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An Infrared Spectroscopic Study of the Adsorption and Mechanism of Surface Reactions of 2-Propanol on Ceria

MOHAMED I. ZAKI[1] AND NORMAN SHEPPARD

School of Chemical Sciences, University of East Anglia, Norwich, England

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An infrared spectroscopic study was made of the adsorbed species and the gas-phase products from the dehydrogenation and dehydration reactions of 2-propanol over CeO_2 catalysts calcined at different temperatures. The adsorbed species observed included hydrogen-bonded alcohol molecules, alcoholate ions, and carboxylate ions. The dehydrogenation reaction to form acetone was followed by a transformation of this product to give isobutene and methane. The dehydration reaction gave propene as the sole product. Mechanisms for the various surface reactions are proposed which are consistent with the infrared results.

INTRODUCTION

The extensive published work on absorption, dehydration, and dehydrogenation of alcohols on oxides of transition metals (*1*), Al_2O_3 (*2*), SiO_2 (*3*), and ZnO (*4*) has made good use of ir spectroscopic methods to improve the understanding of the mechanistic aspects of the surface reactions over these and other oxides (*5–8*).

For example, Hertl and Cuenca (*7*) reported that at 150°C the adsorption of primary alcohols on Al_2O_3 (the oxide which has received most attention from ir spectroscopists) led initially to the formation of surface alkoxyl species, but at higher temperatures, in the presence of alcohol or air, these reacted further to produce carboxyl-related species. In a similar study using secondary alcohols, Deo *et al.* (*5*) reported that hydrogen-bonded adsorbed alcohol molecules were observed, in addition to alkoxyl species. Carboxyl-related species were also identified, in agreement with the results of Hertl and Cuenca (*7*), but a different mechanism was proposed for their formation, which is discussed later.

The present work describes the ir absorption spectroscopic results for the adsorption and surface reactions of 2-propanol on ceria, a lanthanide oxide which has so far been little used as a catalyst. However, its *n*-semiconductive behaviour (*9*), high structural and thermal stabilities (*10*), and its recently reported catalytic activity towards the decomposition of alcohols (*11*) suggested that ceria would be a very worthwhile material for further study. Furthermore, preliminary ir experiments showed that the blackout lattice absorption of ceria in the form of a thin pressed disc commences at a frequency as low as 800 cm^{-1}. Unlike the situation with lighter-element oxides (*2, 3*), this means that much of the fingerprint region of the ir spectra of organic adsorbates will be readily observable.

EXPERIMENTAL

Ceria catalysts used in this study were prepared by the thermal decomposition of ammonium ceric nitrate (*10*) (BDH-AR, $(NH_4)_2[Ce(NO_3)_6]$) in air for 5 hr at different temperatures between 400 and 1000°C.

The results of thermogravimetric analyses, obtained using a Shimadzu TGA-30H automatically recording thermobalance, proved that complete decomposition of the parent salt had occurred at 350°C. X-Ray powder diffraction patterns for the different calcination products of the catalyst, ob-

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[1] Present address: Chemistry Department, Faculty of Science, Minia University, El-Minia, Egypt.

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tained using a Philips diffractometer (type PW 1010) provided with a source of Cu*Kα* radiation (Ni-filtered), have shown good agreement with the ASTM card (No. 4-0.593) (*12*) for crystalline CeO_2.

