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COMMUNICATION

Transfer Hydrogenation of Alkenes with a Ni/Ru/Pt/Au Heteroquatermetallic Nanoparticle Catalyst: Sequential Cooperation of Multiple Nano-Metal Species

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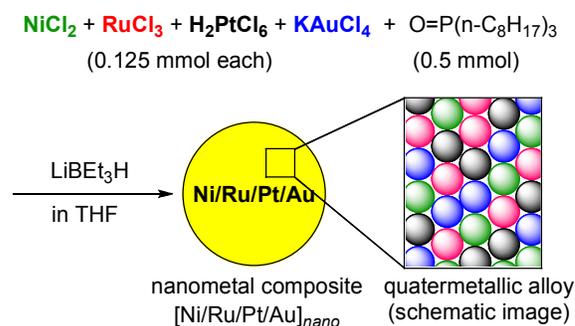
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Quatermetallic alloy nanoparticles of Ni/Ru/Pt/Au were prepared and found to promote the catalytic transfer hydrogenation of non-activated alkenes bearing conjugating units (e.g., 4-phenyl-1-butene) with 2-propanol, where the composition metals, Ni,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



Scheme 1. Preparation of Quatermetallic Alloy Nanoparticles.

Various uni-, bi-, ter-, and quatermetallic alloy nanoparticles modified with a capping agent of trioctylphosphine oxide (TOPO) were prepared in a parallel combinatorial manner. Thus, a mixture of NiCl₂, RuCl₃, H₂PtCl₆, and KAUCl₄ was treated with an excess amount of LiBEt₃H 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 nano structures of 3.0 ± 0.25 nm average diameter (Figure 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 termetallic nanoparticles were prepared under similar conditions with average diameters of ca. 3 nm.

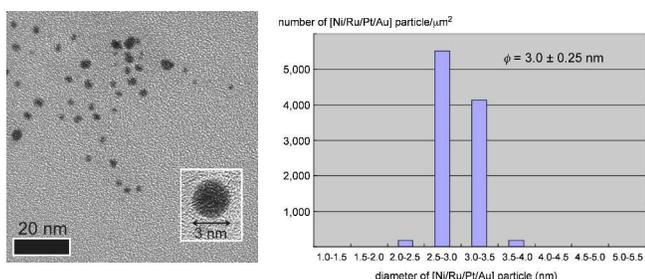


Figure 1. A transmission electron microscopic (TEM) image and a histogram of the size distribution of $[\text{Ni}/\text{Ru}/\text{Pt}/\text{Au}]_{\text{nano}}$.

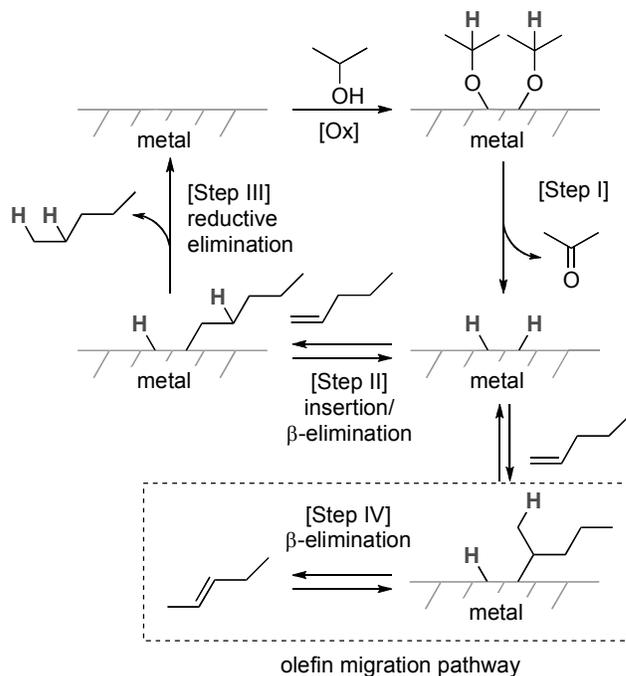
Table 1. Transfer hydrogenation of 4-phenyl-1-butene (**1**) with various uni-, bi-, ter-, quartermetallic nanoparticles.^a

