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Thermal evolution of the adsorbed methoxy species on $Ce_xZr_{1-x}O_2$ solid solution samples: a FT-IR study

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Abstract

Thermal reduction of a series of $Ce_xZr_{1-x}O_2$ solid solution samples by methanol adsorbed at room temperature was investigated using infrared spectroscopy (IR). Methoxy species resulting from methanol dissociation and adsorbed as on-top or bridging species, either on Zr^{4+} or Ce^{4+} ions, are well differentiated. Upon the thermal treatment, Ce^{4+} sites appear to be exclusively the reactive ones through their reduction into Ce^{3+}. First, on-top methoxy species adsorbed on Ce^{4+} sites are oxidised to mobile formate species in the 423–473 K temperature range, with the subsequent partial cerium reduction. Second, bridging methoxy species and formate ones decomposed in the 473–523 K temperature range through processes involving CO, CO_2, H_2, H_2O gaseous evolution. The reduction of surface cerium ions is then complete. The production of H_2 molecules was established by a complementary temperature programmed desorption study.

The different temperature range at which mixed oxide reduction and hydrogen evolution take place demonstrates that the catalysts are not reduced by H_2 uptake, but by framework oxygen consumption, due to methoxys oxidation into formate species. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Ceria-zirconia mixed oxides; Methanol adsorption; Cerium reduction; FT-IR spectroscopy

1. Introduction

The increasingly restrictive regulations on exhaust emissions from motor vehicles will necessitate the development of a new generation of three way catalysts (TWC) in the near future. Cerium dioxide (ceria; CeO_2) is the main component of the current TWC and one of its role during the combustion cycle is to store oxygen when the air/fuel ratio is high and to release it when the ratio is low [1]. Such a property is related to the ceria reducibility, i.e. to the easy conversion of the oxidation state $Ce^{III} \leftrightarrow Ce^{IV}$ [2].

One of the factors that have to be improved, for the new generation catalysts, is their efficiency under cold start operation conditions. This could be done by moving the catalytic system very close to the engine, to speed up the initial temperature increase. This will submit the materials to severe use conditions. In this sense, the incorporation of zirconia into ceria as mixed oxides for the next TWC generation constitutes a promising alternative as many works in literature have already pointed out that this system better resists sintering and deactivation processes [3–5]. Moreover, our preliminary studies seem to demonstrate that the

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presence of zirconium inside the fluorite ceria structure improves the oxygen mobility and the oxygen storage capacity (OSC), as already pointed out by some authors [6–8].

A lot of work was devoted to the study of ceria reduction by H_2 and, to a less extent, by CO [9]. This field may be completed by the investigation of ceria reducibility by other reducing agents, such as hydrocarbons or alcohols, that may be likely present in the automotive exhaust gases, especially since MTBE-like compounds have been envisaged to substitute benzene as antidetonant in the unleaded fuels.

In the present work we have used methanol, which is at the same time a good probe molecule for the study of the surface composition of our mixed compounds. The analysis of the thermal evolution of the methoxy species adsorbed on the surface of the investigated samples allows us to find out the reduction effect of methanol on the ceria–zirconia solid solution.

2. Experimental

$Ce_xZr_{1-x}O_2$ solid solution powders of high surface area (approximately 100 m^2/g) and homogeneous in composition with x=1, 0.80, 0.68, 0.50 and 0, were specifically prepared from their nitrate precursors by Rhodia for this study. Structural and textural characterisation of the samples have been reported elsewhere [10–12]. They are noted here respectively, CZ-100/0-HS, CZ-80/20-HS, CZ-68/32-HS, CZ-50/50-HS, CZ-15/85-HS and CZ-0/100-HS, according to the atomic percentages of Ce and Zr. The suffix HS recalls the high specific surface area of the samples.

For the IR studies the powders were pressed into self-supported wafers of about 10 mg cm^{-2} and activated in situ in a quartz cell, placed into the IR beam, following a standard pretreatment up to 873 K [10].

IR spectra were recorded at room temperature (r.t.) with a Nicolet Magna 550 FT-IR spectrometer (resolution 4 cm^{-1}) after quenching the samples to room temperature. The spectra have been treated by the help of the Nicolet OMNIC^{TM} software; they are presented as subtractions between the spectra after and before methanol adsorption, characterising thus the adsorbed species and not the substrate.

3. Results and discussion

3.1. Methanol adsorption at r.t.: methoxy species characterisation

Fig. 1 shows the spectra of the species formed from methanol chemisorption on the series of the activated samples. The shown spectra are those recorded after methanol evacuation at 373 K. They are very similar, in the case of CeO_2 and ZrO_2, to those obtained after evacuation at r.t. Let us first recall that the methanol chemisorption is dissociative on those materials, with the rupture of the CH_3O-H bond, as shown from experiments involving $CH_3^{18}OH$ [13–15]. In agreement with literature, in the case of ceria (spectrum 1(f)) peaks are observed at 1107 (marked I), 1063 (II), 1014 (III) cm^{-1}, due respectively to on-top, doubly and triply bridging methoxy species co-ordinated over Ce^{4+} ions. A band at 1042 cm^{-1} is related to a second type of doubly bridging species (II′) on cerium ions with a different co-ordination with surface oxygens [13]. Some weak bands are also detectable in the δ(C–H) bending region at 1434 and 1450 cm^{-1}, due to a $\delta(CH_3)$ mode for on-top and bridging species, respectively [16]. Correspondingly in the C–H stretching region (Fig. 1) we observe bands at 2912 ($\nu_{as}(CH_3)$), 2885 ($2\delta(CH_3)$), and 2806 cm^{-1} ($\nu_s(CH_3)$).

The spectrum of methanol adsorbed on zirconia (Fig. 1(a)) is partly different [17]: bands at 1163 (labelled I*) and at 1070 (II*) cm^{-1} are due to on-top and doubly bridging species [18,19] over Zr^{4+}, and the main bands at 2924 and 2817 cm^{-1} are the $\nu(C–H_3)$ stretching modes for these methoxy species.

The spectra of the adsorbed species arising from methanol chemisorption on the CZ mixed samples are also shown in Fig. 1 (spectra (b)–(e)). The analysis of the O–C stretching region shows that it is possible to discriminate the on-top methoxy species (I) co-ordinated over Ce from the same species (I*) co-ordinated over Zr, the first being responsible for a band at about 1100 cm^{-1} while the latter is characterised by a band at 1150 cm^{-1}. All the bands corresponding to methanol dissociative adsorption either on cerium or on zirconium ions are present on the mixed oxides, showing a regular downshift of the peaks position (few cm^{-1}) with respect to the bands on pure samples. The shift is slight (few cm^{-1}) for methoxy species

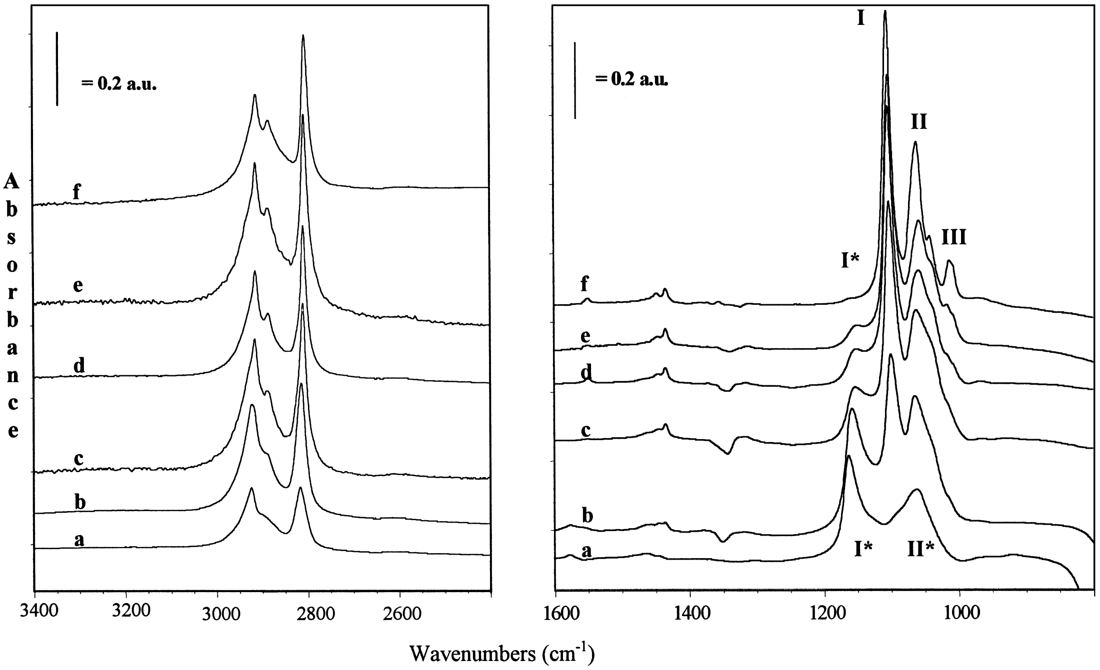


Fig. 1. FT-IR subtraction spectra of the surface species formed by methanol dissociative adsorption at rt over ZrO_2 (CZ-0/100) (a), CZ-15/85-HS (b), CZ-50/50-HS (c), CZ-68/32-HS (d), CZ-80/20-HS (e), CeO_2 (CZ-100/0-HS) (f), after evacuation at 373 K. Left side C–H stretching region, right side C–O stretching region. I, II, III: ν(OC) bands for OCH_3 species on-top, doubly or triply bridged over Ce^{4+} ions; I^*, II^*: on-top or doubly bridged OCH_3 species over Zr^{4+} ions).

adsorbed on Ce^{4+} ions, whereas it is a little more important in the case of Zr^{4+} ions.

3.2. Heating at 473 K: formate species characterisation

The spectra of the adsorbed species present on the different samples after evacuation at 473 K are reported in Fig. 2. Comparison with Fig. 1 shows for pure zirconia (spectra (a) in Figs. 1 and 2), no noticeable effect of the temperature increase from 373–473 K. Only the formation of traces of formate species is detectable and characterised by the weak bands at 1575 (ν_{as}(OCO)), 1383 (δ(CH)) and 1370 cm^{-1} (ν_s(OCO)). The ν(CH) mode has been observed at 2875 cm^{-1} [20].

For pure ceria (spectra (f) in Figs. 1 and 2), as reported in [16], only on-top methoxy species are near completely and selectively oxidised into formate species characterised by strong bands at 1585 (shoulder), 1563 and 1551 cm^{-1} (ν_{as}(OCO)), 1373 (δ(CH)) and 1357 cm^{-1} (ν_s(OCO)). The corresponding ν(CH) mode is clearly seen at 2840 cm^{-1}. The observance of three ν_{as}(OCO) bands is indicative of at least three kinds of formate species. Literature results indicate that the ν_{as}(OCO) formate bands at 1585 and 1563 cm^{-1} are due to two types of formate species adsorbed on reduced Ce^{3+} sites, while the band at 1551 cm^{-1} is due to formate species adsorbed on Ce^{4+} sites [21]. The presence of the bands at 1585 and 1563 cm^{-1} in spectrum (f) (Fig. 2) shows that the oxidation of CH_3O^- species into $HCOO^-$ ones is accompanied by a $Ce^{4+} \rightarrow Ce^{3+}$ reduction. Notice that in spectrum (f) (Fig. 2) the $\nu_{as}(CH_3)$ (2919 cm^{-1}) and $\nu_s(CH_3)$ (2801 cm^{-1}) wave numbers of remaining methoxy species differ slightly from those reported above (Fig. 1); the latter corresponds to the unresolved contribution of both on-top and bridging species [16]; whereas only bridging species remain after heating at 473 K and are thus characterised by the two bands at 2919 and 2801 cm^{-1}.

For mixed compounds (spectra (b)–(e), Fig. 2) the intensity of the band located at about 1150 cm^{-1} and characterising on-top methoxy species adsorbed on

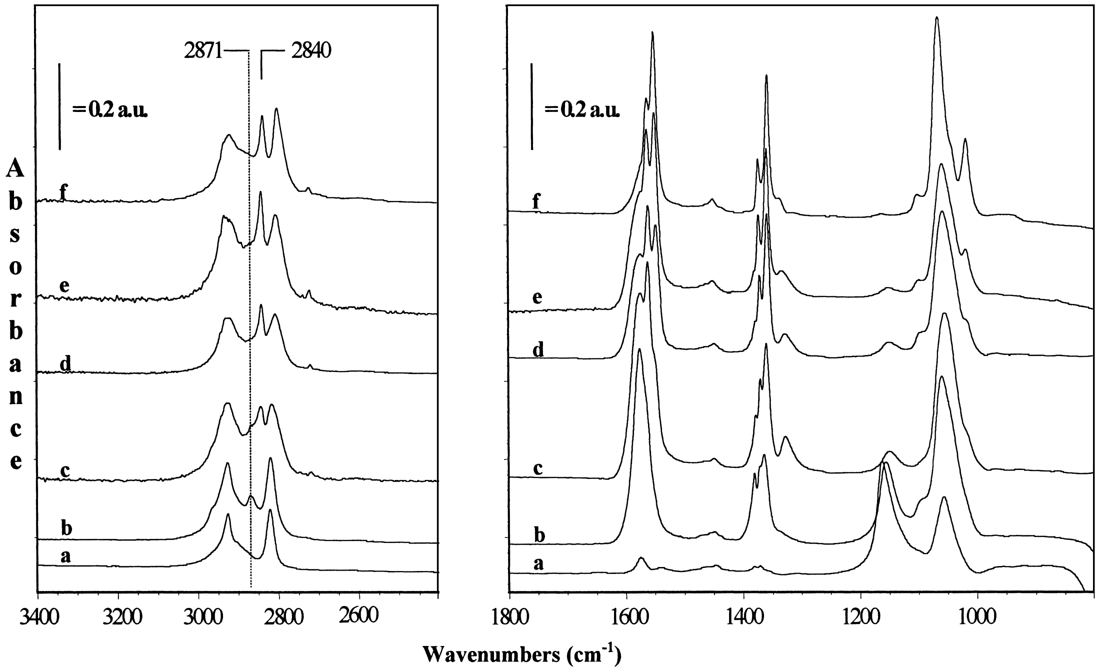


Fig. 2. The same as Fig. 1 but after evacuation at 473 K instead of 373 K.

Zr^{4+}, decreases at least by a factor 2 upon heating from 373–473 K, whereas it was nearly unchanged for unreactive pure zirconia. The distribution between formate species formed, adsorbed either on zirconia or on ceria, is unambiguously seen looking at the ν(OCO) wave number, 1575 and 1383 cm^{-1} for zirconia and 1585, 1563, 1551 and 1358 cm^{-1} for ceria. It clearly appears, from the ν_{as}(OCO) bands, that the intensity of the peak located near 1550 cm^{-1} (formates on Ce^{4+} sites) decreases till to vanish as the cerium content of the sample decreases (Fig. 2, spectra (f)–(b)). Inversely the intensities of the bands at 1585 and 1563 cm^{-1} (formates on Ce^{3+} sites) firstly increases as do the bands at 1575 and 1383 cm^{-1} (formates on Zr^{4+} sites), these last bands being largely predominant when the zirconium content of the mixed sample is high (Fig. 2, spectrum (b)). These results may be rationalised as follows:

1. Ce^{4+} sites are the reactive ones and on-top methoxy species adsorbed on Ce^{4+} are oxidised into formate species and a simultaneous $Ce^{4+} \rightarrow Ce^{3+}$ reduction takes place.
2. At 473 K formate species are mobile, so in the case of pure ceria an excess of Ce^{4+} sites may lead to the formate adsorption on such sites (band at 1550 cm^{-1}), whereas formate adsorption on Ce^{3+} sites is also observed (less important bands at 1585 and 1563 cm^{-1}).
3. As the cerium content of the sample decreases, the excess of Ce^{4+} sites diminishes, so formate species adsorbed on Ce^{4+} sites tend to vanish (intensity decrease of the band at 1550 cm^{-1}).
4. Formate may also migrate to Zr^{4+} site, then for the mixed sample having the greater Zr^{4+} content mainly formate species adsorbed on Zr^{4+} are observed (bands at 1575 and 1383 cm^{-1}, spectrum (b)). This is confirmed by considering the ν(CH) spectral range, where the ν(CH) band at 2871 cm^{-1} due to formate species on Zr^{4+} is the only observed (Fig. 2, spectrum (b)), while the feature at 2837 cm^{-1}, corresponding to the Ce site, is lacking.
5. The partial elimination of on-top methoxy species adsorbed on Zr^{4+} ions upon heating to 473 K, may be either due to the migration of these species to

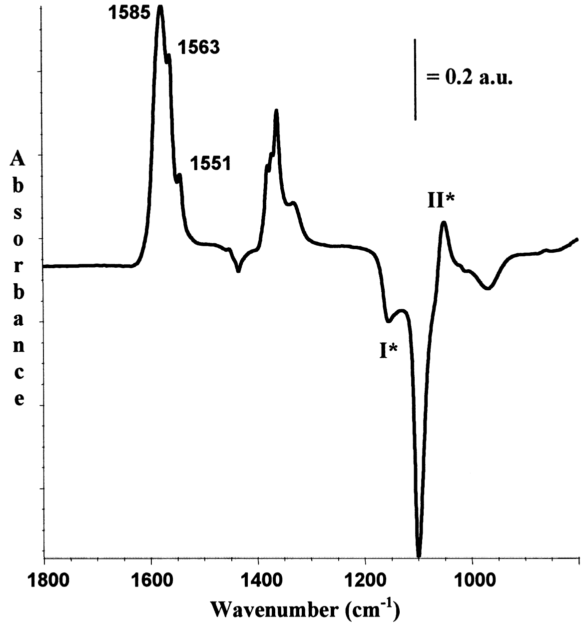
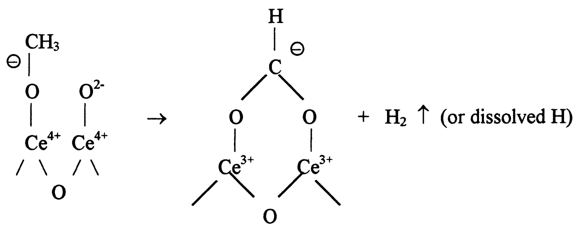


Fig. 3. Difference between spectra 1(c) and 2(c) of the sample CZ-50/50-HS surface methoxy covered and evacuated either at 473 K (Fig. 2) or 373 K (Fig. 1). I^* on-top and II^* bridging OCH_3 species over Zr^{4+} ions.

reactive Ce^{4+} sites or to the migration of formate species to Zr^{4+} sites. Indeed it has been shown that the co-adsorption of methoxy and formate species on Zr^{4+} sites leads to a conversion of on-top methoxys into bridging ones [22]. Differences between spectra scanned after formate production (heating to 473 K) and those scanned before this production (heating only to 373 K) were performed. Such a difference is shown in Fig. 3 for the CZ-50/50-HS sample. Since the temperature is varied, frequency shifts, even slight of the bands may create important artefacts in such differences (needing thus to be cautious in their interpretation); nevertheless it appears that the intensity decrease of the band at 1155 cm^{-1} (I^*, on-top methoxy species on Zr^{4+}) is correlated with a comparable increasing of the intensity of that at 1051 cm^{-1} (II^*, bridging methoxy species on Zr^{4+}). This suggests that the partial diminution of the amount of on-top methoxy species on Zr^{4+} sites upon heating to 473 K is mainly due to their conversion into bridging ones due to formate species adsorption on Zr^{4+} sites, and not to the migration of methoxy species from inactive Zr^{4+} sites to reactive Ce^{4+} ones.

From the examination of the 3800–3600 cm^{-1} spectral region (not shown), no surface OH species are formed during the oxidation of on-top methoxy species at 473 K. If water was produced during the process, it should dissociate on ceria into OH surface species; moreover the gas phase spectra reveal the presence of only traces of water (beyond gaseous CO_2). Excluding thus water formation during the process, we postulate H_2 evolution (or, possibly, atomic hydrogen solubility in ceria or in the mixed oxides).

The following equation may be proposed for the on-top methoxy species oxidation on Ce^{4+} sites:



(1)

H_2 reduction on the surface of ceria has been reported to begin at about 473 K [2], but it is more clearly observed at 573 K, then the ceria reducibility by CH_3OH through formate formation at 473 K is not far from that resulting from H_2. The ceria reduction would be limited to sites where only on-top and not bridging species are adsorbed, i.e. to Ce^{4+} surface sites of low unsaturated co-ordination, and only capping surface oxygen species are thought to be involved at 473 K.

The presence of CO_2 in the gas phase is possibly due to a further oxidation of formate species migrating to Ce^{4+} sites:

$$HCOO^- + Ce^{4+} \rightarrow CO_2 + \tfrac{1}{2}H_2 + Ce^{3+}. \qquad (2)$$

In these mechanisms, H_2 evolution cannot be probed by IR measurements because of its vibrational inactivity. Thus independent TPD experiments have been performed using a mass spectrometer as detector (Fig. 4) but not very conclusive results were so obtained (see Section 3.3).

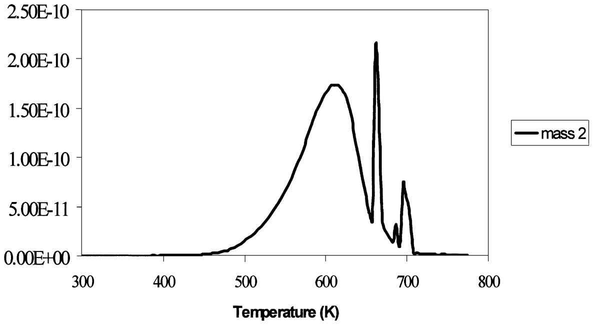


Fig. 4. Plot of hydrogen evolution versus temperature after mass spectroscopy detection from TPD experiments using methoxy precovered CZ-50/50-HS sample (heating temperature 5 K min^{-1}).

3.3. *Overall heating from r.t. to 623 K*

Taking as example the CZ-50/50-HS sample, thermal evolution of methoxy species is shown in Fig. 5, in the 298–623 K temperature range. When the temperature is raised step by step, it may be seen that formate species start to be produced at 423 K as shown by the weak ν_{as}(OCO) bands at around 1550–1600 cm^{-1} (spectrum (c)). It may be inferred that such species are mainly adsorbed on Ce^{4+} sites (band at 1550 cm^{-1}). As the temperature increases from 423 to 473 K, adsorption of formate species on Ce^{3+} becomes predominant (band at 1563 cm^{-1}) because of the increased reduction of cerium when the amount of formate species grows up (spectrum (d)). Moreover, formate species spread over the Zr^{4+} sites (bands at 1575 and 1383 cm^{-1}). Heating to 523 K (spectrum (e)) leads to the near complete decomposition of both formate and bridging methoxy species. The remaining formate species are mainly those adsorbed on Zr^{4+} ions (predominant ν(CH) band at 2871 cm^{-1}, relative to that at 2837 cm^{-1}); the remaining on-top methoxy species (weak band at 1150 cm^{-1}) and bridging methoxys (ν(OC) band at 1050 cm^{-1}, ν_s(CH$_3$) band at 2817 cm^{-1}) are adsorbed also on Zr^{4+} sites. It is possible that migration of methoxy species, initially adsorbed on Zr^{4+} sites, to reactive Ce^{4+} sites (discarded at 473 K, see Section 3.2), become possible at 523 K. However, the presence of residual methoxy species on Zr^{4+} sites at this last temperature shows that it is not easy. The only new adsorbed species

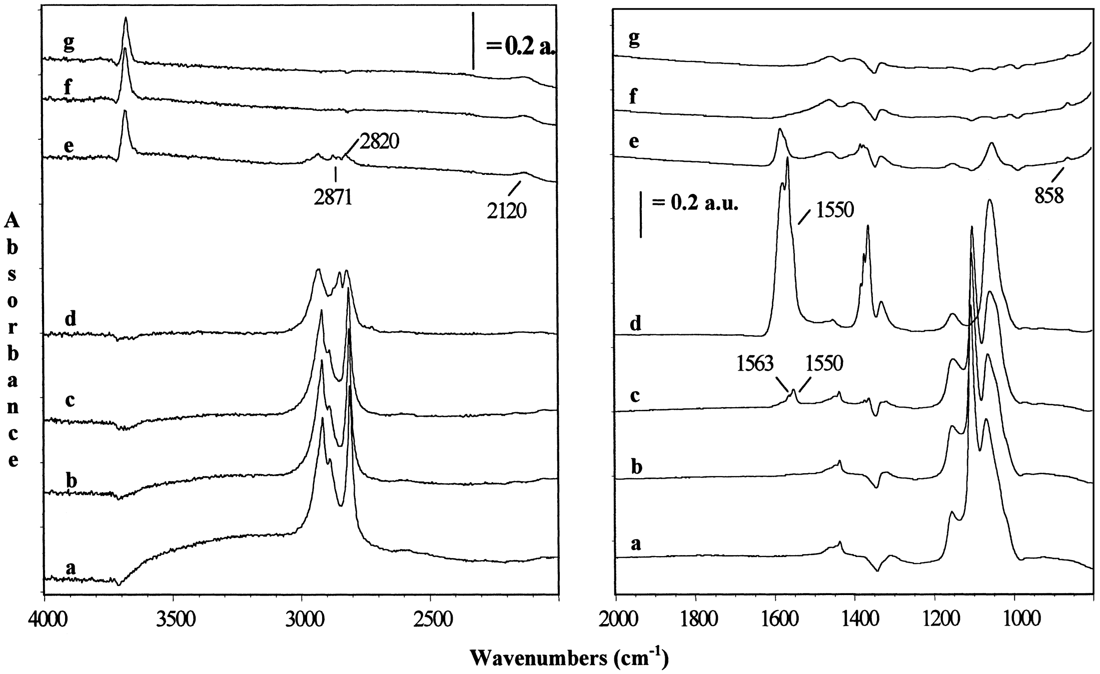


Fig. 5. FT-IR subtraction spectra of the surface species formed by the methanol dissociative adsorption over CZ-50/50-HS after evacuation at 298 (a), 373 (b), 423 (c), 473 (d), 523 (e), 573 (f) and 623 K (g). Left side C–H stretching region, right side C–O stretching region.

formed upon heating to 523 K are OH ones (band at 3681 cm^{-1}) and traces of carbonates well characterised by the very weak but specific $\pi(CO_3)$ band at 858 cm^{-1}. No trace of adsorbed species expected from an incomplete methoxy oxidation, such as dioxymethylene, which is known to be formed on the surface of other oxides [23], is observed. Above 523 K (spectra (f) and (g)) residual formate and bridging species totally vanish, the only remaining adsorbed surface species being the OH and carbonate ones. These above features are common to all the samples (excluding pure zirconia on which both on-top and bridging methoxy species are unreactive at least up to 573 K). Note that in spectra (e), (f), (g) of Fig. 5 a band at 2120 cm^{-1} clearly appears. It is due to the forbidden $^2F_{5/2} \rightarrow ^2F_{7/2}$ electronic transition of Ce^{3+} ions in internal structural defects [14], thus indicating that at 523 K the ceria reduction becomes not limited to its surface.

Detailed features for spectra of formed OH and carbonate species at 573 K are sample dependent, as may be seen in Fig. 6.

We now examine the spectral range characterising the carbonate species formed at 573 K (right part in Fig. 6). The bands at 1460 and 1390 cm^{-1} are due to the $\nu(CO_3)$ asymmetrical modes of polydentate carbonate species adsorbed on ceria [21]; the third symmetrical $\nu(CO_3)$ mode is hardly detectable at 1060 cm^{-1}, while the characteristic $\pi(CO_3)$ band is weak but very well defined at 858 cm^{-1}. The spectra here observed are very similar to that resulting from CO_2 adsorption on reduced ceria at 573 K [21]. The quantity of adsorbed carbonate species qualitatively decreases as does the ceria content in the sample (spectra (f)–(c)). No carbonate species are detected in the case of CZ-15/85-HS.

The carbonate band intensities in Fig. 5(e)–(g) are much weaker than those of formate band in spectrum (d). A very high discrepancy between the molar absorption coefficient of the corresponding carbonate $\nu_{as}(CO_3)$ and formate $\nu_{as}(CO_2)$ bands being excluded, it means that the relative amount of surface carbonate species formed is very low. This suggests a main decomposition of initial formate and methoxy species into gaseous products such as CO or CO_2 as effectively observed from the gas phase spectrum in addition to gaseous H_2O (Fig. 7). However the significance of spectra reported in Fig. 7 has to be

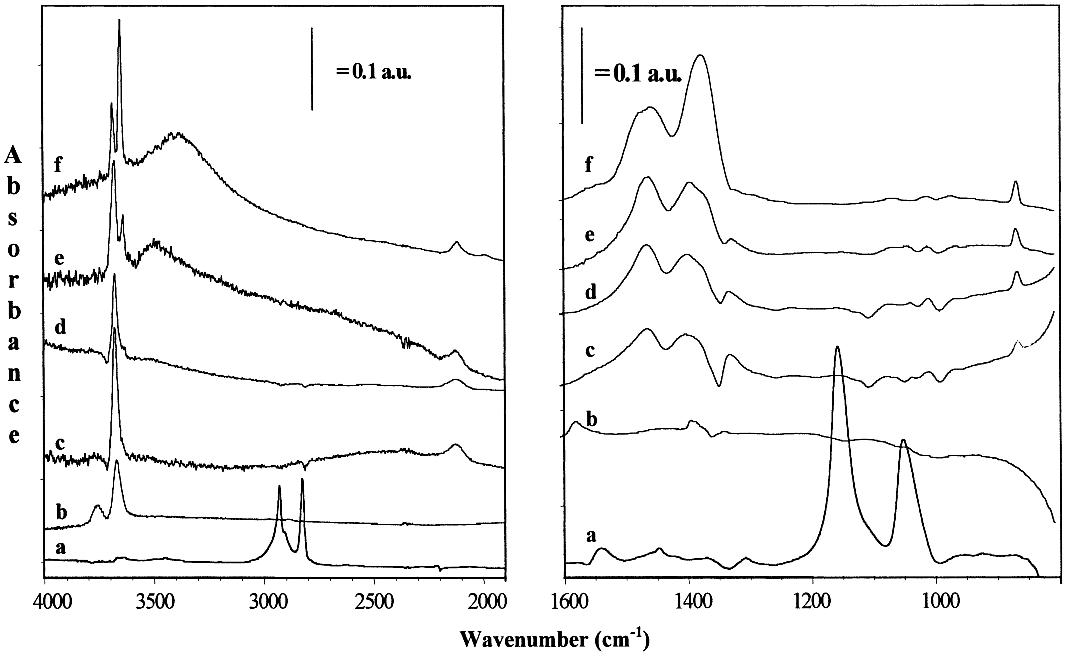


Fig. 6. FT-IR subtraction spectra of the species formed by methanol oxidation over ZrO_2 (CZ-0/100) (a), CZ-15/85-HS (b), CZ-50/50-HS (c), CZ-68/32-HS (d), CZ-80/20-HS (e), CeO_2 (CZ-100/0-HS) (f), after evacuation at 573 K.

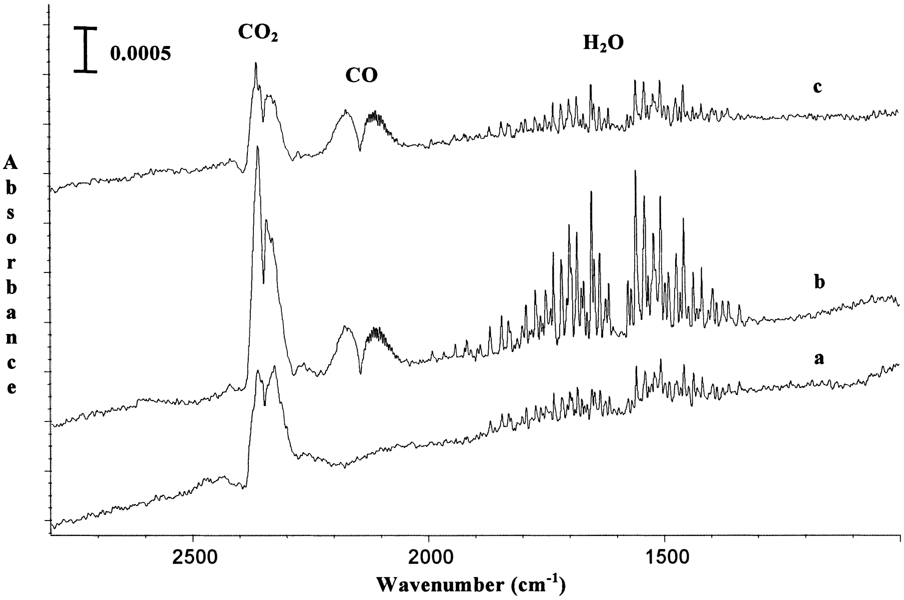


Fig. 7. FT-IR spectra of the gas phase produced by a step by step heating of CZ-50/50-HS sample, on which methanol was pre-adsorbed at rt: heating from 423 to 473 K (a), from 473 to 523 K (b) and from 523 to 573 K (c). The sample was evacuated first at the beginning of each heating step (see Fig. 5 for adsorbed species on the sample).

cautiously considered. These spectra result from subtracting spectra scanned after the indicated treatment from a common background spectrum scanned before all of these treatments. Despite that the spectrometer was continuously swept with dry N_2 for purging the optical path from atmospheric CO_2 and H_2O, very weak H_2O bands in Fig. 7(a) and (c) may result from a very small amount of H_2O produced by the sample, but we cannot exclude a contribution due to a variation in the ambient H_2O. The CO_2 band intensity is sufficiently high to be attributed to CO_2 evolution from the sample. Let us remark that if surface bidentate carbonate species were to be formed, they could not be thermally stable on ceria above 473 K (decomposition into CO_2), only the more tightly bound polydentate carbonate species being then observed on the surface [21].

The ν(OH) spectral range is rather complicated (Fig. 6, left part). For CZ-15/85-HS (spectrum (b)) the ν(OH) band at 3759 cm^{-1} is unambiguously due to on-top OH species on Zr^{4+} ions [24], while the band at 3667 cm^{-1}, whose width at half-height diminishes as the zirconium content in the sample decreases (spectra (b)–(f)), shifting to 3676 cm^{-1}, can be due to bridging OH species adsorbed either on Zr^{4+} (3667 cm^{-1}) or Ce^{3+} (3676 cm^{-1}) ions. This band is the only one observed for CZ-50/50-HS (spectrum (c)) and CZ-68/32-HS (spectrum (d)). This feature suggests that it is mainly due to bridging OH species on Ce^{3+} ions [25]. As the ceria content increases (spectra (e) and (f)) a sharp band at 3640 cm^{-1} and a wide one in the 3500–3300 cm^{-1} spectral range grow up. They are due to OH species adsorbed on reduced ceria but they lead to a H_2 evolution under a prolonged evacuation at 673 K, which is reversible upon subsequent H_2 treatment [25].

Studies on the ν(OH) bands for OH species produced by H_2 reduction of these mixed samples are in progress in our laboratory. Some preliminary results are shown in Fig. 8 for OH species resulting from the H_2 reduction at 573 K (left part) and 673 K (right part). Discarding a detailed discussion of the variation of the ν(OH) band throughout the series of samples, which was not the scope of this study, the spectra in the left part of Fig. 6 match very well with those in the right part of Fig. 8. Then the thermal elimination at 573 K of surface species produced by methanol adsorption reduces ceria as does H_2, but at 673 K. This temperature shift may be due to an easier breaking of C–H bonds to produce H than that of the H–H

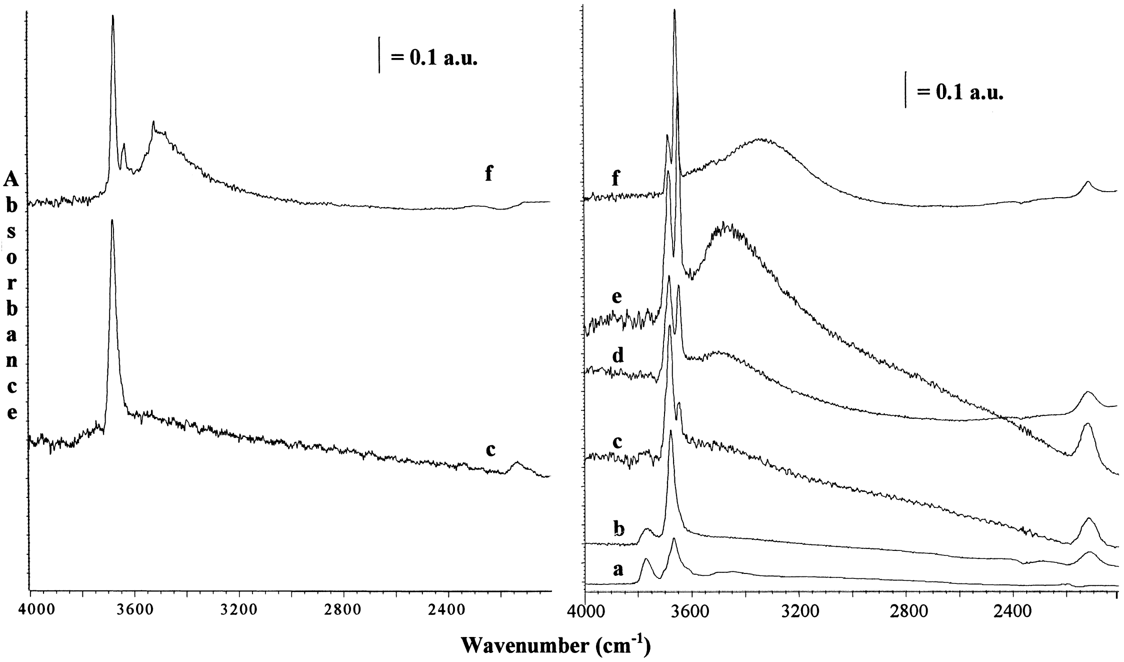


Fig. 8. FT-IR spectra of OH species resulting from the H_2 reduction at 573 K (left part) and 673 K (right part). CZ-0/100 (a), CZ-15/85-HS (b), CZ-50/50-HS (c), CZ-68/32-HS (d), CZ-80/20-HS (e), CZ-100/0-HS (f).

bond in H_2 adsorption. In that sense it is well known that transition metals supported on ceria such as Rh, Pt, Pd, on which H_2 easily dissociates and spills over the carriers, allow the ceria reduction to occur even at r.t., indicating then that H–H bond breaking is a determining step for ceria reduction by H_2. Moreover if CO is produced during the thermal decomposition process, ceria is more easily reduced by CO than by H_2 at low temperatures [26].

However, other factors such as thermal surface–subsurface reorganisation, made easier by methoxy and formate adsorption, may also be involved. Both formate and methoxy species are eliminated upon heating up to 523 K and concomitantly subsurface Ce^{3+} ions are produced (electronic transition at 2120 cm^{-1}). Literature results [27] have shown that 573 K was just the temperature at which the surface O^{2-} mobility begins to be observed for clean ceria, its maximum taking place at 673 K. Thus a surface–subsurface reorganisation may be assumed to occur at 523 K by O^{2-} migration from the surface underlayer to the surface itself, (i) generating Ce^{3+} in a bulk-like crystal field and (ii) converting bridging OCH_3 species into transient on-top ones, which are then oxidised into formate species. The lowering of the temperature threshold from 573 K for clean ceria surface to 523 K for methanol adsorbed ones, may be due to a concerted mechanism between the surface–subsurface reorganisation and the adsorbed species reactivity. At 523 K formate species adsorbed on Ce^{4+} sites are possibly oxidised in the following processes, not far from those proposed by Li et al. [28]:

$$HCOO^-_{ads} + Ce^{4+}_{surf} \rightarrow CO_2 + \tfrac{1}{2}H_2 + Ce^{3+}_{surf} \quad (2)$$

$$HCOO^-_{ads} + O^{2-}_{surf} + 2Ce^{4+}_{surf} \rightarrow CO_2 + OH^-_{surf} + 2Ce^{3+}_{surf} \quad (3)$$

$$HCOO^-_{ads} + O^{2-}_{surf} + Ce^{4+}_{surf} \rightarrow CO^{2-}_{3\,ads} + \tfrac{1}{2}H_2 + Ce^{3+}_{surf} \quad (4)$$

Process (3) at 523 K looks like the already considered process (2) at 473 K, but takes into account a higher reactivity of H_2 towards ceria as the temperature increases. The formation of adsorbed OH species is in accordance with the presence of ν(OH) bands at 573 K and not at 473 K (Fig. 5), while the formation of gaseous CO_2 at 523 K is spectroscopically inferred from Fig. 7 (spectrum (b)). A further dehydroxylation of the surface would produce gaseous H_2O as it is observed (Fig. 7). Process (4) takes into account the formation of polydentate carbonate species.

Because of the slow kinetic of O^{2-} migration from the bulk to the surface at temperatures lower than 673 K [27], all adsorbed surface species are not expected to be eliminated by an oxidative process but also by decomposition. For formate species adsorbed on Ce^{3+} ions or on irreducible Zr^{4+} ones, the following process may be proposed:

$$HCOO^-_{ads} \rightarrow CO + OH^-_{surf} \quad (5)$$

Notice that before evacuation at 523 K, the presence of CO in the gas phase was effectively characterised by the ν(CO) band at 2143 cm^{-1} having a rotational structure (Fig. 7(b)). The surface OH species so formed contribute to the ν(OH) band (Fig. 5(e)).

Heating the samples from 523 K up to 623 K only eliminates residual formate and methoxy species on Zr^{4+} (Fig. 5(e)–(g)), while the production of gaseous CO_2 (carbonate decomposition) or H_2O (dehydroxylation) decreases. The ν(OH) frequency remains that of OH species adsorbed on Ce^{3+} ions, excluding thus a surface re-oxidation from bulk O^{2-} migration to the surface and a subsequent bulk reduction. Then, in this temperature range, sample reduction appears limited to the surface–subsurface underlayer, as in the case of reduction by H_2 at 673 K [14].

In the processes (1), (2) and (4) proposed from the IR results, H_2 evolution is proposed but not confirmed as this species is not an IR vibrationally active one. Then a separate TPD experiment has been performed using the CZ-50/50-HS sample pre-covered by methoxy species, the H_2 evolution being detected by a mass spectrometer. Results are reported in Fig. 4. A large asymmetrical signal is observed extending from 470 to 670 K, followed by a narrow one at 670 K and a minor one at 700 K. This does not match exactly the H_2 evolution considered at 423–473 K (processes (1) and (2)) or at 473–523 K (processes (2) and (4)), since there is a delay between the temperature range 423–523 K for methoxy and formate species decomposition (IR results) and the 470–670 K range corresponding to the H_2 evolution (TPD results). A plausible explanation of this would be that H_2 is produced through an intermediate atomic H adsorbed (or absorbed) infrared inactive species. In the case of pure ceria, NMR measurements showed the hydrogen incorporation into the oxide, mainly in the bulk, when ceria was treated with H_2 in the 373–773 K temperature range [29]. The narrow signal at 670 K is assigned to the decomposition of OH species adsorbed on the already reduced surface. The presence of such OH species at 623 K is clearly indicated by the ν(OH) band at 3681 cm^{-1} (Fig. 5, spectrum (g)); they decomposed into H_2 upon heating to 673 K [25].

4. Conclusions

The dissociative chemisorption of methanol on the investigated solid solutions and the differentiation of methoxy and formate species adsorbed on Zr^{4+}, Ce^{4+} and Ce^{3+} sites allowed us to deeply study the surface species transformation during the thermal evolution of methoxy species.

When the temperature is raised step by step, it may be seen that the formate species start to be produced at 423 K. Since Ce^{4+} sites are the reactive ones, on-top methoxy species adsorbed on Ce^{4+} are selectively oxidised into formate species and a simultaneous $Ce^{4+} \rightarrow Ce^{3+}$ reduction takes place. Moreover, the oxidation of the adsorbed methoxy species, in absence of molecular oxygen, involves lattice O^{2-} species, with a consequent surface reduction.

At 473 K formate species are mobile, so in the case of pure ceria an excess of Ce^{4+} sites may lead to the formate adsorption on such sites, whereas formate adsorption on Ce^{3+} sites is also observed. As the cerium content of the sample decreases, the excess of Ce^{4+} sites diminishes, so formate species adsorbed on Ce^{4+} sites tend to vanish. Formate may also migrate to Zr^{4+} site, then for the mixed sample having the greatest Zr^{4+} content mainly formate species adsorbed on Zr^{4+} are observed. The partial elimination of on-top methoxy species adsorbed on Zr^{4+} ions upon heating to 473 K, is likely due to their conversion into bridging ones due to formate species adsorption on Zr^{4+} sites, and not to the migration of methoxy species from inactive Zr^{4+} sites to reactive Ce^{4+} ones.

The further oxidation of formate species migrating to unreduced Ce^{4+} sites leads to CO_2 evolution.

Above 523 K residual formate and bridging methoxy species totally vanish, the only remaining adsorbed surface species being the OH and carbonates; the latter qualitatively decrease as does ceria content in the sample. At this temperature the reduced state of ceria becomes not limited to its surface, as demonstrated by the appearance of the forbidden $^2F_{5/2} \rightarrow ^2F_{7/2}$ electronic transition of Ce^{3+} ions in internal structural defects. Thus a surface–subsurface reorganisation may be assumed at 523 K by O^{2-} migration from the surface underlayer to the surface, introducing Ce^{3+} in a bulk-like crystal field and converting bridging -OCH_3 species into transient on-top ones, which are then oxidised into formates. The lowering of the temperature threshold from 573 K for H_2 reduction of clean ceria surface to 523 K for methanol adsorbed one, may be due to a concerted mechanism between the surface–subsurface reorganisation and the adsorbed species reactivity.

A TPD experiment confirms the H_2 evolution during the thermal decomposition process of adsorbed species. For temperatures lower than 670 K, adsorbed species decomposition does not match exactly the H_2 evolution, suggesting thus the formation of adsorbed intermediate atomic H species.

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