ELSEVIER

Thermochimica Acta 318 (1998) 83–89

thermochimica acta

Studies of the reduction and reoxidation processes of Nd_4PdO_7

M. Andersson*, K. Jansson, M. Nygren

Inorganic Chemistry, Arrhenius Laboratory, Stockholm University, S-10691 Stockholm, Sweden

Received 2 September 1997; accepted 3 November 1997

Abstract

It has been demonstrated that Nd_4PdO_7, when exposed to a gas mixture of CO and He, fully decomposes to Nd_2O_3 and nano-sized Pd-particles, which are found on the surfaces of the micron-sized Nd_2O_3 particles. This material, known to exhibit catalytic activity for oxidation of CO and hydrocarbons, and reduction of NO, can be reoxidised to Nd_4PdO_7 by heat treatment at 1085°C in air for a short period of time, i.e. when utilised as catalyst this material can easily be regenerated if it has become aged. The reduced material has been studied in scanning and transmission electron microscopes (SEM and TEM) equipped with element analysis facilities, and characterised by X-ray powder diffraction (XRPD) studies. A wet-chemistry method for extraction of the nanoparticles formed has been developed, based on selective dissolution of Nd_2O_3, and the bare Pd-particles have been characterised by XRPD, SEM and TEM studies. The reduction and reoxidation of Nd_4PdO_7 material was monitored in a thermogravimetric setup. Nd_4PdO_7 decomposed in air to Nd_2O_3 and Pd at 1185°C, which is ≈50°C higher than the previously reported decomposition temperature. © 1998 Elsevier Science B.V.

Keywords: Nd–Pd oxide; Thermal analysis; Reduction; Oxidation; Nanoparticles

1. Introduction

In a previous article [1], a La_4PdO_7-based catalyst was reported to acquire a reproducible catalytic three-way activity (i.e. simultaneous oxidation of CO and hydrocarbons and reduction of NO) after several light-off runs in a simulated car exhaust gas, and the catalytic effect was attributed to the formation of nano-sized Pd-particles on the surface of La_2O_3. It was also found that this reduction process was reversible by heat treatment in air at elevated temperatures, which reformed La_4PdO_7. Utilising this property, catalysts based on this material could be easily regenerated by heat treatment in air followed by reactivation.

A possible drawback of the La_4PdO_7 material could be the moisture sensitivity of La_2O_3, since our previous studies have shown that the formation of $La(OH)_3$ cracks the material and embed the catalytically active Pd-particles. We believed that this could severely affect the reversibility as well as the activity and lifetime of the catalyst.

As Nd_2O_3 is known to be much less sensitive to moisture, we prepared the neodymium analogue to La_4PdO_7, i.e. Nd_4PdO_7, and in this article we discuss the chemical and morphological changes involved in the reduction and reoxidation processes of Nd_4PdO_7. Monophasic Nd_4PdO_7 has thus been reduced in a flow of helium and carbon monoxide and then reoxidised in air. These processes were monitored in a theromogravimetric setup, and the products were characterised by their X-ray powder

*Corresponding author.

PII S0040-6031(98)00332-3

diffraction (XRPD) patterns. Analytical transmission and scanning electron microscopes (ATEM and SEM) equipped with elemental analysis facilities were used to examine the morphology and composition of selected samples, and a wet-chemistry method for extraction and characterisation of the formed nano-sized Pd-particles has been developed. Preliminary studies of the catalytic activity of the reduced Nd_4PdO_7 material showed that it can simultaneously oxidise CO and hydrocarbons and reduce NO when exposed to slightly reducing car exhaust conditions [2]. More detailed studies of the catalytic activity of the reduced Nd_4PdO_7 material are presently being performed.

2. Experimental

2.1. Materials

The following starting materials were used: Nd_2O_3 (99.9%, Johnson Matthey), anhydrous $PdCl_2$ (purum, Fluka), HCl (fuming 37% p.a., Merck), The gases He, CO and compressed air used for the reduction and reoxidation of Nd_4PdO_7 were supplied by AGA Gas AB.

