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The stoichiometry of hydrogen reduced zirconia and its influence on catalytic activity

Part 1: Volumetric and conductivity studies

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There is still little known about the origin, quantity and reactivity of defect species in reduced zirconia. Reduction of zirconia with flowing dry hydrogen leads to the adsorption of hydrogen and to the formation of oxygen vacancies. The number of vacancies increases with increasing treatment temperature, with increasing hydrogen flow rate and with increasing treatment time. The presence of water vapour in the reducing hydrogen causes the number of oxygen vacancies to decrease, presumably due to an equilibrium shift according to the equation: $Zr^{4+} + O^{2-} + H_2 \rightarrow H_2O + V_O + Zr^{3+} + e^-$. The oxygen uptake of the reduced zirconia occurs in two steps, resulting in a low temperature peak (LTP) at about 500 K and in a high temperature peak (HTP) at about 773 K in the temperature-programmed oxidation (TPO). At reduction below 800 K the oxygen vacancies represented by the LTP are most likely located on the zirconia surface; their increase with temperature corresponds to a reaction energy of 20 kJ mol^{-1} for the reaction given above. When zirconia is reduced above 823 K the effect of temperature increases, characterized by an activation energy of about 120 kJ mol^{-1}. Because of the high activation energy the corresponding vacancies are, most likely, located in the bulk of zirconia. Parallel to the formation of vacancies the electric conductivity increases proving that the electrons formed are most likely delocalized in the conduction band of the bulk phase. The oxygen vacancies corresponding to the HTP probably represent defects caused by the iron content of the zirconia. These vacancies are created at lower temperatures but need stronger conditions for reoxidation. Furthermore, the degree of reduction influences the catalytic activity for the hydrodeoxygenation of propan-2-ol.

1. Introduction

In recent years zirconia and particular yttria stabilized zirconia (YSZ) have gained tremendous technological and scientific interest. ZrO_2 is an oxygen-ion conductor[1] and is therefore used in oxygen sensors,[2,3] oxygen pumps and as an electrolyte in fuel cells.[4] There is much interest in the contribution of pure zirconia and its redox properties. The reduction of pure zirconia to Magneli phases similar to those of titania should further facilitate the use of zirconia as electrodes in electrochemical systems.[5]

Zirconia is also an important material in heterogeneous catalysis.[6] The use of zirconia as a sulfate, as a phosphate, as sulfated zirconia, and as constituent in mixed oxides in catalysts has been intensively discussed.[7–10] Active sites on the surface of such species are probably electronic or structural defects which lower the bonding strength of adsorbed molecules and favour subsequent reactions. Because of structural and chemical properties similar to titania it may behave like titania when it is used as a support for noble metal catalysts. Particularly it should induce "strong metal support interactions" (SMSI effects), *i.e.* the suppression of hydrocarbon skeleton reactions and decreased adsorption capacity for hydrogen and carbon monoxide, but also C–O bond activation as observed in titania-supported metal catalysts.[11] Currently there is also much interest in the oxygen storage capacity (OSC) of zirconia and its influence on catalysis.[12]

Zirconia is well known as a stable oxide which tends to lose surface oxygen only after thermal treatment under high vacuum above 973 K.[13,14] Other oxides show the presence of O_2^- species on the surface (CaO, ZnO, Cr_2O_3, TiO_2)[1,15–18] or the presence of superoxides (CeO_2)[19] after treatment in reducing atmospheres and after thermal treatment *in vacuo* followed by exposure to oxygen. Formation of anion vacancies due to ceria or yttria dopants has been discussed in several papers.[10,20–23] Some FTIR studies on chemisorption of CO and H_2/O_2 were done on pure zirconia[13,14,24,25] and some theoretical studies proved the presence of reduced defect sites (anion vacancies)[26,27] but failed to discuss their origin and reactivity in detail. There is also little known about the conditions of their formation and about their quantities.

Thus the aim of this work was to study the formation of anion vacancies under varying conditions and their influence on the electrical and catalytic properties. This was done with volumetric oxygen titration, with temperature controlled oxidation, and with measurements of the electric conductivity and of the catalytic activity for the hydrodeoyxgenation of propan-2-ol.

2. Experimental

Materials

The zirconium(IV) oxide used in this work was prepared by low-temperature drying of a solution of zirconia aquat (a suspension of 20% ZrO_2 in water, 0.1 μm particle size, supplied by Alfa Aesar). Before use the zirconia was calcined in air at different temperatures, which was accompanied with sintering, leading to systematically controlled surface area. In addition to pure zirconia, yttria stabilized zirconia (1.3 wt.%), supplied by Alfa Aesar (prepared by its aquat as described above) was used for comparison in the conductivity measurements.

