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Sol–gel processed fluorite-structured PrO_y–ZrO_2 mixed oxides deposited on alumina

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Preparation of PrO_y (Pr_6O_{11}) or single-phase fluorite-structured PrO_y–ZrO_2 mixed oxide, supported on high-surface-area γ-alumina, was achieved for the first time by impregnation of γ-alumina powder with $Pr(O^iC_3H_7)_3$ or a mixture of $Pr(O^iC_3H_7)_3$ and $Zr(O^iC_3H_7)_4\cdot{}^iC_3H_7OH$ and calcination at 600 °C. Subsequent calcination at 900 °C caused partial transformation of Pr_6O_{11} to $PrAlO_3$ but only improved the crystallinity of the mixed oxide. Further calcination at 1200 °C led to complete transformation of Pr_6O_{11} but only partial disproportionation of PrO_y–ZrO_2 to $PrAlO_3$ and ZrO_2; transformation of γ- to α-alumina was also inhibited in the case of the mixed oxide. In contrast, there was no evidence of any crystalline phase containing praseodymium upon calcination of γ-alumina powder impregnated with a mixture of praseodymium nitrate and zirconium chloride in a 1 : 0 or 1 : 1 molar ratio. These results show that praseodymium oxide can be supported on alumina and stabilized against reaction with the alumina by the incorporation of zirconium in the form of the mixed oxide, PrO_y–ZrO_2, provided it is deposited using alkoxide precursors. This stabilization should allow praseodymia to undergo redox processes and thus provide oxygen storage capacity when supported on alumina in a catalyst washcoat.

Introduction

Modern vehicles are equipped with three-way catalysts for the treatment of exhaust gases. It is necessary to maintain the ratio of reducing to oxidizing gases close to stoichiometric for the optimum performance of three-way catalysts. Control of air-to-fuel ratio by the standard oxygen sensor results in slight rich/lean excursions of the exhaust gas. Larger transients can occur in response to acceleration/deceleration. Since catalysts used for controlling exhaust gas emissions only operate effectively near the stoichiometric ratio of reducing to oxidizing gases, cerium oxide, an oxygen storage material, is added to the catalyst to damp out such variations.[1] Improved oxygen storage materials are needed, however, due to the demand for increasingly better catalyst performance and durability. Praseodymium oxide is one of the materials under investigation because it undergoes oxygen exchange at a lower temperature than cerium oxide, and its oxygen storage capacity (reducibility) is not diminished by high temperature sintering.[2] Historically, praseodymium oxide has not been used as an oxygen storage material, in part because it readily reacts with γ-alumina, the component of the washcoat which serves as the high-surface-area support for the catalytically active ingredients. The formation of praseodymium aluminate in a sample prepared by impregnation of γ-alumina with praseodymium nitrate and subsequent sintering has been proposed based on X-ray photoelectron spectroscopic analysis.[3] This aluminate is not an effective oxygen storage material because it does not allow easy Pr^{3+}–Pr^{4+} interconversion. Thus, praseodymium oxide can be used as an oxygen storage material only if its reaction with alumina can be prevented.

As an alternative to alumina, a high-surface-area praseodymium–zirconium mixed oxide, analogous to the cerium–zirconium mixed oxides currently in use, could possibly serve as the support material. Efforts by Sinev *et al.* to prepare such mixed oxides with low surface area using coprecipitation methods led to materials containing a mixture of phases.[4] Among these phases, the component crystallized in the fluorite structure allows Pr^{3+}–Pr^{4+} interconversion.[5] More recently, we have shown that high-surface-area single phase PrO_y–ZrO_2 materials, crystallized in the fluorite structure, can be prepared by the sol–gel process employing praseodymium and zirconium alkoxide precursors.[6] Our studies also show that the ratio of PrO_y to ZrO_2 should be higher than 1 : 3 because PrO_y–ZrO_2 fluorite containing less than 25% PrO_y is not an effective oxygen storage material. (Thus, zirconium oxide could not simply be used in place of γ-alumina in the washcoat because the PrO_y to ZrO_2 ratio in the resulting PrO_y–ZrO_2 material would be too small.)

