CeO_2-based Solid Solutions with the Fluorite Structure as Novel and Effective Catalysts for Methane Combustion

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The partial substitution of Ce in CeO_2 with isovalent elements like Hf and Zr greatly increases the overall activity of methane combustion measured as light-off and ignition temperature; the presence of a defective fluorite-structured oxide is recognized as a key factor in the activity enhancement.

Ceria-based materials have been widely investigated in the last years owing to the broad range of applications in different fields: from the use of CeO_2 as an additive in the so-called three-way catalysts for automotive exhaust treatment,[1] to the use of CeO_2 in the preparation of advanced ceramic materials.[2] Particularly, the presence of CeO_2 has been found effective in promotion of catalytic reactions for CO_2 activation,[3] CO oxidation[4] and CO/NO removal.[5] Also, very recently, it has been reported that the presence of defect sites in ceria–zirconia mixed oxides are effective in enhancing the oxygen storage and release capacities of these materials in comparison to pure CeO_2 and ZrO_2.[6] In all these applications, the two most remarkable features that make CeO_2 a promising material for use as support or catalyst in oxidation–reduction reactions are: (*i*) the redox couple Ce^{III}/Ce^{IV}, with the ability of ceria to shift between CeO_2 under oxidizing conditions and Ce_2O_3 under reducing conditions respectively; and, (*ii*) the ease of formation of oxygen vacancies and the relatively high mobility of bulk oxygen.

Here, we describe the activity of CeO_2-containing materials in the catalytic combustion of CH_4 which has received considerable attention recently as an alternative to conventional thermal combustion.[7] Several materials have been used as effective catalysts for methane combustion; in particular perovskites and aluminates have been described as very active catalysts for the total oxidation of methane.[8] In the present work, we describe the use of fluorite-structured solid solutions, based on CeO_2, as effective catalysts for methane combustion.

CeO_2, ZrO_2 and HfO_2 were prepared by precipitation with ammonia from the corresponding nitrates or chlorides, followed by washing, drying and calcination at 1200 K. $Ce_{0.8}Zr_{0.2}O_2$ and $Ce_{0.8}Hf_{0.2}O_2$ were prepared by coprecipitation by adding dropwise an aqueous solution of $Ce(NO_3)_3{\cdot}6H_2O$, $ZrO(NO_3)_2{\cdot}xH_2O$ or $HfCl_4$, of the appropriate composition, to a solution of concentrated ammonia. After precipitation, the mixture has been filtered, washed, dried at 373 K for approximately 15 h and then calcined at 1200 K for 2 h. The powders have been characterised by X-ray diffraction, surface area (BET) measurements, temperature-programmed reduction and transmission electron microscopy coupled with electron dispersive X-ray analysis (TEM-EDX). Catalytic measurements were carried out on a quartz microreactor (8 mm ID, 20 cm long) loaded with 0.18 cm^3 of catalyst diluted with granular quartz. The inlet gas composition was CH_4 (1%), O_2 (4%) with He as balance, and the flow rate was adjusted to have a space velocity of 34 000 h^{-1}. The temperature was monitored with a 0.5 mm thermocouple immersed in the catalyst bed and the inlet and outlet gas composition was measured with a gas chromatograph equipped with a heated ten-way sampling valve.

Table 1 BET surface areas and activity data for the investigated catalysts

Sample	Surface area[a]	T/K (10%)[b]	T/K (50%)[c]	Reaction rate[d]
CeO_2	6	835	945	1.18
ZrO_2	10	920	970	0.36
HfO_2	9	825	900	1.92
$Ce_{0.8}Zr_{0.2}O_2$[e]	29	730	815	9.34
$Ce_{0.8}Hf_{0.2}O_2$[e]	26	735	830	7.53
Pt/CeO_2[f]	11	790	890	7.32

[a] BET surface area ($m^2\ g^{-1}$). [b] Temperature for 10% conversion of CH_4 to CO_2. [c] Temperature for 50% conversion of CH_4 to CO_2. [d] Rate measured at 725 K: μmol $g^{-1}\ s^{-1}$. [e] Lifetime of these catalysts has also been tested at 823 and 973 K (*i.e.* at approx. 50% and total conversion). Deactivation is not observed after 24 h on stream. The initial behaviour of the catalysts is also unaffected by deactivation [f] Pt/CeO_2 has been prepared by incipient wetness impregnation of CeO_2 with H_2PtCl_6 followed by drying and calcination. The catalyst has been calcined at 973 K and then reduced *in situ* at 573 K before catalytic tests. Data have been taken after 3 h on stream.

The homogeneity of the samples have been tested with EDX analysis, and all powders consist of particles that correspond well with the starting composition; no areas rich in one element only have been observed. X-ray diffraction analysis also confirms the formation of solid solutions with the fluorite structure. BET measurements (Table 1) indicate that higher specific surface areas are obtained by introduction of Zr and Hf into the fcc cell of CeO_2.

