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ScienceDirect
Catalysis Today 122 (2007) 239–244
CATALYSIS TODAY
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Trimetallic nanoparticles having a Au-core structure

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Abstract

The Au/Pt/Rh trimetallic nanoparticles were successfully synthesized by a combination of a co-reduction and a self-organization method using poly(*N*-vinyl-2-pyrrolidone) (PVP) as a protecting reagent. The triple core/shell structure was suggested by HR-TEM, EF-TEM and FT-IR-CO for the trimetallic nanoparticles. The present trimetallic nanoparticles had much higher catalytic activity for hydrogenation than the corresponding monometallic and bimetallic nanoparticles. This high catalytic activity can be due to the sequential electronic effect between different atoms of a particle, which is supported by XPS data.

Keywords: Trimetallic nanoparticle; Core–shell structure; Hydrogenation catalyst; Self-organization; Bimetallic nanoparticle; Ligand effect

1. Introduction

Much attention has been paid to bimetallic nanoparticles, especially those having a core/shell structure [1]. From the viewpoint of Au catalysts, bimetallic nanoparticles have received much attention recently [2–6]. They were used as catalysts for preparation of hydrogen peroxide [2,3], hydrodechloriation [4] and vinyl acetate synthesis [5]. We have prepared bimetallic nanoparticles having a Au-core structure, such as Au/Pt [7] and Au/Pd [8] bimetallic nanoparticles by co-reduction of the corresponding metal ions in ethanol/water in the presence of poly(*N*-vinyl-2-pyrrolidone) (PVP), and found that such bimetallic nanoparticles are more active as a catalyst for partial hydrogenation of diene than the corresponding Pt and Pd monometallic nanoparticles, respectively, due to the presence of an Au-core. Recently, we have discovered that a physical mixture of dispersions of two kinds of PVP-protected monometallic nanoparticles in solution can result in formation of PVP-protected bimetallic nanoparticles having a core/shell structure by self-organization [9,10].

Here, we present the synthesis of trimetallic nanoparticles having a Au-core structure by a combination of the preparation of bimetallic nanoparticles by co-reduction with the formation of core/shell-structured bimetallic nanoparticles by self-organization in physical mixture. The formation of trimetallic nanoparticles has been suggested by UV–vis spectral change, TEM image change, FT-IR spectra of adsorbed carbon monoxide, XPS spectra and calorimetric studies. The catalytic activity of trimetallic nanoparticles in the molar ratio of Au/Pd/Rh = 1/4/20 was higher than the corresponding monometallic and bimetallic nanoparticles for hydrogenation of methyl acrylate. This high catalytic activity can be understood by sequential electronic charge transfer from surface Rh atoms to interlayered Pt atoms and then to core Au atoms.

2. Experimental

2.1. Preparation of Au/Pt/Rh trimetallic nanoparticles

The colloidal dispersions of poly(*N*-vinyl-2-pyrrolidone) (PVP)-protected Au/Pt bimetallic nanoparticles were prepared by refluxing of the H_2O/EtOH (1/1, v/v) solution of $HAuCl_4$ and H_2PtCl_6 in the presence of PVP [7]. The molar ratio of Au/Pt was 1/4, and the molar ratio of monomer unit of PVP against total metal (*R*) was kept 40 in the present experiments. The colloidal dispersions of Rh nanoparticles were separately prepared by refluxing a H_2O/EtOH (1/1, v/v) solution of $RhCl_3$ in the presence of PVP [11]. The colloidal dispersion of PVP-protected Au/Pt (1/4) nanoparticle and that of PVP-protected Rh nanoparticles were mixed at room temperature in the designed

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doi:10.1016/j.cattod.2007.03.013

ratio. The mixed dispersions were kept stirring at least for a day at room temperature to complete the self-organization reaction.

