Supporting Information for

Direct evidence of SMSI decoration effect: The case of Co/TiO$_2$ catalyst

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1. Catalyst preparation

Cobalt supported TiO_2 catalyst was synthesised with a cobalt loading of 10 wt %. The TiO_2 sample used as a carrier has a nano-crystalline anatase structure (99%) with a specific surface area of 336 m^2/g and a pore volume of 0.44 cm^3/g (Hombifine N). Before impregnation, the support was calcined in air at 773 K for 2 h (TiO_2-c). The cobalt catalyst was prepared by wet impregnation of the support using a $Co(NO_3)_2 \cdot 6H_2O$ aqueous solution. The solution was maintained under stirring at 353 K until complete evaporation of water in a rotary evaporator. The obtained solid was dried overnight at 373 K and calcined at 723 K for 2 h, whereby the nitrates thermally decomposed under formation of the oxides. The calcination was carried out in static air at 773 K for 2 h. The catalyst is labelled as Co10-ct. Finally, a reduction treatment was performed under H_2 atmosphere at 773 K during 2 hours (Co10-ctr).

Elemental analysis was performed by inductively coupled plasma emission spectroscopy (ICP-AES) (Perkin Elmer optima 3300DV) in order to evaluate the cobalt charge.

The specific surface area and pore size distribution of the different materials were determined by nitrogen adsorption at 77 K with a Micromeritics Tristar 3100 device. Values were calculated by applying the BET method. Prior to adsorption measurements, samples were degassed at 423 K.

2. Structural characterization

X-ray diffraction profiles were recorded on a Seifert 3000P diffractometer using Cu K (λ = 0.1538 nm) radiation, equipped with a bent graphite monochromator in the diffracted beam and an automatic primary slit. The patterns were collected using a 2 step of 0.02º, with an accumulation time of 5 s, and 2 angles ranging from 5 to 80º.

Pawley refinements for TiO$_2$, Co-10ct (calcined) and Co-10ctr (H$_2$ 773K) samples

Pawley profile-fitting procedure [1] was used employing the FullProf Software [2], in order to refine the cell and peak profile parameters, as well as those of the background, peak asymmetry and zero shift. **Tables S1-S3** summarized the main refined structural parameters found for all the samples studied in this work. First, Pawley profile fitting was carried out for TiO$_2$ data **(Figure S1)**. These structural values found for anatase TiO$_2$ system (support sample) were used later as a reference for the Co-supported systems. Concerning the two biphasic samples, data show the characteristic diffraction peaks of TiO$_2$ anatase (I4$_1$/amd space group) and Co$_3$O$_4$ oxide (F d -3 m space group) in the fresh sample named **Co-10ct (calcined) (Figure S2)**, while for the activated sample named **Co-10ctr (reduced in H$_2$ at 773 K)** presents also TiO$_2$ anatase phase but cobalt fcc metallic phase (Fm-3m space group) **(Figure S3)**.

[1] G. S. Pawley, J. Appl. Crystallogr. 1981, 14, 357.

[2] J. Rodriguez-Carvajal, Collected Abstracts of Powder Diffraction Meeting, Toulouse, France, 1990, p. 127.

Table S1. Structure refinement values for TiO_2 Anatase sample.

