Effect of additional metal ions on catalyses of polymer-stabilized metal nanoclusters

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Abstract

Two kinds of polymer-stabilized metal nanocluster catalysts were prepared by different methods. One is homogeneous poly(acrylic acid)-stabilized silver (PAA-Ag) nanoclusters, which were prepared upon UV irradiation of an alcohol/water solution of silver(I) perchlorate in the presence of poly(acrylic acid). Oxidation of ethylene, catalyzed by PAA-Ag nanoclusters, was performed in glycol under 1 atm of ethylene/oxygen (2/1 v/v). Addition of both cesium(I) and rhenium(VII) ions remarkably increased the catalytic activity of PAA-Ag nanoclusters. The other is heterogeneous palladium nanoclusters, which were immobilized on chelate resin-metal ion complexes, and prepared by reduction of palladium(II) ions supported on resin complexes. In this heterogeneous catalyst, the chelate resin works both as a support and as a protective polymer of nanoclusters. Hydrogenation of olefins in ethanol under 1 atm of hydrogen at 30°C was used for evaluating the catalysis of immobilized Pd nanoclusters. An increase of the reaction rate by lanthanoid ions was observed in the hydrogenation of olefins catalyzed by Pd nanoclusters supported on resin complexes. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Metal nanocluster catalyst; Poly(acrylic acid); Chelate resin; Polymer catalyst; Polymer-immobilized metal ions

1. Introduction

Recently, much attention has been paid to nanoscience and nanotechnology leading to nanodevices, because their developments are requested for the 21st century. Interests in the nanoscopic materials and their application to catalyses have greatly stimulated the research on metal nanoclusters [1–6]. Metal nanoclusters stabilized by organic molecules are now creating a new class of materials different from ei-

ther conventional bulk materials or atoms, giving one of the smallest building blocks of matter. Most of the remarkable properties of metal nanoclusters are based on high surface area and quantum size effects. Metal nanoclusters have been prepared chemically by reduction of the corresponding metal salts [7] and physically by pulverization of the metallic mass [8]. The chemical procedure is superior to the physical one with respect to the easy preparation, stability of dispersion, smallness of nanocluster size and narrowness of size distribution.

Polymer-stabilized metal nanoclusters often act as an excellent homogeneous catalyst for some organic reactions. For example, palladium nanoclusters

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obtained by refluxing an alcohol/water solution of palladium ion in the presence of poly(N-vinyl-2-pyrrolidone) (PVP) were used as an active catalyst for selective hydrogenation of cyclooctadienes [9]. The PVP-stabilized noble metal nanoclusters were also effective catalysts for visible-light-induced hydrogen generation in the electron relay system of EDTA, tris(bipyridine)ruthenium(II), methyl viologen, and a proton [10]. A carbon–nitrogen triple bond of acrylonitrile was selectively hydrated on copper nanoclusters, giving acrylamide in 100% yield without formation of ethylene cyanohydrin [11].

Immobilization of homogeneous metal nanocluster particles onto solid supports without reducing their activity is of great importance for practical utilization of the catalysts. There are reports on immobilization of metal nanoclusters by electrostatic attractive force between electrically charged nanoclusters and ionic moieties on supports [12]. Organic polymer supports have been widely used for the immobilization of metal nanoclusters, since they can be easily functionalized by organic reactions [13–15]. Immobilized rhodium nanoclusters were prepared by making use of the formation of covalent bonds between a protective polymer of nanoclusters and a polymer support [16]. Beads of chelate resin-metal complexes were prepared from polystyrene-based resins functionalized by tridentate iminodiacetate moieties [17,18]. The heterogeneous polymer-immobilized metal nanoclusters worked as very active catalysts for hydrogenation of olefins.