2.2. Characterization

The characterization of metal nanoparticles was carried out by using powder X-ray diffraction (XRD), transmission electron microscopy (TEM), high-resolution TEM (HR-TEM) and energy-filtered TEM (EF-TEM). Fourier transform infrared (FT-IR) spectra of the carbon monoxide adsorbed on the metal surface (FT-IR-CO) were measured to get the information of the surface composition of metal nanoparticles. The elemental analysis of metal nanoparticles was carried out by inductively coupled plasma (ICP) atomic emission spectroscopy. Ultraviolet–visible (UV–vis) spectroscopy was used to understand the reaction processes during the formation of metal nanoparticles. X-ray photoelectron spectroscopy (XPS) was conducted to measure the binding energy of the metals. Isothermal titration calorimetry was used to measure the molar enthalpy [10]. The catalytic activity of the metal nanoparticles was determined by measuring the rate of hydrogenation of methyl acrylate (25 mmol L^{-1}) in ethanol at 30 °C under 1 atm pressure of hydrogen by using the metal catalyst at a concentration of 1.01 mol L^{-1}. The product was only pure methyl propionate detected by glpc. When the most active catalyst was used, 100% conversion was achieved in a few minutes.

3. Results and discussion

3.1. Preparation and characterization of trimetallic nanoparticles

The colloidal dispersion of Au/Pt/Rh trimetallic nanoparticles was prepared by mixing the colloidal dispersion of Au/Pt nanoparticles and that of Rh nanoparticles. The UV–vis spectra of the dispersion of the Au/Pt/Rh trimetallic nanoparticles as well as those of the starting Au/Pt bimetallic and Rh monometallic nanoparticles are shown in Fig. 1. The spectral change is too small to infer the occurrence of a reaction between the nanoparticles. TEM photographs and size distribution histograms of these nanoparticles, shown in Fig. 2, suggest the self-organization, which can be defined by the spontaneous formation of trimetallic nanoparticles by mixing bimetallic nanoparticles and monometallic ones in dispersions, because the size distribution histogram of the trimetallic nanoparticles is narrower than that expected by summation of the histograms of bimetallic nanoparticles and monometallic ones. Spontaneous formation of Ag-Rh bimetallic nanoparticles by mixing Ag and Rh nanoparticles have been reported [9,10], although the precise formation mechanism is not clear (vide post, cf. Fig. 12). HR-TEM image (Fig. 3a) of the trimetallic nanoparticles reveals that the nanoparticle form a single crystal, which means that mixture gives the spontaneous formation of single crystal. The energy dispersive X-ray spectrum (EDS) (Fig. 3b) clearly shows the presence of Rh, Pt and Au at an atomic ratio of 80.8:16.1:3.1,

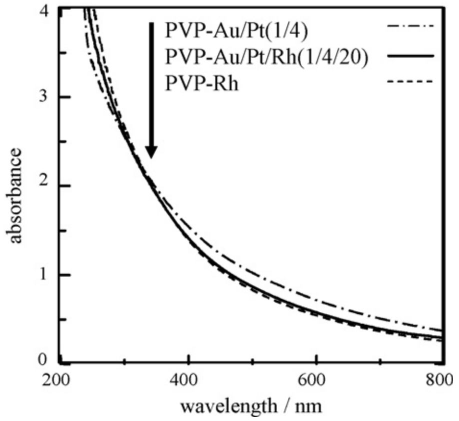

Fig. 1. UV–vis spectra of Rh monometallic, Au/Pt bimetallic and Au/Pt/Rh trimetallic nanoparticles.

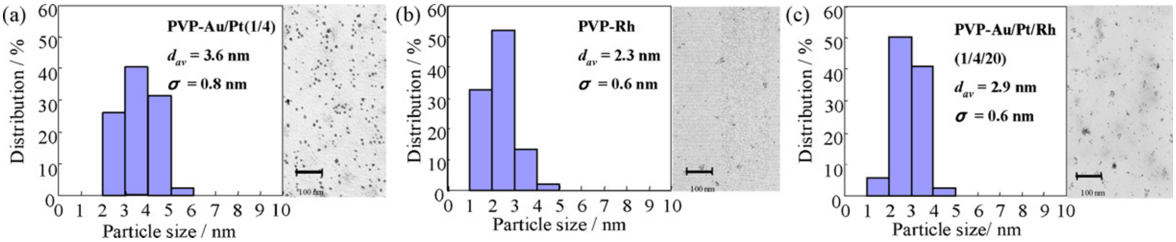

Fig. 2. TEM images and size distribution histograms of PVP-protected: (a) Au/Pt bimetallic, (b) Rh monometallic and (c) Au/Pt/Rh trimetallic nanoparticles.

