NO decomposition by ultrafine noble metals dispersed on the rare earth phosphate hollow particles

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Novel fine polymer particles containing ultrafine Pd, Pt or Rh metal dispersed on the core-shell [core, poly(styrene-*co*-acrylamide) or poly(styrene-*co*-acrylic acid); shell, $LnPO_4(Ln = Ce, Nd, Pr, Sm, La)$] type microsphere were prepared by the emulsifier-free emulsion polymerization of styrene with acrylamide or acrylic acid followed by the addition of $PdCl_2$, $HPtCl_6$, or $RhCl_3$ and finally by the addition of a mixture of $Ln(NO_3)_3$ and NaH_2PO_4. Pyrolysis of the resulting polymer particles at 700–900°C provides polymer-free hollow particles (diameter 450–550 nm) composed of noble metals and $LnPO_4$. The excellent catalytic reduction of NO gas into N_2 and O_2 was observed at 500–700°C using the rersulting particles as catalyst. © 2000 Kluwer Academic Publishers

1. Introduction

Selective catalytic decomposition of nitrogen monoxide into N_2 and O_2 by ultrafine transition metals supported by metal oxide have been extensively studied [1–6]. Alumina is known as an excellent oxide support to result in enhanced N_2 formation [7, 8]. For example, Co(5 wt%)/Al_2O_3 showed high activity as compared with Fe(5 wt%)/Al_2O_3 or Ni(5 wt%)/Al_2O_3 in the presence of ethene and oxygen [9]. On the other hand, selective decomposition of nitrogen oxides under lean-burn conditions has been reported by noble metal catalysts such as Pt/$AlPO_4$, Pt/B_2O_3/SiO_2/Al_2O_3 in the presence of C_3H_6 [10], Pt or Pd/Al_2O_3 [11], and Pt/Al_2O_3 in the presence of C_3H_8 at 1000°C [12]. Co or Ni/Zr/noble metal and Pd/Ni-valve metal (Ta, Nb, Zr) alloy systems show higher activities for the NO decomposition [13]. Very high activity was achieved at low temperature by secondary injection of clean-burning thermal promotor such as MeOH in the Pt/Al_2O_3 catalytic system [14]. Selective reduction of NO_2 in the presence of SO_2 was observed using Cu/Al_2O_3 as catalyst, while that of NO was not so high [15]. Rh/Al_2O_3 catalyst is reported to be very active for both reduction of NO_x and oxidation of CO [16–21]. Thus the catalytic systems containing noble metals generally exhibit higher catalytic activity than the systems containing Fe, Co, and Ni metals. Excellent review concerning the decomposition of NO_x into N_2 by alumina supported metals should be consulted [22].

Catalytic decomposition of NO over valency-controlled Ln_2CuO_4-based mixed oxide [23–26], Ag particles supported by Co_3O_4 [27], Rh/pillared clay [28], metal-ZSM-5 [29–32] and metal/carbonaceous materials [33–39] are also reported. This paper describes the excellent catalytic activity of ultrafine Pd, Pt, and Rh metals dispersed on the surface of fine particles of $LnPO_4$ for the decomposition of NO to N_2 to O_2. Aims of this paper lies in the evaluation of the absolute catalysis of the present hollow particles in the absence of CO, CO_2 and hydrocarbons as compared with that of well known Pt/A_2lO_3 catalyst.

2. Experimental procedure
2.1. General

Measurement of transmission electron micrograph (TEM) was carried out on a Topcon E-002B transmission electron micrscope, using the particles dispersed on the water. Scanning electron micrograph (SEM) was measured on a Hitachi S-2150 instrument. X-ray diffraction analyses (XRD) were performed on a Rigaku RDA-1A instrument equipped with a Rigaku CN4036A2 X-ray generator using Cu K_α radiation ($\rho = 1.5418$ Å, 40 kV, 30 mA). Particle induced X-ray emission analysis (PIXE) was performed on a van de Graff accelerator system in Hiroshima University using proton radiation. Thermal analysis was performed on a Seiko SSC 5100 DSC-22C apparatus, where the

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polymer samples (ca. 6 mg for each) were heated at a rate of $10°C/min$ from $0°C$ to $400°C$ in nitrogen stream. T_g values were obtained upon the second heating. X-ray photoelectron spectroscopy (XPS) was conducted on a Perkin Elmer ESCA 5400MC instrument with a magnesium K_α source (1254.8 eV).

2.2. Materials

Styrene was dried over CaH_2 and purified by distillation under reduced pressure in argon stream. Acrylamide was recrystallized from acetone and dried in air. Acrylic acid was purified by distillation in vacuo after drying over CaH_2. Potassium persulfate (KPS) was recrystallized from water and dried in vacuo. Palladium(II) sodium chloride, palladium(II) nitrate, chromium(III) nitrate nonahydrate, lanthanide(III) nitrate hexahydrate (Wako), rhodium(III) chloride trihydrate (Mitsuwa) and iron(III) nitrate enneahydrate were purchased and used without further purification.

2.3. Preparation of poly (styrene-*co*-acrylamide) fine particles

Degass of water (500 ml) placed in a three necked flask (1000 ml) equipped with a condenser and magnetic stir bar was performed under reduced pressure. The container was purged with argon gas and the water was heated to $70°C$. A mixture of acrylamide (8.5 g, 0.12 mol) dissolved in 20 ml of water and styrene (55 ml, 0.53 mol) was added to the above mentioned water with stirring. Then KPS (160 mg, 1 mmol) dissolved in 20 ml of water was added to this mixture and the resulting mixture was stirred at $70°C$ for 6 h. Resulting large aggregates were filtered off using a 2G glass filter. The dispersion of poly(styrene-*co*-acrylamide) fine particles thus obtained was centrifuged for 30 min at 15000 rpm, and the precipitates were dispersed again in water using an ultrasonic vibrator to give the particles with diameter of 364 ± 8 nm in 88% yield.

2.4. Preparation of poly(styrene-*co*-acrylic acid) fine particles

Degass of water (500 ml) placed in a three necked flask (1000 ml) equipped with a condenser and magnetic stir bar was performed under reduced pressure. The container was purged with argon gas and the water was heated to $70°C$ with stirring. Acrylic acid (8.2 ml, 0.12 mol) and styrene (55 ml, 0.53 mol) were added to the water. KPS (160 mg, 1 mmol) dissolved in 20 ml of water was added to this mixture and the resulting mixture was kept at $70°C$ for 6 h with stirring at 300 rpm. Large aggregates were filtered off, and the resulting dispersion of poly(styrene-*co*-acrylic acid) fine particles were centrifuged for 30 min at 15000 rpm. Then, the precipitates were dispersed again in water using an ultrasonic vibrator to give the particles with the diameter of 389 ± 10 nm in 89% yield.

