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Controlled selectivity for ethanol steam reforming reaction over doped CeO₂ surfaces: The role of gallium

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Abstract

The ethanol steam reforming reaction, together with the adsorption and decomposition of ethanol was studied on CeO₂ and gallium-doped ceria (CeGaO_x) by a combined experimental and theoretical approach using infrared spectroscopy (IR), mass spectrometry (MS) and density functional theory (DFT) calculations. At 100°C, different types of monodentate ethoxy species were identified as standing-up (SU) on Ce⁴⁺ and lying-down (LD) on Ce⁴⁺ and Ga³⁺, with the alkyl chain more perpendicular or parallel to the surface, respectively. It is suggested that the incorporation of Ga into the ceria lattice changes the decomposition pathway of LD species, which converts to acetate instead of ethylene, attributed to the increased lattice oxygen lability in the Ce–O–Ga interface upon doping and the propensity to form Ga–H surface species. Under ethanol steam reforming conditions, Ga doping of ceria-based materials has a drastic effect by improving the H₂:CO₂ ratio, changing the product distribution and reducing coke formation.

Keywords: bioethanol, hydrogen production, gallia, deactivation, coke precursors

Introduction

A few decades ago, the concern about global warming attributed to the emissions of CO₂, the primary greenhouse gas originating from the burning of fossil fuels, triggered the interest in using H₂ as an energy vector. For reasons of storage and transport, it is more convenient, however, that the energy vector is liquid and has low toxicity. Thus, ethanol obtained from renewable resources[1], is a suitable candidate for this purpose. It is well known that molecular hydrogen can be produced from ethanol by reforming with water vapor [2].

One of the main challenges with respect to the formulation of catalytic materials for ethanol steam reforming (ESR) lies in the development of active metal-supported catalysts that control the selectivity in order to, for example, increase the H₂ yield and inhibit the undesired coke formation. The main reactions that contribute to coke production during ESR are: ethylene polymerization, the Boudouard reaction, reverse carbon gasification, and hydrocarbon decomposition [3]. As a consequence of those reactions, mainly two types of carbon deposits have been reported on the surface of ESR catalysts: amorphous and filamentous [4,5]. The nature of the carbon and the reactions involved in its formation depend on reaction conditions and the chosen catalyst, which typically consists of metal nanoparticles dispersed on a reducible oxide.

Several strategies have been applied to minimize carbon formation during ESR, such as increasing the steam to ethanol ratio, adding oxygen to the feed, co-feeding CO₂ or H₂, as well as catalyst modifications [3,5]. However, those strategies that only modify the operational conditions had limited success. Catalyst modifications have shown to be the most promising strategy to minimize coke formation during ESR in terms of yield and costs. The formulation of catalytic materials for ESR plays a crucial role in terms of minimizing carbon deposits as well as achieving complete ethanol conversion and maximizing the H₂ yield. The nature of the metal, the particle size and oxidation state, and the impact of the oxide support

on the stability and selectivity of the catalyst are fundamental aspects to be taken into account when designing an ESR catalyst [6–8]. A better understanding of the reaction mechanism, and of the aspects mentioned above, should lead to the development of new high performance catalysts for ESR.

The support itself can play a major role in ESR by assisting in the removal of carbon or suppressing its formation [5]. The addition of dopants to the oxide support has been studied with the aim of modifying the acid/base properties or enhancing the oxygen storage capacity. On the one hand, neutralizing the acid sites by addition of dopants may limit ethylene polymerization, and dopants such as alkali metals [9–12], alkaline earth metals [13–15], or rare earth oxides [16–20] have shown to be effective. However, it should be noted that doping can impact the electronic properties of the catalyst and/or block or modify specific adsorption sites. On the other hand, it has been reported that cerium oxide (CeO_2 , also known as ceria) may be a suitable support for ESR metal/oxide catalysts due to its high oxygen storage capacity, and at the same time, the oxygen mobility in ceria can improve the catalytic stability by suppressing the formation of carbonaceous species [21,22]. The use of ceria-containing mixed oxides as a support for an ESR catalyst has been tested. Doping CeO_2 with Ca, Pr, Fe and Zr [23–27] promoted the reducibility of pure ceria and enhanced the formation of oxygen vacancies. Also, some of us have proved that doping ceria with Ga^{3+} by a co-precipitation method, which allows the incorporation of gallium cations into in the fluorite structure of ceria giving place to cerium-gallium mixed oxides, significantly improves the redox property of the pure ceria material [28,29]. This was proven by a combination of experimental techniques such as oxygen storage capacity measurements, temperature-programmed reduction (TPR) by H_2 and CO, in situ X-ray absorption spectrometry (XAS) and time-resolved X-ray diffraction (TR-XRD). Additionally, the isothermal reduction experiments with H_2 followed by DRIFTS together with kinetic modeling and DFT

calculations showed that in the case of the cerium-gallium mixed oxides, H₂ is activated at the interface between gallia-rich and ceria-rich (nano)domains with a very low activation barrier, leading to Ga–H species and the formation of Ce³⁺, as well as to the formation of oxygen vacancies by removal of water [30]. From the above findings, it is expected that mixed cerium-gallium oxides will be better supports for the steam reforming of ethanol than pure ceria because the higher reducibility of the mixed oxide would facilitate the oxidation of ethoxy species, preventing the formation of coke precursors. Also, the ease at which H would be abstracted from ethoxy species on the doped system to form Ga–H groups, is likely to have an important effect.

In this work we investigated the ethanol steam reforming reaction, as well as the adsorption and decomposition of ethanol over bare ceria and ceria-gallia supports to characterize its surface chemical behavior. A combined experimental and theoretical approach is used to provide a comprehensive picture of the processes taking place. The adsorption and temperature programmed surface reaction (TPSR) of ethanol is measured and followed by diffuse reflectance infrared spectroscopy (TPSR-IR) and mass spectrometry (TPSR-MS). Periodic Density Functional Theory (DFT) calculations on model systems allow the characterization of the nature of some surface species and intermediates involved.

Experiments

1. Synthesis of the materials

Polycrystalline CeO₂ and two cerium-gallium mixed oxides (Ce to Ga atomic ratio equal to 90:10 and 80:20 at/at, hereafter labelled as Ce₉₀Ga₁₀O_x and Ce₈₀Ga₂₀O_x, respectively), generally termed as CeGaO_x, together with Ga₂O₃ as reference material, were prepared from high purity metal nitrate salts and characterized in previous studies [28–31]. In summary, CeO₂, Ga₂O₃ and CeGaO_x were prepared by precipitation in ammonia solution (pH 8.5) of

the respective nitrates dissolved in water, and ethanol in the case of Ga^{3+} cations alone, followed by washing, drying and calcination at 723 K. The structural analysis by X-ray diffraction (XRD) of a set of Ce–Ga materials in a wide range of compositions (Ce/Ga atomic ratio = 95/5, 90/10, 80/20, and 75/25) [29, 31] together with nanostructural and chemical composition analyses by high-resolution electron microscopy (HREM) and energy dispersive spectroscopy (EDS), respectively, on the $\text{Ce}_{95}\text{Ga}_{05}\text{O}_x$ and $\text{Ce}_{80}\text{Ga}_{20}\text{O}_x$ samples, allowed us to verify that it is possible to incorporate homogeneously Ga^{3+} cations to the fluorite-type structure of ceria [31].

Table 1 summarizes the most relevant features of those oxides for this study, that is, gallium content, surface area by Brunauer-Emmett-Teller method, oxygen storage capacity, reducibility by temperature-programmed CO reduction (see relative CO uptake) and adsorption of ethanol.

Table 1. Characterization of the oxides^a.

Sample	Ga^b	$\text{Ga}:(\text{Ce}+\text{Ga})^c$	S_{BET}^d	OSC ^e	Relative CO uptake ^f	Ethanol uptake ^g
	% w/w	% at/at	m^2/g	$\mu\text{mol O/g}$	$A_{\text{sample}}/A_{\text{CeO}_2}$	$\mu\text{mol C}_2\text{H}_5\text{OH}/\text{m}^2$
CeO_2	0	-	58	50	1	4.0
$\text{Ce}_{90}\text{Ga}_{10}\text{O}_x$	4.3	10	108	261	2.5	4.2
$\text{Ce}_{80}\text{Ga}_{20}\text{O}_x$	8.9	19	100	475	3.7	4.2
Ga_2O_3	100	-	76	-	0.3	3.9

^a The samples were previously pretreated as described in section 2.

^b X-ray fluorescence spectroscopy.

^c Atomic surface ratio by X-ray photoelectron spectroscopy (XPS).

^d Brunauer-Emmett-Teller (BET) surface area.

^e Oxygen storage capacity (OSC), by temperature gravimetric analysis (TGA) in H_2 at 200 °C (see Figure S1 in SI).

^f Temperature-programmed reduction (TPR) in 5%CO/He from 100 to 400 °C by mass spectrometry. A: integrated area of the CO traces (see Figure S2 in SI).

^g Mass Spectrometry (MS) at 100 °C in ethanol (2.3% v/v)/He (see text). Estimated error: $\pm 0.1 \mu\text{mol}/\text{m}^2$ (see Figure S3 in SI).

The cobalt catalysts were prepared on pure CeO_2 and $\text{Ce}_{90}\text{Ga}_{10}\text{O}_x$ by wet impregnation from an aqueous solution of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, in order to obtain a low Co loading (0.9 atom of Co/nm^2 , that is, 0.5 % w/w Co/CeO_2 and 1.0 % w/w $\text{Co}/\text{Ce}_{90}\text{Ga}_{10}\text{O}_x$). XRD patterns and S_{BET}

surface area of the catalysts were identical to those of the bare supports, indicating that Co particles were well dispersed and that the morphology of the support was not affected by Co incorporation.

2. Catalytic tests

Ceria and gallium-doped ceria samples were tested under ethanol steam reforming conditions. Each sample was diluted with quartz (1:4 w/w), placed in a quartz microreactor and then, subjected to a cleaning pretreatment, as follows: 1) heating under pure H₂ flow to 450 °C (15 min); 2) purge with He at 450 °C (15 min); 3) oxidation with O₂ at 450 °C (15 min); 4) cooling under O₂ flow to 100 °C; and 5) purge with He at 100 °C (15 min). The catalytic test was run with a mixture of water and ethanol diluted in Ar (H₂O:C₂H₅OH:Ar = 8.8:1.5:89.7 molar ratio, that is, H₂O:C₂H₅OH = 6:1). The catalytic performance was measured from 200 to 500 °C (100 °C steps, 1h at each temperature) using two gas chromatograph Shimadzu GC-9A equipped with a Porapak QS and Carbosieve SII, and TCD and FID detectors for the quantification of C₂H₅OH, H₂, CO, CO₂, CH₄, C₂H₄ (ethylene), C₂H₄O (acetaldehyde), CH₃COCH₃ (acetone), CH₃CHOHCH₃ (2-propanol). The weight hourly space velocity was 1.7 and 3.3 h⁻¹ for CeO₂ and CeGaO_x, respectively, in order to keep constant the residence time normalized per surface area of the oxides (1550 m²_{sample}·h/mol ethanol). Conversion of ethanol (X_{C₂H₅OH}), yield to H₂ (Yield_{H₂}) and yield to carbon-containing compounds (Yield_i) were calculated (for details see Supporting Information). For 100% conversion of ethanol, the based-carbon selectivity to the i-product is equivalent to the Yield_i.