In this report, we describe our studies on the deposition of PrO_y and PrO_y–ZrO_2 fluorite materials on γ-alumina employing alkoxide precursors. This is an ‘industry first’ approach to facilitate the use of praseodymium oxide as an oxygen storage material. Our results show that the reaction of PrO_y–ZrO_2 fluorite materials, deposited from alkoxides, with γ-alumina particles is not facile and requires relatively high-temperature calcination. At such temperatures, the transformation of γ-alumina to α-alumina also begins. This led us to also study the interaction of PrO_y–ZrO_2 with α-alumina substrates; these materials could be useful for high-temperature applications, *e.g.* 1000 °C in close-coupling with the exhaust manifold.

Experimental

The alkoxides were handled carefully in an inert atmosphere in a dry box. Solvents were carefully dried and distilled before use. The alkoxides of praseodymium and zirconium were prepared by known methods.[7] Commercial 2,4-pentanedione was distilled over sodium. For calcination, the samples were loaded in a ceramic crucible which was placed in a muffle furnace in an ambient atmosphere. Infra-red spectra of these samples were recorded on a Perkin-Elmer system 2000 instrument. Powder X-ray diffraction (XRD) was performed using a Scintag X1 diffractometer with Cu-Kα. Images and energy dispersive X-ray analyses were obtained using a Hitachi HF-2000 field emission transmission electron microscope equipped with a Noran ultra-thin-window detector system.

Preparation of PrO_y coated γ-alumina particles

A solution of $Pr(O^iC_3H_7)_3$ (0.107 g) in THF was added to 0.942 g γ-alumina powder ($\approx 100\ m^2\ g^{-1}$ BET surface area). The reaction mixture was stirred for two hours and volatiles were removed in vacuum. The residue was pyrolyzed at 600 °C (10 °C min^{-1}, 4 h hold) to obtain PrO_y coated particles. The amount of PrO_y is identical to that in the 10% PrO_y–ZrO_2/Al_2O_3 sample described below. We also prepared a sample in which the amount of PrO_y is identical to that in the 10% $3PrO_y$–ZrO_2/Al_2O_3 sample below.

Preparation of PrO_y–ZrO_2 coated γ-alumina particles

A solution of $Pr(O^iC_3H_7)_3$ (0.107 g) and $Zr(O^iC_3H_7)_4\cdot{}^iC_3H_7OH$ (0.132 g) in THF was added to 0.90 g γ-alumina powder. The reaction mixture was stirred for two hours and volatiles were removed in vacuum. A portion of residue (0.4 g) was pyrolyzed at 600 °C (10 °C min^{-1}, 4 h hold) to obtain PrO_y–ZrO_2 coated particles with a Pr : Zr molar ratio of 1 : 1. Corresponding materials with a Pr : Zr molar ratio of 1 : 1 (20% loading) and 3 : 1 (10% and 20% loadings) were prepared by appropriately adjusting the ratio of parent alkoxides and alumina.

Impregnation of γ-alumina with PrO_y–ZrO_2 employing salts

γ-Alumina (0.80 g) was added to a solution of praseodymium nitrate hexahydrate (0.22 g) and anhydrous zirconium chloride (0.157 g) in water (0.5 ml). The solution was carefully dried and the residue was pyrolyzed at 600 °C (5 °C min^{-1}, 4 h hold).

Preparation of PrO_y–ZrO_2 films on α-alumina coupons

Clear sols (0.1 M in THF) were prepared by adding 2,4-pentanedione to solutions of $Pr(O^iC_3H_7)_3$ and $Zr(O^iC_3H_7)_4\cdot{}^iC_3H_7OH$ in THF, cooling the reaction mixture to −78 °C, and slowly adding water mixed with THF while stirring. The sols were then warmed to room temperature and stored under a nitrogen atmosphere. A solution with a Pr : Zr molar ratio of 1 : 1 was obtained by combining the pure sols. PrO_y–ZrO_2 films on α-alumina coupons (square plates, 1 cm wide by 1 mm thick) were prepared by dip-coating at a withdrawal rate of 0.4 cm s^{-1}, drying to obtain xerogel films, and calcining for 30 min at 750 °C. The dip-coating/drying/calcination procedure was performed twice in order to double the film thickness. Additional calcination treatments were performed stepwise in a small high-temperature furnace (manufactured by CMS, Bloomfield, NJ, USA), heating and cooling at a rate of 20 °C min^{-1}, and holding at temperature for a period of 30 minutes. The steps in temperature were 900, 1050, 1200, 1300, and 1400 °C.

