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# Modified Co/TiO<sub>2</sub> catalysts for CO<sub>2</sub> hydrogenation to fuels

Canio Scarfiello,<sup>a,b,c</sup> Katerina Soulantica,<sup>b</sup> Simon Cayez,<sup>b</sup> Aurélien Durupt,<sup>a,b,c</sup> Guillaume Viau,<sup>b</sup> Nolwenn Le Breton,<sup>d</sup> Athanassios K. Boudalis,<sup>d</sup> Frédéric Meunier,<sup>e</sup> Guillaume Clet,<sup>f</sup> Mathias Barreau,<sup>g</sup> Davide Salusso,<sup>h</sup> Spiros Zafeiratos,<sup>g</sup> Doan Pham Minh,<sup>a</sup> Philippe Serp<sup>c</sup>

<sup>a</sup> *Université de Toulouse, IMT Mines Albi, UMR CNRS 5302, Centre RAPSODEE, Campus Jarlard, F-81013 Albi, cedex 09, France.*

<sup>b</sup> *Université de Toulouse, INSA, UPS, CNRS, LPCNO, 135 avenue de Rangueil, F-31077 Toulouse, France.*

<sup>c</sup> *LCC, CNRS-UPR 8241, ENSIACET, Université de Toulouse, France.*

<sup>d</sup> *Institut de Chimie de Strasbourg, Université de Strasbourg-CNRS UMR 7177, 4 rue Blaise Pascal, BP 296 R8, F-67008 Strasbourg Cedex, France*

<sup>e</sup> *Université Claude Bernard Lyon 1, CNRS, IRCELYON, 2 Av. Albert Einstein, F-69626 Villeurbanne, France.*

<sup>f</sup> *Normandie Univ, ENSICAEN, UNICAEN, CNRS, LCS, F-14000 Caen, France*

<sup>g</sup> *ICPEES-UMR 7515 CNRS-ECPM-Université de Strasbourg, 25, rue Becquerel, F-67087 Strasbourg Cedex 2, FRANCE*

<sup>h</sup> *European Synchrotron Radiation Facility, CS 40220, Cedex 9 F-38043 Grenoble, France*

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**Abstract.** The direct CO<sub>2</sub> conversion to liquid fuels by catalytic hydrogenation (CO<sub>2</sub>-based Fischer-Tropsch synthesis, FTS), is a sustainable approach to reduce CO<sub>2</sub> emissions. This challenging reaction proceeds through tandem catalysis involving reverse water gas shift reaction to produce CO and subsequent traditional CO-FTS. Unmodified Co-based catalysts allow performing the reaction at low temperatures (< 250 °C), albeit producing mainly methane. In this study, we modified a commercial TiO<sub>2</sub>-P25 support by NaBH<sub>4</sub> reduction so as to introduce controlled amounts of promoters and oxygen vacancies (O<sub>v</sub>). The modified and unmodified supports were used to prepare Co-based catalysts, which were evaluated for CO<sub>2</sub>-based FTS at 220-250 °C and 20 bar. The promoted catalysts outperform the one prepared on commercial TiO<sub>2</sub> in terms of activity and selectivity towards C<sub>5+</sub>. Detailed characterizations of the catalysts were performed to decipher the role of promoters. We show that, besides

improving CO<sub>2</sub> activation and limiting H<sub>2</sub> activation, the presence of alkali on the support allows a modulation of hydrogen spillover in the system. The best catalyst in terms of activity and selectivity is the one for which sodium is deposited in sufficient amount to modulate the hydrogen spillover, which allows an optimal surface C/H ratio on cobalt.

## 1. Introduction

Carbon dioxide catalytic hydrogenation with H<sub>2</sub> produced from nuclear or renewable energies is a promising way toward carbon neutralization, while producing value-added fuels such as methane, long-chain hydrocarbons, olefins, methanol, or higher alcohols [1]. The selective production of C<sub>2+</sub> hydrocarbons by one-step CO<sub>2</sub> hydrogenation (CO<sub>2</sub>-based Fischer-Tropsch synthesis, CO<sub>2</sub>-FTS) is particularly challenging due to the high C–C coupling barriers, and the numerous competing reactions generating undesired C<sub>1</sub> products. During the one-step CO<sub>2</sub>-FTS, the exothermic FT reaction (Eq. 1) occurs only after the initial transformation of CO<sub>2</sub> into CO *via* the reverse water gas-shift reaction (RWGS, Eq. 2). As the latter is slightly endothermic, CO<sub>2</sub> conversion to CO is often limited at the temperatures required for FTS.



Iron-based catalysts are relatively active for RWGS, but need harsher conditions than Co-based catalysts and show high deactivation rates during the traditional FTS [2, 3]. Indeed, metallic cobalt represents one of the best choices for the production of synthetic hydrocarbons *via* traditional FTS [4]. However, for CO<sub>2</sub>-FTS on cobalt catalysts, weak CO<sub>2</sub> adsorption and RWGS thermodynamic constraints lead to low C/H surface ratio and CO coverage, resulting in the preferential production of CH<sub>4</sub> and short chain hydrocarbons [5].

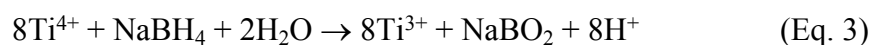
Several parameters can be modulated to improve the selectivity towards C<sub>2+</sub> products on Co-based catalysts such as: the choice of cobalt active phase, support and metal support interfaces, and the addition of promoters [6]. The role of the different Co active phases is still debated in the literature [7]. Both metallic cobalt and cobalt oxide (CoO) can be active during CO<sub>2</sub>-FTS, depending on the support used [8]. Metallic cobalt is more active on most supports, while CoO appears to be an alternative choice on titania [8, 9]. The formation of a unique interface between cobalt and the TiO<sub>2</sub> support could be at the origin of this behavior. Cobalt carbides seem to be related to the formation of methane or ethanol, depending on the support [10], as well as to catalyst deactivation [7]. However, a recent work reports that specific facets of Co<sub>2</sub>C display excellent RWGS and CO<sub>2</sub>-FTS activity for the direct synthesis of olefins and alcohols [11]. As far as the support is concerned, reducible oxides and especially TiO<sub>2</sub> are better adapted for this reaction than irreducible oxides [6]. The higher activity obtained on TiO<sub>2</sub>-based catalysts stems from the ability of reducible oxides to create unique metal-support interfaces, originating from strong metal-support interaction (SMSI) [12], which can largely benefit the CO<sub>2</sub> activation toward different products, from C<sub>2+</sub> to CH<sub>4</sub> and CO [7, 9]. Moreover, reducible oxides and metal-oxide interfaces are rich in surface defects such as reduced cationic sites or oxygen vacancies (O<sub>v</sub>) that can be exploited for the direct activation of CO<sub>2</sub> [13, 14]. Such surface defects, when properly introduced on a reducible support, can also enhance metal dispersion during catalyst preparation [15]. It was also demonstrated that the crystal phase of TiO<sub>2</sub> (rutile or anatase) has a significant effect on the product selectivity obtained on Co-based catalysts [16]. Finally, the addition of alkali promoters allows increasing CO<sub>2</sub> adsorption, C/H surface ratio and the intrinsically marginal activity of Co-based catalysts for RWGS, helping to mitigate excess methanation and to increase overall C<sub>2+</sub> selectivity [6, 16, 17]. Moreover, alkali and

alkaline earth promotion can also favor the generation of  $O_v$  on reducible supports, and improve the final metal dispersion [18].

The present study aims at disentangling the effects of the support modification on the  $CO_2$ -FTS using Co/ $TiO_2$  catalysts. Compared to the work of Li and coworkers [16], in which  $TiO_2$  anatase and rutile phase were compared, we used in our study a  $TiO_2$  support containing a mixture of anatase and rutile phase ( $TiO_2$ -P25), since such mixtures have been shown to be advantageous for the CO-FTS [19]. Commercial  $TiO_2$ -P25 was partially reduced using  $NaBH_4$  as reducing agent, leading to the formation of surface defects ( $O_v$  and  $Ti^{3+}$ ) and the incorporation of Na and B promoters. The amount of both surface defects and promoters can be controlled by modulating the conditions of the reduction process. The resulting modified supports were employed for the preparation of Co-based catalysts by incipient wetness impregnation (IWI), and the resulting catalysts were evaluated for the direct  $CO_2$ -FTS at 220 and 250 °C. The catalysts prepared on different modified supports outperform the one prepared on the commercial  $TiO_2$ -P25 (benchmark), in terms of selectivity towards  $C_{2+}$  and  $C_{5+}$ . The catalysts showing low alkali loading are also more active than the one prepared on the commercial support. We show through *ex situ* and *in situ* analyses that the presence of sodium in the catalyst affects catalytic performance in several ways. First of all, the promoter contributes to the activation of  $CO_2$ , which contributes to the catalytic activity. The localization of the promoter, on the support and/or on the metal also has a marked effect on the activity and the selectivity. When the promoter interacts with cobalt, the activity decreases but the selectivity increases relative to the unmodified catalyst. When sodium is essentially present on the support, it also serves to modulate the hydrogen spillover in the system. This regulation of hydrogen spillover makes it possible to achieve high activities and selectivity in  $C_{5+}$ .

## 2. Results and discussion

**2.1 Titania support modification.** The reduction of  $TiO_2$  with  $NaBH_4$  (Eq. 3) has already been used for the preparation of colored crystalline core/amorphous shell structures ( $TiO_2@TiO_{2-x}$ ) with superior photocatalytic properties [20, 21], including for photocatalytic  $CO_2$  conversion [22]. This reduction process produces different defect states within the bandgap of  $TiO_2$ , which are accompanied by a drastic color change. After reduction of commercial  $TiO_2$ -P25 containing 85% anatase (A- $TiO_2$ ) and 15% rutile (R- $TiO_2$ ), the white color of the material changes into blue or black, depending on the temperature treatment [23].



Here, this reduction process was implemented to obtain different supports for the preparation of Co-based catalysts for  $CO_2$ -FTS. Careful control of the operating conditions such as amount of  $NaBH_4$ , reaction temperature and washing steps, allows: i) the modulation of the final  $TiO_2$  reduction degree (concentration of  $O_v$  and  $Ti^{3+}$ ) and, ii) the incorporation of various amounts of Na and B promoters in the modified titania support (denoted as  $TiO_2^*$ ).

Mild reduction leads to the formation of the m- $TiO_2^*$  support, characterized by a medium concentration of defects ( $O_v$ ,  $Ti^{3+}$ ) and promoters (Na, B), and showing a light-blue color (**Figure S1**). Harsher reduction conditions lead to the formation of the dark-blue d- $TiO_2^*$  support, rich in surface defects and promoters (**Table 1**). Finally, the reoxidation of the m- $TiO_2^*$  support under air leads to the formation of the white m- $TiO_2^*$ -reox support (**Figure S1**), deprived of surface defects and containing only the promoters. Only small differences of promoter concentrations are detected between the m- $TiO_2^*$  and m- $TiO_2^*$ -reox supports, in line

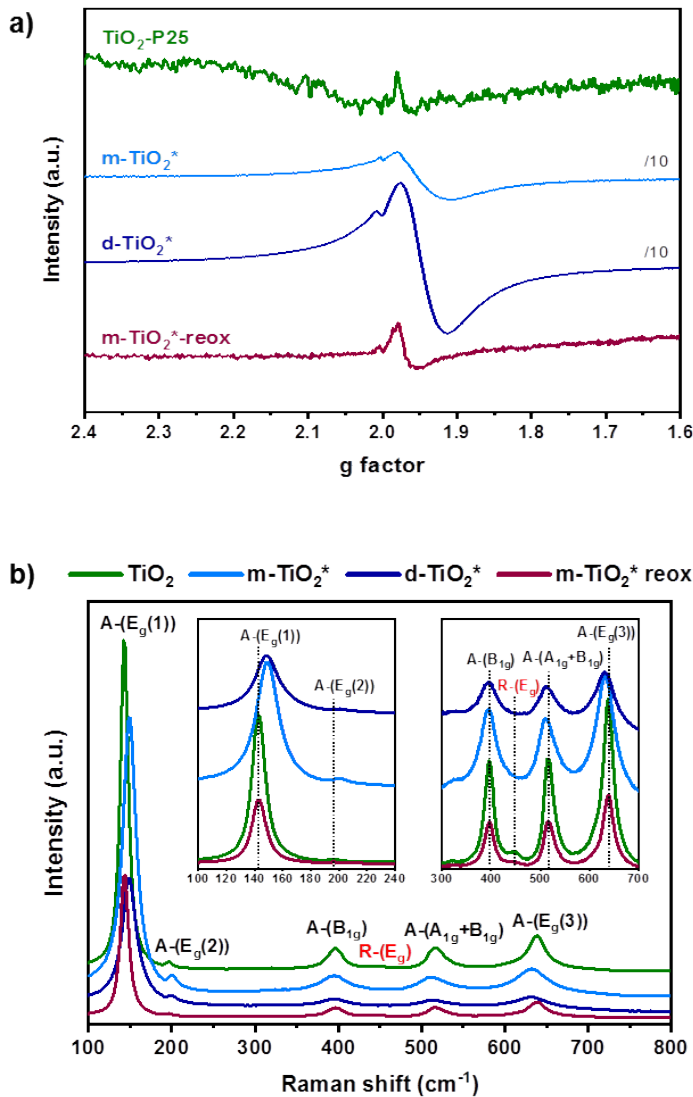
with small variations obtained among different batches (Na wt% can vary between 0.5 and 0.7 wt% on m-TiO<sub>2</sub>\* and between 1.1 and 1.3 wt% for d-TiO<sub>2</sub>\*).

**Table 1.** Promoter and defect concentration on the different supports according to ICP-OES and EPR analyses, respectively.

| Support                   | ICP-OES (%wt) |      | Total spin concentration <sup>a</sup><br>(nmol.mg <sup>-1</sup> ) | Approximate relative concentrations <sup>a</sup> |                      |
|---------------------------|---------------|------|---|--|----------------------|
|                           | Na            | B    |   | O <sub>v</sub> (%)                               | Ti <sup>3+</sup> (%) |
| TiO <sub>2</sub>          | -             | -    | < 1   | 0  | 100                  |
| m-TiO <sub>2</sub> *      | 0.52          | 0.02 | 480   | < 0.1  | 99.9                 |
| d-TiO <sub>2</sub> *      | 1.18          | 0.07 | 1000  | < 0.1  | 99.9                 |
| m-TiO <sub>2</sub> *-reox | 0.50          | 0.02 | < 10  | < 0.1  | 99.9                 |

<sup>a</sup> Based on double integration of the EPR signal.

Electron paramagnetic resonance (EPR) spectroscopy was used to confirm the presence of unpaired electrons, O<sub>v</sub> and Ti<sup>3+</sup> in the different supports. The EPR spectra of the supports are shown in the **Figure 1a**, and the main results are summarized in **Table 1**. On the commercial TiO<sub>2</sub>-P25, only an extremely weak signal centered at  $g = 1.97$  can be detected, assigned to a small amount of Ti<sup>3+</sup> [24], resulting in a very low total radical concentration (< 1 nmol/mg). Upon reduction, the total concentration of radical species increases significantly up to 480 nmol.mg<sup>-1</sup> and 1 μmol.mg<sup>-1</sup> for m-TiO<sub>2</sub>\* and d-TiO<sub>2</sub>\*, respectively. Moreover, a second peak centered at  $g = 2.002$ , which can be assigned to O<sub>v</sub>, starts to be visible (**Figure 1a**) [24]. Both signals are still visible on the m-TiO<sub>2</sub>\*-reox, even if the total radical concentration decreased significantly (< 10 nmol.mg<sup>-1</sup>). Such signals can be attributed to residual defects in the subsurface layers of the support, likely related to the presence of promoter incorporation [25]. Overall, the EPR results confirm the creation of defects (O<sub>v</sub> and Ti<sup>3+</sup>) upon reduction with NaBH<sub>4</sub>, and the destruction of almost all these defects upon reoxidation in air.