2.5. Preparation of fine polymer particles containing Pd, Pt and Rh metals

Tin(II) dichloride (3.8 g, 0.2 mol) dissolved in water (100 ml) was added to the dispersion of fine poly(styrene-*co*-acrylamide) particles or poly(styrene-*co*-acrylic acid) (1.0 g) in 150 ml water and the mixture was stirred for 1 h at room temperature. The dispersion was centrifuged for 30 min at 15000 rpm and precipitates were dispersed again in deionized water. This procedure was repeated two times. To the precipitate dispersed in 180 ml of water was then added palladium(II) chloride (0.58 g, 10 mmol) dissolved in 20 ml of water. Then the dispersion was stirred for 3 h at room temperature and the solution was centrifuged for 30 min at 15000 rpm. During this treatment, Pd fine particles was produced by reduction with tin(II) dichloride. In a similar manner, preparation of fine polymer particles containing Pt and Rh metal was performed using hydrogen hexachloroplatinate ($HPtCl_6$, 0.26 g, 10 mmol) and rhodium trichloride (0.13 g, 10 mmol), respectively.

2.6. Preparation of ultrafine Pd, Pt, or Rh particles dispersed on the polymer/$LnPO_4$ (Ln = Sm, Pr, La) particles

Into a dispersion of fine polymer particles (5.0 ml aqueous dispersion containing 0.15 g particles) was added a poly(vinyl alcohol) (0.3 g) aqueous solution (10 ml). Then a mixture of powdered $Sm(NO_3)_3 \cdot 6H_2O$ (1.1 g 2.5 mmol) and $NaH_2PO_4 \cdot H_2O$ (0.27 g, 2.5 mmol) dissolved in 9.0 ml of water was added to the above mentioned dispersion and the mixture was stirred for 3 h at $90°C$. The resulting fine polymer particles coated with $SmPO_4$ was purified by centrifugation of the precipitates for 15 min at 10000 rpm followed by redispersion in water using ultrasonic vibrator. In a similar manner, polymer particles containing other lanthanide phosphate/Pd, Pt or Rh were prepared using corresponding lanthanide nitrates such as $Pr(NO_3)_3$ and $La(NO_3)_3$ and NaH_2PO_4.

2.7. Preparation of Pd paticles dispersed on the polymer/MPO_4 (M = Al, Mg, Zn, Cr, Mn, Fe, Co) particle

Into a dispersion of fine poly(styrene-*co*-acrylic acid) particles (5.0 ml aqueous dispersion containing 0.2 g particles) was added poly(vinyl alcohol) (0.3 g) aqueous solution (10 ml). Then a mixture of $Mg(NO_3)_2 \cdot 6H_2O$ (0.64 g, 2.5 mmol), $AlCl_3$ (0.33 g, 2.5 mmol), $ZnCl_2$ (0.34 g, 2.5 mmol), $KCr(SO_4)_2 \cdot 12H_2O$ (1.25 g, 2.5 mmol), $Mn(NO_3)_2 \cdot 6H_2O$ (0.72 g, 2.5 mmol), $Co(NO_3)_2 \cdot 6H_2O$ (0.72 g, 2.5 mmol), or $Fe(NO_3)_3 \cdot 9H_2O$ (1.01 g, 2.5 mmol) and $NaH_2PO_4 \cdot H_2O$ (0.26g, 2.5 mmol) dissolved in 10 ml of water was added to the dispersion. Then the mixture was stirred at $90°C$ for 3 h. The resulting dispersion was centrifuged for 15 min at 15000 rpm, and the precipitates were redispersed in water using an ultrasonic vibrator. This procedure was repeated 3 times.

2.8. Preparation of noble metal particles on a powdery lanthanide phosphate

Powdery rare earth phosphates were prepared by the addition of the aqueous solution of rare earth nitrate to sodium dihydrogenphosphate($Ln^{3+}/PO_4^{3-} = 1.0$ molar

ratio). The resulting precipitate was dried *in vacuo* and calcinated in air for 5 min at 900°C. Noble metal/LnPO$_4$ particles were prepared by impregnation of noble metal chloride (Na$_2$PdCl$_6$, H$_2$PtCl$_6$, RhCl$_3$) solution to the LnPO$_4$ solid followed by reduction at 0°C with formarine. These noble metal chlorides were loaded in 1, 3 and 5 mol% of LnPO$_4$. Resulting noble metal/LnPO$_4$ was washed with water and dried *in vacuo*.

2.9. Heat treatment

Pyrolysis of the resulting particles was conducted between 700°C and 1000°C in air using a combustion tube (Nippon Kogaku Togyo Co. Ltd., NC-14; inside diameter 70 mm, length 600 mm) in a kanthal conbustion furnace (Motoyama TKW-11-1040, 200 V/3.7 kW). The temperature was monitored by a sheathed thermocouple (type R, Pt-Rh) attached to the furnace and controlled by a digital program unit (Chin KP-113) and a thyristor unit (Sansa Elec. Co. VDI-2020). Heat-treatment of polymer/LnPO$_4$ particles (0.3–1.0 g) was conducted in a ceramic dish in a combustion tube at fixed temperatures (700, 900, 1000°C) for 15 min.

2.10. Catalytic activity for the direct decomposition of NO

The catalytic activity for the decomposition of NO was examined using a fixed bed flow reactor. NO gas (2480 ppm) in He was fed into 30 mg catalyst bed at the rate of 12 ml/min. The activity was measured at temperatures between 400 and 700°C, after reaching steady-state. The resulting gas composition of NO was analyzed to be N$_2$ and O$_2$ on a Shimadzu QP-1000 mass fragmentgraph.

