

## Dehydration of 4-methylpentan-2-ol over lanthanum and cerium oxides

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Lanthanum and cerium oxides have been tested for the title reaction at 623 K and atmospheric pressure in a flow reactor. Lanthanum oxide (prepared from the corresponding nitrate) gives mainly 4-methylpent-1-ene (80% of the products). Similar results are observed with cerium oxide obtained from the corresponding hydroxide, whereas cerium oxide prepared from nitrate is less selective towards alk-1-enes. In addition to dehydration, dehydrogenation to 4-methylpentan-2-one is also observed to a limited extent for all the catalysts. Information on the acid–base properties of the samples was obtained by adsorption microcalorimetry of ammonia and carbon dioxide and correlated to reaction selectivities. Possible changes in the oxidation state of cerium ions due to the reaction atmosphere are considered. The present results are compared with former data for zirconia catalysts. Modification of cerium oxide *via* immersion in NaOH solution does not appear to be useful for improving alk-1-ene selectivity.

Secondary alcohol dehydration on metal oxides has been widely investigated.<sup>1,2</sup> Competition between alk-1-ene and alk-2-ene formation usually occurs and further complexity can arise from the simultaneous dehydrogenation of the reactant to the corresponding ketone. E1, E2 and E1cB mechanisms are usually considered to explain product distribution. When E1 is operating, Saytzeff orientation is observed and alkenes with an internal double bond are mainly formed; this occurs *via* the C–OH bond rupture with the corresponding formation of a carbonium ion able to undergo positional and geometrical isomerisation. Saytzeff products are also formed *via* the E2 mechanism, but in this case no intermediate is formed, the reaction being concerted. E1cB leads to alk-1-enes (Hofmann orientation) *via* the rupture of the C–H bond. Intermediate situations between the above limiting cases can occur. It is generally assumed that the reaction pathway is influenced by the acid–base properties of the catalyst, Hofmann orientation and ketone formation being considered to require higher basicity. Several hypotheses have been advanced for taking the occurrence of dehydrogenation into account. The most interesting appear to be the indication that this reaction can be initiated by the same E1cB mechanism leading to alk-1-enes,<sup>6,7</sup> or the suggestion that the rate determining step of dehydrogenation is the C<sub>α</sub>–H bond rupture previously weakened by adsorption, *via* a hydrogen bond, on a strong base site of the reactant alcohol.<sup>8,9</sup>

Among the dehydration reactions of secondary alcohols the selective transformation of 4-methylpentan-2-ol to 4-methylpent-1-ene deserves particular attention from the application point of view because the dehydration product is the starting material for manufacturing valuable thermoplastic polymers. In a previous work from this laboratory<sup>10</sup> the dehydration of 4-methylpentan-2-ol was investigated over several zirconia catalysts differing as to the preparation procedure and/or the addition of dopants. The catalysts were characterised by microcalorimetry, *via* measurement of the heats of adsorption of NH<sub>3</sub> and CO<sub>2</sub>, and the acid–base properties of the solid were correlated to the catalytic behaviour. Dehydration to 4-methylpent-1-ene was found to require a catalyst well balanced in the number of acid and base sites, with a high strength of the latter. The presence on the catalyst of strong

basic sites prevailing in number over acidic ones resulted in enhanced dehydrogenation to ketones, whereas dehydration to the alk-2-ene was favoured on those zirconia samples on which the acid sites predominate; according to their strength a more or less pronounced formation of skeletal isomers of C<sub>6</sub>-alkenes was observed.

The present work considers the results of further investigation of 4-methylpentan-2-ol conversion on lanthanum and cerium oxides.

### Experimental

The lanthanum and cerium oxides used for 4-methylpentan-2-ol conversion were prepared from suitable precursor salts. Concise information is given in Table 1. The acid–base properties of these catalysts were determined by the microcalorimetric technique, using ammonia and carbon dioxide as probe molecules. The measurements were carried out in a Tian–Calvet type calorimeter from Setaram. Each sample was pretreated overnight at 673 K under vacuum (10<sup>−3</sup> Pa) before the successive introduction of small doses of the probe gas. The equilibrium pressure relative to each adsorbed amount was measured by a differential pressure gauge (Datametrix). The run was stopped at a final equilibrium pressure of 133.3 Pa. The adsorption temperature was maintained at 353 K, to limit physisorption.

Testing of the catalytic activity was performed at atmospheric pressure in a fixed-bed flow microreactor. To avoid thermal conversion of the reactant, a quartz microreactor (10 mm id) was used and the stainless-steel pipes to and from the reactor were passivated. The catalyst was activated *in situ* (6 h at 773 K under a CO<sub>2</sub>-free air flow). 4-Methylpentan-2-ol was fed in with an N<sub>2</sub> stream. Reactant partial pressure, P<sub>O, A</sub> and time factor, W/F, were 15.5 kPa and 2.5 g<sub>cat</sub> h/g<sub>alcohol</sub><sup>−1</sup>, respectively.

On-line capillary gas chromatography (GC) analysis conditions were: Petrocol DH 50.2 column, oven temperature between 313 and 448 K, heating rate 2 K min<sup>−1</sup>. Product identification was confirmed by GC and MS.