**Figure 1. a)** EPR spectra recorded at 100 K of the different supports normalized to the sample mass. The intensities of the spectra of the two reduced supports ( $m\text{-TiO}_2^*$  and  $d\text{-TiO}_2^*$ ) were divided by 10. **b)** Raman spectra of the different supports. A =  $\text{TiO}_2$ -anatase; R =  $\text{TiO}_2$ -rutile.

Raman analyses were performed (**Figure 1b**) to confirm the presence of disorder and  $\text{O}_v$ . For  $\text{TiO}_2$ -P25, the main Raman bands appear at  $\sim 143$ , 196, 397, 516, and  $638\text{ cm}^{-1}$ , which are all ascribable to the predominant A- $\text{TiO}_2$  phase [26]. Only one weak band of R- $\text{TiO}_2$  at  $\sim 447\text{ cm}^{-1}$  (R-( $E_g$ )) appears on  $\text{TiO}_2$  (**Figure 1b**, inset). The latter is no more visible upon reduction ( $m\text{-TiO}_2^*$  and  $d\text{-TiO}_2^*$ ), which is consistent with an easier reducibility of the R- $\text{TiO}_2$  phase [27]. Finally, this band appears again upon reoxidation on the  $m\text{-TiO}_2^*$ -reox support, in line with XRD results (*vide infra*). Anatase bands also show some shift upon the different treatments. In particular, the lowest frequency vibrational mode of A- $\text{TiO}_2$   $E_g(1)$  at  $143\text{ cm}^{-1}$  shows significant broadening, and shifts towards higher wavenumbers (blue-shift) in  $m\text{-TiO}_2^*$  and  $d\text{-TiO}_2^*$ . Such broadening and blue shift of the  $E_g(1)$  mode in Na-doped  $\text{TiO}_2$  has been attributed to a decrease of the particle size and non-stoichiometry related to defect formation [28]. The small changes in the A- $\text{TiO}_2$  crystallite size (*vide infra*) and the disappearance of this blue shift upon reoxidation (**Figure 1b**, inset) suggest that non-stoichiometry ( $\text{O}_v$  and  $\text{Ti}^{3+}$ ) should be

responsible for the variation of the  $E_g(1)$  mode. Conversely, a small red shift can be detected, on both m-TiO<sub>2</sub>\* and d-TiO<sub>2</sub>\*, for the A-TiO<sub>2</sub> bands at higher wavenumbers (397, 516, and 638 cm<sup>-1</sup>). This red shift can be tentatively attributed to the incorporation of Na into these two samples [29].

Commercial TiO<sub>2</sub> is a mixture of A-TiO<sub>2</sub> and R-TiO<sub>2</sub>. Furthermore, a small amount of amorphous phase was detected by TEM [30]. The XRD diffractograms of the supports are shown in **Figure S2**. The rutile content was estimated from the XRD peak intensity using Eq. 4 [31, 32].

$$\chi = (1 + 0.8 I_{A(101)}/I_{R(110)})^{-1} \quad (\text{Eq. 4})$$

The estimated crystallite size, the  $2\theta$  values of A-TiO<sub>2</sub>(101) and R-TiO<sub>2</sub>(110) planes, and the estimated rutile content in the different samples are listed in the **Table S1**. Upon reduction of TiO<sub>2</sub>, a diffraction peak at  $\sim 49.6^\circ$  starts to be visible on the m-TiO<sub>2</sub>\* support, which can be attributed to the sodium titanate Na<sub>0.46</sub>TiO<sub>2</sub> phase [33]. Small shifts towards lower  $2\theta$  values can be detected for both A-TiO<sub>2</sub>(101) and R-TiO<sub>2</sub>(110) diffraction peaks upon support reduction (**Table S1**), which can be attributed to the formation of surface defects [34], and of the new sodium titanate phase. This phase becomes significantly more visible on the d-TiO<sub>2</sub>\* support, in line with the higher sodium content in this sample. Moreover, new peaks ascribable to Na<sub>2</sub>B<sub>6</sub>O<sub>10</sub>, Na<sub>2</sub>O, NaBO<sub>2</sub>, and B<sub>2</sub>O can be detected on this latter support, in line with the results of other authors [20]. None of these phases was detected on the m-TiO<sub>2</sub>\*-reox support, indicating structural change of the support upon reoxidation. Whatever the support, A-TiO<sub>2</sub> crystallites (25±1 nm) are smaller than those of R-TiO<sub>2</sub> (30-45 nm). Similar crystallite sizes were reported by other authors for TiO<sub>2</sub> P25 [35, 36]. The A-TiO<sub>2</sub>, but above all, the R-TiO<sub>2</sub> crystallite sizes decrease upon reduction (m-TiO<sub>2</sub>\* and d-TiO<sub>2</sub>\*) and increase again upon reoxidation (m-TiO<sub>2</sub>\*-reox). The decrease of R-TiO<sub>2</sub> crystallite size can be associated to the formation of an amorphous or disordered layer of reduced TiO<sub>2</sub> around a crystallite core, resulting in the formation of a crystalline-disordered core-shell structure [21]. Therefore, the R-TiO<sub>2</sub> phase is the most reactive one towards NaBH<sub>4</sub> reduction, and is mainly involved in the formation of a disordered TiO<sub>2</sub>@TiO<sub>2-x</sub> shell. Other authors reported similar results, with a preferential reduction of the R-TiO<sub>2</sub> over the A-TiO<sub>2</sub> phase due to longer Ti-O bonds in the rutile crystal structure [27, 37]. The decrease of R-TiO<sub>2</sub> crystallite size and the formation of an amorphous or disordered layer of reduced TiO<sub>2</sub> should also be associated to the increase of the surface area observed on the most reduced d-TiO<sub>2</sub>\* sample (Table S2).

XRD, EPR and Raman characterization show that reduction with NaBH<sub>4</sub>, of TiO<sub>2</sub>-P25 leads to the formation of defects (O<sub>v</sub>, Ti<sup>3+</sup>) and to the formation of new Na- and B-containing phases. It is mainly the most reactive R-TiO<sub>2</sub> phase which undergoes structural modification upon reduction. Upon reoxidation the O<sub>v</sub> and Ti<sup>3+</sup> defects disappear, letting behind the Na and B promoters.

H<sub>2</sub>-temperature programmed reduction (H<sub>2</sub>-TPR analyses) show that the reduction by hydrogen is moderate for all the supports (**Figure S3a** and **Table S2**), due to the presence of a large fraction of anatase phase [38]. TiO<sub>2</sub>-P25 exhibited no H<sub>2</sub> consumption peak in the 50-500 °C range, since its reduction normally occurs at T > 600 °C. The Na-promoted samples show reduction events at lower temperatures (400-500 °C) that might be attributed to the reduction of sodium species [39, 40].

The CO<sub>2</sub>-temperature programmed desorption (CO<sub>2</sub>-TPD) results show that the three modified supports can adsorb more CO<sub>2</sub>, compared to the commercial TiO<sub>2</sub>-P25 (**Figure S3b** and **Table S2**). The negligible difference between m-TiO<sub>2</sub>\* and m-TiO<sub>2</sub>\*-reox supports suggests that the increased basicity of the d-TiO<sub>2</sub>\* arises mainly from the presence of the promoters rather than from surface defects. Overall, the d-TiO<sub>2</sub>\* support, rich in both surface defects and promoters,

shows the highest basicity, which can contribute to an increase of CO<sub>2</sub> adsorption [6]. Since alkali metals can strongly promote CO<sub>2</sub> adsorption [40-42], we mainly attributed the increase in the basicity of the modified supports to the presence of Na (see **Figure S4** for the correlation between the amount of adsorbed CO<sub>2</sub> and the Na wt % in the different supports). Indeed, the basicity of Na-promoted Pt/TiO<sub>2</sub> catalysts has been attributed mainly to the presence of NaO<sub>x</sub> species [40], and sodium titanate nanotubes have been identified as promising CO<sub>2</sub> adsorbents showing higher efficiency than the parent TiO<sub>2</sub> [43]. The CO<sub>2</sub>-TPD profiles show also that the commercial TiO<sub>2</sub>-P25 can only bond some CO<sub>2</sub> with a medium strength. Upon reduction, m-TiO<sub>2</sub>\* shows increased adsorption in both weak and medium strength ranges, and a small tail in the strong adsorption range. The latter becomes more significant on m-TiO<sub>2</sub>\*-reox support, indicating that the reoxidation might lead to the creation of new sites, which can strongly bond CO<sub>2</sub>. Finally, the d-TiO<sub>2</sub>\* displays an important increase in the weak-medium bonded CO<sub>2</sub>, and a very small tail in the strong-bonded range.

To summarize the support characterization results, the reduction of TiO<sub>2</sub> by NaBH<sub>4</sub> is a suitable one-step procedure to obtain partially reduced supports containing defects (O<sub>v</sub> and Ti<sup>3+</sup>) and Na and B promoters identified as crystalline phases, which can significantly increase CO<sub>2</sub> adsorption. The reoxidation of the m-TiO<sub>2</sub>\* support eliminates the surface defects, while conserving the promoters.

**2.2 Co/x-TiO<sub>2</sub> catalysts.** To investigate the effect of the different supports and their properties on CO<sub>2</sub>-FTS performances, four cobalt based catalysts with 10 wt% Co (nominal loading) were prepared by IWI method. The catalysts and their real metal loadings (ICP-OES) are listed in the **Table 2**. Cobalt metal loadings were very close to their nominal value, as expected for the IWI synthesis. Cobalt species were observed on all calcined catalysts by Raman spectroscopy, notably in the form of Co<sub>3</sub>O<sub>4</sub>, which disappeared after reduction (*vide infra*). The crystallite size of Co<sub>3</sub>O<sub>4</sub> (**Table 2**) was determined from the diffractograms of the calcined catalysts (**Figure S5**). Bulk characterization methods such as magnetic measurements and XRD show the presence of mainly metallic cobalt in all reduced samples (**Figure S5**). The measurement of the sample magnetization as a function of the applied magnetic field by vibrating-sample magnetometry (VSM) allows the determination of the saturation magnetization (M<sub>s</sub>) of each sample (**Figure S5a**), which can be divided by the magnetization of bulk Co (M<sub>s</sub> = 154 emu/g) to determine the percentage of metallic cobalt in each sample (**Table 2**).

**Table 2.** Real metal loading (ICP-OES) of the different catalysts of this study. Percentage of metallic Co (% Co<sup>0</sup>) calculated from VSM measurements (300 K) in the reduced catalysts, and Co<sub>3</sub>O<sub>4</sub> estimated crystallite size (from XRD on the calcined catalysts).

| Catalyst                | ICP-OES (%wt) |      |      | % Co <sup>0</sup> (VSM) | Co <sub>3</sub> O <sub>4</sub> (nm) |
|-------------------------|---------------|------|------|-------------------------|-------------------------------------|
|                         | Co            | Na   | B    |                         |                                     |
| Co/TiO <sub>2</sub>     | 9.62          | -    | -    | 99.75                   | 37.4                                |
| Co/m-TiO <sub>2</sub> * | 9.70          | 0.64 | 0.04 | 97.97                   | 44.2                                |

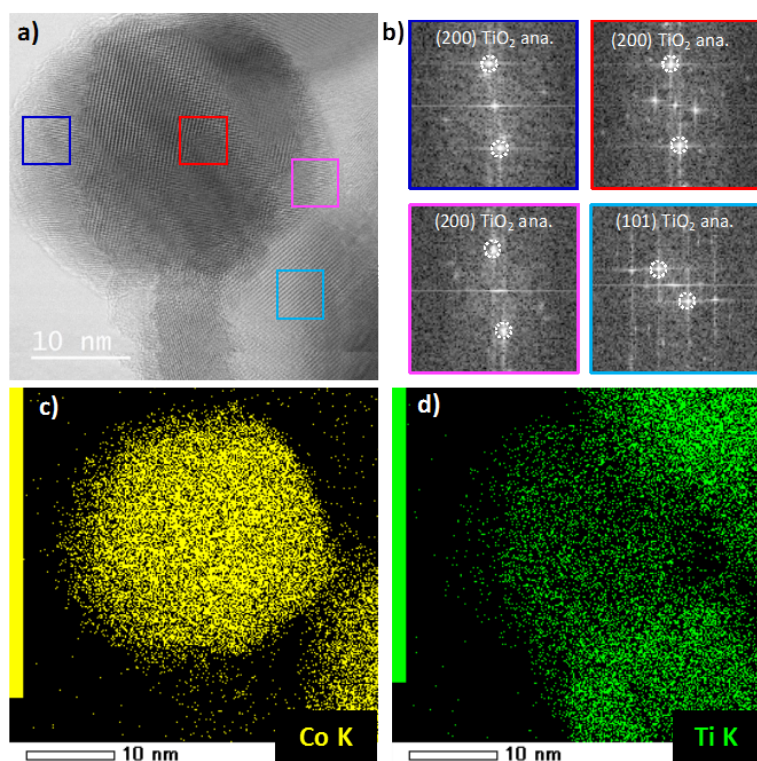


|                                  |      |      |      |       |      |
|----------------------------------|------|------|------|-------|------|
| Co/d-TiO <sub>2</sub> *          | 9.24 | 0.92 | 0.07 | 94.30 | 39.6 |
| Co/m-TiO <sub>2</sub> *-<br>reox | 9.88 | 0.47 | 0.02 | 91.44 | 38.1 |

The reduced Co/TiO<sub>2</sub> catalyst, which can be considered as the reference catalyst, contains the highest amount of metallic cobalt (99.75 %). This is in line with H<sub>2</sub>-TPR, CO-TPD and diffuse reflectance infrared Fourier transform spectroscopy (DRIFT) characterizations (*vide infra*) that indicate a more difficult reduction, and probably the presence of some oxidized cobalt in the three promoted catalysts. Crystalline cobalt oxide was not detected by XRD on any of the reduced catalysts (**Figure S5b**), which contain only both *hcp* and *fcc* metallic Co. The crystallite sizes of a reduced 15 wt% FTS Co/TiO<sub>2</sub>-P25 catalyst were measured by XRD (MoK<sub>α</sub> radiation) to be approximately 20 nm for the *fcc* phase and a 2.5 nm for the *hcp* phase [44]. In our case (CoK<sub>α</sub> radiation), due to the overlapping of several crystallographic phases, the quantification and crystallite size determination of the metallic Co was not conclusive. The percentages of the R-TiO<sub>2</sub> phase as well as the R-TiO<sub>2</sub> crystallite size in the four catalysts (**Table S3**) are similar, contrarily to the situation of bare supports (**Table S1**). To investigate whether the re-crystallization of the R-TiO<sub>2</sub> phase took place during the calcination or reduction steps, we followed its evolution during catalyst preparation (**Figure S6**). The results show that the re-crystallization takes place during the calcination step, that is, when the cobalt nitrate decomposition leads to the formation of a NO<sub>x</sub>-rich highly oxidative environment [45]. Moreover, no peaks related to Na or B containing phases are visible on the XRD diagrams of the calcined or reduced catalysts, pointing toward an amorphization phenomenon. It was reported that Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·5H<sub>2</sub>O and Na<sub>0.23</sub>TiO<sub>2</sub> can be removed from reduced TiO<sub>2</sub> *via* HCl washing, due to their instability in acid [46]. Therefore, it is possible that such phases are partially leached by the acidic Co nitrate solution during the IWI and redispersed on the catalyst to form amorphous phases during the different calcination/reduction steps.