2.2. Preparation of Nd_4PdO_7 and reduced material

The Nd_4PdO_7 starting material was prepared as follows: (i) neodymium oxide was calcined overnight at 1000°C and dissolved in fuming hydrochloric acid together with palladium chloride in an Nd/Pd molar ratio of 4 : 1, and the solution was boiled to dryness; (ii) the residue was slowly heated to 550°C, held at this temperature for 2 h and then ground in a mortar; and (iii) the temperature was then slowly raised to 1000°C, and the sample was heat treated at this temperature for 7 days.

Nd_4PdO_7 was then reduced in a tube furnace at 750°C with a flowing gas mixture of 16 ml CO and 1000 ml He per minute. An alumina container with ca. 150 mg Nd_4PdO_7 was placed in the furnace and the temperature was raised to 750°C during 25 min. After 25 min of isothermal heat treatment the furnace was cooled to room temperature and the sample was transferred to a desiccator.

2.3. Thermogravimetry

The reduction and reoxidation of Nd_4PdO_7 material was studied in thermogravimetric (TG) setups (Setaram TAG24 and Perkin–Elmer TGA7). Typically, 50 mg samples were used, and heating and cooling rates of 10°/min. A CO/He gas mixture was used for the reduction, and the oxidation was performed in air.

2.4. Characterisation

All samples were characterised by their XRPD patterns obtained in a Guinier–Hägg camera, using CuK_{α_1} radiation and Si as internal standard. The photographs obtained were evaluated in a computerised scanner system [3], and the records obtained for Nd_2O_3 and Pd were matched with tabulated JCPDS data. We have recently solved the structure of Nd_4PdO_7 [4], and the diffraction patterns of the starting and reoxidised material have been indexed with use of this unit cell. The morphologies of selected samples were studied in a scanning electron microscope (SEM, JEOL 880) and in an analytical transmission microscope (ATEM, JEOL 2000FX), both furnished with energy-dispersive spectrometers (EDS, Link AN-10 000) for elemental analysis.

3. Results and discussion

3.1. Thermogravimetry

The TG curve of Nd_4PdO_7 heated to 750°C in a CO/He gas mixture is shown in Fig. 1. The reduction starts at ≈380°C and is finished at ca. 600°C with a total mass loss of 2.2%, which is in fair agreement with the calculated value, 2.0%. The DTG (%/min) curve given in the Fig. 1 suggests that the reduction occurs in one step. The reduced sample was reheated in air to 1085°C and held at this temperature for half an hour; it was then heated to 1350°C and held at this temperature for half an hour before quenching to room temperature in argon atmosphere. The TG and DTG curves thus obtained are shown in Fig. 2. The oxidation process starts ca. 260°C and is finished at 800°C. This process clearly occurs in at least two steps, the first one occurring at temperatures ranging from 260 to

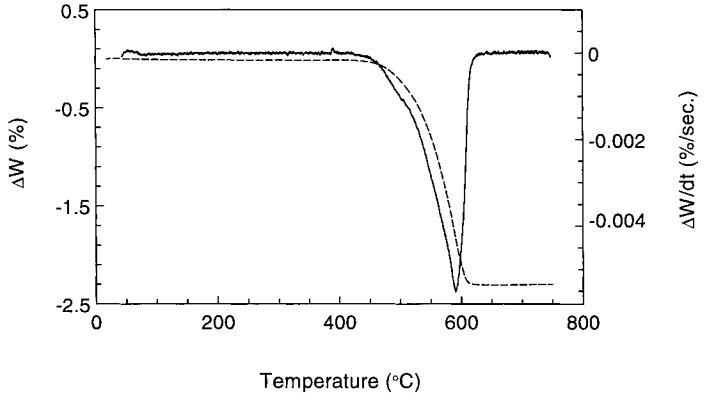

Fig. 1. The TG (· · ·) and DTG curves of Nd_4PdO_7 heated to 750°C in a CO/He gas mixture, using a heating rate of 10°C/min.

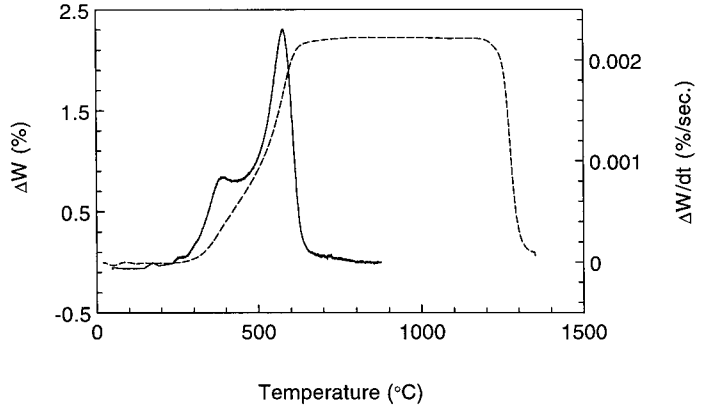

Fig. 2. The TG (· · ·) and DTG curves of Nd_4PdO_7 heated in air to 1085°C and held at this temperature for 1 h, and then heated to 1350°C and held at this temperature for 0.5 h.

450°C and the second one from 450 to 800°C. A total mass increase of 2.2% is observed, in good agreement with the mass-loss measurements, but still somewhat larger than the calculated value, 2.05%. Prolonged heat treatment at 1085°C did not give rise to any further mass increase. The phase analysis studies described below showed that Nd_4PdO_7 is rapidly formed at this temperature when reduced material is heat treated in air. Around 1185°C, Nd_4PdO_7 starts to decompose into neodymia and Pd, and a total mass loss of 2.1% is found (see Fig. 2). McDaniel and Schneider [5] have reported the decomposition temperature in air of Nd_4PdO_7 to be 1135°C, i.e. substantially lower than our observation.

3.2. Phase analysis

The XRPD data of the starting material (Fig. 3(a)) was matched with the diffraction pattern of Nd_4PdO_7 given in Ref. [4], and the material was found to contain, besides Nd_4PdO_7, some Nd_2O_3 (1.9%) and $Nd_2Pd_2O_5$ (2.2%), the percentages being Rietveld-refined phase fractions. The reduced material gave rise to reflections characteristic of hexagonal Nd_2O_3 (Fig. 3(b)), and a single very weak peak indicating the presence of palladium. Line-broadening analysis [6] of the strongest Nd_2O_3 reflection indicated that the average crystallite size of Nd_2O_3 should be ca. 0.1 μm, which is five-to-ten times smaller than that observed in

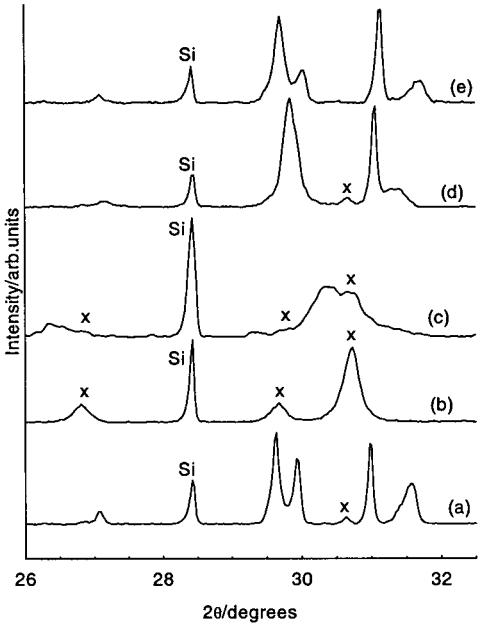

Fig. 3. X-ray diffraction patterns of (a) Nd_4PdO_7, (b) reduced material (reflections denoted by x are ascribed to Nd_2O_3), (c) reduced material heated in air for 10 min at 670°C, (d) for 10 min at 1085°C, and (e) 720 min at 1085°C.

the SEM. Nd_4PdO_7 did not exhibit any line broadening. Oxidised samples yielded diffraction patterns similar to that of Nd_4PdO_7.

In order to study the oxidation mechanism in greater detail, reduced samples were heat treated in the Perkin–Elmer TG-unit, as described below, using a heating rate of 200°/min to 670°C, and were held for 10 min at this temperature. The X-ray powder diffractogram (see Fig. 3(c)) showed that this sample contained Nd_2O_3, but it also exhibited a set of reflections at somewhat lower 2θ-values than those of Nd_2O_3. At least six of the original Nd_2O_3 reflections

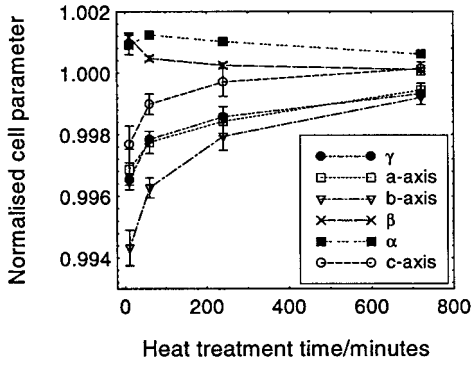

Fig. 4. Unit cell parameters of Nd_4PdO_7 obtained from reduced material reheated in air at 1085°C for 10, 60, 240 and 720 h, respectively, plotted vs. time. The parameters are normalised to those of the starting material.

had counterparts of comparable intensity at lower 2θ-values. These observation suggest that Nd_4PdO_7 is formed via some intermediate compound on the oxidation of Nd_2O_3 and Pd (see also above and below).

The X-ray diffraction patterns of the reduced material, heat treated at 1085°C in air, for periods ranging from 10 min to 12 h revealed that the oxidation process at this temperature is very rapid, as an almost monophasic Nd_4PdO_7 sample was obtained after only 10 min. Thus only a minor amount of Nd_2O_3 was found in this sample, as seen in Fig. 3(d), but no Nd_2O_3 remained after 12 h of heat treatment (see Fig. 3(e)). The lattice parameters of Nd_4PdO_7 formed after 10 min, 1 h, 4 h and 10 h of heat treatment and those of the starting material are very similar (see Table 1). A small increase in the a-, b-, c- and γ-parameters can be discerned with increasing heating time, though, whereas there is no significant variation in the α- and β-angles, as seen in Fig. 4 where the cell parameters, normalised to those of the starting material, are plotted as a function of heating time.

Table 1
Unit cell parameters of reduced Nd_4PdO_7 reoxidised at 1085°C for 10 min (labelled O10), 60 min (O60), 240 min (O240) and 720 min (O720) and those of the starting material (OS)

Sample	a (Å)	b (Å)	c (Å)	α	β	γ
O10	15.918(10)	7.150(4)	6.898(4)	96.40(3)	131.78(2)	121.03(2)
O60	15.932(5)	7.164(2)	6.907(2)	96.43(1)	131.69(1)	121.19(1)
O240	15.943(7)	7.176(3)	6.912(3)	96.41(1)	131.66(1)	121.28(1)
O720	15.959(2)	7.185(1)	6.915(1)	96.37(1)	131.638(6)	121.365(8)
OS	15.968(3)	7.191(1)	6.914(1)	96.311(7)	131.627(5)	121.452(5)

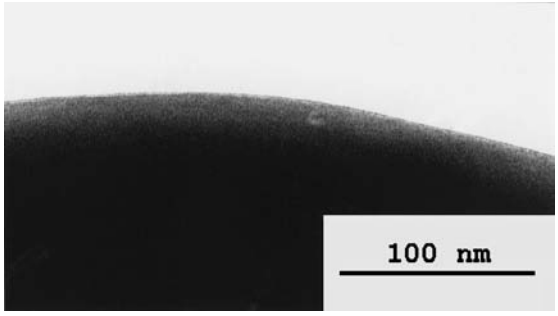

Fig. 5. An ATEM micrograph of an Nd_4PdO_7 crystal showing a characteristically smooth surface.

The XRPD pattern of the sample heat treated at 1350°C and quenched to room temperature contained reflections which all could be ascribed to Nd_2O_3 and Pd.

3.3. ATEM studies

The starting material consisted of micron-sized particles with smooth and clean surfaces, having Pd and Nd contents of typically 20 and 80%, respectively, in agreement with the Nd_4PdO_7 formula. A micrograph of a characteristic Nd_4PdO_7 crystal is reproduced in Fig. 5.

The reduced material showed crystalline grains in the same size range as the starting material, and elemental area analysis yielded Nd : Pd ratios of 4 : 1. Closer inspection of these grains revealed that semi-spherical nanoparticles in the 5–20 nm size range were distributed over almost all surfaces (see Fig. 6), and no grain without such particles could be found. These nanoparticles were typically separated by 20 to 100 nm, and spot EDS analysis of such a nanoparticle gave rise to a higher Pd signal than the area EDS analysis mentioned above. These results, together with the findings from the XRPD analysis, suggest that the micron-sized grains are crystallites of Nd_2O_3 and that the nanoparticles are Pd or PdO. Pd is the most likely candidate, according to the X-ray findings and taking in account the reducing conditions used in the preparation of the material.

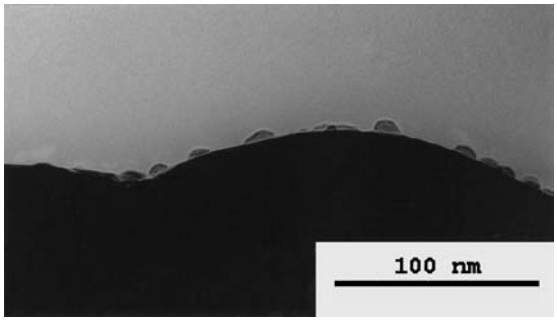

Fig. 6. An ATEM micrograph of an Nd_2O_3 crystal with semi-spherical nano-sized Pd-particles on its surface.

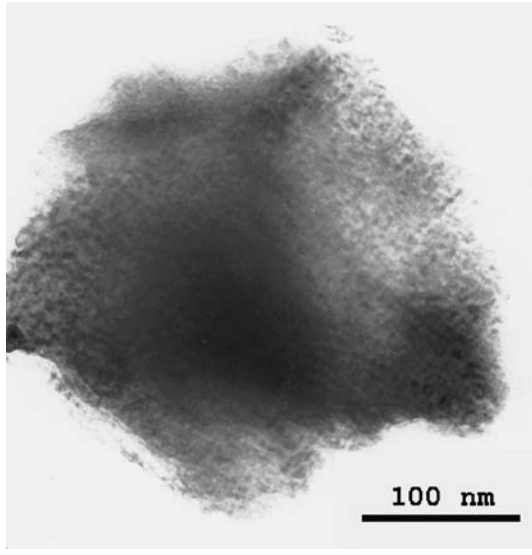

Fig. 7. An ATEM micrograph of a fragment of an unknown phase formed after oxidation of reduced material for 10 min in air at 670°C.

The material oxidised at 670°C for 10 min showed two different types of grains. Some were very similar to the reduced material, having the same size, the same type of semi-spherical nanoparticles on their surfaces and 80/20 Nd/Pd overall composition, whereas other grains showed a totally different morphology as evidenced from Fig. 7. It can be seen that these grains are smaller, exhibit a rougher surface and are also more transparent than the others. Nevertheless, they have Nd/Pd ratios of 80/20 and were found to be crystalline, i.e. their electron diffraction patterns could be recorded.

