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New ceria-based catalysts for pollution abatement

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Abstract

In the present work, we describe the use of fluorite-structured solid solutions, based on mixtures of $CeO_2/La_2O_3/Pr_2O_3$, and similar systems, i.e. $CeO_2/Ln_2O_3/Pr_2O_3$ where Ln=Tb, Sm, and Gd as effective catalysts for methane combustion. Mixed lanthanide oxide doped ceria solid solutions were prepared using an evaporation method from nitrate precursors and were subsequently calcined to 1073 K. Sample characterisation was achieved using powder X-ray diffraction (PXRD) and temperature programmed reduction (TPR). PXRDs obtained subsequent to a 12 h calcination at 1073 K for 12 h all show peaks corresponding to a fluorite-based structure. There are no additional features suggestive of large-scale segregation or ordered superstructure formation. This was confirmed by Rietveld analysis which showed that the lattice possesses cubic nature with $a=b=c=5.50$ Å. Methane combustion tests show that the most effective catalysts are those lanthanide oxide doped ceria catalysts prepared with 5% Pr molar metal ratios. TPR experiments suggest PrO_2 is an essential component and both surface and bulk chemistries have important roles in catalytic activity. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: PXRD; TPR; Ceria

1. Introduction

Ceria-based materials have been widely investigated recently owing to their broad range of applications in different fields [1]: from the use of CeO_2 as an additive in the so-called three way catalysts for automotive exhaust treatment [2], to the use of CeO_2 in the preparation of advanced ceramic materials [3]. Particularly, the presence of CeO_2 has been found effective in the promotion of various catalytic reactions including, CO_2 activation [4], CO oxidation [5] and CO/NO removal [6]. In all these applications, two features result in making CeO_2 a promising material for use either as a support or active catalyst in oxidation–reduction reactions. These are: (a) the redox couple Ce^{3+}/Ce^{4+}, with the ability of ceria to shift between CeO_2 under oxidizing conditions and Ce_2O_3 under reducing conditions, respectively, and (b) the ease of formation of labile oxygen vacancies and particularly the relatively high mobility of bulk oxygen species [7].

The potential of CeO_2 to oxidize hydrocarbons has been known for several years and is found to be strongly dependent on pretreatment atmosphere and temperature. Herein we describe the activity of CeO_2 based materials in the catalytic combustion of CH_4 which has received considerable attention recently as an alternative to conventional thermal combustion [6]. It is believed that lanthanide based materials have activities comparable to other catalyst materials. In particular perovskites [8–10] and hexaaluminates [11] have also been described as very active for the total oxidation of methane.

Praesodymia, by itself, at low temperatures can form a wide range of ordered intermediate phases between Pr_2O_3 and PrO_2 [12]. Even in ambient conditions, PrO_2 has a considerable amount of defects

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and these exist in the form of anion vacancies. It is often best to denote the stoichiometry of the material in the general form PrO_{2-x}. Similar structural chemistry has been described for ceria [13]. However, at room temperature, in oxidising environments, the non-stoichiometry is negligible. The redox reactions, which are essential in oxidation catalysis, are achieved by phase transitions between these phases.

Lanthana is also known to have certain catalytic properties but its role is still poorly understood. Lanthana doped europium oxides have received considerable interest for use as phenol oxidative catalysts [14]. Lanthanum perovskites, e.g. $LaCoO_3$, are and have been investigated as potential catalysts for the control of automotive exhaust emissions and methane combustion [8–10]. In the case of ceria and ceria doped samples it is thought that the addition of 3+ cations enhances the catalytic activity through the production of anion vacancies, which compensate for the lower valency of the dopant [7].

2. Experimental

Powder X-ray diffraction (PXRD) patterns of all materials were obtained on a Philips PW 3710 MPD apparatus using Cu Kα (λ=1.54 Å) with an anode current of 40 mA and a voltage of 40 mV. Profiles were analysed using the PC-Rietveld programme available from Philips.