Metal catalysts composed of two (or more) different metal elements are of interest from both a technological and a scientific view for improving the quality and/or property of the catalysts. Alkali metal ions are an important additive for a silver catalyst in an oxidation of ethylene [19–22]. Promotive effects of lanthanoid ions on hydrogenation of ethene catalyzed by transition metal catalyst were reported by Imamura and coworkers [23,24]. They concluded that the presence of additional lanthanoid ions strongly influenced the state of adsorption of hydrogen in the subsequent activation process, resulting in enhancement of the surface to dissociate hydrogen. In the case of conventional supported metal catalysts, additional metal ions may weakly interact with the metal particles on inorganic supports. In the case of polymer-metal nanocluster catalysts, in contrast, electrostatic interactions between additional metal ions

and ionic polymers are strong enough for the additional metal ions to assist the interaction with metal nanoclusters surrounded by polymers. Thus, a larger promotive effect of additional metal ions is expected in polymer-stabilized metal nanocluster catalysts than in conventional supported metal catalysts. However, there have been few reports discussing the interaction between metal ions and ionic polymers on both homogeneous and heterogeneous catalysts. The present paper focuses on the promotive effect of additional metal ions on catalytic activity of both homogeneous and heterogeneous nanocluster catalysts.

2. Experimental

2.1. Materials

Poly(sodium acrylate) (PAA-Na, average molecular weight 2100; Aldrich) was used without further purification as the protective polymer for nanoclusters. A chelate resin containing iminodiacetic acid moieties (abbreviated as CR, Diaion CR-10; mean bead diameter 0.5 mm, chemical structure as shown in Fig. 1) was purchased from Mitsubishi Chemical Industry Co. One gram of the dry resin was measured by pH titration to contain 2.57 mmol of iminodiacetic acid moieties. Highly purified oxygen (99.99%) and hydrogen (99.99%) from Nippon Oxygen Co. were used for the catalytic reaction. Other reagents employed here were of a commercial G.R. grade and used as received.

2.2. Preparation

The PAA-Na (1.32 mmol in monomeric units, 40 times of the total amount of metal ion) and silver perchlorate (0.033 mmol) were mixed in ethanol/water
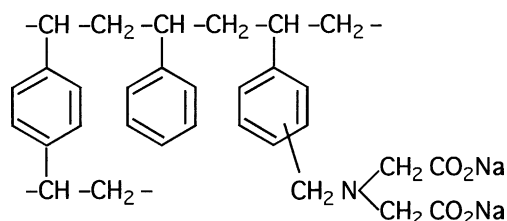

Fig. 1. Chemical structure of the chelate resin.

(1/1, v/v) to form a $50 \, cm^3$ solution. Mixed solutions in a quartz vessel were degassed by three freeze-thaw cycles, filled with pure nitrogen and then exposed to the light of an Ushio $500 \, W$ super-high-pressure mercury lamp for 1 h in a water bath maintained at 30°C. Addition of cesium and rhenium ions was conducted by mixing an aqueous solution of cesium carbonate and rhenium oxide, respectively, to the colloidal dispersion of PAA-Ag nanoclusters prepared at desired concentration.

Chelate resin-metal (CR-M) complexes were prepared by shaking a mixture of the corresponding metal chloride (3.09 mmol) and the chelate resin exchanged with sodium ions (CR-Na, 0.8 g, containing 2.06 mmol of iminodiacetate in the dry state) in water for 24 h. Then Pd(II) ion (11.4 μmol) was immobilized on each CR-M complex, followed by reduction to produce Pd nanoclusters by an aqueous solution of $LiBH_4$ (22.8 mmol), giving the chelate resin-supported Pd nanocluster catalysts containing metal ions (CR-M-Pd). The CR-M-Pd was washed with ethanol ($50 \, cm^3$) four times and dried at room temperature under vacuum.

2.3. Measurements

Ultraviolet and visible (UV–VIS) spectra were obtained at room temperature using a Shimadzu 2500PC recording spectrophotometer equipped with a 10 mm quartz cell. The PAA-Ag nanoclusters employed here were characterized by transmission electron microscopy (TEM) at 100 kV on a Hitachi H-7000 electron microscope. Samples for TEM were prepared by placing a drop of the colloidal dispersion of PAA-Ag nanoclusters onto a carbon-coated copper micro-grid for high resolution TEM (kindly provided by Dr. K. Adachi), followed by naturally evaporating the solvent. The mean diameter and standard deviation were calculated by counting the diameters of 200 particles with a magnifier (10×) on the TEM photograph of 100,000 magnifications. The Brunauer–Emmett–Teller (BET) surface area of the CR-M-Pd was measured at 77 K with a Micromeritics ASAP 2000 instrument. The sample was completely dried by heating at 95°C until the pressure in the sample tube became <10 mTorr before the measurement. The BET surface area was calculated from the amount of nitrogen adsorbed at 77 K.