Results and discussion

Previous XPS studies have shown that the impregnation of γ-alumina with praseodymium nitrate and subsequent pyrolysis results in the formation of praseodymium aluminate.[3] In our case, after calcining at 600 °C, neither praseodymium oxide nor praseodymium aluminate could be detected in the XRD pattern of the powder. Impregnation of γ-alumina employing praseodymium alkoxide, on the other hand, furnishes a brown-colored powder which after calcining at 600 °C in air showed diffraction peaks due to praseodymium oxide crystallized in the fluorite structure [Fig. 1(A), (I)]. There were no diffraction peaks which could be assigned to praseodymium aluminate. Further calcination at 900 °C led to crystallization of praseodymium aluminate, but the diffraction peaks due to praseodymium oxide could also still be seen [Fig. 1(B), (I)]. Finally, after calcination at 1200 °C, diffraction peaks due to praseodymium oxide were absent and other diffraction peaks due to α-alumina appeared [Fig. 1(C), (I)].

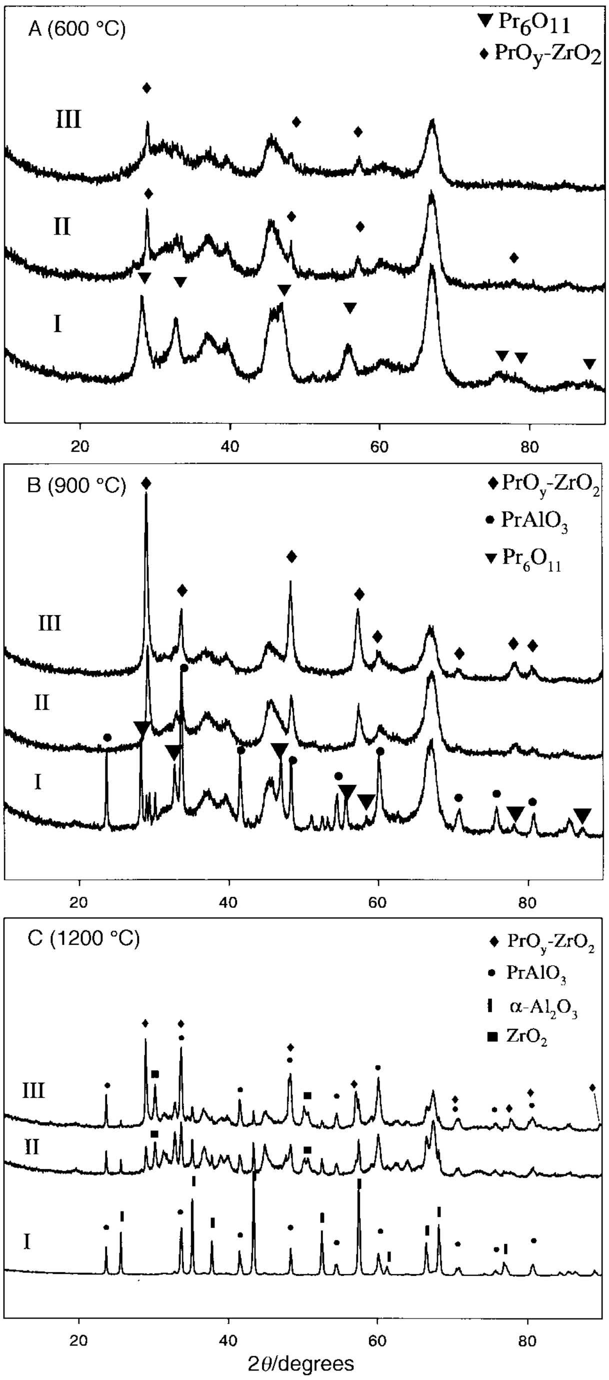
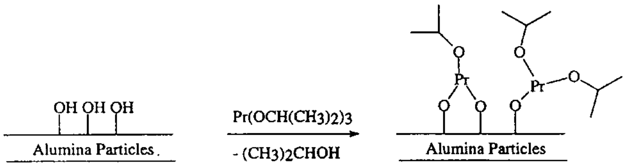