High Resolution Transmission Electron Microscopy (HRTEM), Scanning Transmission Electron Microscopy Energy Dispersive X-ray spectroscopy (STEM-EDX) and Scanning Transmission Electron Microscopy-High-Angle Annular Dark-Field (STEM-HAADF) analyses were performed on the four reduced catalysts to evaluate the Co particle size and their distribution on the support. Due to the low contrast difference between Ti and Co atoms, the identification of Co particles requires constant EDX analysis. Moreover, the extended agglomeration and the broad size distribution of Co, which is present both as small and large particles (**Figure S7**), makes impossible an accurate evaluation of the Co particle size distribution. Evidence of the SMSI encapsulation effect was probed by STEM-HAADF. **Figures S8 to S11** show the presence of encapsulation and fringes/striations resulting from non-epitaxial growth between the metal and the support in the four catalysts [47-49]. EDX analyses on isolated Co particles confirm the presence of TiO<sub>2</sub> in the outmost encapsulation layer, which seems to be in part amorphous and in part crystalline. The formation of such layers is generally related to partial reduction of TiO<sub>2</sub> under reducing atmosphere [50], which is enhanced in the presence of metal thanks to hydrogen spillover [51]. SMSI is widely assumed to be due to migration of unstable TiO<sub>x</sub> species onto the metal surface forming metal particles encapsulated by a TiO<sub>x</sub> layers [12]. The encapsulation of Co particles by TiO<sub>2</sub> was confirmed on the Co/m-TiO<sub>2</sub>\*-reox catalyst by fast Fourier transform (FFT) analysis of STEM-HAADF micrographs.

A selected example of an isolated from the rest of the support Co particle is shown in **Figure 2**.



**Figure 2.** STEM-HAADF micrographs: **a)** bright field image; **b)** FFT patterns of the area framed with rectangles of corresponding colors, on which diffraction spots of the anatase phase are marked by dotted circles; **c)** and **d)** EDX mapping with Co (**c**, yellow) and Ti (**d**, green) of the Co/m-TiO<sub>2</sub>\*-reox catalyst.

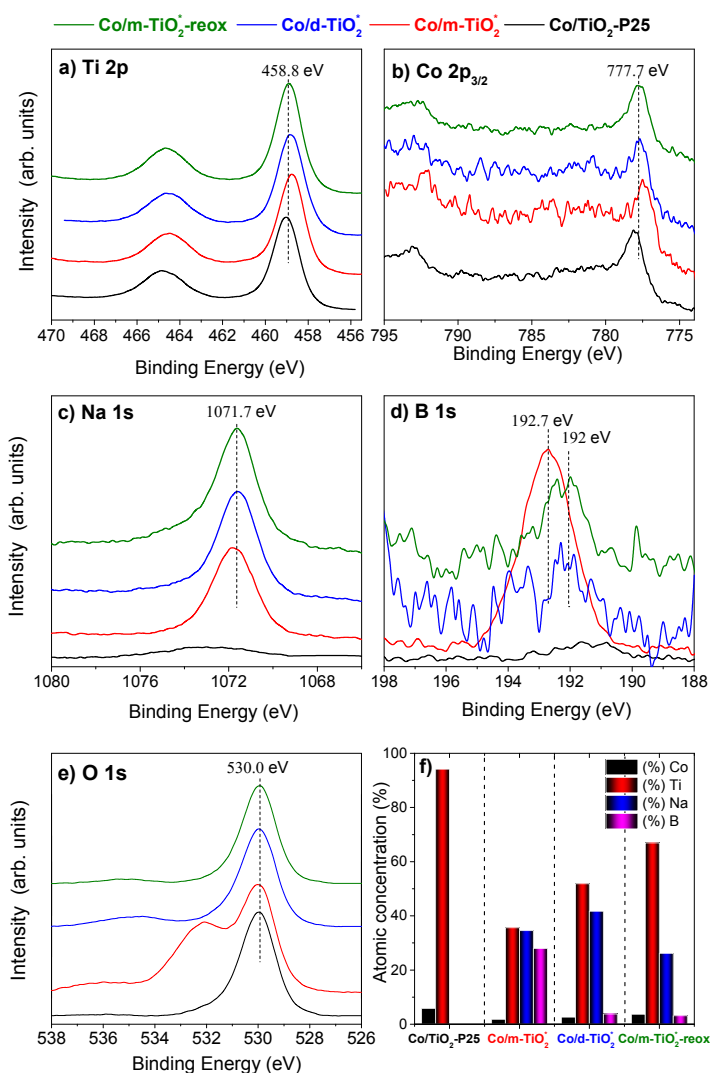
The FFT patterns of the framed areas on **Figure 2a** are presented on **Figure 2b**. The Co and Ti EDX mapping are given in **Figures 2c** and **2d**. Both elements are present in the particle. The spots surrounded by dotted circles on **Figure 2b** were attributed to the (200) reflection of A-TiO<sub>2</sub>. This reflection is observed throughout the particle (frames dark blue, red and magenta). For the particle in the bottom right-hand corner, A-TiO<sub>2</sub> is evidenced by the (101) reflection showing a different crystallographic orientation. The SMSI effect appearing during H<sub>2</sub> reduction has been shown to be more pronounced on Co/A-TiO<sub>2</sub> compared to Co/R-TiO<sub>2</sub> [52]. It is worth noting that this SMSI effect may be partly reversed during FTS, especially at high conversion [53]. Standard EDX is not appropriate for detecting light elements ( $Z < 11$ ). Thus, boron cannot be detected by EDX, while the detection of Na is not easy due to its low  $Z$  (11), and its low concentration in all promoted catalysts. Sodium was detected on the Co/d-TiO<sub>2</sub>\* catalyst (**Figure S12**). Its location (on the support or on Co particles), cannot be precisely determined, as most of the time Co and TiO<sub>2</sub> particles overlap. However, some analyses on isolated Co particles have revealed association of Na, Ti and Co. For the Co/m-TiO<sub>2</sub>\* (**Figure S13**) and Co/m-TiO<sub>2</sub>\*-reox (**Figure S14**) catalysts, Na seems to be associated to the support.

The presence of radical species on the calcined catalysts was probed by EPR (**Figure S15**). Their concentration is extremely low (<1 nmol/mg) on all the catalysts and few residual O<sub>v</sub> are detectable only on the catalysts prepared on the promoted supports. Such residual species might

be related to defects in the subsurface layers, which are not re-oxidized, or simply, to the presence of Na and B, which doping favors the formation of  $O_v$  and  $Ti^{3+}$  [54]. The surface defects can, in theory, be reformed during the reduction step or during catalysis, for example thanks to hydrogen spillover [55-57]. EPR studies were attempted on the reduced catalysts to verify any further formation of surface defects. However, the presence of ferromagnetic  $Co^0$  strongly perturbed the cavity, preventing us from collecting meaningful spectra.

To overcome this limitation of EPR, we followed by *in situ* Raman analysis the evolution of the  $TiO_2$  bands during the reduction of the catalysts under  $H_2$  at  $340^\circ C$ , as well as during reaction under  $CO_2/H_2$  (1 bar) at  $220^\circ C$  (**Figure S16**). On the calcined catalysts, the A- $TiO_2$   $E_g(1)$  band was initially at a lower position on  $Co/TiO_2$  (*ca.*  $146\text{ cm}^{-1}$ ) than on the promoted catalysts (*ca.*  $147\text{-}148\text{ cm}^{-1}$ ). Since EPR analyses point to very few  $O_v$  and  $Ti^{3+}$  on the calcined catalysts, this shift should be associated to the disorder induced by the presence of dopants in the promoted catalysts [58]. In the course of the reduction, the band of  $Co/TiO_2$  at *ca.*  $146\text{ cm}^{-1}$  evolved, notably when cobalt oxide was reduced but it finally remained *ca.*  $2\text{ cm}^{-1}$  lower than on the promoted catalysts. During the reaction with  $CO_2/H_2$ , the band on  $Co/TiO_2$  stabilized at  $144\text{ cm}^{-1}$  while the band for  $Co/m\text{-}TiO_2^*$  and  $Co/m\text{-}TiO_2^*\text{-reox}$  remained centered at *ca.*  $148\text{ cm}^{-1}$ . These analyses do not support the formation of  $O_v$  and  $Ti^{3+}$  during the reduction of the catalysts or during reaction under 1 bar.

The surface state of the catalysts was analyzed by X-ray photoelectron spectroscopy (XPS). The samples were initially reduced at  $400^\circ C$  under 7 mbar  $H_2$  for 30 min in a variable pressure reactor attached to the spectrometer and then transferred under vacuum for the XPS measurements (*quasi in situ* XPS). The XPS survey scans (**Figure S17**) are dominated by the photoemission and Auger peaks of  $TiO_2$  and Na (for promoted catalysts) in addition to carbon peak typically present on samples synthesized by chemical methods. The B 1s and Co 2p peaks are less visible in the survey scans indicating lower surface concentration. According to the high-resolution spectra shown in **Figure 3a**, the binding energy (BE) of the Ti  $2p_{3/2}$  peak at  $458.7(\pm 0.2)\text{ eV}$  (in parenthesis the variation among the different catalysts) corresponds to  $Ti^{4+}$  ions of stoichiometric  $TiO_2$ , while there are no evidences of  $Ti^{3+}$  presence, typically manifested at the low BE side of the Ti 2p peak [59].



**Figure 3.** **a)** Ti 2p; **b)** Co 2p<sub>3/2</sub>; **c)** Na 1s; **d)** B 1s; **e)** O 1s *quasi in situ* X-ray photoelectron spectra measured after reduction at 400 °C in 7 mbar H<sub>2</sub> of Co/TiO<sub>2</sub>\* (black line), Co/m-TiO<sub>2</sub>\* (red line), Co/d-TiO<sub>2</sub>\* (blue line) and Co/m-TiO<sub>2</sub>\*-reox (green line) catalysts. All peaks are normalized to the same height. **f)** The surface atomic concentration of the four catalysts calculated by the *quasi in situ* XPS results.

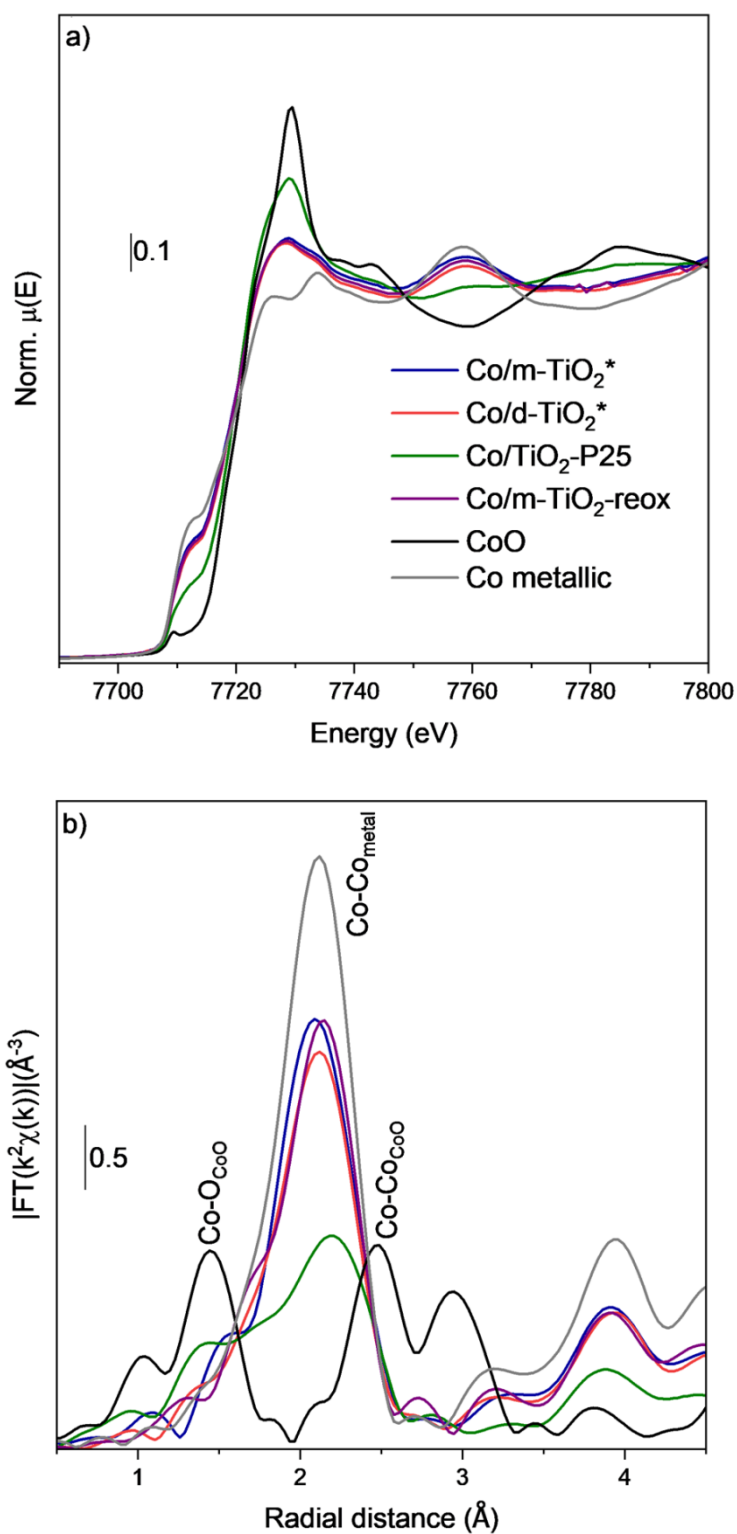
The Co 2p<sub>3/2</sub> peak at 777.7(±0.2) eV is characteristic of metallic Co (**Figure 3b**) [60, 61], but traces of ionic cobalt cannot be excluded due to the low signal to noise ratio. The BE of Na 1s for all promoted catalysts appear at 1071.7(±0.1) eV (**Figure 3c**). According to previous XPS studies, this BE is associated either to sodium (bi)carbonates [62, 63] or sodium-titanate compounds [64-66]. The formation of sodium oxides (e.g. Na<sub>2</sub>O) or hydroxides (e.g. NaOH) is rather unlikely, since in this case the Na 1s appears either at higher or lower BEs, respectively than 1071.7 eV [67, 68]. The C 1s spectra can help to distinguish between sodium titanate and carbonate species since carbonates should be accompanied by a characteristic C 1s peak at around 290 eV [62]. As shown in **Figure S18**, the C 1s region is dominated by a component at 284.6±0.1 eV due to hydrocarbons, excluding carbonate formation. Based on that, we conclude that Na interacts with the TiO<sub>2</sub> support to form sodium-titanate. The B 1s peak of Co/m-TiO<sub>2</sub>\* is centered at 192.7±0.1 eV, while for the other two promoted samples it is around 192 eV and is significantly less intense (**Figure 3d**). Previous reports indicated that B 1s peak is sensitive to the local chemical environment of boron [69-72]. In particular, anionic B<sup>2-</sup> (*i.e.* TiB<sub>2</sub> or CoB)

and cationic  $B^{3+}$  (*i.e.*  $B_2O_3$ ) appears around 187.5 eV and 193 eV, respectively; while B occupying substitutional or interstitial  $TiO_2$  sites is found between 190 and 192 eV [69-73]. Accordingly, on  $Co/m-TiO_2^*$  surface boron forms an oxide (e.g.  $B_2O_3$ ), while on  $Co/d-TiO_2^*$  and  $Co/m-TiO_2^*$ -reox it is most likely incorporated into  $TiO_2$ . The O 1s spectra (**Figure 3e**) are very similar for  $Co/TiO_2$ ,  $Co/d-TiO_2^*$  and  $Co/m-TiO_2^*$ -reox catalysts, with a peak at 530.0( $\pm$ 0.1) eV ascribed to lattice  $TiO_2$  species [74]. A distinctly different spectrum is found for  $Co/m-TiO_2^*$ , with an additional O 1s component around 532.3 eV, typically attributed to hydroxyl groups [74]. For the  $Co/m-TiO_2^*$  catalyst, this peak can be also related to boron oxide [74]. Calculation of the boron oxide stoichiometry by the O 1s and B 1s spectra, assuming that the component at 532.3 eV is exclusively related to boron oxide, gives a stoichiometry of  $BO_{2.2}$ , which is significantly higher than the one expected for common boron oxides (*i.e.* boron trioxide,  $BO_{1.5}$ ). Based on this, one can safely assume that apart of boron oxide, a significant population of OH groups is stabilized on  $Co/m-TiO_2^*$ .