Temperature-programmed experiments were carried out in a quartz microreactor (7 mm id) with a miniature thermo-

**Table 1** Lanthanum and cerium oxides for 4-methylpentan-2-ol dehydration

catalyst	precursor	preparation method	thermal treatment <sup>a</sup>		$S_{\text{BET}}$ /m <sup>2</sup> g <sup>-1</sup>
			temperature /K		
La <sub>2</sub> O <sub>3</sub> /50	La(NO <sub>3</sub> ) <sub>3</sub> · 6H <sub>2</sub> O	precipitation calcination	773		33
CeO <sub>2</sub> /48	Ce(NO <sub>3</sub> ) <sub>3</sub> · 6H <sub>2</sub> O	calcination	773		77
CeO <sub>2</sub> /49	Ce(OH) <sub>3</sub>	calcination	773		71
CeO <sub>2</sub> /49D	CeO <sub>2</sub> /49	immersion NaOH calcination	673		86

<sup>a</sup> 2 h in air at the indicated temperature.

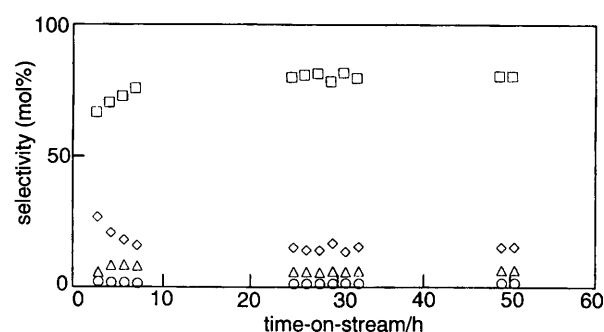
couple, an electric furnace and a linear temperature-programming device. A thermal conductivity detector (TCD) or an UTI 100 C quadrupole mass spectrometer were used. The sample was activated in flowing He gas (30 cm<sup>3</sup> min<sup>-1</sup>), for 12 h at 873 K (heating rate 15 K min<sup>-1</sup>). For temperature-programmed desorption (TPD) the sample was cooled to the saturation temperature, a suitable number of pulses of the adsorbing substance was injected and the temperature was increased to 873 K (heating rate 15 K min<sup>-1</sup>). In temperature-programmed reduction (TPR) runs the sample was cooled to 303 K, H<sub>2</sub> was admitted instead of He and the temperature increased at 2.5 K min<sup>-1</sup>.

## Results and Discussion

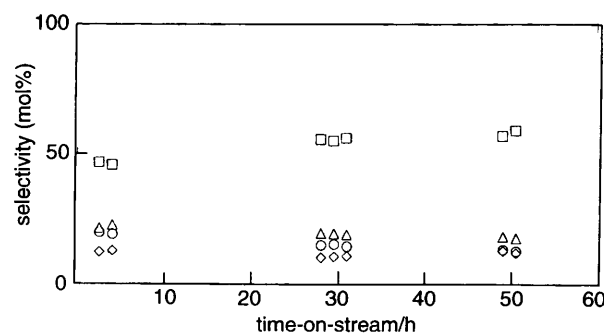
Each oxide was tested at a reaction temperature giving around 50% conversion. Selectivities to 4-methylpent-1-ene, 4-methylpent-2-ene, 4-methylpentan-2-one and skeletal isomers of C<sub>6</sub>-alkenes were determined as a function of time-on-stream in runs lasting from 30 up to 100 h. Average values of these parameters, calculated from later time-on-stream data, are presented in Table 2. The most interesting catalysts appear to be La<sub>2</sub>O<sub>3</sub>/50 and CeO<sub>2</sub>/49. 4-Methylpent-1-ene is by far the most abundant product, 4-methylpent-2-ene formation is low and C<sub>6</sub> skeletal isomers are almost negligible; dehydrogenation to 4-methylpentan-2-one occurs to some limited extent. CeO<sub>2</sub>/48 does not differ substantially from CeO<sub>2</sub>/49 as to dehydrogenation, but dehydration to the desired alk-1-ene is less favoured, overall selectivity to β-alkenes is marked, although lower than that to 4-methylpent-1-ene, and C<sub>6</sub> skeletal isomers are not negligible. The selectivities to the various products over CeO<sub>2</sub>/49D are almost the same as those for CeO<sub>2</sub>/49, conversion being a little lower on the former; however these samples differ markedly in their behaviour during the early hours on-stream, as will be shown below. Conversion values after 2.5 h on-stream, *i.e.* the time needed to establish steady conditions, were 45, 65 and 61% for La<sub>2</sub>O<sub>3</sub>/50, CeO<sub>2</sub>/48 and CeO<sub>2</sub>/49, respectively. These initial values are somewhat higher than the average conversion at the later time-on-stream given in Table 2. However all of the catalysts were found to be quite stable after 25 h on-stream. Products selectivities for La<sub>2</sub>O<sub>3</sub>/50 are reported as a function

of time-on-stream in Fig. 1. Initially alk-1-ene selectivity is seen to increase while ketone selectivity decreases. A similar interesting behaviour, but much more pronounced, had been observed over one of the zirconia samples previously investigated.<sup>10</sup> Results for CeO<sub>2</sub>/48 are shown in Fig. 2. 4-Methylpentan-2-one selectivity does not change. 4-Methylpent-1-ene is the favoured dehydration product at any time-on-stream but the ratio between 4-methylpent-1-ene and all the alk-2-enes is almost doubled for the long runs; 4-methylpent-2-ene and C<sub>6</sub> skeletal isomers have very close selectivity values initially. Selectivities for CeO<sub>2</sub>/49 are presented in Fig. 3. Changes appear confined to the early hours on stream, when alk-1-enes increase while both ketone and 4-methylpent-2-ene decrease slightly.