2.4. Catalyses

Oxidation of ethylene, catalyzed by PAA-Ag nanoclusters, was performed in glycol under 1 atm of ethylene/oxygen (2/1, v/v). Glycol ($30 \, cm^3$) and evaporated PAA-Ag nanoclusters (0.015 mmol) were poured into a $100 \, cm^3$ flask. The mixtures were degassed by freeze-thaw cycles and were stirred under ethylene/oxygen at 170°C. After 3 h reaction, the mixtures were cooled down <10°C while stirring. The oxidation product was analyzed with a Shimadzu GC-14B gas chromatograph using a $3.1 \, m \times 3.2 \, mm$ ∅ column of TSG-1 at 60°C.

The catalytic activities of CR-M-Pd were evaluated by hydrogenation of various olefins. The catalyst (0.8 g, containing 11.4 μmol of Pd) and ethanol were placed in a flask ($50 \, cm^3$) at 30°C, the atmosphere of which was replaced in advance with hydrogen at an atmospheric pressure. Then, the reaction was started by addition of the substrate in a small amount of ethanol to give a total volume of $20 \, cm^3$ and was traced by hydrogen uptake with a temperature-controlled gas burette. The initial rate was determined by the initial slope of hydrogen uptake [25].

3. Results and discussion

3.1. Characterization of PAA-stabilized Ag nanoclusters

Colloidal silver catalysts stabilized by PAA were prepared by reduction of silver(I) perchlorate in an ethanol/water mixed solution in the presence of PAA-Na on irradiation with light, having a yellow color and being stable for months at room temperature. Since the solution of silver(I) perchlorate has no absorption above 230 nm, the reduction of Ag(I) ions to form a colloidal dispersion of PAA-Ag nanoclusters is supported by the appearance of the absorption at ca. 427 nm due to the plasmon oscillation characteristic of Ag nanoclusters (Fig. 2). Fig. 2 also shows the absorption spectra of PAA-Ag nanoclusters in the presence of Cs(I) (Fig. 2b) and Cs(I)/Re(VII) (1/1; mol/mol) ions (Fig. 2c). The absorption spectra of PAA-Ag nanocluster dispersions in the presence of Cs(I) and Cs(I)/Re(VII) ions, respectively, are in good agreement with that in the absence of metal
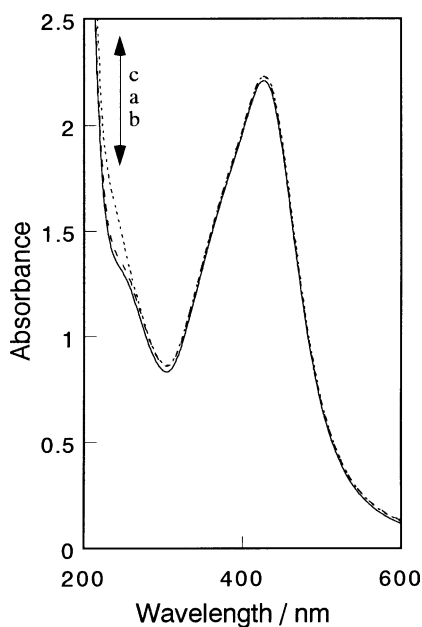
Fig. 2. UV–VIS absorption spectra of colloidal dispersions of PAA-Ag nanoclusters in the absence and presence of metal ions: (a) PAA-Ag, (b) PAA-Ag-Cs, and (c) PAA-Ag-Cs/Re. [Ag] = 0.33 mmol dm^{-3}, [PAA] = 13.2 mmol dm^{-3}, [total metal ion] = 0.033 mmol dm^{-3}, ethanol/water (1/1, v/v).
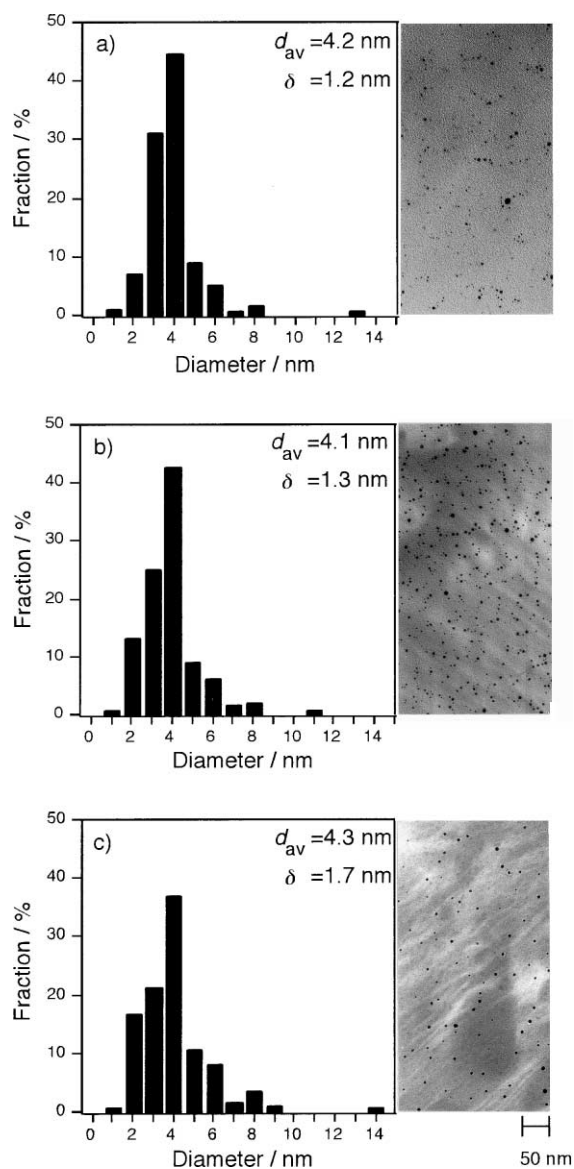