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The composition of the zirconia was controlled by X-ray absorption spectroscopy, revealing a major contamination by hafnium and minor impurities of Ca and Fe, their content being roughly below 200 ppm. The contents of iron and hafnium were determined more accurately by ICP-OES (inductively coupled plasma–optical emission spectroscopy) amounting 1.09 wt.% of hafnium and 168 ppm of iron. This proportion of hafnium is typical for zirconia prepared from natural sources without extensive separation of hafnium.

The surface area of the samples was determined by adsorption of nitrogen at 77 K according to BET. Structural changes due to thermal and vacuum treatment were investigated by X-ray diffraction (XRD) and Raman spectroscopy.

Hydrogen, helium and oxygen were highest grade gases supplied by Messer-Griesheim. Hydrogen was purified further by passing through an oxygen removing purifier, and helium was freed from traces of oxygen by an Anoxy-Cil unit. Condensable contaminants were removed from hydrogen and helium by liquid nitrogen traps, while oxygen was passed through a trap cooled with liquid nitrogen/ethanol.

Volumetric apparatus

Volumetric measurements were performed in an all-glass apparatus equipped with metal bellow valves (Witeg), a Baratron pressure transducer (MKS), and mass flow controllers (MKS). To ensure volumetric measurements at temperatures of 1073 K the reactor part of the apparatus containing the sample was made of quartz glass. The mass of the zirconia samples was rather high (about 10 g) in order to enhance the accuracy of the measurements.

To simulate the usual catalyst pretreatment in research laboratories, zirconia was treated in flowing dry hydrogen at a flow rate of typically 1 ml s^{-1}. To control the activity of oxygen, in some experiments the hydrogen was passed through a U-shaped tube whose bottom was covered by H_2O. The trap was cooled to 273 K to provide a controlled partial pressure of 6.1 mbar of water in the resulting gas stream.

After hydrogen treatment the sample was evacuated at 773 K by a diffusion pump (base pressure 5×10^{-7} mbar) to remove any adsorbed hydrogen and was afterwards cooled *in vacuo* down to the oxygen treatment temperature. The uptake of oxygen was measured volumetrically at 548 K in order to ensure a fast and quantitative reoxidation of zirconia to its stoichiometric state. Some reoxidation measurements were started at room temperature followed by a controlled increase of the temperature (TPO) to study the rate of the reoxidation processes.

Catalytic activity studies

All measurements of catalytic activity were carried out in an all-glass recirculation batch reactor described elsewhere.[28] The reaction mixture was analysed by gas chromatography using a capillary column (polydimethylsiloxan, 25 m length, 0.53 mm diameter, 5 μm film, operating temperature 343 K) and FID detection.

Conductivity apparatus

The conductivity of pelletised samples (6 mm diameter, using 30 to 150 mg, pressed with 8000 bar for 2 min) was measured using two gold electrodes in a vertical quartz tube (Fig. 1). The pellets were compressed (1 bar) by the upper electrode to ensure good electrical contacts. The apparatus was suited for gas treatments similar to those in the volumetric apparatus.

The temperature was controlled by a thermocouple (situated inside the reactor) and a PID temperature controller. The change in conductivity was measured during treatment with flowing oxygen and hydrogen.

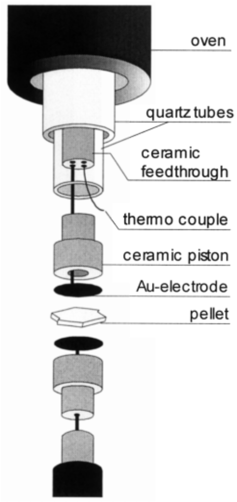

Fig. 1 Scheme of the reactor used for conductivity measurements.

3. Results and discussion

Effect of thermal treatment on the surface area of zirconia

The zirconia prepared from the aqueous solution has a monoclinic structure as confirmed by XRD spectra of the sample before and after use. Fig. 2 shows the XRD spectrum of the sintered sample and the position of diffraction peaks of monoclinic ZrO_2 reported in the literature.[29] In addition, the Raman spectrum of this sample (Fig. 3) shows the typical vibrations of monoclinic zirconia.[25]

The fresh sample (calcined at 673 K) exhibits a BET surface area of about 120 m^2 g^{-1} but starts to sinter at about 723 K. The specific surface area decreases continuously with increasing calcination temperature, leading to a final value of 13 m^2 g^{-1} after calcination at 1273 K (Fig. 4).