The differential heats of ammonia adsorption for La<sub>2</sub>O<sub>3</sub>/50, CeO<sub>2</sub>/48 and CeO<sub>2</sub>/49 are shown in Fig. 4 as a function of coverage. Initial differential heats range from 125 to 95 kJ mol<sup>-1</sup>. A plateau around 100 kJ mol<sup>-1</sup> appears for CeO<sub>2</sub>/48 whereas continuous heterogeneity is observed for the other samples, for which differential heat smoothly decreases. Results for CO<sub>2</sub> adsorption on La<sub>2</sub>O<sub>3</sub>/50, CeO<sub>2</sub>/48 and CeO<sub>2</sub>/49 are shown in Fig. 5. All show high initial heats (180–225 kJ mol<sup>-1</sup>). A plateau can be seen around 145–160 kJ mol<sup>-1</sup>, followed by a continuous decrease of the differential



**Fig. 1** Selectivities vs. time-on-stream for La<sub>2</sub>O<sub>3</sub>/50 at 633 K: (□) 4-methylpent-1-ene; (△) 4-methylpent-2-ene; (◇) 4-methylpentan-2-one; (○) skeletal isomers of C<sub>6</sub>-alkenes



**Fig. 2** Selectivities vs. time-on-stream for CeO<sub>2</sub>/48 at 613 K: symbols as in Fig. 1

**Table 2** Catalytic activity of lanthanum and cerium oxides; the results refer to later time-on-stream data

catalyst	T/K	conversion /mol	selectivity (mol%) <sup>a</sup>			
			1-A	2-A	C <sub>6</sub>	K
La <sub>2</sub> O <sub>3</sub> /50	633	38	80	7	2	11
CeO <sub>2</sub> /48	613	51	56	19	15	10
CeO <sub>2</sub> /49	633	52	78	9	0	13
CeO <sub>2</sub> /49D	633	52	78	8	1	13

<sup>a</sup> 1-A, 4-methylpent-1-ene; 2-A, 4-methylpent-2-ene; C<sub>6</sub>, skeletal isomers of C<sub>6</sub>-alkenes; K, 4-methylpentan-2-one.

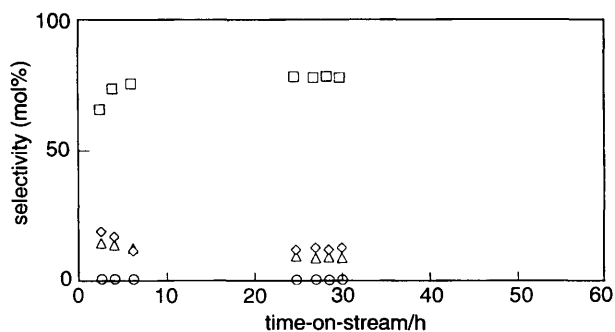


Fig. 3 Selectivities vs. time-on-stream for CeO<sub>2</sub>/49 at 633 K: Symbols as in Fig. 1

heat. The interaction of CO<sub>2</sub> is more pronounced for La<sub>2</sub>O<sub>3</sub>/50 than for CeO<sub>2</sub>/48 and CeO<sub>2</sub>/49, in terms of both number and strength of the adsorbing sites.

The use of NH<sub>3</sub> and CO<sub>2</sub> to probe the acidity and basicity, respectively, of metal oxides *via* microcalorimetry has been reported previously.<sup>11</sup> In the light of the different possible modes of interaction of these molecules with the oxide surface, it was found that NH<sub>3</sub> mostly coordinates to surface Lewis sites, but in a few cases the results were interpreted by considering the simultaneous occurrence (to a low extent) of dissociative adsorption leading to NH<sub>2</sub> and OH surface species. For some of the oxides in ref. 11 dissociative adsorption of ammonia was related to the presence of very strong acid sites, a situation also reported for mordenites,<sup>12</sup> where the sites with differential heat of NH<sub>3</sub> adsorption  $\geq 170$  kJ mol<sup>-1</sup> were considered to be of Lewis type and responsible for the dissociative adsorption. The initial differential heats measured in the present work for ammonia adsorption are in the range 125–95 kJ mol<sup>-1</sup>. Furthermore, IR evidence has been reported showing that dissociative adsorption occurs on samples pretreated in a vacuum at temperatures of 723 K or higher.<sup>13</sup> All of the samples investigated in the present work were

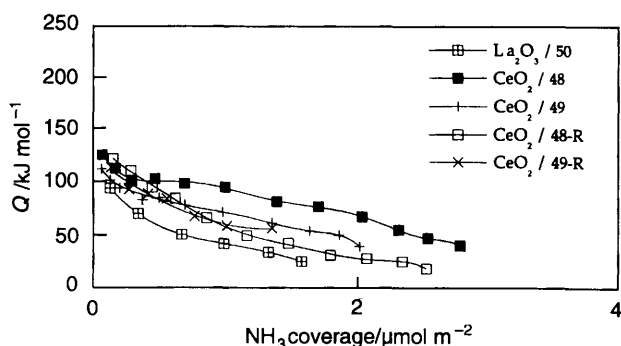


Fig. 4 Differential heats of adsorption of NH<sub>3</sub> as a function of coverage for lanthanum and cerium oxides

