



# Article Catalytic Performances of Co/TiO<sub>2</sub> Catalysts in the Oxidative Dehydrogenation of Ethane to Ethylene: Effect of CoTiO<sub>3</sub> and Co<sub>2</sub>TiO<sub>4</sub> Phase Formation

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Abstract: Co/TiO<sub>2</sub> catalysts with different cobalt loadings (3.8, 7.5 and 15 wt%) were prepared by impregnation method of Co(NO<sub>3</sub>)<sub>2</sub> 6H<sub>2</sub>O over titania. Samples containing Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and TiO<sub>2</sub> in stoichiometric proportions in order to obtain CoTiO<sub>3</sub> and Co<sub>2</sub> TiO<sub>4</sub> phases were also synthesized. The effect of the calcination treatment at two different temperatures, 550 and 1150 °C, was investigated. Characterizations by several techniques, such as XRD, UV-vis-NIR, DRS, Raman and XPS, were carried out. XRD showed the coexistence of three phases: CoTiO<sub>3</sub>; Co<sub>2</sub>TiO<sub>4</sub> and  $Co_3O_4$  after calcination at 550 °C, while calcination at high temperature (1150 °C) led to single-phase systems (CoTiO<sub>3</sub> or Co<sub>2</sub>TiO<sub>4</sub>). Diffuse reflection and XPS spectroscopy showed that divalent cobalt occupies octahedral sites in the ilmenite phase, and both tetrahedral and octahedral sites in the spinel phase. The catalytic performances of the prepared catalysts were evaluated in the oxidative dehydrogenation reaction (ODH) of ethane to ethylene, as a function of the Co content for Co/TiO<sub>2</sub> catalysts and as a function of the calcination temperatures for the CoTiO<sub>3</sub> and Co<sub>2</sub>TiO<sub>4</sub> phases.  $Co(7.5)/TiO_2$  was the most active, although the conversion of ethane decreased in the first 150 min of the reaction, reaching values comparable to those of  $Co_2 TiO_4$  and  $CoTiO_3$ ; however,  $Co(7.5)/TiO_2$ was confirmed as having the best selectivity to ethylene in comparison with the bulk phases, CoTiO<sub>3</sub> and Co<sub>2</sub>TiO<sub>4</sub>. The influence of the reaction mixture composition, specifically the presence of water, at different percentages, was investigated. There is a decrease in the overall ethane conversion and an increase in the ethylene selectivity when the percentage of water increases. This behavior can likely be attributed to an increase in the surface concentration of hydroxyl species (OH), resulting in heightened surface acidity.

Keywords: ODH; cobalt titanate; ethane; oxidative dehydrogenation

# 1. Introduction

The chemical industry heavily relies on unsaturated hydrocarbons as a raw material for various industrial processes. However, the current industrial capacity for light alkenes such as ethene, propene and butene is expected to be insufficient due to the increasing demands of the petrochemical industry [1,2]. Traditional methods for producing light alkenes, such as catalytic or steam cracking of naphtha and fluid catalytic cracking (FCC) of petroleum crude



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**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). oil, have negative impacts on the environment [3–5]. With the increasing concern of climate change, there is a growing need for new, environmentally friendly methods of producing these chemicals [4,6]. It should be noted that in recent years, several commercial and academic proposals have been put forth as alternatives, promising to produce high-value chemicals from sustainable raw materials [7]. The revolution of shale gas and the prevalence of liquefied natural gas (LNG) technologies have increased the production of light alkanes, thus enhancing the interest in their dehydrogenation as a potential way to apply liquefied natural gas. Alkane dehydrogenation can be mainly achieved by nonoxidative or oxidative dehydrogenation [8–10]. It should be noted that thermodynamic dehydrogenation at high temperatures can result in the formation of undesirable byproducts. While the oxidation process can improve propylene yield, it can, however, also increase undesirable deep oxidation. Various catalytic formulations have been tested in oxidative dehydrogenation of alkanes, often consisting of complex mixtures of oxides. Thus, catalysts often contain oxides of vanadium, molybdenum and niobium. For example, the Mo–V–Nb–O system has been shown to have a 100% selectivity at 10% conversion for ODH from ethane to ethylene [11]; however, the best results have been obtained using boron oxides on different supports. In alumina catalysts containing 30% B2O3 in weight, the yield of ethylene was 14.6% at 38% conversion [12]. Additionally, a system composed of oxides of Co, Zr, P, Fe and K was found to have a selectivity of 74% at 53% conversion [12]. Oxidative dehydrogenation of ethane (ODH-E) is regarded as a highly promising approach for the conversion of ethane into valuable products [13]. When sustainable and easily accessible sources of ethane are employed in this process, the resulting ethylene production has the potential to satisfy both industrial production standards and environmental requirements. It is important to note that such processes should achieve an ethylene yield of greater than 60% in a single pass, with minimal formation of carbon oxides as a byproduct. Others transition metals have also demonstrated promising outcomes as well. For instance, research on various chromium-based catalysts supported on lamellar phosphates has revealed that CrPO<sub>4</sub> exhibits ethylene selectivity ranging from 60% to 50% and a conversion range from 30 to 20%. This result highlights the role that phosphorus can play as an additive in certain catalytic formulations [14]. ElIdrissi et al. [15,16] have reported that the selectivity for ethylene using a catalyst system composed of  $V/TiO_2$ , modified with phosphorus at a 1.64 of P/V ratio, was close to 50% at a conversion rate of 33%. They attribute the high selectivity to the acid-base properties and the V<sup>4+/</sup>V<sup>5+</sup> ratio and suggest that the presence of phosphorus adjusts the surface acidity, leading to an increase in the amount of isolated V<sup>4+</sup> ions. These vanadium-based catalysts are still the subject of ongoing research, and several recent articles have been published on their capacity for oxidative dehydrogenation [17].