3. Temperature programmed surface reaction of ethanol

Two kinds of temperature-programmed surface reaction (TPSR) studies of adsorbed ethanol were carried out to follow the adsorbed and gaseous-phase evolved species, by infrared (IR) and mass spectrometry (MS), respectively, as follows:

3.1. TPSR by diffuse reflectance infrared Fourier Transform spectroscopy (TPSR-IR)

100 mg of each oxide were loaded in a high temperature Harrick DRIFT cell with ZnSe windows mounted in a FTIR Nicolet 8700 spectrometer (MCT detector). Before the alcohol adsorption, the samples were subjected to the same cleaning procedure described above. Then, a gas stream containing 2.3% v/v of ethanol in He was admitted in the DRIFT cell at 100 °C (15 min), and afterwards purged with He to eliminate the ethanol excess (15 min, 100 °C). Finally, the cell was heated until 450 °C (5 °C/min) under He flow. In all cases the gas flow was 50 cm³/min. The IR spectra were taken consecutively by averaging 25 scans (acquisition time = 30 s) and with a resolution equal to 4 cm⁻¹.

3.2. TPSR by mass spectrometry (TPSR-MS)

A sample amount equivalent to 10 m² of oxide, diluted with quartz, was loaded on a U shaped microreactor coupled with a mass spectrometer (Balzers QMG 112A) and the same cleaning treatment, adsorption and TPSR of ethanol protocols were carried out, as detailed in the previous TPSR-IR experiment. During the TPSR-MS, the following species were scanned at the outlet of the reactor: H₂, He, N₂, CH₄, H₂O, ethylene, CO, acetaldehyde, ethanol, O₂, CO₂, acetone, diethyl ether, acetic acid and ethyl acetate (m/e = 2, 4, 14, 16, 18, 27, 28, 29, 31, 32, 44, 58, 59, 60 and 61 amu, respectively). The amount of adsorbed ethanol (ethanol uptake) on the oxides was determined at 100 °C after switching a 4-way valve from pure He to the 2.3% v/v ethanol stream (diluted in He) and Ar (tracer, 5 cm³/min). The total ethanol uptake (Q) was determined by taking the integral of the difference between the trace of the adsorbate during the adsorption experiment and the trace of Ar, for a given gas molar flow rate of the adsorbate and weight of sample, from 0 to 30 min.

Immediately after each TPSR-MS experiment, a temperature-programmed oxidation (TPO) test was run to investigate the carbonaceous species remaining after the ethanol decomposition study, as described: the TPSR-MS sample was cooled down in He and heated to 450 °C under pure O₂ flow (10 °C/min); the evolution of the same MS signals as mentioned above were followed, but only CO₂ was detected.

To ensure that in both types of TPSR experimental setups, with IR and MS detection, both temperature and fluid dynamics were comparable, a thermocouple was inserted in the catalyst bed in order to monitor the temperature of the sample at all times with the dimensions of both sample beds being similar.

Theoretical Models and Computational Methods

All electronic structure and vibrational calculations were carried out using the spin-polarized DFT approach as implemented in the Vienna ab initio simulation package (VASP) {vasp site, <http://www.vasp.at>; version vasp.5.3.5}[32]. Ce (4f, 5s, 5p, 5d, 6s), O (2s, 2p), Ga (3d, 4s, 4p), C (2s, 2p), and H (1s) electrons were explicitly treated as valence ones within the projector augmented wave (PAW) method [33], with a plane-wave cutoff energy of 600 eV, whereas the remaining electrons were considered as part of the atomic core.

The total energies, vibrational frequencies and forces were calculated with an accuracy of 10⁻⁸ eV and 10⁻² eV/Å for electronic and force convergence, respectively, within the DFT+U approach by Dudarev et al. [34] ($U_{\text{eff}} = U - J = 4.5$ eV for the Ce 4f electrons) with the generalized gradient approximation (GGA) proposed by Perdew, Burke, and Ernzerhof (PBE) [35]. Long-range dispersion corrections were also considered employing the so-called DFT-DF2 approach (optB88-vdW) [36], as implemented in VASP by Klimeš et al. [37,38], using the algorithm of Román-Pérez and Soler [39].

The 3×3 (111) termination of the fluorite CeO₂ structure was chosen as model. A six atomic layer slab (two O–Ce–O trilayers) with the calculated ceria bulk equilibrium lattice

constant of 5.485 Å was used, one trilayer was allowed to relax with the surface unit cell kept fixed during geometry optimization. The gallium-containing slab was modeled by replacing one surface cerium ion (Ce⁴⁺) by a gallium one (Ga³⁺) plus one hydrogen atom to keep charge neutrality. The composition of the slabs was Ce₁₈O₃₆ for pure ceria and Ce₁₇GaO₃₆H for gallium-doped ceria. In addition, corresponding hydroxylated surface models were also created by adding a dissociated water molecule, resulting in slabs with the Ce₁₈O₃₇H₂ and Ce₁₇GaO₃₇H₃ compositions. Selected calculations were performed for nine atomic layer slabs (three O–Ce–O trilayers) in order to evaluate a possible influence of the thickness of the model in the calculated properties such as the ethanol adsorption energy and its vibrational frequency (cf. Table S1 and S2).

The adsorption energy of the dissociatively chemisorbed ethanol was calculated according to the following equation for the example of the hydroxylated undoped CeO₂(111) surface:

$$E_{\text{ads}} = E[(\text{C}_2\text{H}_5\text{O}+\text{H})/\text{Ce}_{18}\text{O}_{37}\text{H}_2] - E[\text{Ce}_{18}\text{O}_{37}\text{H}_2] - E[\text{C}_2\text{H}_5\text{OH}_{\text{gas}}] \quad (1),$$

where $E[(\text{C}_2\text{H}_5\text{O}+\text{H})/\text{Ce}_{18}\text{O}_{37}\text{H}_2]$ is the total energy of the ethoxy species and hydrogen co-adsorbed on the surface, $E[\text{Ce}_{18}\text{O}_{37}\text{H}_2]$ is the total energy of the surface without the adsorbate, and $E[\text{C}_2\text{H}_5\text{OH}_{\text{gas}}]$ is the energy of the gas phase ethanol molecule. The same definition was used for the corresponding hydroxylated Ga-doped surface (Ce₁₇GaO₃₇H₃ slab).

Monkhorst–Pack grids with a (2 × 2 × 1) k-point sampling were used. For the ethanol gas-phase species, a Γ -point calculation in a 20 × 19 × 18 Å³ box was performed.

The computed IR vibrational frequencies have been calculated by diagonalizing the Hessian matrix. The elements of the Hessian matrix were obtained from finite differences of the DFT+U forces with small displacements of all of the atoms of the chemisorbed species. The theoretical frequencies were scaled following the procedure described by Merrick et al. [40] minimizing by least-squares the residual:

$$\Delta = \sum_i^{all} (\lambda \omega_i^{theor} - \nu_i^{exp})^2 \quad (2)$$

where ω_i^{theor} and ν_i^{exp} are the i th theoretical harmonic frequency and the i th experimental frequency (in cm^{-1}) of ethanol in gas-phase in the 800 – 1200 cm^{-1} range. The experimental data were obtained from the NIST database (<https://cccbdb.nist.gov/>). The minimization of equation (1) leads to:

$$\lambda = \sum_i^{all} \omega_i^{theor} \nu_i^{exp} / \sum_i^{all} (\omega_i^{theor})^2 \quad (3)$$

The optimized scale factor λ was then used to calculate an overall root-mean-square error, rms_{ov} :

$$\text{rms}_{ov} = \left(\sum_1^{n_{mol}} \Delta_{min} / n_{mol} \right)^{1/2} \quad (4)$$

where n_{mol} is the number of modes and $\Delta_{min} = (\lambda \omega_i^{theor} - \nu_i^{exp})^2$. With this procedure the scale factor obtained and applied to the DFT frequencies values was $\lambda = 1.021$ with $\text{rms}_{ov} = 5 \text{ cm}^{-1}$ (cf. Table S3 for experimental and calculated frequencies for ethanol in the gas phase).

Results and Discussion

1. Steam reforming of ethanol on CeO_2 and CeGaO_x

Both CeO_2 and $\text{Ce}_{90}\text{Ga}_{10}\text{O}_x$ were active for ethanol conversion over 300 °C, reaching 100 % conversion at 500 °C, and being the gallium-doped oxide more active than pure ceria (Figure 1a).

The product distribution varied significantly between both samples, keeping the same features at each temperature. At 500 °C, the yield to H_2 was 2.5-fold higher on CeGaO_x than on CeO_2 , and consistently the yield to CO_2 followed the same trend (Figure 1b). However, the $\text{H}_2:\text{CO}_2$ molar ratio at the reactor outlet was equal to 3.1 and 2.4 (see molar fractions in Supporting Information), respectively, which is a clear indication that the cerium-gallium

mixed oxide is a better ESR material since that ratio is closer to the theoretical value ($H_2:CO_2 = 3$).

