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# Acid-base properties and catalytic activity of nanophase ceria-zirconia catalysts for 4-methylpentan-2-ol dehydration

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The room-temperature high energy ball-milling technique was used to prepare nanophase  $Ce_{1-x}Zr_xO_2$  (x = 0; 0.2; 0.5; 0.8; 1) catalysts. The acid-base properties of these catalysts were investigated by means of adsorption microcalorimetry, using NH<sub>3</sub> and CO<sub>2</sub> as probe molecules. The catalytic activity for 4-methylpentan-2-ol dehydration was tested at atmospheric pressure in a fixed-bed flow microreactor. The inclusion of increasingly high contents of zirconium into the ceria lattice has a complex influence on the acidity and basicity of the pure parent oxide, in terms of both number and strength of the sites. A maximum in 1-alkene selectivity is observed for the ceria-rich catalyst and a minimum for the zirconia-rich sample. Catalytic results are correlated with the acid-base properties and can be interpreted in the light of the mechanism formerly proposed for zirconia, ceria and lanthania. Surface conditioning of the zirconia-rich catalyst occurs during the run, resulting in a remarkable variation of selectivity.

In an attempt to enhance the redox properties of ceria by incorporating foreign cations in its lattice, ceria-zirconia solid solutions have been prepared both by  $conventional^{1,2}$  and innovative methods. $^{3-5}$  The increased redox capability of ceria-zirconia solid solutions has also been investigated with computer simulation techniques.<sup>6</sup> Little has been published about the acid-base features of ceria, despite the key role of this parameter in several catalytic applications. The surface acidity and basicity of ceria has been investigated by temperature-programmed desorption of ammonia and stepwise thermal desorption of carbon dioxide and it is believed that acid-base pairs are important in the activation of hydrocarbons at high temperatures.<sup>7</sup> Mechanistic studies with deuterated butan-2-ols indicated that acid-base sites are involved in the dehydration reaction over ceria.8 The microcalorimetric technique has been recently used to assess the acid-base properties of ceria catalysts for the dehydration of 4methylpentan-2-ol.9 Temperature-programmed desorption of ammonia and CO<sub>2</sub>, spectroscopic investigation of the adsorption of CO<sub>2</sub> and pyridine, titration by benzoic acid and test reactions were used to study the surface acidity and basicity of CeO<sub>2</sub>-CaO mixed oxides obtained by coprecipitation.<sup>10</sup> To the present authors' knowledge, however, no papers have been published concerning the acid-base features of ceria-zirconia solid solutions.

The present paper deals with the acid-base properties and the catalytic activity for 4-methylpentan-2-ol dehydration of nanophase  $CeO_2$ -ZrO<sub>2</sub> solid solutions, prepared by roomtemperature high energy ball-milling, whose redox and oxygen storage properties had been formerly investigated.<sup>5</sup> The conversion of 4-methylpentan-2-ol is important from the practical viewpoint as an alternative route to 4-methylpent-1-ene, a monomer for the manufacture of thermoplastic polymers of superior technological properties (TPX). Fine tuning of the acid-base character of the catalyst is essential in order to obtain high selectivity to the desired 1-alkene and avoid parasitic formation of olefins with internal double bond and/or dehydrogenation to ketone;<sup>9,11</sup> accordingly, 4-methylpentan-2-ol conversion also represents a useful test reaction for characterising the acidity and basicity of catalysts.<sup>12</sup> Microcalorimetry has gained importance as one of the most reliable methods for the study of surface acidity and basicity of solid catalysts. Accordingly, direct assessment of the acid-base properties of the ceria-zirconia solid solutions, in terms of both site concentrations and strength distributions, has been carried out by means of this technique, using ammonia and carbon dioxide as probe molecules.

## **Experimental**

CeO<sub>2</sub> (Aldrich, 99.999% pure) was used as received.  $ZrO_2$  was prepared from hydrous zirconia (MEL chemicals) by calcination at 973 K. The solid solutions were prepared by milling appropriate amounts of the two component oxides in a highenergy vibratory ball-mill (Spex 8000) working at an oscillation frequency of 20 Hz and an amplitude of 20 cm. Both the vial (V = 50 cm<sup>3</sup>) and the balls ( $\phi = 10$  mm) were  $ZrO_2$ made, in order to avoid leaching contamination with iron and tungsten from the milling apparatus. The ball-to-powder ratio was 18:1 by weight (*i.e.* 6 balls and 1 g of powder) and the milling time 9 h. The composition of the solid solutions prepared through this way, as well as their structural and textural features, are summarised in Table 1. Further details are reported elsewhere,<sup>5</sup>

Tian-Calvet heat flow equipment (Setaram) was used for microcalorimetric measurements. Each sample was pretreated