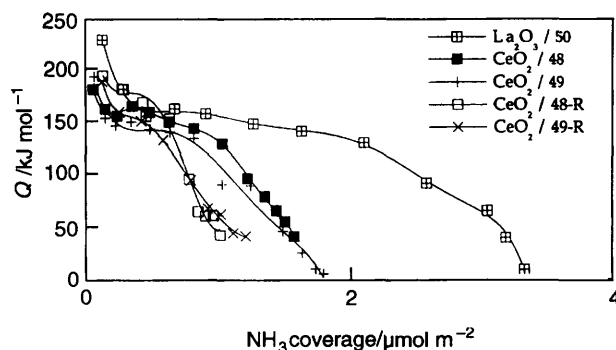


Fig. 5 Differential heats of adsorption of CO<sub>2</sub> as a function of coverage for lanthanum and cerium oxides

pretreated at 673 K, *i.e.* a lower temperature than the above threshold value. Generally, owing to the pretreatment conditions followed and the acid strength values of our samples, it seems unlikely that dissociative adsorption of ammonia occurs on the present catalysts.

CO<sub>2</sub> is a poor donor but a good electron acceptor.<sup>14</sup> Owing to its acidic character, it has been frequently used to probe the basic properties of solid surfaces, mostly by the TPD technique.<sup>15–18</sup> IR evidence concerning the formation of carbonate-like species of different configurations has been reported for metal oxides,<sup>14</sup> which accounts for the heterogeneity of the surface revealed by microcalorimetric measurements. The possibility that CO<sub>2</sub> could behave as a base and interact with Lewis-acid sites should also be considered. However, these sites would have to be very strong. The presence of linearly held CO<sub>2</sub> has been revealed by IR on silica-alumina,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and  $\alpha$ -Cr<sub>2</sub>O<sub>3</sub>.<sup>19,20</sup> Specific bands were assigned to CO<sub>2</sub> interacting at one end with exposed cations acting as Lewis sites of high strength, as they adsorbed ammonia very strongly.<sup>19</sup> Neighbouring oxygen anions could eventually participate in this adsorption *via* lateral interaction with the C atom of CO<sub>2</sub>, which could result in the perturbation of the linearity of the adsorbed molecule leading to organic carbonate-like configurations. From the viewpoint of the present investigation it is important to stress that this particular adsorption mode of the CO<sub>2</sub> molecule is reported to require the presence of very strong Lewis acid sites<sup>19</sup> and to be very weak.<sup>19,20</sup> Thus, even if such an adsorption mode could establish on samples of relatively low acidity like ours, its contribution can be neglected by excluding sites which are too weak in pertinent calculations (see below).

A cooperative action of acid sites is known to operate in secondary alcohol transformation over metal oxides,<sup>2</sup> which suggests the possibility of correlating the selectivity results for our samples with the microcalorimetric data. However problems may arise with CeO<sub>2</sub>/48 and CeO<sub>2</sub>/49. The reduction of Ce<sup>IV</sup> to Ce<sup>III</sup> is known to occur readily. The reducing atmosphere experienced by the catalyst when the reactant alcohol is fed into the reactor may suddenly transform (at least partly) CeO<sub>2</sub> into Ce<sub>2</sub>O<sub>3</sub>. Even at earlier times-on-stream, the acid-base properties of the two cerium oxide catalysts could thus be different from those presented in Fig. 4 and 5 for CeO<sub>2</sub>/48 and CeO<sub>2</sub>/49. The reducibility of CeO<sub>2</sub>/48 and CeO<sub>2</sub>/49 was checked in TPR runs. H<sub>2</sub> consumption and H<sub>2</sub>O production were observed, starting at 347 K for both the oxides. A broad peak for water was recorded for CeO<sub>2</sub>/49, with its maximum at about 393 K, ending at about 523 K. The colour of the sample changed from pale to dark yellow. For CeO<sub>2</sub>/48 the water peak was somewhat sharper, with a maximum at 473 K, terminating at about 573 K. The colour changed from pale yellow to dark green.

After this treatment, the samples (henceforth called CeO<sub>2</sub>/49-R and CeO<sub>2</sub>/48-R) were characterised by microcalorimetry. The pertinent results are shown in Fig. 4 and 5. CeO<sub>2</sub>/49-R is quite similar to CeO<sub>2</sub>/49 as to the initial heat of NH<sub>3</sub> adsorption and the acid-strength distribution (Fig. 4); the number of ammonia-adsorbing sites is lower for the former. CeO<sub>2</sub>/48-R and CeO<sub>2</sub>/48 differ significantly in their acid-strength distribution (Fig. 4); the plateau observed on the latter around 100 kJ mol<sup>-1</sup> is no longer present on CeO<sub>2</sub>/48-R, which shows continuous heterogeneity. Reduction also results in the elimination from both CeO<sub>2</sub>/48 and CeO<sub>2</sub>/49 of the family of basic sites with CO<sub>2</sub> adsorption heats of about 160 and 145 kJ mol<sup>-1</sup> (Fig. 5). Instead, stronger sites appear at low coverage, particularly on CeO<sub>2</sub>/48-R. The total number of basic sites on CeO<sub>2</sub>/48-R and CeO<sub>2</sub>/49-R is lower than on CeO<sub>2</sub>/48 and CeO<sub>2</sub>/49.