3. Results and discussion
3.1. Preparation of ultrafine noble metal particle dispersed on the rare earth metal phosphate hollow particles

We have developed novel method for the preparation of hollow particles of LnPO$_4$ which disperse ultrafine noble metal particle on its surface uniformly. As an application of this particle, we have demonstrated here the catalytic NO decomposition in the absence of hydrocarbon and CO to evaluate the exact catalytic action of noble metal/LnPO$_4$ particle, to compare with commercially available Pt/Al$_2$O$_3$. The use of the present particle in place of conventional powdery Al$_2$O$_3$ or LnPO$_4$ is expected to result in higher catalytic activity, reflecting its high surface area.

Emulsifier-free emulsion copolymerization of styrene with acrylic acid (4 : 1 ratio) by K$_2$S$_2$O$_8$ (pottasium persulfate) in deionized water produces the fine polymer particles with particle size of 281–413 Å in diameter (Scheme 1). Resulting particles were treated with SnCl$_2$ and then with PdCl$_2$, H$_2$PtCl$_6$ or RhCl$_3$ in water for 1 h. The metal chloride was reduced with SnCl$_2$ to M(0). Activated fine polymer particles thus obtained contained 0.1–0.8 wt% of Pd, 0.1–0.7 wt% of Pt, and 0.08–0.6 wt% of Rh metal as determined by the XRD and PIXE analyses. The result of ICP analysis agreed well with that obtained by PIXE measurement. TEM analysis tells us that the diameter of Pd, Pt and Rh metal is <1.3, <1.0 and <1.5 nm, respectively. Then the polymer particles were treated with a mixture of Ln(NO$_3$)$_3$ and sodium dihydrogen-phosphate (NaH$_2$PO$_4$) to generate the core shell type polymer particles (core, poly(styrene-*co*-acrylic acid; shell LnPO$_4$) upon heating to 90°C. Thus polymer particles surrounded by light lanthanide phosphate LnPO$_4$ (thickness 22–55 nm) were obtained. Fig. 1 shows the appearance of poly(styrene-*co*-acrylamide)/Pd/CePO$_4$ (1a), poly(styrene-*co*-acrylamide)/Pd/NdPO$_4$ (1b), poly(styrene-*co*-acrylic acid)/Pd/SmPO$_4$ (1c), and poly(styrene-*co*-acrylic acid)/Pd/LaPO$_4$ (1d) particles. The XRD patterns reveal the formation of CePO$_4$·H$_2$O, NdPO$_4$·0.5H$_2$O, SmPO$_4$·H$_2$O and LaPO$_4$·H$_2$O. Table I shows the result of core-shell particles composed of polymer and pd/LnPO$_4$. In contrast to these, heavy lanthanide phosphate could not form the stable layer (shell), presumably due to the formation of churchite type salts, while light lanthanide generally forms rhabdophene type salts, which show rather strong interaction with carboxylate or amide group. Fig. 2 shows the appearance of Eu, Tb, Er and Yb phosphate particles covered slightly on the surface of polymer/Pd particles. The amount of immobilized Pd, Pt and Rh
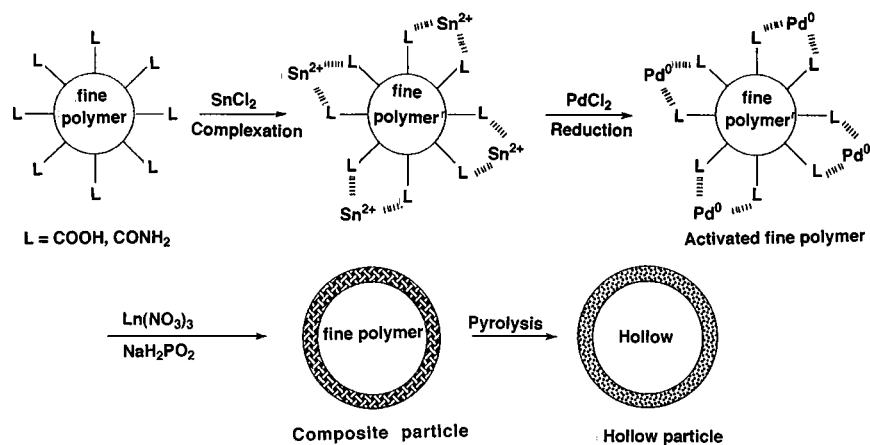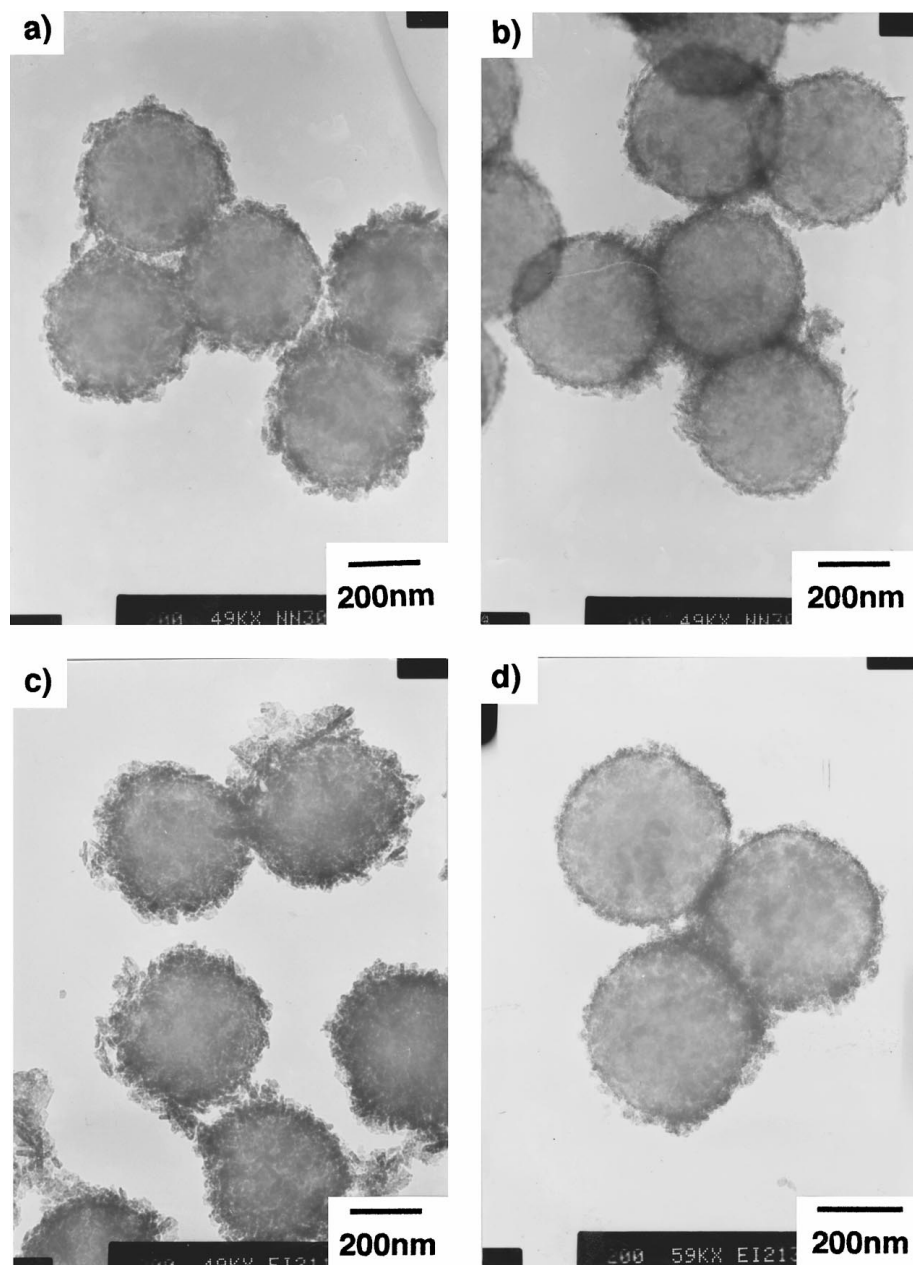