Fig. 3. Transmission electron micrographs and particle size distribution histograms of Ag nanoclusters: (a) PAA-Ag, (b) PAA-Ag-Cs, and (c) PAA-Ag-Cs/Re; d_{av}: average diameter, δ: S.D.

ions, suggesting the stability of PAA-Ag nanocluster dispersions even after the addition of metal ions. According to the Schultze–Hardy rule, the higher the concentration of electrolytes, the lower the stability of dispersions. In fact, Au nanoclusters, prepared by an aerosol method and trapped in 2-propanol, coagulated after addition of NaCl [26]. However, polymers as PAA-Na, adsorbed on the surface of metal nanoclusters by hydrophobic interactions, can prevent the aggregation of particles by steric stabilization [27,28]. The polymer molecule is considered to coordinate to the metal particle at multiple sites [29]. Although each coordination bond is weak, the multi-coordination results in strong chemical adsorption of the polymer molecule on the metal nanocluster surface. The chemical adsorption of polymers on the metal nanocluster surfaces has been evidenced by IR [30] and XPS [31] spectra. Thus, colloidal dispersions of PAA-Ag nanoclusters can keep the stability on addition of metal ions to the system by multi-coordination of PAA-Na on the Ag surface.

Fig. 3 depicts the transmission electron micrographs and the corresponding histograms indicating the particle size distributions of PAA-Ag nanoclusters in the absence and the presence of Cs(I) ions (PAA-Ag-Cs), or both Cs(I) and Re(VII) ions (PAA-Ag-Cs/Re). Particles in colloidal dispersions

of PAA-Ag nanoclusters have an average diameter of 4.2 nm. The average diameters of PAA-Ag-Cs, and PAA-Ag-Cs/Re(1/1) nanoclusters are 4.1 and 4.3 nm, respectively. The average diameters of PAA-Ag nanoclusters in the presence of metal ions are in good agreement with those in the absence, indicating the stability of PAA-Ag nanoclusters even after the addition of metal ions. This result was also supported by the constant absorption spectra independent of the presence or the absence of metal ions.