The intensity of the XPS spectra allows quantifying the concentration of the chemical elements on the surface. As shown in **Figure 3f**, the Co surface concentration (in at. %) is below 6 % for all catalysts, which is significantly lower than the bulk concentration measured by ICP-OES (**Table 2**). Taking into account the surface sensitivity of XPS (estimated analysis depth *ca.* 7 nm), this result suggests encapsulation of Co under  $TiO_2$  as shown by STEM-HAADF analyses. Notably, the lowest cobalt concentration was measured on  $Co/m-TiO_2^*$  (around 2%) and the highest on  $Co/TiO_2$  (around 6%). The reason for the presence of a greater quantity of boron on the surface of  $Co/m-TiO_2^*$  compared to the other two promoted catalysts is still unclear. The concentration of Na promoter is several hundred times higher on the surface than in the bulk (**Table 2**), indicating it is preferentially located on the surface. The trend in Na concentration is qualitatively similar with the ICP-OES measurements shown in **Table 2**. Overall, XPS analyses give critical information regarding the surface chemical state, and notably on the nature of the promoters. The  $Co/d-TiO_2^*$  catalyst shows the highest surface concentration of Na among the catalysts and the  $Co/m-TiO_2^*$  presents a high amount of B on its surface. Boron exists as an oxide or is incorporated into  $TiO_2$ , while Na interacts with  $TiO_2$  as sodium-titanate. Finally, the surface concentration of cobalt is lower than in the bulk, confirming spillover of  $TiO_2$ .

The local geometric and electronic structure of cobalt was further analyzed by hard X-rays Absorption Spectroscopy in X-ray Absorption Near Edge Structure (XANES) and Extended X-Ray Absorption Fine Structure (EXAFS) regions. *Ex-situ* Co K-edge spectra of the four reduced catalysts recorded after air exposure, together with reference spectra of CoO and metallic Co (foil), are shown in **Figure 4a**. For all catalysts, the spectrum line shape corresponds to a mixture of Co and CoO phases indicating partial cobalt oxidation, as expected for  $Co/TiO_2$  catalysts exposed to the air [75]. The Co K-edge of the  $Co/TiO_2$  catalyst is different from the other three, showing a clear decrease of the shoulder in the rising edge combined with increased whiteline intensity. Differences are also observed in the Fourier-transformed (FT) EXAFS (**Figure 4b**) with a less intense Co-Co scattering path in the second shell as compared to the other samples due to lower metal concentration. Linear combination analysis (LCA) of the XANES region (**Figure S19**) confirms the higher CoO fraction in  $Co/TiO_2$  due to air exposure. Fit of FT-EXAFS spectra (**Figure S20**) was conducted to gain more insights on cobalt local structure. Due to the intrinsic correlation between Co species concentration, coordination number (CN) and Debye Waller (DW) factor to the dampening of shell intensity, reasonable constrains were applied. Indeed, species concentration was fixed to LCA results and CN was constrained to crystallographic values, while only DW factors were fit as free variables. The obtained DW factors (**Table S4**) are all physically correct, indicating that the employed CN were suitable to describe the presence of CoO and metallic Co. Thus, for all catalysts the majority of cobalt particles have bulk characteristics, which are generally attained for sizes

above 3 nm [76, 77]. Apart from the particle size, the radial Co-Co distance is sensitive to potential interaction of cobalt atoms with heteroatoms. As shown in **Table S4**, the radial distances in the first and second cell are identical with those of bulk Co and CoO phases, which rule out the possibility of Co-Ti, Co-B or Co-Na compounds formation.



**Figure 4.** Co K-edge XANES **a)** and **b)** FT-EXAFS spectra collected *ex situ* on reduced Co/m-TiO<sub>2</sub> (blue line), Co/d-TiO<sub>2</sub>\* (red line), Co/TiO<sub>2</sub> (green line) and Co/m-TiO<sub>2</sub>\*-reox (purple

line) catalysts. Reference spectra of CoO (black line) and metallic Co (grey line) are reported for clarity. Experimental EXAFS spectra are reported in **Figure S19** for clarity.

However, due to the relatively large cobalt particles, the EXAFS spectra in our case are not sensitive to surface or interface interactions, therefore one cannot exclude that cobalt is in contact with Na or B, but we can only talk about two separate phases. Overall, EXAFS analysis indicates that cobalt electronic and geometric structure of all examined catalysts is very similar with particle exceeding 3 nm, and the absence of mixed Co-B or Co-Na compounds.

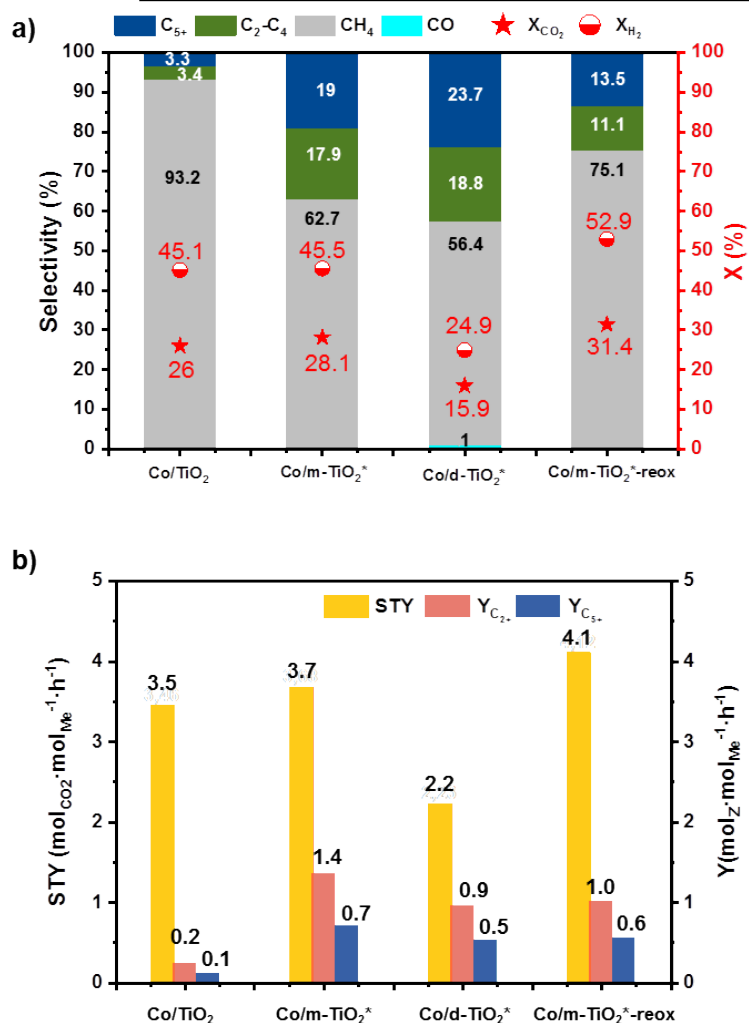
To summarize catalyst characterization results, high levels of cobalt reduction (> 90%) have been obtained for the four reduced catalysts, and no specific charge transfer between cobalt and support or promoters is evidenced from XPS. SMSI encapsulation effect was evidenced for the four catalysts by STEM-HAADF and confirmed by XPS. After cobalt deposition on the modified TiO<sub>2</sub> supports, the defects (O<sub>v</sub> and Ti<sup>3+</sup>) present on the bare supports disappear due to the highly oxidative atmosphere present during the calcination step. XPS and *in situ* Raman analyses support the fact that these defects did not reappear upon catalyst reduction. The promoters (Na and B) are present on the surface of promoted catalysts. Sodium, which is the main promoter, is mainly present as an amorphous sodium-titanate phase. Boron is present in lower amounts than Na, and exists as an oxide or is incorporated into TiO<sub>2</sub>. The cobalt electronic/geometric structure of the four catalysts is very similar, and did not include mixed Co-B or Co-Na compounds.

**2.3 CO<sub>2</sub>-FTS on Co/TiO<sub>2</sub> catalysts.** The catalytic results at T = 220 °C after 50 h on stream are presented in **Table 3** and **Figure 5**. The catalyst prepared on TiO<sub>2</sub>-P25 shows, as expected [78], a very high selectivity of 93 % towards methane. The three catalysts prepared on the modified supports display significantly higher selectivity towards C<sub>2+</sub> and C<sub>5+</sub> products. Overall, the catalysts prepared on the reduced supports, namely Co/m-TiO<sub>2</sub>\* and Co/d-TiO<sub>2</sub>\* present the lowest Y<sub>CH<sub>4</sub></sub> and the highest Y<sub>C<sub>2+</sub></sub> and Y<sub>C<sub>5+</sub></sub>.

**Table 0.** X<sub>H<sub>2</sub></sub>/X<sub>CO<sub>2</sub></sub> ratio, and yields (mol<sub>Z</sub>·mol<sub>Me</sub><sup>-1</sup>·h<sup>-1</sup>, Z = CH<sub>4</sub>, C<sub>2+</sub>, CO) of the catalysts after 50 h on stream at T = 220 °C, P = 20 bar, H<sub>2</sub>/CO<sub>2</sub> = 2, WHSV = 1620 mL·g<sub>cat</sub><sup>-1</sup>·h<sup>-1</sup>.

| Catalyst                | CO <sub>2</sub> conversion (%) | X <sub>H<sub>2</sub></sub> /X <sub>CO<sub>2</sub></sub> | Y <sub>CH<sub>4</sub></sub>   | Y <sub>C<sub>2+</sub></sub> | Y <sub>CO</sub> |
|-------------------------|--------------------------------|---|---|-----------------------------|-----------------|
|                         |                                |   | (mol <sub>Z</sub> ·mol <sub>Me</sub> <sup>-1</sup> ·h <sup>-1</sup> ) |                             |                 |
| Co/TiO <sub>2</sub>     | 26                             | 1.73  | 3.22  | 0.23                        | 0.00            |
| Co/m-TiO <sub>2</sub> * | 28.1                           | 1.61  | 2.31  | 1.36                        | 0.01            |
| Co/d-TiO <sub>2</sub> * | 15.9                           | 1.56  | 1.26  | 0.95                        | 0.02            |

Co/m-TiO<sub>2</sub>\*-reox                      31.4                      1.68                      3.09                      1.01                      0.01



**Figure 5. a)** Conversion (red) and selectivity (black or white); **b)** Space-time yield (STY, mol<sub>CO<sub>2</sub></sub>·mol<sub>Me</sub><sup>-1</sup>·h<sup>-1</sup>) and yields (Y, mol<sub>Z</sub>·mol<sub>Me</sub><sup>-1</sup>·h<sup>-1</sup>, Z = C<sub>2+</sub>, C<sub>5+</sub>) of the catalysts involved in this study after 50 h on stream, T = 220 °C, P = 20 bar, H<sub>2</sub>/CO<sub>2</sub> = 2, WHSV = 1620 mL·g<sub>cat</sub><sup>-1</sup>·h<sup>-1</sup>.

Few amounts of CO are formed on the catalysts prepared from modified supports. The lower X<sub>H<sub>2</sub></sub>/X<sub>CO<sub>2</sub></sub> ratios of the modified catalysts (**Table 3**), may indicate a lower surface H/C coverage. Several authors have reported that a low H/C coverage allows limiting methanation and enhancing RWGS activity, which in turn promotes chain growth [6, 78]. As far as CO<sub>2</sub> conversion is concerned, it is significantly reduced for the Co/d-TiO<sub>2</sub>\* catalyst, which contains the higher sodium concentration. The presence of promoters in smaller concentrations on Co/m-TiO<sub>2</sub>\* and Co/m-TiO<sub>2</sub>\*-reox catalysts did not affect the CO<sub>2</sub> conversion. At 220 °C, Co/m-TiO<sub>2</sub>\* is the best catalyst for C<sub>2+</sub> production.

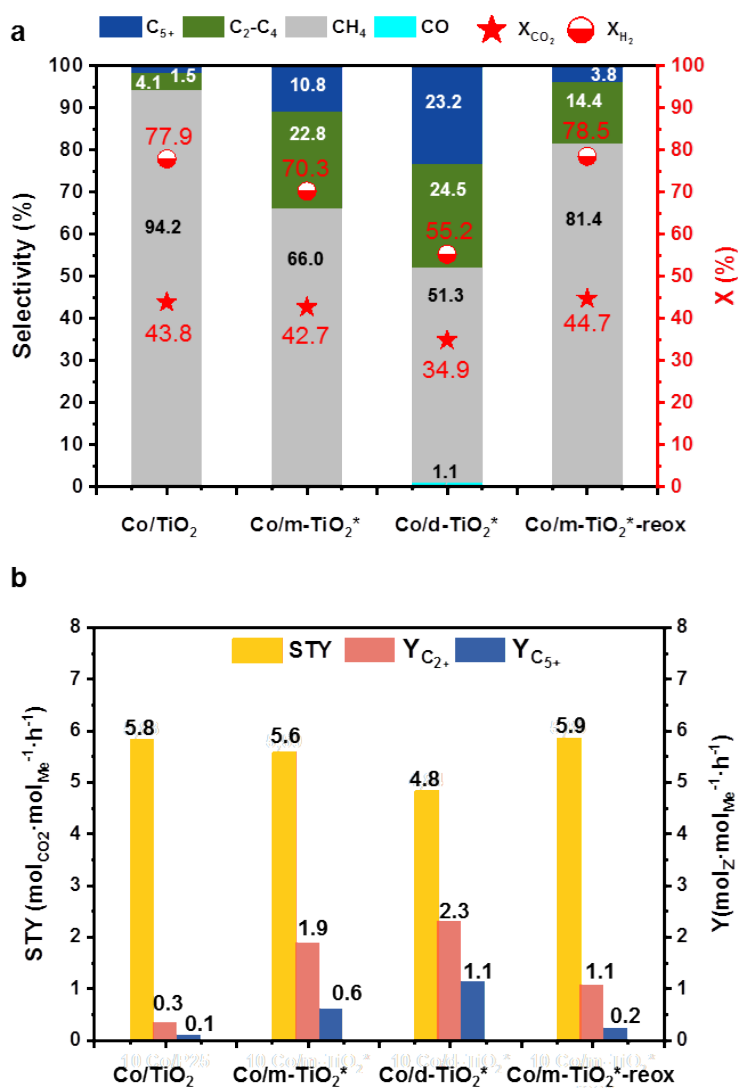


A series of tests was also performed for 25 h at 250 °C and 20 bar, after the initial tests at 220 °C, which are presented in **Table 4** and **Figure 6**.

