, bi- and trimetallic nanoparticles were tested in the transfer hydrogenation under similar conditions (entries 7–17). However, none of the bi- or trimetallic nanoparticles efficiently promoted the hydrogenation. It is noteworthy that a considerable

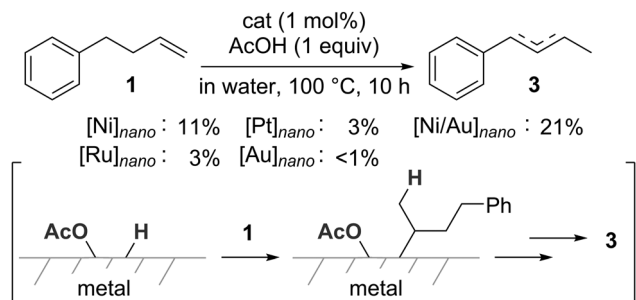
**Scheme 2** Reaction pathway of the transfer hydrogenation of alkenes.

amount of the olefin-migrated products **3** was obtained with bi- and trimetallic nanoparticle catalysts containing nickel as a composition element (entries 9, 13–16).

A generally accepted reaction pathway of the heterogeneous transition metal-catalyzed transfer hydrogenation of alkenes is outlined in Scheme 2.⁶ The reaction proceeds *via* (i) abstraction of hydrogen from an alcohol (alcohol oxidation) to generate the metal-hydrogen species (step I), (ii) insertion of an alkene between a metal-hydrogen bond to form a metal(hydrogen)alkyl intermediate (step II), and (iii) reductive elimination of the intermediate to release the product alkane (step III). We hypothesized that the composition elements (Ni, Ru, Pt, and Au) of the quatermetallic nanocatalyst [Ni/Ru/Pt/Au]_{nano} should promote the steps of the above mentioned reaction pathway sequentially, and complete the catalytic cycle cooperatively.

First, oxidation of 2-octanol was examined using the unimetallic nanocatalysts to evaluate their catalytic ability for step I (Scheme 3). The reaction was carried out in refluxing water under molecular oxygen for 5 h in the presence of 1 mol% of the unimetallic nanocatalysts. It was found that [Pt]_{nano} catalyzed the oxidation to give 2-octanone in 31% yield with high reaction selectivity,^{2a,e} whereas [Ni]_{nano}, [Ru]_{nano}, and [Au]_{nano} were not effective for the oxidation and only afforded 2-octanone in 0%,

**Scheme 3** Oxidation of 2-octanol with various nanocatalysts.

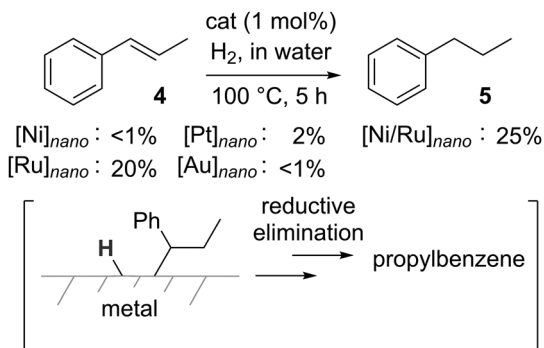


Scheme 4 Olefin migration via insertion–elimination steps with various nanocatalysts.