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Sample	Surface area $/m^2 g^{-1}$	Phase
CeO <sub>2</sub>	3	Cubic
$Ce_{0.8}Zr_{0.2}O_2$	21	Cubic
$Ce_{0.5}Zr_{0.5}O_{2}$	12	Cubic (traces tetragonal)
$Ce_{0.2}^{0.5}Zr_{0.8}^{0.5}O_2^2$	8	Tetragonal (traces cubic and monoclinic)
ZrO <sub>2</sub>	28	Monoclinic

overnight at 673 K under vacuum  $(10^{-3} \text{ Pa})$  before the successive introduction of small doses of the probe gas (ammonia or carbon dioxide). The equilibrium pressure relative to each adsorbed amount was measured by means of a differential pressure gauge (Datametrics). The run was stopped at a final equilibrium pressure of 133.3 Pa. The adsorption temperature was maintained at 353 K, in order to limit physisorption.

Testing of the catalytic activity was performed at atmospheric pressure in a quartz-made fixed-bed flow microreactor (10 mm id). All the equipment devices, including the stainlesssteel pipes to and from the reactor, had been passivated by hot HNO<sub>3</sub> treatment before the assembling. The catalyst was activated in situ (6 h at 773 K under CO<sub>2</sub>-free air flow). 4-Methylpentan-2-ol was fed in with an N2 stream (partial pressure,  $p_{0, \text{ alcohol}} = 15.5$  kPa, time factor, W/F = 2.5 g<sub>cat</sub> h  $g_{alcohol}^{-1}$ ). For each catalyst, several reactor temperatures were checked during the same run, until about 50% conversion was reached. A new run with a fresh portion of the same sample was then started and carried out at the temperature giving 50% conversion, in order to exclude influence of the thermal history of the sample on its catalytic behaviour and allow a better comparison of the catalysts. On-line capillary GC analysis conditions were: Petrocol DH 50.2 column, oven temperature between 313 and 473 K, heating rate 5 K min<sup>-1</sup>. Product identification was confirmed by GC-MS. No significant differences in conversion were observed in runs where both the flow rate and the catalyst amount were significantly changed while keeping the same W/F value; accordingly, the occurrence of external diffusion limitations was ruled out.

### **Results and discussion**

## Microcalorimetric characterisation

Information about the acid properties of the pure oxides and the solid solutions is summarised in Fig. 1, where the differential heat of adsorption,  $Q_{diff}$ , is plotted vs. ammonia uptake. The initial heat of adsorption is relatively low (76 kJ mol<sup>-1</sup>) for CeO<sub>2</sub>, lies in the range 131–108 kJ mol<sup>-1</sup> for the solid solutions and is rather high (175 kJ mol<sup>-1</sup>) for ZrO<sub>2</sub>. In the region of intermediate ammonia uptake the differential heat



**Fig. 1** Differential heat of adsorption,  $Q_{\text{diff}}$ , vs. ammonia uptake. ( $\bullet$ ), CeO<sub>2</sub>; ( $\bigcirc$ ), Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub>; ( $\blacktriangle$ ), Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub>; ( $\square$ ),Ce<sub>0.2</sub>Zr<sub>0.8</sub>O<sub>2</sub>; ( $\blacksquare$ ), ZrO<sub>2</sub>.

decreases continuously for all the samples, with the exception of  $ZrO_2$ , where a step is observed at about 140 kJ mol<sup>-1</sup>. In the region of high ammonia uptakes  $Q_{diff}$  is very low for all the samples and changes very slightly, which suggests the occurrence of physical adsorption.

To individuate in Fig. 1 the point at which the adsorption shifts from chemical (*i.e.* at the acid sites) to physical (which must be disregarded in the determination of the acid-sites concentration), plots of integral heat,  $Q_{int}$ , vs. ammonia uptake (Fig. 2a) and the adsorption isotherms (Fig. 2b) have been drawn. Very low or negligible evolution of heat associated with remarkably increasing ammonia uptake (*i.e.* attainment of a plateau in Fig. 2a) and the simultaneous deviation upwards of the adsorption isotherm from the attained plateau (*i.e.* the change of concavity in Fig. 2b) are an indication of the establishment of physical adsorption. Inspection of Figs. 2a and b and comparison with Fig. 1 allows one to conclude that differential heats below *ca.* 30 kJ mol<sup>-1</sup> are related to physical adsorption.

