

# Propan-2-ol transformation on simple metal oxides $\text{TiO}_2$ , $\text{ZrO}_2$ and $\text{CeO}_2$

D. Haffad, A. Chambellan\*, J.C. Lavalley

UMR 6506, Catalyse et Spectrochimie, ISMRA-Université, 14050 Caen, France

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## Abstract

The propan-2-ol dehydration or dehydrogenation over three simple metal oxides ( $\text{TiO}_2$ ,  $\text{ZrO}_2$  and  $\text{CeO}_2$ ) was carried out in helium, dihydrogen or air flow, at temperatures in the (473–623 K) range.

Propan-2-ol decomposition on metal oxide surfaces has been used as an acid–base test. On  $\text{TiO}_2$ ,  $\text{ZrO}_2$  or  $\text{CeO}_2$ , it appears that propene and acetone formation sites are not specific and it is difficult to deduce surfaces properties from activities and selectivities observed. In helium and dihydrogen, for all the metal oxides, temperature increase always favours propene formation. In air, the three metal oxides used are more active and their selectivity in acetone is more important than in helium or dihydrogen.

The results clearly show that propanol transformation cannot be a simple test of acidity. Particularly, on ceria, results suggest that redox property and the high lability of lattice oxygen contribute to products formations, involving oxygen vacancies. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Acidity; Basicity; Oxidation properties; Propan-2-ol transformation

## 1. Introduction

The acid–base properties of metal oxides play a key role in catalysis. They can be characterised by different methods, in particular by test-reactions, like propan-2-ol decomposition. It is often admitted that propan-2-ol dehydration into propene probes the catalyst acid character, whereas its dehydrogenation to acetone characterises its basicity [1–4]. However, results are not so clear; for instance it has been reported that additional redox ability promotes propan-2-ol dehydrogenation [5–8]. Therefore, it is necessary to take in account both redox and acid–base properties

of the metal oxides to establish relationships between catalytic results and surface characterisation.

The aim of this study is to compare the catalytic activity towards propan-2-ol dehydration and dehydrogenation of three metal oxides:  $\text{TiO}_2$  (anatase),  $\text{ZrO}_2$  and  $\text{CeO}_2$ . They are oxides of the second row transition elements, the oxidation number of the cation,  $z$ , is equal to 4. Their acid character increases as the ionic radius and/or the co-ordination number of the cation decreases, as experimentally shown by infrared spectroscopy using probe molecule adsorption [9]:



On the other hand, oxygen mobility of ceria, measured by oxygen isotopic exchange, is high [10], explaining its redox properties [11]. Therefore, from these considerations, a gradual change of dehydration

\* Corresponding author. Fax: +33-2-31-45-28-22.  
E-mail address: chambellan@ismra.fr (A. Chambellan).

to dehydrogenation is expected by changing  $\text{TiO}_2$  into  $\text{ZrO}_2$  and then into  $\text{CeO}_2$ . To check if such a variation occurs, catalyst activities have been compared at different temperatures and under different gas atmospheres (He,  $\text{H}_2$ , air). Special attention has been paid to secondary products analysis. Reaction mechanisms are proposed taking into account the surface properties of the three metal oxides used. The results will be used to evaluate the potential use of propan-2-ol test to determine the acid–base properties of metal oxides.

## 2. Experimental

Before the reaction, a flow pre-treatment of either helium, dihydrogen or air was passed over metal oxides for 2 h at 623 K (denoted as  $\bar{N}$ ,  $\bar{R}$ ,  $\bar{O}$  like neutral, reducing or oxidising pre-treatment). The propan-2-ol transformation was performed on 200 mg of catalyst ( $W$ ), in a quartz microflow reactor at atmospheric pressure in a helium, dihydrogen or air flow ( $N$ ,  $R$ ,  $O$  process). The flow rate was  $20 \text{ ml min}^{-1}$ , the contact time  $W/F = 2.21 \text{ kg mol}^{-1} \text{ h}^{-1}$  and the temperature varied in the (413–673 K) range [12].

Affluents were analysed online, every 15 min, by gas chromatography using a FID detector and a CP-WAX 52CB column. Some products were collected at liquid dinitrogen temperature to identify secondary products by coupling gas chromatograph and mass spectrometer. When an accurate identification is not possible, the secondary product was named by its stoichiometric formula deduced from its mass spectrum.

$\text{CeO}_2$  provided by Rhône Poulenc had a high specific BET area,  $120 \text{ m}^2 \text{ g}^{-1}$ , including a  $60 \text{ m}^2 \text{ g}^{-1}$  equivalent area in microporosity. It contained less than 0.5% lanthana [13]. The acidity and basicity were measured in oxidised and reduced states by use of probe molecule adsorption studied by FT-IR spectroscopy [14].  $\text{TiO}_2$  and  $\text{ZrO}_2$  were prepared by hydrolysis of the corresponding propylates, followed by calcination at 823 K. Their surface area was  $70 \text{ m}^2 \text{ g}^{-1}$  and their porous volume  $0.15 \text{ cm}^3 \text{ g}^{-1}$ . Their X-ray diffraction spectra showed rather broad peaks assigned to anatase in the case of  $\text{TiO}_2$  and to quadratic and monoclinic structures in the case of  $\text{ZrO}_2$  [15]. Their acidic and basic properties using specific probe molecules adsorption were also reported in [15].

## 3. Results

### 3.1. In helium flow ( $\bar{N}$ procedure)

Total conversion  $f_T$  and selectivity  $S$ , strongly depend on the metal-oxide used. Fig. 1 shows that the conversion increases from  $\text{CeO}_2 < \text{ZrO}_2 < \text{TiO}_2$ , for all the temperatures. The first product at  $T > 473 \text{ K}$  is always acetone, but propene then appears and becomes predominant in the case of  $\text{TiO}_2$  and  $\text{ZrO}_2$ .

In Fig. 2, conversion and selectivity are compared for the three catalysts, after 1 h of reaction at three different temperatures chosen in such a way that conversions are comparable. On  $\text{TiO}_2$  and  $\text{ZrO}_2$ , selectivities do not vary with time on stream. In contrast, the amount of secondary products is quite important on  $\text{CeO}_2$  and tends to increase with time on stream at temperatures lower 523 K.