**Table 4.**  $X_{H_2}/X_{CO_2}$  ratio after 25 h on stream; yields ( $\text{mol}_Z \cdot \text{mol}_{Me}^{-1} \cdot \text{h}^{-1}$ ,  $Z = CH_4, C_{2+}, CO$ ) of the catalysts involved in this study after 25 h on stream at  $T = 250$  °C,  $P = 20$  bar,  $WHSV = 1620 \text{ mL} \cdot \text{g}_{cat}^{-1} \cdot \text{h}^{-1}$ .

| Catalyst                         | CO <sub>2</sub> conversion |  | $X_{H_2}/X_{CO_2}$ | $Y_{CH_4}$  | $Y_{C_{2+}}$ | $Y_{CO}$ |
|----------------------------------|----------------------------|--|--------------------|---|--------------|----------|
|                                  | (%)                        |  |                    |   |              |          |
|                                  |                            |  |                    | (mol <sub>Z</sub> ·mol <sub>Me</sub> <sup>-1</sup> ·h <sup>-1</sup> ) |              |          |
| Co/TiO <sub>2</sub> -P25         | 43.8                       |  | 1.77               | 5.49  | 0.33         | 0.01     |
| Co/m-TiO <sub>2</sub> *          | 42.7                       |  | 1.64               | 3.69  | 1.88         | 0.02     |
| Co/d-TiO <sub>2</sub> *          | 34.9                       |  | 1.58               | 2.48  | 2.30         | 0.05     |
| Co/m-TiO <sub>2</sub> *-<br>reox | 44.7                       |  | 1.75               | 4.77  | 1.07         | 0.02     |

At 250 °C, all catalysts are more active than at 220 °C; and several differences can be noticed in the product distribution. First, the selectivity towards CH<sub>4</sub> increases on most catalysts, because of a higher H<sub>2</sub> activation level revealed also by an increase of the  $X_{H_2}/X_{CO_2}$  ratio (**Table 4**). Moreover, the selectivity towards C<sub>2</sub>-C<sub>4</sub> products increases at the expense of C<sub>5+</sub>. The only catalyst that does not follow this trend is Co/d-TiO<sub>2</sub>\*. This catalyst produces slightly less CH<sub>4</sub> and more C<sub>2</sub>-C<sub>4</sub> products at 250 °C than at 220 °C. Consequently, Co/d-TiO<sub>2</sub>\* is the best catalyst at 250 °C, showing even higher  $Y_{C_{2+}}$  and  $Y_{C_{5+}}$  than Co/m-TiO<sub>2</sub>\*. The presence of a higher amount of promoter on Co/d-TiO<sub>2</sub>\* likely permits to maintain a good H/C surface ratio at 250 °C, similarly to what occurs on other alkali promoted catalysts [16, 41, 79, 80]. Therefore, Co/m-TiO<sub>2</sub>\* and Co/d-TiO<sub>2</sub>\* are the best catalysts to produce C<sub>2+</sub> and C<sub>5+</sub> via CO<sub>2</sub>-FTS, at 220 °C and 250 °C, respectively. Although it is difficult to compare the catalytic performance of different systems reported in the literature due to the use of different reactors and often not strictly identical operating conditions, the two catalysts Co/m-TiO<sub>2</sub>\* and Co/d-TiO<sub>2</sub>\* performed very well in terms of STY and in particularly of  $Y_{C_{2+}}$  compared to the best cobalt catalysts described in the literature for CO<sub>2</sub>-FTS (**Table S5**).

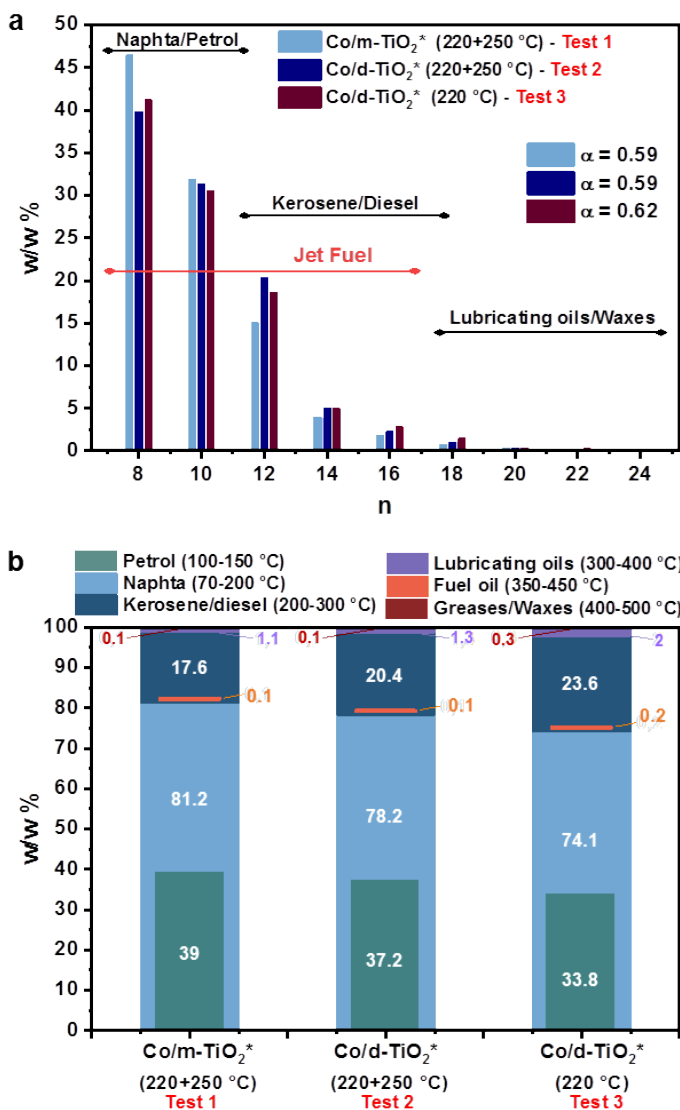


**Figure 6.** **a**) Conversion (red) and selectivity (black or white); **b**) STY (mol<sub>CO<sub>2</sub></sub>·mol<sub>Me</sub><sup>-1</sup>·h<sup>-1</sup>) and yields (mol<sub>Z</sub>·mol<sub>Me</sub><sup>-1</sup>·h<sup>-1</sup>, Z = C<sub>2+</sub>, C<sub>5+</sub>) of the catalysts involved in this study after 25 h on stream, T = 250 °C, P = 20 bar, H<sub>2</sub>/CO<sub>2</sub> = 2, WHSV = 1620 mL·g<sub>cat</sub><sup>-1</sup>·h<sup>-1</sup>.

To investigate any modification of the catalyst structure during the reaction, XRD was performed on the four catalysts after catalytic tests at 250 °C. XRD diffractograms of the spent catalysts are shown in **Figure S21**, and the main parameters of the TiO<sub>2</sub> phases are summarized in **Table S6**. XRD patterns of the used catalysts show the presence of a sharp peak, centered at 30.9°, which is attributed to graphitic carbon (**Figure S21a**) [44]. Small variations of the *hcp*- and *fcc*-Co peaks suggest modifications of the Co active phase during the catalytic tests. The formation of cobalt carbides can be envisaged [81]. The most intense peak of Co<sub>3</sub>C should be centered at ~ 51.7°, and is overlapped with other phases. Isolated diffraction peaks of Co<sub>3</sub>C with lower intensity are not visible. However, the presence of this phase cannot be completely excluded. No significant variation of anatase and rutile crystallite size, or rutile phase percentage was noticed after catalysis (**Table S6** and **Table S3**).

According to **Table S5**, Co/m-TiO<sub>2</sub>\* and Co/d-TiO<sub>2</sub>\* have been identified as the most performing catalysts. To assess their stability and collect some oil products for  $\alpha$  determination,

long tests were performed at 220 °C and the results are presented in **Figure S22** and **Figure S23**. The Co/m-TiO<sub>2</sub>\* catalyst (**Figure S22**) is extremely stable at 20 bar and 220 °C, while Co/d-TiO<sub>2</sub>\* catalyst (**Figure S23**) shows a fluctuating behavior, needing 75-100 h on stream for its performance to be stabilized. These, and other similar tests carried out at both 220 and 250 °C on these two catalysts allowed the collection of liquid hydrocarbons as illustrated in **Figure S24**. For GC analysis, three different CO<sub>2</sub>-FTS catalytic tests, which produced the highest amount of oil products, were considered (**Table S7**). The oil fractions were analyzed by GC-SimDist. **Figure 7** shows the product distribution of the oil phase as a function of carbon chain length (n) and corresponding chain growth probability ( $\alpha$ ). No alcohols were detected in the water fractions by GC and GC-MS. No C<sub>2</sub>H<sub>4</sub> was detected during the catalytic tests with any of the four catalysts involved in this study. The results of the SimDist analysis show that the C<sub>5+</sub> products for both catalysts correspond mainly to the jet-fuel fraction (C<sub>8</sub>-C<sub>16</sub>), with only a small difference between the two catalysts. Consequently, the  $\alpha$  values are very similar between these two catalysts, and are close to the maximum values that can be obtained in CO<sub>2</sub>-FTS (0.5-0.6) [82-84]. Slightly higher  $\alpha$  value was obtained during the single test at 220 °C on the Co/d-TiO<sub>2</sub>\* catalyst, indicating that 220 °C is a more suitable temperature for CO<sub>2</sub>-FTS, and an increase in the operating temperature favors chain termination, which is in line with the observed variation of selectivity. However, we must take into consideration that the  $\alpha$  variations of these three different tests might be related to the different time on stream (TOS) at 220 °C and 250 °C.

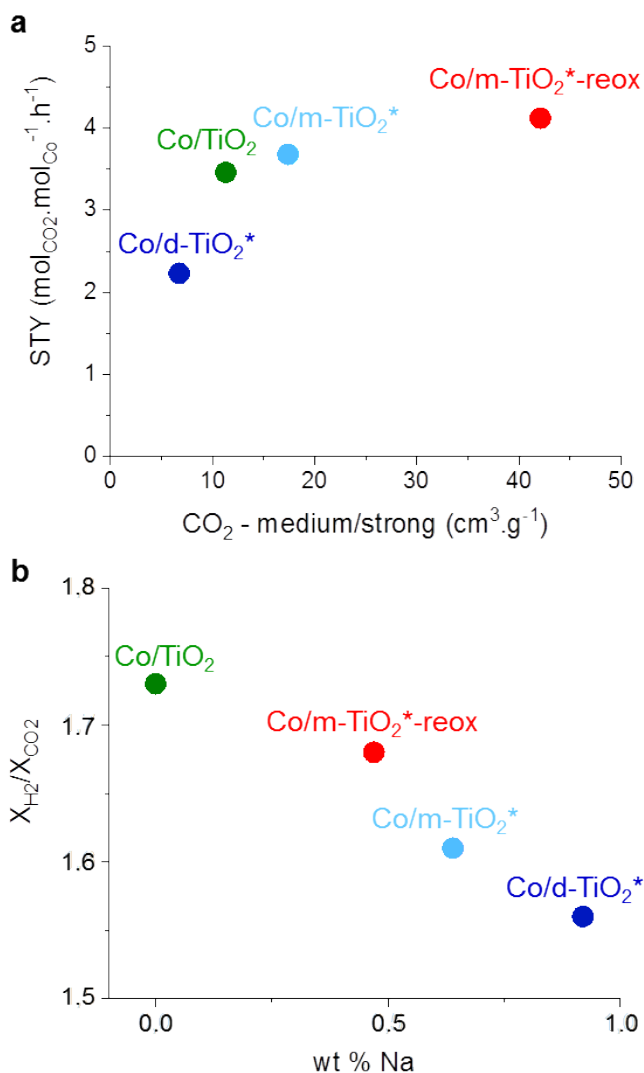


**Figure 7. a)** Product distribution of the oil liquid phase as a function of carbon chain length ( $n$ ) and corresponding chain growth probability ( $\alpha$ ). Light blue = Test 1: catalyst Co/m-TiO<sub>2</sub>\*, 150 h at 220 °C + 50 h at 250 °C; Test 2: dark blue = catalyst Co/d-TiO<sub>2</sub>\*, 70 h 220 °C + 70 h at 250 °C; Test 3: wine = catalyst Co/d-TiO<sub>2</sub>\*, 225 h at 220 °C;  $P = 20$  bar,  $H_2/CO_2 = 2$ ,  $WHSV = 1620 \text{ mL} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$ . **b)** Product distribution of the oil liquid phases expressed in terms of different distillation fractions.

**2.4 Impact of TiO<sub>2</sub> modification on CO<sub>2</sub>-FTS and structure/performance correlation.** To rationalize the obtained catalytic results and try to correlate the catalyst performance to their structure, additional characterizations were performed on the four catalysts.

CO<sub>2</sub>-TPD, CO-TPD, N<sub>2</sub> adsorption isotherm and H<sub>2</sub>-TPR analyses are shown in **Figure S25**, and the main results are summarized in **Table S8**. The catalysts prepared on the modified supports, although presenting a similar specific surface area as Co/TiO<sub>2</sub>, adsorb higher amount of CO<sub>2</sub> than Co/TiO<sub>2</sub>. All Co-based catalysts adsorb less CO<sub>2</sub> than the corresponding bare supports (**Figure S26**). Such result indicates that the support plays a major role in CO<sub>2</sub> adsorption [40], and Co particle deposition should induce the blocking of part of the CO<sub>2</sub>

adsorption sites of the supports. This phenomenon is much less pronounced for the Co/m-TiO<sub>2</sub>\*-reox sample. This might be related to a different distribution of Co particles, a different extent of SMSI, or to the presence of different CO<sub>2</sub> adsorption sites on this catalyst, resulting from a different location of the promoters on the support, probably related to surface reconstruction during the reoxidation step. The total amounts of adsorbed CO<sub>2</sub> cannot be directly correlated to the STY or selectivity of the catalysts. If we consider only the medium/strongly adsorbed CO<sub>2</sub> on the various catalysts, notable differences are observed between the four catalysts (**Figure S27**). Particularly, the more active Co/m-TiO<sub>2</sub>\*-reox catalyst shows the highest amounts of the medium/strongly adsorbed CO<sub>2</sub> and the opposite is observed for the less active Co/d-TiO<sub>2</sub>\* catalyst. The reason why this latter catalyst shows the lower amount of medium/strongly adsorbed CO<sub>2</sub> is still unclear. If we now consider this amount of medium/strongly adsorbed CO<sub>2</sub>, which should be important for the catalytic reaction, it correlates well with catalyst activity (**Figure 8a**), but not with selectivity. At a first glance, it might be surprising that the Co/d-TiO<sub>2</sub>\* catalyst, which present the higher sodium loading and the higher surface Na concentration, is the less active. However, beside CO<sub>2</sub> activation *via* adsorption, promoters can play different roles in the reaction. For instance, it was reported that small amount of B (< 0.1%) can decrease the H<sub>2</sub> uptake of a 10 wt% Co/TiO<sub>2</sub> catalyst, and increase the final  $\alpha$  during traditional CO-FTS [85]. Alkali metals are electron donors and, therefore, may act by enhancing chemisorption of electron acceptor species, such as CO,[86] and/or by suppressing chemisorption of electron donors, such as H<sub>2</sub> [87]. The electron donation from the alkali promoters to the metal species, results in a decreased possibility of electron donation from H<sub>2</sub>, thus, limiting its activation [16, 41]. Such phenomena have already been reported for Na<sub>2</sub>O-doped Co catalysts [88, 89]. The lower STY (2.2 mol<sub>CO<sub>2</sub></sub>.mol<sub>Co</sub><sup>-1</sup>.h<sup>-1</sup>) obtained for the Co/d-TiO<sub>2</sub>\* catalyst, might be related to strong electronic interactions between Co sites and the promoter(s). Such interaction strongly limits H<sub>2</sub> activation, resulting in a reduced activity, but good selectivity. For the other modified catalysts, the STY varied between 3.4 and 4.1 mol<sub>CO<sub>2</sub></sub>.mol<sub>Co</sub><sup>-1</sup>.h<sup>-1</sup> for Co/TiO<sub>2</sub> and Co/m-TiO<sub>2</sub>\*-reox, respectively. It is therefore unlikely that Na interacts significantly with cobalt in these two catalysts, which are significantly more active than the Co/d-TiO<sub>2</sub>\* catalyst. Therefore, the promoter(s) should be on the support, and available for CO<sub>2</sub> activation. We independently prepared a Co-1%Na/m-TiO<sub>2</sub>\* catalyst, obtained by the addition of 1 wt% Na to the Co/m-TiO<sub>2</sub>\* by IWI method using NaNO<sub>3</sub> as precursor. In this new catalyst, it is likely that the excess promoter can also deposit on the metal. The Co-1%Na/m-TiO<sub>2</sub>\* catalyst shows a drastic decrease of the activity, but not of the selectivity, in comparison with Co/m-TiO<sub>2</sub>\* (**Figure S28**).