Fig. 1 X-Ray powder diffraction of PrO_y–ZrO_2 impregnated γ-alumina (from alkoxides): (A) 600 °C, (B) 900 °C, and (C) 1200 °C. [I, PrO_y on γ-Al_2O_3. II, 10% PrO_y–ZrO_2 on γ-Al_2O_3. III, 20% PrO_y–ZrO_2 on γ-Al_2O_3.]

The difference in thermal behavior of praseodymium-impregnated alumina from nitrate and alkoxide may be explained by the interaction of praseodymium alkoxide with hydroxy groups on alumina. This can lead to the formation of a protective layer upon pyrolysis. Thus, the reaction of praseodymium oxide with alumina can occur only after the breakdown of the protective layer and will require a relatively higher temperature treatment (see below).



The formation of such a protective layer cannot take place during impregnation with praseodymium nitrate. An alternative explanation which also involves differences in the chemistry of the precursors is that in the nitrate case praseodymium species uniformly coat the surface of the alumina, yielding a high dispersion and thus high dilution of praseodymium which subsequently reacts with alumina to produce an XRD-invisible phase. In the alkoxide case, on the other hand, the praseodymium precursor does not 'wet' the alumina surface well, so that large particles of praseodymium oxide form upon calcination. The locally high concentration of praseodymium which results then leads to subsequent formation of XRD-visible praseodymium aluminate upon further calcination.

We expected that a layer of zirconium oxide on alumina might protect against the reaction between praseodymium oxide and alumina because a high temperature treatment is needed for the reaction of zirconia with alumina. However, the thermal behavior of materials formed on impregnation of alumina with PrO_y–ZrO_2 employing a mixture of $Pr(NO_3)_3 \cdot 6H_2O$ and $ZrCl_4$ suggests that ZrO_2 does not form such a protective layer. The XRD pattern of this material exhibits only diffraction peaks due to γ-alumina after calcination at 600 °C (Fig. 2). Additional peaks due to zirconium oxide can be seen after calcination at 900 °C. Photographs of the material, obtained with high resolution transmission electron microscopy (HRTEM), at this stage are shown in Fig. 3. Energy dispersive spectra (EDS) from the encircled areas, A–C, in the top photograph reveal Pr and Zr in widely varying ratios on the alumina particles. This shows that the Pr distribution is independent of the Zr distribution. Although Pr was typically detected on most of the alumina particles examined, some areas, such as A and B in the bottom photograph, revealed only Zr; the lattice fringes in this photograph are thought to be due to ZrO_2.

It is important to note that the impregnation of alumina with zirconium oxide employing zirconium chloride and subsequent impregnation with praseodymium oxide employing praseodymium nitrate also did not prevent the apparent reaction of praseodymium oxide with alumina at 600 °C.