For conversions lower than 30%, propene is the main product formed on  $\text{TiO}_2$  and  $\text{ZrO}_2$ . The relative amount of acetone increases from  $\text{TiO}_2 < \text{ZrO}_2 \ll \text{CeO}_2$ . On  $\text{CeO}_2$ , secondary products, mainly unsaturated  $\text{C}_6\text{H}_{10}$ ,  $\text{C}_6\text{H}_{12}$  compounds and ketones seem to occur when the acetone amount is large.

The selectivity depends upon temperature, forever, the three oxides examined, temperature increase always favours propene formation in such a way that propene is the only product formed on  $\text{TiO}_2$  at 523 K and on  $\text{ZrO}_2$  at 598 K. On  $\text{CeO}_2$  (Fig. 3) some acetone is detected even at 623 K and the conversion of propan-2-ol into acetone reaches its maximum (about 20%) at 550 K.

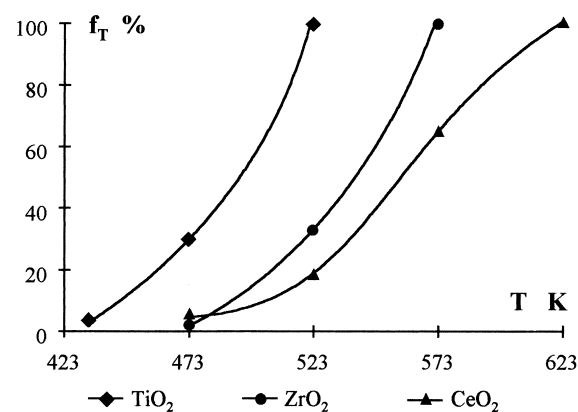


Fig. 1. Propan-2-ol conversion in helium flow vs. temperature on  $\text{TiO}_2$ ,  $\text{ZrO}_2$  and  $\text{CeO}_2$ .

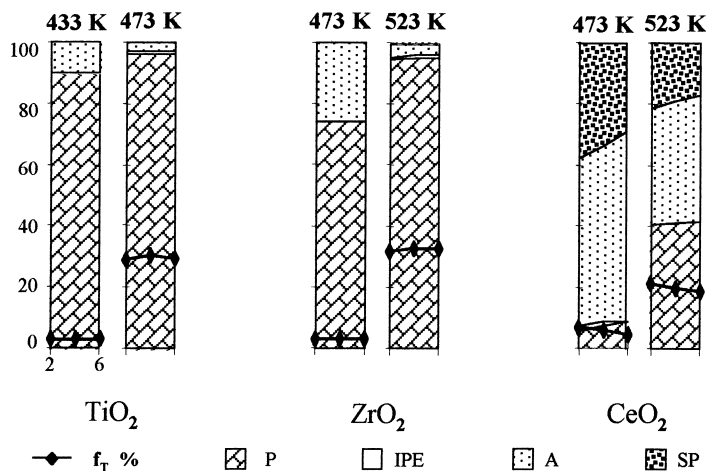


Fig. 2. Propan-2-ol transformation in helium flow on TiO<sub>2</sub>, ZrO<sub>2</sub> and CeO<sub>2</sub>. Variations of conversion ( $f_T$ ) and selectivity with time on stream (h) at 433, 473 or 523 K. P: propene; IPE: isopropyl ether; A: acetone; SP: secondary products.

The activation energies  $E_a$  (P) for propene formation on TiO<sub>2</sub>, ZrO<sub>2</sub> and CeO<sub>2</sub> have been estimated to 121, 110 and 125 kJ mol<sup>-1</sup>, respectively (in 423–473, 473–523 and 473–533 K temperature ranges). These values are very close to those reported by Gervanisi et al. [16] on TiO<sub>2</sub> (130 kJ mol<sup>-1</sup>, 437–477 temperature range) and ZrO<sub>2</sub> (112 kJ mol<sup>-1</sup>, 455–499 K temperature range).

For reaction temperature >473 K, secondary products are formed, for all metal oxides, at reaction higher

than 473 K. They consist of C<sub>6</sub> compounds formed from condensation, accompanied by a low amount of light products (methane, butene).

On TiO<sub>2</sub> only traces of isopropyl ether have been found at 473 K and of an ethylenic compound C<sub>6</sub>H<sub>12</sub> (probably (CH<sub>3</sub>)<sub>2</sub>C=C(CH<sub>3</sub>)<sub>2</sub>) from 523 K.

On ZrO<sub>2</sub>, traces of isopropyl ether are also detected at low temperature (473 K), whereas the amount of unsaturated hydrocarbon (C<sub>6</sub>H<sub>12</sub>) and dienes (C<sub>6</sub>H<sub>10</sub>) is more important. The propan-2-ol conversion into

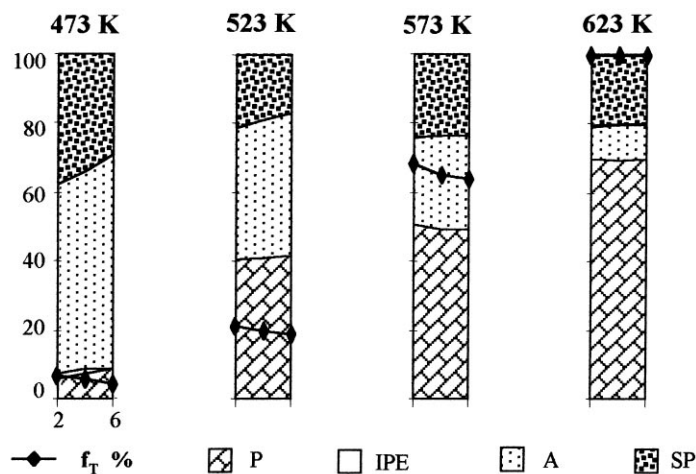


Fig. 3. Propan-2-ol transformation in helium flow. Variations of conversion ( $f_T$ ) and selectivity on CeO<sub>2</sub> with time on stream (h) at 473, 523, 573 and 623 K.

secondary products is 1.5% at 523 K and reaches a maximum (5.5%) at 573 K. From 523 K, traces of ketones are also formed as ethyl-methyl-ketone, diethyl-ketone, isobutyl-methyl-ketone (BMC) and mesityl-oxide (OM: 4-methyl-2-one pent-3-ene).