According to our previous findings on 4-methylpentan-2-ol transformation over zirconia catalysts,<sup>10</sup> a key parameter gov-



**Table 3** Acid–base properties and initial reaction selectivities for lanthanum and cerium oxides

catalysts	$n_B : n_A$	$n_{A>80} : n_A$	$n_{B>80} : n_B$	initial selectivity (mol%) <sup>a</sup>		
				1-A	2-A + C <sub>6</sub>	K
CeO <sub>2</sub> /49	0.89	0.31	0.72	66	16	18
CeO <sub>2</sub> /49-R	0.89	0.43	0.70			
CeO <sub>2</sub> /48	0.55	0.55	0.85	47	41	12
CeO <sub>2</sub> /48-R	0.49	0.32	0.80			
La <sub>2</sub> O <sub>3</sub> /50	2.06	0.15	0.86	64	6	30

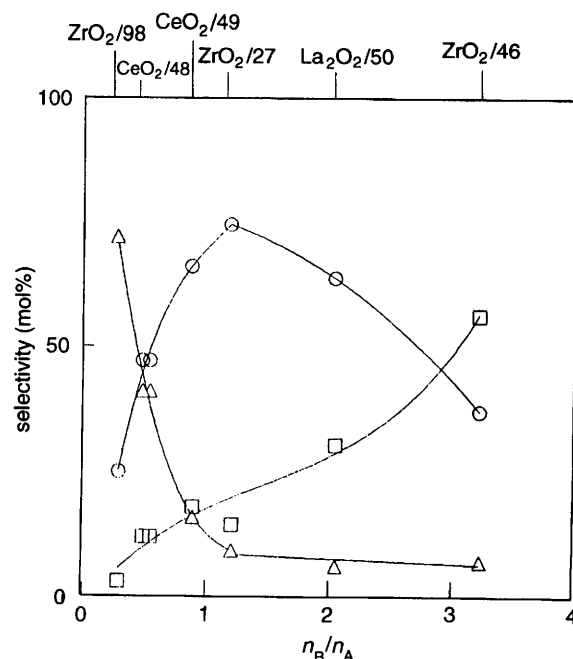
<sup>a</sup> 1-A, 4-methylpent-1-ene; 2-A + C<sub>6</sub>, 4-methylpent-2-ene + skeletal isomers of C<sub>6</sub>-alkenes; K, 4-methylpentan-2-one.

erning selectivity should be the ratio between the number of base and acid sites,  $n_B : n_A$ . This ratio has been calculated for each catalyst by dividing the amount of adsorbed CO<sub>2</sub> by the amount of adsorbed ammonia. Sites with adsorption heats below 25 kJ mol<sup>-1</sup> reasonably related to physical adsorption were neglected in this calculation. Values of  $n_B : n_A$  are given in Table 3, which also gives initial selectivities to the reaction products. The fraction of acid sites with adsorption heat of ammonia > 80 kJ mol<sup>-1</sup> ( $n_{NH_3>80} : n_{NH_3}$ ) and the fraction of basic sites with adsorption heat of CO<sub>2</sub> > 80 kJ mol<sup>-1</sup> ( $n_{CO_2>80} : n_{CO_2}$ ) have been also calculated and are presented in Table 3. These parameters have also been calculated for CeO<sub>2</sub>/48-R and CeO<sub>2</sub>/49-R, which were assumed to represent the possible states of CeO<sub>2</sub>/48 and CeO<sub>2</sub>/49 if reduction by the reactant alcohol actually occurs.

As expected, typical E1cB selectivity is observed for CeO<sub>2</sub>/49. This catalyst has a well balanced number of acid and base sites whether it remains unaffected by the reducing reaction atmosphere or it actually undergoes sudden reduction by 4-methylpentan-2-ol ( $n_B : n_A = 0.89$  for both CeO<sub>2</sub>/49 and CeO<sub>2</sub>/49-R). This allows a two-point adsorption of the reactant alcohol *via* interaction of the acid sites with the OH group of the alcohol and the simultaneous interaction of the base sites with the  $\beta$ -hydrogen of the terminal methyl group. This is followed by C–H bond rupture on the strong base sites, which are predominant ( $n_{CO_2>80}/n_{CO_2} = 0.72$  and 0.70 for CeO<sub>2</sub>/49 and CeO<sub>2</sub>/49-R, respectively) leading to 4-methylpent-1-ene *via* intermediate carbanionic species.

On CeO<sub>2</sub>/48 the situation is less well defined. 4-Methylpent-1-ene selectivity is sufficiently high (47%) to suggest the occurrence of the E1cB mechanism. In addition, the overall selectivity to alk-2-enes is just slightly lower (41%), which indicates the simultaneous presence of Saytzeff-oriented reaction pathways. Most of the basic sites on CeO<sub>2</sub>/48 and CeO<sub>2</sub>/48-R are strong ( $n_{CO_2>80}/n_{CO_2} = 0.85$  and 0.80, respectively). Such a high value should favour an E1cB mechanism *via* the C–H bond rupture, whether CeO<sub>2</sub>/48 is suddenly reduced or not. However, the  $n_B : n_A$  ratio is below unity in both cases (0.49 and 0.56 for CeO<sub>2</sub>/48-R and CeO<sub>2</sub>/48, respectively) which limits the establishment of two-point adsorption of the reactant alcohol. 4-Methylpentan-2-ol could also be adsorbed, at least in part, *via* the interaction of the hydroxy group of the alcohol with the prevailing acid sites. This could be followed by C–OH bond rupture leading to carbocation formation and then to alk-2-enes. Thus an E1 mechanism could be operating as well as E1cB. Further indication for this is the large amount of C<sub>6</sub> skeletal isomers in the alk-2-enes mixture (about 50% of the all the alkenes having an internal double bond), which can be explained by the occurrence of an alkyl shift in the intermediate carbocation.