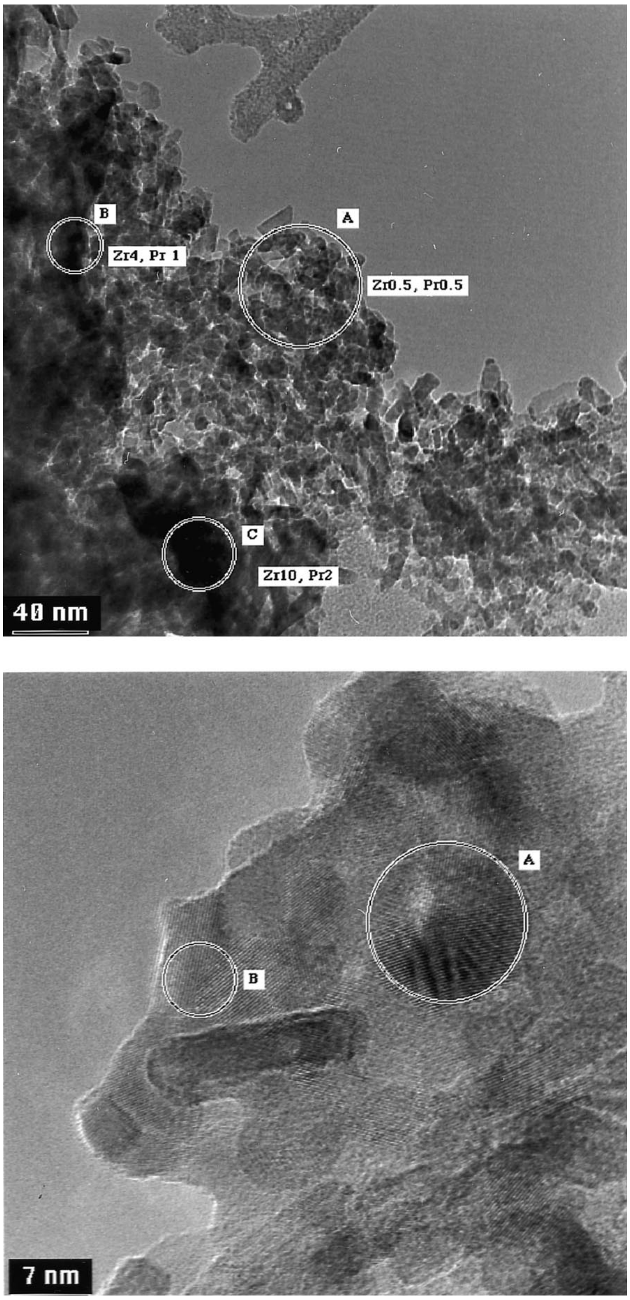


Fig. 3 HRTEM of PrO_y–ZrO_2 particles deposited on γ-alumina from salts after calcining at 900 °C.

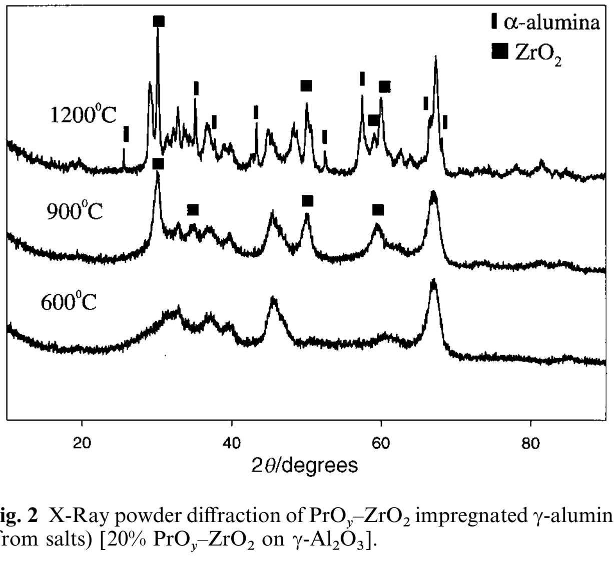


Fig. 2 X-Ray powder diffraction of PrO_y–ZrO_2 impregnated γ-alumina (from salts) [20% PrO_y–ZrO_2 on γ-Al_2O_3].

Since praseodymium oxide on alumina, deposited from alkoxides, is thermally more stable than that deposited from salts, we focused our efforts towards preparation of materials employing alkoxide precursors. The impregnation of γ-alumina with praseodymium and zirconium alkoxides in a 1 : 1 ratio (at both 10 and 20% w/w loadings) results in brown powders. The XRD patterns of the powders, calcined at 600 °C, clearly show the diffraction peaks corresponding to a cubic fluorite PrO_y–ZrO_2 structure [Fig. 1(A), (II) and (III)]. That the intensity of these peaks relative to the alumina peaks or PrO_y–ZrO_2 concentration does not scale with loading merely indicates that not all the mixed oxide is well enough crystallized at this stage to contribute to the XRD patterns. Indeed, much larger diffraction peaks due to the fluorite structure are observed after calcination at 900 °C [Fig. 1(B), (II) and (III)]. Significantly, there are no peaks corresponding to praseodymium aluminate, indicating that formation of the mixed oxide stabilizes against reaction between praseodymium oxide and alumina. Photographs of the 20 wt% sample, obtained with HRTEM, show small regions of PrO_y–ZrO_2 material with a Pr : Zr ratio of 1 : 1 on alumina particles (bottom photograph