Cobalt-based supported catalysts have been proven to be effective in various processes such as hydro treatment and Fischer–Tropsch reactions, among others [18]. They have also been used in the coupling of methane to form longer-chain hydrocarbons [19]. The incorporation of cobalt in perovskite-like materials as LnCoO<sub>3</sub> leads to catalysts with an effective performance in total oxidation and pollution control reactions [20]. The cobalt's ability to act as an oxidant during the oxidation process is due to the presence of oxygen on the surface of the catalyst, when oxygen is present in the process [21]. In ODH of ethane, cobalt has been used either as a supported catalyst to increase stability and selectivity, incorporated as a promoter to improve catalytic performance or explored in new materials [22–29].

Despite the promising conversion and selectivity rates reported in the literature, the industrial application of oxidative dehydrogenation (ODH) is still limited. The current literature reports an ethylene yield of approximately 20%, whereas industrial applications necessitate a productivity exceeding 1 kg  $C_2H_4$ ·kg cat<sup>-1</sup> h<sup>-1</sup> [30]. Previous research on cobalt supported on titania has shown promising results for the oxidative dehydrogenation of ethane [12,31]. Furthermore, XRD analysis of the catalyst at the stationary state revealed the presence of the defined phases such as ilmenite CoTiO<sub>3</sub> and spinel Co<sub>2</sub>TiO<sub>4</sub>. The best ODH performance of ethane was obtained at 550 °C, with a catalyst containing 7.5% wt

of Co. Notably, the reaction starts with a conversion of 33% and a selectivity around 75%, and then it decreases to reach a stationary state of 22% conversion and 60% selectivity after 150 min of running [12,31]. In view of climate change and the need to update industrial processes, research has focused on developing catalytic materials applied specially in the recovering and valorization of petrol-derived compounds. The purpose of this work is to investigate Co/TiO<sub>2</sub> systems at different cobalt loadings for providing information on the formation of the defined phases, CoTiO<sub>3</sub> and Co<sub>2</sub>TiO<sub>4</sub>, and their catalytic properties.

With this aim, we synthesized and characterized the ilmenite  $CoTiO_3$  and spinel  $Co_2TiO_4$  phases using different spectroscopic techniques. Then, we investigated their behavior in the oxidative dehydrogenation (ODH) reaction of ethane in order to correlate their activity and selectivity with the environment and the oxidation state of the active sites.

## 2. Materials and Methods

### 2.1. Chemical Products

The TiO<sub>2</sub> anatase used as support in this work was supplied by Rhone-Poulenc and is characterized by a specific surface area of 89 m<sup>2</sup> g<sup>-1</sup>.

Other reagents, including  $Co(NO_3)_2.6H_2O$ , (Analytical Reagent, Sinopharm Chemical Reagent Co., Ltd., Ningbo, China.), were used without any further purification.

## 2.2. Preparation of Catalysts

Co/TiO<sub>2</sub> catalysts with cobalt loadings equal to 3.8, 7.5, and 15.0 wt% were prepared according to a previously described method [12,31]. The TiO<sub>2</sub> support was put in contact with a Co(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O solution at suitable concentration in order to obtain the desired cobalt content. The suspension was kept under stirring at 80° C until complete evaporation of the water. The recovered solid was dried at 120° C, then calcined at 550° C or at 1150 °C for 4 h under air. The CoTiO<sub>3</sub> and Co<sub>2</sub>TiO<sub>4</sub> phases were synthesized as previously described by using TiO<sub>2</sub> and Co(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O solution in stoichiometric proportions in order to form the desired phases composition. Calcination at 550 °C and or 1150 °C was performed as reported above.

## 2.3. Characterization Techniques

Elemental analysis of the catalysts was carried out using an X-ray fluorescence wavedispersive spectrometer (XRF-1800, Shimadzu, Japan). The source was an X-ray tube with a Rh anode, a voltage of 40 kV, a current of 95 mA and a diaphragm of 10 mm. The real chemical composition corresponded well to the nominal one within  $\pm$ 5%.

Specific surface areas of the samples were measured at -196 °C with a nitrogen sorption technique using the ASAP 2020 equipment (Micromeritics, Norcross, Catalysts 2023, 13, 60,615 of 18 GA, USA). Before the measurements, the powder samples were degassed at 250 °C for 2 h. The specific surface area was calculated via the Brunauer-Emmett–Teller (BET) method in the standard pressure range 0.05–0.3 P/P<sub>0</sub>.

The X-ray diffraction patterns were used to identify the phases present in the samples and to determine their crystalline structure. They were collected using a Siemens D500 high-resolution spectrometer with Cu K $\alpha$  radiation (K $\alpha$  = 1.540598 A) at room temperature. The data were recorded with a step of 0.05° (2 $\theta$ ) and a counting time of 10 s per step. The assignment of the crystalline phases was based on the JCPDS powder diffraction file cards.

The morphology, composition and elemental mapping distribution of the two selected samples,  $CoTiO_3$  and  $Co_2TiO_4$ , calcined at 1150 °C, were analyzed by scanning electron microscopy (SEM) and energy-dispersive X-ray (EDX) analysis on QUATTRO S-FEG-Thermo Fisher equipment.

Diffuse reflection UV–visible–NIR spectra were recorded in the wavelength range of 190 to 2500 nm using a Varian Cary 5E double monochromator spectrometer, which was equipped with an integrating sphere. To establish a reference, polytetrafluoroethylene was utilized. Laser-Raman (LR) spectra were obtained using a Dilor XY spectrometer in backscatter geometry with a 514.5 nm excitation line from a Spectra Physics Model 165 coherent argon laser, with power kept below 20 mW. The spectrometer was equipped with a monochromator for selecting specific spectral ranges and a Jobin-Yvon 1024  $\times$  56 CCD matrix thermoelectrically cooled as a multichannel detector.

XPS spectra were recorded on a Vacuum Generators MK I spectrometer with an un-monochromated Al K $\alpha$  (1486.6 eV, 200 W) under about 10<sup>-9</sup> Torr. The spectra were digitized, summed, smoothed and reconstructed using Gauss–Lorentzian components. The measurements were carried out on powdered samples dispersed on an indium plaque using the C1s peak at 285 eV as a reference.