Entry	Catalyst ^b	mol %	Yield [%] of 2 ^c	Yield [%] of 3 ^c
1	$[\text{Ni}_{0.24}/\text{Ru}_{0.26}/\text{Pt}_{0.26}/\text{Au}_{0.24}]$	0.5	98	<1
2	$[\text{Ni}]$	0.5	2	<1
3	$[\text{Ru}]$	0.5	<1	<1
4	$[\text{Pt}]$	0.5	<1	<1
5	$[\text{Au}]$	0.5	<1	<1
6	$[\text{Ni}] + [\text{Ru}] + [\text{Pt}] + [\text{Au}]$	0.5	<1	<1
7	$[\text{Ni}_{0.54}/\text{Ru}_{0.46}]$	0.5	<1	<1
8	$[\text{Ni}_{0.61}/\text{Pt}_{0.39}]$	0.4	5	<1
9	$[\text{Ni}_{0.51}/\text{Au}_{0.49}]$	0.5	2	14
10	$[\text{Ru}_{0.43}/\text{Pt}_{0.57}]$	0.3	1	5
11	$[\text{Ru}_{0.43}/\text{Au}_{0.57}]$	0.4	1	7
12	$[\text{Pt}_{0.49}/\text{Au}_{0.51}]$	0.7	<1	<1
13	$[\text{Ni}_{0.36}/\text{Ru}_{0.35}/\text{Pt}_{0.25}]$	0.7	4	16
14	$[\text{Ni}_{0.36}/\text{Ru}_{0.35}/\text{Pt}_{0.25}]$	2.0	16	33
15	$[\text{Ni}_{0.38}/\text{Ru}_{0.27}/\text{Au}_{0.35}]$	0.5	<1	22
16	$[\text{Ni}_{0.34}/\text{Pt}_{0.25}/\text{Au}_{0.41}]$	0.3	2	20
17	$[\text{Ru}_{0.35}/\text{Pt}_{0.43}/\text{Au}_{0.22}]$	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, $\text{H}_2\text{O}/2\text{-propanol} = 3/10$) 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 $[\text{Ni}/\text{Ru}/\text{Pt}/\text{Au}]_{\text{nano}}$ 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 $[\text{Ni}/\text{Ru}/\text{Pt}/\text{Au}]_{\text{nano}}$ in aqueous 2-propanol ($\text{iPrOH}/\text{H}_2\text{O} = 10/3$) at 100 °C for 24 h under atmospheric conditions

to give butylbenzene (**2**) in 98% yield (Table 2, entry 1). Unimetallic $[\text{Ni}]_{\text{nano}}$, $[\text{Ru}]_{\text{nano}}$, $[\text{Pt}]_{\text{nano}}$, and $[\text{Au}]_{\text{nano}}$ did not catalyze the transfer hydrogenation at all (entries 2-5). Furthermore, the reaction hardly proceeded even with 1 mol% each of unimetallic nanoparticles $[\text{Ni}]_{\text{nano}}$, $[\text{Ru}]_{\text{nano}}$, $[\text{Pt}]_{\text{nano}}$, and $[\text{Au}]_{\text{nano}}$ (total metal residue = 4 mol%) under similar conditions (entry 6). These results indicate that the high catalytic ability of the quatermetallic $[\text{Ni}/\text{Ru}/\text{Pt}/\text{Au}]_{\text{nano}}$ catalyst is induced in a cooperative manner by the combination of the multiple metal species. In order to determine the essential metal elements for this catalysis, bi- and termetallic nanoparticles were tested in the transfer hydrogenation under similar conditions (entries 7-17). However, none of the bi- or termetallic nanoparticles efficiently promoted the hydrogenation. It is noteworthy that a considerable amount of the olefin-migrated products **3** was obtained with bi- and termetallic nanoparticle catalysts containing nickel as a composition element (entries 9, 13-16).