3.2. Catalysis for oxidation of ethylene

The PAA-Ag nanoclusters were applied to the catalyst for production of ethylene oxide (EO) in solution under an atmospheric pressure of ethylene and oxygen (2/1, v/v). Fig. 4 depicts the effect of metal ions upon catalytic activity of PAA-Ag nanoclusters for oxidation of ethylene. Addition of Cs(I) ions increases the catalytic activity of PAA-Ag nanoclusters. Cesium ions have been reported to show a promotive effect in the activity of industrial catalysts based on metallic Ag [19,20]. Bukhtiyarov et al. [32] reported the existence of a complex between supported Ag catalysts and Cs overlayers through oxygen on the basis of XPS and temperature programmed desorption measurements. Thus, in our case additional metal ions such as Cs(I) are considered to form stable complexes with PAA-Ag nanoclusters by the assistance of the interaction between the metal ions and ionic polymers.
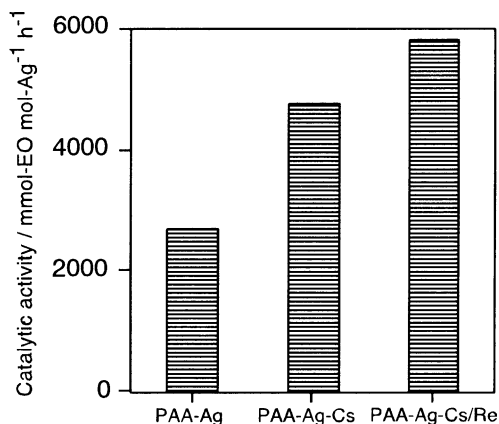

Fig. 4. Effect of metal ions upon catalytic activity of PAA-Ag nanoclusters for oxidation of ethylene; EO: ethylene oxide.
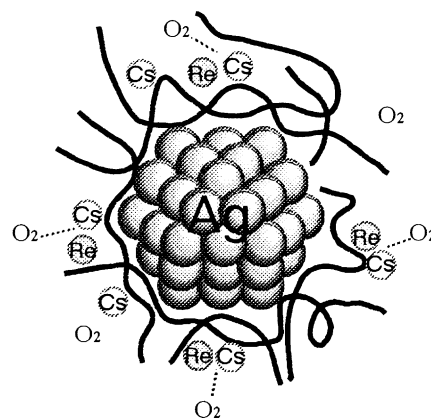

Fig. 5. Schematic model illustrating the promotive effect of metal ions on the catalytic activity of PAA-Ag nanoclusters.

The catalytic activity of PAA-Ag-Cs/Re(1/1) nanoclusters is much higher than that of PAA-Ag-Cs nanoclusters. Addition of Re(VII) ions to Ag-based industrial catalysts was reported to show promotion in selectivity [33]. The XPS analysis of Ag powder surface by Suzuki and Ayame [34] revealed that a surface oxygen concentration of Ag powders increased by a simultaneous addition of Cs(I) and Re(VII) ions to ca. five times the value of that of the single addition of Cs(I) or Re(VII) ion. They also claimed that a simultaneous addition of Cs(I) and Re(VII) ions facilitated to maintaining the Cs(I) ions surrounded by a large number of oxygen atoms. Yuan et al. [35] reported that Re(VII) ions made the adsorbed oxygen diffuse more readily into Ag surfaces. In the present reaction, Re(VII) ions, interacting with polymers, may increase oxygen concentration near Cs(I) ions neighboring PAA-Ag nanoclusters (Fig. 5). This increment of surface oxygen concentration by an ensemble effect of both Cs(I) and Re(VII) ions may be responsible for promoting the catalytic activities of not only Ag powders but also PAA-Ag nanoclusters as well.