The total concentration of acid sites,  $n_A$ , has hence been calculated for all the samples as the amount of ammonia adsorbed with  $Q_{\text{diff}} \ge 30 \text{ kJ} \text{ mol}^{-1}$ ; it is plotted vs. the oxide composition in Fig. 3. It can be seen that  $n_A$ , which is the lowest for pure ceria, markedly increases upon addition of 20 mol% of zirconia, then decreases as the ZrO<sub>2</sub> content is further increased up to 80 mol% and finally attains the highest value on pure zirconia. The upwards shifting of the  $Q_{\rm diff}$  vs. ammonia uptake curves observed in Fig. 1 when passing from pure ceria to the solid solutions and then to pure zirconia indicates an increase of the acid strength; the step at 140 kJ mol<sup>-1</sup> indicates that a set of homogeneous sites of high strength is present on pure zirconia, whereas on the other samples the sites are continuously heterogeneous. To further compare the acid strength of the samples, the population of the sites with  $Q_{\text{diff}} \ge 80 \text{ kJ mol}^{-1}$ ,  $n_{A \ge 80}$ , has been evaluated



**Fig. 2** Integral heat of adsorption,  $Q_{int}$ , vs. ammonia uptake (a) and isotherms for ammonia adsorption (b). ( $\bullet$ ), CeO<sub>2</sub>; ( $\bigcirc$ ), Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub>; ( $\blacktriangle$ ), Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub>; ( $\square$ ), Ce<sub>0.2</sub>Zr<sub>0.8</sub>O<sub>2</sub>; ( $\blacksquare$ ), ZrO<sub>2</sub>.



**Fig. 3** Total concentration of acid sites,  $n_A$ , ( $\bullet$ ), and fraction of sites with differential heat of adsorption  $\ge 80 \text{ kJ mol}^{-1}$ ,  $n_{A\ge 80} : n_A$ , ( $\blacksquare$ ), vs. oxide composition.

(reasons for choosing such a limit stem from previous findings,<sup>9</sup> as will be discussed later on). In Fig. 3 the fraction of sites of this strength over the total sites,  $n_{A \ge 80} : n_A$ , is plotted (as %) vs. the oxide composition. An increasing trend is observed along the series: CeO<sub>2</sub> (where no sites with  $Q_{diff} \ge$  80 kJ mol<sup>-1</sup> are present)  $\ll$  Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub> < Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub> < Ce<sub>0.2</sub>Zr<sub>0.8</sub>O<sub>2</sub> < ZrO<sub>2</sub>.

In the case of CO<sub>2</sub> adsorption, the shape of both the  $Q_{\rm int}$  vs. uptake curves (Fig. 4a) and the adsorption isotherms (Fig. 4b), points out the occurrence of chemical adsorption only. The  $Q_{\rm diff}$  vs. uptake plots in Fig. 5 show that the initial heats of adsorption are quite similar for all the samples (145–155 kJ mol<sup>-1</sup>). Significant differences are observed as the CO<sub>2</sub> uptake increases: the differential heat continuously decreases for CeO<sub>2</sub>; a plateau at *ca.* 155 kJ mol<sup>-1</sup> is observed for Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub> and Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub>, rather short on the latter; no



**Fig. 4** Integral heat of adsorption,  $Q_{int}$ , vs. CO<sub>2</sub> uptake (a) and isotherms for CO<sub>2</sub> adsorption (b). ( $\bigcirc$ ), CeO<sub>2</sub>; ( $\bigcirc$ ), Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub>; ( $\blacktriangle$ ), Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub>; ( $\square$ ), Ce<sub>0.2</sub>Zr<sub>0.8</sub>O<sub>2</sub>; ( $\blacksquare$ ), ZrO<sub>2</sub>.



**Fig. 5** Differential heat of adsorption,  $Q_{\text{diff}}$ , vs. CO<sub>2</sub> uptake. ( $\bullet$ ), CeO<sub>2</sub>; ( $\bigcirc$ ), Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub>; ( $\blacktriangle$ ), Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub>; ( $\square$ ), Ce<sub>0.2</sub>Zr<sub>0.8</sub>O<sub>2</sub>; ( $\blacksquare$ ), ZrO<sub>2</sub>.

step is visible for  $Ce_{0.2}Zr_{0.8}O_2$ , whereas a plateau is present on pure zirconia at ca. 145 kJ mol<sup>-1</sup>. The total concentration of basic sites,  $n_{\rm B}$ , as well as the fraction of sites with differential heat  $\ge 80 \text{ kJ} \text{ mol}^{-1}$ ,  $n_{B \ge 80} : n_B$ , is plotted (as %) vs. the oxide composition in Fig. 6. It shows that, in comparison with pure ceria, the CeO<sub>2</sub>-rich solid solution has a remarkable basic character, both in terms of  $n_{\rm B}$  and  $n_{\rm B \ge 80}$ :  $n_{\rm B}$ ; the base properties of the solid solutions are attenuated as the zirconia content is increased up to 80 mol% and then growing again for pure zirconia. Note also (Fig. 5) that, in contrast with pure ceria, whose sites are continuously heterogeneous, most of the sites of the ceria-rich CeO2-ZrO2 form an homogeneous set of high strength; the population of this set lowers when passing to CeO<sub>2</sub>-ZrO<sub>2</sub> of intermediate composition and finally disappears on the zirconia-rich solid solution, despite the fact that pure zirconia has a remarkable population of homogeneous sites of high strength.