Scheme 1

Figure 1 TEM profiles of poly(styrene-*co*-acrylamide)/Pd/CePO$_4$ (a), poly(styrene-*co*-acrylamide)/Pd/NdPO$_4$ (b), poly(styrene-*co*-acrylic acid)/Pd/SmPO$_4$ (c), poly(styrene-*co*-acrylic acid)/Pd/LaPO$_4$ (d) before pyrolysis.

TABLE I Preparation of polymer/Pd/LnPO$_4$ particles

Metal	Ln(NO$_3$)$_3$ (mol/1)	NaH$_2$PO$_2$ (mol/1)	Particles (g/1)	Particle size (nm)	Shell thickness (nm)
Ce	0.063	0.063	7.5	449	53.5
	0.125	0.125	7.5	490	62.7
Nd	0.063	0.063	7.5	413	50.3
	0.125	0.125	7.5	447	62.0
Pr	0.063	0.063	7.5	508	61.6
	0.125	0.125	7.5	531	70.8
Sm	0.125	0.125	7.5	490	50.2
	0.125	0.125	20.0	433	42.1
La	0.125	0.125	7.5	479	48.3
	0.125	0.125	20.0	423	28.5

metal is 0.53, 0.21 and 0.28 wt% for the poly(styrene-*co*-acrylamide) system and 0.41–0.56, 0.22 and 0.21 wt%, respectively, for poly(styrene-*co*-acrylic acid) system (feed amount 10 mmol).

When the feed amount of noble metal (Pd) was decreased to 1.0–0.1 mmol from 10 mmol, the diamter of resulting particles decreased (from 531 to 436 nm) and the shell surrounding the particles turns to very thin (from 70.8 to 22.4 nm).

3.2. Preparation of ultrafine Pd particles supported by other metal phosphates

We have also examined the preparation of Pd particles dispersed on the surface of poly(styrene-*co*-acrylic acid)/other metal phosphates such as Mg, Zn, Cr, Fe etc. The formation of magnesium hydrogenphosphate MgHPO$_4$ on the polymer particle was recognized only in the alkaline conditions (pH 9–10), where the shell is attached to the polymer particles in the heterogeneous manner. Its XRD analysis clearly shows the formation of MgHPO$_4$ (Fig. 3). The addition of a mixture
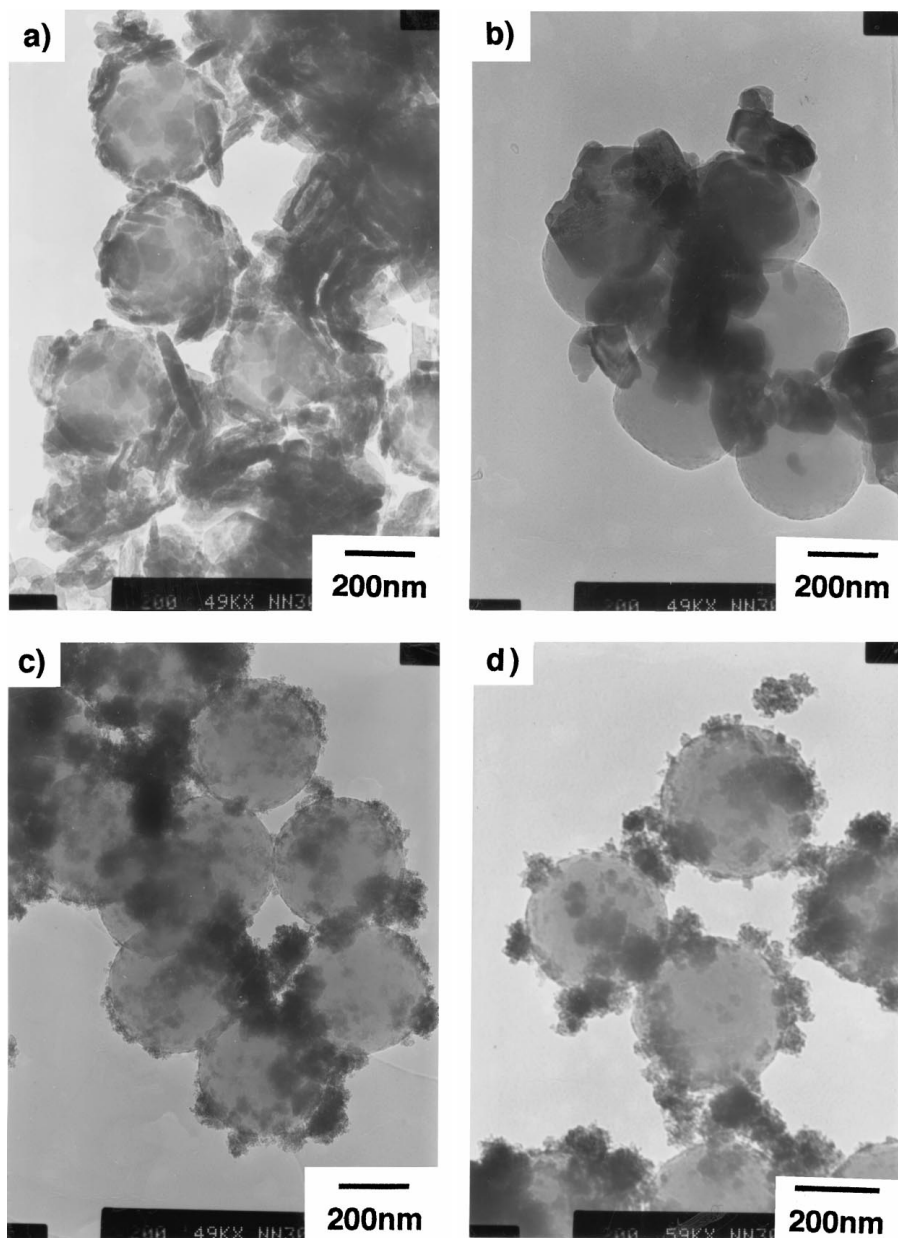
Figure 2 TEM profiles of poly(styrene-*co*-acrylic acid)/Pd/EuPO$_4$ (a), poly(styrene-*co*-acrylic acid)/Pd/TbPO$_4$ (b), poly(styrene-*co*-acrylic acid)/Pd/ErPO$_4$ (c), poly(styrene-*co*-acrylic acid)/Pd/YbPO$_4$ (d).
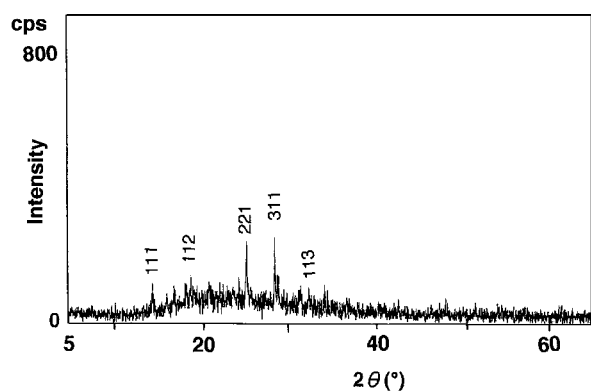