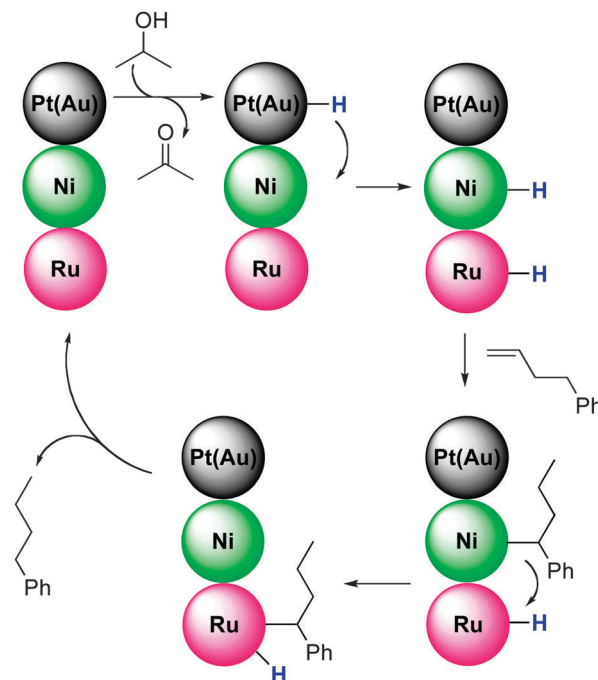
6%, and 1% yield, respectively. It should be noted that the bimetallic $[\text{Pt}/\text{Au}]_{\text{nano}}$ promoted the oxidation more effectively under identical conditions to give 46% yield of 2-octanone.⁷ Thus, both $[\text{Pt}]_{\text{nano}}$ and $[\text{Pt}/\text{Au}]_{\text{nano}}$ were identified as effective catalysts for the hydrogen abstraction from alcohols (step I).⁹

As can be seen in Table 1, particularly in entries 9 and 13–16, the olefin migration products **3** were observed when bi- and trimetallic nanoparticles containing nickel were used as catalysts. Olefin migration occurs *via* an olefin insertion/ β -hydride elimination pathway (Scheme 2, step IV). Indeed, among the unimetallic catalysts $[\text{Ni}]_{\text{nano}}$, $[\text{Ru}]_{\text{nano}}$, $[\text{Pt}]_{\text{nano}}$, and $[\text{Au}]_{\text{nano}}$, only $[\text{Ni}]_{\text{nano}}$ promoted olefin migration of 4-phenyl-1-butene (**1**) with acetic acid, where a protonated metal species, $\text{M}(\text{OAc})\text{H}$, was generated *in situ* (Scheme 4).⁸ Thus, the Ni–H species is somewhat more active than the other metals for olefin insertion to form the Ni-alkyl intermediate, thereby facilitating step IV and step II, as shown in Scheme 2. $[\text{Ni}/\text{Au}]_{\text{nano}}$ also showed moderate catalytic activity for olefin migration under acidic conditions.⁹

Hydrogenation of the olefin must include the reductive elimination step (step III) from a $\text{M}(\text{H})$ alkyl intermediate. When β -methylstyrene (**4**) was subjected to hydrogenation under molecular hydrogen (1 atm) in refluxing water with 1 mol% metal of unimetallic ($[\text{Ni}]_{\text{nano}}$, $[\text{Ru}]_{\text{nano}}$, $[\text{Pt}]_{\text{nano}}$, and $[\text{Au}]_{\text{nano}}$) as well as bimetallic $[\text{Ni}/\text{Ru}]_{\text{nano}}$ catalysts, 20% and 25% yields of propylbenzene (**5**) were obtained using the $[\text{Ru}]_{\text{nano}}$ and $[\text{Ni}/\text{Ru}]_{\text{nano}}$ catalysts, respectively. The $[\text{Ni}]_{\text{nano}}$, $[\text{Pt}]_{\text{nano}}$, and $[\text{Au}]_{\text{nano}}$ catalysts were much less active for the hydrogenation under these conditions.⁹