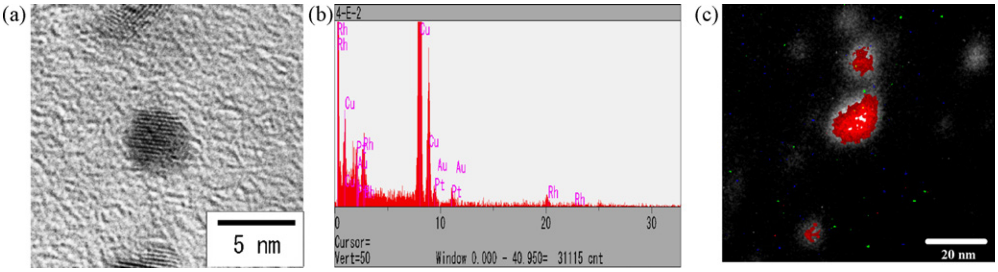

Fig. 3. (a) HR-TEM image, (b) EDS spectrum and (c) EF-TEM image of PVP-protected Au/Pt/Rh (1/4/20) nanoparticles.

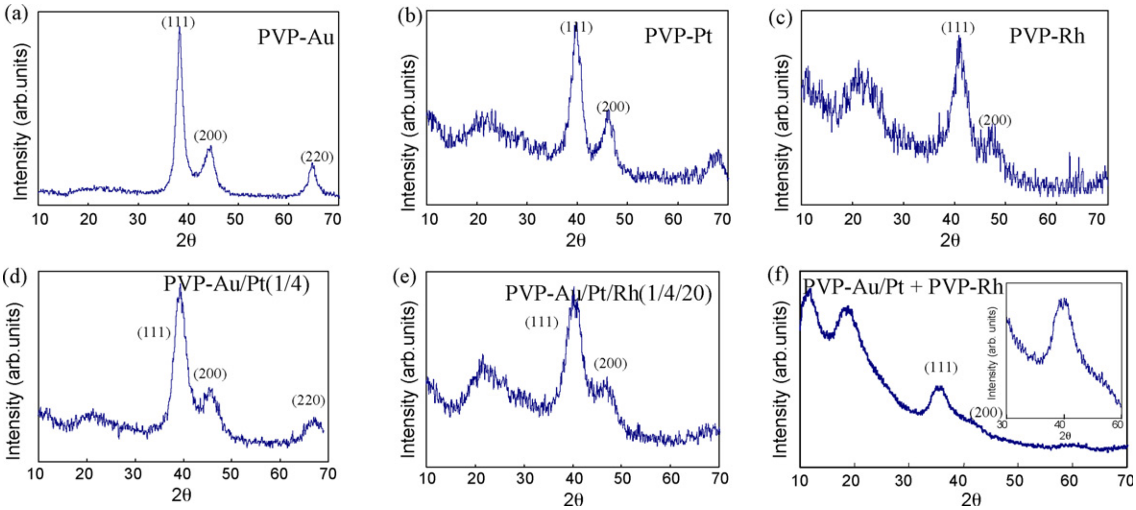

Fig. 4. XRD patterns of (a) PVP-Au, (b) PVP-Pt, (c) PVP-Rh, (d) PVP-Au/Pt (1/4), (e) PVP-Au/Pt/Rh and (f) the1:4 mixture of PVP-Au/Pt (1/4) and PVP-Ph nanoparticles.

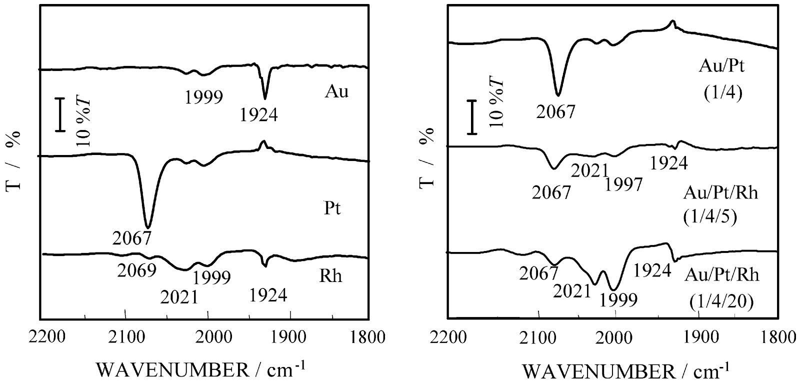

Fig. 5. FT-IR-CO spectra of monometallic nanoparticles and multi-metallic nanoparticles.