**Figure 8.** **a)** Evolution of STY (based on total Co) with the amount of CO<sub>2</sub> adsorbed medium/strongly on the catalyst surfaces; and **b)** evolution of the X<sub>H2</sub>/X<sub>CO2</sub> ratio during CO<sub>2</sub>-FTS and the sodium loading in the catalysts.

Therefore, it is reasonable to propose that when Na is directly interacting with cobalt in the modified catalysts (located on cobalt or at perimetric sites of Co crystallites) [87], its presence strongly decreases catalyst activity and increases its selectivity compared to the unpromoted catalyst. This is the case of the Co/d-TiO<sub>2</sub>\* catalyst, for which, interestingly, Na and Co were detected on the same areas (**Figure S12**). Alternatively, when Na is present mainly on the support of modified catalysts (added alkalis interact strongly with the TiO<sub>2</sub> surface) [54], its presence does not affect catalyst activity, but only its selectivity as compared to unpromoted catalyst. This is a key result of this study, which will be discussed in more detail later. Globally, we found that the amount of sodium in the catalyst impacts the X<sub>H2</sub>/X<sub>CO2</sub> ratio; the higher the Na loading, the lower is this ratio (**Figure 8b**).

We can have an idea about H<sub>2</sub> activation on these catalysts from H<sub>2</sub>-TPR profiles (**Figure S25b**). All catalysts display the main reduction events in a temperature range between ~ 300-600 °C, attributed mainly to the reduction of Co<sub>3</sub>O<sub>4</sub> to CoO and CoO to metallic Co. Differences can be observed in the shapes of the profiles, which might be related to different Co particle size distributions (smaller Co particles have been reported to be more easily reduced on TiO<sub>2</sub> [90]) and/or different interactions with the support or promoter. The Co/TiO<sub>2</sub> catalyst shows

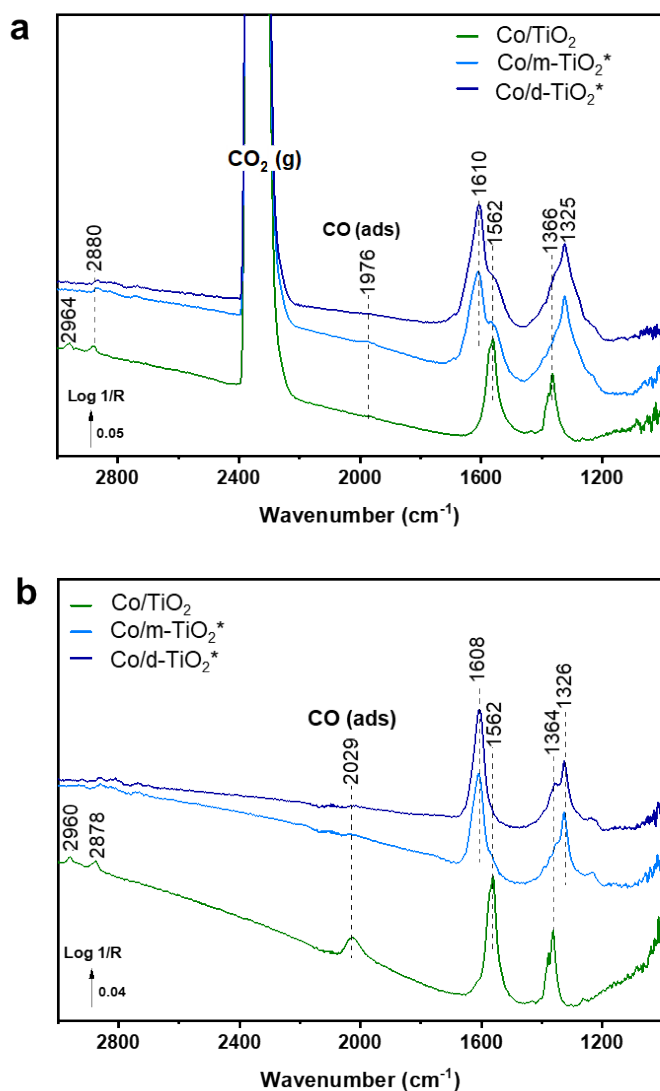
the easiest reduction, which starts slowly at low temperature (*ca.* 120 °C). On Co/m-TiO<sub>2</sub>\*, the reduction starts at slightly higher temperature (*ca.* 150 °C). The different shape of the reduction peaks between Co/m-TiO<sub>2</sub>\* and Co/m-TiO<sub>2</sub>\*-reox suggests a different interaction between cobalt and the support in these two catalysts showing similar amounts of promoters (**Table 1**). This was confirmed by Raman analyses (*vide infra*). The Co/m-TiO<sub>2</sub>\*-reox catalyst shows the lower H<sub>2</sub> consumption of the series. On Co/d-TiO<sub>2</sub>\*, the reduction starts at higher temperature (*ca.* 300 °C) and also finishes at higher temperatures than on Co/TiO<sub>2</sub>, indicating a more difficult reduction. This should be associated to the interaction between the promoter and the metal, which can limit H<sub>2</sub> activation and inhibit the reduction of the active phase [91, 92]. It was also shown that the presence of R-TiO<sub>2</sub>, which is the lowest for the Co/d-TiO<sub>2</sub>\* catalyst (**Table S6**), can facilitate the reduction process of cobalt oxide species on TiO<sub>2</sub> [93]. **Figure S29** shows that globally, the quantification of TPR results (H<sub>2</sub> consumption, **Table S8**) is in line with the VSM results (**Table 2**). At that point, it is interesting to notice that neither the catalyst activity nor their selectivity can be correlated to the reduction degree of cobalt.

Reduction of the Co/TiO<sub>2</sub>, Co/m-TiO<sub>2</sub>\* and Co/m-TiO<sub>2</sub>\*-reox catalysts was also followed by *in situ* Raman spectroscopy (**Figure S30**). Before treatment, Co/TiO<sub>2</sub> and Co/m-TiO<sub>2</sub>\*-reox clearly showed well-defined bands at 469, 510 and 678 cm<sup>-1</sup> attributed to the spinel Co<sub>3</sub>O<sub>4</sub> phase [52]. On both solids, heating under dihydrogen leads to a progressive decrease of these bands already above 60 °C and more pronounced above 120 °C. Above 250 °C, the bands of cobalt oxide become too weak to be detected. Interestingly, different bands appear on the Co/m-TiO<sub>2</sub>\* sample, where a broad peak is observed at 681 cm<sup>-1</sup> and smaller bands at lower wavenumbers. These bands, which are easier to observe when the contribution of TiO<sub>2</sub> is subtracted (**Figure S30b**), get better defined up to 110 °C where the main band also shifts to 686 cm<sup>-1</sup> and the smaller bands are observed at 227, 260, 329, 379, 427 and 602 cm<sup>-1</sup>. These bands are consistent with those reported for the ilmenite CoTiO<sub>3</sub> phase [94, 95]. After this preliminary transformation, heating induces a first transformation to Co<sub>3</sub>O<sub>4</sub>, as observed on the other solids, and its progressive reduction. After reduction, all solids finally showed only the spectrum of TiO<sub>2</sub> and the disappearance of the cobalt oxides, confirming their complete reduction to metallic cobalt. The low temperatures at which changes are observed probably indicate a good initial dispersion of the cobalt species.

The CO-TPD analyses (**Figure S25c** and **Table S8**) indicate that all the catalysts adsorb moderate amounts of CO compared to CO<sub>2</sub>. The CO-TPD profiles show that the promoted catalysts adsorb most of the CO with a weaker bonding than Co/TiO<sub>2</sub>. We also noticed that among the promoted catalysts, a higher amount of medium bonding CO is observed for the Co/d-TiO<sub>2</sub>\* catalyst, which can suggest direct interaction between Na and Co [86]. The stronger CO bonding on Co/TiO<sub>2</sub>, along with the availability of a high number of H species, might favor its immediate hydrogenation to CH<sub>4</sub>. *Operando* DRIFT analyses have been carried out on catalysts Co/TiO<sub>2</sub>, Co/m-TiO<sub>2</sub>\* and Co/d-TiO<sub>2</sub>\* to probe adsorbed CO and CO<sub>2</sub> species. The results are shown in **Figure 9a**.

At 220 °C, 1 bar and H<sub>2</sub>/CO<sub>2</sub> = 2, the principal surface species are quite different between the unpromoted and promoted catalysts. Only bands at 2964, 2880, 1562 and 1366 cm<sup>-1</sup>, which are assigned to formate species adsorbed on titania, are present on the Co/TiO<sub>2</sub> catalyst. The corresponding vibration modes are detailed elsewhere [96]. Additional bands were observed in the case of the promoted samples, which could correspond to sodium formates [97, 98] and carbonates [99, 100]. It has been reported that for unpromoted Co/TiO<sub>2</sub> catalysts, the CO<sub>2</sub> hydrogenation reaction proceeds through formate species on Co/R-TiO<sub>2</sub> (which is further converted to CH<sub>4</sub>), while Co/A-TiO<sub>2</sub> undergoes CO<sub>2</sub> → \*CO (which desorbs to form gas-phase CO instead of subsequent hydrogenation) [16]. The formation of carbonate species on the promoted catalysts could be related to the presence of Na [43, 101]. Interestingly, under H<sub>2</sub>/CO

= 40 (**Figure 9b**), only the Co/TiO<sub>2</sub> catalyst, which presents the highest surface cobalt concentration (XPS), shows a significant concentration of Co<sup>0</sup>-CO, while almost no CO seems to be adsorbed on the promoted catalysts. These results may indicate either that CO is readily dissociated at 220 °C, or that, probably due to a partial TiO<sub>2</sub> coverage, only few metallic Co is accessible on these catalysts [52]. This is typical of SMSI, which usually results in suppressed CO and H<sub>2</sub> chemisorption [102]. Therefore, partial coverage of metallic Co particles might be the reason for the low CO uptake and the different CO interaction strength observed during CO-TPD.



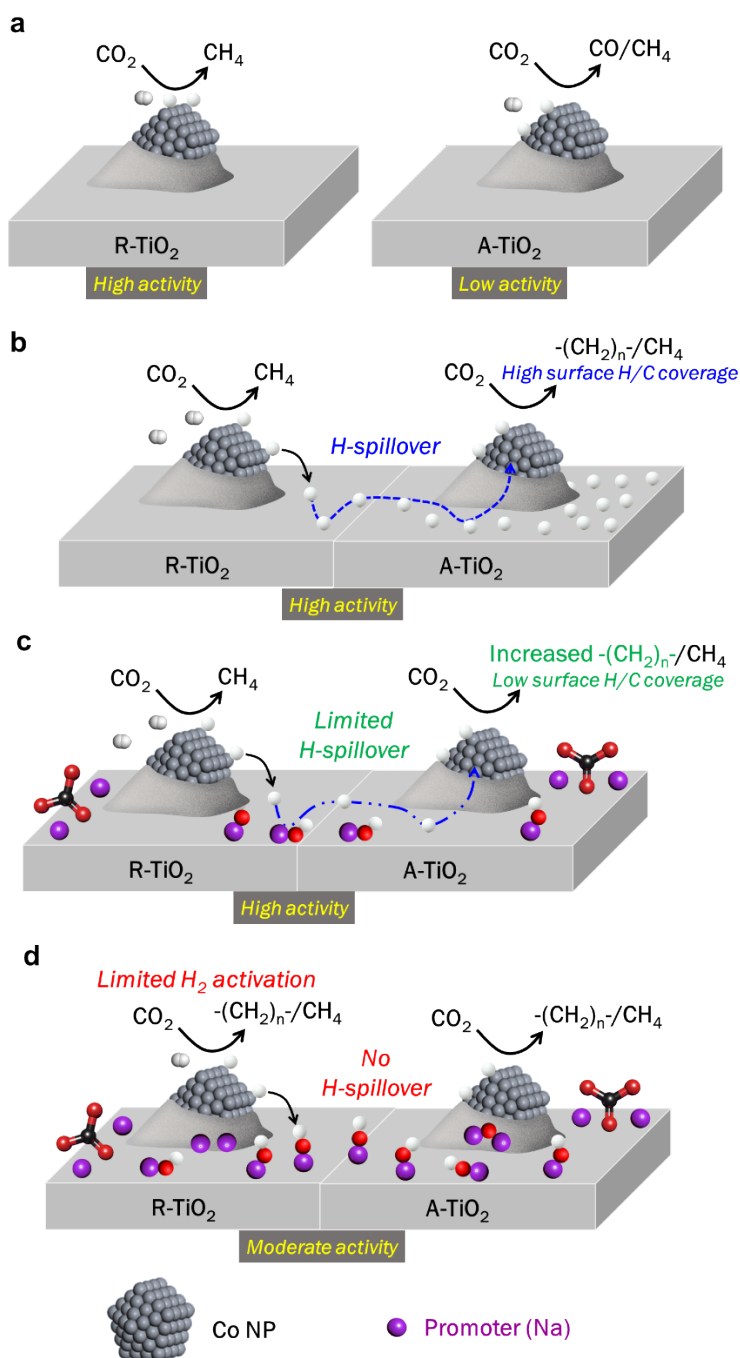
**Figure 9.** **a)** Operando DRIFT after 1 h of reaction with CO<sub>2</sub> at T = 220 °C, P = 1 bar (H<sub>2</sub>/CO<sub>2</sub> = 2). **b)** Operando DRIFT after 1 h of reaction with CO at T = 220 °C, P = 1 bar (H<sub>2</sub>/CO = 40).

The intensity of the cobalt carbonyl band was monitored down to 140 °C under the CO/H<sub>2</sub> stream (**Figure S31**), temperature at which conversion was negligible and surface coverage should have reached its maximum value [103]. These data show that the relative coverage at 220 °C was ca. 83% that at 140 °C over the unpromoted Co/TiO<sub>2</sub>. The near absence Co-CO bands on the promoted sample cannot thus be mostly related to a temperature-dependent surface



coverage, but other effects are at play. We had previously mentioned that coverage of cobalt by  $\text{TiO}_x$  (SMSI effect) was a possible explanation for the lack of reduced cobalt at the sample surface. This was recently confirmed by a synchrotron-based near-ambient pressure X-ray photoelectron and absorption study performed under  $\text{CO}_2/\text{H}_2$  at 250 °C [104]. We should add now that potential cobalt oxidation cannot be excluded under pressure. It had been shown over non-promoted  $\text{Co}/\text{TiO}_2$  catalyst that  $\text{CO}_2$  did not lead to cobalt oxidation [5], but this has not yet been proven on these B- and K-promoted samples, which could lead to more oxophilic cobalt particles.

At that point, the characterizations performed allow us to confirm a dual role of the promoter on catalyst activity. It allows  $\text{CO}_2$  activation (medium/strongly adsorbed  $\text{CO}_2$ ) when present on the support, which can explain the higher STY obtained on the  $\text{Co}/\text{m-TiO}_2^*$  and  $\text{Co}/\text{m-TiO}_2^*$ -reox catalysts compared to the unpromoted  $\text{Co}/\text{TiO}_2$  catalyst. When there is a significant interaction between the promoter and the metal ( $\text{Co}/\text{d-TiO}_2^*$  catalyst), a reduced  $\text{H}_2$  activation induced a drop of the activity and a higher selectivity towards hydrocarbons, in agreement with what is known from the literature. Despite the fact that the promoter location (on the support or in contact with Co) is a key parameter for catalytic performance, a nice correlation was obtained between the total promoter content, independently of its location, and the  $X_{\text{H}_2}/X_{\text{CO}_2}$  ratio. The promoter can also favor the formation of surface defects, which in turn favor the development of SMSI effect, which is present in all the catalysts, but its degree is difficult to quantify. The  $\text{O}_v$  and  $\text{Ti}^{3+}$  defects on the catalysts, which could be present during  $\text{CO}_2$ -FTS at 20 bar, could also play a role on  $\text{CO}_2$  activation. However, taken together, these results do not allow providing an explanation of the large difference in selectivity observed between the unpromoted catalyst ( $\text{Co}/\text{TiO}_2$ ) and the two promoted catalysts, in which Na is mainly located on the support ( $\text{Co}/\text{m-TiO}_2^*$  and  $\text{Co}/\text{m-TiO}_2^*$ -reox). To explain this difference in selectivity, it is necessary to take into account that the  $\text{CO}_2$  hydrogenation operates on a catalyst containing both the A- $\text{TiO}_2$  and R- $\text{TiO}_2$  phases on the same support.