On ceria, conversion to secondary products is much more important and reaches a maximum (15%) at 550 K. All the products observed on  $\text{TiO}_2$  and  $\text{ZrO}_2$  are found,  $\text{C}_6\text{H}_{12}$  and  $\text{C}_6\text{H}_{10}$  are largely predominant. When the reaction temperature increases, a behaviour similar to that observed on  $\text{ZrO}_2$  is noted. The amount of  $\text{C}_6\text{H}_{12}$  compounds continuously increases, whereas that of  $\text{C}_6\text{H}_{10}$  and oxygenated compounds reaches a maximum near 523 K. Traces of propane and light hydrocarbons are also detected.

### 3.2. In dihydrogen flow ( $\overline{RR}$ procedure)

It has been found that propan-2-ol conversions and selectivities, on  $\text{ZrO}_2$  and  $\text{TiO}_2$ , depend neither on the nature of the flowing gas (He or  $\text{H}_2$ ) nor on the conditions of the catalyst pre-treatment. It is observed that the use of dihydrogen as flow slightly favours propene formation when the conversion is not complete ( $T > 523$  K for  $\text{TiO}_2$ ,  $T < 600$  K for  $\text{ZrO}_2$ ).

More important changes are noted on  $\text{CeO}_2$ . Higher conversions (Fig. 4) are observed in dihydrogen flow at 523 and 573 K, due to an increase in propene forma-

tion. Secondary products are more important; in contrast the conversion into acetone decreases. At 623 K, propan-2-ol conversion is complete and the amount of acetone formed is then very weak.

It is important to note that if the dihydrogen flow is replaced by helium during the test, activity and selectivity change into those observed under helium, irrespective of the reaction temperature.

### 3.3. In air flow ( $\overline{OO}$ procedure)

In air flow, the catalysts activated under oxidising conditions at 623 K are much more active than those pre-treated in helium or dihydrogen flow. They all present some activity even at 413 K. In the range (413–448 K), when comparison is possible, at equal and low conversion, acetone selectivity is much more important than under He or  $\text{H}_2$ .

In air, ceria is more active than other oxides (Fig. 5) with the conversion reaching 38% at 448 K. Acetone is almost the only product detected. Note that  $\text{TiO}_2$  and  $\text{ZrO}_2$  selectivities are quite different.  $\text{TiO}_2$  mainly gives rise to propene, whereas acetone is predominant on  $\text{ZrO}_2$ . The activation energy for propene formation on  $\text{TiO}_2$  ( $E_a(\text{P}) = 121 \text{ kJ mol}^{-1}$ ) is similar to that measured under helium. In the same temperature range (413–455 K), the activation energies for acetone formation  $E_a(\text{A})$  are lower than  $121 \text{ kJ mol}^{-1}$ . They can

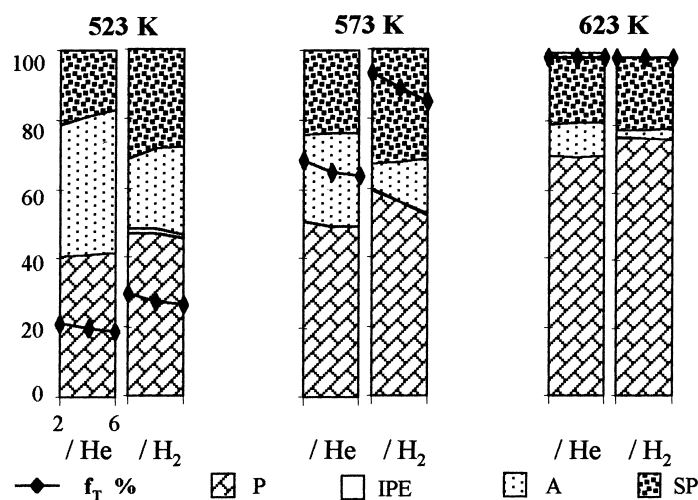


Fig. 4. Propan-2-ol transformation in helium or in dihydrogen flow. Variations of conversion ( $f_T$ ) and selectivity on  $\text{CeO}_2$  with time on stream (h) at 523, 573 and 623 K.

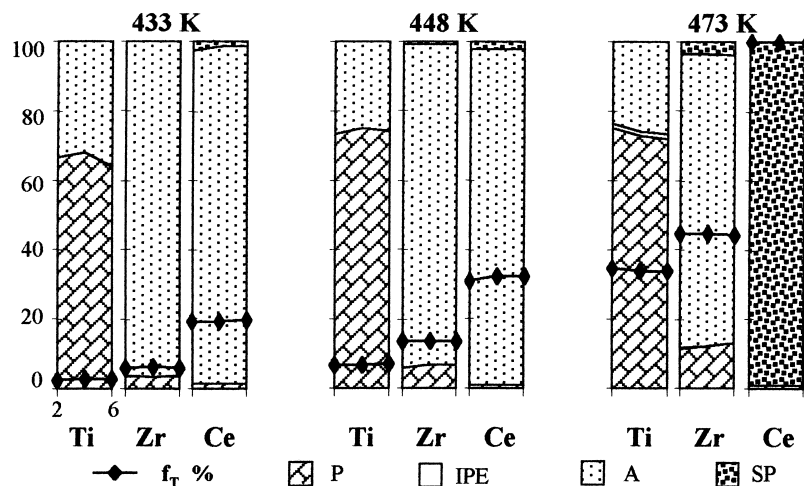


Fig. 5. Propan-2-ol transformation under air on TiO<sub>2</sub>, ZrO<sub>2</sub> and CeO<sub>2</sub>. Variations of conversion ( $f_T$ ) and selectivity with time on stream (h) at 433, 448 and 473 K.

be estimated to  $63 \pm 3$ ,  $73 \pm 10$  and  $89 \pm 9$  kJ mol<sup>-1</sup> for TiO<sub>2</sub>, ZrO<sub>2</sub> and CeO<sub>2</sub>, respectively.