The inclusion of increasingly high contents of zirconium into the ceria lattice has hence a complex influence on both the acidity and basicity of the pure parent oxide. No general rules for predicting the base character of binary oxides have been proposed up to now. On the contrary, qualitative models have been developed concerning the generation of new acidic features upon mixing different oxides. Most frequently cited are the Tanabe<sup>13</sup> and Kung models.<sup>14</sup> Both models presume dilute solid solutions of one cation in a matrix oxide. The Tanabe model is based on a local approach: mismatches in cation valency and coordination number along a heterolinkage M–O–M' originate an excess charge at the site of the minor component cation, resulting in acidity generation. For solid solutions of cubic ceria and monoclinic zirconia the



**Fig. 6** Total concentration of base sites,  $n_{\rm B}$ , ( $\oplus$ ), and fraction of sites with differential heat of adsorption (80 kJ mol<sup>-1</sup>,  $n_{\rm B\geq 80}$  :  $n_{\rm B}$ , ( $\blacksquare$ ), vs. oxide composition.

excess charge is +1/2 for ceria-rich compositions and -4/7for zirconia-rich solutions. According to the model, acidity should be generated in both cases, of Lewis type in the former and of Brønsted type in the latter. This prediction does not match with the outcome of the microcalorimetric experiments, which, though not able to discriminate between the nature of the sites, show that an acidity larger than the sum of the acidities of the component oxides is generated on  $Ce_{0.8}Zr_{0.2}O_2$ but not on  $Ce_{0,2}Zr_{0,8}O_2$  (Fig. 3). The assumption that zirconia maintains its monoclinic structure upon mixing with cubic ceria seems too crude in the light of structural analysis, which has shown<sup>5</sup> that the effect of milling  $CeO_2$  and  $ZrO_2$  is the formation of a fluorite-structured, cubic solid solution as long as the zirconia content does not exceed 50 mol%, a partial tetragonalisation being observed for higher zirconium loading. On this basis calculation gives zero excess charge for both ceria-rich and zirconia-rich solid solutions and no new acidity should hence be expected, which is in contrast with the experimental findings. In no way is this model able to predict the acidity trend for ceria-zirconia solid solutions.

Contrary to Tanabe's model, Kung's approach<sup>14</sup> also takes into account long range effects, by relating acidity generation to both the electrostatic potential at the substituting cation site and changes in the matrix necessary to balance stoichiometry. A general conclusion of the model is that for oxides having the same metal-oxygen stoichiometry, new acidity (of Lewis type) can be generated only if the host oxide is more ionic than the guest. Accordingly, due to the higher ionic character of CeO<sub>2</sub> in comparison with ZrO<sub>2</sub>, generation of acidity should be expected for ceria-rich solid solutions but not for zirconia-rich compositions, which qualitatively reproduces the observed experimental trend.

Additional calorimetric runs have been carried out on  $Ce_{0.8}Zr_{0.2}O_2$  and  $Ce_{0.2}Zr_{0.8}O_2$  after exposure to hydrogen atmosphere at 673 K overnight, i.e. conditions under which  $Ce^{4+}/Ce^{3+}$  reduction is expected to occur to some extent.<sup>5</sup> Comparison of the results for the reduced and as-prepared samples is presented in Figs. 7 and 8 for the ceria-rich and zirconia-rich solutions respectively. The most interesting effects of the reduction of  $Ce_{0.8}Zr_{0.2}O_2$  (Fig. 7) are the weakening of its acid sites and the partial loss of homogeneity of the base sites. The former effect is indicated by the downwards shift of the  $Q_{\text{diff}}$  vs. the NH<sub>3</sub> uptake curve (Fig. 7a); note that  $n_{A \ge 80}$  for the reduced sample is less than 60% of the original value for the untreated Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub>. Fig. 7b shows that after reduction, the initial differential heat for  $CO_2$  is higher and the plateau in the  $Q_{\text{diff}}$  vs. the CO<sub>2</sub> uptake curve is shorter, which indicates a more heterogeneous character of the base sites. Weakening of the acid sites upon reduction is observed also for  $Ce_{0.2}Zr_{0.8}O_2$ , Fig. 8a (the  $Q_{diff}$  vs. the NH<sub>3</sub> uptake curve is shifted downwards;  $n_{A \ge 80}$  is about one half of the original value). No significant change of  $Q_{\text{diff}}$  vs. the CO<sub>2</sub> uptake curve results from reduction (Fig. 8b), *i.e.* the strength distribution of the base sites remains unchanged.