### 2.4. Catalytic Tests

The oxidative dehydrogenation of ethane (ODH) was carried out in a continuous-flow microreactor made of quartz, operating at atmospheric pressure, in a temperature range of 450–550 °C. The catalyst, which was sieved to a particle size between 125 and 180  $\mu$ m, was placed in the reactor between two plugs of quartz wool and was purged with pure nitrogen before the reaction. The reaction mixture consisted of 6 vol.% ethane, 3 vol.% O<sub>2</sub> and 91 vol.% N<sub>2</sub>. The effluent gases were analyzed using two online chromatographs, one (FID) equipped with a Porapak Q column for hydrocarbons and the other (TCD) with a silica gel column for oxygenated products. At the experimental conditions chosen, the reaction light-off occurred at around 300 °C and produced only ethylene and CO<sub>x</sub>. The effect of water presence at different volume percentages ranging between 1.2 and 3.1 vol.%, in reaction mixture at reaction temperature of 550 °C, was also investigated.

## 3. Results and Discussion

# 3.1. Characterization

The activity study of the defined  $CoTiO_3$  and  $Co_2TiO_4$  phases was imposed after their formation in the stationary state during a study of the  $x\%/TiO_2$  catalysts in ODH of ethane, hence the importance of associating the latter to this study. The X-ray diffraction patterns of the prepared x% Co/TiO<sub>2</sub> samples are displayed in Figure 1. An examination of the obtained results reveals that the sample diffractogram with a low concentration of cobalt 3.8 wt % (Figure 1, curve b) is characterized by peaks of the anatase titania (JCPDS file #84-1286). For the 7.5 and 15.0 wt% cobalt samples, in addition to anatase, a few peaks were observed (Figure 1c,d), denoting Co<sub>3</sub>O<sub>4</sub> formation (JCPDS file no. 78-1970). The intensity of the system exhibits a direct correlation with the concentration of cobalt, whereby higher cobalt concentrations lead to increased intensity levels. Additionally, when the Co content increases from 7.5% to 15%, the average particle size ranges from 17 to 19 nm, which is in agreement with the findings reported by Ho et al. [32]. The study revealed the presence of  $Co_3O_4$  crystallites in samples that contain as little as 1.5% of Co within the anatase and rutile mixture, which also has a surface area of 50 m<sup>2</sup> g<sup>-1</sup>. The findings of this work are different from those reported previously and by other researchers, which could be a result of the greater surface area of anatase present in our samples. This leads to improved dispersion of  $Co_3O_4$  and potentially the formation of some amorphous species that are not identifiable by X-ray diffraction.

The XRD patterns of CoTiO<sub>3</sub> and Co<sub>2</sub>TiO<sub>4</sub> samples calcined at different temperatures are shown in Figure 2A,B, respectively. For both samples, it can be observed that the calcination at 550 °C leads mainly to a mixture of phases: CoTiO<sub>3</sub>, Co<sub>2</sub>TiO<sub>4</sub> and Co<sub>3</sub>O<sub>4</sub>.Co<sub>2</sub>TiO<sub>4</sub> is in the minority compared with the other phases. Increasing temperature to 750 °C for the CoTiO<sub>3</sub> sample decreases the intensity of the Co<sub>2</sub>TiO<sub>4</sub> lines. Similarly, a significant decrease in the Co<sub>3</sub>O<sub>4</sub> lines can be observed. Calcination at higher temperature (1150 °C) leads to single-phase systems: the ilmenite CoTiO<sub>3</sub> and spinel Co<sub>2</sub>TiO<sub>4</sub> phases.

On the other hand, the study of the ilmenite  $CoTiO_3$  phase by XRD showed that the  $Ti^{4+}$  and  $Co^{2+}$  ions occupy slightly distorted octahedral sites. The ilmenite structure is found in oxides with the formula ABO<sub>3</sub>, when the A and B ions have similar sizes and

a total charge of +6. The name ilmenite comes from the mineral Fe<sup>II</sup>Ti<sup>IV</sup>O3, which has a similar structure to corundum. It consists of a compact hexagonal arrangement of oxygen ions and cations occupying two thirds of the octahedral sites. Divalent and tetravalent ions form alternating layers. On the other hand,  $Co_2TiO_4$  has an inverse spinel structure, which can be represented by the formula  $Co^{2+}(Co^{2+}Ti^{4+})O_4$ , where half of the  $Co^{2+}$  ions occupy the tetrahedral sites; the other half of the  $Co^{2+}$  ions occupy the octahedral sites.

In Table 1, the specific surface areas (SSAs) ( $m^2/g$ ) are listed for Co(x%)/TiO<sub>2</sub> samples calcined at 550 °C, as well as for the CoTiO<sub>3</sub> and Co<sub>2</sub>TiO<sub>4</sub> phases treated at two different calcination temperatures, 550 and 1150 °C. The SSA values of the CoTiO<sub>3</sub> and Co<sub>2</sub>TiO<sub>4</sub> phases are lower than those for Co(x)/TiO<sub>2</sub> samples, and the values decrease by increasing the calcination temperature of CoTiO<sub>3</sub> and Co<sub>2</sub>TiO<sub>4</sub>. This finding suggests that sintering of the exposed surface and lowering of the active sites is available for catalysis.

**Table 1.** Specific surface areas  $(m^2/g)$  of  $Co(x)/TiO_2$  and defined phases,  $CoTiO_3$  and  $Co_2TiO_4$ .

| Samples                        | Co(3.8)/TiO <sub>2</sub> | Co(7.5)/TiO <sub>2</sub> | Co(15)/TiO <sub>2</sub> | CoTiO <sub>3</sub> | Co <sub>2</sub> TiO <sub>4</sub> |
|--------------------------------|--------------------------|--------------------------|-------------------------|--------------------|----------------------------------|
| SSA values (m <sup>2</sup> /g) | 65                       | 60                       | 56                      | <sup>a</sup> 46    | <sup>a</sup> 45                  |
|                                | -                        | -                        | -                       | <sup>b</sup> 9.4   | <sup>b</sup> 10                  |



<sup>a</sup>: calcined at 550 °C <sup>b</sup>: calcined at 1150 °C.