which is close to the fed ratio (80:16:4). Fig. 3c shows EF-TEM, where red parts of the particles consist of Rh [12]. The Rh atoms, existing in a whole particle, may be located near the surface of a particle rather than the center of the particle. These results may suggest that the trimetallic nanoparticles have a structure of a single crystal, but that Rh may possibly exist near the surface of the crystal, and Pt and Au may be located rather in a center of the particle. XRD patterns of PVP-protected Au/Pt/Rh (1/4/20) trimetallic nanoparticles, and the related monometallic and bimetallic nanoparticles are shown in Fig. 4. Table 1 summarizes the spacing of lattice plane (*d*) of metals in bulk and nanoparticles. These results may also suggest that the trimetallic nanoparticles are not mixtures of the related metal nanoparticles but new particles with a single crystal structure.

The FT-IR spectrum of carbon monoxide adsorbed on the surface of metal varies depending on the kind of metal. So, this technique is often used for identification of the kind of surface metals of bimetallic nanoparticles [13]. We used this technique to identify the surface metal of the trimetallic nanoparticles. The FT-IR spectra are shown in Fig. 5. The results indicate that FT-IR spectrum of CO adsorbed on Au/Pt/Rh (1/4/20) trimetallic nanoparticles is rather similar to that of Rh nanoparticles, although they are not completely the same. Thus, this result again supports that the surface of trimetallic nanoparticles mainly consists of Rh metal.

3.2. Catalytic activity of trimetallic nanoparticles

The catalytic activity of the Au/Pt/Rh trimetallic nanoparticles was investigated for the hydrogenation of methyl acrylate

Table 1
Spacing of lattice place (*d*) of bulk and nanoparticles of metals

Material	*d*(*A*) at various *h k l* values			
	(1 1 1)	(2 0 0)	(2 2 0)	(3 1 1)
Au	2.36	2.04	1.44	1.23
PVP-Au	2.34	2.04	1.43	1.23
Pt	2.27	1.96	1.38	1.18
PVP-Pt	2.25	1.95	1.37	–
Rh	2.20	1.90	–	1.15
PVP-Rh	2.17	1.90	–	–
PVP-Au/Pt	2.28	1.98	1.37	–
PVP-Au/Pt/Rh	2.24	1.93	–	–
PVP-Au/Pt + PVP-Rh	2.27, 2.22	–	–	–

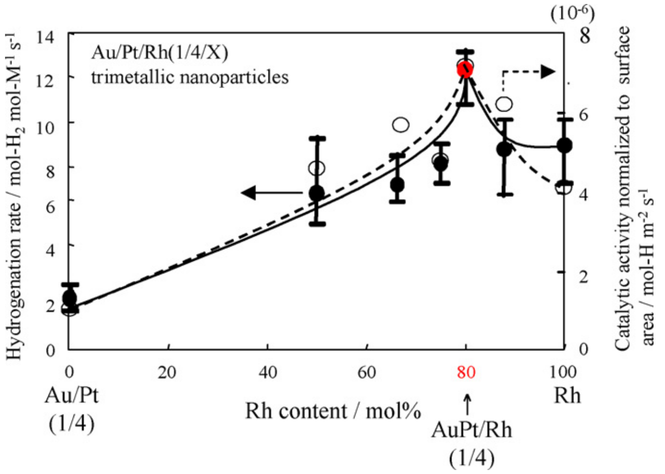

Fig. 6. Catalyst activity vs. Rh content of Au/Pt/Rh trimetallic nanoparticles. The open circles and broken line show the catalytic activity normalized to surface area.

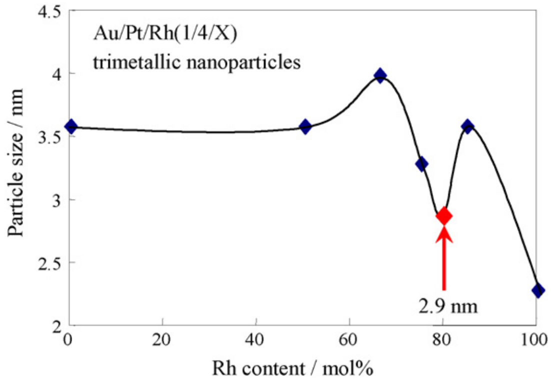

Fig. 7. Particles size vs. Rh content of Au/Pt/Rh trimetallic nanoparticles.