Figure 3 XRD pattern of poly(styrene-co-acrylic ascid)/Pd/MgHPO$_4$ particle.

of ZnCl$_2$ and NaH$_2$PO$_4$ on the polymer particles brings about the formation of thin Zn$_3$(PO$_4$)$_2$, when the reaction was carried out in slightly alkaline conditions at 0°C. Prolonged reaction did not change the thickness.

The addition of a mixture of AlCl$_3$ with NaH$_2$PO$_4$ resulted in the formation of needle like AlPO$_4$. The addition of CrK(SO$_4$)·12H$_2$O with NaH$_2$PO$_4$ resulted in the formation of green cromium shell, but the identification of cromium compound by XRD was still unsuccessful because the shell is amorphous.

3.3. Pyrolysis of noble metal/polymer/rare earth phosphate particles

The resulting polymer particles were pyrolyzed at 700–1000°C to liberate organic polymer unit. Remained particles are composed of only LnPO$_4$ and noble metal (Pd, Pt, or Rh) as evidenced by elemental analyses (C, H and N contents <0.3% in every cases). BET specific surface area of the resulting materials ranges from 42 to 53 m^2/g. The spherical shape is maintained after pyrolysis as evidenced by the TEM measurement and the structure of LnPO$_4$ was not changed as revealed

by XRD spectra. The size of hollow particles and the Pd content thus obtained are summarized in Table II, and the appearance of particles is shown in Fig. 4. The diameter of the particle significantly shrinks and the

TABLE II Pyrolysis of polymer/Pd/LnPO$_4$ particles

Metal	Ln(NO$_3$)$_3$ (mol/1)	NaH$_2$PO$_2$ (mol/1)	Particles (g/1)	Particle size (nm)	Shell thickness (nm)	Pd content (wt%)
Ce	0.063	0.063	7.5	435	49.5	0.32
	0.125	0.125	7.5	456	51.5	0.20
Nd	0.063	0.063	7.5	409	45.6	0.70
	0.125	0.125	7.5	423	58.5	0.47
Pr	0.063	0.063	7.5	473	49.7	0.52
	0.125	0.125	7.5	512	53.5	0.37
Sm	0.125	0.125	7.5	467	49.8	0.18
	0.125	0.125	20.0	421	38.5	0.45
La	0.125	0.125	7.5	453	45.3	0.19
	0.0125	0.125	20.0	419	23.2	0.40

thickness of the shell becomes thin. During this procedure, noble metal oozed out from the inside to the outside of the particles. As an evidence, XPS profiles of poly(styrene-co-acrylic acid)/Pd/CePO$_4$ before and after pyrolysis at 900°C are shown in Fig. 5.