Temperature programmed reduction (TPR) experiments were carried out using a gas mixture of 3% H_2 and 97% N_2. Samples (40 mg) were pretreated in O_2 at 823 K for 1 h at a flow rate of 20 ml min^{-1} prior to the reduction experiment to effect both sample cleansing and ensure stoichiometry prior to reaction. A thermal conductivity detector (TCD), with accompanying Gow-Mac TCD controller compared the relative amounts of hydrogen in the gas which had passed over the sample with that in the reference flow. A Cambridge Process Controls Model 702 furnace controller controlled the sample temperature. The sample was contained in a straight quartz tube, which had a small well for a thermocouple. A total gas flow rate flow rate of 20 ml min^{-1} and heating rate of 20 K min^{-1} was used for all samples.

Catalyst activities (1 g sample) were routinely measured using a simple low pressure (0–5 atm) stainless steel flow through reactor (inside diameter 3 mm, 30 cm length) at a linear gas velocity of 20 cm s^{-1} (space velocity of 20 000 h^{-1}). A 2.61% CH_4 in air mixture was used for testing. Data were recorded as TPR_e profiles between 298 and 1258 K with a temperature sweep rate of 20 K min^{-1}.

CeO_2/Ln_2O_3 solid solutions, where Ln=La, Pr, Sm, Gd and Tb in less than 30% molar atomic ratio, were prepared by evaporation of nitrate solutions, at 353 K in air, from an intimate mix of their respective metal nitrates. Samples were dried, crushed, aged initially at 673 K to remove nitrates, reground and calcined in air at 1073 K for 12 h, ground again and sieved prior to analysis and testing.

3. Results

3.1. PXRD studies

Figs. 1 and 2 show typical PXRD patterns for various doped cerias, all prepared with 5% molar ratio of Pr and varying amounts of La and Ce, after calcination at 1073 K for 12 h. The compositions are indicated as, e.g. 90Ce/5La/5Pr, which refer to metal molar percentages. The diffractograms of all the samples and pure ceria are similar except that the doped cerias show a slight decrease in the 2θ values. There are no additional features present suggesting little component phase separation or vacancy ordering. There are minor asymmetries of some of the reflections for certain materials and this has been associated with small distortions of the fluorite lattice due to dopant/vacancy introduction [15]. These small distortions are ignored here since they are very small. The data, hence, provide evidence for expansion in the ceria lattice and good solid solution. The addition of the dopant ions to the lattice also results in a stabilisation of the primary particle size as measured by PXRD compared to pure ceria. It was found that both La and Pr are highly soluble in the ceria lattice. It is believed based on the evidence of the PXRD data and the high calcination temperature and long age times (in comparison to the testing procedure) used that little loss of surface area is noted during catalytic testing. At the low dopant levels prepared here, the dopant ions are in true solid solution and are randomly distributed in the ceria lattice, Ln^{3+} substituting for Ce^{4+} cationic sites. The increase in ion size,

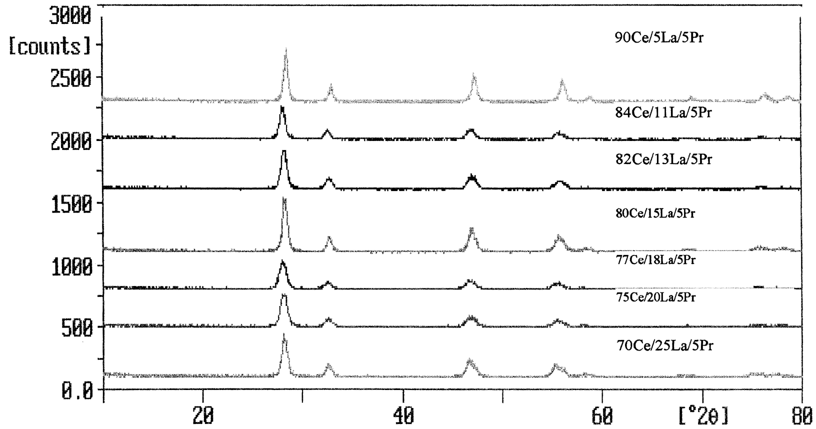

Fig. 1. PXRD patterns for various $CeO_2/La_2O_3/PrO_{2-x}$ mixed oxides aged at 1073 K for 12 h (compositions as indicated in figure).