The catalytic activity of CeO_2 based mixed oxide have been carried out to study the effect of isovalent cation substitution in CeO_2 lattice on the ignition and light-off temperature in the combustion of methane. The results at different temperatures, in the range 573–1073 K, are reported in Fig. 1 and the overall activity and specific kinetic data are reported in Table 1. It is shown that the activity is greatly enhanced by introduction of Zr^{4+} and Hf^{4+} into CeO_2 lattice; $Ce_{0.8}Zr_{0.2}O_2$ reaches 50% conversion at 130 K lower than ceria and 165 K lower than ZrO_2. To obtain any given conversion between 10 and 80% with the pure oxides requires a temperature of *ca.* 80–200 K higher than that of the corresponding doped oxides. It should be noted that with CeO_2 and $Ce_{0.8}M_{0.2}O_2$, carbon monoxide is not formed and the selectivity to CO_2 is almost 100%, while in the case of ZrO_2 and HfO_2, a considerabe amount of CO is formed

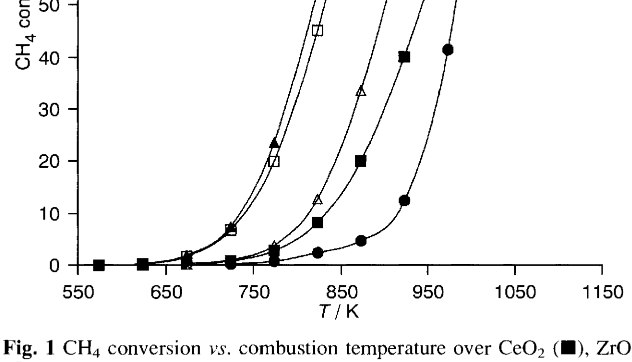

Fig. 1 CH_4 conversion *vs.* combustion temperature over CeO_2 (■), ZrO_2 (●), HfO_2 (△), $Ce_{0.8}Zr_{0.2}O_2$ (▲), and $Ce_{0.8}Hf_{0.2}O_2$ (□)

(from 5 mol% of CO with HfO_2 to a maximum of 40% with ZrO_2). Moreover, CeO_2-based catalysts do not show any deactivation after 24 h under reaction conditions at 823 and 973 K. The overall activity of solid solutions is comparable with that of Pt/CeO_2 under the same reaction conditions (Table 1).

Quantitative temperature-programmed reduction of ceria and of the solid solutions are shown in Fig. 2. The presence of two peaks in CeO_2 has been associated with a stepwise reduction of the oxide; the second signal is mainly due to bulk oxygen removal while the first peak has been related to easily reducible surface Ce^{IV}.[3] The isovalent substitution of Zr and Hf in the fcc cell of CeO_2 dramatically lowers Ce^{IV}–Ce^{III} reduction temperature, as can be seen from the TPR profile shown in Fig. 2. This fact has been recently observed in the case of low surface area Ce–Zr solid solutions[6,9] and has been attributed to the increased oxygen mobility in the defective fluorite structure generated by introduction of the smaller Zr cation.[6] The present results extend those findings to other fluorite-structured CeO_2-based solid solutions in which some Ce atoms have been substituted with isovalent cations with smaller dimensions, like the present case in which Hf^{4+} (with a crystal ionic radius of 0.78 Å) has replaced some Ce^{4+} atoms (ionic radius 0.92 Å).[10]

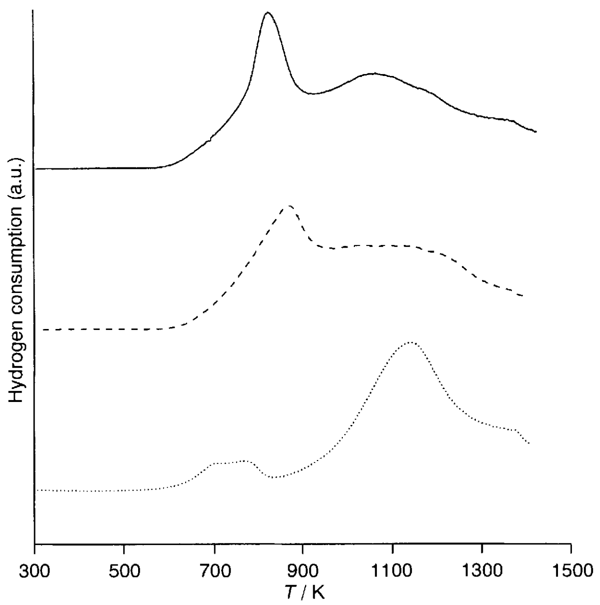

Fig. 2 Temperature-programmed reduction of $Ce_{0.8}Zr_{0.2}O_2$ (——), $Ce_{0.8}Hf_{0.2}O_2$ (– – –), and CeO_2 (···). For clarity the area of the curves has been normalized.

It is likely that the increase in the oxidation activity is related to the following factors: (*i*) the higher oxygen mobility at lower temperatures for fluorite-structured mixed oxides in comparison to pure CeO_2.[11] (*ii*) the lower reduction temperature of Ce^{IV}, and thus the increased ability of CeO_2 to shift between Ce^{IV} and Ce^{III} at much lower temperature, as determined by quantitative TPR measurements. This could facilitate the creation of oxygen vacancies and their subsequent reaction with reactant gas-phase oxygen. Annihilation of oxygen vacancies with formation of oxygen-hole centres, have been recently invoked to elucidate the role of defects and oxygen ion migration in the catalytic activity of doped lanthanum oxide in oxidation reactions.[12]

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