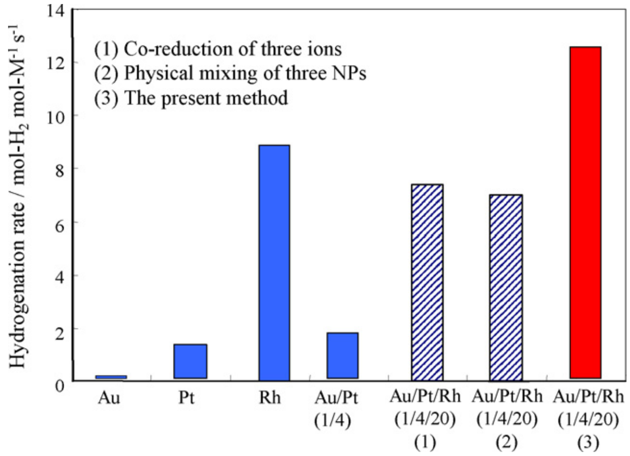

Fig. 8. Comparison of catalytic activities of various metal nanoparticles.

in ethanol at 30 °C under 1 atm of hydrogen pressure. Dependence of the catalytic activity upon the Rh content of Au/Pt/Rh trimetallic nanoparticles is shown in Fig. 6, where the molar ratio of Au/Pt is kept constant at 1/4. Fig. 6 reveals that the catalytic activity suddenly increases at the molar ratio of (Au + Pt) to Rh is 1/4, i.e., totally at the molar ratio of Au/Pt/Rh = 1/4/20. If Fig. 6 is compared with Fig. 7, which shows the change of the average diameter of trimetallic nanoparticles depending on the Rh content, then the minimum diameter is observed at the same content of Rh (Au/Pt/Rh = 1/4/20). Thus, the catalytic activity was normalized to the surface area (open circles and broken line in Fig. 6). The highest normalized catalytic activity was still observed at the molar ratio of Au/Pt/Rh = 1/4/20. This suggests that this ratio 1/4 is special for the preparation of small particles and thus, the high total surface area is convenient for the high catalytic activity. However, note that, although monometallic Rh nanoparticles have the smaller average particle size than the Au/Pt/Rh (1/4/20) trimetallic nanoparticles, the catalytic activity of Rh is lower than that of the Au/Pt/Rh (1/4/20) trimetallic nanoparticles (about 57% of that of trimetallic ones). Thus, the Au/Pt/Rh (1/4/20) trimetallic nanoparticles have a special structure, which could be a reason of the high catalytic activity.

This idea was supported by comparing the catalytic activity of trimetallic nanoparticles with the same composition but prepared by the different methods. Thus, other kinds of trimetallic nanoparticles were prepared by: (1) co-reduction of $HAuCl_4$, H_2PtCl_6 and $RhCl_3$ at the same ratio by refluxing ethanol/water and (2) physical mixture of Au, Pt and Rh monometallic nanoparticles at the same ratio. The catalytic activities of these trimetallic nanoparticles as well as Au/Pt (1/4) bimetallic, and Au, Pt and Rh monometallic nanoparticles are summarized in Fig. 8 for comparison. The Au/Pt/Rh trimetallic nanoparticles prepared by the present sophisticated method have the highest catalytic activity among the nanoparticles tested here. Again, the present trimetallic nanoparticles could have a special structure, which provides the high activity.

The thermal stability of the Au/Pt/Rh (1/4/20) trimetallic nanoparticles was examined by heat treatment of the present

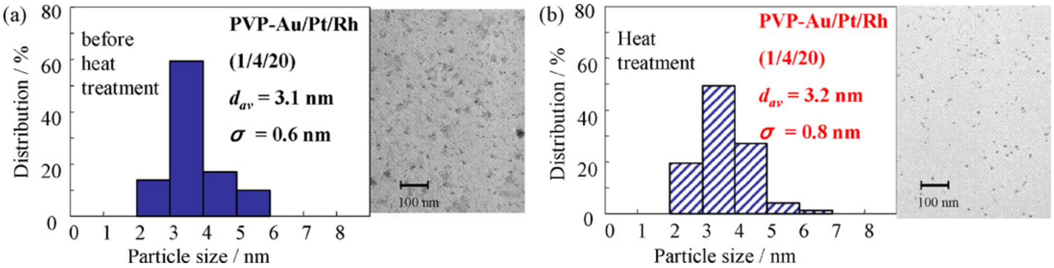

Fig. 9. TEM images and size distributions of PVP-protected Au/Pt/Rh (1/4/20) trimetallic nanoparticles (a) before and (b) after heat treatment.