e.g. Ce^{3+} compared to Ce^{4+} results in the expansion of the ceria unit cell parameter from that of 5.41 Å, the accepted value for pure ceria [16]. This can be seen in Table 1, which shows lattice parameter values for the doped mixed oxides as calculated from Rietveld refinement techniques. In all cases, there is expansion of the lattice, and the expansion appears to increase with lanthanide content. These values can give important information when compared with the CeO_2-PrO_{2-x} and the $CeO_2-La_2O_3$ systems. The CeO_2-PrO_{2-x} system (70Ce/30Pr and 80Ce/20Pr), show very small or negative expansions as expected since Pr^{4+} has an ionic radius which is just below Ce^{4+} (see below). However the $CeO_2-La_2O_3$ system (70Ce/30La and 80Ce/20La) exhibits quite significant expansion. The data suggest that La is being added as La^{3+} which has a larger ionic size than Ce^{4+} whilst Pr is being added as mostly Pr^{4+} which is only slightly smaller than Ce^{4+}.

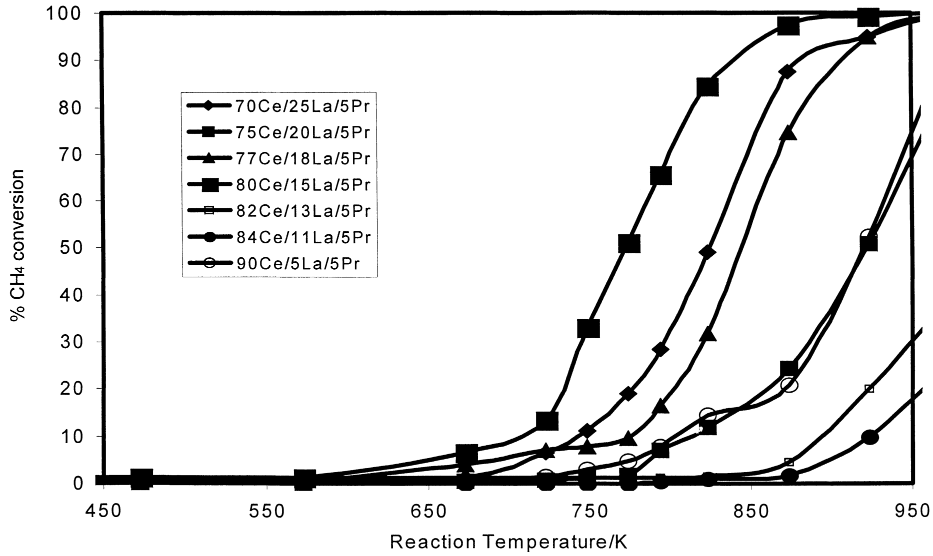

Fig. 2. Methane combustion profiles for various $CeO_2/La_2O_3/PrO_{2-x}$ mixed oxides, all prepared with 5% molar ratio of Pr after initial calcination at 1073 K for 12 h (compositions as shown).

Table 1
Lattice parameter values and T_{50} combustion values for the $CeO_2/La_2O_3/PrO_{2-x}$ mixed oxide system after initial calcination at 1073 k for 12 h (compositions as shown)

	T_{50} (K)	Lattice parameter (Å)
70Ce/25La/5Pr	794	5.50
75Ce/20La/5Pr	918	5.48
77Ce/18La/5Pr	843	5.48
80Ce/15La/5Pr	769	5.45
82Ce/13La/5Pr	989	5.42
84Ce/11La/5Pr	1025	5.42
90Ce/5La/5Pr	919	5.43
70Ce/30Pr	898	5.40
70Ce/5La/25Pr	876	5.43
70Ce/10La/20Pr	868	5.42
70Ce/15La/15Pr	921	5.45
70Ce/20La/10Pr	993	5.48
70Ce/30La	988	5.53
80Ce/20Pr	864	5.41
80Ce/5La/15Pr	850	5.42
80Ce/10La/10Pr	932	5.43
80Ce/20La	886	5.47