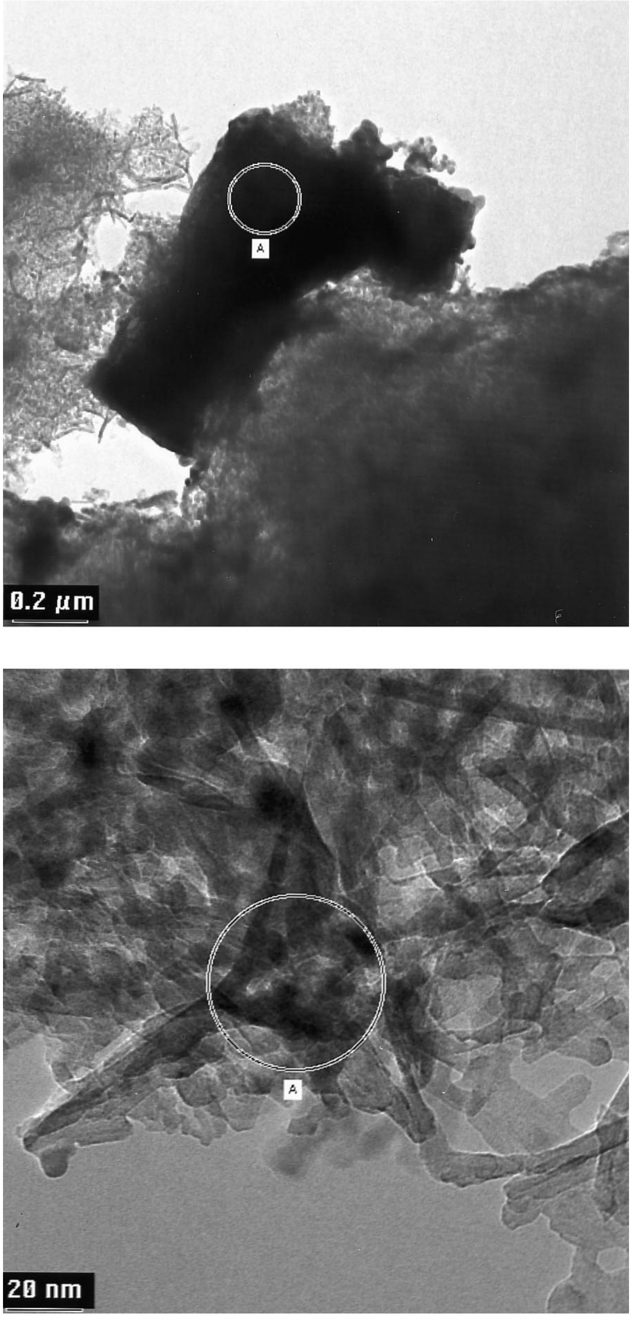


Fig. 4 HRTEM of PrO_y–ZrO_2 particles deposited on γ-alumina from alkoxides after calcining at 900 °C. The EDS of encircled areas show PrO_y–ZrO_2.

of Fig. 4) as well as some large PrO_y–ZrO_2 crystallites with particle size ≈0.8 µm (top photograph of Fig. 4). Such a distribution can be expected because the γ-alumina does not contain sufficient hydroxy groups to react with all alkoxy groups of the alkoxide precursors. This will result in the formation of PrO_y–ZrO_2 particles anchored on γ-alumina as well as some free PrO_y–ZrO_2 particles. An alternative explanation, following the reasoning of Xie *et al.*[8,9] and Bettman *et al.*,[10] is that free PrO_y–ZrO_2 particles can be expected since the amount of PrO_y–ZrO_2 present exceeds one monolayer coverage.

The EDS of several PrO_y–ZrO_2 particles, free and anchored on γ-alumina, show that there is no variation of the Pr : Zr ratio in the alkoxide-prepared material. This supports the conclusion drawn from XRD that all of the PrO_y–ZrO_2 exists in a single fluorite-structured phase at 900 °C. Further calcination at 1200 °C does, however, lead to disproportionation of PrO_y–ZrO_2 and formation of praseodymium aluminate, zirconia, and α-alumina [Fig. 1(C), (II) and (III)]. Note that the extent of the transformation of γ- to α-alumina is less, both here and in the case of the sample made from salts, than when zirconia is absent [Fig. 1(C), (I)].

