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Preparation of nano-sized palladium particles anchored onto Ln_2O_3 grains with Ln = La, Nd, Sm, Eu or Gd[†]

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Nano-sized Pd-particles anchored onto Ln_2O_3 particles with Ln = La, Nd, Sm, Eu or Gd have been prepared by reduction of the Ln_4PdO_7 precursor materials in a flowing gas mixture of CO and an inert gas (He or Ar). The reductions have been monitored by theromogravimetric (TG) and differential scanning calorimetric (DSC) measurements. The TG experiments show that the onset temperatures of the reduction varies from 450 to 575 °C with the lanthanoid used and Ln = Sm or Eu exhibit the lowest reduction temperatures. The air re-oxidation of the reduced materials back to their oxidised formed, *e.g.* Ln_4PdO_7, has also been studied by TG and this reaction starts at 280–340 °C depending on the lanthanoid used; the re-oxidation process occurs in two steps for all lanthanoids except Sm and Gd. The formation of Ln_4PdO_7 is observed to be very fast. The prepared and reduced materials have been characterised by their X-ray powder diffraction (XRPD) patterns. The DSC studies and XRPD patterns of quenched samples suggest that the reduction process occurs in at least two steps. The reduced materials have also been characterised by transmission electron microscopy (TEM/EDS) studies and a wet-chemistry method for selective dissolution of Ln_2O_3 has been used to extract the formed Pd nano-particles. Line-broadening analysis of the XRPD pattern of extracted particles suggests that the Pd particles are nanosized single crystals as the calculated particle size (20 nm) agrees fairly well with corresponding data from the TEM studies (5–20 nm). Reduced Ln_4PdO_7 materials have been shown to exhibit three way catalytic activity for car exhaust clean-up (*i.e.* simultaneous oxidation of CO and hydrocarbons and reduction of NO) with T_{50} values around 450 °C.

Introduction

In previous articles we have discussed the structures and selected properties[1–4] of Ln_4PdO_7 with Ln = La, Nd, Sm, Eu or Gd and have shown that they possess very similar structures and that the compounds with Ln = La, Nd or Sm decompose to nano-particles of Pd anchored onto Ln_2O_3 grains when exposed to reducing gas mixtures containing CO. It has also been shown that reduced materials of Ln_4PdO_7 with Ln = La or Nd exhibited so called three way catalytic activity for car exhaust clean-up, *i.e.* simultaneous oxidation of CO and hydrocarbons and reduction of NO,[2,4] and that the reduced materials could quickly be re-oxidised at elevated temperatures in air whereupon the Ln_4PdO_7 starting material is formed after a very short time,[2–4] *e.g.* after 10 min or less in the Nd_4PdO_7 case. As these materials could find use as renewable catalysts, *i.e.* that the deactivated catalyst can be regenerated by oxidation followed by re-reduction, we have found it worthwhile to investigate the mechanism of formation of nano-particles of Pd anchored onto the different Ln_2O_3 grains and to study the reduction and re-oxidation processes in greater detail.

The reduction and re-oxidation behaviour of Ln_4PdO_7 with Ln = La, Nd, Sm, Eu or Gd has thus been studied by thermal analysis (TG and DSC) and the morphology of the materials subjected to catalytic tests have been characterised by TEM and XRPD studies. The wet-chemistry method described in ref. 3 for selective dissolution of Ln_2O_3 has been used to extract and characterise formed nano-particles of Pd. The XRPD patterns have been used for calculation of the size of the formed Pd nano-particles from the XRPD line-broadening of the recorded XRPD peaks and for phase analysis of starting materials and reduced materials, respectively.

Catalytic activity of reduced Ln_4PdO_7 samples has been measured in an in-house built test reactor.

Experimental

The Ln_4PdO_7 oxides were prepared by dissolving $PdCl_2$ (*p.a.* Fluka) and the corresponding lanthanide nitrate [$La(NO_3)_3 \cdot 6H_2O$, *p.a.* Merck] or oxide (Ln_2O_3, *p.a.* Johnson Matthey) in fuming HCl (Merck) followed by evaporation to dryness by boiling. The solid products were then calcined at successively higher temperatures and finally heat-treated for typically 7 d at 1000 °C with re-grindings in between. To obtain samples with as low levels of secondary phases as possible the thus formed products were reduced in a flowing gas mixture of 20 vol.% CO and 80 vol.% He at 750 °C for 0.5 h followed by heat treatment at 1000–1100 °C for more than 40 h. The metal content of the samples was analysed using a scanning electron microscope (SEM, JEOL 820) fitted with an energy dispersive spectrometer (EDS, Link AN-10000). The TG reduction curves were recorded using a gas mixture of 20 vol.% CO and 80 vol.% He for all oxides (in addition a gas mixture of 1.6 vol.% CO and 98.4 vol.% He has been used to reduce Nd_4PdO_7), using a Setaram TAG-24 set up. Gas flow velocities in the 40–100 cm^3 min^{-1} range and a heating rate of 10 °C min^{-1} have been used. The re-oxidation experiments were performed in air.