3.3. Characterization of Pd nanoclusters supported on chelate resin-metal complexes

Immobilization of Pd(II) ion on CR-M was carried out by mixing CR-M (2.06 mmol of iminodiacetate in the dry state) with a hydrochloric acid solution of $PdCl_2$ (3.09 mmol). The supernatant changed from
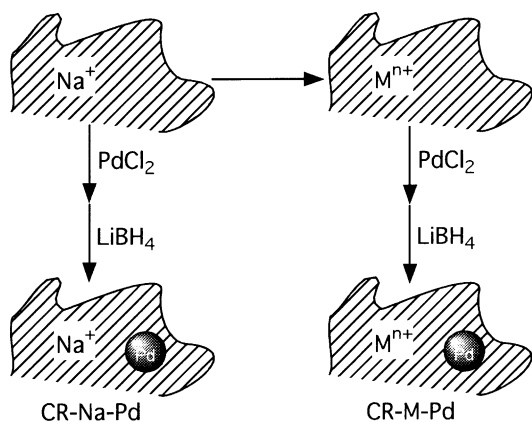
Fig. 6. Schematic illustration of the preparation processes of the Pd nanoclusters supported on chelate resin-sodium and multivalent metal ion complexes.

Fig. 7. Effect of metal ions upon specific surface area of CR-M-Pd.

yellowish brown to colorless. Immobilization of >99.9% of charged Pd(II) ions was determined by UV–VIS spectra. The heterogeneous catalysts were produced by reduction of Pd(II) ions on CR-M with lithium borohydride. The preparation process are illustrated in Fig. 6 for CR-Na-Pd and CR-M-Pd. Reduction of Pd(II) ions was confirmed by the color change from yellow to gray by treatment with lithium borohydride. In this system, the chelate resin works both as a support and as a protective polymer of the nanoclusters. CR-M, dried from ethanol, can keep the pore structure after drying and has a large surface area in the dry state. The surface area of CR-M increased as well by complexing with multivalent cations [36]. Fig. 7 shows the relationship between the specific surface area and the metal ion coordinating to iminodiacetate moieties of the chelate resin in the supported Pd nanocluster catalysts. The specific surface area of the complexed chelate resin increases with the increasing valency of the complexed metal ions as described previously [37,38]. However, the surface area of CR-Al-Pd is smaller than that of CR-Mg-Pd. The ionic condition of CR-M(III) was found to be different from that of the CR-Mg complex [17,39], which probably caused the difference in the immobilization behavior of Pd(II) ions. The amount of Na(I) and Mg(II) ions taken-up is exactly balanced with that of the anionic group of the resin, whereas the amount of M(III) ions adsorbed exceeds it, resulting in a surplus of positive charge. The an-
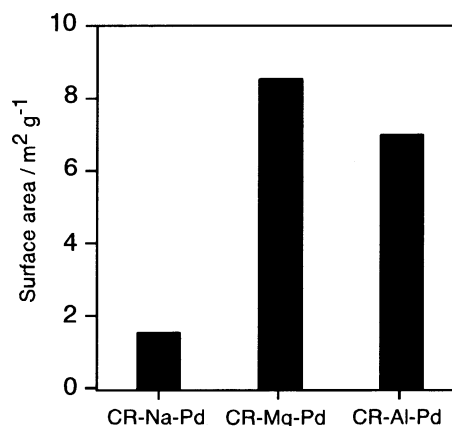
ionic Pd(II) ions can approach CR-Mg by diffusion and distributes only on the surface of CR-Mg. In the case of Al(III) ions, however, the surplus of the positive charge is responsible for the interaction of the CR-Al with Pd(II) ions. It was supported by the TEM photographs of CR-Mg-Pd and CR-Al-Pd [18].

3.4. Catalysis for hydrogenation of olefins

Table 1 shows the hydrogenation rate catalyzed by CR-M-Pd under 1 atm of hydrogen at 30°C. The catalytic activity increases in the order of CR-Na-Pd < CR-Mg-Pd, which is the same as that of the increasing surface area of the catalyst. The high catalytic activity of palladium nanoclusters, supported on chelate resin-metal complex, is considered to be due to the increase in the surface area of the catalyst as shown in Fig. 7. Although CR-Al-Pd has much larger surface area than CR-Na-Pd, CR-Al-Pd has a lower activity than those of CR-Na-Pd and CR-Mg-Pd. The