For reaction temperatures higher than 448 K, propan-2-ol conversions are more important and several secondary products appear, not well identified. The carbon balance is not maintained any more. On ceria, at 473 K, no product is detected showing a complete transformation into CO<sub>2</sub> and H<sub>2</sub>O. On ZrO<sub>2</sub> and TiO<sub>2</sub> the total combustion occurs at higher temperature ( $T > 523$  K). Traces of C<sub>6</sub>H<sub>10</sub> without any C<sub>6</sub>H<sub>12</sub> olefin are detected on ZrO<sub>2</sub> for reaction temperatures higher than 473 K.

If air is replaced by helium under reaction conditions at 473 K, the amount of acetone produced drops and conversions and selectivities tend to those observed under helium in the same conditions.

## 4. Discussion

### 4.1. Surface properties

Some bulk properties of the three metal oxides used, denoted as “ionic basic oxides” [17] are gathered in Table 1.

Their surface, after activation, presents: (i) coordinatively unsaturated (cus) cations acting as Lewis acid sites, (ii) cus anions, acting as Lewis basic sites, (iii) residual hydroxy groups, acting as Brønsted acid

sites or basic sites. Generally acid–base pair sites are formed, dehydroxylation by heating occurring through elimination of H<sub>2</sub>O by recombination of neighbouring hydroxo groups. However, in the case of TiO<sub>2</sub>, Lewis acid sites alone can be created from molecular H<sub>2</sub>O desorption, without any coupled basic sites [18]. Using different probes adsorption, it is well established that the strength of the Lewis sites decreases from TiO<sub>2</sub> > ZrO<sub>2</sub> > CeO<sub>2</sub> [9,19] as expected from the polarising power of the cation (charge to radius ratio) [20]. As for the strength of the Lewis basic sites, it increases in the reverse order, as shown by CO<sub>2</sub> adsorption [19,21,22], in agreement with the residual charges on the surface anions calculated from the Pauling compensation model (Table 1).

Ti<sup>4+</sup>, Zr<sup>4+</sup>, Ce<sup>4+</sup> cations and rare gases are isoelectronic, so only oxidation reactions can be generated. The concomitant reduction of the cation ( $M^{4+} + e \rightarrow M^{3+}$ ) increases their nucleophilic character, particularly the basicity of the metal oxide. It can occur under flow of reactants or products, or after a reducing pre-treatment. Standard reduction potentials [25] reported in Table 1 show that CeO<sub>2</sub> can be easily reduced into Ce<sub>2</sub>O<sub>3</sub>, due to its high oxygen mobility [10]. Reduction of TiO<sub>2</sub> into Ti<sub>2</sub>O<sub>3</sub> is much more difficult and occurs through the formation of Ti<sub>n</sub>O<sub>(2n-1)</sub> intermediate phases (Magneli phases) [26]. Zirconia does not present any stable sub-oxide, which does not exclude any surface reduction. Under hydrogen,

Table 1  
Some physical and chemical parameters

	$\chi_M$ (eV) <sup>a</sup>	$I_{O-M}$ <sup>a</sup>	Cation <sup>b</sup>	$R(N)$ (pm) <sup>c</sup>	Structure name <sup>d</sup>	$\delta$ (e) <sup>e</sup>	MO <sub>2</sub> /M <sub>n</sub> O <sub>2n-1</sub>	$E(\text{MO}_2)/E(\text{M}_n\text{O}_{2n-1})$ <sup>f</sup>
Ti	1.54	70%	Ti <sup>+IV</sup> (6) O <sup>-II</sup> (3)	74 122	TiO <sub>2</sub>	$N = 6$ Ti(OH) <sup>-0.33</sup> Ti <sub>2</sub> (OH) <sup>+0.33</sup> Ti <sub>2</sub> O <sup>-0.66</sup>	TiO <sub>2</sub> /Ti <sub>3</sub> O <sub>5</sub>	-0.60
					Anatase (t) Rutile (t)			
Zr	1.33	72%	Zr <sup>+IV</sup> (7) O <sup>-II</sup> (3) O <sup>-II</sup> (4)	92 122 124	ZrO <sub>2</sub>	$N = 7$ Zr(OH) <sup>-0.43</sup> Zr <sub>2</sub> (OH) <sup>+0.14</sup> Zr <sub>3</sub> (OH) <sup>+0.71</sup> Zr <sub>2</sub> O <sup>-0.86</sup>	ZrO <sub>2</sub> /Zr <sub>n</sub> O <sub>2n-1</sub>	?
					Baddeleyite (m)		ZrO <sub>2</sub> /Zr	-1.55
Ce	1.12	77%	Ce <sup>+IV</sup> (8) O <sup>-II</sup> (4)	111 124	CeO <sub>2</sub>	$N = 8$ Ce(OH) <sup>-0.5</sup> Ce <sub>2</sub> (OH) <sup>+0</sup> Ce <sub>3</sub> (OH) <sup>+0.5</sup> Ce <sub>2</sub> O <sup>-1</sup>	CeO <sub>2</sub> /Ce <sub>2</sub> O <sub>3</sub>	+1.56
					Fluorite (c)			

<sup>a</sup> Metal electro-negativity ( $\chi_M$ ) and metal–oxygen bond ionicity ( $I_{O-M}$ ) according to Pauling [23].

<sup>b</sup> The values in parentheses indicate the  $N$ -coordination.

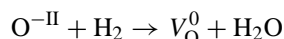
<sup>c</sup>  $R(N)$ : ionic radius of the  $N$ -coordinate cation according to Shannon and Prewitt [24].

<sup>d</sup> Crystal lattice: tetragonal (t), monoclinic (m), cubic (c).

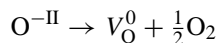
<sup>e</sup> Residual charge of surface oxygen ( $\cdot$ )<sup>- $\delta$</sup>  according to Pauling [20].