Although no appreciable peak was observed before pyrolysis, the 3d peak of Pd metal (Fig. 5b) was observed after pyrolysis. The exact value shifted to 338.4 eV from 334.9 eV (standard Pd metal), presumably due to the weak interaction between CePO$_4$ and Pd metal, while no shift was observed for Ce 3d (888.4 ± 1 eV), P 2p (133.5 ± 2 eV), and O 1s (533 ± 1.5 eV). When poly(styrene-co-acrylic acid) (4 : 1)/ Pd/A1PO$_4$ particles were pyrolyzed at 900°C, hollow particles (diameter 510 nm) composed of needle like A1PO$_4$ was obtained. In this case, hollow carbon particles attached to the resulting needle like A1PO$_4$ should be formed, because the elemental analysis shows the exsistence of 3.2% carbon. The Pd content is 1.2 wt% (calcd. 1.4 wt%) and the XRD analysis
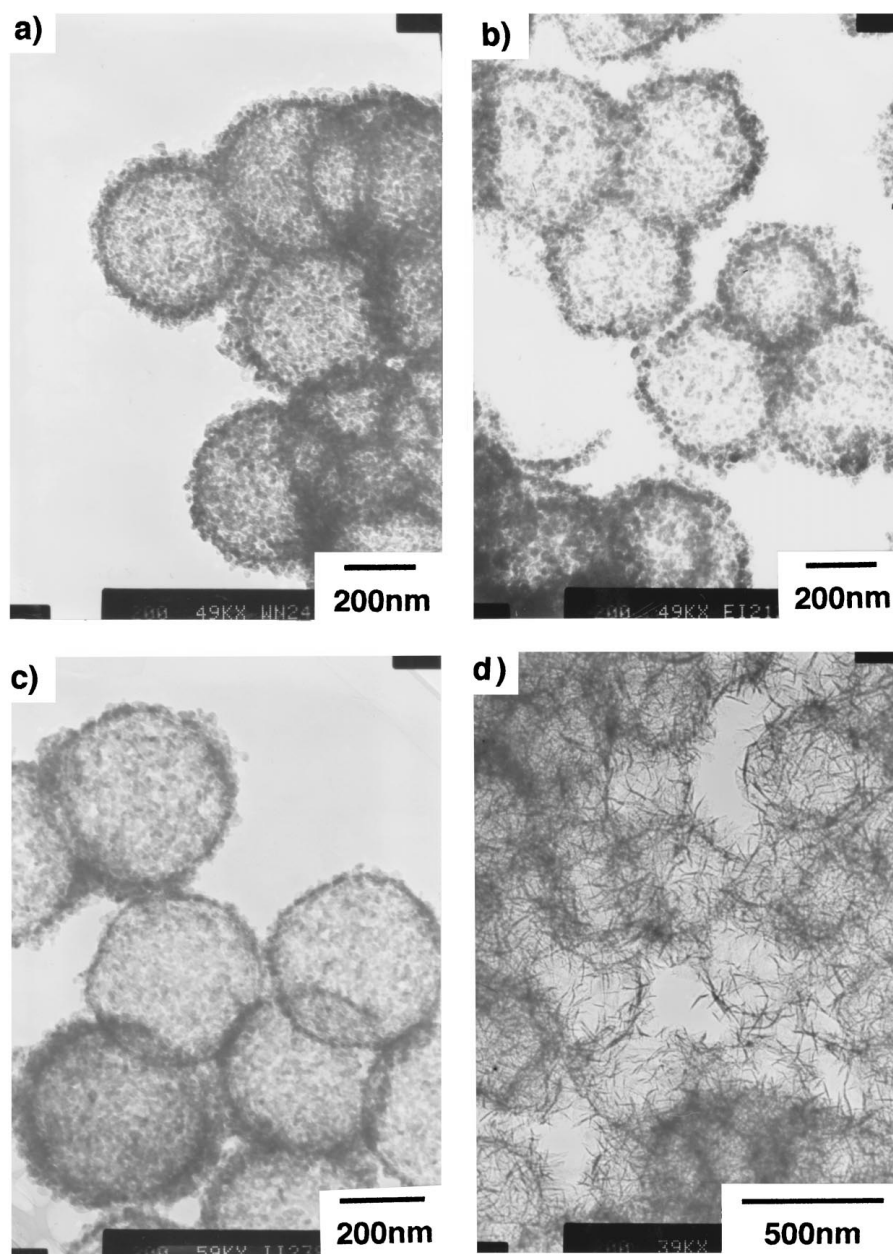

Figure 4 TEM profiles of poly(styrene-co-acrylic acid)/Pd/PrPO$_4$ (a), poly(styrene-co-acrylic acid)/Pd/SmPO$_4$ (b), poly(styrene-co-acrylic acid)/Pd/LaPO$_4$ (c), and poly(styrene-co-acrylic acid)/Pd/AlPO$_4$ (d) after pyrolysis.

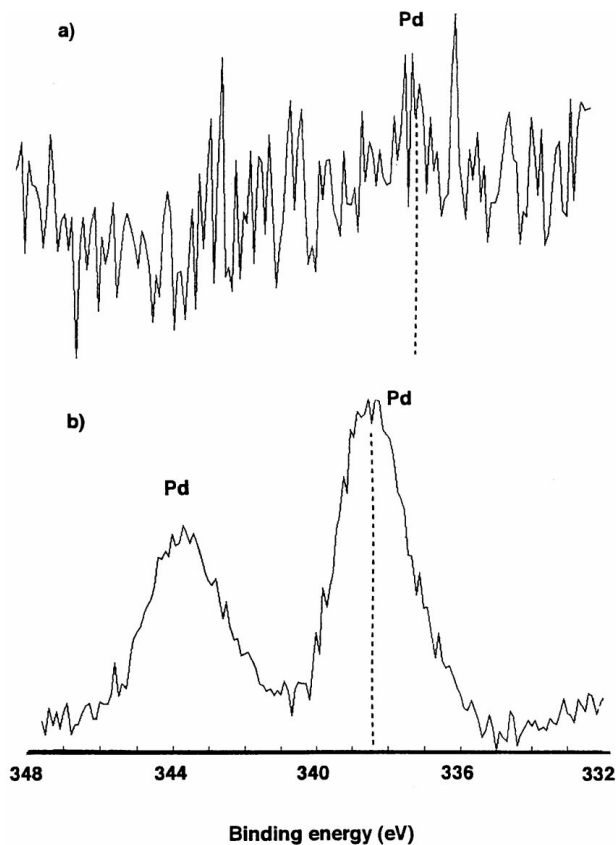Figure 5 ESCA spectra of poly(styrene-*co*-acrylamide)/Pd/CePO$_4$ particles before (a) and after (b) pyrolysis.

revealed the maintenance of AlPO$_4$ structure. The pyrolysis of poly(styrene-*co*-acrylic acid)/Pd/CrPO$_4$ resulted hollow particles composed of a mixture of CrPO$_4$/Pd and Cr$_2$O$_3$/Pd as analyzed by XPS (Cr 3d 578.4 eV, P 2p 1325.0 eV, O 1s 533.4 eV, Pd 3d 339.4 eV) and XRD (the formation of crystalline Cr$_2$O$_3$). The carbon content is 3.5%. Therefore, the hollow particles should be formed on the thin carbon hollow particle.