Ceria reduction by H<sub>2</sub> treatment can be envisaged to occur as follows:<sup>15</sup> (1), dissociation of chemisorbed hydrogen to form hydroxy groups; (2), formation of anionic vacancies and reduction of the neighbouring cations; (3), desorption of water by combination of hydrogen and hydroxy groups; (4), diffusion of surface anionic vacancies into the bulk material. It is also possible that  $Ce^{4+}/Ce^{3+}$  reduction occurs following H<sub>2</sub> dissociation without formation of oxygen vacancies in the first step. However, such a possibility seems unlikely for the present samples, as it would originate a hydroxylated surface, i.e. an increased concentration of the acid sites which is not experimentally observed (Figs. 7 and 8). The assumption that the cerium cations act as Lewis sites is supported by the observed acid-strength decrease after  $H_2$  treating, ascribable to the lower charge/radius ratio of  $Ce^{3+}$  (radius 1.14 Å) in comparison with Ce4+ (radius 0.97 Å).



Fig. 7 Differential heats of adsorption,  $Q_{\text{diff}}$ , vs. ammonia (a) and  $\widetilde{CO}_2$  (b) uptakes for the as-prepared, ( $\blacksquare$ ), and reduced  $Ce_{0.8}Zr_{0.2}O_2$ , (O), samples.



**Fig. 8** Differential heats of adsorption,  $Q_{\text{diff}}$ , *vs.* ammonia (a) and  $CO_2$  (b) uptakes for the as-prepared, ( $\blacksquare$ ), and reduced  $Ce_{0.2}Zr_{0.8}O_2$ ,  $(\bigcirc)$ , samples.

According to the reduction mechanism outlined above, a chemical pumping effect causes oxygen to diffuse up to the surface, where the vacancies are first originated upon water elimination (step 3). Oxygen mobility should be favoured in ceria-zirconia solid solutions because the substitution of Ce<sup>4+</sup> with the smaller  $Zr^{4+}$  cation (radius 0.84 Å) causes shrinking of the CeO<sub>2</sub> fluorite-type lattice and formation of structural defects. The energetics of oxygen ion transport in the CeO<sub>2</sub>-ZrO<sub>2</sub> solid solutions has been investigated over the whole composition range by computer simulation methods;<sup>6</sup> the activation energy for oxygen migration was found to decrease with increasing zirconia content, a minimum being attained for Ce<sub>0.1</sub>Zr<sub>0.9</sub>O<sub>2</sub>, which was hence considered the most easily reducible system. Decrease of the cell volume with increasing zirconia content was experimentally observed for the present samples and was considered responsible for the higher reduction extent of  $Ce_{0.2}Zr_{0.8}O_2$  in comparison with  $Ce_{0.8}Zr_{0.2}O_2$ .<sup>5</sup> The surface oxygen anions act as base sites in the calorimetric experiments. The results in Figs. 7 and 8 can be tentatively explained as follows. For the hydrogen-treated  $Ce_{0.8}Zr_{0.2}O_2$ , anion vacancies not yet replaced by oxygen diffusing from the bulk as well as oxygen anions are probably present on the surface; a higher degree of heterogeneity should hence be expected in comparison with the same sample not treated with  $H_2$ . For the  $H_2$ -treated  $Ce_{0.2}Zr_{0.8}O_2$ , a higher extent of bulk reduction occurs, which implies that the anion vacancies formed at the beginning of the reduction process (step 2) have already been replaced by oxygen anions coming from the bulk; accordingly, no significant differences in the strength distribution of the base sites should be expected in comparison with the same sample not exposed to  $H_2$ . In addition, in this sample the lower concentration of cerium limits the total number of oxygen vacancies that can be formed upon reduction. Therefore, the similarity of the strength distribution of base sites after reduction should be the result of (i) the increased diffusion of  $O^{2-}$  and (ii) the decrease of the amount of reducible elements.

#### **Catalytic behaviour**

4-Methylpent-1-ene (the desired product) and 4-methylpent-2ene were the main products formed upon reacting 4methylpentan-2-ol over the Ce–Zr oxides. Other C<sub>6</sub>-alkene isomers with internal double bond were also formed, to a very limited extent in all cases, with the exception of Ce<sub>0.2</sub>Zr<sub>0.8</sub>O<sub>2</sub>. Light olefins such as propene were also detected (their amount being, however, negligible in all cases, with the exception of CeO<sub>2</sub>), as well as trace amounts of pentene oligomers. Side dehydrogenation of the reactant alcohol to 4-methylpentan-2one was practically negligible for all the catalysts. The conversion of the reactant alcohol, as well as the selectivity to each of the above products, was monitored as a function of timeon-stream for each oxide in isothermal runs lasting 30 up to 80 h. The reaction temperature was such that the initial (1 h on-stream) conversion was *ca*. 50% (see Experimental section).