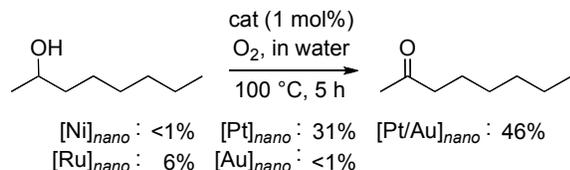


Scheme 2. Reaction pathway of the transfer hydrogenation of alkenes.

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 $[\text{Ni}/\text{Ru}/\text{Pt}/\text{Au}]_{\text{nano}}$ should promote the steps of the above mentioned reaction pathway sequentially, and complete the catalytic cycle cooperatively.

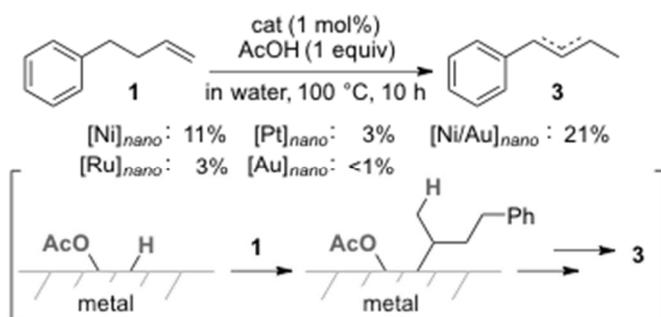
First, oxidation of 2-octanol was examined with the unimetallic nanocatalysts to evaluate their catalytic ability for Step I (Scheme 3). The reaction was carried out in refluxing water under molecular oxygen for 5 h in the presence of 1 mol% of the unimetallic nanocatalysts. It was found that $[\text{Pt}]_{\text{nano}}$ catalyzed the oxidation to

give 2-octanone in 31% yield with high reaction selectivity,^{2a,2e} whereas $[\text{Ni}]_{\text{nano}}$, $[\text{Ru}]_{\text{nano}}$, and $[\text{Au}]_{\text{nano}}$ were not effective for the oxidation and only afforded the 2-octanone in 0%, 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 the 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

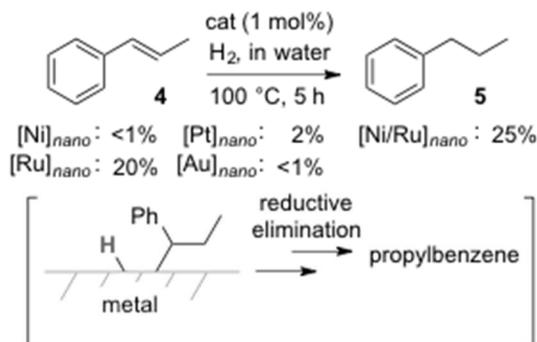


Scheme 3. Oxidation of 2-octanol with various nanocatalysts.

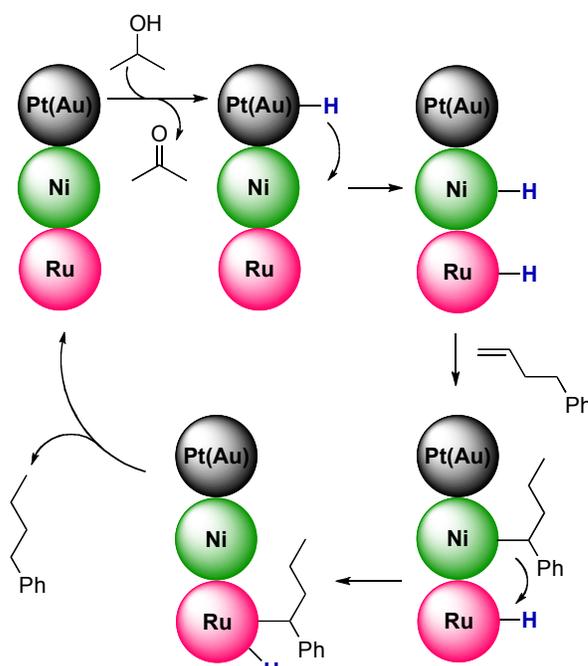
As can be seen in Table 1, particularly in entries 9 and 13-16, the olefin migration products **3** were observed when bi- and termetallic nanoparticles containing nickel were used as catalysts. Olefin migration occurs via an olefin insertion/ β -hydride elimination pathway (Scheme 2, Step IV). Indeed, among the unimetallic catalysts $[\text{Ni}]_{\text{nano}}$, $[\text{Ru}]_{\text{nano}}$, $[\text{Pt}]_{\text{nano}}$, and $[\text{Au}]_{\text{nano}}$, only the $[\text{Ni}]_{\text{nano}}$ 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