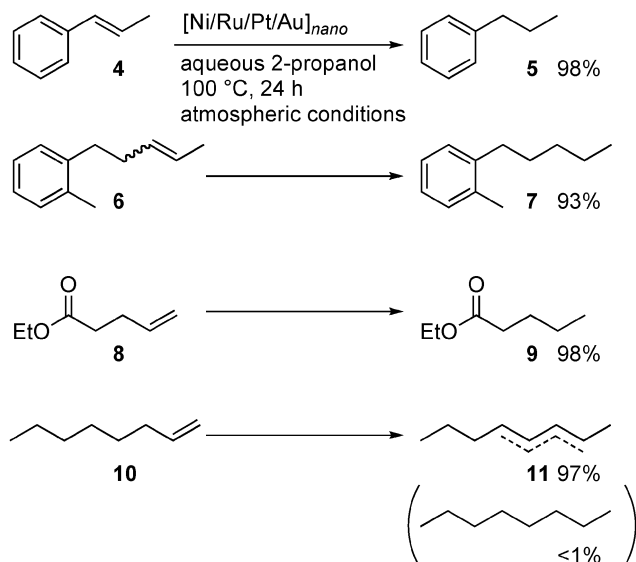
Scheme 5 Hydrogenation of β -methylstyrene *via* the reductive elimination step with various nanocatalysts.



Scheme 6 Sequential cooperation of multiple metals to promote alkene transfer hydrogenation.

Considering the individual reactivity of $[\text{Ni}]_{\text{nano}}$, $[\text{Ru}]_{\text{nano}}$, $[\text{Pt}]_{\text{nano}}$, and $[\text{Au}]_{\text{nano}}$, shown in Schemes 3–5, the significant catalytic ability of the quaternary metal nanoparticles $[\text{Ni}/\text{Ru}/\text{Pt}/\text{Au}]_{\text{nano}}$ in the transfer hydrogenation of alkenes was possibly induced by the sequential cooperation of the composition metals. Although the reaction mechanism is still unclear, we propose the inter-metal-ligand relay sequence as a plausible reaction pathway, namely (i) $[\text{Pt}/\text{Au}]$ -promoted alcohol oxidation to generate a metal-hydride species and relay of the hydrogen ligand onto Ni and Ru, (ii) $[\text{Ni}]$ -catalyzed olefin migration *via* an insertion–elimination pathway to afford a reactive benzyl-metal intermediate and relay of the benzylic ligand onto Ru, and (iii) the hydrogenation (reductive elimination) from a Ru-benzyl intermediate (Scheme 6).

The substrate scope of the transfer hydrogenation protocol using the quaternary metal nanoparticles $[\text{Ni}/\text{Ru}/\text{Pt}/\text{Au}]_{\text{nano}}$ was examined for the reduction of various alkenes, representative results of which are shown in Scheme 7. Reduction of β -methylstyrene (**4**) proceeded smoothly with $[\text{Ni}/\text{Ru}/\text{Pt}/\text{Au}]_{\text{nano}}$ under similar transfer hydrogenation conditions to give propylbenzene (**5**) in 98% yield. 4-(2-Methylphenyl)-2-pentene (**6**) and ethyl 1-pentenoate (**8**) also underwent catalytic reduction to afford 2-(*n*-pentyl)toluene (**7**) and ethyl pentanoate (**9**) in 93% and 98% isolated yields, respectively. It is interesting that the reduction of 1-octene (**10**), which lacks a conjugating group (*e.g.*, aryl and carbonyl), did not proceed under similar conditions and gave only olefin-isomerized products **11** (97%); 6 isomers were observed in the GC-MS analysis. Thus, the reductive elimination step forming the C–H bond must occur from the corresponding benzylic or π -carbonyl alkyl metal intermediates generated *in situ* *via* nickel-promoted olefin migration (insertion–elimination process).



Scheme 7 Transfer hydrogenation of olefins with $[\text{Ni/Ru/Pt/Au}]_{\text{nano}}$.

In conclusion, we have developed a novel protocol for the heterogeneous catalytic transfer hydrogenation of alkenes which was promoted by the quatermetallic alloy nanoparticles $[\text{Ni/Ru/Pt/Au}]_{\text{nano}}$ via sequential cooperation of the component metal elements. Along this line, various types of catalysts are being developed by combining the unique chemical properties of transition metals in our laboratory and will be reported in due course.

We acknowledge the JSPS (Grant-in-Aid for Scientific Research on Innovative Area #2105) for partial financial support of this work. Y. I. was supported by the JSPS Fellowship program.

Notes and references

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