The initial catalytic results for all the samples are summarised in Fig. 9, where both the temperature for 50% conversion,  $T_{50}$ , and the initial selectivity to 4-methylpent-1-ene,  $S_{1A}$ , are plotted vs. composition. Increasingly high zirconia contents in the solid solution enhance its overall activity, as indicated by the decreasing trend of  $T_{50}$  (Fig. 9a); though the low activity of CeO<sub>2</sub> might stem from its low surface area (Table 1), there is no manifest correlation between the latter and the overall activity of the samples (note for instance that Ce<sub>0.2</sub>Zr<sub>0.8</sub>O<sub>2</sub> is rather active despite its low surface area). Fig. 9b shows that the inclusion of 20 mol% of zirconia into the ceria lattice results in a remarkable improvement of the selectivity to the desired 1-alkene (54% for CeO<sub>2</sub>, 71% for Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub>); further addition of zirconia is not convenient (60% selectivity for Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub>) or even detrimental (32%



**Fig. 9** Temperature for initial conversion = 50%,  $T_{50}$ , (a), and initial selectivity to 4-methylpent-1-ene,  $S_{1A}$ , (b), vs. oxide composition.

for  $Ce_{0.2}Zr_{0.8}O_2$ ). It is worthy of note that there is a close resemblance between the 1-alkene selectivity trend on one hand (Fig. 9b) and the trends of the acid-sites concentration (Fig. 3), base-sites concentration (Fig. 6) and fraction of base sites stronger than 80 kJ mol<sup>-1</sup> (Fig. 6) on the other.

Previous findings for the same reaction on zirconia,<sup>11</sup> ceria and lanthania9 allowed us to conclude that when the acid and base functions of the catalyst are well balanced in terms of site concentrations, a two-point adsorption of the reactant alcohol occurs, in which the most acidic hydrogen (i.e. that of the terminal methyl group) interacts with a base site while the acid centre interacts with the OH group of the alcohol. The fate of this adsorbed species depends on the relative strength of the acid and base sites. If the acid sites are weak and the base sites are strong enough, rupture of the C-H bond with carbanion formation occurs first and an E1cB mechanism sets in, leading to the preferential formation of the 1-alkene (Hofmann orientation). A basic strength of 80 kJ mol<sup>-1</sup> seems to represent the threshold value required for establishing the above sequence of steps. If the strength of the acid and base sites is comparable, no intermediate carbanion is formed, the transformation of the adsorbed species into the olefin being concerted (E2 mechanism); 2-alkene is then the preferred product (Savtzeff orientation).

Such a co-operative action of the sites is disfavoured when either the acid or the base sites are predominant. In the former case, the reaction is initiated by the attack of the acid sites to the hydroxy group of the alcohol: an intermediate carbocation is formed, which transforms into alkenes with internal double bonds (E1 mechanism, Saytzeff orientation). When the base sites on the catalyst surface are predominant and strong, adsorption occurs by means of a hydrogen bond involving the OH group of the alcohol and a base site; abstraction of  $H_{\alpha}$  by interaction with a positively polarised H atom on the surface (originating from the previously split OH group of the alcohol) then occurs and a ketone is formed instead of an alkene.

In light of this, it is not surprising that the values for  $n_A$ ,  $n_B$ and  $n_{B \ge 80}$ :  $n_B$  appear so relevant to the initial 1-alkene selectivity in the present case, as indicated by a comparison of Figs. 3 and 6 with 9b. To check in detail how the above picture fits the present results, the initial selectivity to 4methylpent-1-ene has been plotted vs.  $n_{\rm B}$ :  $n_{\rm A}$  in Fig. 10, where previous data for ceria, lanthania and zirconia-based catalysts<sup>9,11</sup> have also been reported. (Both the present and former data refer to 50% conversion). With the exception of  $Ce_{0.2}Zr_{0.8}O_2$ , the two sets of data are fitted by the same volcano-shaped curve. In agreement with the picture outlined, the maximum in 1-alkene selectivity corresponds to those catalysts (Na-doped zirconia, ZrO<sub>2</sub>/27;<sup>11</sup> ceria prepared from Ce<sup>III</sup> hydroxide by calcination in air, CeO<sub>2</sub>/49<sup>9</sup> and Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub>) where the acid and base functions are wellbalanced as to the number of sites  $(n_{\rm B}: n_{\rm A} \text{ is close to } 1)$ , but unbalanced as to the strength  $(n_{B \ge 80} : n_B = 80\%$  and  $n_{A \ge 80}$ :  $n_A = 0\%$  for ZrO<sub>2</sub>/27 from data in ref. 11; 70 and 31% for  $CeO_2/49$  from data in ref. 9, and 86 and 31% for  $Ce_{0.8}Zr_{0.2}O_2$  from Figs. 6 and 3). These catalysts represent somewhat of a limiting case in which dehydration through the E1cB mechanism predominates. Other limiting cases are represented by the two zirconia samples  $ZrO_2/98$  and  $ZrO_2/46$ , prepared from different precursors:<sup>11</sup> on the latter,  $n_{\rm B}$ :  $n_{\rm A}$  is so high that dehydrogenation is strongly favoured over dehydration, on the former,  $n_{\rm B}$ :  $n_{\rm A}$  is so low that only dehydration practically occurs, almost exclusively by the E1 mechanism.