<sup>f</sup>  $E(\text{MO}_2)/E(\text{M}_n\text{O}_{2n-1})$ : standard reduction potentials (in volts) according to Pourbaix [25].

a partial surface deoxygenation can occur leading to creation of anionic vacancies:



where  $\text{V}_\text{O}^0$  is a neutral oxygen vacancy (a vacancy having two electrons). Their formation explains the n-semi-conductor properties of TiO<sub>2</sub> [26,27], ZrO<sub>2</sub> [26,28] and CeO<sub>2</sub> [26,29] and thus, checks the weak reduction of the ZrO<sub>2</sub> surface. They are able, by electron transfer, to reduce cations. If the question about the detection of Ti<sup>3+</sup> ions using CO adsorption [30] is still open [31], Ce<sup>3+</sup> can be easily differentiated from Ce<sup>4+</sup> by CO or methanol adsorption [14,32]. Zr<sup>3+</sup> ions have been evidenced by EPR either under reduced pressure or in presence of dioxygen [33]. The formation of such anionic vacancies can also explain, on zirconia, the formation of F centres under oxidising atmosphere and even its semi-conducting properties under O<sub>2</sub> at 625 K. Note that oxygen vacancies could pre-exist, notably, on ceria according to:



They can be evidenced by oxygen adsorption, through the formation of O<sub>2</sub><sup>-</sup> superoxide species, well char-

acterised by ESR or IR spectroscopy [14,34]. Such species have also been observed on TiO<sub>2</sub> [35] and ZrO<sub>2</sub> [36].

## 4.2. Catalytic tests

Catalytic results show that both the activity and selectivity of TiO<sub>2</sub>, ZrO<sub>2</sub> and CeO<sub>2</sub> in propan-2-ol decomposition strongly depend on the reaction temperature and the nature of the flowing gas. Therefore, the effect of both parameters is discussed.

### 4.2.1. Propene and acetone formation

It is worth noting that the first product detected by increasing temperature is acetone, for all the metal oxides and the flowing gas. In our experiments, propan-2-ol is first introduced at 413 K on the catalyst activated at 625 K and then the temperature is progressively increased. At low temperature, several infrared studies of alcohol adsorption on TiO<sub>2</sub> [37], ZrO<sub>2</sub> [38] and CeO<sub>2</sub> [32] have evidenced the formation of alkoxide species either by dissociative adsorption on acid–base M<sup>IV</sup>...O<sup>II</sup> sites or by alcohol condensation with the residual surface hydroxo groups with

water formation [39]. On heating, the disappearance of the isopropoxy species so formed would lead to acetone, as already reported on  $\text{TiO}_2$  and  $\text{ZrO}_2$  [40] and on  $\text{CeO}_2$  [5]. Note that several papers reported that thermal desorption of adsorbed methoxy species on ceria leads, under vacuum at 473 K, to formate species. This transformation is accompanied by a  $\text{Ce}^{\text{IV}} \rightarrow \text{Ce}^{\text{III}}$  reduction. Therefore, it is possible that even under helium, some cerium ions are reduced even at relatively low temperature [14].

Desorption of isopropoxy species generates the surface active sites for propanol-2-ol decomposition. On  $\text{TiO}_2$  and  $\text{ZrO}_2$ , near 473 K, under helium or dihydrogen, propene is mainly detected with a selectivity higher than 95 and 75%, respectively. On  $\text{CeO}_2$ , propene is a minor product (selectivity >10%). Whatever the metal oxide, under helium, temperature increase always favours propene formation, in agreement with the value of activation energies, higher for propene than for acetone formation.

It is generally proposed that propene formation involved either surface Brønsted (Fig. 6a) or Lewis (Fig. 6b) acid sites, leading to hydrogen bonded or co-ordinated propan-2-ol species, respectively.

A concerted mechanism then occurs involving a hydrogen atom of a methyl group (Fig. 6). Since, the strength of the Lewis acid sites decreases from  $\text{TiO}_2 > \text{ZrO}_2 > \text{CeO}_2$ , propene formation should decrease in the same order if such sites play the role of active sites.

As for the acidity of residual OH groups, it has been found that only some of them on  $\text{TiO}_2$  are able to protonate 2,6-dimethyl-pyridine, evidencing their Brønsted acidity. The catalytic results reported here are in good accordance with those expected from acidic properties.

Use of dihydrogen as a flow gas increases propene formation on ceria at  $T \geq 523$  K (Fig. 4). It is generally assumed that ceria surface reduction under flow of  $\text{H}_2$  begins at  $T \geq 523$  K and is well observed at  $T = 623$  K [32,41]. Surface rehydroxylation occurs, followed by dehydroxylation, involving the concomitant reduction of  $\text{Ce}^{\text{IV}}$  into  $\text{Ce}^{\text{III}}$ . Adsorption of probe molecules has been used to compare the acidity of ceria in oxidised and reduced states. The acid strength of cerium ions is weak and it decreases upon reduction as shown by adsorbing weak Lewis bases as CO [42] and  $\text{CH}_3\text{CN}$  [43]. Therefore, it is difficult to explain the increase of propene formation under dihydrogen by an increase of surface acidity. We prefer to invoke redox reactions as shown in Fig. 7.

One can think of this mechanism as the reverse Mars and Krevelen mechanism, the first step correspond to the oxidation of the catalyst with propan-2-ol that loses one oxygen and the second step has to be the reduction of the metal oxide [44]. Note that the last step of this scheme is the reverse of the oxidation of reduced ceria by  $\text{H}_2\text{O}$  which has been observed at 573 K.