When La was replaced with other lanthanide dopants, i.e. Tb, Sm, Gd, smaller lattice expansions were generally observed. Unit cell parameters for these systems are shown in Table 2. It can be seen that these do not vary much from the lattice parameter of pure ceria. This is explained by the ionic radii of these cations. Due to the lanthanide contraction there is a slight decrease in the ionic radii as the atomic number increases and thus expansion is very much less than La^{3+}.

Table 2
Lattice parameter values and T_{50} combustion values for the $Ce_2O_3/M_2O_3/PrO_{2-x}$ mixed oxide systems (M=Tb, Gd, Sm), after initial calcination at 1073 K for 12 h (compositions as shown)

	T_{50} (K)	Lattice parameter (Å)
70Ce/25Tb/5Pr	1118	5.41
80Ce/15Tb/5Pr	978	5.41
90Ce/5Tb/5Pr	885	5.41
70Ce/25Gd/5Pr	943	5.41
80Ce/15Gd/5Pr	858	5.42
90Ce/5Gd/5Pr	893	5.42
70Ce/25Sm/5Pr	978	5.43
80Ce/15Sm/5Pr	1079	5.41
90Ce/5Sm/5Pr	1033	5.41

3.2. Catalytic testing

Table 1 summarises the methane combustion results for the $CeO_2/La_2O_3/PrO_{2-x}$ system and typical TPR_e data are shown for the 5% Pr systems. As can be seen, the most active catalysts for this reaction are those prepared with 5% Pr molar atomic ratio. The most active catalysts are $80CeO_2/15La_2O_3/5PrO_{2-x}$ followed by, $70CeO_2/25La_2O_3/5PrO_{2-x}$ which exhibit much lower "lightoff" temperatures and T_{50}'s, (the temperature needed for 50% conversion), of 769 and 794 K, respectively. This compares quite favourably with other known catalysts for the methane combustion reaction, e.g. Pt–Rh which has a T_{50} of 791 K and perovskites [8–10] and hexaaluminates [17] which possess activity in the range 753–823 K. As can be seen, analysis of trends in the data is quite difficult. If the data for the 5% Pr samples are compared it can be seen that total loadings of less than 20% are likely to be less active. It has been suggested that this is because of segregation of the lanthana component at these higher loadings [13]. PrO_{2-x} also appears to be a necessary component for a T_{50} of <873 K. It can also be seen that the presence of lanthana is necessary for good activity but moderate activity can be observed with PrO_{2-x} addition also.

When Tb, Sm and Gd are substituted for La, the activities drop in all cases, sometimes quite dramatically. The results for samples co-doped with 5% PrO_{2-x} are summarised in Fig. 3 and Table 2. Direct comparison to Table 1 can be made with similar catalysts. It can be seen that in almost every example replacement of La^{3+} results in a lower T_{50} value. If average T_{50} values, for a set of the same dopant, are taken from Table 2, then the order of descending activity for the 5% PrO_{2-x} catalysts are La, Gd, Tb and Sm as secondary dopants.

3.3. TPR studies

In order to elucidate the reason for the enhanced activity of the $CeO_2/La_2O_3/PrO_{2-x}$ system and especially those prepared with 5% Pr molar ratio, TPR analysis experiments were carried out. Illustrative results are summarised here in Fig. 4 and are compared with similar experiments on pure ceria. In the experiments two features can be seen for some of the tertiary doped samples investigated. By analogy to earlier ceria

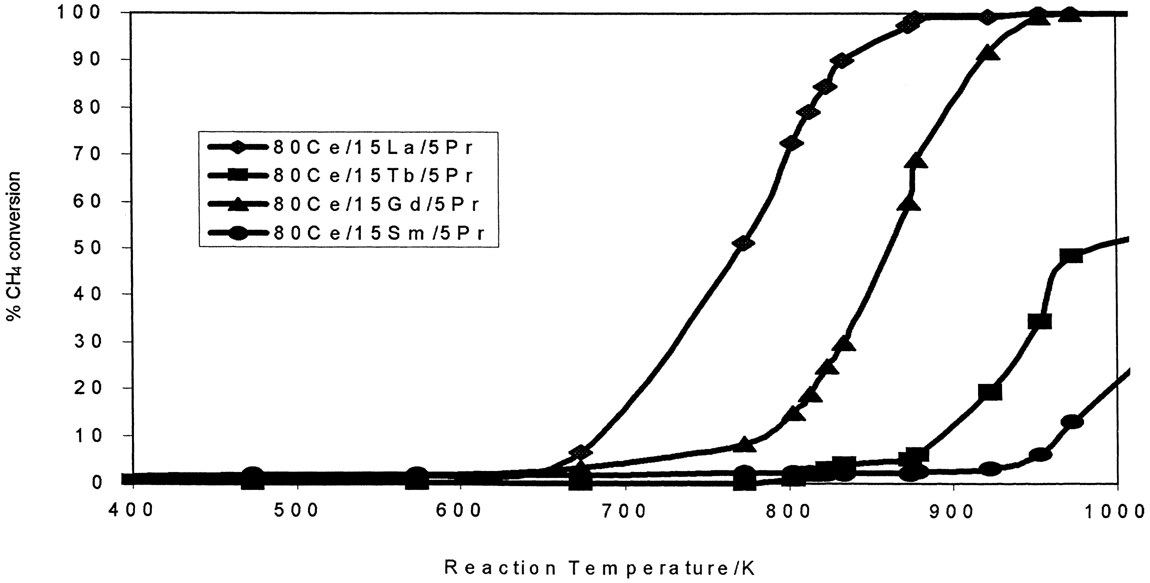

Fig. 3. Methane combustion profiles for $80CeO_2/15M_2O_3/5PrO_{2-x}$ where M=La, Tb, Gd, Sm, after initial calcination at 1073 K for 12 h (compositions as shown).

reduction studies [1], a high temperature component at approximately 823 K could be identified as being due to bulk reduction and a second peak at 623 K and below due to surface reduction. Several samples show only bulk features. CeO_2 has a surface-type reduction feature at 700 K and a small bulk reduction feature at 1100 K, since CeO_2 is thought to be more difficult to reduce than PrO_2. The La_2O_3 doped materials show a bulk reduction feature suggesting the anion vacancies promote this reaction. In all cases the reduction temperature of the bulk peak was significantly lowered to 823 K compared with 1100 K for pure ceria. It can be

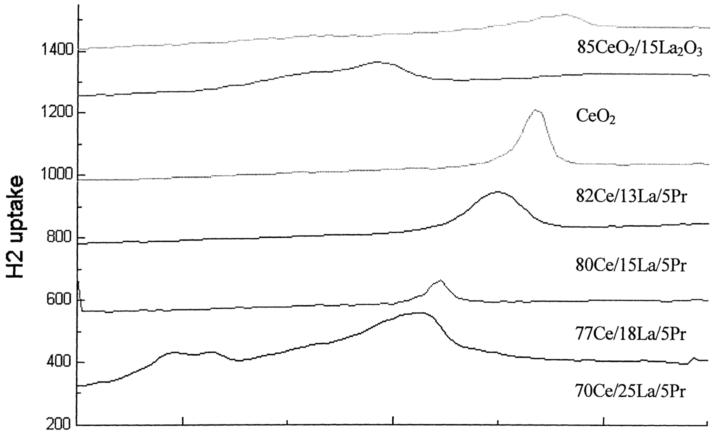

Fig. 4. TPR data for various $CeO_2/La_2O_3/PrO_{2-x}$ mixed oxides compared to that of pure ceria. All samples were initially calcined at 1073 K for 12 h before reduction (samples shown in figure text).

seen that the amount of H_2 uptake for the surface reduction peak is quite low relative to the bulk peak for all of the PrO_{2-x} doped samples. One possible reason for this behaviour is, enhanced bulk diffusion of anion vacancies to the surface, due mainly to the introduction of PrO_{2-x} to the ceria lattice, thus enhancing the activity. However, the presence of a low temperature surface reduction peak for $70CeO_2/25La_2O_3/5PrO_{2-x}$, which is not readily seen for the more active catalyst $80CeO_2/15La_2O_3/5PrO_{2-x}$, also implies that the kinetics of the methane combustion reaction are only weakly related to the "reducibility" of the surface.

4. Discussion

Much as we would like to, it is not possible to offer facile arguments explaining activity trends for these catalysts. It is possible to suggest some general guidelines in preparing these catalysts. The concentration and type of dopant is crucial, dopants other than lanthana and praseodymia being least effective. Also, the most efficient catalysts have 5% loadings of PrO_{2-x} and the total lanthanide dopant content does not exceed 25 metal at.% in total.

The special activity of lanthana (compared to other dopants used) can be simply correlated to its effect on the host lattice expansion. Ce^{4+}, with an ion size of about 0.1 nm, is almost perfectly sized to fit into the close-packed (anion) fluorite lattice. La^{3+} is significantly larger at 0.11 nm and its introduction will result in lattice strain and the introduction of free volume. This will facilitate the equilibrium of oxygen atoms between the surface and the bulk. This is seen in the appearance of a significant "bulk" reduction feature in the TPR results for La_2O_3/CeO_2 systems, as in Fig. 4. Addition of 5% PrO_{2-x} dramatically changes the TPR spectrum, which now shows a larger bulk reduction feature. It is this feature which seems to correlate with catalytic activity, suggesting "bulk" reduction is important in defining high catalytic activity.

It can be concluded that the bulk redox chemistry is very important in these systems with the surface playing a minor role. Lanthana addition appears to promote the material for facile surface–bulk oxygen transport. The role of PrO_{2-x} may be important in a similar way. Ordered phases of Pr oxides are well known [12] and are much more easily observed than equivalent ceria phases [18]. It is suggested here that the formation of similar vacancy ordered phases as a result of doping of Pr may allow facile migration along ordered arrays of anion vacancies enhancing oxygen mass transport.

Two explanations for the importance of loading at the surface chemistry are offered here. Firstly in the working conditions (i.e. at high temperature), the surface is essentially completely reduced to M_2O_3 and it is the bulk that acts as an oxygen source. Secondly, the surface may be passivated by a layer of lanthana. Recent NMR research from these laboratories suggest that the surface is essentially covered with this oxide for almost all La_2O_3/CeO_2 compositions [15]. Recent work by Dunwoody et al. [19] have suggested that traditional surface spectroscopies such as XPS and SIMS are poor at quantifying low levels of surface segregation in the systems and such effects might account for the non-observance of segregation by other workers.

Finally, we point out that the activity is not related to surface area. BET measurements and particle size comparisons are not well correlated with activity as can be seen on inspection of PXRD peak widths in Fig. 1, which are very similar. It, thus, appears that simple models based on the availability of anion vacancies at the surface have little effect on activity. It is not suggested that the surface does not play an important role (e.g. it clearly leads to bulk reduction). However, it is not "all-important" in deciding the effectiveness of these materials as methane combustion catalysts.

5. Conclusions

It has been shown that ceria based catalysts can be effective for the catalytic combustion of methane and are comparable in activity to other conventional catalysts for this reaction. The concentration and type of dopant is critical, the most efficient catalysts being mixed oxides of ceria/lanthana/praseodymia, with praseodymia present in 5% molar ratio. It is believed that improved activity is due to, in the main, the defect chemistry of the system. Effectively, lanthana incorporation is responsible for production of anion vacancies but more importantly lattice expansion, which apparently enhances diffusion from the bulk to the surface. Praseodymia provides an important effect to the system by enhancing the rate still further of bulk to surface mass transport. It might tentatively be suggested that this could be due to PrO_2 addition, producing ordered arrangements of vacancies.

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