3.4. NO decomposition by LnPO$_4$/Pd hollow particles

Temperature dependent activity for the NO decomposition into N$_2$ and O$_2$ by SmPO$_4$/Pd particles (diameter 377-547Å) is given in Fig. 6. Sm-1 system contained 0.88 wt% of Pd is active at the temperature range of 500–700°C while Sm-3 (Pd content 0.35 wt%) and Sm-4 (Pd content 0.2 wt%) systems showed much lower activity. The activity observed for Sm-1 system is nealy the same as commercially available Pt(1 wt%) particles supported by Al$_2$O$_3$ (pre-reaction surface area 226 m^2, metal-surface area 0.48 m^2/g, Pt particle diamter 1.7 nm). Similarly LaPO$_4$/Pd particles show high activity at 700°C (Fig. 7). The NO conversion by PrPO$_4$/Pd hollow particles (Pd content, 0.21 wt%) was 17% and that by LaPO$_4$/Pd (Pd content, 0.58 wt%) was 15%. However, CePO$_4$/Pd and NdPO$_4$/Pd particles actually show no catalysis at 400–700°C, although these particles contain 0.2–0.7 wt% Pd metal (the reason is not clear at present). Among the metal phosphate other than rare earth phosphate, only the AlPO$_4$/Pd par-
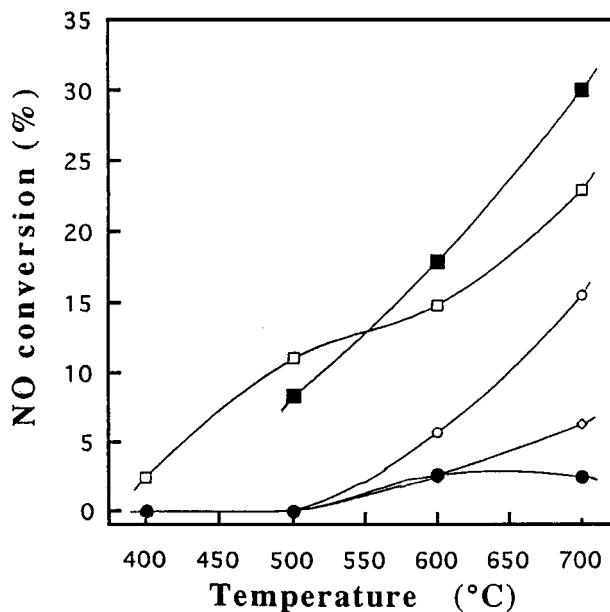

Figure 6 Catalytic reduction of NO using SmPO$_4$/Pd hollow particle, a) Pd content, 0.88 (□) wt%, b) 0.82% (○), c) 0.35 wt% (◇), d) 0.2 wt% (●), e) Pt 1 wt% on Al$_2$O$_3$ (■).
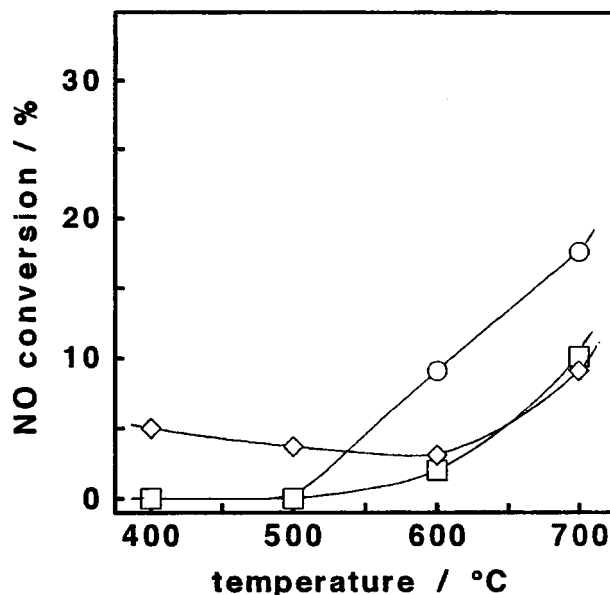

Figure 7 Catalytic reduction of NO by LaPO$_4$/Pd particle, a) Pd content, 0.58 wt% (○), b) 0.30 wt% (□), c) 0.22 wt% (◇).

ticles showed excellent catalysis (Fig. 8). The activity at 700°C is nealy equal to that of Pt/Al$_2$O$_3$ and varies depending upon the pyrolysis temperature of polymer particles surrounded by LnPO$_4$/Pd. We have examined the pyrolysis at three different temperatures, 700, 900, and 1000°C using PrPO$_4$/Pd particles. As a consequence, pyrolysis at aroud 900°C gave best result as shown in Fig. 9.

Furthermore, the life time of the present LnPO$_4$/Pd(LaPO$_4$, Pd content 0.58 wt%) was tested for 100 h. The NO gas was flowed at a rate of 20 ml/min. As a result, the activity did not change during this period (Fig. 10). Thus, the present Pd partricles dispersed on the LnPO$_4$ microsphere showed high activity toward the NO decomposition.
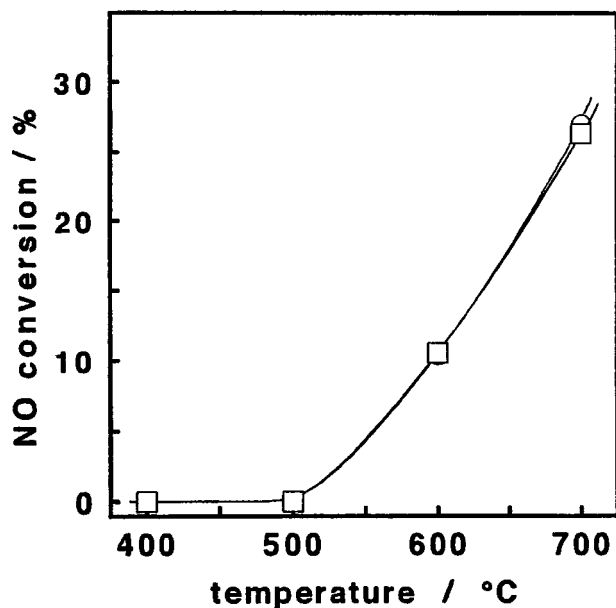
Figure 8 Catalytic reduction of NO by $AlPO_4/Pd$ particle, a) Pd content, 0.58 wt% (O), b) 0.35 wt% (□).
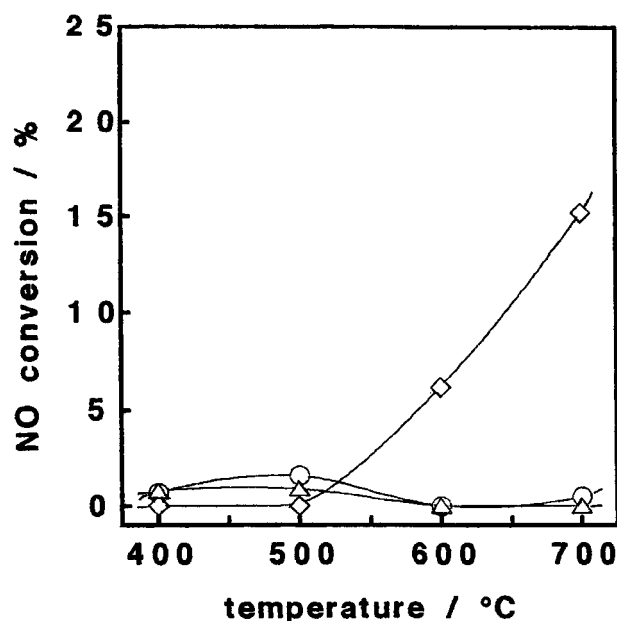