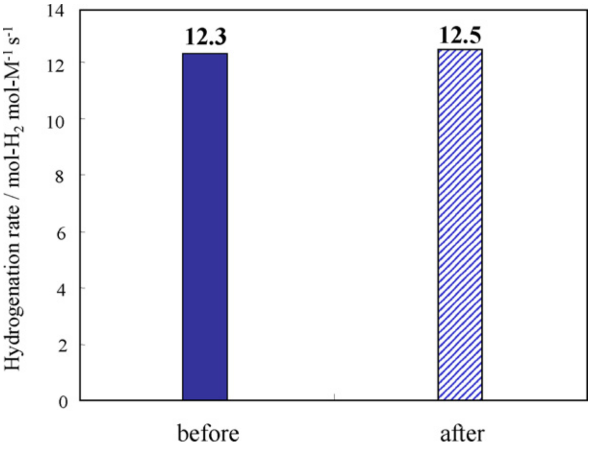

Fig. 10. Catalytic activity of trimetallic nanoparticles before and after heat treatment at 100 °C for 24 h.

Table 2
Binding energy of PVP-Au/Pt bimetallic and the corresponding monometallic nanoparticles

	Binding energy (eV)			Shift (eV) Δ
	PVP-Au	PVP-Pt	PVP-Au/Pt	
Au 4f7/2	84.25	–	84.10	−0.15
Pt 4f7/2	–	71.11	71.14	+0.03

Table 3
Binding energy of PVP-protected Au/Pt/Rh trimetallic nanoparticles and the corresponding monometallic nanoparticles

	Binding energy (eV)				Shift (eV) Δ
	PVP-Au	PVP-Pt	PVP-Rh	PVP-Au/Pt/Rh	
Au $4f_{7/2}$	84.25	–	–	84.10	−0.15
Pt$4f_{7/2}$	–	71.11	–	71.29	+0.18
Rh $3d_{5/2}$	–	–	307.35	307.55	+0.20

catalyst as a powder at 100 °C under nitrogen atmosphere for 24 h. The change of the size distribution and the catalytic activity are shown in Figs. 9 and 10, respectively. These data indicate that the present trimetallic nanoparticles are enough stable against the heat treatment. In our previous work, we found that the bimetallic nanoparticles with a core/shell structure were stable against the heat treatment under the same conditions, but those with an inverted core/shell structure were not so stable [14]. This means that the core/shell structure is thermodynamically stable, while the inverted core/shell structure is thermodynamically unstable. By extrapolating the above consideration, we think that the present Au/Pt/Rh (1/4/20) trimetallic nanoparticles will have a thermodynamically stable structure, which may be a triple core/shell structure.

3.3. Discussion on the high catalytic activity

In our previous works, we have observed that the core/shell-structured bimetallic nanoparticles have much higher catalytic activity for partial hydrogenation of diene to olefin [7,15,16]. This high catalytic activity can be attributed to the electronic (ligand) effect between the core and shell atoms. If this concept can be applied to the present triple core/shell-structured trimetallic nanoparticles, the electronic charge may sequentially transfer among these layers. This idea can be confirmed by XPS data. The binding energies of PVP-protected Au/Pt (1/4) bimetallic nanoparticles and the related ones, and those of PVP-protected Au/Pt/Rh (1/4/20) trimetallic nanoparticle and the related ones are shown in Tables 2 and 3, respectively. In the case of Au/Pt bimetallic nanoparticles, the binding energy of Au $4f_{7/2}$ in Au/Pt bimetallic nanoparticles shifts to lower energy in 0.15 eV, while that of Pt $4f_{7/2}$ shifts to higher energy in 0.03 eV. Although these shifts were very small and comparable with an error bar, the measurements were carried out several times using different lots and the resulting data showed the same tendency. Thus, these data may suggest the concept of electronic charge transfer from Pt in the surface to Au in the core. The similar electronic charge transfer may also be considered to occur from Rh to Pt and from Pt to Au in the Au/Pt/Rh (1/4/20) trimetallic nanoparticles, based on the data shown in Table 3. This sequential electronic charge transfer can be illustrated as shown Fig. 11. This order of the charge transfer may consist with the order of the ionization potential of Au, Pt and Rh in a bulk.