Phase 1: Anatase TiO_2

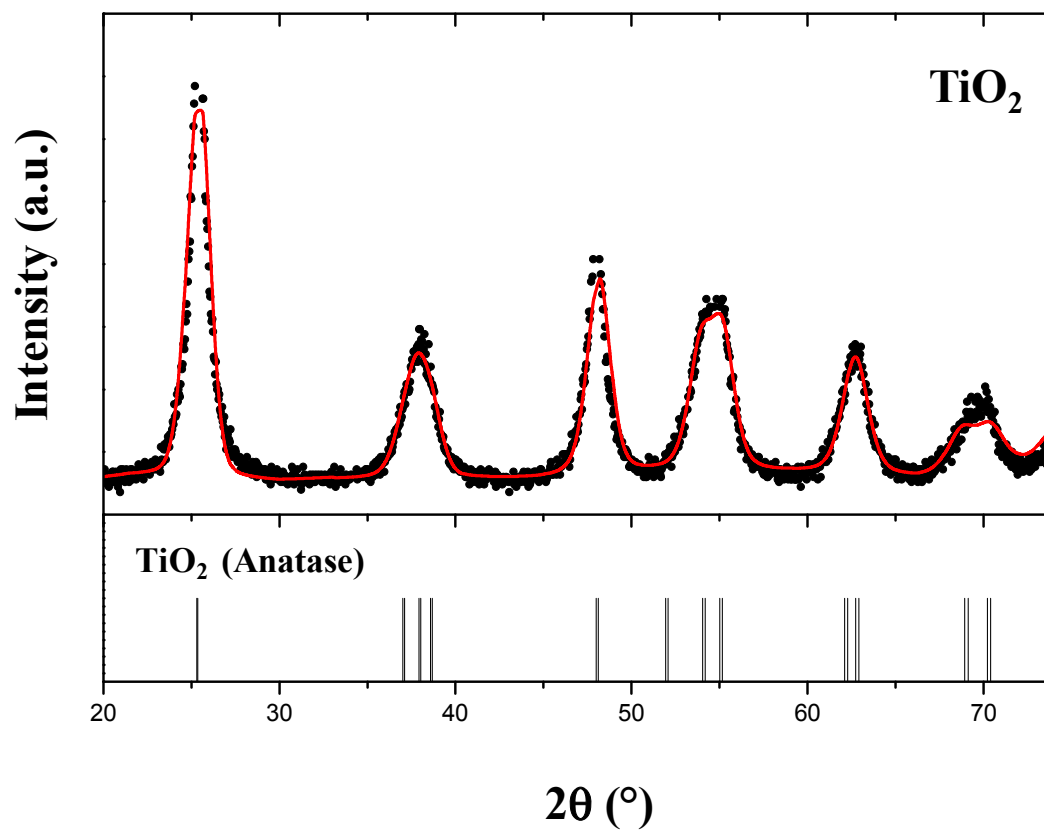|	
Space group	I 4_1/a m d
Unit cell dimensions	a = 3.7882(4) Å $\quad\alpha$ = 90°
	b = 3.7882(4) Å $\quad\beta$ = 90°
	c = 9.481(2) Å $\quad\gamma$ = 90°
Bragg R-factor (R_{wp})	0.314
Rf-factor(R_{wp})	0.311
Profile Function	Thompson-Cox-Hastings pseudo-Voigt *
	Axial divergence asymmetry
U	6.8398
V	-6.6391
W	3.0541
X	1.1590
Y	0.0482

Figure S1. Pawley refinement for TiO_2 sample. Experimental data, Y_{obs} (red), simulated pattern and Y_{calc} (black) and Bragg reflections.

Table S2. Structure refinement values for Co10-ct (calcined) sample.

Phase 1: Anatase TiO$_2$

Space group	I 4$_1$/a m d
Unit cell dimensions	a = 3.7861(4) Å α= 90°
	b = 3.7861(4) Å β= 90°
	c= 9.515(1) Å γ = 90°
Bragg R-factor (R$_{wp}$)	0.573
Rf-factor(R$_{wp}$)	0.339
Profile Function	Thompson-Cox-Hastings pseudo-Voigt *
	Axial divergence asymmetry
U	0.14748
V	0.31341
W	0.28836
X	0.15999
Y	0.00100