**Figure 1.** XRD patterns of  $Co(x)/TiO_2$  samples calcined at 550 °C,  $TiO_2$  (**a**), Co(3.8) (**b**), Co(7.5) (**c**) and Co(15) (**d**).



Figure 2. XRD diagrams of  $CoTiO_3$  (A) and  $Co_2TiO_4$  (B) samples as a function of the calcination temperature.

In Figure 3, the adsorption/desorption profiles of selected samples are shown. The isotherms are type IV according to the IUPAC classification. According to the decreased values of specific surface area, after calcination at high temperature, a very low amount of N<sub>2</sub> was adsorbed by the CoTiO<sub>3</sub> calcined at 1150 °C, as can be seen from looking at the curves (d) in Figure 3.

SEM and EDX analyses (see Figure 4) were performed to obtain more insight into the morphology and chemical composition of the CoTiO<sub>3</sub> and Co<sub>2</sub>TiO<sub>4</sub> samples calcined at 1150 °C. CoTiO<sub>3</sub> has an almost regular morphology, although some grains appear fused and with not well-defined contours (Figure 4A). The Co<sub>2</sub>TiO<sub>4</sub> sample shows some distinctive differences: the grains are more defined, compact and uniform than those of CoTiO<sub>3</sub> (Figure 4B). Moreover, the shape is cubic or octahedral, according to the spinel structure of Co<sub>2</sub>TiO<sub>4</sub>. In both cases, semiquantitative EDX analysis shows a chemical composition very close to the stoichiometric formulae of the solids (Figure 4C,D).



Figure 3. N<sub>2</sub> adsorption/desorption isotherms of Co(3.8) (a), Co(15) (b), CoTiO<sub>3</sub> calcined at 550  $^{\circ}$ C (c) and CoTiO<sub>3</sub> calcined at 1150  $^{\circ}$ C (d).



**Figure 4.** SEM images and EDX spectra of  $CoTiO_3$  (**A**,**C**) and  $Co_2TiO_4$  (**B**,**D**) samples calcined at 1150 °C.

Diffuse reflection UV-visible-NIR spectroscopy offers valuable insights into the oxidation state of transition metals, their coordination and the symmetry of their surrounding environment. Co/TiO<sub>2</sub> absorption spectra in the UV-visible-NIR are displayed in Figure 5. It should be noted that distinguishing between different species is challenging for two distinct considerations: (i) In the 1100–1500 nm wavelength range, the v1 transition of octahedral ions partially overlaps with the v<sub>2</sub> transition of tetrahedral species. In addition, the high coefficient of absorption of the tetrahedral species makes it difficult to detect the first transition. (ii) In TiO<sub>2</sub>, a Co<sup>2+</sup>  $\rightarrow$  Ti<sup>4+</sup> charge transfer can take place. Indeed, an absorption of Co<sup>2+</sup>-modified MgTi<sub>2</sub>O<sub>5</sub> in the 400–500 nm wavelength region was assigned to this transition mode [12,33]. It is important to consider  $Co^{2+}$  to  $Ti^{4+}$  charge transfers, since cations of the active phase and support have variable valence. The UV spectrum of TiO<sub>2</sub> shows strong absorption related to the interband transition, and maxima around 320 and 220 nm are attributed to  $Co^{2+}$  to  $Ti^{4+}$  charge transfers. The 3.8 wt% Co sample has slight absorption in the visible range (Figure 5); however, for the 7.5 and 15 wt% Co samples, new bands appear and intensify with increasing Co load. The near-infrared (NIR) region has a broad band in the 1200 and 1600 nm interval, as well as the band of 2"(OH) harmonics of residual hydroxyl groups, which is located close to 1380 nm. The visible range has another band around 700 nm, and a shoulder with a maximum at 420 nm in the range of 400 and 600 nm observed only in the loaded 15 wt% Co sample (Figure 5, curve d). These results indicate the presence of different cobalt species [12].



Figure 5. DRS spectra of Co (x)/TiO<sub>2</sub> samples, TiO<sub>2</sub> (a), Co(3.8) (b), Co(7.5) (c) and Co(15) (d).

The UV–visible–NIR spectra of the CoTiO<sub>3</sub> and Co<sub>2</sub>TiO<sub>4</sub> samples calcined at different temperatures (550, 750 and 1150 °C) are shown in Figure 6A,B. In general, the calcination temperature drastically changes the position, shape and relative intensities of the bands.

In the case of the CoTiO<sub>3</sub> sample calcined at 550° C, two broad bands, A and B, appear at 596 and 760 nm, respectively. The calcination temperature has no effect on the position of these bands; however, a variation in their relative intensities is observed after calcination. In the NIR part, a notable modification of the maxima of the bands was observed. Indeed, the sample calcined at 550 °C is characterized by the appearance of bands at 1250, 1350 and 1530 nm and a shoulder at 1750 nm (Figure 6A; spectrum a), which is already attributed to the transition  ${}^{4}A_{2}(W) \rightarrow {}^{4}T_{1}$  (F) of divalent cobalt in the tetrahedral site. The treatment

at 1150 °C leads to the appearance of an intense and broad band centered at 1530 nm (Figure 6A, spectrum c). Also, note that in the ilmenite CoTiO<sub>3</sub> structure, the Co<sup>2+</sup> ions are in octahedral symmetry. In the olivine Co<sub>2</sub>SiO<sub>4</sub> structure taken as reference, Co<sup>2+</sup> occupies the octahedral interstices. The UV–visible spectrum of this compound (data not shown) has a similar appearance to that of the ilmenite CoTiO<sub>3</sub> phase (Figure 6, spectrum c). The bands at 600, 760 and 1530 nm are assigned to the three (<sup>4</sup> T <sub>1g</sub>  $\rightarrow$  <sup>4</sup> T <sub>1g</sub> (P), <sup>4</sup>T <sub>1g</sub>  $\rightarrow$  <sup>-4</sup> A <sub>2g</sub> (F) and <sup>4</sup> T <sub>1g</sub>  $\rightarrow$  <sup>4</sup> T <sub>2g</sub> (F)) divalent cobalts in the octahedral sites.