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



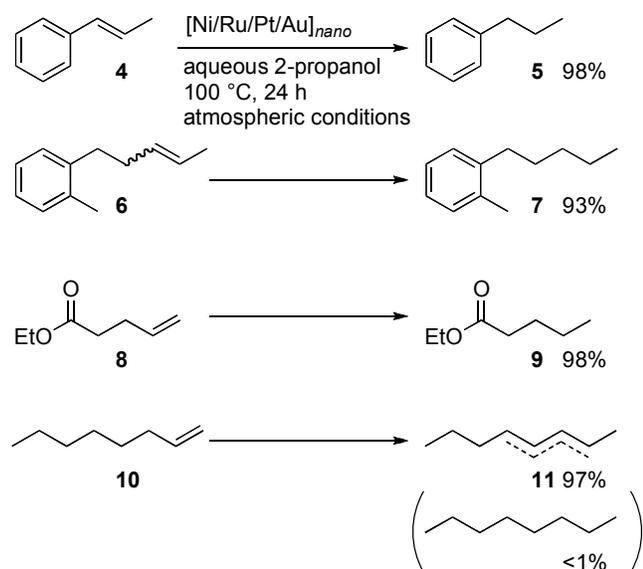
Scheme 5. Hydrogenation of β -methylstyrene via the reductive elimination Step with various nanocatalysts.



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

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

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 nanoparticles $[\text{Ni}/\text{Ru}/\text{Pt}/\text{Au}]_{\text{nano}}$ in the transfer hydrogenation of alkenes may be 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).



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

The substrate scope of the transfer hydrogenation protocol using the quaternary metallic nanoparticles $[\text{Ni/Ru/Pt/Au}]_{\text{nano}}$ 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 $[\text{Ni/Ru/Pt/Au}]_{\text{nano}}$ 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 yield, respectively. It is interesting that the reduction of 1-octene (**10**), which lacks a conjugating group (e.g., aryl, 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 α -carbonyl alkylmetal intermediates generated in situ via nickel-promoted olefin migration (insertion-elimination process).

In conclusion, we have developed a novel protocol for the heterogeneous catalytic transfer hydrogenation of alkenes which was promoted by the quaternary metallic 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.

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Notes and references

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† Electronic Supplementary Information (ESI) available: experimental detail, TEM images of nanoparticle catalysts, GC & GC-MS charts and ^1H & ^{13}C NMR spectra of the products. See DOI: 10.1039/c000000x/

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- It has been reported that the transfer hydrogenation of non-activated alkenes often required 10-30 mol% of Raney Ni or homogeneous phosphine-Ru complexes under thermal conditions. See references 3 and 6, and references cited therein.
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- Catalytic ability of the heteroquaternary metallic $[\text{Ni/Ru/Pt/Au}]_{\text{nano}}$ was also examined for the aerobic oxidation of 2-octanol (cf. Scheme 3), olefin migration of 4-phenylbut-1-ene (cf. Scheme 4) and hydrogenation of β -methylstyrene (cf. Scheme 5), where 2-octanol, olefin-isomerized products **3** (4-phenylbut-2-ene and 1-phenylbut-1-ene (β -ethylstyrene)), and phenylpropane (**5**) were obtained in 63%, 13%, and 99% yield, respectively.