Table 1
Catalytic activities for hydrogenation of various olefins[a]

Substrate	Catalytic activity (mmol-H_2 mol-Pd^{-1} s^{-1})		
	CR-Na-Pd	CR-Mg-Pd	CR-Al-Pd
Acrylic acid	151	166	120
COD[b]	122	144	63.5
1-Hexene	77.0	109	61.4

[a] Conditions: substrate, 0.5 mmol; Pd, 11.4 μmol in ethanol (30°C).
[b] COD: 1,3-Cyclooctadiene.

palladium nanoclusters were located near the surface of CR-Na-Pd or CR-Mg-Pd, whereas they were distributed uniformly inside of the CR-Al-Pd catalyst [18]. Therefore, hydrogen and the substrate can easily approach the palladium nanoclusters on the surface of CR-Na-Pd or CR-Mg-Pd, while it is not easy for them to approach the palladium nanoclusters inside the CR-Al-Pd. This is a reason why CR-Al-Pd has a larger surface area but a lower catalytic activity than CR-Na-Pd.

Instead of Al ion lanthanoid ions (abbreviated as Ln) were used as trivalent metal ions in the CR-immobilized Pd nanocluster catalysts. The catalytic activity of CR-M-Pd can be increased by the use of lanthanoid ions on this reaction system. Fig. 8 depicts the relationship between the catalytic activity for hydrogenation of acrylic acid and the kind of lanthanoid ions. The CR-Ln-Pd shows 1.2–1.4 times higher catalytic activity than CR-Al-Pd; the catalytic activity of CR-Nd-Pd is the highest among the CR-Ln-Pd. Li and Binglin [40] found the promotive effect of anchored lanthanoid ions upon the hydrogenation activity of the palladium catalyst supported on the resin beads. However, CR-Lu-Pd has lower catalytic activity than that expected. The surface area of CR-Lu-Pd $(5.62 \, m^2 \, g^{-1})$ [18] was smaller than that of CR-Al-Pd $(6.97 \, m^2 \, g^{-1}$ in Fig. 7). Thus, a direct comparison between CR-Ln-Pd and CR-Al-Pd is not reasonable because they have different surface area.

In order to investigate the interaction between lanthanoid ions and palladium particles, the hydro-
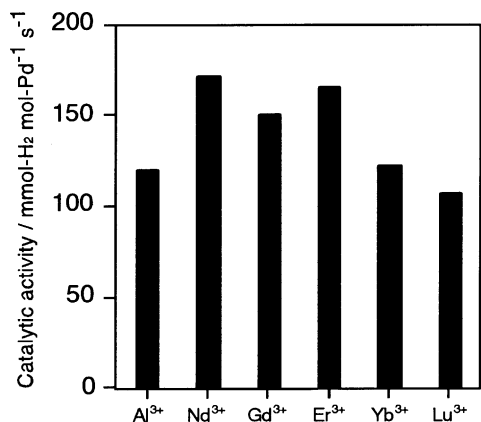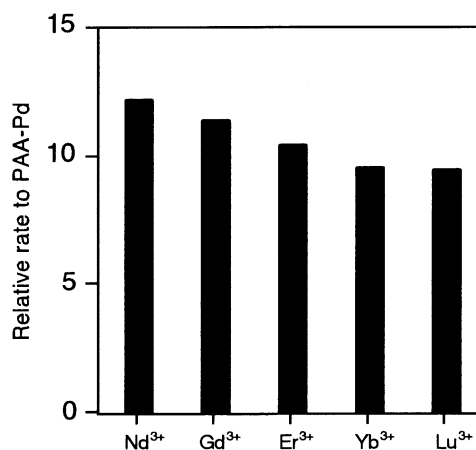

Fig. 9. Effect of lanthanoid ions upon catalytic activity of PAA-Pd-M nanoclusters for hydrogenation of acrylic acid.