3.4. Calorimetric study on formation of the triple core/shell structure

Recently, we have discovered the high exothermic interaction between Ag and Rh monometallic nanoparticles measured by isothermal titration calorimetry (ITC) [10]. The data suggested the formation of a pseudo-core/shell structure as an intermediate to form the core/shell structure by self-organization as shown in Fig. 12. This ITC technique was applied to the present system to form trimetallic nanoparticles by mixture of bimetallic nanoparticles and monometallic ones (self-organization). The results are shown in Table 4 as well as for the

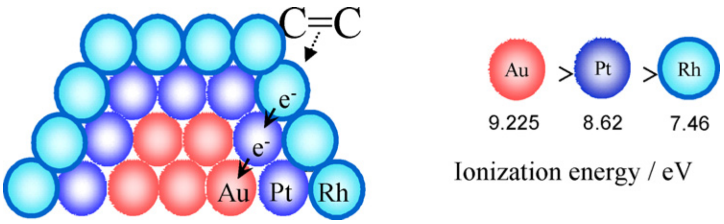

Fig. 11. Schematic presentation of the sequential electronic charge transfer in the Au-core/Pt-interlayer/Rh-shell trimetallic nanoparticles. Cartoon shows a cross-section of a part of spherical particle as an example. Ionization energies of the corresponding bulk metals are also shown for comparison.

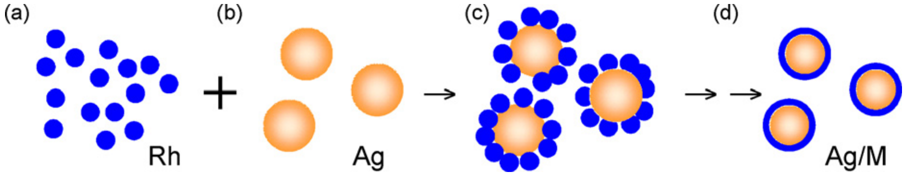

Fig. 12. Schematic presentation of formation of the core/shell structure (d) by mixing Rh (a) and Ag (b) nanoparticles through a pseudo-core/shell structure (c), where Rh nanoparticles surround Ag nanoparticles.

Table 4
Molar enthalpy obtained with ITC by injecting a particle dispersion into another particle dispersion

Injection particle	Particle in cell	
PVP-Rh	PVP-Au/Pt	−297.3
PVP-Au/Pt	PVP-Rh	−47
PVP-Pt	PVP-Au (L)	−534
PVP-Au (L)	PVP-Pt	−78

formation of Au/Pt bimetallic nanoparticles by the self-organization. The data clearly indicate the presence of the strong exothermic interaction between these particles. This strong exothermic interaction could be a driving force for the self-organization to form the trimetallic nanoparticles with a pseudo-core/shell structure.

4. Conclusion

The colloidal dispersions of PVP-protected Au/Pt/Rh trimetallic nanoparticle were prepared by mixing the dispersions of PVP-protected Rh nanoparticles and those of PVP-protected Au/Pt (1/4) bimetallic nanoparticles with a Au-core/Pt-shell structure. The trimetallic nanoparticles thus prepared may have a triple core/shell structure (Au-core/Pt-interlayer/Rh-shell), which is suggested by HR-TEM, EF-TEM and FT-IR-CO. The trimetallic nanoparticles with the composition of Au/Pt/Rh (1/4/20) and a triple core/shell structure have the highest catalytic activity for hydrogenation of methyl acrylate at 30 °C in ethanol among the trimetallic nanoparticles with other composition and other structures, and the corresponding bimetallic and monometallic nanoparticles. Although, the triple core/shell structure of trimetallic nanoparticles is not completely proved at the present stage, the higher catalytic activity of Au/Pt/Rh (1/4/20) trimetallic nanoparticles can support the presence of a special structure, possibly a triple core/shell structure, in this ratio. The high catalytic activity of trimetallic nanoparticles is probably due to the sequential electronic effect between elements in a particle. The strong exothermic interaction observed by ITC may be a driving force for the self-organization to form the triple core/shell structure. The preparation and characterization techniques presented here will be useful to design novel catalysts with desired structures.

Acknowledgment

This work was supported by a Grand-in-Aid for Scientific Research from Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan (No. 15310678).

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