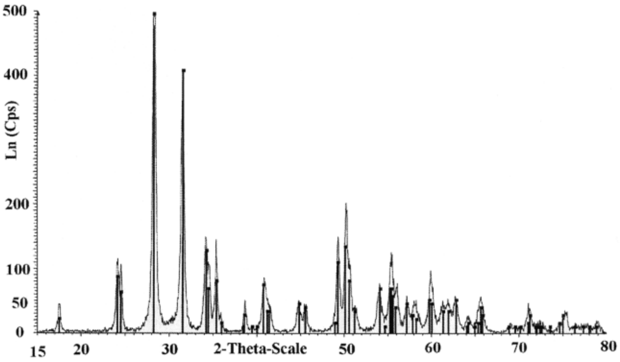

Fig. 2 XRD spectrum of zirconia sintered at 1273 K.

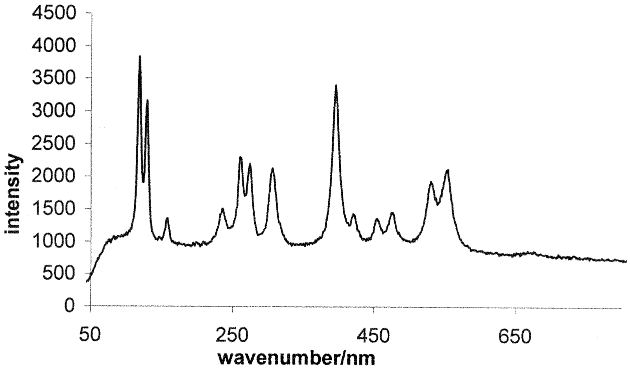

Fig. 3 Raman spectrum of the monoclinic zirconia sample.

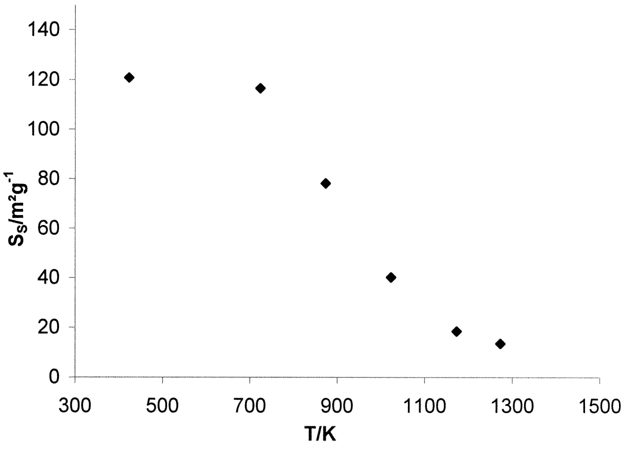

Fig. 4 Decrease of the specific surface area (BET) of zirconia with temperature.

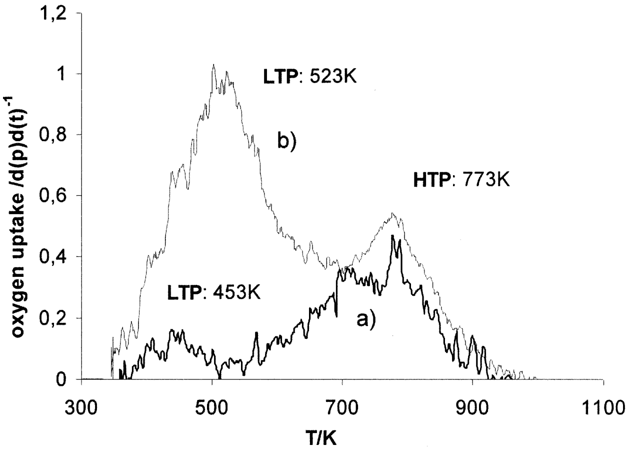

Fig. 5 Temperature-programmed oxidation (TPO) of zirconia after reduction in flowing hydrogen for 10 h at (a) 873 K and (b) 1023 K.

To avoid any changes in the surface during hydrogen treatments all further studies were carried out with zirconia that was calcined at 1273 K.

Hydrogen adsorption on zirconia

If zirconia is treated *in vacuo*, temperatures above 973 K are necessary to obtain measurable oxygen reuptake afterwards. On the other hand, in flowing hydrogen the zirconia starts to be reduced at temperatures above 473 K. Simultaneously with the reduction state the colour of the zirconia also changes, starting from white to slightly grey, its intensity increasing with increasing reduction temperature and reduction time. This colour change extends to the IR band as is documented by a simultaneous loss of IR transmittance.

Temperature-programmed desorption (TPD) experiments, carried out after hydrogen treatment followed by evacuation at room temperature, result in hydrogen desorption peaks at 773 K. The colour of the sample does not change during the hydrogen desorption. The amount of the desorbed hydrogen is only about 10% of the hydrogen corresponding to the formation of oxygen vacancies. Most likely, this hydrogen is stored in OH groups formed at the zirconia surface which decompose at 773 K.

To measure the number of oxygen vacancies the adsorbed hydrogen was removed by TPD or by evacuation at 773 K prior to the titration of the oxygen vacancies.

Oxygen reuptake after hydrogen treatment

(a) Temperature-programmed oxidation (TPO). When oxygen was admitted to the reduced zirconia at room temperature no significant amounts of oxygen were taken up, but in the temperature range up to 1000 K the oxygen uptake increases continuously with increasing oxygen treatment temperature. Thus, the reoxidation is obviously an activated process and, because of the wide temperature range of reuptake, it may occur in several steps. To study the reoxidation kinetics, the reduced samples were reoxidized by TPO.

After the hydrogen treatment oxygen was admitted at room temperature and the oxygen uptake was measured while the temperature was raised linearly to 1073 K (heating rate of 5 K min^{-1}), resulting in two uptake peaks, the first one appearing between 453 and 523 K (low temperature peak, LTP) and the second one appearing between 753 and 793 K (high temperature peak, HTP). Fig. 5 shows the TPO profiles obtained after a 10 h hydrogen treatment at 873 K (a) and at 1023 K (b).

Apparently, the reduced zirconia consumes oxygen in two steps, the temperature of the oxygen uptake depending either on the thermodynamics of reoxidation or on kinetic hindrances to the oxygen uptake process.

(b) Influence of reduction time. To study the reduction kinetics the zirconia was treated in a hydrogen flow of 1 ml s^{-1} for different reduction times. Oxygen uptake was measured and split up into its contribution to the low temperature peak and to the high temperature peak. Hydrogen treatment at 873 K results in an increase of the low temperature peak during the first 3 h. After that time no further vacancies corresponding to the LTP peak are formed resulting in an oxygen reuptake corresponding to a concentration of oxygen vacancies of about 0.7 μmol g^{-1}. At this point, it should be stressed that each μmol of oxygen vacancies needs only 0.5 μmol of gaseous oxygen.

Surprisingly, the high temperature peak is saturated after about one hour, corresponding to about 3.5 μmol g^{-1} oxygen vacancies. Obviously, vacancies corresponding to the high temperature peak are formed more readily than those corresponding to the low temperature peak (Fig. 6).

Reduction at 1023 K leads to a much higher LTP peak, the saturation of this peak requiring a much longer time. After 20 h of treatment the LTP peaks levels off to a nearly constant value corresponding to 11 μmol g^{-1} oxygen vacancies. On the other hand, the effect of reduction time on the HTP is nearly the same as after reduction at 873 K, leading to a rather

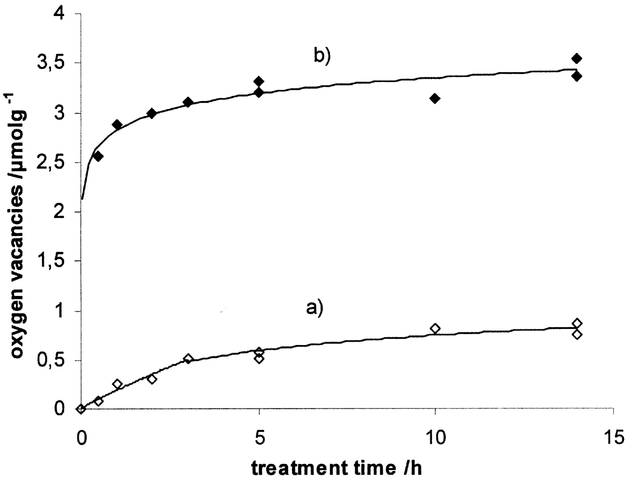

Fig. 6 Influence of reduction time on the formation of oxygen vacancies. Hydrogen treatment at 873 K, oxygen uptake corresponding to (a) LTP and (b) HTP.

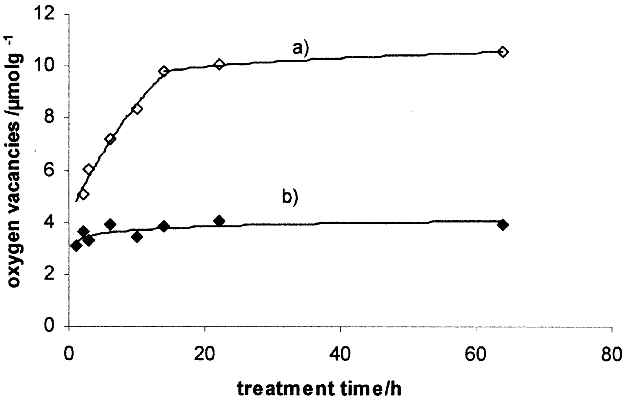

Fig. 7 Influence of reduction time on the formation of oxygen vacancies. Hydrogen treatment at 1023 K, oxygen uptake corresponding to (a) LTP and (b) HTP.

fast saturation of about 4 µmol g^{-1} oxygen vacancies after a treatment time of 1 h (Fig. 7).

Hydrogen treatments with systematically varied flow rates at a fixed treatment time showed that the number of oxygen vacancies (causing the LTP peak) increases with increasing hydrogen flow rate.

(c) Influence of the reduction temperature. To study the effect of the reduction temperature a constant reduction time of 3 h was applied. The hydrogen flow rate was adjusted to 1 ml s^{-1}. The treatment time was chosen because at most treatment temperatures the reduction degree of the zirconia has reached saturation after this time, and, for operational reasons, to keep the time of the experiments within reasonable limits. Note that for the highest reduction temperature the LTP peak has not yet reached saturation after 3 h.

Fig. 8 shows the number of oxygen vacancies in zirconia, hydrogen treated for 3 h, as a function of reduction temperature for the LTP peak and the HTP peak. The LTP peak increases nearly exponentially with increasing reduction temperature, while the number of oxygen vacancies corresponding to the HTP peak is nearly independent of reduction temperature, resulting in about 3.5 µmol of oxygen vacancies per gram.

As is seen in Fig. 8, the formation of oxygen vacancies due to the low temperature peak depends only slightly on the temperature below 800 K, while after treatment above this temperature the corresponding peak area is strongly affected by the temperature. On the other hand, the vacancies due to the high temperature peak show nearly no dependence on treatment temperature.

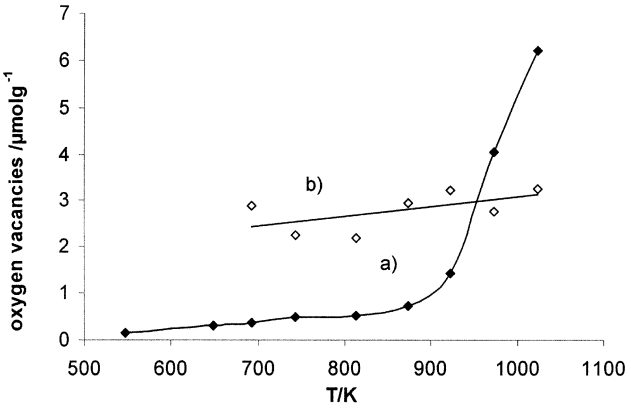

Fig. 8 Influence of hydrogen treatment temperature (3 h treatment) on the number of oxygen vacancies corresponding to (a) LTP and (b) HTP.

(d) Treatment in wet hydrogen. In some experiments, zirconia was treated in hydrogen to which water vapour was added, the partial pressure being fixed at 6.1 mbar, as described above. After a 15 h treatment in wet hydrogen the number of oxygen vacancies formed was smaller by a factor of about 10 compared to zirconia treated in dry hydrogen (Table 1).

(e) Nature of oxygen vacancies. Surprisingly, the oxygen vacancies corresponding to the HTP are hardly affected by the temperature. Their formation at 873 K is accomplished after a short time period (Fig. 6), but they need a high temperature for reoxidation. Their number seems to be limited to 3.5 µmol g^{-1}. As these vacancies are easily formed, but need strong oxidizing conditions for reoxidation, it is assumed that these sites are due to the presence of iron in the zirconia. The content of 186 ppm is equivalent to 3.3 µmol g^{-1}, which is nearly that of the oxygen vacancies saturated in the HTP-peak. The increase of these vacancies with time may be fictitious because of some overlap with the LTP peak which increases strongly with reduction temperature.

The low temperature peak exhibits a small influence of temperature below 800 K. The effect of treatment time on the number of oxygen vacancies shows that at the lower temperatures the reduction reaches a rather stationary value after a short time. The fact that fewer oxygen vacancies are formed in a wet hydrogen treatment compared to reduction in dry hydrogen indicates a thermodynamic control of these vacancies. Furthermore, treatment with a higher flow rate of dry hydrogen causes an increased formation of vacancies. Thus it is proposed that the following equation controls the formation of vacancies.

$$M^{4+} + O^{2-} + H_2 \rightarrow H_2O + V_O + M^{3+} + e^-.$$

During hydrogen treatment water vapour is formed, its pressure being controlled by the number of vacancies, by the hydrogen pressure, and by the temperature. The rate of the formation of oxygen vacancies is then controlled by the removal of water in the hydrogen flow and thus proportional to the equilibrium water vapour pressure. At a given treatment temperature the equilibrium pressure decreases with increasing number of oxygen vacancies. Therefore, the rate of reduction becomes slower during the course of reaction and eventually comes to a halt when the equilibrium water pressure becomes negligible.

Fig. 9 shows a linear dependence of the logarithm of vacancies *versus* $1/T$. Assuming equilibrium is established, the enthalpy for the reaction above is calculated to be 20 kJ mol^{-1} according to van 't Hoff's law.

From the rate for attaining equilibrium we conclude that the oxygen that is removed during reduction is located at the zirconia surface and thus surface vacancies are most likely formed, at least below 800 K.

For titania, a mechanism for the formation of oxygen vacancies has been proposed,[30] which we assume to be applicable also for zirconia. It occurs *via* several steps: adsorption and dissociation of hydrogen, followed by the formation and desorption of water, as is shown in Fig. 10.

Table 1 Number of oxygen vacancies after treatment for 15 h in dry and in wet hydrogen

T/K	Vacancies/µmol g^{-1} (dry)	Vacancies/µmol g^{-1} (wet)
548	0.30	0.06
743	2.64	0.36
1023	9.32	1.06

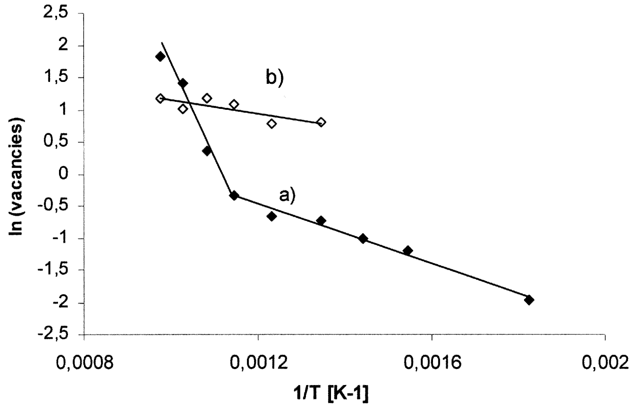

Fig. 9 Logarithmic plot of oxygen vacancies, corresponding to (a) the LTP peak and (b) the HTP peak *versus* $1/T$.

Above 800 K the number of vacancies is much more affected by the reduction temperature than below this temperature. As is seen in Fig. 7, the attainment of a stationary amount of vacancies requires more than 10 h. Evidently, in this temperature regime the equilibrium is no longer established.

Again, the plot of the logarithm of vacancies *versus* $1/T$ exhibits a linear dependence, but in this region of kinetic control an activation energy of about 120 kJ mol^{-1} can be calculated according to the Arrhenius equation. This high activation energy is most likely due to a transport process in the bulk and we assume that above 800 K the formation of bulk vacancies starts during hydrogen treatment.

Together with oxygen vacancy formation a metal ion is reduced from the oxidation state of +4 to +3. As the content of hafnium in the zirconia (1.09 wt.%, *i.e.* 61 μmol g^{-1}) is greater than the number of oxygen vacancies, both Zr^{4+} and Hf^{4+} are candidates to be reduced. To decide which ion is easier to reduce the oxidation potential[31] of the M^{3+} ion in vacuum may be used with the result that Hf^{3+} (30.75 eV) is more easily oxidized than Zr^{3+} (34.83 eV). In turn, Zr^{4+} is more easily reduced than Hf^{4+}. Furthermore, the ionic radius of Zr^{4+} (80 pm) increases to 93 pm upon reduction. Hf^{4+} with a radius of 91 pm may just fit in the ZrO_2 lattice, while the formation of Hf^{3+} (103 pm) may be impeded because of steric interactions.

Therefore we assume that Zr^{3+} ions and not Hf^{3+} ions are formed in the reduction of zirconia. The electron formed attains most likely to n-type sites in the zirconia which can contribute to the electric conductivity.

Catalytic activity of the hydrodeoxygenation of propan-2-ol — effect of pre-reduction

The hydrodeoxygenation of propan-2-ol to propane and water was used as a test reaction, since it does not produce any side products and the reactant contains a C–O bond, which is known to be effected by oxygen vacancies present in titania supported catalysts. For studies on catalytic activity a sample of about 2 g of zirconia was put into the recirculation batch reactor. After calcination in flowing oxygen for 2 h at 673 K, followed by evacuation and hydrogen treatment for 1 h at 673 K, a mixture of 10 mbar propan-2-ol and 990 mbar hydrogen was prepared, to which systematically controlled amounts of water (0, 5, 10 mbar) were added. This mixture was then admitted to the reactor, the reaction temperature was 473 K.

Zirconia exhibits a rather low catalytic activity (0.7 nmol g^{-1} s^{-1} at 473 K), compared to titania (14.6 nmol g^{-1} s^{-1} at 473 K).[11] As is seen in Fig. 11, the catalytic activity decreases with increasing water vapour pressure in the reaction mixture.

Water vapour quenches and thereby reduces the number of oxygen vacancies. Thus, as the rate of the catalytic reaction also decreases, we conclude that an oxygen vacancy on the zirconia surface contributes to the catalytic ensemble of the hydrodeoxygenation of propan-2-ol.

The reaction may proceed *via* a reverse Mars–van Krevelen mechanism,[32] occurring *via* (i) the adsorption of propan-2-ol on the surface vacancy, followed by (ii) the formation of propane by hydrogen, leaving the former oxygen vacancy saturated by oxygen and eventually (iii) the formation of a new vacancy by reaction with hydrogen.

Effect of hydrogen reduction on the electric conductivity of zirconia

When zirconia is treated in flowing oxygen the electrical conductivity starts to increase at an onset temperature of 740 K. The increase proceeds exponentially, as is seen from the linear plot of the logarithm of the conductivity *versus* $1/T$ (Fig. 12), which is typical for semiconductors. After the temperature is decreased the identical conductivity is measured, *i.e.* no hysteresis is found.

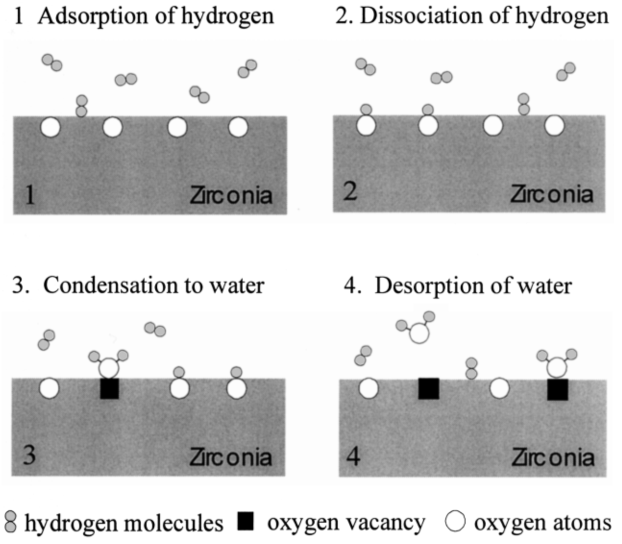

Fig. 10 Proposed mechanism for the formation of oxygen vacancies.

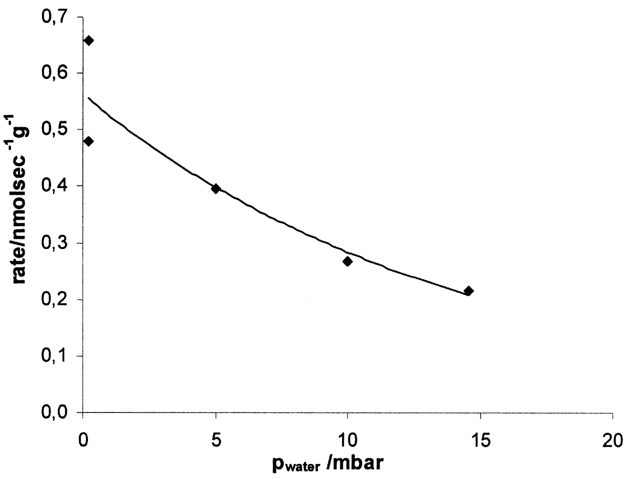

Fig. 11 Influence of water vapour pressure on the catalytic activity of zirconia for hydrodeoxygenation of propan-2-ol at 473 K after hydrogen treatment for 1 h at 673 K.

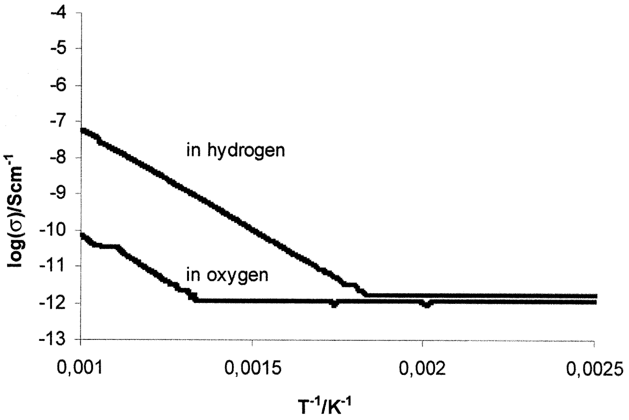

Fig. 12 Logarithm of the conductivity *versus* $1/T$ in flowing oxygen and hydrogen.

Treatment in flowing hydrogen leads to a similar effect of temperature on the electrical conductivity. Starting from nearly the same room temperature conductivity as measured on oxygen treated zirconia, the onset temperature of the increase in conductivity is 550 K, ending up in a 1000-fold conductivity compared to the oxygen treated zirconia. Again a linear semilogarithmic plot of conductivity *versus* $1/T$ is obtained with the same slope as obtained in the oxygen treatment. This temperature effect was fully reversible, *i.e.* no hysteresis loop is found upon cooling to room temperature.

Both the oxygen treated and the hydrogen treated zirconia show the same temperature effect on the conductivity. Thus it seems that for both treatments the conductivity proceeds *via* the same mechanism. Most likely n-type sites are responsible for the conduction mechanism. Such sites may be formed even in an oxygen atmosphere above 740 K.

In the hydrogen treated zirconia the number of n-type electrons is higher by a factor of 1000 as may be deduced from the increased conductivity, at least above 740 K. The conductivity increases with increasing temperature since at higher temperatures (i) more donor electrons reach the conduction band and (ii) the number of donor sites is enhanced. Thus the activation energy of conduction (120 kJ mol^{-1}) is composed of the energy necessary to promote the donor electrons to the conduction band and of the formation energy of the vacancies. The conductivity measurements were performed in a temperature-programmed mode, *i.e.* in the short treatment times presumably only oxygen vacancies located at the surface are formed. The heat of formation of these sites is about 20 kJ mol^{-1}, as given above. Thus the energy level of the donor sites in zirconia is about 100 kJ mol^{-1} below the conduction band, *i.e.* roughly 1 eV.

4. Conclusions

After hydrogen treatment small amounts of hydrogen remain chemisorbed on zirconia, as is seen from a small thermo-desorption peak at 773 K. When, after hydrogen desorption, the sample is treated in oxygen in a temperature-programmed mode, oxygen uptake is observed at two different temperatures. The oxygen uptake at the lower temperature (LTP, at 500 K) most likely saturates surface oxygen vacancies; if the zirconia was previously reduced below 823 K, the energy of formation of these vacancies is 20 kJ mol^{-1}. Reduction above 823 K leads to the formation of bulk oxygen vacancies, which needs an activation energy of 120 kJ mol^{-1}. The oxygen uptake at the higher temperature (HTP, at 773 K) is presumably due to reoxidation of reduced iron ions present in zirconia as contaminants.

The number of surface oxygen vacancies increases with increasing reduction temperature, increasing reduction time, increasing hydrogen flow rate, and decreasing water vapour pressure. Thus, most likely it is controlled by the equilibrium

$$Zr^{4+} + O^{2-} + H_2 \Leftrightarrow H_2O + V_O + Zr^{3+} + e^-$$

The electrons occupy donor sites whose energy is about 1 eV below the conduction band, giving rise to an increased electrical conductivity. As is typical for a semiconductor, the conductivity starts to rise at about 743 K in flowing oxygen and at 553 K in flowing hydrogen, resulting in a 1000-fold higher conductivity for the hydrogen treated sample. The activation energy for conductivity is nearly the same for both treatments (120 kJ mol^{-1}).

Zirconia shows a rather low catalytic activity for the hydrodeoxygenation of propan-2-ol at a reaction temperature of 200 °C. When water vapour is added to the reaction mixture the surface oxygen vacancies are quenched and the catalytic activity becomes even smaller. Thus, it is assumed that surface oxygen vacancies contribute to the catalytic ensemble of this reaction.

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