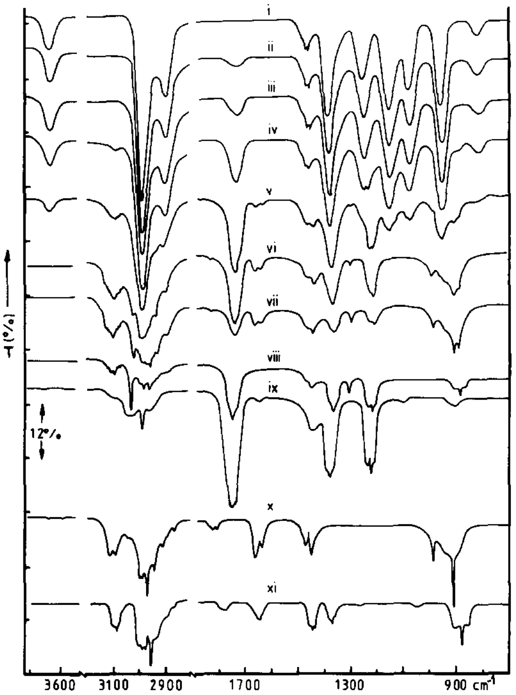


FIG. 1. Infrared spectra of 10 Torr of gas-phase 2-propanol in contact (for 10 min) with ceria (calcined at 400°C) at room temperature (i), 150 (ii), 200 (iii), 250 (iv), 300 (v), 350 (vi), or 400°C (vii). Acetone in contact with the catalyst at 400°C (viii). Reference spectra of 10 Torr of the gas-phase constituents; acetone (ix), propene (x), isobutene (xi) at room temperature are given for comparison with the product spectra.

All of the organic materials used in this work were of spectroscopic grade (BDH) and were degassed by freezing and thawing under vacuum.

A 200-mg sample of the catalyst was used to prepare a thin porous disc, of an adequate transmission over the frequency range from 4000 to 800 cm^{-1}, by pressing the fine powder at 2 tons in.$^{-2}$ The catalyst disc was then placed in an evacuable infrared cell of Pyrex glass with KBr windows which had a form very similar to the model described by Peri and Hannan (*13*). The infrared spectra were obtained using a Digilab FTS-14 Fourier transform infrared spectrometer at a resolution of 4 cm^{-1}. Gas-phase spectra were obtained by lifting the catalyst disc and holder out of the infrared beam.

After recording the catalyst background spectrum (*in vacuo*) at room temperature, the reactant vapour was introduced to a pressure of 10 Torr. The cell was then heated to various temperatures and/or pumped off. Depending on the sequence of experiments being performed, various combinations of heating and/or degassing cycles were performed.

To evaluate the extent of reaction and the chemical nature of the components of the reaction mixture, the gas phase was also analysed by infrared.

RESULTS

Infrared Spectra of Gas Phases

Figure 1(i) shows the gas-phase infrared spectrum from a 10-Torr dose of 2-propanol in contact at room temperature with a ceria catalyst that had been calcined at 400°C. The alcohol-dominant vapour phase at room temperature became modified in composition by heating. Figures 1(ii)–(vii) show gaseous spectra obtained over the catalyst after consecutive 10-min heating periods at the temperatures indicated between room temperature and 400°C. The spectra were measured after cooling the system once again to room temperature. These gas-phase spectra provided very effective qualitative, and semiquantitative, analysis of the gas mixtures. In addition to the expected products of acetone (from dehydrogenation) and propene (from dehydration of the alcohol), they showed the presence of two other gas-phase species, viz., methane and isobutene. For comparison the spectra of the pure components of the gas mixtures are shown in Fig. 1. The most suitable absorptions for monitoring growth or decay of the different components, chosen because of their freedom from interference from the spectra of others, were as follows: 2-pro-

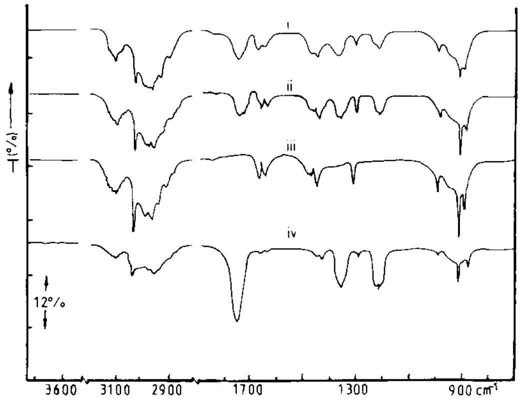


FIG. 2. Infrared spectra of 10 Torr gas-phase 2-propanol in contact (for 10 min) at 400°C with ceria calcined at 400 (i), 600 (ii), 800 (iii), or 1000°C (iv).

panol, 3660 and 1080 cm^{-1}; acetone, 1740 cm^{-1}; propene, 1650 (doublet) and 915 cm^{-1}; methane, 1310 cm^{-1} (another prominent band occurs at 3010 cm^{-1}); and isobutene, 890 cm^{-1}.

The gas-phase spectra show that acetone first appears as a product at 150°C and is present up to 400°C. It reaches its maximum concentration at 300°C and afterwards diminishes. Propene appears at ca. 250°C and remains a major product at 400°C. Methane and isobutene also first appear at 250°C and grow in concentration up to 400°C. A subsequent experiment in which acetone alone was heated over the catalyst at 400°C showed that it was some further reaction of this primary product that led to the formation of methane and isobutene.

Figure 2 compares the gas-phase spectra obtained after heating a 10-Torr dose of 2-propanol for 10 min at 400°C over ceria catalysts that had been calcined at the different temperatures of 400, 600, 800, and 1000°C. In all cases the original 2-propanol had been completely transformed. Compared with that calcined at 400°C, the 600°C sample showed some additional formation of methane and isobutene at the expense of acetone. That calcined at 800°C showed complete transformation of acetone to these products. Surprisingly, the catalyst calcined at 1000°C showed a much greater retention of acetone in the gas phase as well as the presence of less propene than occurred over that calcined at 800°C.

Infrared Spectra of Adsorbed Species

(*A*) *Adsorption of 2-propanol at room temperature, 150, 250, and 350° on* CeO_2 *calcined at 400°C.* Figure 3 shows the spectra between 4000 and 800 cm^{-1} of the surface species resulting from the adsorption of 2-propanol on a CeO_2 sample that had been calcined at 400°C. The spectra were taken after adsorption at four different temperatures from room temperature up to 350°C, followed by cooling to room temperature. In addition, a spectrum from acetone adsorbed at 150°C is inset. Ceria itself shows strong lattice absorption below 800 cm^{-1}. Its base-line spectrum also shows absorptions from OH stretching vibrations associated with the oxide in the 3700- to 3300-cm^{-1} regions; in particular, two high-wavenumber νOH bands at 3680 and 3610 cm^{-1} on the bare surface clearly arise from chemically bound OH groups that are relatively free of hydrogen bonding.

The spectra obtained after adsorption of 2-propanol at room temperature, 150, 250, and 350°C have many features in common amongst themselves and with the spectrum of the liquid 2-propanol (*14*). In particular, the characteristic pattern of absorptions in the νCH stretching region (2968, 2930, and 2868 cm^{-1}), together with broad and strong composite absorptions near 1135 and between 1000 and 925 cm^{-1} in the C–O stretching/CH_3 rocking region, clearly show the presence of a considerable number of $(CH_3)_2CH–O–$ groups. At least two species containing this group are present, as indicated by the spectral changes with temperature in the 1000- to 925-cm^{-1} region. Comparison with the general infrared spectrum of cerium isopropoxide (*15*) shows that, as has been postulated for the adsorption of alcohols on other oxide surfaces (*5*, *6*), an isopropoxide ion is likely to

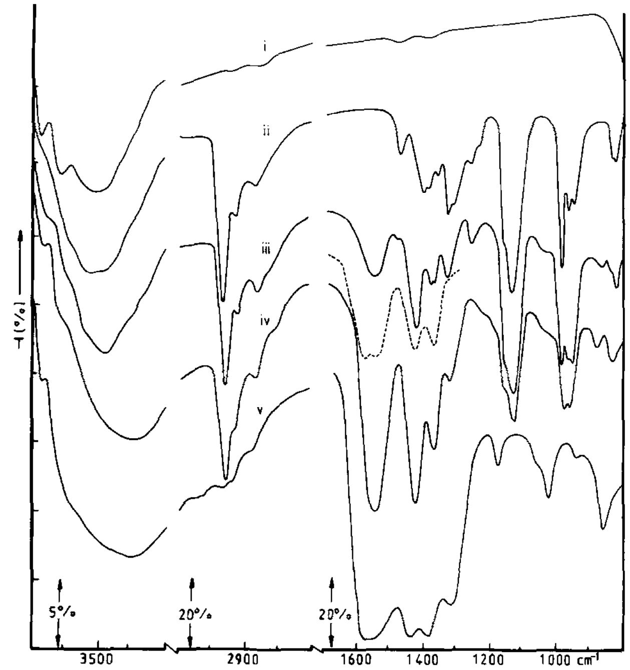


FIG. 3. Infrared spectra of 2-propanol adsorbed on ceria calcined at 400°C at room temperature (ii), 150 (iii), 250 (iv), or 350°C (v). (i) The background CeO_2 spectrum prior to adsorption and after pumping (10^{-5} Torr) at 100°C for 2 hr. Spectrum (1700–1300 cm^{-1}) of acetone adsorbed on the catalyst at 150°C (broken line).

be one of these. It seems probable that the absorption doublet at 963 and 925 cm^{-1} is to be associated with surface isopropoxide ions, whereas the 985-cm^{-1} band, strongest at room temperature, originates from intact 2-propanol molecules hydrogen-bonded to the surface. The OH absorptions of ceria at 3680 and 3610 cm^{-1}, mentioned earlier and considered to be due to surface OH groups free of hydrogen bonding, are absent in the room-temperature spectrum but the former is somewhat restored in the spectra after adsorption at 150 and 250°C. These changes are consistent with the desorption of 2-propanol molecules with increasing temperature. These doubtless contribute δOH absorptions to the spectra in the 1350- to 1250-cm^{-1} region (*16*a), particularly at room temperature.

Additional absorptions at 1550 and 1425 cm^{-1} appear in the spectrum after adsorption of the alcohol at 150°C; at higher temperatures these became enhanced in intensity, and move to ca. 1580 and 1440 cm^{-1}, while a third band at 1375 cm^{-1} emerges alongside them. For adsorption at 350°C the species giving rise to these bands is dominant in the spectrum and no alkoxide-type species remain. By analogy with earlier studies of the oxidation products of alcohols on oxides, these three absorptions can be assigned to a carboxylate surface species (*5*, *6*, *17–19*). On chemical grounds the most probable such species is the acetate ion and Davydov *et al.* (*6*) have assigned bands at 1570, 1440, 1390, and 1060 cm^{-1}, with similar relative intensities, to an oxidised species (presumably the acetate) from ethanol on Cr_2O_3. The general weakness of the νCH stretching absorption region is also consistent with the presence of a CH_3 group adjacent to a carbonyl-derived group (*16*b), such as COO^-. Only weak absorptions at 1170 and 860 cm^{-1} in the spectrum obtained after adsorption at 350°C cannot be reasonably assigned to the ace-

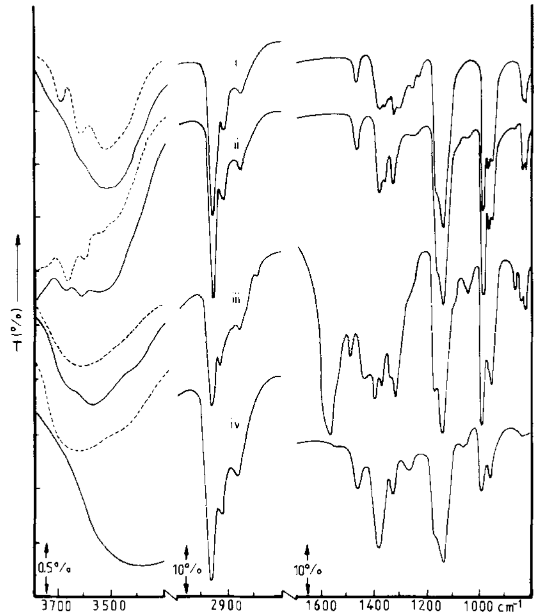


FIG. 4. Infrared spectra of 2-propanol adsorbed at room temperature on ceria calcined at 400 (i), 600 (ii), 800 (iii), or 1000°C (iv). In addition, spectra are shown (3800–3300 cm^{-1}) of the different catalysts prior to adsorption and after pumping (10^{-5} Torr) at 100°C for 2 hr (broken lines). Note the much expanded scale for the spectra in the region 3800–3300 cm^{-1}.

tate ion.

Fink (*19*) and others (*5*, *6*) have observed strong absorptions above 1600 cm^{-1}, which they have assigned to metal-coordinated aldehydic or ketonic groups postulated to be intermediates in the ultimate formation of carboxylate species (see below). We have not observed such bands, and acetone itself adsorbed at 150°C (inset in Fig. 3) shows bands similar to those assigned to the acetate species. However, the intermediate species may occur at temperatures between room temperature and 150°C, a region not studied in this investigation.

(*B*) *Adsorption of 2-propanol at room temperature and 250°C on ceria calcined at temperatures of 400, 600, 800, and 1000°C.* Calcination at different temperatures is known to change the surface species on oxides and in particular to remove surface-bound OH groups with Brønsted-type acidity at high temperatures with the formation of new sites of Lewis acidity from exposed metal cations.

Figure 4 shows the spectra of 2-propanol adsorbed at room temperature on ceria calcined at 400, 600, 800, or 1000°C, and Fig. 5 compares the analogous spectra after the alcohol adsorption at 250°C. This was chosen as a temperature at which the various catalytic reactions are in progress on the sample calcined at 400°C.

For adsorption at room temperature on all samples, bands in all relevant regions of the spectra, viz., νOH, νCH, and ca. 1135 and 1000–925 cm^{-1}, show the presence of the hydrogen-bonded 2-propanol and the isopropoxide ion species discussed above. The intensities of these bands are, however, notably reduced on the sample calcined at 1000°C. An alcohol molecule can be hydrogen-bonded to an oxide surface in two ways, viz., $\mathrm{R{-}\overset{\overset{H}{/}}{O}\ldots\ldots HO^{-}}$ (i) or $\mathrm{\overset{\overset{R}{\backslash}}{O}{-}H\ldots\ldots O^{2-}}$ (ii), where

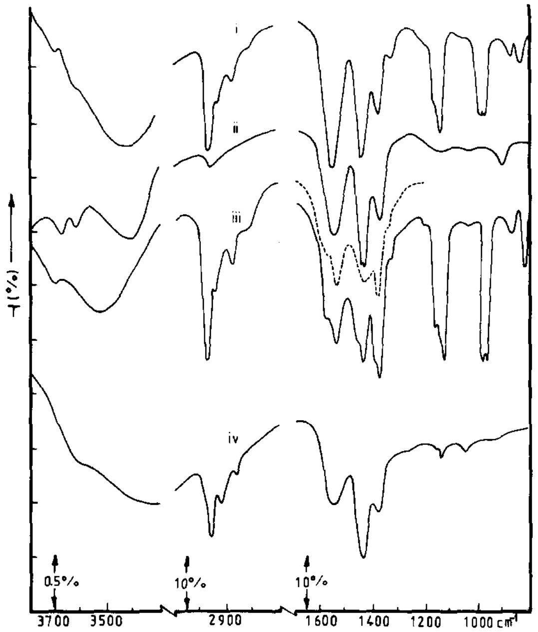
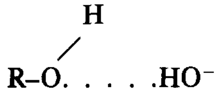


FIG. 5. Infrared spectra of 2-propanol adsorbed at 250°C on ceria calcined at 400 (i), 600 (ii), 800 (iii), or 1000°C (iv). Spectrum (1700–1200 cm^{-1}) of propene adsorbed at 250°C on ceria calcined at 400°C (broken line).

OH^- and O^{2-} are groups on the surface of the oxide. At higher temperatures, calcination is expected to reduce the number of OH^- groups on the surface of the oxide by the reaction $2OH^- \rightarrow H_2O + O^{2-}$. Hence absorptions between 1350 and 1200 cm^{-1} from adsorption on CeO_2–400°C which are not present or weak with CeO_2–600°C may be caused by the presence of more of the


$\overset{\overset{\displaystyle H}{/}}{\text{R–O}}\text{. . . . .}HO^-$ type of interaction of the alcohol with the surface. δOH modes of vibration, which give bands in this region of the spectrum, are expected to be sensitive to whether or not the alcoholic OH group is involved in hydrogen bonding (*16*a).

In addition to the absorption already discussed and attributable to surface species with the structural grouping $(CH_3)_2CH$–O–, the sample calcined at 1000°C shows additional absorption near 1390 cm^{-1}, and that calcined at 800°C shows several additional absorptions at 1575 cm^{-1} (strong and presumably associated with some type of unsaturated oxygen-containing species) with weaker ones at 1490 and 1325 cm^{-1}. These will be discussed later.

The results obtained from adsorption of 2-propanol at 250°C on the variously calcined samples are more complex but can be summarised as follows:

(i) The samples calcined at 400 and 800°C both show prominent absorptions which have been attributed above to isopropoxide ion, notably bands in the νCH, ca. 1135- and ca. 950-cm^{-1} regions; however, those calcined at 600 and 1000°C do not show such features.

(ii) Samples calcined at 400, 600, and 1000°C show bands between 1600 and 1350 cm^{-1} attributable to carboxylate species, while that calcined at 800°C shows more complex absorptions in this region. The latter pattern of absorptions is very similar to that obtained (inset in Fig. 5) from the absorption at 250°C of propene on ceria that had been calcined at 400°C.

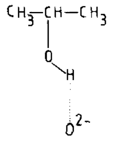
It is clear from the above that the CeO_2 sample calcined at 800°C shows some unique and interesting features in its spectra from adsorbed 2-propanol. Paragraph (ii) above suggests that the bands observed after adsorption at 250°C might arise from some partially oxidised olefinic hydrocarbon species. In this context it is worth noting that the frequencies of the unusual bands obtained after adsorption on this sample at room temperature resemble those reported for an alkene–alkoxide ion (*20*) such as [$^-O—C(CH_3)=CH_2$].

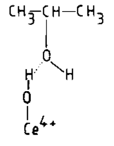
DISCUSSION

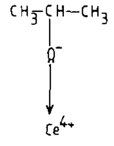
The results described above clearly show that 2-propanol decomposes over ceria via dehydrogenation to give acetone (150–400°C) and via dehydration to give propene (250–400°C). Moreover, the propene molecules formed have shown no tendency to react further, whereas acetone molecules, through further interaction with the surface, become involved in bireaction pathways to give isobutene and methane (250–400°C). These new results show that a recent kinetic study (*11*) of the isothermal change of acetone concentration was only capable of providing a partial monitor for the alcohol-dehydrogenation activity of ceria. Gas chromatography, which was emloyed in that work (*11*), was not as successful as the infrared technique in attaining quantitative separation, and hence identification, of both isobutene and methane.

The Effect of Reaction Temperature on the Surface Reactivity of CeO_2 Calcined at 400°C

The absorption of the alcohol at room temperature most probably takes place via the formation of hydrogen-bonded (Ia) and (Ib) and isopropoxide (II) species. These species would be expected to have the following types of structures.

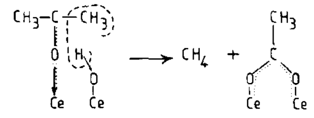

[Ia]


[Ib]

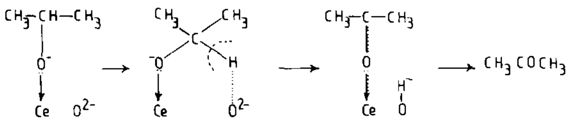

[II]

The displacement of the bands at 3680 and 3610 cm^{-1} with the formation of additional absorption in the broad hydrogen-bonded OH region at around 3500^{-1}, accompanying the adsorption of the alcohol, gives evidence for the part taken by the surface OH groups of the catalyst in the formation of the hydrogen-bonded species. The formation of the isopropoxide species was deduced from an absorption band pattern very similar to that of cerium isopropoxide (*15*).

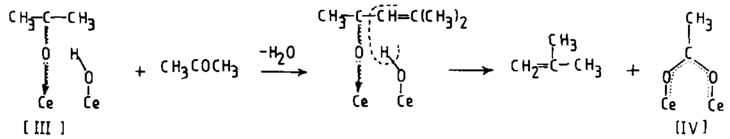
As the dehydrogenation reaction started to take place at 150°C three new bands at 1550, 1425, and 1370 cm^{-1} are observed in the spectrum of the adsorbed phase. We ascribed these bands to the formation of a carboxylate species (IV). This may proceed via an acetone-like intermediate (III) as has been suggested previously for the dehydrogenation of 2-propanol over Al_2O_3 (*5*).


[III] [IV]

The detection of methane in the gas phase may provide an experimental support for the validity of the above mechanism. According to this mechanism, the dehydrogenation reaction takes place according to the following steps.


[II] [III]

As the reaction temperature increased to 250°C, propene, isobutene, and methane started to appear in the gas phase. This implies that both the dehydration reaction and the further reaction of acetone had begun. For the dehydration reaction, the carbonium ion mechanism (*5*) is widely accepted. For the formation of isobutene, which has been found to take place at the expense of the acetone gas phase, we suggest a mechanism involving an aldol condensation-type reaction as below:


[III] [IV]

This provides an alternative route to the formation of acetate ions which dominate the spectra of the adsorbed species at 350°C.

The Effect of Calcination on the Surface Reactivity of the Catalyst

With regard to the dehydration reaction, many investigators (*5, 21*) have stated that the active sites for this reaction are of acidic character, i.e., Brønsted and Lewis sites. Although the concentration of surface OH groups suffers a continuous drop on calcining ceria catalysts from 400 to 800°C, as shown by the decrease of the νOH absorption in the corresponding spectra (Fig. 4), the surface retains a continued dehydration activity (Fig. 2). Pak (*21*) explained a similar phenomenon with regard to the dehydration activity of alumina catalysts in terms of the compensation effect in catalysis. He attributed the apparent increase of the acidic strength of residual OH groups to an increase of the polarization of the AlOH bond as a result of the progressive dehydration of the catalyst. A similar interpretation was given for the dehydration of 2-propanol on chromia catalyst (*22*). On the other hand, the increase of the dehydration of the catalyst itself is also expected to be accompanied by an increase of the number of coordinatively unsaturated metal ions (*23*) (Lewis sites) on the surface. We can therefore relate the increase of the dehydration activity of ceria, upon calcination, to the increase of the acidity of the Brønsted sites and/or to the increase of the number of the Lewis sites. It seems likely that a two-point adsorption of alcohol is necessary for the dehydration and that this might take place most readily in the pores (*24*). The observed drop in the dehydration activity of the CeO_2 calcined at 1000°C could be due to the collapse of the porosity as a result of sintering as reported by Fahim *et al.* (*11*) or to a change in the nature of the Lewis acidity because of conversion of Ce^{4+} to Ce^{3+} in the semiconductive region (*9*).

The dehydration activity, as monitored by the intensity of the characteristic bands of gas-phase acetone in the reaction temperature range ≤200°C, i.e., before further reaction of the acetone sets in, suffers a continuous drop as the calcination temperature increases from 400 to 1000°C. According to the mechanism proposed above for this reaction, it is suggested that the exposed couples of surface Ce^{4+} and O^{2-} ions are the active sites. Studies of the defect structure of ceria, based on high-temperature X-ray (*25*), thermodynamic (*26*), and electrical conductivity measurements (*9*), showed that this oxide can be classified as a metal-excess, *n*-type semiconductor. The presence of excess metal was interpreted (*9*) in terms of a defect structure involving triply and quadruply ionized cerium interstitials and localized electrons. Hence the electronic conduction mechanism of ceria has been explained in terms of a "hopping type" of process (*27*). Brauer *et al.* (*28*) studied the influence of temperature on the defect structure of ceria by measuring the oxygen dissociation pressure from 600 to 1050°C. From the results of their investigation it can be concluded that above 600°C a homogeneous cubic solid solution extends from $Ce_{1.02}O_2$ to about $Ce_{1.33}O_2$, leading to a large departure from stoichiometry. The electrical conductivity measurements (*9*) showed that the electronic mobility decreased with increasing defect concentration. This was accounted for in the concentration of normal cerium sites available for electron occupation becoming decreased with increasing departure from stoichiometry (*9*). Therefore if, as is envisaged in a number of recent publications (*29, 30*), the alcohol dehydrogenation reaction is controlled by the electronic mobility of the catalyst surface, the observed drop of the dehydrogenation activity of ceria upon calcination is explicable. The unexpected increase of the formation of acetone at 400°C on CeO_2 calcined at 1000°C (Fig. 2) is understandable more in terms of the simultaneous drop of the rate of formation of isobutene and methane rather than of an increase of the dehydrogenation activity of the catalyst itself.

The trend of variation of the activity of ceria towards the further reaction of acetone (Fig. 2) can be plausibly explained on the same basis suggested for the dehydration activity, in light of the established carbonium ion mechanism. It is known that aldol condensation reactions occur by the same type of mechanism (*31*).

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