The impregnation of γ-alumina using alkoxides with praseodymium and zirconium in 3 : 1 ratio (at both 10 and 20% w/w loadings) also results in a brown powder. Evolution of the X-ray powder diffraction patterns of these samples with calcination treatments closely paralleled that of the 1 : 1 samples except that some crystalline praseodymium aluminate was detected after 900 °C calcination.

These results suggest that the alkoxides play a more important role than just forming a barrier coating. Since praseodymium and zirconium alkoxides are highly reactive, both of them can contribute towards formation of a barrier layer. Furthermore, praseodymium alkoxide can associate with zirconium alkoxide to form $MM'(OR)_n$ type heterometallic alkoxides[11] leading to the preferential formation of fluorite-type PrO_y–ZrO_2 despite the presence of alumina. Since $3PrO_y$–ZrO_2 contains an excess of PrO_y, it behaves like a mixture of PrO_y and PrO_y–ZrO_2 in the presence of alumina and forms praseodymium aluminate at 900 °C in addition to fluorite $m PrO_y$–$n ZrO_2$ materials.

Thus, γ-alumina powders, impregnated with $m PrO_y$–$n ZrO_2$ ($m/n \geqslant 1$) fluorite materials exhibit considerable thermal stability and thus may be employed as oxygen storage materials, provided they are impregnated using alkoxide precursors. Comparable results are obtained for PrO_y–ZrO_2 films deposited on the α-alumina coupons, described below.

The PrO_y–ZrO_2 films (with a Pr : Zr ratio of 1 : 1) were deposited by a dip-coating method employing sols derived from 2,4-pentanedione modified praseodymium and zirconium alkoxides. Compared to a highly moisture sensitive solution of alkoxides, these sols are convenient for the deposition of films because they can be handled under ambient conditions. In a separate experiment, we pyrolyzed a mixture of praseodymium and zirconium oxide sols and found that they also formed pure single phase fluorite materials.

Thermal evolution of the thin (of the order of 10 nm) films made by dip-coating the coupons of α-alumina was followed by XRD. Dense, polycrystalline alumina was used in order to minimize absorption of the solution and also provide a best-case situation with respect to limiting subsequent reaction between the films and the alumina.

As shown in Fig. 5, films which are nearly invisible (due to low crystallinity) after calcination at 750 °C develop a (111) line characteristic of the PrO_y–ZrO_2 fluorite-structured phase by 900 °C. This phase is stable up to almost 1200 °C, where separation into praseodymia and zirconia phases begins to occur. By 1300 °C, only the high-temperature-stable tetragonal zirconia phase remains, praseodymia having apparently dissolved into the alumina substrate. (The feature at 31.3° originates from the substrate.)

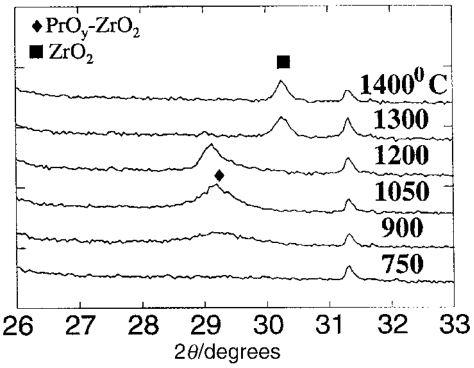


Fig. 5 Changes in XRD of PrO_y–ZrO_2 film on an α-alumina coupon upon calcination.

Conclusions

In conclusion, we have shown that single-phase PrO_y–ZrO_2 material crystallized in the fluorite structure can be deposited on alumina. The PrO_y–ZrO_2 material supported on γ-alumina is stable to at least 900 °C in air, and the PrO_y–ZrO_2 films on α-alumina substrates are stable even after calcining to 1200 °C. The stability of PrO_y–ZrO_2 on Al_2O_3 and its ability to release oxygen at relatively low temperature make it a candidate for automotive catalyst applications.

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