Figure 10 Dependence of reaction time on the catalytic action of $LaPO_4/Pd$ particle.

Figure 9 The effect of pyrolysis temperature for $PrPO_4/Pd$ particle, a) 700°C (O), b) 900°C (◇), c) 1100°C (△).

Figure 11 Catalytic activity of rare-earth metal black dispersed on the surface of $PrPO_4$, a) 5 wt% Pt (●), b) 1 wt% Pt (O), c) 5 wt% Rh (◆), d) 1 wt% Rh (◇), e) 5 wt% Pd (▲), f) 1 wt% Pd (△).

3.5. NO decomposition by noble metal on powdered $LnPO_4$

$LnPO_4$ hollow particles containing Pd metal show high activities toward the NO decomposition. Seeking for characteristic nature of the present particles, we have also examined the activity of the noble metal dispersed on the conventional powdery $LnPO_4$. The $LnPO_4$ powder was synthesized by mixing the corresponding rare earth nitrate with NaH_2PO_4 in water. The precipitate was thouroughly dried in vacuo and calcinated in air for 5 min at 100°C. Then the noble mertal black (Pt, Pd, and Rh) dispersed on $LnPO_4$ powder was prepared by impregnation of noble metal chloride (loading as 1 or 5 wt%) followed by reduction with formaldehyde solution at 0°C for 1 h. Resulting product was washed with water and dried in vacuo. Fig. 11 shows the result
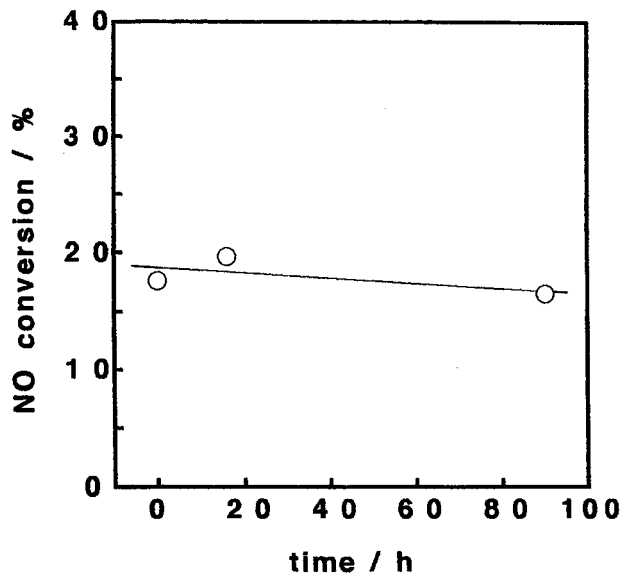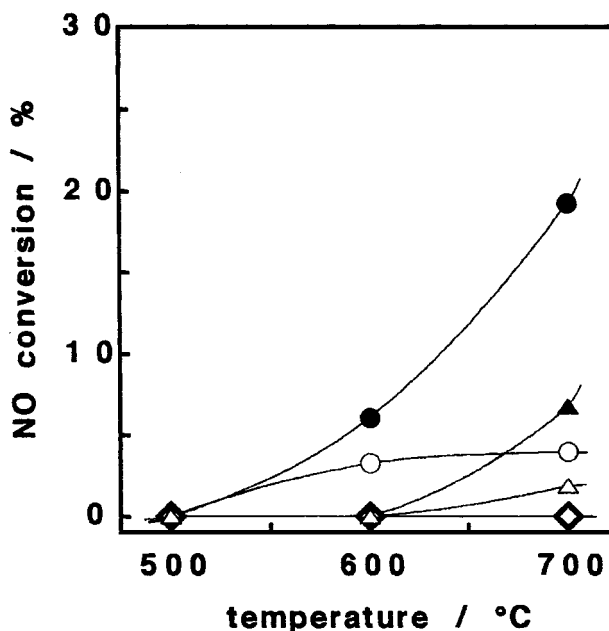
of NO decomposition by the conventional noble metals supported by $LnPO_4$ powder. Pt derivative (5 wt%) exhibits rather high activity. However, the activity decreased significantly when the $LnPO_4$ powder containing 1 wt% Pt was used. Pd derivatives (containing 5 and 1 wt%) show rather low activity. When Rh metal was used, almost no catalytic activity was observed. Thus, noble metals dispersed on the suface of hollow $LnPO_4$ particles show signifcantly high activity as compared with the conventional noble metal dispersed on the powdery $LnPO_4$. We can expect good result for the catalytic decomposition of NO or NO_2 in the presence of hydrocarbon, CO and O_2. In fact, the YPO_4 powder added to a mixture of H_3BO_3 and $Pt(NH_3)_4(NO_3)_2$ shows excellent activity after pyrolysis at 400°C for decomposition of NO in the presence of C_3H_6, CO, and

H$_2$ [40]. The Co/Al$_2$O$_3$ and Fe/Al$_2$O$_3$ catalysts show high catalytic activity for the decomposition of NO in the presence of ethene and oxygen [41, 42]. More recently, the Pt/Al$_2$O$_3$ is reported to have high catalytic activity for decomposition of NO into N$_2$ and O$_2$ in the presence of O$_2$, CO, propene, H$_2$O, and H$_2$ in the mild conditions (225°C)[43].

4. Concluding remarks
The Pd/LnPO$_4$(Ln = Pr, Sm, La, Al) hollow particles (diameter 450–550 nm) show excellent catalytic activity for the decomposition of NO, the activity being nearly equal to that of commercially available Pt/Al$_2$O$_3$.

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