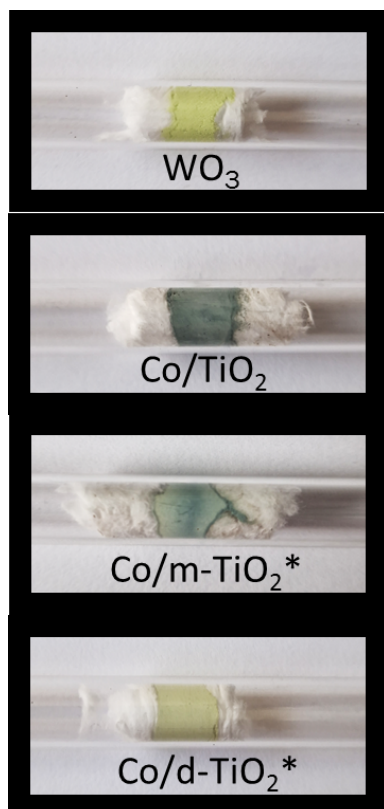


**Figure 10.** Mechanistic pathways for CO<sub>2</sub>-based FTS at 220 °C on unpromoted and alkali-promoted Co/TiO<sub>2</sub> catalysts presenting SMSI. **a).** Unpromoted Co/TiO<sub>2</sub> catalyst presenting different TiO<sub>2</sub> phases on different supports. **b).** Unpromoted Co/TiO<sub>2</sub> catalyst presenting different TiO<sub>2</sub> phases on the same support (TiO<sub>2</sub>-P25). **c).** Alkali-promoted Co/TiO<sub>2</sub> catalyst presenting different TiO<sub>2</sub> phases on the same support (TiO<sub>2</sub>-P25) and alkali on the support (Co/m-TiO<sub>2</sub>\* catalyst). **d).** Alkali-promoted Co/TiO<sub>2</sub> catalyst presenting different TiO<sub>2</sub> phases on the same support (TiO<sub>2</sub>-P25) and alkali on the support and on Co particles (Co/d-TiO<sub>2</sub>\* catalyst). Red spheres correspond to oxygen atoms and white spheres to hydrogen atoms.

It is known from the literature on CO<sub>2</sub> hydrogenation that Co/R-TiO<sub>2</sub> is very active and produces CH<sub>4</sub>, while Co/A-TiO<sub>2</sub> is poorly active and more selective for CO production (**Figure 10a**) [16]. For conventional CO-FTS, the activity of Co/TiO<sub>2</sub> catalysts largely depends on the crystal phase of TiO<sub>2</sub> support [19, 105, 106]. At 230 °C and 10 bar, Shimura and coworkers

have shown that Co/R-TiO<sub>2</sub> is active for CO-FTS, and produces C<sub>5+</sub> hydrocarbons with a good selectivity (68 %), while Co/A-TiO<sub>2</sub> is poorly active and also produces C<sub>5+</sub> hydrocarbons with a good selectivity (72-75 %) [19]. Interestingly, the use of a mixture 15% R-TiO<sub>2</sub>-85% A-TiO<sub>2</sub> as support allows increasing the activity compared to a 98%R-TiO<sub>2</sub> support, while maintaining a good selectivity towards C<sub>5+</sub> hydrocarbons (66 %). However, the origin of the synergy between the two TiO<sub>2</sub> phases was not elucidated in that study. Furthermore, some of us have shown that for CO<sub>2</sub> methanation on Ni/TiO<sub>2</sub> catalysts, the catalytic activity depends appreciably on the nature of the support [107]. Adsorbed CO accumulates on the poorly active Ni/A-TiO<sub>2</sub> and not on the very active Ni/R-TiO<sub>2</sub>. The use of Ni/TiO<sub>2</sub>-P25 allows for a significant increase of the reaction rate related to Ni/R-TiO<sub>2</sub>. In that case, the role of Ni/R-TiO<sub>2</sub> is to assist the hydrogenation of the CO adsorbed on Ni/A-TiO<sub>2</sub>. The synergy operates thanks to H-spillover from Ni/R-TiO<sub>2</sub> to Ni/A-TiO<sub>2</sub>. It is reasonable to propose that a similar synergy could operate on the unpromoted Co/TiO<sub>2</sub> catalyst (**Figure 10b**). H-spillover on Fe/TiO<sub>2</sub> [108], Ni/TiO<sub>2</sub> [109] and Co/TiO<sub>2</sub> [57, 110] catalysts has already been reported. Efficient H-spillover from Co/R-TiO<sub>2</sub> to Co/A-TiO<sub>2</sub> in the Co/TiO<sub>2</sub> catalyst should contribute to the poor C<sub>2+</sub> selectivity of this catalyst, because of an excess of active \*H species on Co/A-TiO<sub>2</sub> favoring CH<sub>4</sub> formation. It is also known that Na<sup>+</sup> species may act as a trap for dissociated hydrogen species, significantly reducing H-spillover and hydrogen mobility on the catalyst surface [111-114]. Consequently, we suspected that for the promoted catalysts, an additional role of the Na deposited on the support (present as sodium titanate) could be to regulate the H-spillover from Co/R-TiO<sub>2</sub> to Co/A-TiO<sub>2</sub> to maintain a lower surface H/C coverage on Co/A-TiO<sub>2</sub>. This modulation of H-spillover (**Figure 10c**) allowed a higher selectivity compared to the unpromoted catalyst, while maintaining a good activity.

To confirm this hypothesis, we have evaluated the H-spillover on the Co/TiO<sub>2</sub>, Co/m-TiO<sub>2</sub>\* and Co/d-TiO<sub>2</sub>\* catalysts. WO<sub>3</sub> was used to diagnose H<sub>2</sub> activation on these catalysts, since it is known that the spilt-over H species can migrate and readily react with WO<sub>3</sub> (yellow powder) to form dark blue H<sub>x</sub>WO<sub>3</sub> [115]. It has to be noted that H<sub>2</sub> molecules can reduce the WO<sub>3</sub> only above 200 °C [116]. As expected, and shown in the photographs in **Figure 11** taken after treatment with H<sub>2</sub> at 180 °C for 30 min, the WO<sub>3</sub> alone exhibited an unchanged color after hydrogen treatment. In contrast, the Co/TiO<sub>2</sub> catalyst gave the darkest color of the tungsten species after H<sub>2</sub> treatment, demonstrating that hydrogen dissociation and spillover occurred.



**Figure 11.** Photographs of samples made with 1 g of  $\text{WO}_3$  mixed or not with 0.01 g of various catalysts after treatment with  $\text{H}_2$  at 180 °C for 30 min.

The  $\text{Co/m-TiO}_2^*$  catalyst also showed the color change, but the resultant color was lighter than that observed with the  $\text{Co/TiO}_2$  catalyst, evidencing a reduced H-spillover for this catalyst presenting Na mainly on the support. Finally, for the  $\text{Co/d-TiO}_2^*$  catalyst containing significant amounts of Na on the support and in interaction with Co particles, no H-spillover is observed. For this latter catalyst (**Figure 10d**), the presence of promoter in interaction with Co particles should lead to a drop in the exposed Co surface [89], to a lower  $\text{H}_2$  activation [16, 41], and finally to a lower activity but good selectivity. Our catalytic tests also show that this phenomenon is more pronounced at 220 °C than at 250 °C, a temperature at which the  $\text{Co/d-TiO}_2^*$  catalyst presented high activity and selectivity.

### 3. Conclusion

Supported Co-based catalysts synthesized on either unmodified or modified  $\text{TiO}_2$  supports were developed and evaluated in  $\text{CO}_2$  hydrogenation. The modification of the reducible oxide ( $\text{TiO}_2$ -P25, containing both rutile and anatase phases) consists in a thermal reduction with  $\text{NaBH}_4$ , which enable introducing surface defects ( $\text{O}_v$  and  $\text{Ti}^{3+}$ ) and promoters (Na, B). The rutile  $\text{TiO}_2$  phase is the most reactive one, resulting in the formation of a disordered  $\text{TiO}_2@TiO_{2-x}$  shell and a sodium titanate phase. The promoted cobalt catalysts contain various amounts of promoters as amorphous phases, which contribute to an increased  $\text{CO}_2$  adsorption, but do not contain surface defects in appreciable concentration. All catalysts show similar electronic/geometric structure, a high level of cobalt reduction and present SMSI effect. The catalyst activity is not proportional to the amount of reduced Co, but to the amount of  $\text{CO}_2$  they can medium/strongly adsorb. These results confirm that one role of the promoter is to assist  $\text{CO}_2$  activation. The promoter concentration is nevertheless important, since a too high concentration results in a decrease in activity. This latter effect must be associated to a weaker activation of  $\text{CO}_2$  that is

moderately/strongly bound, as seen from CO<sub>2</sub> TPD; but also, to the weaker activation of dihydrogen, because the excess of promoter interacts with the cobalt. Consequently, a second role of the promoter, if it interacts with cobalt, should be to limit H<sub>2</sub> activation, thus decreasing activity and increasing C<sub>5+</sub> selectivity. Such a role of alkali promoters is well documented in CO-FTS and is also operative in CO<sub>2</sub>-based FTS.

The promoted catalysts show significantly higher selectivity than the unpromoted one. To rationalize the effect of promoter on both activity and selectivity, it is necessary to take into account the existence of a cooperative catalysis between the Co on rutile TiO<sub>2</sub>, which shows good activity but is selective for CH<sub>4</sub>, and the Co on anatase TiO<sub>2</sub>, which is poorly active and more selective to CO. The synergistic effect involves hydrogen spillover from the Co on rutile TiO<sub>2</sub> to the Co on anatase TiO<sub>2</sub>. At moderate promoter loading, Na should be present mainly on the support, contributing to CO<sub>2</sub> activation. In parallel, the alkali promoter also slows down the H-spillover, contributing to maintaining a low surface H/C coverage of the Co on anatase TiO<sub>2</sub>, resulting in significantly higher selectivity compared to the unpromoted catalyst. These results illustrate how surface promotion effects are valuable tools to adjust the FT product distribution toward the production of synthetic fuels.

#### 4. Material and methods

##### 4.1 Supports and catalysts preparation

***m-TiO<sub>2</sub>\* support.*** 1 g of NaBH<sub>4</sub> (Aldrich, 99.99%) was dissolved in 50 mL of EtOH (Carlo Erba, 99.9 %) into a rotavapor flask. Then, the 10 g of TiO<sub>2</sub>-P25 (Evonik, > 99.5 %) were added to the solution. The mixture was stirred in the rotavapor for 1 h (25 °C, 500 mbar). Subsequently, the EtOH was removed using the rotavapor (80 °C, 150 mbar for 30 min and then 75 mbar for 30 min). The resulting powder was dried overnight at 120 °C in a static oven, grinded and then treated in a tubular oven under argon at 320 °C, for 15 minutes (5 °C.min<sup>-1</sup> ramp). Afterwards, the resulting blue product was recovered under Ar and then washed four times with distilled water, followed by washing with absolute ethanol. Finally, the product was dried for 15 h at 150 °C under argon (5 °C/min ramp).

***d-TiO<sub>2</sub>\* support.*** 1.52 g of NaBH<sub>4</sub> was dissolved in 50 mL of EtOH into a rotavapor flask. Then, the 10 g of TiO<sub>2</sub>-P25 were added to the solution. The mixture was stirred in the rotavapor for 1 h (25 °C, 500 mbar). Subsequently, the EtOH was removed using the rotavapor (80 °C, 150 mbar for 30 min and then 75 mbar for 30 min). The resulting powder was dried overnight at 120 °C in a static oven, grinded and then treated in a tubular oven under argon at 370 °C, for 30 minutes (5 °C.min<sup>-1</sup> ramp). Afterwards, the resulting blue product was recovered under Ar and then washed four times with distilled water, followed by washing with absolute ethanol. Finally, the product was dried for 15 h at 150 °C under argon (5 °C/min ramp).

***m-TiO<sub>2</sub>\*-reox support.*** The desired amount of m-TiO<sub>2</sub>\* support was placed in an alumina combustion boat and treated under air in a static oven at 350 °C for 30 minutes (5 °C/min ramp).

***Cobalt catalysts.*** Cobalt catalysts with a loading of ~ 10 wt% were prepared via incipient wetness impregnation. For each catalyst, 10 g of the corresponding support were placed in a Schlenk vessel and degassed for 2 h under vacuum at 150 °C (oil bath temperature). After cooling down at room temperature, an aqueous metal precursor solution (Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Acros organic, 99 %) was added under vacuum and continuous stirring. The resulting mixture was sonicated for 30 min, followed by 30 min of stirring. The sonication/stirring sequence was repeated 4 times. The mixture was dried for 24 h at 80 °C followed by 12 h at 120 °C in a static furnace. Finally, the powder was treated in a tubular oven at 460 °C, for 4 h, under Ar (5 °C/min ramp).

**Catalyst reduction.** For the characterizations of the reduced samples, 500 mg of catalyst were reduced in a tubular oven under a mixture of 40% H<sub>2</sub>/Ar with a total flow of 25 mL·min<sup>-1</sup>.

## 4.2 Supports and catalysts characterization

**TEM and STEM measurements.** Transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) studies were performed using a JEOL cold-FEG JEM-ARM200F operated at 200kV equipped with a probe Cs corrector reaching a spatial resolution of 0.078 nm. EDX spectra were recorded with a JEOL CENTURIO SDD detector. The TEM analysis was performed on catalyst samples after the reduction steps. The catalyst samples were prepared by ultrasound-assisted dispersion in pure ethanol (Carlo Erba, 99.9 %), and the suspensions were dropped onto a holey carbon film-covered copper grid.

**XRD measurements.** XRD measurements were performed using a Panalytical Empyrean diffractometer equipped with a Co radiation source ( $\lambda = 1.789 \text{ \AA}$ ). The diffraction patterns of supports, calcined and reduced catalysts were recorded within the  $2\theta$  range of 20-95° with an increment of 0.02° and 400 s/step. The Scherrer equation was used for the determination of crystallite size. Anatase and rutile TiO<sub>2</sub> crystallite size were calculated from the peaks at 29.4° and 31.9°, respectively. Co<sub>3</sub>O<sub>4</sub> crystallite size were calculated from the peak at 36.5°.

**Surface area measurements.** The surface area was determined from N<sub>2</sub> adsorption/desorption isotherms at -196 °C using a Micromeritics 3Flex instrument. Prior to the analysis, all samples were degassed under vacuum at 200 °C for 5 h to remove physisorbed species.

**VSM.** The magnetic measurements were performed using a Quantum Design Squid magnetometer at 300 K and field up to 6 T. The measurements were performed on reduced catalysts. Standard VSM capsules were filled with a known amount (a few mg) of sample and sealed. To avoid any oxidation, the samples were prepared in a glovebox, and transferred to the cryostat in a Schlenk vessel. The VSM capsule containing the sample was rapidly introduced into the VSM to avoid exposure of the sample to the air.