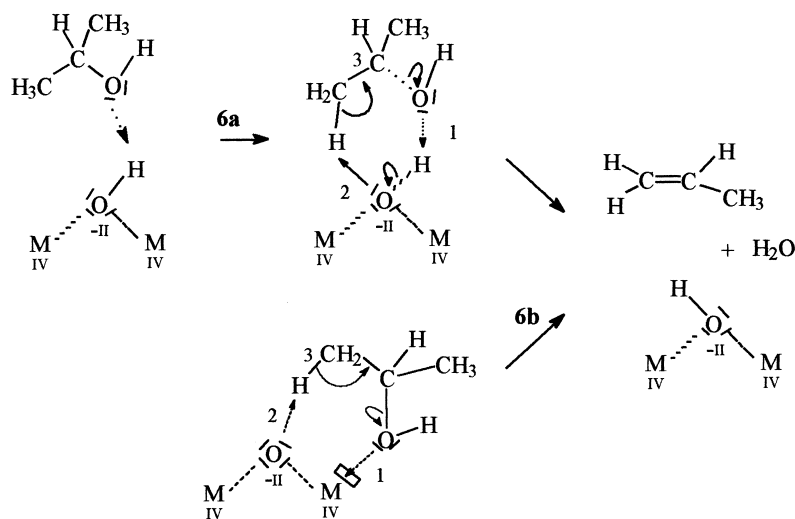


Fig. 6. Propan-2-ol dehydration: 'acid-base' model.

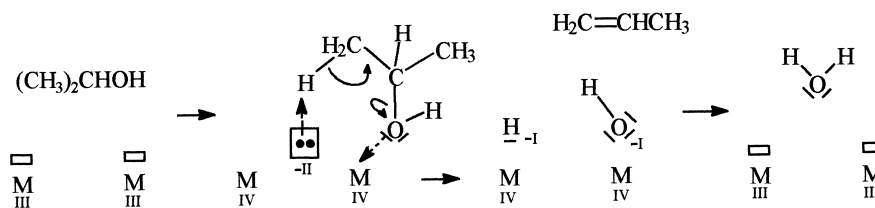


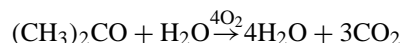
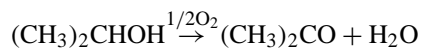
Fig. 7. Propan-2-ol dehydration: redox model.

As mentioned above, the mechanism of acetone formation on metal oxide could involve alkoxy species as intermediates (Fig. 8a). However, other intermediates as hydride species have also been reported [8] (Fig. 8b). The first mechanism mainly involves the basicity of the  $O^{-II}$  surface sites, the second one, the reduction properties of the cation. Since, both basicity and redox properties of three metal oxides used increase in the following order:  $TiO_2 < ZrO_2 < CeO_2$ , acetone selectivity is expected to increase in the same order under helium, as observed. Note that the amount of secondary products is important when a large amount of acetone is formed, which strongly supposes that secondary products mainly arise from acetone transformation. Therefore, the amount of acetone detected is certainly lower or even much lower, than that actually formed.

In air, the three metal oxides used are more active (some activity is noted as low as 473 K), whereas their selectivity in acetone increases. At 433 and 458 K, selectivity results show that  $TiO_2$  can be classified as

an acid amphoteric oxide,  $ZrO_2$  as a basic amphoteric oxide and ceria as a pure basic oxide. This expected classification is quite different from that deduced from reactivity measurements obtained under helium or dihydrogen at higher temperature. In such conditions, all catalysts appeared much more acidic.

In air, the carbon balance is not checked when the reaction temperature increases. This suggests that some propan-2-ol oxidation then occurs, leading to  $CO_2$ , not detected by gas chromatograph equipped with a FID detector. The first step of the complete oxidation can be acetone.



This is in agreement with Gervasini et al. [16] who reported in air, the marked activity towards acetone formation at low temperature of  $Cr_2O_3$  and  $MoO_3$ , usually employed as active phases in various oxidation reactions. The basicity of these three oxides

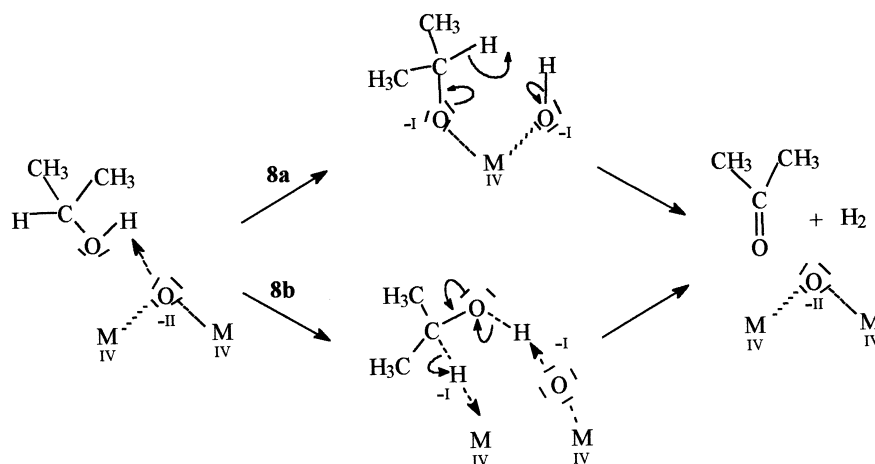
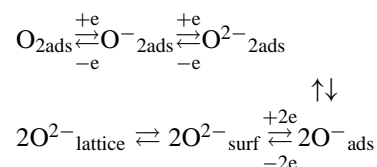


Fig. 8. Acetone formation: 'acid-base' model.



cannot explain their activity in acetone formation, since, none of them is not enough basic to adsorb  $\text{CO}_2$  [45]. Trovarelli recently reviewed the catalytic properties of ceria [46], oxidation reactions account for the majority of uses of ceria-containing materials in catalysis. The redox properties of ceria and the high lability of lattice oxygen are among the most important factors which contribute to its reactivity in oxidation reactions, however, total oxidation reactions generally occur. In agreement with these results, we propose that a part of acetone formed on ceria under air results from direct propan-2-ol oxidation.

Several authors have shown that oxygen adsorption on activated ceria leads to the formation of superoxide  $\text{O}_2^-$  species, which could be involved in the formation of anionic oxygen  $\text{O}^{2-}$  co-ordinated to surface cationic sites.