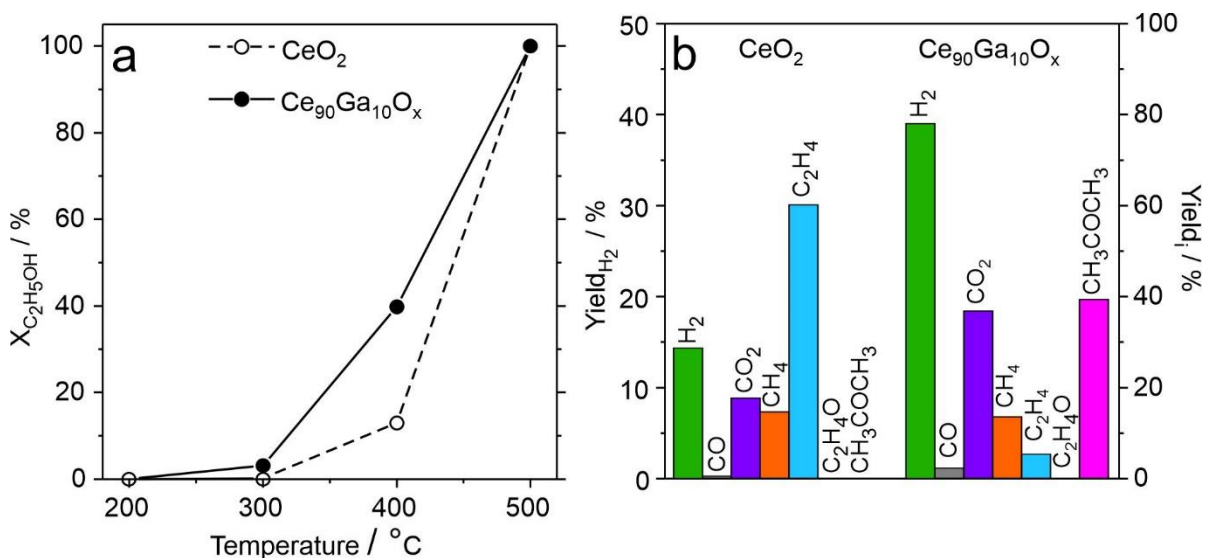


Figure 1. (a) Ethanol conversion vs. temperature (200-500 °C) and, (b) product yield at 500 °C under ESR conditions ($H_2O:C_2H_5OH=6:1$, $1550 \text{ m}^2\cdot\text{h}/\text{molC}_2\text{H}_5\text{OH}$) for CeO_2 and $Ce_{90}Ga_{10}O_x$. Carbon balance: 93 and 97% for CeO_2 and $Ce_{90}Ga_{10}O_x$, respectively at 500 °C.

Also, the yields to ethylene and acetone were remarkably different: While CeO_2 was able to convert the 60 % of ethanol to ethylene (C_2H_4), the $Ce_{90}Ga_{10}O_x$ produced less than 5 % of this product. On the contrary, the yield to acetone (CH_3COCH_3) was 40 % on $Ce_{90}Ga_{10}O_x$ and only traces were detected on pure ceria. Some methane (approximately 14 %) and small amounts of carbon monoxide (lower than 2 %) were also produced by both oxides.

Thus, gallium addition to ceria definitely improves the ESR capacity of pure ceria, which is consistent with the higher redox capacity (OSC and relative CO uptake, see Table 1) of the cerium-gallium mixed oxides. Additionally, the noticeable production of ethylene, a coke precursor [3–5,21], decreased by the incorporation of gallium to the pure CeO_2 whereas the basicity of the CeO_2 slightly decreased with the addition of gallium up to $Ga/Ce= 20/80$ atomic ratio [28,41]. To explain these disparate chemical behaviors, and to understand the

plausible impact on the ERS reaction performance on both kinds of oxides, it is reasonable to study –first– the adsorption and decomposition of ethanol over the surface of pure ceria and cerium-gallium mixed oxides.

2. Adsorption of ethanol on CeO_2 and $CeGaO_x$

The adsorption of ethanol gave rise to a number of bands assigned to ethoxy (C_2H_5O) species, together with the partial consumption of hydroxyl groups (negative bands at 3710, 3685 and 3660 cm^{-1}) characteristic of the dissociative chemisorption of ethanol on hydroxylated oxide surfaces (Figure 2a) [42,43]. The detailed assignment of each IR bands is reported in Table 2 for all the samples studied in this work.

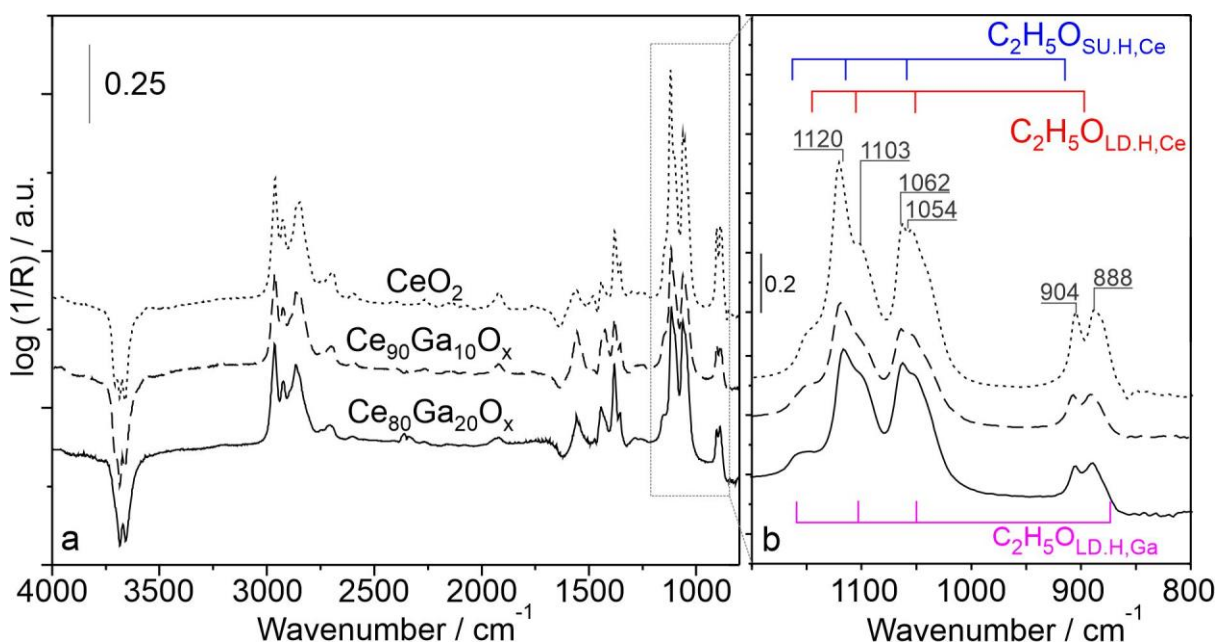


Figure 2. (a) DRIFT spectra for CeO_2 , $Ce_{90}Ga_{10}O_x$ and $Ce_{80}Ga_{20}O_x$ after ethanol adsorption at 100 °C and purging with He (the spectrum of the clean oxide right before the adsorption was subtracted). (b) Details of the 1200-800 cm^{-1} region of the spectra and the calculated scaled frequencies values for $C_2H_5O_{LD,H,Ce}$ (red lines), $C_2H_5O_{SU,H,Ce}$ (blue lines) and $C_2H_5O_{SU,H,Ga}$ (magenta lines), see text.

The main bands associated to C_2H_5O species on pure CeO_2 can be identified in three regions of the spectra. In the region from 3000 to 2700 cm^{-1} , a number of overlapping IR bands can be detected corresponding to the C–H bond stretching (ν) modes of ethoxy species. Second, the peaks assigned to the deformation (δ) of the C–H bonds of C_2H_5O species can be found between $1800 - 1200\text{ cm}^{-1}$. Finally, in the region from 1200 to 800 cm^{-1} , a series of overlapping bands can be detected corresponding to the (CO) and (CCO) modes. These bands usually provide information on the coordination of alkoxy species on the surface of oxides [44,45]. They are decisive to explain the reactivity of the alcohols.

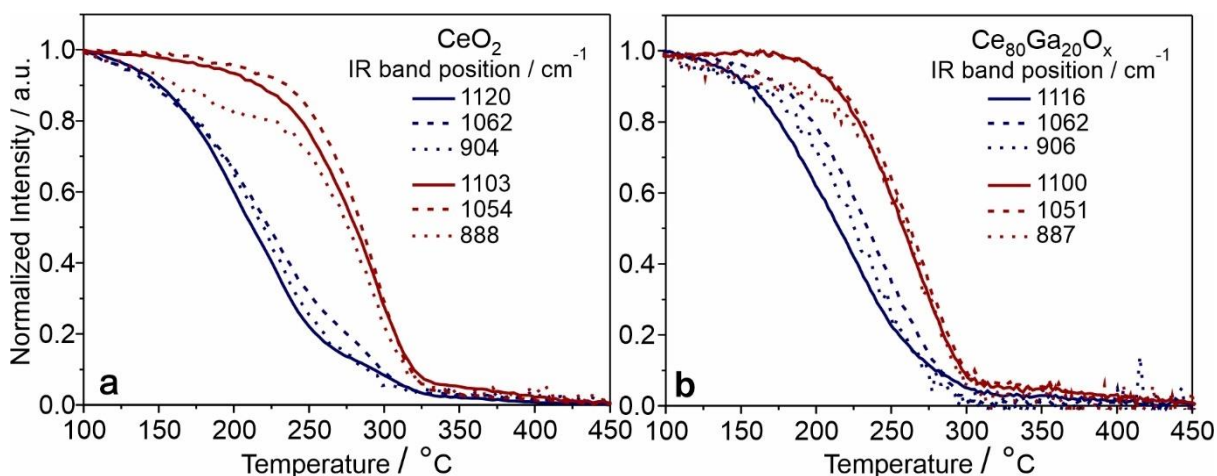


Figure 3. Normalized integrated intensity of the ethoxy DRIFT signals detected in the $1200 - 800\text{ cm}^{-1}$ region of the spectra during the TPSR-IR for CeO_2 (a) and $Ce_{80}Ga_{20}O_x$ (b).

It is worth mentioning that in the case of pure ceria, a number of bands were identified at 1150 , 1120 , 1103 , 1062 , 1054 , 904 and 888 cm^{-1} which resemble doublets (with the exception of the first one, Figure 2b). The thermal evolution of these bands during the TPSR-IR experiments clearly showed that the intensities of the signals at 1103 , 1054 and 888 cm^{-1} decreases more slowly than those of the peaks at 1120 , 1062 and 904 cm^{-1} . The evolution of the normalized integrated intensity of those sets of IR signals is depicted in Figure 3a. These two sets of bands could originate from two types of ethoxy species adsorbed on the CeO_2 surface (generically labeled as type 1 and 2): one more stable species (type 1) and another

one more labile species (type 2). Here, it is important to point out that the adsorption and activation of ethanol was studied on a fully oxidized sample, since the final step of the cleaning pretreatment involves oxidizing the sample under pure O₂ at 450°C (see experimental section). In other words, the ethoxy species detected by IR spectroscopy are adsorbed on Ce⁴⁺ cations, and accordingly, the 2130 cm⁻¹ Ce³⁺ IR signal was not detected before or after ethanol adsorption at 100°C.

Due to the different thermal stability, and in line with the reactivity of surface methoxy groups [45], it is tempting to assign the first set of bands (type 1) to bidentate ethoxy species, whereas the second set (type 2) would correspond to monodentate ethoxy ones. Such an assignment would partially contradict that by Yee et al. [46], who suggested that peaks at 1107 and 1057 cm⁻¹ may be caused by mono and bidentate ethoxy species, respectively, after the adsorption of ethanol at 25 °C on their ceria powder samples. The assignment of those vibrational frequencies is certainly more complex than it appears. Li et al. [47] studied the adsorption of ethanol on differently shaped CeO₂ nanoparticles (25°C) that preferentially exhibited specific crystallographic planes: (111) for nanooctahedra, (100) for nanocubes, and a mixture of facets for nanorods. The ceria nanooctahedra developed bands at 1096, 1050 and 885 cm⁻¹, whereas in the case of the nanocubes and nanorods, two additional bands were also detected at 1120 and 905 cm⁻¹. Also, in a recent DFT study, Beste and Overbury [48] suggested that on CeO₂(111) only monodentate ethoxy (on-top) is a stable surface species. However, two of such configurations were proposed to coexist, where ethoxy can be characterized as either standing-up (with the C–C axis perpendicular to the surface) or lying-down (with the C–C axis parallel to the surface). On CeO₂(100), on the other hand, ethoxy species are also predicted to be adsorbed in a bidentate form in addition to the on-top species [48]. Then, for a more accurate assignment of these bands, a combination of our experimental results with theoretical calculations is required.

Table 2. Experimental and calculated infrared frequencies (cm^{-1}) together with surface species and mode assignments during the adsorption and TPSR of ethanol on CeO_2 and CeGaO_x samples.

Species	Vibrational mode	Experimental			Calculated			
		CeO_2	$\text{Ce}_{90}\text{Ga}_{10}\text{O}_x$	$\text{Ce}_{80}\text{Ga}_{20}\text{O}_x$	$\text{C}_2\text{H}_5\text{O}_{\text{SU.H,Ce}}^a$	$\text{C}_2\text{H}_5\text{O}_{\text{LD.H,Ce}}^b$	$\text{C}_2\text{H}_5\text{O}_{\text{LD.H,Ga}}^c$	
Ethoxy ($\text{C}_2\text{H}_5\text{O}$)	$\nu_{\text{as}}(\text{CH}_3)$	2962	2962	2967				
	$\nu_{\text{as}}(\text{CH}_2)$	2926	2925	2923				
	$\nu_{\text{s}}(\text{CH}_3)$	2862	2864	2867				
	$\nu_{\text{s}}(\text{CH}_2)$	2845	2847	2848				
	$\delta(\text{CH}_2)+\text{FR}$	2690	2704	2696				
	$\delta(\text{CH}_2)$	1480	1480	1475				
	$\delta_{\text{as}}(\text{CH}_3)$	1442	1442	1443				
	$\delta_{\text{s}}(\text{CH}_3)$	1380	1380	1382				
	$\omega(\text{CH}_2)$	1354	1354	1354				
	$\tau(\text{CCO})$	1150	1152	1155	1163	1146	1158	
	$\nu(\text{CO})$	1120	1118	1116	1114			
			1103	1100	1100	1105	1103	
		$\nu_{\text{as}}(\text{CCO})$	1062	1063	1062	1058		
			1054	1052	1051		1051	1050
		$\nu_{\text{s}}(\text{CCO})$	904	904	906	914		
		888	888	887		896	874	
Acetate ($\text{C}_2\text{H}_3\text{O}_2$)	$\nu_{\text{as}}(\text{OCO})$	1550	1558	1557				
	$\nu_{\text{s}}(\text{OCO})$	1426	1423	1430				
Ce^{3+}	Forbidden electronic Transition, $^2\text{F}_{5/2} \rightarrow ^2\text{F}_{7/2}$	2112	2123	2123				
Gallium hydride	$\nu(\text{GaH})$	-	1955 w	1940 w				

^a“standing-up” ethoxy species stabilized by a O-Ce bond and two hydrogen bonds ($\text{C}_2\text{H}_5\text{O}_{\text{SU.H,Ce}}$), Figure 4b.

^b“lying-down” ethoxy species stabilized by a O-Ce bond and two hydrogen bonds ($\text{C}_2\text{H}_5\text{O}_{\text{LD.H,Ce}}$), Figure 4a.

^c“lying-down” ethoxy species stabilized by a O-Ga bond and two hydrogen bonds ($\text{C}_2\text{H}_5\text{O}_{\text{LD.H,Ga}}$), Figure 4c.

As our polycrystalline CeO₂ samples could exhibit a mixture of different crystallographic planes, we have run additional experiments of ethanol adsorption on CeO₂ nanooctahedra and nanocubes, that preferentially exhibit the (111) and (100) planes, respectively. The results show the fingerprint of ethoxy species, in the 1200-800 cm⁻¹ of the spectra, and the one for CeO₂ nanooctahedra (dominated by (111) surfaces) resembles that of our polycrystalline CeO₂ sample (Figure S5). Thus, in an effort to interpret our experimental results we have here investigated the adsorption of ethoxy species with different coordination on (111) oriented CeO₂ surfaces by DFT-based calculations. Previously, some of us showed that the (111) orientation enabled the assignment of observed infrared bands upon adsorption and decomposition of methanol over ceria powders to distinct surface formate species and that the presence of hydroxyl groups could not be ignored when considering the stability of those species [49]. Thus, here we specifically consider monodentate ethoxy species with different adsorption sites for the hydrogen atom resulting from the O–H bond cleavage of ethanol on the hydroxylated ceria surface (Ce₁₈O₃₇H₂ slab), for which all the positions neighboring the ethoxy groups were tested for the adsorption of the OH and H species of the added water molecule to the clean surface (Ce₁₈O₃₆ slab). For the results of the dissociative adsorption of ethanol on the non-hydroxylated CeO₂(111) surface, and the vibrational frequencies of the ethoxy species, see the Supporting Information.

The DFT+U+DF2 results indicate that stable ethoxy species can have the alkyl chain parallel or perpendicular to the surface normal (Figures 4a and b). We name these ethoxy states as “standing-up” (SU), C₂H₅O_{SU,H}, and “lying-down” (LD), C₂H₅O_{LD,H}, respectively. They are stabilized on the surface by the O–Ce bond and two hydrogen bonds. The two states have similar chemisorption energies (–1.12 and –1.08 eV for the C₂H₅O_{LD,H,Ce} and C₂H₅O_{SU,H,Ce} species, respectively, with respect to ethanol and the hydroxylated CeO₂

surface), but the stability of the $C_2H_5O_{SU}$ -type species is somewhat more pronounced when the surface is

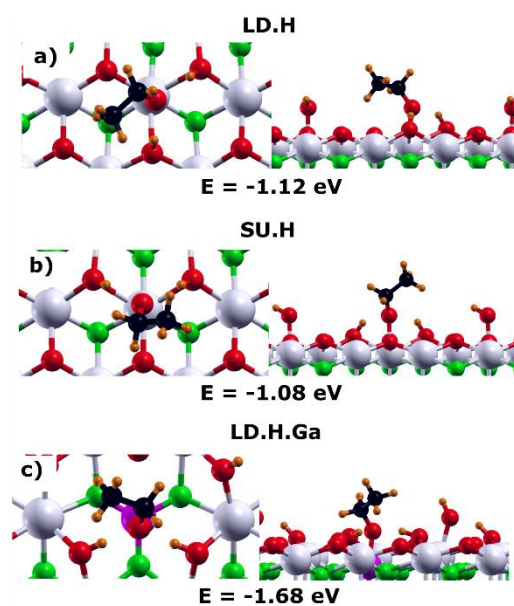


Figure 4. Top and side views of adsorbed ethoxy species with a co-adsorbed dissociated water molecule: a) monodentate $C_2H_5O_{LD,H}$, b) monodentate $C_2H_5O_{SU,H}$ and c) monodentate $C_2H_5O_{LD,Ga}$, for the $Ce_{18}O_{37}H_2$ (a-b) and $Ce_{17}GaO_{37}H_3$ (c) slabs. Color code: Ce atoms, white; O atoms of the first CeO_2 layer and belonging to the ethoxy species, red; O atoms of the second CeO_2 layer, green; C atoms, black, H atoms, orange and Ga atom in purple. The ethanol adsorption energies are calculated with respect to ethanol in the gas-phase and the hydroxylated surfaces (cf. Eq. 1).

hydroxylated than when is not (cf. Table S1). The calculation of the scaled frequencies for these species gives the following values: $\nu(CO)_{LD,H,Ce}$ $1105\text{ cm}^{-1} < \nu(CO)_{SU,H,Ce}$ 1114 cm^{-1} , $\nu_{as}(CCO)_{LD,H,Ce}$ $1051\text{ cm}^{-1} < \nu_{as}(CCO)_{SU,H,Ce}$ 1058 cm^{-1} , and $\nu_s(CCO)_{LD,H,Ce}$ $896\text{ cm}^{-1} < \nu_s(CCO)_{SU,H,Ce}$ 914 cm^{-1} , which are superimposed to the IR spectrum for CeO_2 at $100\text{ }^\circ\text{C}$ in Figure 2b. As can be seen, the calculated frequencies not only describe the splitting of the bands corresponding to the CO, asymmetric and symmetric CCO stretching vibrations, but also predict that the frequencies of the somewhat more stable $C_2H_5O_{LD,H,Ce}$ species appear at

lower wavenumbers than the corresponding ones for the less stable $C_2H_5O_{SU,H,Ce}$ groups, for all three stretching modes [that is, $\nu(j\text{-mode})_{LD,H,Ce} < \nu(j\text{-mode})_{SU,H,Ce}$]. The results of the selected test calculations performed employing a thicker (three O–Ce–O trilayers) slab (cf. Table S1 and S2), show a variation of the $C_2H_5O_{LD,H,Ce}$ and $C_2H_5O_{SU,H,Ce}$ binding energies of less than 4 meV, and of the vibrational frequencies of less than 5 cm^{-1} , where the relative stabilities and the $\nu_{LD,H,Ce} < \nu_{SU,H,Ce}$ ordering of the $\nu(CO)$, $\nu_{as}(CCO)$, and $\nu_s(CCO)$ frequencies are preserved.

Given the agreement between the theoretical predictions and the experimental results, we propose that the “lying-down” ethoxy ($C_2H_5O_{LD,H,Ce}$) is the one that decomposes more slowly than the “standing-up” one ($C_2H_5O_{SU,H,Ce}$), that is, those formerly labeled as type 1 and 2, respectively. The previously calculated barriers for the formation of acetaldehyde through H–C scission from the LD and SU ethoxy species on the $CeO_2(111)$ surface [48], provide support to our proposal, since a larger energy barrier was found for the formation of acetaldehyde through β -H–C scission in the case of the LD species (2.08 eV) as compared to the barrier for the process through α -H–C scission in the case of the SU ethoxy species (1.11 eV). It is important to note that the here reported theoretical calculations predict OH groups to have a decisive impact on the adsorbed ethoxy species (see Supporting Information), similar as previously reported for formate on ceria [49].

For the ceria-gallia $Ce_{90}Ga_{10}O_x$ and $Ce_{80}Ga_{20}O_x$ systems, similar DRIFT spectra to those of pure ceria after adsorption of ethanol at $100\text{ }^\circ\text{C}$ were observed (Figure 2), with three double peaks in the $1200 - 800\text{ cm}^{-1}$ region of the spectra. Specifically, the same types of IR bands associated with ethoxy species were detected as in the case of CeO_2 (Table 2), and the ethanol uptake calculated from the adsorption curves acquired by mass spectrometry was approximately $4\text{ }\mu\text{mol EtOH/m}^2$ for the whole set of $Ce(Ga)O_x$ samples (Table 1). Again, two types of ethoxy species can be anticipated from the normalized integrated intensity of the

ethoxy bands collected during the TPSR-IR (Figure 3b). The evolution of the two sets of ethoxy bands were practically identical for the $\text{Ce}_{90}\text{Ga}_{10}\text{O}_x$ and $\text{Ce}_{80}\text{Ga}_{20}\text{O}_x$ samples (cf. Figure 3b and Figure S8, for $\text{Ce}_{80}\text{Ga}_{20}\text{O}_x$ and $\text{Ce}_{90}\text{Ga}_{10}\text{O}_x$, respectively). However, the rate of decomposition of the “more stable” type of ethoxy species is faster in the gallium-doped materials compared to pure ceria (cf. Figure 3a and 3b).

In order to gain insight into the effects of gallium incorporation on the IR bands associated with ethoxy species, we have investigated the $\text{Ce}_{17}\text{GaO}_{37}\text{H}_3$ slab model. On this gallium-doped ceria surface, ethanol still dissociates upon adsorption with the ethoxy species in monodentate form on top of the Ga atom, either “standing-up” or “lying-down” species (namely, $\text{C}_2\text{H}_5\text{O}_{\text{SU,H,Ga}}$ or $\text{C}_2\text{H}_5\text{O}_{\text{LD,H,Ga}}$, respectively, see Figure S9). However, the “lying-down” state is by 0.17 eV more stable than the “standing-up” one (Figure S9 and Table S1), and thus, a strongly preferred population of surface Ga sites by lying down ethoxy species is expected. For the remaining surface Ce sites, since the $\text{C}_2\text{H}_5\text{O}_{\text{LD,H,Ce}}$ state is only by 0.04 eV more stable than the $\text{C}_2\text{H}_5\text{O}_{\text{SU,H,Ce}}$ one (Table S1), as mentioned above, the presence of both types of ethoxy species is likely to occur. Thus, upon gallium-doping, Ga sites will be occupied by $\text{C}_2\text{H}_5\text{O}_{\text{LD,H,Ga}}$ species and the remaining Ce sites with $\text{C}_2\text{H}_5\text{O}_{\text{LD,H,Ce}}$ and $\text{C}_2\text{H}_5\text{O}_{\text{SU,H,Ce}}$ ones.

The calculated (scaled) frequency values for $\text{C}_2\text{H}_5\text{O}_{\text{LD,H,Ga}}$ are: $\tau(\text{CCO}) = 1158 \text{ cm}^{-1}$, $\nu(\text{CO}) = 1103 \text{ cm}^{-1}$, $\nu_{\text{as}}(\text{CCO}) = 1050 \text{ cm}^{-1}$, and $\nu_{\text{s}}(\text{CCO}) = 874 \text{ cm}^{-1}$. Figure 2b shows the calculated frequencies for the $\text{C}_2\text{H}_5\text{O}_{\text{LD,H,Ce}}$, $\text{C}_2\text{H}_5\text{O}_{\text{SU,H,Ce}}$ and $\text{C}_2\text{H}_5\text{O}_{\text{LD,H,Ga}}$ superimposed with the IR spectra of chemisorbed ethanol on $\text{Ce}_{80}\text{Ga}_{20}\text{O}_x$ at 100 °C. After Ga doping, the DRIFT spectra show vibrations at frequencies which are either blue or red shifted with respect to those observed for the pure ceria by at most 5 cm^{-1} (Table 2). In the $1120 - 1100 \text{ cm}^{-1}$ region, a double peak is again observed (Figure 2b) where, according to the calculations (Table 2), the peak at 1116 cm^{-1} is attributed to the CO stretching mode [$\nu(\text{CO})$] of the $\text{C}_2\text{H}_5\text{O}_{\text{SU,H,Ce}}$

species (1114 cm^{-1}) and that at 1100 cm^{-1} to the same mode of the $\text{C}_2\text{H}_5\text{O}_{\text{LD,H,Ce}}$ plus $\text{C}_2\text{H}_5\text{O}_{\text{LD,H,Ga}}$ species (1105 and 1103 cm^{-1} , respectively).

Furthermore, three bands contribute to the $1060 - 1050\text{ cm}^{-1}$ region, two are assigned to the asymmetric CCO mode [$\nu_{\text{as}}(\text{CCO})$] of the $\text{C}_2\text{H}_5\text{O}_{\text{SU,H,Ce}}$ and $\text{C}_2\text{H}_5\text{O}_{\text{LD,H,Ce}}$ species, calculated at 1058 and 1051 cm^{-1} , respectively, and the third one at 1050 cm^{-1} is due to the same mode but of the $\text{C}_2\text{H}_5\text{O}_{\text{LD,H,Ga}}$ species. The appearance of such an additional band may explain the observed widening of the lower energy band of the double peak in the $1060 - 1050\text{ cm}^{-1}$ range upon gallium doping (Figures 2b).

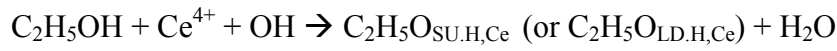
Finally, in the $900\text{-}880\text{ cm}^{-1}$ range, the observed peak at 906 cm^{-1} corresponds to the symmetric CCO stretching [$\nu_{\text{s}}(\text{CCO})$] of the $\text{C}_2\text{H}_5\text{O}_{\text{SU,H,Ce}}$ (calculated at 914 cm^{-1}), and that at 887 cm^{-1} to the $\text{C}_2\text{H}_5\text{O}_{\text{LD,H,Ce}}$ plus $\text{C}_2\text{H}_5\text{O}_{\text{LD,H,Ga}}$ species (calculated at 896 and 874 cm^{-1} , respectively (Table 2).

3. *Decomposition of ethanol on CeO_2 and CeGaO_x*

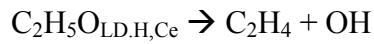
As discussed in the previous section, in the case of pure ceria, ethanol is dissociatively adsorbed at $100\text{ }^\circ\text{C}$ to form monodentate ethoxy species, in “standing up” ($\text{C}_2\text{H}_5\text{O}_{\text{SU,H,Ce}}$) and “lying down” ($\text{C}_2\text{H}_5\text{O}_{\text{LD,H,Ce}}$) configurations, leaving H available on the surface that reacts with surface hydroxyl groups to yield water (Scheme 1, r1). In the case of the CeGaO_x samples, in addition to the formation of $\text{C}_2\text{H}_5\text{O}_{\text{SU,H,Ce}}$ and $\text{C}_2\text{H}_5\text{O}_{\text{LD,H,Ce}}$, ethoxy is also adsorbed on Ga^{3+} cations in its lying-down configuration (Scheme 2, r1 and r2). This dissociative chemisorption of ethanol, followed by water release, is generally accepted as the first step of the mechanism for lineal alcohol chemisorption on oxides [42,43].

After the adsorption of ethanol, the samples were heated under He flow to study the thermal evolution of the species adsorbed on the surface (TPSR-IR) and their gaseous products at the outlet of the reactor (TPSR-MS). The correlation of the TPSR results by

DRIFTS and MS allowed us to propose a mechanism for the reaction of ethanol with the surface of the supports studied in this work (Schemes 1 and 2).



(r1)

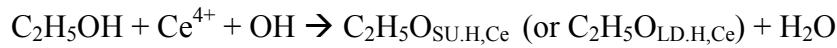


(r4)

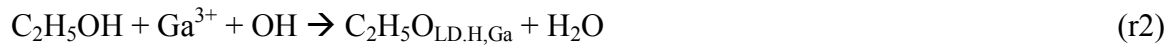


\square : oxygen vacancy

Scheme 1. Mechanism for ethanol adsorption and decomposition on pure CeO₂.



(r1)



(r4)



Scheme 2. Mechanism for ethanol adsorption and decomposition on CeGaO_x.

Figure 5 shows the thermal evolution of the IR spectra and the two-dimensional iso-intensity maps, arising from the decomposition of adsorbed ethoxy species on pure CeO₂ and

Ce₈₀Ga₂₀O_x with increasing temperature (TPSR-IR). The normalized integrated intensity of the most appropriate IR signal (more intense and less overlapped) for each surface species identified during the ethanol TPSR-IR experiments, together with the normalized intensity of the most important products detected during the TPSR-MS are shown in Figure 6 for both samples. Similar results were found for Ce₉₀Ga₁₀O_x (Figure S10). IR traces for both the SU and LD ethoxy species were plotted in all three panels of Figure 6I and 6II in order to facilitate comparison of their rate of decomposition with the thermal evolution of other surface species and products.

3.1. Acetate formation

A clear evidence of the formation of acetate species on CeO₂ above 150 °C is found by the appearance of two bands at 1550 and 1425 cm⁻¹ during the TPSR-IR (Figure 5 Ic, see Table 2). This can be easily observed by the emergence of two red areas in the two-dimensional iso-intensity maps (Figure 5 Ig). The curves of the normalized integrated intensity of the signals at 1120 (C₂H₅O_{SU,H,Ce}) and 1550 (CH₃COO) cm⁻¹ as a function of temperature plotted in Figure 6 Ia, intersect at approximately 50% of conversion (T_{50%} = 215 °C). This is a strong suggestion that C₂H₅O_{SU,H,Ce} species react with surface lattice oxygen of ceria to yield acetate species according to r2 (Scheme 1).

The thermal evolution of C₂H₅O_{SU,H,Ce} in the CeGaO_x samples is identical to pure ceria, suggesting that this type of ethoxy is not affected by the presence of Ga³⁺ and it decomposes according to r3 in Scheme 2 (cf. Figure 6 Ia and IIa). Although a correlation between the decomposition of C₂H₅O_{SU,H,Ce} and the formation of acetate species is also observed on CeGaO_x, the intersection between the thermal evolution of the C₂H₅O_{SU,H,Ce} and acetate species does not take place at 50 % of C₂H₅O_{SU,H,Ce} decomposition, but at a lower value, ~40

% (Figure 6 IIa). Then, there must be another source, besides $C_2H_5O_{SU,H,Ce}$ species, contributing to the formation of acetate species, as explained below.

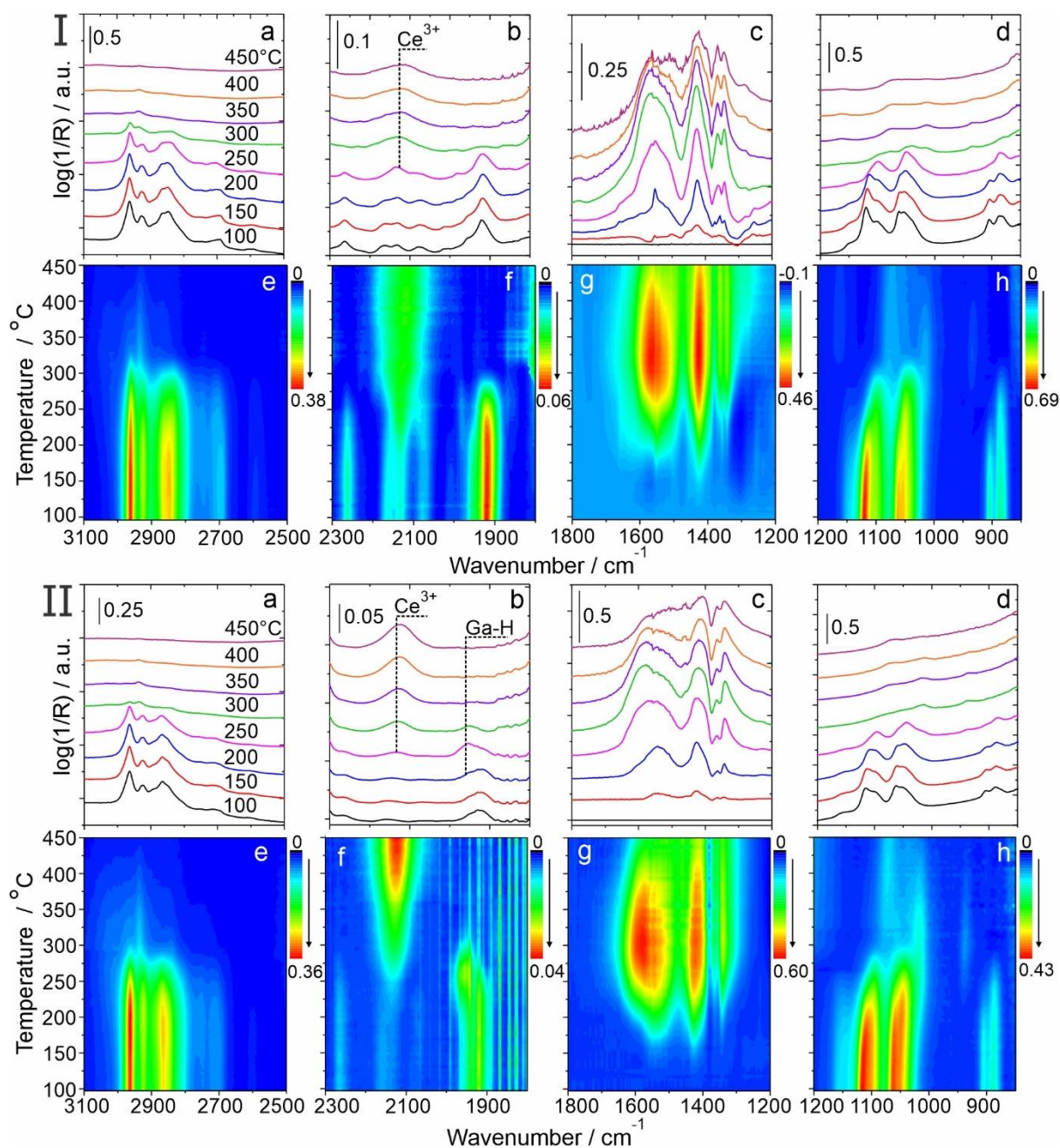


Figure 5. DRIFT spectra (a-d), together with the two-dimensional iso-intensity maps (e-h, bottom panel) collected during the TPSR-IR of ethanol on: I) pure CeO_2 , and II) $Ce_{80}Ga_{20}O_x$ samples.

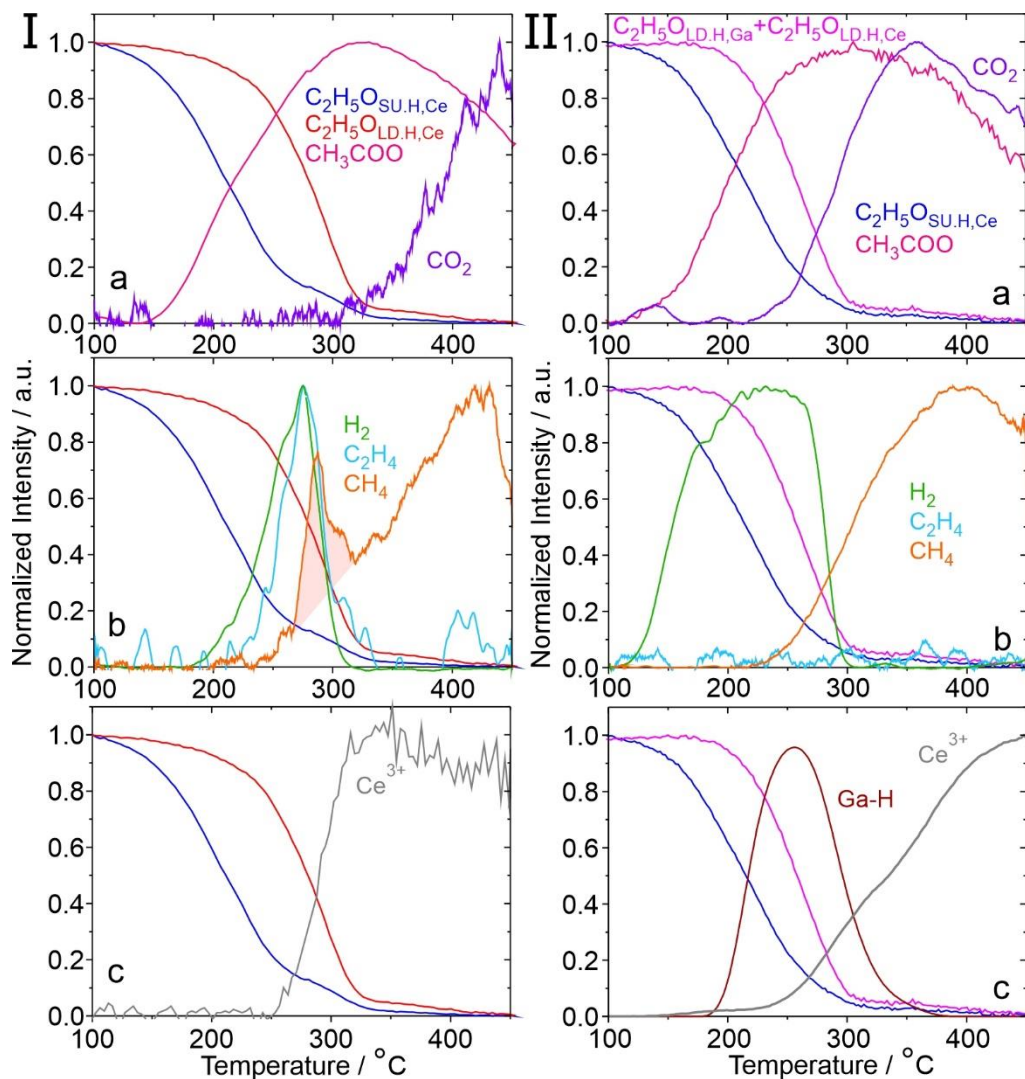


Figure 6. Normalized integrated intensity of the most important DRIFT signals detected during the TPSR-IR and normalized intensity of the gaseous products detected during the TPSR-MS on: I) CeO_2 and II) $\text{Ce}_{80}\text{Ga}_{20}\text{O}_x$ samples.

The evolution of the $\nu_{\text{as}}(\text{CCO})$ band at about 1100 cm^{-1} on CeGaO_x , that is, the simultaneous decomposition of the $\text{C}_2\text{H}_5\text{O}_{\text{LD,H,Ga}}$ and $\text{C}_2\text{H}_5\text{O}_{\text{LD,H,Ce}}$, is faster with respect to that on CeO_2 (which is only due to $\text{C}_2\text{H}_5\text{O}_{\text{LD,H,Ce}}$): 50 % of the intensity drop occurs at 258 and 284 °C (temperature shift of -26°C), respectively (cf. Figure 6 Ia and IIa). Additionally, the formation of acetate species on $\text{Ce}_{80}\text{Ga}_{20}\text{O}_x$, which implies the dehydrogenation/oxidation of ethoxy species, occurs at a higher rate compared to pure ceria ($T_{50\%} = 200\text{ °C}$ vs. 215 °C , respectively –see also Figure 6 Ia and IIa). Thus, it is suggested that both LD ethoxy species,

$C_2H_5O_{LD,H,Ga}$ and $C_2H_5O_{LD,H,Ce}$, on the surface of $CeGaO_x$ would convert by dehydrogenation/oxidation into acetate species, assisted by both the pronounced oxidative capacity of the Ce–O–Ga interface and the ability to form gallium hydride (Scheme 2, r4), as compare to the undoped surface. The observed more facile removal of oxygen from the cerium-gallium mixed oxide with respect to pure ceria (see Table 1) is consistent with the results of DFT calculations [29] and it has been attributed to an important relaxation (an umbrella type displacement of the gallium atom) that takes place after the removal of an oxygen atom at the Ce–O–Ga interface. Moreover, some of us have reported that at the boundary of gallium nanodomains on $CeGaO_x$ samples, H_2 easily dissociates, being the driving-force the formation of surface gallium hydride [30]. Another piece of experimental evidence is the absence of ethylene during the TPSR-MS on the $CeGaO_x$ samples (see for example Figure 6 Iib), which is a clear suggestion that both ethoxy $C_2H_5O_{LD,H,Ga}$ and $C_2H_5O_{LD,H,Ce}$ must lead to the formation of a product other than C_2H_4 (as observed on pure ceria and it is clarified below), that is, acetate species. In line with this suggestion, the evolution of the non-normalized integrated intensity of acetate species during the TPSR-IR (see last panel of Figure S11 in SI) shows that the concentration of acetate species is higher with increasing Ga loading.

3.2. Methane and carbon dioxide formation

On pure CeO_2 , the trace of methane plotted in Figure 6 Ib displays a sharp peak at 287 °C, which is overlapped to a broad desorption peak with a maximum at around 420 °C. This observation suggests that there are at least two sources of methane production. The broad desorption peak of CH_4 at higher temperatures, which somehow parallels the evolution of CO_2 , resembles the opposite trend of acetate decomposition above 250 °C (Figure 6 Ia). This previous observation is an indication that CH_4 together with CO_2 are the main final gaseous

products of C–C bond cleavage of acetate species (Scheme 1, r3). The origin of the sharp peak of methane will be explained later.

Evidence of the reduction of ceria as a consequence of the decomposition of acetate species can be found in Figure 5 Ib and 5 If: a band at 2130 cm^{-1} , assigned to the forbidden electronic transition ${}^2F_{5/2} \rightarrow {}^2F_{7/2}$ of Ce^{3+} cations [29,30,50], was observed above $250\text{ }^\circ\text{C}$. Its intensity increases as the temperature raises to finally level off at $T > 340\text{ }^\circ\text{C}$ (Figure 6 Ic). Thus, the formation of Ce^{3+} is correlated to the decomposition of acetate species: as soon as CH_4 is released, the ceria surface is reduced with the concomitant formation of carbonate species (evidenced by the broadening of the peaks in the region from 1800 to 1200 cm^{-1} , see Figure 5 Ic) [41], which decompose to CO_2 after further heating. The formation of Ce^{3+} cations during acetate decomposition is represented by the oxygen vacancy formation in reaction 3 (Scheme 1). Although some of the oxygen vacancies could be refilled by the nearby oxygen species, the detection of the 2130 cm^{-1} IR band from 250°C to 450°C is a clear indication that the support remains reduced.

On the gallium doped oxides, the decomposition of acetate species begins at lower temperature than on pure ceria. The maximum intensity of acetate traces on $\text{Ce}_{80}\text{Ga}_{20}\text{O}_x$, which also includes the formation of some carbonate species, is reached at $295\text{ }^\circ\text{C}$, that is, $30\text{ }^\circ\text{C}$ lower compared to ceria (cf. Figure 6 Ia and IIa). The decomposition of those acetate species is again clearly related to the formation of CO_2 , CH_4 and Ce^{3+} (Figure 6 IIa-c). However, CO_2 desorbed $100\text{ }^\circ\text{C}$ earlier than in CeO_2 , showing a maximum at $350\text{ }^\circ\text{C}$ (cf. Figures 6 Ia and IIa). Additionally, the ratio of the maximum integrated intensity of the 2130 cm^{-1} IR signal ($I_{\text{Ce}^{3+}}$) which is reached at 450°C , between CeGaO_x and CeO_2 [$I_{\text{Ce}^{3+}(\text{CeGaO}_x)}/I_{\text{Ce}^{3+}(\text{CeO}_2)}$] shows that the amount of Ce^{3+} in the $\text{Ce}_{90}\text{Ga}_{10}\text{O}_x$ and $\text{Ce}_{80}\text{Ga}_{20}\text{O}_x$ samples is 20 and 30 %, respectively, higher than in the undoped CeO_2 one. In accord with this last observation, both OSC and relative CO uptake results (Table 1) show

that Ce-Ga mixed oxides are more reducible than pure ceria, the higher the Ga content, the higher the relative CO uptake, that is, the reducibility of the mixed oxide increases with gallium loading [29]. In agreement, CO₂ release during the TPSR-MS begins at lower temperature on the sample with higher gallium loading ($T_{50} = 300$ vs. 340 °C on Ce₈₀Ga₂₀O_x and Ce₉₀Ga₁₀O_x, respectively). Furthermore, the amount of CO₂ released in the gas phase is also higher as the Ga loading, that is, the acidity of the mixed oxides [41], increases (Figure S11). This observation is consistent with the higher acetate surface concentration mentioned in the previous section.

Thus, it can be concluded that ethoxy oxidation to acetate species near the Ce–O–Ga interface is favored by the higher oxygen mobility of the mixed oxides, leading to CO₂ release at much lower temperature (~50 and 100 °C earlier on Ce₉₀Ga₁₀O_x and Ce₈₀Ga₂₀O_x, respectively, and in accord with the increase in redox properties with increasing gallium loading) compared to pure ceria (Scheme 2, r5). On the other hand, and most likely, acetate species that are far away from the nanodomains of Ga behave as in the case of pure ceria (Scheme1, r3), decomposing at higher temperatures.

3.3. Ethylene and carbon formation

Figure 6 Ib shows that on pure CeO₂, ethylene release was detected between 200 and 330 °C, with a maximum at 275 °C. In the same temperature range, the decrease of LD ethoxy species concentration is observed. In fact, the maximum of ethylene desorption peak matches the 50% depletion of C₂H₅O_{LD,H,Ce} species. Thus, it is proposed that the ethoxy species in LD configuration on pure ceria decompose to yield ethylene in the gas phase and OH species at $T > 200$ °C (Scheme 1, r4). However, ethylene was not detected on the Ce-Ga mixed oxides (Figure 6 IIb and Figure S10 b) and, as suggested before, the LD ethoxy were converted to acetate instead.

A concerted elimination pathway was identified as a plausible pathway that can produce ethylene when ethanol is adsorbed on Lewis acid sites adjacent to a surface O basic site. Overbury and coworkers [47] suggested that on CeO₂ nanoshapes (octahedra, cubes, and rods), ethylene could be produced from a concerted cleavage of β-H–C and C–OH bonds of adsorbed ethanol/ethoxy species (bimolecular elimination, E2). Our TPRS-MS results on CeO₂ are in accord with this mechanism which is related to the basicity of the adjacent O²⁻ site. Conversely, desorption of ethylene was not observed on the CeGaO_x samples. It was previously shown that the basicity of the CeGaO_x mixed oxides is slightly lower than that of pure CeO₂, as measured by CO₂ uptake at 298 K [41]. Then, the lower basicity of the mixed oxide can favor the α-H–C scission vs. β-H–C scission. Additionally, it can be hypothesized that α-H–C scission can be performed by Ga sites, forming Ga–H, and then enhancing the transformation of ethoxy to acetate rather than ethylene.

Finally, polymerization of ethylene may lead to the formation of amorphous carbonaceous deposits [3,21] (some of them are partially hydrogenated, CH_x) on the surface of ceria. Thus, the sharp CH₄ peak detected in the case of pure ceria, which is shifted to higher temperature than the one of C₂H₄ (Figure 6 IIb), could be the product of the hydrogenation of carbon deposited (probably partially hydrogenated) at the surface of ceria by polymerization of ethylene (Scheme 1, r5 and r6). This hypothesis is supported by the absence of the sharp methane peak in the gallium-doped oxides, which is in agreement with the non-detection of ethylene (Figure 6 IIb and Figure S10 b).

But still it is feasible to think that the reason we do not detect ethylene in the case of the Ce-Ga mixed oxides is because polymerization could be favored, converting all the ethylene into a carbonaceous deposit. However, the evolution of the CO₂ trace during the TPO experiments on previously treated oxides samples by the TPRS-MS of ethanol, shown in Figure 7, allow us to discard this last hypothesis because the nature of carbonaceous deposit

is similar on both cerium and cerium-gallium oxides and the total amount of carbon burned during the TPO is at least 3-fold higher on CeO₂ than on CeGaO_x.

At least three peaks evolved during oxidation at 165, 255 and 340 °C on pure CeO₂ and at 145, 230 and 300 °C on CeGaO_x samples, suggesting the formation of different types of carbonaceous deposits. It has been proposed that C₂H₄ is able to polymerize to finally yield coke over the surface of ethanol reforming catalysts [3,5], and this idea is based on the well-known phenomena of olefin polymerization in different industrial processes [51,52]. Usually, the different types of coke are characterized by TPO according to the temperature of CO₂ release: the higher the temperature the most stable the type of carbon deposit [53–55]. In our case, it might be postulated that the first two peaks of CO₂ (T < 300 °C) are due to partially hydrogenated carbon deposits, whereas the one at T > 300 °C would correspond to amorphous carbon. However, at least 3 to 4-fold more CO₂ was released from CeO₂ with respect to Ce₉₀Ga₁₀O_x and Ce₈₀Ga₂₀O_x, respectively. Then, if the source of those carbonaceous deposits were the polymerization of ethylene over any of the oxides employed in this work, it is possible to affirm that gallium-doping to the ceria significantly reduces the formation of ethylene to a level that we were unable to detect. In other terms, the lower amount of carbonaceous deposit in CeGaO_x cannot be attributed to the higher concentration of surface H on the gallium doped samples (due to de formation of Ga–H species), which would prevent C₂H₄ polymerization [51], because the production of ethylene was undetectable for the CeGaO_x samples. Therefore, and again, the most reasonable explanation is that the acetate route for LD ethoxy decomposition is favored by the greater oxidative power of the Ce–O–Ga interface and Ga–H formation.

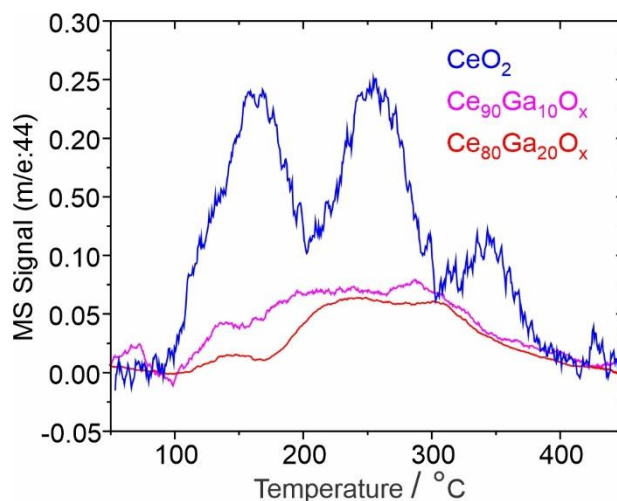


Figure 7. TPO traces on CeO_2 , $\text{Ce}_{90}\text{Ga}_{10}\text{O}_x$ and $\text{Ce}_{80}\text{Ga}_{20}\text{O}_x$, followed by mass spectrometry.

3.4. Hydrogen formation

H_2 desorption on ceria was detected between 180 and 330 °C, with a parallel evolution to that of the ethylene (Figure 6 Ib). This observation could be the result of the recombination of H and/or OH species (Scheme 1, r7) resulting from both the dehydrogenation of ethoxy LD to ethylene (Scheme 1, r4) and the formation of acetate species from ethoxy SU (Scheme 1, r2).

However, H_2 begins to be detected at the outlet of the TPSR-MS reactor from 120 °C on the $\text{Ce}_{80}\text{Ga}_{20}\text{O}_x$ sample, that is, at a lower temperature than on pure ceria (cf. Figures 6 Ib and IIb), and as soon as ethoxy SU begins to decompose. This result would imply that the H species coming from the dehydrogenation of $\text{C}_2\text{H}_5\text{O}_{\text{SU,H,Ce}}$ have migrated to Ga^{3+} , which are known to be active sites for H_2 dissociation and/or H recombination [30], rapidly recombined and left the surface as H_2 (Scheme 2, r6). In other words, the recombination of OH species to give H_2 in pure ceria (Scheme 1, r7) is a slower step than the proposed migration of H species to Ga^{3+} surface sites and the hydrogen release according to r6 in Scheme 2. The hydrogen evolution of the $\text{Ce}_{90}\text{Ga}_{10}\text{O}_x$ sample (Figure S10) shows an intermediate behavior between pure ceria and $\text{Ce}_{80}\text{Ga}_{20}\text{O}_x$, with a maximum at 252°C.

In line with the expected facile formation of gallium hydrides, an IR band of Ga–H species at 1955 cm^{-1} was detected above 180 °C reaching a maximum at 250 °C (Figures 5 IIb, 5 IIc)

and 6 IIc). The normalized integrated intensity of the Ga–H signal (plotted in Figure 6 IIc) suggests that the Ga–H species develop along with the decomposition of the ethoxy species in LD configuration, and when H₂ has almost reached a maximum (due to C₂H₅O_{SU,H,Ce} decomposition, as explained above). These results indicate that below 180 °C, the rate of recombination of Ga–H and OH species to yield H₂ (r6) is faster than the rate of formation of Ga–H species. Moreover, when the temperature increases above 180 °C the decomposition of LD ethoxy species, to acetate, near the gallium nanodomains begins to dominate and Ga–H species begin to be detected (Figure 6 IIc). The consumption of Ga–H observed above 250 °C could be a consequence of the decomposition of some of the acetate species, originated from LD and/or SU ethoxy species, leading to the formation of Ce³⁺ (Scheme 2, r5).

Another point to mention is that neither ethanol nor acetaldehyde were detected in the gas phase by MS for any of our ceria-based samples. Conversely, Li et al. [47] found a broad desorption peak of ethanol and acetaldehyde in the low temperature range (between 70 to 250 °C), with a maximum between 100 and 150°C, for nanoshaped ceria samples. Then, we run an extra TPRS-MS experiment after exposing our polycrystalline CeO₂ powder to ethanol at 25 °C. Our results showed broad peaks, between RT and 150 °C, due to the desorption of ethanol and acetaldehyde (Figure S12). This last result, along with the no-detection of acetaldehyde during the ethanol adsorption at 100 °C followed by He purging, allows us to assume that in our TPRS experiments, most of the acetaldehyde had already been removed from the IR cell or MS microreactor. Thus, the formation of acetaldehyde as an intermediate species during ethanol decomposition cannot be ruled out, but since it has not been detected in our experiments, it probably transforms quickly in acetate species over the surface. In fact, this hypothesis implies that in a consecutive reaction step, the activation energy for acetaldehyde decomposition should be higher than the one corresponding to its formation.

In summary, and along the section 3, we have shown that doping of ceria with gallia: (i) allows the recombination of H species coming from the dehydrogenation of ethoxy SU, favored by the formation of Ga–H species, which release H₂ to the gas phase at much lower temperature compared to pure ceria, (ii) facilitates the dehydrogenation/oxidation of LD ethoxy species to acetate species due to both, the higher reactivity of the oxygen at the Ce–O–Ga interface and the capacity to form surface gallium hydride species, (iii) favors the formation of CO₂ from acetate at lower temperature, and (iii) prevents the β-CH and C–O breaking of LD ethoxy, hindering ethylene production and carbon deposits.

4. Relationship between ethanol decomposition and the steam reforming reaction on CeO₂ and CeGaO_x

By simple inspection of the non-normalized evolution curves of each gaseous compounds and acetate species on CeO₂ and CeGaO_x followed by the TPSR-MS and TPSR-IR experiments (Figure S11), we can conclude that gallium addition to ceria increased the H₂ and CO₂ production, and the amount of surface acetate, but decreased ethylene production. Those trends for gaseous products are consistent with those observed on Figure 1b for the ethanol steam reforming reaction on pure CeO₂ and Ce₉₀Ga₁₀O_x. If we assume that acetate species are involved in acetone production under ESR (ketonization reaction), which is the main hypothesis of several authors [2,55–58], it is also possible to correlate the higher surface concentration of acetate on the CeGaO_x to the higher yield to acetone under ESR conditions (cf. Figure S11 and Figure 1b). Of course, under ESR conditions, the role of water cannot be ignored. Some of us have studied by H₂O-TPO the reoxidation of ceria as well as gallium-doped ceria (Ce₇₅Ga₂₅O_x), by means of IR spectroscopy and time-resolved XRD [29]. On one hand, the evolution of Ce³⁺ IR signal showed a partial oxidation of Ce³⁺ to Ce⁴⁺ in both materials (70 and 45% of reoxidation on CeO₂ and Ce₇₅Ga₂₅O_x at 723 K, respectively). On the other hand, the evolution of the lattice parameter of the Ce₇₅Ga₂₅O_x sample obtained by

XRD, showed a 50 % of Ce^{3+} reoxidation by water, in close agreement with the corresponding IR spectroscopy results. Water activation was also studied on Pt/CeO₂ or Pt/Ce₈₀Ga₂₀O_x catalysts for water gas shift (WGS), showing that in the presence of the metallic function the oxygen vacancy filling by water is always fast for both systems [59]. Thus, it seems that the role of water under ESR conditions could be to quench oxygen vacancies and thus to populate the surface with Ce^{4+} cations. However, further studies would be necessary to explore the role of water during ESR reaction. Nonetheless, it appears that ethanol decomposition rules the product distribution under ESR conditions on the pure CeO₂ and CeGaO_x samples.

The metallic function is also crucial to run an effective steam reforming reaction, since the desired final products are H₂ and CO₂. Cobalt sites, for example, favor C–C scission and water activation [60]. However, choosing the “right” metal-oxide combination and manipulating metal-support interactions, as well as controlling the effect of metal loading is important to obtain active, stable, and improved ESR catalysts [2,61]. Thus, more significant insights were obtained after running the ESR reaction on cobalt supported on CeO₂ and Ce₉₀Ga₁₀O_x, under the same experimental conditions described over the supports. In this case, to preserve “visible” the reactivity of the supports we chose a low Co loading (0.9 atom of Co/nm², that is, 0.5 % w/w Co/CeO₂ and 1.0 % w/w Co/Ce₉₀Ga₁₀O_x). The initial product distribution at 500 °C (t = 0 h, 100% of ethanol conversion), obtained under the same experimental conditions described for the supports, is shown in Figure S13. As expected, the Co-supported catalysts are more active and effective than the bare supports for the ESR reaction by decreasing the amount of carbonaceous by-products such as ethylene and acetone, and increasing the amounts of H₂ and CO₂ (cf. Figures 1b and S13). However, the main trends on product distribution mentioned above on the supports are still kept for our Co-supported catalysts at initial conditions: higher production of H₂, CO₂ and acetone, and lower

ethylene formation are observed on Co/Ce₉₀Ga₁₀O_x than on Co/CeO₂. Furthermore, 12 % less of carbon deposition, measured by TPO experiments (Figure S14 in SI), was found on the gallium doped catalysts after 4 h on stream at 500 °C (1.60 vs. 1.82 g C/g Co/h for 1.0 % Co/Ce₉₀Ga₁₀O_x and 0.5 % Co/CeO₂, respectively), which suggests that gallium plays a role in avoiding coke formation, most likely by suppressing ethylene production. Then, future experimental (and theoretical) work involving specific IR studies under operando conditions will be required to discriminate intermediates from spectators and unravel the ESR reaction mechanism over the CeO₂ and CeGaO_x supports as well as over the Co-based catalysts.

Conclusions

Cerium oxide and cerium-gallium mixed oxides were evaluated as supports for the steam reforming of ethanol, showing that gallium increased the H₂ yield and enhanced the H₂:CO₂ ratio at the reactor outlet. A noticeable change of the carbon-based product selectivity was also observed: ethanol was preferentially converted to ethylene on pure CeO₂ and to carbon dioxide and acetone on CeGaO_x. To understand these dissimilar behaviors we investigated the adsorption and decomposition of ethanol over the surface of the both kinds of oxides.

Ethanol adsorption and TPSR-IR studies on CeO₂ and CeGaO_x showed the formation of two types of ethoxy species, one being less reactive and another being less stable. DFT calculations of ethanol adsorption on the hydroxylated ceria(111) showed that the ethoxy species are adsorbed in monodentate coordination on a Ce atom, and two configurations are possible. In these two states, the alkyl chain is oriented parallel (ethoxy LD, "lying down") or perpendicular (ethoxy SU, "standing up") to the surface. In the case of the gallium-doped ceria surface, ethoxy can also dissociate on top of a Ga atom in a "lying-down" configuration.

The calculation of the vibrational frequencies of ethoxy species by DFT allowed us to assign the IR bands of ethoxy species found in the spectral region from 1200 to 800 cm⁻¹.

Based on the evolution of the surface species and gas phase products obtained by TPSR-IR and TPSR-MS, we postulate a mechanism for ethanol adsorption and decomposition on the surface of the oxides studied in this work.

In the case of pure ceria, the ethoxy in SU configuration decomposes above 150°C to yield acetate species, which further decompose to CO₂ and CH₄ in the gas phase. Moreover, ethoxy LD begins to decompose above 200°C, leading to H₂ and C₂H₄. Ethylene can further polymerize resulting in the formation of carbon deposits on the surface of ceria. Surprisingly, ethylene was not detected at the outlet of the reactor on the mixed oxides. It is proposed that dehydrogenation and oxidation of ethoxy to acetate species at the Ce–O–Ga interface is assisted by the formation of Ga–H species. Thus, all of the ethoxy species adsorbed on the surface of the mixed oxides, including those in lying down configurations, would rather take the acetate route than produce ethylene. Additionally, the more labile oxygen at the Ce–O–Ga interface likely assists the decomposition of acetate species to CO₂ and CH₄ at lower temperature. Thus, the absence of ethylene in the gas phase during TPSR-MS and the lower amounts of carbonaceous deposits, suggest that the cerium-gallium mixed oxides are more promising supports for ESR metal/oxide catalysts than pure ceria, that is, less coke formation might be anticipated.

ASSOCIATED CONTENT

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version.

Data availability

The DFT data that support the findings of this study are available in Materials Cloud {<https://www.materialscloud.org/home>} with the identifier doi:*****/materialscloud:2019.*****.

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