Phase 2: Co$_3$O$_4$

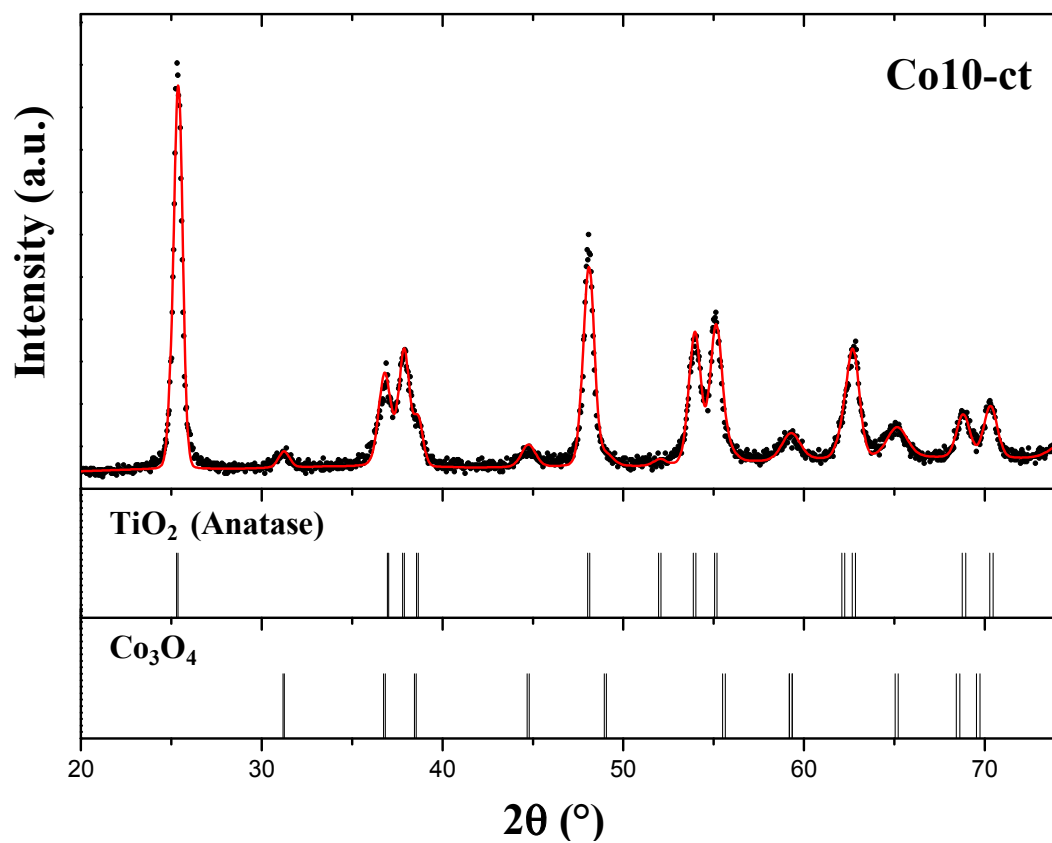|	
Space group	F d -3 m
Unit cell dimensions	a = 8.106(1) Å α= 90°
	b= 8.106(1) Å β= 90°
	c= 8.106(1) Å γ = 90°
Bragg R-factor (R$_{wp}$)	0.756
Rf-factor(R$_{wp}$)	0.536
Profile Function	Thompson-Cox-Hastings pseudo-Voigt *
	Axial divergence asymmetry
U	2.80393
V	-0.02049
W	0.18277
X	0.47621
Y	0.00010

Figure S2. Pawley refinement for Co10-ct sample. Experimental data, Y_{obs} (red), simulated pattern and Y_{calc} (black) and Bragg reflections.

Table S3. Structure refinement values for Co10-ctr (reduced) sample.

Phase 1: Anatase TiO$_2$

Space group	I 4$_1$/a m d	
Unit cell dimensions	a = 3.7863(5) Å	α = 90°
	b = 3.7863(5) Å	β = 90°
	c = 9.509(1) Å	γ = 90°
Bragg R-factor (R$_{wp}$)	0.551	
Rf-factor(R$_{wp}$)	0.421	
Profile Function	Thompson-Cox-Hastings pseudo-Voigt *	
	Axial divergence asymmetry	
U	0.14427	
V	-0.09486	
W	0.18037	
X	0.74237	
Y	0.00100	