The DSC runs were carried out using a Perkin-Elmer DSC 2C instrument in the temperature range 20–675 °C using a gas mixture of 1.6 vol.% CO in Ar with a flow rate of 9.50 cm^3 min^{-1}. The wet-chemistry method used for selective dissolution of Ln_2O_3 described in ref. 3 was used for extraction of Pd nano-particles.

Catalytic activity was measured in an in-house built test reactor (described in ref. 2). The gas mixture (see below) was transferred to a quartz tube positioned in a horizontal furnace. A sample amount equivalent to 63.3 μmol of Pd was placed evenly on the bottom of an aluminium oxide boat which was

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[†] Basis of the presentation given at Materials Chemistry Discussion No. 1, 24–26 September 1998, ICMCB, University of Bordeaux, France.

Table 1 Gas mixture used in connection with the catalytic activity tests

Gas	Flow rate/cm^3 min^{-1}
He	125
CO	2.0
Propene	0.037
NO	0.125
O_2	0.987

inserted into the quartz tube. The outlet gas composition was continuously monitored by a quadrupole mass spectrometer. The following gases and temperature programs were used; (*i*) the Ln_4PdO_7 precursors were reduced in 20 vol.% CO and 80 vol.% He gas mixture by heating the samples from room temperature to a pre-set temperature, as determined by the TG experiments described above, by 10 °C min^{-1}, followed by an isothermal heat treatment at this temperature until a low and constant CO_2 signal was obtained; (*ii*) equilibration in a reducing synthetic car exhaust gas mixture (see Table 1) at 100 °C followed by a light-off scan from 100–560 °C using a heating rate of 10 °C min^{-1}; (*iii*) a second light-off scan was then performed to test the reproducibility of the catalytic behaviour and; (*iv*) finally the temperature was kept constant at 560 °C in order to equilibrate the system before the measurements of the degree of conversion were performed.

T_{50}-values, defined as the temperature at which 50% of the maximum conversion of CO, propene and NO, respectively, occurs, was used to characterise the catalytic activity of the various materials.

The prepared and reduced samples were characterised by their XRPD patterns obtained with a Guinier–Hägg camera using Cu-Kα radiation and Si as internal standard. The obtained photographs were evaluated in a computerised scanner system[5] and the obtained records were matched with tabulated JCPDS data. The program Pirum[6] was used for refinement of the unit cell parameters.

A JEOL 2000FX transmission electron microscope furnished with a LINK AN 10000 EDS detector was used for characterisation of the reduced samples.

Results and discussion

Thermal analysis

The reduction and re-oxidation TG-curves of the Ln_4PdO_7 compounds are presented in Fig. 1 and 2, respectively. To verify the reproducibility of the TG experiments two reduction and re-oxidation experiments were carried out for the samples with Ln = La and Nd (dashed lines in Fig. 1 and 2). The onset temperatures have been calculated from the intersection of the tangent of the baseline and that of the inflection point of the weight loss curve and are presented in Table 2. The oxidation process occurred in two steps for all samples but for Ln = Sm or Gd and accordingly two onset temperatures are given for Ln = La, Nd or Eu in Table 2. To verify that Ln_4PdO_7 was reformed upon oxidation the materials obtained were finally oxidised in air to temperatures exceeding the decomposition temperatures previously reported for the various Ln_4PdO_7 compounds.[7,8] Thus all samples decomposed at these elevated temperatures (see Fig. 2) and these decomposition temperatures are also listed in Table 2 together with the corresponding data given by McDaniel *et al.* and Kakhan *et al.*, respectively.[7,8] The observed and calculated weight losses and weight gains for the reduction and re-oxidation processes are presented in Table 3.

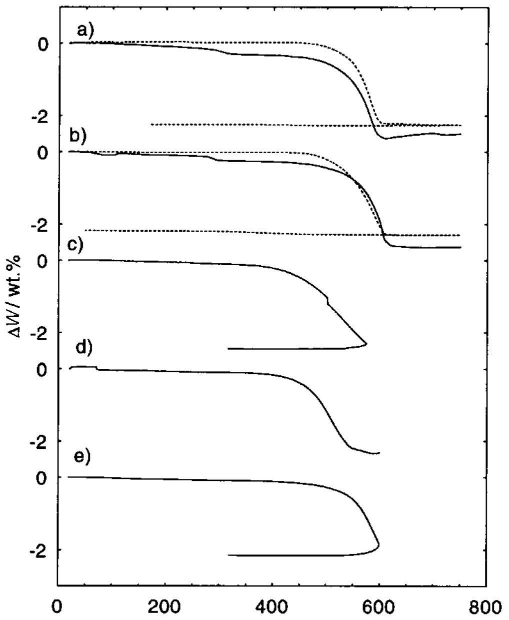

Fig. 1 TG curves for reduction of Ln_4PdO_7 with Ln = La (a), Nd (b), Sm (c), Eu (d), and Gd (e). The dotted curves refer to a second reduction of a re-oxidised sample.

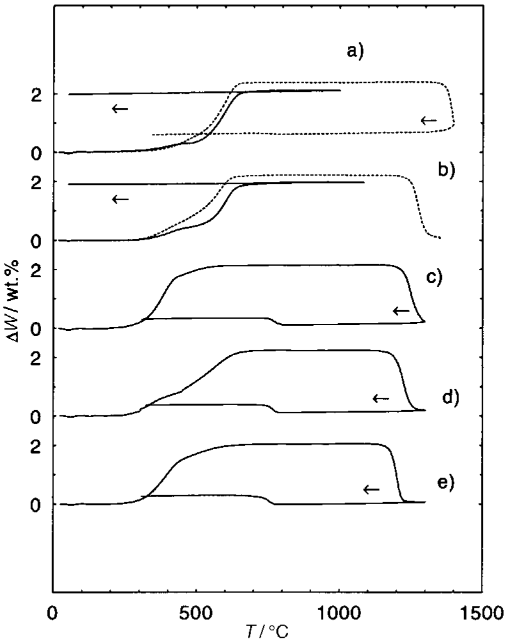

Fig. 2 TG curves for oxidation of reduced Ln_4PdO_7 samples with Ln = La (a), Nd (b), Sm (c), Eu (d), and Gd (e). The dotted curves refer to a second oxidation of samples reduced twice (see Fig. 1).

The observed weight losses and weight gains are in fair agreement with the calculated ones. Eu_4PdO_7 showed the lowest onset temperatures in both oxidation steps whereas Sm_4PdO_7 showed the lowest reduction onset temperature. It can also be concluded that the decomposition temperatures observed in this study are markedly higher than previously reported. In part, this can be explained by the fact that in this study these temperatures are determined from TG experiments while all previous studies except that in ref. 8 are based on prolonged heat treatments at elevated temperatures.

The reduction characteristics of Nd_4PdO_7 when exposed to a gas mixture consisting of 1.6 vol.% CO and 98.4 vol.% He/Ar are evident from Fig. 3, showing the recorded TG (obtained with use of He) and DSC (Ar has been used instead of He in order to reduce the thermal exchange between the DSC cups and the cooling block surrounding the cups) curves. These curves suggest that the reduction mechanism occurs in at least

Table 2 Onset temperatures for the reduction and re-oxidation and the decomposition temperature of the Ln_4PdO_7 compounds as determined from the TG experiments

Sample	T_{ons} red/°C	T_{ons} ox. step 1/°C	T_{ons} ox. step 2/°C	T_{dec}/°C	T_{dec}/°C
La_4PdO_7	539	314	537	1375	1190[7] 1310[8]
Nd_4PdO_7	575	340	553	1252	1135[7]
Nd_4PdO_7[a]	587	340	559	1264	1135[7]
Sm_4PdO_7	450	320	—	1223	1115[7]
Eu_4PdO_7	462	280	469	1197	1085[7]
Gd_4PdO_7	543	319	—	1179	—

[a] Reduced in a gas mixture consisting of 1.6 vol.% CO and 98.4 vol.% He.

Table 3 Observed and calculated weight losses and weight gains on reduction and re-oxidation of Ln_4PdO_7, respectively

Sample	Obs. weight loss (wt.%)	Obs. weight gain (wt.%)	Calc. weight gain/loss (wt.%)
La_4PdO_7	2.33	2.11	2.067
Nd_4PdO_7	2.14	1.98	2.012
Nd_4PdO_7[a]	2.26	2.36	2.012
Sm_4PdO_7	2.28	2.16	1.951
Eu_4PdO_7	2.22	2.25	1.936
Gd_4PdO_7	2.06	2.06	1.888

[a] Reduced in a gas mixture consisting of 1.6 vol.% CO and 98.4 vol.% He.

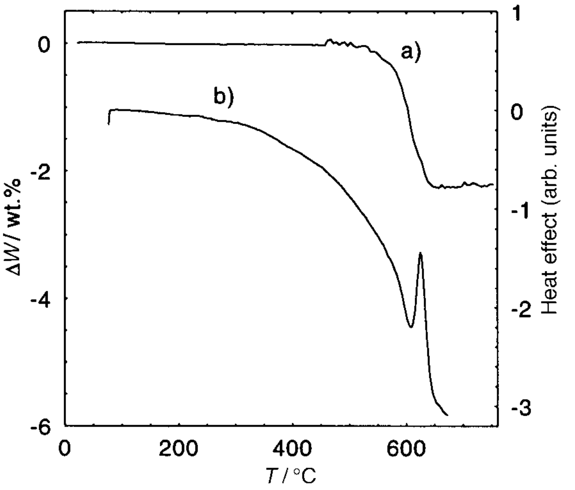

Fig. 3 Recorded TG (a) and DSC (b) curves of Nd_4PdO_7 when exposed to a gas mixture consisting of 1.6 vol.% CO and 98.4 vol.% He and Ar, respectively.

two steps. The first 60% of the observed weight loss is seemingly associated with an endothermal DSC peak, while for weight losses exceeding 60% an exothermal DSC peak is discerned.

Phase analysis

The prepared Ln_4PdO_7 materials all contained Ln_4PdO_7 as the main phase but a few percent of Ln_2O_3 and/or $Ln_2Pd_2O_5$ were present in some samples.

Reduced and catalytic activity tested materials exhibited diffraction patterns characteristic of the corresponding lanthanide oxide, *i.e.* for Ln = La or Nd the hexagonal modification is found while for Ln = Sm, Eu or Gd the monoclinic modification is found. The XRPD pattern of the Gd sample also contained a few reflections which could be ascribed to its cubic modification. The lattice parameters of the obtained Ln_2O_3 samples are given in Table 4 and are all in fair agreement with tabulated JCPDS data. It can also be noted that the obtained XRPD patterns of these materials did not contain any other reflections than those which could be ascribed to the Ln oxides.

Table 4 Lattice parameters of the formed Ln_2O_3 oxides

Sample	a/Å	b/Å	c/Å	β/°
La_4PdO_7	3.946(2)	3.946(2)	6.142(3)	
Nd_4PdO_7	3.832(3)	3.832(3)	6.024(5)	
Sm_4PdO_7	14.16(2)	3.633(5)	8.855(8)	100.14(7)
Eu_4PdO_7	14.12(3)	3.61(1)	8.84(2)	100.3(2)
Gd_4PdO_7	14.06(2)	3.592(4)	8.76(2)	100.4(2)

A series of samples were quenched from various temperatures when reduced in the DSC instrument using a 1.6 vol.% CO and 98.4 vol.% Ar gas mixture. The quenched materials were characterised by their XRPD patterns and some results are given Fig. 4. (For sake of comparison the XRPD pattern of Nd_4PdO_7 is also included). The other diffraction patterns depicted in Fig. 4 refer to samples quenched from temperatures just before the exothermal DSC peak, in the middle of the exothermal DSC peak and after the exothermal DSC peak, respectively. It is evident from Fig. 4 that the reduction of Nd_4PdO_7 to 2 $Nd_2O_3 + Pd$ proceeds *via* at least two crystalline phases. The diffraction pattern in Fig. 4(d) matches that of hexagonal Nd_2O_3.

X-Ray line-broadening analysis was used for determination of the size of the formed Pd nano-particles, extracted from a reduced Nd_4PdO_7 sample as described in ref. 3. The broadening of the strongest line was analysed according to the Scherrer half-width method using a value of 0.8290 as the Scherrer constant for spherical crystallites as described in ref. 9. The obtained average particle size turned out to be 20 nm.

Catalytic activity

All reduced Ln_4PdO_7 samples exhibited a three way catalytic behaviour when tested as described above. T_{50} temperatures and degree of conversions at 560 °C are presented in Table 5. Typical light-off curves are shown in Fig. 5. The data given Table 5 and Fig. 5 refer to data obtained in the second light-off run. The first and second light off runs resemble each other to a great extent.

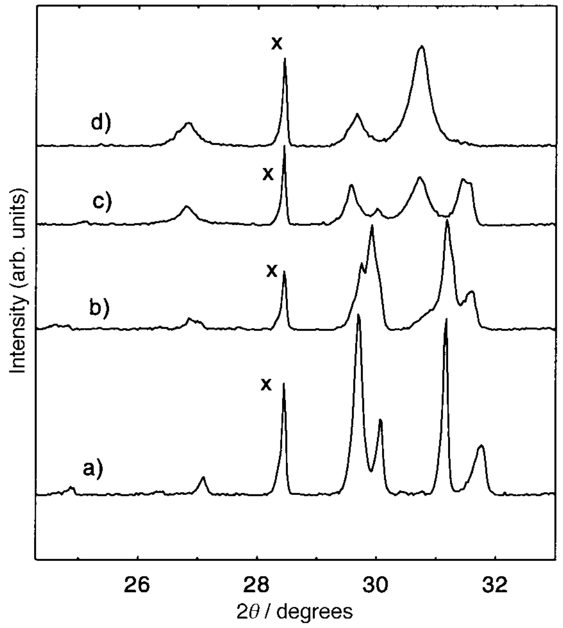

Fig. 4 XRPD pattern of Nd_4PdO_7 (a) and of samples quenched from temperatures just before the exothermal DSC peak (b), in the middle of the exothermal DSC peak (c) and after the exothermal DSC peak (d) shown in Fig. 3. The peaks marked with crosses originate from Si used as internal standard.

Table 5 T_{50} temperatures (°C) and degree of conversion at 560 °C of propene, CO and NO, respectively

Sample	T_{50}, NO	T_{50}, CO	T_{50}, propene	Conv. degr. NO (%)	Conv. degr. CO (%)	Conv. degr. propene (%)
La_4PdO_7	463	432	442	80	91	84
Nd_4PdO_7	502	458	470	69	83	82
Sm_4PdO_7	483	446	458	73	84	82
Eu_4PdO_7	456	423	431	81	83	82
Gd_4PdO_7	466	429	443	68	66	82

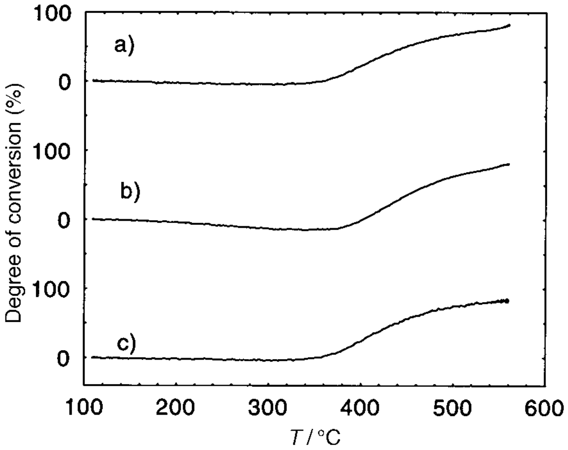

Fig. 5 Light-off curves for conversion of propene (a), NO (b) and CO (c) obtained for reduced Eu_4PdO_7.

It can be concluded that all reduced Ln_4PdO_7 samples exhibit similar T_{50} values for conversion of CO, propene and NO to CO_2, H_2O and N_2, respectively, and that the degree of conversion at 560 °C is around 80% for all species.

TEM studies

After the catalytic tests, the samples were examined in a TEM and were found to contain micron sized Ln oxide crystals with nano-sized Pd particles, typically in the range 5–20 nm in diameter, anchored onto their surfaces as illustrated in Fig. 6. Two samples of Nd_4PdO_7 reduced in the TG using different heating rates (1.5 and 20° min^{-1}) were also examined and both samples exhibited Pd particles of the same size.