 $ZrO_2$ ,  $CeO_2$  and  $Ce_{0.5}Zr_{0.5}O_2$  as well as  $CeO_2/48$  (a pure ceria sample prepared from Ce<sup>III</sup> nitrate by calcination in air<sup>9</sup>) lie on the left-hand branch of the curve in Fig. 10, showing a tendency of the selectivity to 4-methylpent-1-ene to increase with  $n_B: n_A$ . Both Saytzeff- and Hofmann-oriented pathways are simultaneously present, as indicated by the values of 1-alkene selectivity (47–60%). As  $n_B: n_A$  increases, the two-point adsorption of the reactant alcohol is enhanced, which favours E2 and E1cB over E1. However, the strength of the acid and base sites is not balanced over these catalysts ( $n_{B\geq 80}: n_B = 85\%$  and  $n_{A\geq 80}: n_A = 55\%$  for CeO<sub>2</sub>/48, from data in ref. 9;  $n_{B\geq 80}: n_B = 54\%$  and  $n_{A\geq 80}: n_A = 0\%$  for CeO<sub>2</sub>, 100 and 60% for ZrO<sub>2</sub>, and 81 and 39% for CeO<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub>, from Figs. 6 and 3), which makes 2-alkene formation through the E2 mechanism unlikely. Hofmann orientation could result either from a concerted pathway (E2 with a transition state having a



**Fig. 10** Initial selectivity to 4-methylpent-1-ene,  $S_{1A}$ , vs.  $n_B : n_A$  for various catalysts. Full symbols refer to previously investigated catalysts: two zirconia samples,  $ZrO_2/98$  and  $ZrO_2/46$ , prepared from different precursors;<sup>11</sup> Na-doped zirconia,  $ZrO_2/27$ ;<sup>11</sup> two ceria samples,  $CeO_2/49$  and  $CeO_2/48$ , prepared from different precursors<sup>9</sup> and lanthania,  $La_2O_3/50$ .<sup>9</sup> Open symbols represent the samples investigated in this work.

view Article Online remarkable carbanionic character) or *via* the formation of the intermediate carbanionic species (E1cB).

It has already been noted that  $Ce_{0.2}Zr_{0.8}O_2$  does not lie on the curve, its selectivity to 4-methylpent-1-ene being rather low in comparison with that for the other samples of similar  $n_B: n_A$ . For  $Ce_{0.2}Zr_{0.8}O_2$  the strength of the acid and base sites is quite similar ( $n_{B \ge 80}: n_B = 55\%$ ;  $n_{A \ge 80}: n_A = 61\%$ , from Figs. 6 and 3). The fraction of alcohol that adsorbs on these sites by a two-point mechanism does not undergo carbanion formation, but rather one-step alkene formation through a concerted E2 pathway. Both the latter and the simultaneously present E1 mechanism lead to 2-alkene, which explains the observed low selectivity to 4-methylpent-1-ene.

The conversion of the reactant alcohol, as well as the selectivities to the various products, were not affected in the same way for all the catalysts by time-on-stream. Some loss of the overall activity occurred over CeO2, where conversion decreased from 50 to 35% after 24 h on-stream and then did not change further; the selectivities to 4-methylpent-1-ene,  $S_{1A}$ , 4-methylpent-2-ene,  $S_{2A}$ , C<sub>6</sub>-alkene isomers,  $S_{C6}$ , 4methylpentan-2-one,  $S_{\rm K}$ , were nearly constant over the entire run (54, 35, 3 and 1%, respectively). The catalyst appeared grey-coloured after reaction; after treating at 773 K for 6 h under air flow, the initial activity was restored. Probably, small amounts of alkene oligomers that accumulated on the surface during the early hours on-stream are responsible for the observed activity loss (such an effect would be amplified by the low surface area of the catalyst). This is also suggested by the presence in the reactor effluent of unusual amounts of light alkenes (selectivity,  $S_{LA} = 5\%$ ), which were detected only in traces for the other samples; these light alkenes are likely originated by fragmentation (favoured by the high reaction temperature) of the oligomers, whose presence was also detected in the reactor effluent (selectivity,  $S_{HA} = 2\%$ ).