The formation of  $\text{O}_2^-$  species involves the presence of defect sites, such as anionic vacancies [46]. Such species are not observed on  $\text{ZrO}_2$ , excepted when  $\text{ZrO}_2$  is activated by a ‘quick’ treatment [36]. This was explained involving surface reduced defects resulting from the first decomposition of surfaces impurities upon thermal evacuation.

The side-one co-ordinated  $\text{O}_2^-$  species could participate to the following mechanism (Fig. 9).

Acetone formation increases as the strength of the  $\text{M}^{\text{IV}} \dots \text{O}^{\text{II}}$  bond decreases, which is in agreement

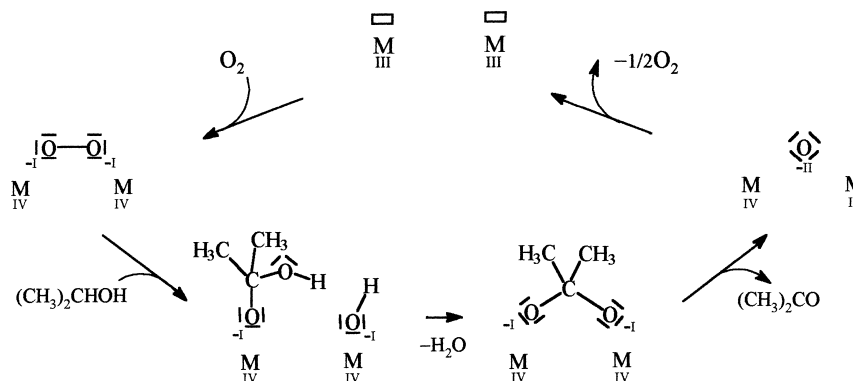


Fig. 9. Direct propan-2-ol oxidation under air.

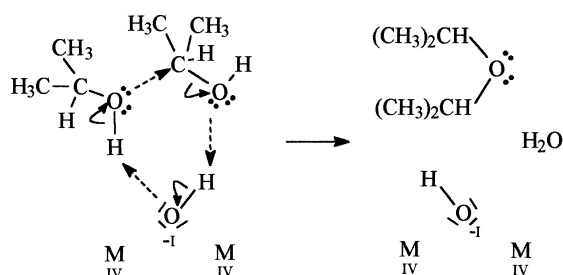
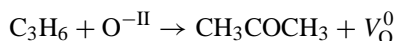


Fig. 10. Propan-2-ol intermolecular dehydration.

with the oxidising properties of  $\text{Ce}^{4+}$ ,  $\text{Zr}^{4+}$  and  $\text{Ti}^{4+}$  cations.

Finally, it has been reported that acetone is one of the main products formed when  $\text{TiO}_2$  is reduced by propene at 773 K [47], this suggests that the surface oxygen mobility could also be involved in acetone formation from propene,



which could occur primarily on ceria.

#### 4.2.2. Secondary reactions

They are mainly detected at reaction temperatures higher than 473 K under helium or dihydrogen. Their nature does not strongly depend upon the metal oxide used but their amount increases in the following order:  $\text{TiO}_2 < \text{ZrO}_2 < \text{CeO}_2$ . They can be classified into four families.

4.2.2.1. *Isopropyl-ether*. It is formed by an intermolecular dehydration (Fig. 10).



The aldol, by contrast to mesityl oxide (OM) and isobutyl methyl ketone (BMC) has never been detected in the conditions used.

## 5. Conclusion

In this study: (i) use of three metal oxides  $\text{TiO}_2$ ,  $\text{ZrO}_2$  and  $\text{CeO}_2$  with different acid–base and redox surface properties, (ii) variation of reaction temperature and (iii) changes of gas flow allow use to determine the formation pathways of propene, acetone and secondary products from propan-2-ol. If as expected, propene formation generally involves Brønsted and Lewis acid sites, results obtained on ceria in dihydrogen rather suggest, in such conditions, a mechanism involving redox properties. As for acetone, its amount in He or  $\text{H}_2$  decreases in the following order  $\text{TiO}_2 < \text{ZrO}_2 < \text{CeO}_2$  which can be explained implying either basic or redox surface properties. In air, oxidation reactions can occur, acetone being a possible intermediate in propan-2-ol total oxidation. Such an oxidation reaction is probable on ceria, showing the role played by its oxidising properties. Moreover, in helium or dihydrogen, a part of propene formed can reduce the surface of the metal oxide, leading also to acetone; this reaction, which requires a high oxygen mobility, can also occur on ceria.

It, therefore, appears that propene and acetone formation sites are not specific. It is difficult to deduce the surface properties of a given metal oxide from the amount of propene and/or acetone formed. The best conditions to check the expected results seem to be propan-2-ol transformation under air at relatively low temperature.

Many secondary products are formed when the reaction temperature increases. The formation of isopropyl-ether, mainly on  $\text{TiO}_2$ , and ketone compounds, mainly on  $\text{CeO}_2$ , involves the acid properties of anatase and the basic properties of ceria. When acetone is the main product formed, a relatively large amount of  $\text{C}_6$ -alkenes and  $\text{C}_6$ -dienes are detected under helium and dihydrogen. Their formation is explained involving mainly redox properties of ceria.

It, therefore, appears that it is difficult to consider unambiguously propan-2-ol dehydration or dehydrogenation as a test of acid–base properties of metal oxides. This confirms a previous study devoted to a

comparison of results obtained on several metal oxides using either propan-2-ol and methylbutynol decomposition as test reactions [50]. In our opinion one of the best examples that propan-2-ol dehydrogenation is not specific to metal oxide basicity is relative to  $\text{Cr}_2\text{O}_3$ , an acidic oxide [45] which gives acetone at low temperature [16].