The materials oxidised at 1085°C for 10 min and 12 h both totally lacked the semi-spherical nanoparticles and showed a morphology very similar to that of Nd_4PdO_7, i.e. dark smooth micron-sized grains with 80/20 Nd/Pd compositions. On some grain surfaces,

brighter appearing fragments containing 100% Nd were found and believed to be Nd_2O_3 or $Nd(OH)_3$.

ATEM studies of the sample heat treated at 1350°C in air revealed the presence of micron-sized grains of Nd_2O_3 and Pd, showing that nano-sized Pd-particles are not produced by decomposition of Nd_4PdO_7 in air at elevated temperatures.

3.4. Extraction of nano-sized Pd-particles

To be able to extract and characterise the nano-sized particles formed and to verify that they are metallic, a wet-chemistry extraction method was developed. It is based on the findings that PdO and palladium metal are insoluble in oxygen free 1 M HCl, whereas Nd_2O_3 and Nd_4PdO_7 are soluble. By exposing the reduced starting material to this solvent, all Nd_2O_3 and unreacted Nd_4PdO_7 (if present) will be dissolved, while PdO (if present) and Pd will remain unaffected. In order to verify that the liquid did not contain any Pd^{2+}-ions, a simple gravimetric method was applied. A series of standard solutions containing various amounts of Pd^{2+}-ions were thus prepared and 1 cm^3 samples of these solutions were evaporated to dryness in an oven at 120°C. The residue was dissolved in 1 cm^3 oxygen free 1M HCl (prepared as described below) and this solution was mixed with equal amounts of fuming HCl and 0.13 M Na_2S. A brownish precipitate of PdS could easily be detected, by visual inspection, down to a concentration of 61.7 μM Pd^{2+}-ions, which corresponds to 6.6 ppm of Pd^{2+}-ions.

The reduced samples were tested in a similar way: (i) oxygen free 1 M HCl was prepared by boiling ca. 50 cm^3 of fuming HCl till the azeotrope was reached, and then for an additional 10 min, whereupon 5.0 cm^3 of this solution was diluted with 25 ml of deionised water which previously had been deoxygenised by bubbling nitrogen through it for 35 min; (ii) 4.85 mg of the reduced sample was mixed with 1.0 cm^3 of the diluted acid in a test tube, which was then flushed with nitrogen, sealed and ultrasonically treated for 1 min. The solution was centrifuged after standing for 30 min, and the supernatant liquid was transferred to another test tube. No brownish precipitate of PdS was found when fuming HCl and Na_2S were added to this liquid.

The crystalline nature, morphology and composition of the undissolved black material were revealed by ATEM/EDS, SEM/EDS and XRPD studies. The material was found to consist of almost spherical particles of sizes in the 5–25 nm range (see Fig. 8). No other metal besides Pd could be detected, but the sample was found to contain minor amounts of chlorine probably originating from the acid. The X-ray powder pattern contained broad reflections which could all be assigned to Pd. No PdO could thus be found.

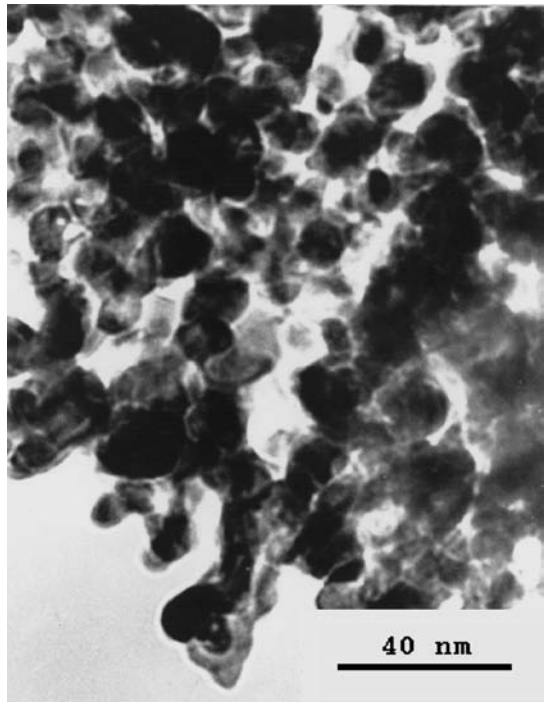

Fig. 8. An ATEM micrograph of the extracted nano-sized Pd-particles.