Most of the base sites on La<sub>2</sub>O<sub>3</sub>/50 have the required strength ( $n_{CO_2>80}/n_{CO_2} = 0.86$ ) to allow the rupture of the

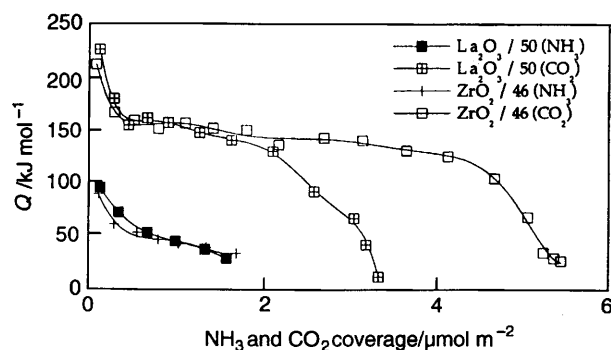


**Fig. 6** Selectivity to 4-methylpent-1-ene (O), alk-2-enes (Δ) and 4-methylpentan-2-one (□) vs.  $n_B : n_A$  for lanthanum and cerium oxides (this work) and zirconia catalysts (ref. 10)

C<sub>β</sub>–H bond first, but the lack of balance between acid and base sites ( $n_B : n_A = 2.01$ ) somewhat limits the two-point adsorption. Interestingly, ketone formation appears to be favoured on La<sub>2</sub>O<sub>3</sub>/50 in comparison with CeO<sub>2</sub>/49.

The influence of the  $n_B : n_A$  ratio on the reaction selectivities is shown in Fig. 6, which shows the present results for lanthanum and cerium oxides together with former results for zirconia catalysts,<sup>10</sup> specifically chosen to cover a wide  $n_B : n_A$  range. Alk-2-ene selectivity dramatically decreases at a low level as  $n_B : n_A$  approaches unity and then remains an approximately constant change, whereas a volcano-shaped curve is apparent for alk-1-ene selectivity values. Ketone formation is enhanced as  $n_B : n_A$  goes well above unity, *i.e.* for La<sub>2</sub>O<sub>3</sub>/50 and ZrO<sub>2</sub>/46.

In Fig. 7, calorimetric results for La<sub>2</sub>O<sub>3</sub>/50 (this work) and ZrO<sub>2</sub>/46 (ref. 10) are compared. Both the oxides show a smooth decrease of the differential heat of ammonia adsorption with increasing coverage, the corresponding curves being almost superimposed. This indicates very similar acidic properties, in terms of both number and strength of the sites. The initial differential heats for CO<sub>2</sub> are very high (225 and 210 kJ mol<sup>-1</sup> for La<sub>2</sub>O<sub>3</sub>/50 and ZrO<sub>2</sub>/46, respectively). After a sudden decrease at very low coverages, a plateau around 150 kJ mol<sup>-1</sup> established for both the oxides, which seems to



**Fig. 7** Differential heats of adsorption of NH<sub>3</sub> and CO<sub>2</sub> as a function of coverage for La<sub>2</sub>O<sub>3</sub>/50 (this work) and ZrO<sub>2</sub>/46 (ref. 10)

indicate that strong base sites of the same family are present on the two samples. The amount of these sites is higher for  $\text{ZrO}_2/46$  and the plateau extends over a wider range of  $\text{CO}_2$  uptake than for  $\text{La}_2\text{O}_3/50$ . The plateau is followed in both cases by a decrease of the differential heat following similar curves. Both dehydration *via* an E1cB mechanism and dehydrogenation are reported to occur *via* the same rate-determining step,<sup>6,7</sup> *i.e.* the rupture of the C—H bond of the methyl group of the alcohol molecule adsorbed on an acid–base pair, giving the corresponding carbanion; OH abstraction from which gives an alk-1-ene, and  $\text{H}_\alpha$  abstraction gives a ketone, both occurring on acid sites. The predominance of 4-methylpent-1-ene and 4-methylpentan-2-one over alk-2-enes on both  $\text{La}_2\text{O}_3/50$  and  $\text{ZrO}_2/46$  is not surprising, as the carbanion formation should be related to the strong base sites. However the reasons for the preference for alk-1-ene or ketone formation remain somewhat unclear, as  $\text{La}_2\text{O}_3/50$  and  $\text{ZrO}_2/46$  are almost identical in acidity. Although differences in the oxide structure may account for this, another reaction pathway towards the ketone should be considered, in which the key point is represented by the adsorption mode of the reactant alcohol. If this could be adsorbed on the base sites by means of a hydrogen bond, the  $\text{C}_\alpha$ —O bond would be strengthened and the  $\text{C}_\alpha$ —H bond weakened by localisation of the negative charge on  $\text{H}_\alpha$ , which is then abstracted by interaction with a positively polarised H atom of the surface (originating from the previously split O—H group of the alcohol).<sup>9</sup> Two conditions are needed for this to occur: a high  $n_B : n_A$  ratio and high base-site strength. Both occur to a greater extent on  $\text{ZrO}_2/46$  than on  $\text{La}_2\text{O}_3/50$ , which explains the observed differences in the ketone : alk-1-ene ratio.

To verify further the role of the base sites on selectivity, an extended run was performed on  $\text{La}_2\text{O}_3/50$  under the following conditions: 4-methylpentan-2-ol was fed in a nitrogen stream, as usual, over the catalyst for 50 h,  $\text{N}_2$  flow was then stopped and immediately replaced by  $\text{CO}_2$ ; the run was continued under these new conditions for 30 h before returning to  $\text{N}_2$  for another 30 h. After a slight decrease confined to the early hours on stream, conversion remained at *ca.* 40% during the whole run, independent of whether nitrogen or carbon dioxide was used as carrier gas. Selectivities to the various products are shown in Fig. 8. Expectedly, sudden changes in alkene distribution are observed when  $\text{N}_2$  is replaced by  $\text{CO}_2$  with a dramatic decrease in alk-1-ene; the original selectivities are again reached when the nitrogen stream is restored.  $\text{CO}_2$  is able to interact strongly with the clean surface of  $\text{La}_2\text{O}_3/50$ , as indicated by the plateau around  $150 \text{ kJ mol}^{-1}$  in Fig. 7. A similar plateau has been reported for commercial lanthanum oxide,<sup>11</sup> and attributed on the basis of IR results,<sup>14</sup> to the formation of a monodentate carbonate, *via* reaction of carbon dioxide with a surface oxygen site acting as a base. When  $\text{CO}_2$

is admitted during reaction, the oxide surface is already covered by adsorbed alcohol molecules. In the case of a two-point adsorption it is the H atom of the methyl group that interacts with the base site. This is a type of interaction that could be easily displaced by the stronger acid  $\text{CO}_2$ , thus reducing the balance between the number of acid and base sites on the catalyst. As a result, E1cB would be strongly limited and alk-2-enes production *via* the acid-triggered E1 mechanism enhanced. Interestingly, ketone selectivity remains almost unchanged when  $\text{CO}_2$  is admitted onto the catalyst instead of  $\text{N}_2$ . Although initially surprising, this finding seems to support the suggestion that ketone formation is not triggered by the same E1cB mechanism responsible for alk-1-ene production. Indeed, if a part of the alcohol molecules are strongly adsorbed onto base sites by means of the H atom of the hydroxy group, it would be difficult for  $\text{CO}_2$  to displace them from the base (oxygen) sites. Rather, the possibility for  $\text{CO}_2$  to be adsorbed on the positively polarised H atom of the surface (originating in our case from the previously split O—H group of the alcohol on the base site) should be considered, as  $\text{CO}_2$  is known to be adsorbed on surface hydroxy groups of metal oxides with the formation of a surface hydrogenocarbonyl ion (bicarbonate species).<sup>11,14</sup> However, whether or not this occurs, the formation of ketones is allowed to continue, according to the pathway outlined above.

Another interesting point concerning  $\text{La}_2\text{O}_3/50$  is the above-mentioned change in selectivity observed during the early hours on stream (Fig. 1). To ascertain whether this behaviour is related to changes in the overall reaction extent associated with the slight activity decay, several runs were performed on  $\text{La}_2\text{O}_3/50$  at different temperatures and/or contact times to achieve different conversion levels. Average values of the selectivities to the various products were calculated from each run at a later time-on-stream, and are reported *vs.* corresponding conversion in Fig. 9. No change in product distribution can be observed over the wide conversion range investigated. Some type of surface conditioning of the catalyst could be responsible for the increase of 4-methylpent-1-ene with time-on-stream observed initially in Fig. 1, probably originated by the interaction of reaction products with the catalyst surface. Neither 4-methylpent-1-ene nor 4-methylpent-2-ene can be retained on the catalyst, as indicated by the failed attempts to saturate it by repeated injections of these substances at 373 K in the TPD equipment. Strong

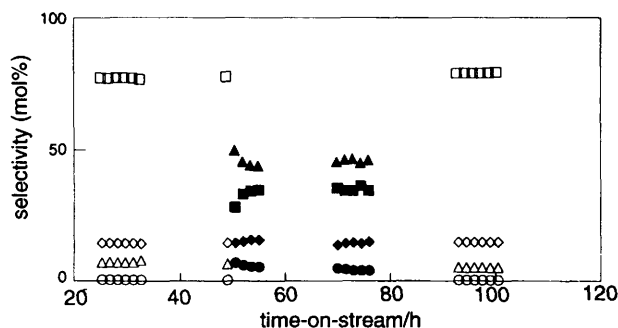


Fig. 8 Selectivities *vs.* time-on-stream for  $\text{La}_2\text{O}_3/50$  at 633 K using  $\text{N}_2$  (open symbols) or  $\text{CO}_2$  (full symbols) as carrier gas: Symbols as in Fig. 1

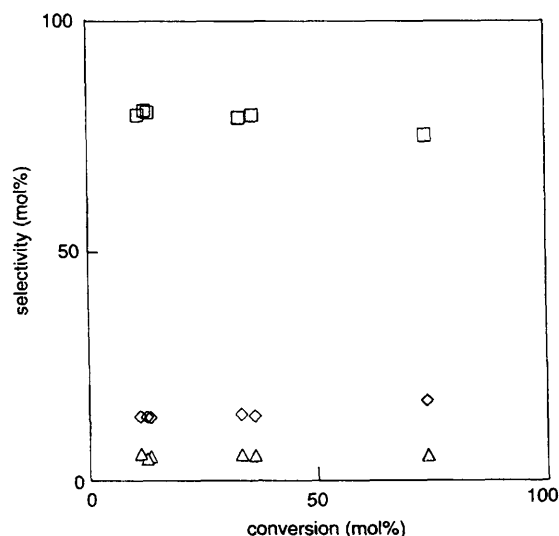


Fig. 9 Selectivities *vs.* conversion for  $\text{La}_2\text{O}_3/50$ . Data refer to later times-on-stream: symbols as in Fig. 1.

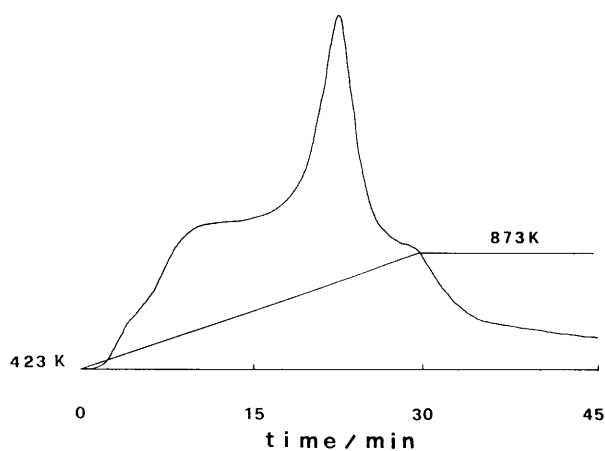


Fig. 10 Temperature-programmed desorption spectrum of  $\text{H}_2\text{O}$  from  $\text{La}_2\text{O}_3/50$

interaction of 4-methylpent-2-one can be ruled out on the basis of TPD experiments, which indicated that ketone adsorption occurs to a very low extent at 373 K and is too weak to operate under reaction conditions. On the contrary, water was found to be adsorbed on  $\text{La}_2\text{O}_3/50$  at 423 K. The pertinent TPD spectrum is shown in Fig. 10. The occurrence of strong interactions is indicated by the sharp peak emerging from the broad spectrum in the high-temperature region. Assuming that the strong  $\text{H}_2\text{O}$  adsorption is related to a dissociative mechanism operating on the strong base sites of the catalyst, on the latter the adsorption of the alcohol by the H atom of the hydroxy group would be limited by competition with the by-product water, once the reaction is started. As a result, ketone formation will decrease.

Changes in selectivity occurring with time-on-stream on the two cerium oxides have been also mentioned (Fig. 2 and 3). No interpretation can be attempted in this case, as the progressive transformation of  $\text{Ce}^{\text{IV}}$  into  $\text{Ce}^{\text{III}}$  and the possibility of surface modifications due to the adsorption of reaction products must be considered simultaneously.

Generally,  $\text{La}_2\text{O}_3/50$  appears to be interesting from the practical point of view: it is reasonably stable and, for long runs, is very selective for 4-methyl-1-pentene.  $\text{CeO}_2/49$  also appears to be promising. Patent reports claim that immersion in NaOH solution, followed by drying and calcination, is a good method for improving  $\text{ZrO}_2$  selectivity to alk-1-ene.<sup>21,22</sup>  $\text{CeO}_2/49\text{D}$  was prepared from  $\text{CeO}_2/49$  according to this procedure. Conversion and selectivities for  $\text{CeO}_2/49\text{D}$  are shown in Fig. 11. Comparison with  $\text{CeO}_2/49$  (Fig. 3) initially indicates a higher overall activity over  $\text{CeO}_2/49\text{D}$  associated with completely different selectivities. For  $\text{CeO}_2/49\text{D}$  the undesired alk-2-enes predominate over 4-methylpent-1-ene when conversion reaches approximately 50% (7 h), i.e. it is comparable with conversion on  $\text{CeO}_2/49$  for which in contrast alk-1-ene is by far the most abundant product. Nevertheless, in the long run the two samples give similar results, as mentioned above during discussion of Table 2. Thus, the NaOH immersion procedure is not particularly encouraging, at least for cerium oxide. It is worthy of note that immersion into NaOH solution of a precipitated zirconium hydroxide previously dried but not calcined gave a zirconia catalyst which appeared to be the best among all the samples.<sup>10</sup> Further work is needed before attempting to explain why such different results are obtained in the present case.

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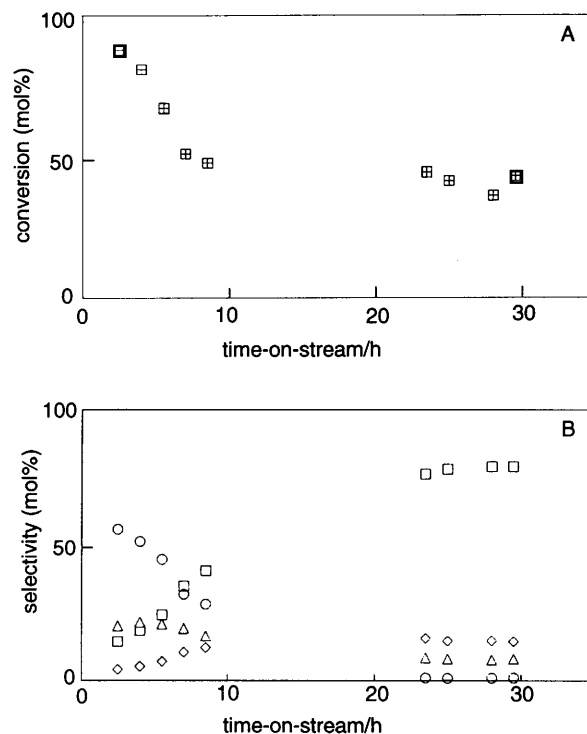


Fig. 11 Conversion (A) and selectivities (B) vs. time-on-stream for  $\text{CeO}_2/49\text{D}$  at 633 K: symbols as in Fig. 1

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