## References

- [1] A. Gervasini, J. Fenyvesi, A. Auroux, *Catal. Lett.* 43 (1997) 219.
- [2] H. Noller, G. Ritter, *J. Chem. Soc., Faraday Trans.* 80 (1984) 275.
- [3] K. Tanabe, M. Misono, Y. Ono, H. Hattori, in: B. Delmon, J.T. Yates (Eds.), *New Solid Acids and Bases*, B, 51B, Elsevier, Amsterdam, 1989, p. 21.
- [4] M.A. Aremendía, V. Boráu, I.M. Garcia, C. Jiménez, A. Marinas, J.M. Marinas, A. Porras, F.J. Urbano, *Appl. Catal. A* 184 (1999) 115.
- [5] M.I. Zaki, G.A.M. Hussein, H.A. El-Ammawy, S.A.A. Mansour, J. Polz, H. Knözinger, *J. Mol. Catal.* 57 (1990) 367.
- [6] R.M. Gabr, M.M. Girgis, A.M. Awad, *Mater. Chem. Phys.* 28 (1991) 413.
- [7] M. Bowker, R.W. Petts, K.C. Waugh, *J. Catal.* 99 (1986) 53.
- [8] D.V. Fikis, W.J. Murphy, R.A. Ross, *Can. J. Chem.* 56 (1978) 2530.
- [9] G. Busca, *Phys. Chem. Chem. Phys.* 1 (1999) 723.
- [10] D. Martin, D. Duprez, *J. Phys. Chem.* 100 (1996) 9429.
- [11] Y. Zhang, S. Andersson, M. Muhammed, *Appl. Catal. B* 6 (1995) 325.
- [12] D. Haffad, U. Kameswari, M.M. Bettahar, A. Chambellan, J.C. Lavalley, *J. Catal.* 172 (1997) 85.
- [13] A. Badri, C. Binet, J.C. Lavalley, *J. Chem. Soc., Faraday Trans.* 93 (1997) 1159.
- [14] C. Binet, M. Daturi, J.C. Lavalley, *Catal. Today* 50 (1999) 207.
- [15] C. Lahousse, A. Aboulayt, F. Maugé, J. Bachelier, J.C. Lavalley, *J. Mol. Catal.* 84 (1993) 283.
- [16] A. Gervasini, A. Auroux, *J. Catal.* 131 (1991) 190.
- [17] D.W. Smith, *J. Chem. Educ.* 64 (1987) 480.
- [18] C. Morterra, *J. Chem. Soc., Faraday Trans.* 84 (5) (1988) 1617.
- [19] J.C. Lavalley, *Catal. Today* 27 (1996) 377.
- [20] J.P. Jolivet, *De la solution à l'oxyde*, Inter-editions/CNRS Editions, Paris, 1994.
- [21] A. Aboulayt, Thesis, El Jadida University, Morocco, 1998.
- [22] D. Martin, D. Duprez, *J. Mol. Catal. A* 118 (1997) 1131.
- [23] J. Emsley, *Les éléments chimiques*, polytechnica, The Elements, Oxford University Press, Oxford, 1992.
- [24] M. Bernard, F. Busnot, *Usuel de Chimie Générale et Minérale*, Dunod, Paris, 1996.
- [25] M. Pourbaix, *Atlas des Equilibres Electrochimiques*, Gauthiers-Villard, Paris, 1963.

- [26] O. Toft Sørensen, *Non-stoichiometric Oxides*, Academic Press, New York, 1981.
- [27] J.M. Herrmann, *J. Catal.* 118 (1989) 52.
- [28] D. Haffad, Thesis, Caen University, France, 1997.
- [29] J.M. Herrmann, *Appl. Catal.* 53 (1989) 117.
- [30] G. Busca, H. Saussey, O. Saur, J.C. Lavalley, V. Lorenzelli, *Appl. Catal.* 14 (1985) 245.
- [31] K.I. Hadjiivanov, D.G. Klissurski, *Chem. Soc. Rev.* 25 (1996) 61.
- [32] C. Binet, A. Jadi, J.C. Lavalley, *J. Chim. Phys.* 89 (1992) 1441.
- [33] H. Liu, L. Feng, X. Zhang, Q. Xue, *J. Phys. Chem.* 99 (1995) 332.
- [34] C. Li, K. Domen, K.-I. Maruya, T. Onishi, *J. Am. Chem. Soc.* 111 (1989) 7683.
- [35] M. Shionati, G. Moro, J.H. Freed, *J. Chem. Phys.* 18 (1988) 435.
- [36] M. Daturi, C. Binet, S. Bernal, J.A. Pérez Omil, J.C. Lavalley, *J. Chem. Soc., Faraday Trans.* 94 (8) (1998) 1143.
- [37] G. Busca, P. Forzatti, J.C. Lavalley, E. Tronconi, *Stud. Surf. Sci. Catal.* 20 (1988) 15.
- [38] M. Bensitel, V. Moravek, J. Lamotte, O. Saur, J.C. Lavalley, *Spectrochim. Acta* 43A (1987) 1487.
- [39] M.I. Zaki, N. Sheppard, *J. Catal.* 80 (1983) 114.
- [40] G.A.M. Hussein, N. Sheppard, M.I. Zaki, R.B. Fahim, *J. Chem. Soc., Faraday Trans.* 85 (7) (1989) 1723.
- [41] A. Jadi, Thesis, Caen University, France, 1990.
- [42] C. Binet, A. Badri, M. Boutonnet-Kizling, J.C. Lavalley, *J. Chem. Soc., Faraday Trans.* 90 (7) (1994) 1023.
- [43] C. Binet, A. Jadi, J.C. Lavalley, *J. Chim. Phys.* 89 (1992) 31.
- [44] E.J. Grootendorst, Y. Verbeek, V. Ponoc, *J. Catal.* 157 (1995) 706.
- [45] A. Auroux, A. Gervasini, *J. Phys. Chem.* 94 (1990) 6371.
- [46] A. Trovarelli, *Catal. Rev.* 38 (4) (1996) 439.
- [47] I. Aso, M. Nakao, N. Yamazoe, T. Seiyama, *J. Catal.* 57 (1979) 287.
- [48] R. Sreekumar, C.N. Pillai, *Catal. Lett.* 19 (1993) 281.
- [49] H. Idriss, K. Pierce, M.A. Barteau, *J. Am. Chem. Soc.* 113 (1991) 715.
- [50] C. Lahousse, J. Bachelier, J.C. Lavalley, H. Lauron-Pernot, A.M. Le Govic, *J. Mol. Catal.* 87 (1994) 329.