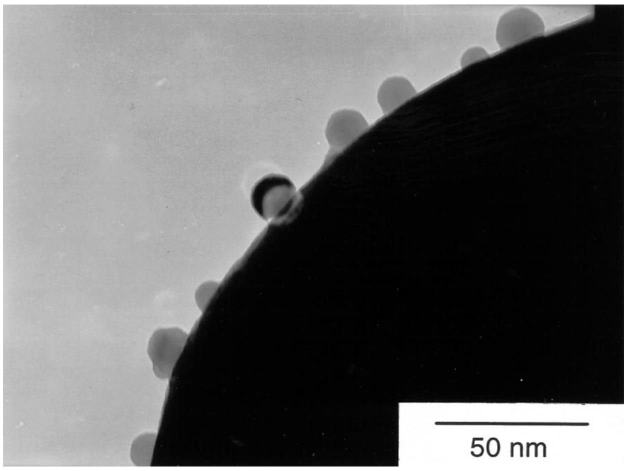

Fig. 6 A TEM micrograph of reduced Gd_4PdO_7 showing Pd particles anchored onto the surface of a grain of Gd_2O_3.

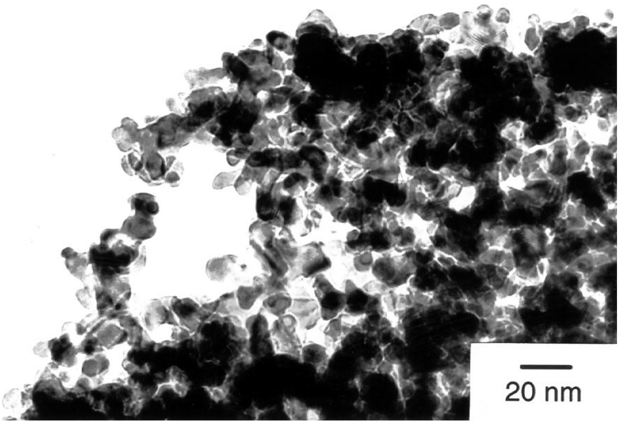

Fig. 7 A TEM micrograph of agglomerated Pd particles extracted from reduced Nd_4PdO_7.

SEM/EDS studies

EDS analysis of individual crystals of the starting material yielded a narrow distribution of compositions around Ln/Pd ratios of 4:1 in agreement with the stoichiometry of Ln_4PdO_7.

Pd particles extracted from reduced Nd_4PdO_7 were examined by SEM/EDS and TEM and found to have a particle size of 5–20 nm, as seen in Fig. 7. The EDS studies confirm that the particles did not contain any other metal but Pd.

Conclusion

We conclude that all materials of composition Ln_4PdO_7 with Ln = La, Nd, Sm, Eu, or Gd decompose upon reduction in a gas mixture of 20 vol.% CO and 80 vol.% He at elevated temperatures to micron sized crystals of the corresponding Ln_2O_3 oxide having Pd nano-particles in the size range 5–20 nm anchored to their surfaces. The reduced materials could easily be re-oxidised back to Ln_4PdO_7. The TG studies suggest that the re-oxidation process occurs in two steps for all lanthanoids except Sm and Gd. The DSC and XRPD studies of quenched samples suggest that the reduction process also occurs in at least two steps.

Pd particles extracted from reduced Nd_4PdO_7 were examined by TEM and found to have a particle size of 5–20 nm in agreement with the line-broadening analysis of the X-ray peaks recorded for the extracted material. These observations suggest that the formed particles are single crystals of Pd.

All reduced samples exhibited three way catalytic activity for the oxidation of CO and propene and reduction of NO with T_{50} values around 450 °C.

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References

1 M. Andersson, J. Grins and M. Nygren, manuscript in preparation.
2 M. Andersson, K. Jansson and M. Nygren, *Catal. Lett.*, 1996, **39**, 253.
3 M. Andersson, K. Jansson and M. Nygren, *Termochim. Acta*, 1998, **318**, 83.
4 M. Andersson, K. Jansson, L. Kihlborg and M. Nygren, *7th Nordic Symposium on Catalysis*, eds. T. Salmi and L.-E. Lindfors, Åbo Akademi, Åbo, Finland, 1996.
5 K. E. Johansson, T. Palm and P.-E. Werner, *J. Phys. E: Sci. Instrum.*, 1980, **13**, 1289.
6 P.-E. Werner, *Ark. Kemi,* 1996, **31**, 513.
7 C. L. McDaniel and S. J. Schneider, *J. Res. Nat. Bur. Stand.*, *Sect. A*, 1968, **72**, 27.
8 B. G. Kakhan, V. B. Lazarev and I. S. Shaplygin, *Russ. J. Inorg. Chem.*, 1982, **27**, 8.
9 J. I. Langford and A. J. C. Wilson, *J. Appl. Crystallogr.*, 1978, **11**, 102.

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