genation in ethanol, catalyzed by the homogeneous PAA-stabilized Pd (PAA-Pd) nanoclusters, was carried out in the presence of lanthanoid ions (abbreviated as PAA-Pd-Ln). Fig. 9 shows the effect of various lanthanoid ions upon the catalytic activity of PAA-Pd-Ln for hydrogenation of acrylic acid. All PAA-Pd-Ln nanoclusters show catalytic activities about 10 times higher than PAA-Pd. The rate of hydrogenation catalyzed by PAA-Pd-Ln is much higher than that by CR-Ln-Pd. The high catalytic activity of PAA-Pd-Ln nanoclusters may be attributed to the concentration of lanthanoid ions and then the concentration of substrates by a similar effect as in the case of PAA-Ag nanoclusters described above. An electrostatic interaction between lanthanoid ions and PAA has been evidenced by IR and ICP analysis [41,42]. Thus, it is concluded that the promotive effect of CR-Ln-Pd is achieved both by its large surface area and by the concentration of substrates near Pd nanoclusters by the interaction of lanthanoid ions with the oxygen-containing substrates.

The durability of CR-Nd-Pd, repeatedly used for hydrogenation of acrylic acid, is presented in Fig. 10. The CR-Nd-Pd can be separated easily from the mixtures by filtration or decantation and are stable throughout the reaction as well as during the recovery procedures. The CR-Nd-Pd retains 80% of the initial activity even in the third run. These results demonstrated that the linkage responsible for the immobilization is sufficiently firm. Aggregation of palladium nanoclusters

Fig. 8. Effect of metal ions upon catalytic activity of CR-M-Pd for hydrogenation of acrylic acid.
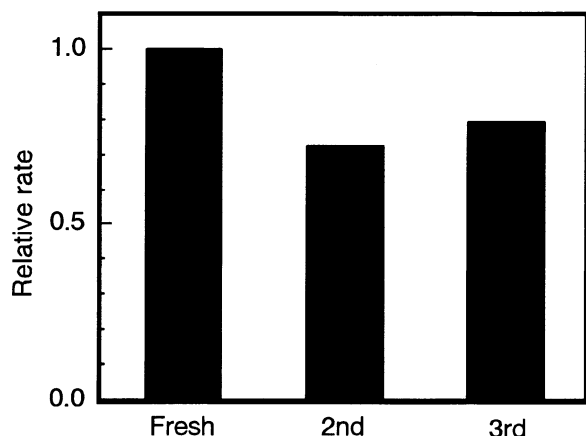
Fig. 10. Repeated usage of CR-Nd-Pd for hydrogenation of acrylic acid.

can be efficiently prevented by the immobilization if the nanoclusters are discretely immobilized on the support. This may be the most important contribution to the high durability of immobilized metal nanocluster.

4. Conclusions

Polymer-stabilized metal nanoclusters were prepared by using linear ionic polymers (PAA-Na) and crosslinked ionic resins (CR). They can be used as a homogeneous and a heterogeneous catalyst, respectively. These polymers play not only a role of stabilization of metal nanoclusters, but also a role of immobilization of additional metal ions by electrostatic interactions. The immobilized metal ions play various roles. Among them, the Cs(I) ions are known to interact with oxygen atoms. Thus, in the case of a homogeneous catalyst of PAA-Ag nanoclusters, Cs(I) ions interacted with molecular oxygen to promote the oxidation of ethylene to form ethylene oxide. Further, simultaneous addition of Cs(I) and Re(VII) ions eminently increased the catalytic activity. Since the additional metal ions such as Cs(I) and Re(VII) ions form stable complexes with PAA-Ag nanoclusters by the assistance of the interaction between the metal ions and ionic polymers, the increase of catalytic activity can be attributed to the increment of oxygen concentration by the ensemble effect of both Cs(I) and Re(VII) ions located near the Ag nanoclusters. On the other hand,

in the case of CR-M-Pd as a heterogeneous catalyst for hydrogenation of olefins, metal ions can be related to both the specific surface area of catalyst and the concentration effect of substrates as in the case of PAA-Ag nanoclusters. The surface area of CR-M-Pd increased by complexing with multivalent cations. The catalytic activity for hydrogenation was improved by addition of lanthanoid ions to the chelate resin system, which might be attributed to the concentration of substrates around the Pd nanoclusters by the interaction of lanthanoid ions with the oxygen-containing substrates.

Acknowledgements

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