Inclusion of zirconia in the ceria lattice originates a stable catalyst for zirconia contents up to 50 mol%; the case of Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub>, *i.e.* the more selective catalyst for the desired 1-alkene, is shown in Fig. 11 as an example. For  $Ce_{0.2}Zr_{0.8}O_2$ a continuous increase of conversion with time-on-stream from ca. 15% up to more than 60% was observed (Fig. 12a), associated with a remarkable variation of the selectivities (Fig. 12b): growth of 4-methylpent-2-ene, drop of C<sub>6</sub>-alkene isomers, decrease of the desired 1-alkene; only trace amounts of ketone were formed at any time-on-stream. As already observed for the acid-base properties and the initial selectivity to 1-alkene, the on-stream features of  $Ce_{0.2}Zr_{0.8}O_2$  also seem unique in comparison with the other Ce-Zr samples. It is worthy of note that this behaviour is also completely different from that of the parent pure zirconia. For the latter, neither the conversion nor the selectivities significantly changed with time-on-stream: 4-methylpent-1-ene was always slightly favoured over 4methylpent-2-ene ( $S_{1A} = 55\%$ ;  $S_{2A} = 43\%$ ); C<sub>6</sub>-alkene isomers were almost negligible ( $S_{C6} = 2\%$ ); only traces of 4methylpentan-2-one were detected.

The observed changes in the catalytic behaviour of  $Ce_{0,2}Zr_{0,8}O_2$  with time-on-stream indicate that some kind of surface conditioning occurs during reaction. The possibility should be considered that this stems from a modification of the acid-base parameters relevant to the reaction selectivity, originated by a  $Ce^{4+}/Ce^{3+}$  shift occurring on the surface as a consequence of the reducing atmosphere experienced by the catalyst in contact with the reactant alcohol. However, even assuming that the reaction conditions make the sample undergo reduction to an extent similar to that occurring after overnight exposure to hydrogen atmosphere at 673 K, the changes in the values of  $n_{\rm B}$ :  $n_{\rm A}$  and  $n_{{\rm B}\geqslant80}$ :  $n_{\rm B}$  do not justify the observed selectivity changes with time-on-stream. For the H<sub>2</sub>-exposed sample  $n_{\rm B}$ :  $n_{\rm A}$  and  $n_{\rm B \ge 80}$ :  $n_{\rm B}$  are 1.0 and 63% respectively (from data in Fig. 8); accordingly, a progressive shift towards a more E1cB character should be expected upon



**Fig. 11** Conversion (a) and selectivities (b) vs. time-on-stream for  $Ce_{0.8}Zr_{0.2}O_2$ . Symbols in (b): ( $\blacksquare$ ), 4-methylpent-1-ene; ( $\bigcirc$ ), 4-methylpent-2-ene; ( $\square$ ),  $C_6$  alkene isomers; ( $\bigcirc$ ), 4-methylpentan-2-one. reduction, which is in contrast with the selectivity trends in Fig. 12b. Moreover, the increasing trend of conversion (Fig. 12a) suggests an increase of the concentration of the active sites on the surface during the reaction, which cannot be related to a possible reduction of the surface. It should also be added that the reaction conditions (*i.e.* alcohol partial pres-



**Fig. 12** Conversion (a) and selectivities (b) vs. time-on-stream for  $Ce_{0,2}Zr_{0,8}O_2$ . Symbols in (b): ( $\blacksquare$ ), 4-methylpent-1-ene; ( $\bigcirc$ ), 4-methylpent-2-ene; ( $\square$ ),  $C_6$  alkene isomers; ( $\bigcirc$ ), 4-methylpentan-2-one.

sure and reaction temperature) are probably too mild for allowing significant reduction. Actually, the colour of the sample after reaction had only a green shade over the original yellow, which seems to indicate that surface reduction has occurred to a negligible extent.

Surface conditioning might stem from strong interactions between the active sites and the reaction products. In no way, however, would the interaction with the product alkenes result in the increase of conversion with time-on-stream. Hydrogen adsorption, reported to occur dissociatively on ZrO<sub>2</sub> to form ZrOH, ZrH and ZrHZr surface species,<sup>3</sup> can also be ruled out in the present case, due to the negligible extent of the dehydrogenation reaction. On the contrary, water is rather an abundant side product. Assuming its dissociative adsorption on site pairs formed by metal and oxygen ions, an increasingly high extent of surface hydroxylation would be expected during the run. The resulting increase of the concentration of the acid sites on the surface would explain the growth of conversion and the overall enhancement of the Saytzeff products. The progressively favoured formation of 4-methylpent-2-ene over C<sub>6</sub> isomers with time-on-stream, i.e. the progressive limitation of the consecutive isomerisation reactions, would result from a fast inactivation of the stronger acid sites, possibly due to strong interaction with the reaction products. The possibility for water to be dissociatively adsorbed on metal oxides is well documented and has also been reported for ZrO2.16 It can take place on site pairs formed by coordinatively unsaturated Zr and oxygen ions and is preceded by the undissociative adsorption of H<sub>2</sub>O on Zr cations. The tentative hypothesis could be proposed that on  $Ce_{0,2}Zr_{0,8}O_2$  the extent of surface hydroxylation is particularly high because the distance between the acid (cations) and base (oxygen ions) sites is such as to assist the dissociation mechanism of the water molecules previously adsorbed undissociatively on the cation site.

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