**Figure 6.** DRS spectra of CoTiO<sub>3</sub> (**A**) and Co<sub>2</sub>TiO<sub>4</sub> (**B**) samples as a function of the calcination temperature: 550 °C (**a**), 750 °C (**b**) and 1150 °C (**c**).

The fundamental <sup>4</sup>F level of the Co<sup>2+</sup> ion in the tetrahedral field breaks down into the lowest ones, <sup>4</sup>A<sub>2</sub> <sup>4</sup> T<sub>1</sub> and <sup>4</sup> T<sub>2</sub>. The transition <sup>4</sup>A<sub>2</sub> (F)  $\rightarrow$  <sup>4</sup>T<sub>2</sub> (F) is forbidden to the electric dipole approximation and allowed for the magnetic dipole approximation. It is indeed very weak and often appears in the infrared region. The two transitions <sup>4</sup>A<sub>2</sub> (F)  $\rightarrow$  <sup>4</sup>T<sub>1</sub> (F) and <sup>4</sup>A<sub>2</sub> (F)  $\rightarrow$  <sup>4</sup>T<sub>1</sub> (P) give very high intense absorption bands, often in three components because of the spin–orbit coupling.

The spectrum of the  $Co_2 TiO_4$  sample calcined at 550 °C is similar to that of  $CoTiO_3$  calcined at the same temperature of 550 °C (Figure 6B, curve a). After treatment at 750 °C (Figure 6B, curve b), its appearance changes radically in the visible part. Indeed, the appearance of several absorptions is noticed: 588,638 and 688 nm and a shoulder around 750 nm.

At higher calcination temperature, a broad absorption spreads between 1300 nm up to 1820 nm, which has already been observed in the case of soda–lime glasses with divalent cobalt and in tetrahedral symmetry [12]. The two shoulders around 535 and 720 nm are, respectively, attributed to the  ${}^{4}T_{1g} \rightarrow {}^{4}T_{1g}$  (F) and  ${}^{4}T_{1g} \rightarrow {}^{4}T_{1g}$  (F) of Co<sup>2+</sup> in octahedral sites. The band at 720 nm has already been observed in the case of CoNaY zeolites [34].

Laser-Raman spectroscopy is a widely used tool in the field of supported and unsupported catalysis. The obtained data for the three  $\text{Co}/\text{TiO}_2$  catalysts are depicted in Figure 7A. The bands observed at 397, 514 and 640 cm<sup>-1</sup> are characteristic of the TiO<sub>2</sub> anatase structure, (curve a). When 3.8% wt of cobalt was added, the spectrum was not impacted (spectrum b). In contrast, higher cobalt level spectra show bands close to 692 cm<sup>-1</sup> and two shoulders at 487 and 528 cm<sup>-1</sup>, suggesting the formation of Co<sub>3</sub>O<sub>4</sub> [12,35].

The Raman spectra of the two CoTiO<sub>3</sub> and Co<sub>2</sub>TiO<sub>4</sub> phases calcined at 1150 °C are shown in Figure 7B. As far as the spinel is concerned, no Raman vibration mode was observed in the frequency range between 200 and 1000 cm<sup>-1</sup> (Figure 7Ba). On the other hand, the Raman spectrum of the ilmenite CoTiO<sub>3</sub> phase (Figure 7B, spectrum b) shows several bands, respectively, at 688, 450, 379, 332, 263 and 233 cm<sup>-1</sup> and two shoulders at 602 and 204 cm<sup>-1</sup>. The mode of vibration at 688 cm<sup>-1</sup> is the most intense. Several isostructural compounds, such as (Ni; Fe; Mg)TiO<sub>3</sub>, exhibit the same Raman line around 700 cm<sup>-1</sup>.



It corresponds to the mode of vibration  $A_{1g}$  of symmetrical elongation of octahedron  $MO_6$  [36].

**Figure 7.** Raman spectra of  $Co(x)/TiO_2$  samples calcined at 550 °C (**A**):  $TiO_2$  (**a**), Co(3.8) (**b**), Co(7.5) (**c**) and Co(15) (**d**). Raman spectra of samples calcined at 1150 °C (**B**):  $Co_2TiO_4$  (**a**) and  $CoTiO_3$  (**b**).

The XPS spectra of the CoTiO<sub>3</sub> and Co<sub>2</sub>TiO<sub>4</sub> phases are illustrated in Figure 8A,B, respectively. The spectral lines of the Co2p of these compounds, such as the Co2p<sub>3/2</sub> binding energies and the spin–orbit coupling  $\Delta E$  (Co2p<sub>1/2</sub>-Co2p<sub>3/2</sub>), as well as the S/M ratios (satellite intensity/main peak intensity ratio), are reported in Table 2.

The Co2p<sub>3/2</sub> binding energies (CoTiO<sub>3</sub>: 781.2 eV; Co<sub>2</sub>TiO<sub>4</sub>: 781 eV), as well as the ratio (S/M), are in good agreement with the presence of paramagnetic ions (Co<sup>2+</sup>). The energy difference  $\Delta E$  (Co2p<sub>1/2</sub>-Co2p<sub>3/2</sub>) is 16 eV in the case of CoO [12]. It is close to the CoTiO<sub>3</sub> phase  $\Delta E$  value, which contains only Co<sup>2+</sup> in octahedral sites. For the spinel phase, a  $\Delta E$  value of 15.8 eV is observed. It should be noted that this difference in energy of the 2p<sub>1/2</sub> and 2p<sub>3/2</sub> electrons usually allows the distinction of the tetrahedral sites from the octahedral sites; however, in the case of the mixed spinel, this discrimination is practically impossible.



Figure 8. XPS spectra of  $CoTiO_3$  (A) and  $Co_2TiO_4$  (B) phases.

| Complete                         | Co2      | . <b>–</b> h   |      |
|----------------------------------|----------|----------------|------|
| Samples                          | B.E. S/M | $\Delta E^{b}$ |      |
| Co(3.8)/TiO <sub>2</sub>         | 781.0    | 0.42           | 15.4 |
| Co(7.5)/TiO <sub>2</sub>         | 780.2    | 0.27           | 15.2 |
| Co(15)/TiO <sub>2</sub>          | 779.9    | 0.19           | 15.1 |
| Co <sub>2</sub> TiO <sub>4</sub> | 781      | 0.40           | 15.8 |
| CoTiO <sub>3</sub>               | 781.2    | 0.47           | 15.9 |
| Co <sub>3</sub> O <sub>4</sub>   | 779.9    | 0.18           | 15.1 |
| СоО                              | 780.4    | 0.4            | 16.0 |

**Table 2.** XPS characterization data for the  $Co(x)/TiO_2$  samples calcined at 550 °C and crystalline phases,  $CoTiO_3$  and  $Co_2TiO_4$  calcined at 1150 °C.

<sup>a</sup> S/M: (satellite intensity/main peak intensity); <sup>b</sup>  $\Delta$ E: spin–orbit coupling (Co2p<sub>1/2</sub>-Co2p<sub>3/2</sub>).

### 3.2. Catalytic Results and Discussion

In order to find a Co/TiO<sub>2</sub> compound adequate to compare the studied CoTiO<sub>3</sub> and Co<sub>2</sub>TiO<sub>4</sub> phases, the experiments were conducted at temperature of 550 °C. Firstly, the conversion with pure TiO<sub>2</sub> as support was less than 5%. At steady state, for some Co/TiO<sub>2</sub> catalysts, the ethane conversion increased with reaction temperature in the 450–550 °C range (Figure 9). The conversion rate increased as the cobalt amount increased, almost reaching a plateau from 7.5 to 15 wt% of Co. The catalyst loaded with 7.5 wt% of Co shows a conversion at 550 °C of around 22.2% with an ethylene yield close to 13.3% (60% selectivity).



**Figure 9.** Ethane conversion registered over  $Co(x)/TiO_2$  catalysts at three different temperatures: 450 °C (**a**), 500 °C (**b**) and 550 °C (**c**).

This result allows us to select the sample containing 7.5 wt% Co as a reference to compare the catalytic performances of the CoTiO<sub>3</sub> and Co<sub>2</sub>TiO<sub>4</sub> phases. Figure 9 shows the variation of ethane conversion as a function of time on Co(7.5)/TiO<sub>2</sub> at 550 °C compared with CoTiO<sub>3</sub> and Co<sub>2</sub>TiO<sub>4</sub> catalytic activities. For Co (7.5)/TiO<sub>2</sub>, the conversion decreased from 33% to around 22.2% when it reached steady state after 3 h of reaction. During this time, the specific surface was significantly reduced, and the color of the catalyst changed from light gray to green, probably due to the change in the conversion of ethane with time over the defined phases CoTiO<sub>3</sub> and Co<sub>2</sub>TiO<sub>4</sub> calcined at 550 and 1150 °C, respectively. The evolution of the ethane conversion shows that these solids are stable over time regardless of the temperature of their calcination. At 550 °C, the ethane conversion is on the same

order of magnitude as that measured with the Co  $(7.5)/\text{TiO}_2$  sample. Therefore, it can be surmised that the octahedral Co<sup>2+</sup> ions present are responsible for the activity [12,31], while Co<sup>3+</sup> ions play a role in the ethylene selectivity, in agreement with the behavior observed for phosphorus-modified samples [12].

In Figure 10, the conversion curves of ethane vs time, at the temperature of 550 °C, are plotted for CoTiO<sub>3</sub> and Co<sub>2</sub>TiO<sub>4</sub> calcined at 550 °C and at 1150 °C, shown in Figure 10A. For comparison, the behavior of Co(7.5)/TiO<sub>2</sub> calcined at 550 °C is displayed, and the selectivity to ethylene is also reported, in Figure 10B. Co(7.5)/TiO<sub>2</sub> appeared as the most active at the beginning of the reaction; however, the conversion of ethane decreased in the first 150 min of the reaction, from the initial value of ~33% to around 22%, reaching values comparable to those of Co<sub>2</sub>TiO<sub>4</sub> and CoTiO<sub>3</sub>, which achieved conversions ranging between 19.7–21.6% as a function of the calcination temperature (see Table 3). In Figure 10B, the selectivity to ethylene versus time is reported for the Co(7.5)/TiO<sub>2</sub> sample. It resulted in a selectivity that was as high as 75% at the beginning of the reaction, then decreased to around 60% after 150 min of reaction, following a similar trend as the ethane conversion. Anyway, such selectivity values are significantly higher than those registered for the bulk samples, CoTiO<sub>3</sub> and Co<sub>2</sub>TiO<sub>4</sub> (see Table 3).



**Figure 10.** Conversion of ethane vs time, at 550 °C, for selected samples (**A**): Co<sub>2</sub>TiO<sub>4</sub> calcined at 1150 °C (**a**) and at 550 °C (**c**); CoTiO<sub>3</sub> calcined at 550 °C (**b**) and at 1150 °C (**d**); Co(7.5)/TiO<sub>2</sub> calcined at 550 °C (**e**). Selectivity to ethylene versus time (**B**), at 550 °C, for Co(7.5)/TiO<sub>2</sub> calcined at 550 °C.

Samples Calcined at EE0 °C

|  | Samples Calchied at 550 °C  |                  |                  |                  |                                  |                  |                  |                  |
|--|-----------------------------|------------------|------------------|------------------|----------------------------------|------------------|------------------|------------------|
| Desetter Terrerentere                                      | CoTiO <sub>3</sub>          |                  |                  |                  | Co <sub>2</sub> TiO <sub>4</sub> |                  |                  |                  |
| Reaction Temperature                                       | α <sub>g</sub>              | α <sub>ene</sub> | Sene             | S <sub>COx</sub> | $\alpha_{\rm g}$                 | α <sub>ene</sub> | S <sub>ene</sub> | S <sub>COx</sub> |
| 450 °C   | 12.9                        | 4.1              | 32               | 72               | 13.8                             | 3.8              | 28               | 72               |
| 500 °C   | 16.8                        | 5.2              | 31               | 69               | 16.8                             | 4.5              | 27               | 69               |
| 550 °C   | 19.9                        | 6                | 30               | 70               | 21.4                             | 4.6              | 21.5             | 78.5             |
| Activation Energy, Ea (kJ·mol <sup><math>-1</math></sup> ) | 21.6 21.6                   |                  |                  |                  |                                  |                  |                  |                  |
|  | Samples Calcined at 1150 °C |                  |                  |                  |                                  |                  |                  |                  |
| Postion Tommorature  | CoTiO <sub>3</sub>          |                  |                  |                  | Co <sub>2</sub> TiO <sub>4</sub> |                  |                  |                  |
| Reaction Temperature                                       | α <sub>g</sub>              | $\alpha_{ene}$   | S <sub>ene</sub> | S <sub>COx</sub> | $\alpha_{\rm g}$                 | α <sub>ene</sub> | S <sub>ene</sub> | S <sub>COx</sub> |
| 450 °C   | 13.1                        | 2.5              | 19               | 71               | 13.8                             | 2.6              | 19               | 81               |
| 500 °C   | 17                          | 3                | 18               | 72               | 17.7                             | 3.3              | 19               | 81               |
| 550 °C   | 21.6                        | 3.8              | 16               | 84               | 19.7                             | 3.8              | 18               | 82               |
| Activation Energy, Ea (kJ·mol <sup><math>-1</math></sup> ) |                             | 24               | 4.5              |                  | 24.4                             |                  |                  |                  |

Table 3. Catalytic results of CoTiO<sub>3</sub> and Co<sub>2</sub>TiO<sub>4</sub> at steady state and activation energy.

 $\alpha_g$ : overall conversion of ethane;  $\alpha_{ene}$ : ethylene yield;  $S_{ene}$ : selectivity towards ethylene.

By comparing the catalytic data obtained for the CoTiO<sub>3</sub> and Co<sub>2</sub>TiO<sub>4</sub> samples calcined at 550 °C and 1150 °C and summarized in Table 3, the following observations can be made:

- The evolution of overall conversion (Figure 10) shows that these materials are stable over time regardless of their calcination temperature. At 550 °C, the overall conversion of ethane is on the same order of magnitude as that measured with the Co(7.5)/TiO<sub>2</sub> sample ( $\alpha_g = 22.2\%$ ).
- For the calcination temperature of 550 °C, selectivity towards ethylene (Table 3) was slightly higher in the case of CoTiO<sub>3</sub> in comparison with Co<sub>2</sub>TiO<sub>4</sub>, while the superior behavior of the Co(7.5)/TiO<sub>2</sub> sample was confirmed.
- No significant modification of catalytic activity was observed after calcination at 1150 °C, but the production of CO<sub>x</sub> became higher, while selectivity to ethylene dropped down.

The apparent activation energy, Ea, of  $C_2H_6$  oxydehydrogenation on the defined phase catalysts was calculated using the Arrhenius equation (Equation (1)). The relationship between the reaction rate *r* and the reaction rate constant *k* was obtained using the theory of reaction series. The expression for the catalytic reaction rate *r* is identical to that used by Wang et al. [37].

$$k = A. e^{-\frac{Lu}{RT}} \tag{1}$$

$$r = k.C_1^{\alpha}C_1^{\beta}\dots C_n^{\gamma} \tag{2}$$

$$Y = \frac{F * \alpha}{22.414 * 60 * 1000 * M}$$
(3)

*k* is the reaction rate constant, *A* is the pre-exponential factor, *Ea* is the apparent activation energy and *R* is the molar gas constant. In Equation (2),  $\alpha$ ,  $\beta$  and  $\gamma$  are reaction orders; *C*<sub>1</sub>, *C*<sub>2</sub> and *C*<sub>n</sub> are reactant concentrations. In Equation (3),  $\alpha$  is the conversion of reactants, *F* is the gas flow rate and *M* is the mass of the catalyst.

1

By plotting  $\ln(r)$  versus 1/T, the apparent activation energy Ea was calculated and the values are listed in Table 3. The values are quite low, slightly increasing for the samples calcined at 1150 °C.

The selectivity to ethylene versus the ethane conversion registered at the reaction temperature of 550 °C on the CoTiO<sub>3</sub> and Co<sub>2</sub>TiO<sub>4</sub> samples calcined at different temperatures (550 °C and 1150 °C) is reported in Figure 11. The common trend is that the selectivity to ethylene decreased by increasing ethane conversion. The samples calcined at 550 °C showed similar curves, with almost overlapping values. Samples calcined at 1150 °C exhibited higher selectivity, the CoTiO<sub>3</sub> phase being the most efficient.



**Figure 11.** Ethylene selectivity versus ethane conversion at 550 °C on CoTiO<sub>3</sub> calcined at 550 °C (**a**) and 1150 °C (**b**) and Co<sub>2</sub>TiO<sub>4</sub> calcined at 550 °C (**c**) and at 1150 °C (**d**).

## Impact of Water Vapor in ODH reaction

In general, water increases the surface acidity and, in this sense, facilitates desorption. Table 4 summarizes the results obtained when steam was added to the reaction mixture at different percentages. It was observed that both phases,  $CoTiO_3$  and  $Co_2TiO_4$ , show the same catalytic behavior in the presence of water, independent of their calcination temperature.

**Table 4.** Catalytic data from the effect study of  $H_2O$  presence in reaction mixture at reaction temperature of 550 °C.

|                       |                  |                  | 9             | Samples Calc     | ined at 550 $^\circ$             | С                  |                  |                  |
|-----------------------|------------------|------------------|---------------|------------------|----------------------------------|--------------------|------------------|------------------|
| Experimental          |                  | Col              | Гі <b>О</b> 3 |                  | Co <sub>2</sub> TiO <sub>4</sub> |                    |                  |                  |
| Conditions            | $\alpha_{\rm g}$ | α <sub>ene</sub> | Sene          | S <sub>COx</sub> | $\alpha_{\rm g}$                 | $\alpha_{\rm ene}$ | S <sub>ene</sub> | S <sub>COx</sub> |
| Dry Mixture           | 19.9             | 6                | 30            | 70               | 21.4                             | 4.6                | 21.5             | 78.5             |
| 1.2% H <sub>2</sub> O | 15.5             | 6.2              | 40            | 60               | 17.1                             | 4.7                | 27               | 73               |
| 1.7% H <sub>2</sub> O | 14.7             | 6.5              | 44            | 56               | 13.9                             | 4.9                | 35               | 65               |
| 3.1% H <sub>2</sub> O | 13               | 6.1              | 47            | 53               | 11.9                             | 4.6                | 39               | 61               |
|                       |                  |                  | S             | amples Calci     | ned at 1150 °                    | °C                 |                  |                  |
|                       |                  |                  |               |                  |                                  | TiO                |                  |                  |

| Experimental          |                  | Col                | ГіО <sub>3</sub> |                  | Co <sub>2</sub> TiO <sub>4</sub> |                    |      |                  |
|-----------------------|------------------|--------------------|------------------|------------------|----------------------------------|--------------------|------|------------------|
| Conditions            | $\alpha_{\rm g}$ | $\alpha_{\rm ene}$ | Sene             | S <sub>COx</sub> | $\alpha_{ m g}$                  | $\alpha_{\rm ene}$ | Sene | S <sub>COx</sub> |
| Dry Mixture           | 21.6             | 3.8                | 16               | 84               | 19.7                             | 3.8                | 18   | 82               |
| 1.2% H <sub>2</sub> O | 16.7             | 3.7                | 22               | 78               | 17.6                             | 3.7                | 21   | 79               |
| 1.7% H <sub>2</sub> O | 15.3             | 4                  | 26               | 74               | 15.6                             | 3.9                | 25   | 75               |
| 3.1% H <sub>2</sub> O | 13.6             | 3.8                | 28               | 72               | 12.8                             | 3.6                | 28   | 72               |

It can be pointed out that there is a decrease in overall ethane conversion and an increase in ethylene selectivity when the percentage of water increases (Table 4). On the other hand, it is also noticeable that the yield of ethylene increases slightly with a reaction mixture containing 1.7% of H<sub>2</sub>O.

The comparison of selectivity obtained for the  $CoTiO_3$  and  $Co_2TiO_4$  catalysts can be appreciated from the plots shown in Figure 12. It is possible to classify the samples into two categories: The first one, less selective in ethylene, includes the samples tested with the dry mixture. The second category, which is more selective, is obtained in the presence of steam.



**Figure 12.** Variation of  $C_2H_4$  selectivity with overall conversion of CoTiO<sub>3</sub> (**A**) and Co<sub>2</sub>TiO<sub>4</sub> (**B**) samples depending on the percentage of steam in the reaction mixture.

From these obtained results, it can be considered that the limiting step is the desorption of the ethylene molecule from the catalyst surface. The presence of water vapor in the reaction mixture promotes this desorption through competition for site occupation. However, at high percentages of water vapor, a significant portion of the active sites are occupied, leading to a significant decrease in overall conversion. Therefore, the increase in  $C_2H_4$  selectivity is likely due to an increase in the OH\* species at the catalyst surface [38] relative to the O\* species, which favors total oxidation.

### 4. Conclusions

In this work, Co/TiO<sub>2</sub> catalysts with varying cobalt loadings (3.8, 7.5, and 15 wt%) were successfully prepared using the impregnation method of Co(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O over titania. Additionally, the CoTiO<sub>3</sub> and Co<sub>2</sub>TiO<sub>4</sub> phases were synthesized by maintaining stoichiometric proportions of the precursors. The effect of calcination treatments at different temperatures (550 °C and 1150 °C) was investigated. Characterization using various techniques, such as XRD, UV–vis–NIR, DRS, Raman and XPS, provided valuable insights. XRD analysis revealed the coexistence of three phases (CoTiO<sub>3</sub>, Co2TiO4 and Co3O4) after calcination at 550 °C and depending on cobalt loading, while high-temperature calcination (1150 °C) resulted in single-phase systems (CoTiO<sub>3</sub> or Co<sub>2</sub>TiO<sub>4</sub>).

Diffuse reflection and XPS spectroscopy detected the presence of divalent cobalt ions that occupied octahedral sites in the ilmenite phase, as well as both tetrahedral and octahedral sites in the spinel phase. The catalytic performances of the prepared catalysts were evaluated for the oxidative dehydrogenation reaction (ODH) of ethane to ethylene. The Co(7.5)/TiO<sub>2</sub> catalyst exhibited higher activity and superior selectivity to ethylene compared with the bulk phases CoTiO<sub>3</sub> and Co<sub>2</sub>TiO<sub>4</sub>.

The influence of the reaction mixture composition, particularly the presence of water at different percentages, was also investigated. The overall ethane conversion decreased, and ethylene selectivity increased as the percentage of water in the mixture increased. This behavior is likely attributed to an increase in the surface concentration of hydroxyl species (OH), leading to heightened surface acidity.

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