Our studies thus prove that the reduced material does not contain any Nd_4PdO_7 or PdO.

Line-broadening calculations yielded a crystallite size of 24.4±2.1 nm, according to the Sherrer half-width formula based on the average broadening of three reflections [6]. However, an average particle diameter of 10.7±3.1 nm was found by measuring the diameters of 51 particles depicted in an ATEM micrograph. It is interesting to note that the Pd-particles obtained are almost spherical, whereas in micrographs, such as that given in Fig. 6, they appear to be semi-spherical. We have seldom observed any truly spherical particles on the surfaces of Nd_2O_3. This

might imply that approximately one half of the Pd particle is buried in the Nd_2O_3 particle and, if so, the nano-sized particles ought to be well anchored to their hosts. Normally noble-metal-based car exhaust catalysts are prepared by depositing the noble metal onto a washcoat by a dip-coating procedure. After having been used for some time, larger aggregates of the noble metals can be found, implying that the efficiency of the catalysts has decreased, i.e. the catalyst has aged. The tendency to form larger aggregates of Pd-particles in our material is expected to be less, because the nano-sized Pd-particles are much better anchored to their hosts than in a catalyst prepared via the dip coating procedure. If larger aggregates are formed our catalyst can easily be regenerated using the oxidation–reduction procedure outlined above.

4. Concluding remarks

It has been demonstrated that Nd_4PdO_7 grains of micrometer size fully decompose to Nd_2O_3 and nano-sized Pd-particles when exposed to a gas mixture of carbon monoxide and helium at 750°C, and that the Pd-particles are found at the surfaces of the Nd_2O_3 particles. The Nd_2O_3 grains formed are of the same size as those of the starting material, Nd_4PdO_7. A wet-chemistry method for extraction of the nanoparticles by selective dissolution of Nd_2O_3 has been developed and used to characterise these particles and to prove that decomposition of Nd_4PdO_7 yields Nd_2O_3 and Pd. Heat treatment of the reduced material in air for 10 min at 670°C gave indications of formation of some metastable Nd–Pd compound, possibly having the morphology shown in Fig. 6. When the reduced material is heat treated at 1085°C, a material with the same morphology, composition and X-ray diffraction pattern as Nd_4PdO_7 is obtained only after 10 min. This material is totally free of the Pd nanoparticles found in the reduced material. Nd_4PdO_7 was found to be stable in air up to 1185°C, which is ≈50°C higher than the previously reported temperature. The catalytic activity of the reduced Nd_4PdO_7 material for oxidation of CO and hydrocarbons and reduction of NO is presently being studied in some detail.

Acknowledgements

This work has been financially supported by the Swedish Research Council for Engineering Sciences.

References

[1] M. Andersson, K. Jansson, M. Nygren, Catalysis Letters 39 (1996) 253.
[2] M. Andersson, K, Jansson, L. Kihlborg, M. Nygren, 7th Nordic Symposium on Catalysis, in: T. Salmi, L.-E. Lindfors (Eds.), Åbo Akademi, Åbo, Finland, 1996.
[3] K.-E. Johansson, T. Palm, P.-E. Werner, J. Phys. E 3 (1980) 1289.
[4] M. Andersson, J. Grins, M. Nygren, in preparation.
[5] C.L. McDaniel, S.J. Schneider, J. Res. Nat. Bur. Stand., Phys. and Chem. 72A, No. 1 (1968) 27.
[6] A.J.C. Wilson, J.I. Langford, J. Appl. Cryst. 11 (1978) 102.