**H<sub>2</sub>-temperature programmed reduction (TPR).** H<sub>2</sub>-TPR measurements were performed using a Micromeritics AutoChem II 2920. In a typical experiment, 50 mg of catalyst were placed on quartz wool into a U-tube quartz reactor. The gases used were from Messer (quality 6.0). The sample was pretreated *in-situ* by ramping at 10 °C·min<sup>-1</sup> to 350 °C under a He flow and remained at that temperature for 60 min. Subsequently, the sample was cooled down to 50 °C. At this temperature, a gas mixture of 5% H<sub>2</sub>/N<sub>2</sub> passed through the sample with a total flow of 50 mL·min<sup>-1</sup> and H<sub>2</sub>-TPR was carried out by heating (10 °C min<sup>-1</sup>) up to 900 °C. H<sub>2</sub> consumption was continuously monitored by a thermal conductivity detector.

**CO<sub>2</sub>/CO-temperature programmed desorption (TPD).** The gases used were from Messer (quality 6.0). CO<sub>2</sub> (or CO) Temperature Programmed Desorption (TPD) measurements were carried out on a Micromeritics Autochem II 2920 instrument equipped with a thermal conductivity detector. In a typical experiment, 150 mg of reduced catalyst were placed on quartz wool into a U-tube quartz reactor. The sample was pretreated *in-situ* by ramping at 10 °C·min<sup>-1</sup> to 350 °C in a He flow and remained at that temperature for 60 min. Subsequently, the sample was cooled down to 50 °C. At this temperature, a gas mixture of 5% H<sub>2</sub>/N<sub>2</sub> was sent on the sample with a total flow of 50 mL·min<sup>-1</sup> and H<sub>2</sub>-TPR was carried out by heating (10 °C·min<sup>-1</sup>) up to 350 °C and held at this temperature for 30 min. H<sub>2</sub> consumption was continuously monitored by a thermal conductivity detector (TCD). Then, the gas flow was switched to He and held at 350 °C for 30 min. Subsequently, the sample was cooled down to 50 °C. At this

temperature, a gas mixture of 5% CO<sub>2</sub>/N<sub>2</sub> (or 5% CO/He) was sent on the sample with a total flow of 50 mL.min<sup>-1</sup> for 60 min. After saturation with CO<sub>2</sub> (or CO), the sample was outgassed for 60 min at 50 °C under He flow to ensure removal of physisorbed CO<sub>2</sub> (or CO). Finally, the sample was heated under He up to 900 °C with a ramp of 10 °C.min<sup>-1</sup> to measure CO<sub>2</sub> (or CO) desorption (TCD). To assess sample basicity, the integral of the CO<sub>2</sub>-TPD data was calculated for each data set and divided by the BET surface area of the respective sample.

**EPR spectroscopy.** Samples were placed in quartz EPR tubes (CFQ, OD 4 mm, Wilmad) and placed under helium atmosphere. EPR spectra were recorded on an X-band EMX-plus spectrometer (Bruker Biospin GmbH) equipped with a high-sensitivity resonator (ER4119HS, Bruker) and a variable temperature unit (ER4131VT, Bruker). Spectra were recorded at 100 K with a microwave power of 0.5 mW and a modulation amplitude of 0.4 mT.

**XPS measurements.** The quasi in situ laboratory-based XPS measurements were carried out in a custom-build ultrahigh-vacuum (UHV) setup coupled with a variable-pressure reactor (VPR) described in details elsewhere [117]. The four catalysts were initially reduced in a furnace at 350 °C for 4 hours under 1 bar 40% H<sub>2</sub>/Ar flow and then stored for several weeks in air. About 100 mg of catalyst powder was pressed into a pellet and mounted on the XPS sample holder equipped with a boron nitride heater and a K-type thermocouple. Then the samples were subjected to a second reduction cycle, this time in the VPR reactor attached to the spectrometer under 7 mbar H<sub>2</sub> for 30 min at 400 °C. After the reduction treatment the VPR was evacuated and the sample was transferred under vacuum to the XPS chamber for analysis. All quasi in situ XPS spectra were collected under UHV (1x10<sup>-8</sup> mbar) at room temperature. A non-monochromatized Al K $\alpha$  X-ray source was used, while survey and high-resolution spectra were recorded with analyzer pass energies of 90 and 22 eV respectively. Samples were exhibit mild charging upon measurements (up to 4 eV), therefore the presented binding energies were calibrated to the main C 1s peak at 284.6 eV. The reliability of this method was confirmed by the Ti 2p and O 1s peaks which after calibration gave practically identical binding energies for all catalysts.

**XAFS measurements.** Ex-situ X-Ray Absorption Fine Structure (XAFS) spectra were collected at BM23 beamline of European Synchrotron Radiation Facility (ESRF) [118] during beamtime allocated with the proposal CH-6666 [119]. Three ionization chambers were employed (I<sub>0</sub>, I<sub>1</sub> and I<sub>2</sub>) and filled with Ar:N<sub>2</sub> mixture. Co K-edge X-Ray Absorption Spectra (XAS) were collected in transmission mode on mass-optimized pellets of 13 mm<sup>2</sup> located between I<sub>0</sub> and I<sub>1</sub> while a Co metal foil was located before I<sub>2</sub>. Step scan collection mode was employed in the 7570 – 8680 eV range with 0.3 eV/point energy resolution in the XANES region (7570 – 7700 eV) and 0.035 k/point resolution in the EXAFS region. 0.5 seconds/point integration time were employed leading to a total of 12 minutes/scan. Energy calibration and alignment, background subtraction and edge jump normalization were conducted with the Athena Software from Demeter Package [120]. Linear Combination Analysis (LCA) was done within the same software using CoO (Sigma Aldrich, >99.99%) and Co metal foil as reference spectra. Spectra were fit in the 7680 – 7820 eV range. The species concentration was constrained with values between 0 and 1 while their sum was not constrained to 1. FT-EXAFS spectra were extracted in the k range 3-13.8 Å<sup>-1</sup> using Hanning window. All the reported FT-EXAFS fit were conducted with ARTEMIS software in the R range 1 – 3.6 Å [120]. Scattering amplitude factor (S<sub>0</sub><sup>2</sup>) of 0.795 was evaluated from fit of metal foil (see Supporting Information for further details on the FT-EXAFS fit procedure).

**Raman measurements.** Raman characterization was done on a Horiba Labram HR Evolution spectrometer using a 532 nm laser excitation (ca. 5 mW) equipped with a Super Long Working Distance 50x objective and a 600 tr/mm grating (1.5 cm<sup>-1</sup> resolution). Approximately 85 mg of sample was introduced in a Linkam CCR-1000 reaction cell. The Raman spectra were serially

acquired every 20 s after 20 s acquisition. Reduction of the solids took place from 20 °C to 340 °C (20 °C/min) in a H<sub>2</sub>/N<sub>2</sub> flow at 20/30 mL.min<sup>-1</sup> respectively followed by *ca.* 3.5 h at this temperature. Reaction was carried out by introducing at 220 °C, a reaction mixture containing CO<sub>2</sub>/H<sub>2</sub>/N<sub>2</sub> flow at 9/18/9 mL.min<sup>-1</sup>, respectively. Band widths and positions were evaluated within the series by spectral treatment

**DRIFTS measurements.** *In situ* DRIFTS experiments were performed using a modified high temperature DRIFT cell from Spectra-Tech fitted with KBr windows placed in a Collector II assembly described elsewhere [121]. The spectrophotometer used was a Nicolet 8700 (ThermoFischer Scientific) fitted with a liquid-N<sub>2</sub> cooled MCT detector. The DRIFT spectra were recorded at a resolution of 4 cm<sup>-1</sup> and 16 scans were averaged. The DRIFTS spectra are reported as log (1/R), where R is the sample reflectance. This pseudo-absorbance gives a better linear representation of the band intensity against surface coverage than that given by the Kubelka-Munk function for strongly absorbing media such as those based on metals supported on oxides [122]. The contribution of gas-phase CO was subtracted using a CO(g) spectrum collected under the same experimental conditions over powdered KBr. High purity gases He (99.999%), H<sub>2</sub> (99.999%), CO<sub>2</sub> (99.995%) and 5% CO/He (99.9%) from Air Liquide or Messer were used without further purification.

### 4.3 High-pressure catalytic tests

CO<sub>2</sub>-FTS catalytic tests were performed in a high-pressure test rig illustrated in **Figure S32**. The gases used, N<sub>2</sub>, H<sub>2</sub> and CO<sub>2</sub> (Messer) had a 99.9999% purity. The reactor is composed of a stainless-steel tube of 33 cm length and 14 mm inner diameter. For a given CO<sub>2</sub>-FTS catalytic test, the bottom part of the reactor was filled with a Sasol Pural sintered α-Al<sub>2</sub>O<sub>3</sub> (1000 °C, 5 h) to sustain the catalytic bed. Then, 2 g of calcined catalyst were diluted with 8 g of inert SiC (Alfa Aesar, > 98.5 %), and placed in the middle of the stainless-steel reactor tube. The rest of the tube was completed with calcined α-Al<sub>2</sub>O<sub>3</sub>. The separation between filling material (α-Al<sub>2</sub>O<sub>3</sub>) and catalyst was ensured by a layer of quartz wool. A thermocouple was placed at the center of the catalytic bed to control the reaction temperature. Each catalyst was reduced in-situ at 350 °C for 4 h under 40% H<sub>2</sub>/N<sub>2</sub> with a total flow of 100 mL.min<sup>-1</sup>. After reduction, the temperature was decreased to 220 °C and the catalyst was outgassed with N<sub>2</sub> to remove the excess of H<sub>2</sub>. Then, the gas was switched to a mixture of H<sub>2</sub>/CO<sub>2</sub>/N<sub>2</sub> = 36/18/18 mL.min<sup>-1</sup>. After 30 min, the pressure was slowly increased to 20 bar using a back-pressure controller. The test started once the desired pressure was reached. After the initial test at 220 °C, the temperature was increased to 250 °C.

The gaseous products were monitored every 30 min using an online μ-GC (Agilent 990) equipped with a MS5A SS (Ar carrier, Messer 6.0) column for the quantification of H<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub> and CO and a Poraplot U FS (He carrier, Messer 6.0) column for the quantification of CO<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub> and C<sub>4</sub>H<sub>10</sub>. Both columns are equipped with a TCD detector.

The condensable products were recovered using hot (150 °C) and cold (4 °C) condensers and analyzed by GC-Simdist (Shimadzu GC-2010 Plus) equipped with ZB-1XT column and a flame ionization detector (FID). For the GC-SimDist analysis, the oil fractions of hot and cold condensers were mixed prior to performing the analysis. CS<sub>2</sub> was used as solvent.

The calculation on the gaseous products detected by m-GC were performed as follows.

N<sub>2</sub> was used as internal standard and the molar fraction of the different molecules during the CO<sub>2</sub>-FTS were calculated as follow:

$$Z^{\text{out}} \text{ (mL/min)} = \frac{\%Z}{\%N_2} \cdot N_2^{\text{in}}$$

$Z^{\text{out}} = \text{CO}_2, \text{H}_2, \text{CH}_4, \text{CO}, \text{C}_2\text{H}_4, \text{C}_2\text{H}_6, \text{C}_3\text{H}_8, \text{C}_4\text{H}_{10}$ .

%Z is obtained directly from the μ-GC, which has an internal calibration.  $N_2^{\text{in}} = N_2$  input flow.

CO<sub>2</sub> and H<sub>2</sub> conversions ( $X_{\text{CO}_2}$ ,  $X_{\text{H}_2}$ ) were calculated as follows:



$$X_{\text{CO}_2}(\%) = 100 \cdot \frac{\text{CO}_2^{\text{in}} - \text{CO}_2^{\text{out}}}{\text{CO}_2^{\text{in}}} \quad X_{\text{H}_2}(\%) = 100 \cdot \frac{\text{H}_2^{\text{in}} - \text{H}_2^{\text{out}}}{\text{H}_2^{\text{in}}}$$

The selectivity of the different products ( $S_Z$ ) were calculated as follows:

$$S_Z(\%) = 100 \cdot \frac{n \cdot Z^{\text{out}}}{\text{CO}_2^{\text{in}} - \text{CO}_2^{\text{out}}} \quad S_{\text{C}_{5+}}(\%) = 100 - \sum S_Z$$

$n$  = number of carbon atoms in  $Z$ .

The yields were calculated as follows:

$$Y_Z(\%) = \frac{X_{\text{CO}_2} \cdot S_Z}{100} \quad Y_Z \left( \text{mol}_{\text{CO}_2 \text{ converted to } Z} \cdot \text{mol}_{\text{Me}}^{-1} \cdot \text{h}^{-1} \right) = \frac{(Y_Z(\%)/100) \cdot \text{CO}_2^{\text{in}} \left( \frac{\text{mol}}{\text{h}} \right)}{\text{mol}_{\text{Me}}(\text{mol})}$$

$Z = \text{CH}_4, \text{CO}, \text{C}_{2+}, \text{C}_{5+}$ .

STY was calculated as follows:

$$\text{STY} \left( \text{mol}_{\text{CO}_2} \cdot \text{mol}_{\text{Me}}^{-1} \cdot \text{h}^{-1} \right) = \frac{(X_{\text{CO}_2}(\%)/100) \cdot \text{CO}_2^{\text{in}} \left( \frac{\text{mol}}{\text{h}} \right)}{\text{mol}_{\text{Me}}(\text{mol})}$$

### Author Contributions

C.S. carried out the synthesis, some structural characterizations, and catalytic tests. S.C. and G.V. performed the XRD characterizations and analyze the data. A.D. performed the spillover experiments. N.L.B. and A.K.B. performed the EPR characterizations and analyze the data. F.M. performed the DRIFTS characterizations and analyze the data. G.C. performed the Raman characterizations and analyze the data. M.B. and S.Z. performed the XPS characterizations and analyze the data. D. Salusso performed the XAS characterizations and analyze the data. K.S., D.P.M. and P.S. conceived and supervised the project. All authors discussed the results and commented on the manuscript. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

### Data availability

Data will be made available on request.

### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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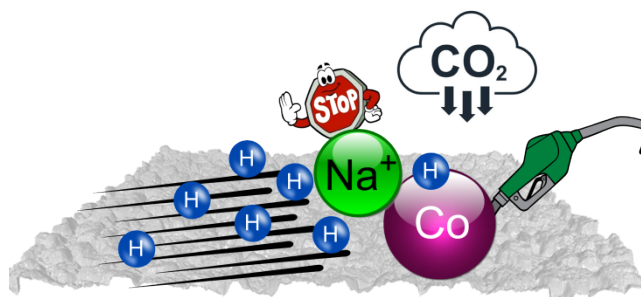


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## Highlights

# Modified Co/TiO<sub>2</sub> catalysts for CO<sub>2</sub> hydrogenation to fuels

C. Scarfiello, K. Soulantica, S. Cayez, A. Durupt, G. Viau, N. Le Breton, A. K. Boudalis, F. Meunier, G. Clet, M. Barreau, D. Salusso, S. Zafeiratos, D. Pham Mihn, P. Serp

- Commercial TiO<sub>2</sub>-P25 was partially reduced with NaBH<sub>4</sub>, leading to the formation of oxygen vacancies, Ti<sup>3+</sup> sites and the incorporation of Na.
- The catalyst activity is proportional to the amount of CO<sub>2</sub> they can medium/strongly adsorb.
- Catalysts prepared on modified supports outperform the one prepared on TiO<sub>2</sub>-P25 in terms of activity and selectivity towards C<sub>5+</sub>.
- The presence of alkali on the support contributes to the activation of CO<sub>2</sub> and allows a modulation of the hydrogen spillover in the system.
- A reduced H-spillover contributes to maintaining a low surface H/C coverage resulting in significantly higher selectivity compared to the unpromoted catalyst.

## Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: