## CeO<sub>2</sub>-based Solid Solutions with the Fluorite Structure as Novel and Effective Catalysts for Methane Combustion

Francesca Zamar, Alessandro Trovarelli,\* Carla de Leitenburg and Giuliano Dolcetti

Dipartimento di Scienze e Tecnologie Chimiche, Università di Udine, via Cotonificio 108, 33100 Udine, Italy

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<sub>2</sub> as an additive in the so-called threeway catalysts for automotive exhaust treatment,<sup>1</sup> to the use of CeO<sub>2</sub> in the preparation of advanced ceramic materials.<sup>2</sup> Particularly, the presence of CeO2 has been found effective in promotion of catalytic reactions for CO<sub>2</sub> activation,<sup>3</sup> CO oxidation<sup>4</sup> and CO/NO removal.<sup>5</sup> 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<sub>2</sub> and ZrO2.6 In all these applications, the two most remarkable features that make CeO<sub>2</sub> a promising material for use as support or catalyst in oxidation-reduction reactions are: (i) the redox couple Ce<sup>III</sup>/Ce<sup>IV</sup>, with the ability of ceria to shift between CeO<sub>2</sub> under oxidizing conditions and Ce<sub>2</sub>O<sub>3</sub> 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.<sup>7</sup> 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.<sup>8</sup> In the present work, we describe the use of fluorite-structured solid solutions, based on CeO<sub>2</sub>, as effective catalysts for methane combustion.

CeO<sub>2</sub>, ZrO<sub>2</sub> and HfO<sub>2</sub> were prepared by precipitation with ammonia from the corresponding nitrates or chlorides, followed by washing, drying and calcination at 1200 K. Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub> and Ce<sub>0.8</sub>Hf<sub>0.2</sub>O<sub>2</sub> were prepared by coprecipitation by adding dropwise an aqueous solution of Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, ZrO-(NO<sub>3</sub>)<sub>2</sub>·*x*H<sub>2</sub>O or HfCl<sub>4</sub>, 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

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

Sample	Surface area <sup>a</sup>	T/K (10%) <sup>b</sup>	T/K (50%) <sup>c</sup>	Reaction rate <sup>d</sup>	
CeO <sub>2</sub>	6	835	945	1.18	
$ZrO_2$	10	920	970	0.36	
HfO <sub>2</sub>	9	825	900	1.92	
$Ce_{0.8}Zr_{0.2}O_{2}e^{e}$	29	730	815	9.34	
$Ce_{0.8}Hf_{0.2}O_2^e$	26	735	830	7.53	
Pt/CeO <sub>2</sub> <sup>f</sup>	11	790	890	7.32	

<sup>*a*</sup> BET surface area (m<sup>2</sup> g<sup>-1</sup>). <sup>*b*</sup> Temperature for 10% conversion of CH<sub>4</sub> to CO<sub>2</sub>. <sup>*c*</sup> Temperature for 50% conversion of CH<sub>4</sub> to CO<sub>2</sub>. <sup>*d*</sup> Rate measured at 725 K: µmol g<sup>-1</sup> s<sup>-1</sup>. <sup>*e*</sup> 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 / Pt/CeO<sub>2</sub> has been prepared by incipient wetness impregnation of CeO<sub>2</sub> with H<sub>2</sub>PtCl<sub>6</sub> 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.

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<sup>3</sup> of catalyst diluted with granular quartz. The inlet gas composition was CH<sub>4</sub> (1%), O<sub>2</sub> (4%) with He as balance, and the flow rate was adjusted to have a space velocity of 34 000 h<sup>-1</sup>. 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.

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<sub>2</sub>.

The catalytic activity of CeO<sub>2</sub> based mixed oxide have been carried out to study the effect of isovalent cation substitution in CeO<sub>2</sub> 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<sup>4+</sup> and Hf<sup>4+</sup> into CeO<sub>2</sub> lattice; Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub> reaches 50% conversion at 130 K lower than ceria and 165 K lower than ZrO<sub>2</sub>. 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<sub>2</sub> and Ce<sub>0.8</sub>M<sub>0.2</sub>O<sub>2</sub>, carbon monoxide is not formed and the selectivity to CO<sub>2</sub> is almost 100%, while in the case of ZrO<sub>2</sub> and HfO<sub>2</sub>, a considerabe amount of CO is formed



**Fig. 1** CH<sub>4</sub> conversion *vs.* combustion temperature over CeO<sub>2</sub> ( $\blacksquare$ ), ZrO<sub>2</sub> ( $\bigcirc$ ), HfO<sub>2</sub> ( $\triangle$ ), Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub> ( $\blacktriangle$ ), and Ce<sub>0.8</sub>Hf<sub>0.2</sub>O<sub>2</sub> ( $\square$ )

(from 5 mol% of CO with HfO<sub>2</sub> to a maximum of 40% with  $ZrO_2$ ). Moreover, CeO<sub>2</sub>-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<sub>2</sub> 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<sub>2</sub> 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<sup>1V,3</sup> The isovalent substitution of Zr and Hf in the fcc cell of CeO<sub>2</sub> dramatically lowers Ce<sup>IV</sup>-Ce<sup>III</sup> 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<sup>6,9</sup> and has been attributed to the increased oxygen mobility in the defective fluorite structure generated by introduction of the smaller Zr cation.<sup>6</sup> The present results extend those findings to other fluorite-structured CeO<sub>2</sub>based solid solutions in which some Ce atoms have been substituted with isovalent cations with smaller dimensions, like the present case in which Hf4+ (with a crystal ionic radius of



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.

0.78 Å) has replaced some Ce4+ atoms (ionic radius

0.92 Å).<sup>10</sup> 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<sub>2</sub>.<sup>11</sup> (*ii*) the lower reduction temperature of Ce<sup>IV</sup>, and thus the increased ability of CeO<sub>2</sub> to shift between Ce<sup>IV</sup> and Ce<sup>III</sup> 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.<sup>12</sup>

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