Phase 2: Cubic Co^0

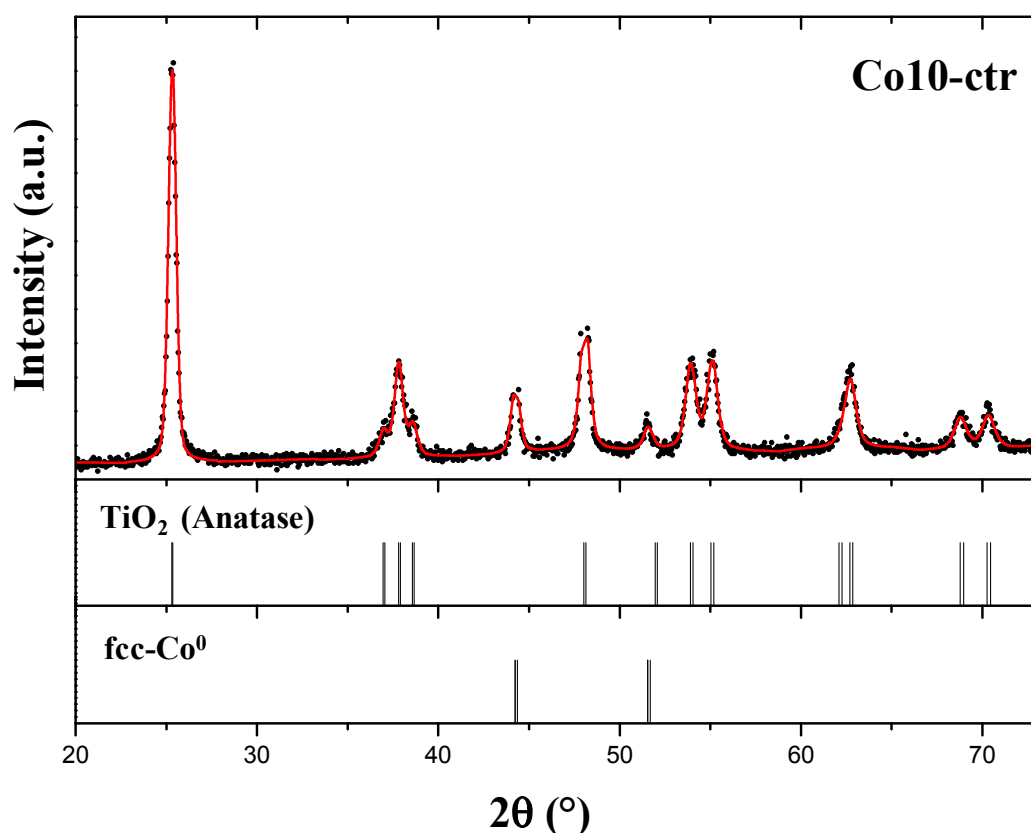|		
Space group	F m -3 m	
Unit cell dimensions	a = 3.5426(4) Å	α = 90°
	b = 3.5426(4) Å	β = 90°
	c = 3.5426(4) Å	γ = 90°
Bragg R-factor (R$_{wp}$)	1.38	
Rf-factor(R$_{wp}$)	1.07	
Profile Function	Thompson-Cox-Hastings pseudo-Voigt *	
	Axial divergence asymmetry	
U	0.32983	
V	-0.38044	
W	0.17265	
X	0.59475	
Y	0.00010	

Figure S3. Pawley refinement for Co10-ctr sample. Experimental data, Y_{obs} (red), simulated pattern and Y_{calc} (black) and Bragg reflections.

3. Reduction properties

Temperature-programmed reduction (TPR) analysis was carried out in a Micromeritics 3000 apparatus by passing a 10% H_2/Ar flow (50 NmL/min) through the sample. Before the reduction, the sample was pretreated using helium, heating at 383 K during 30 min. The reduction profile was obtained increasing the temperature up to 1000 K at a rate of 10 K/min under the 10%H_2/argon flow, and the amount of H_2 consumed was determined with a TCD.
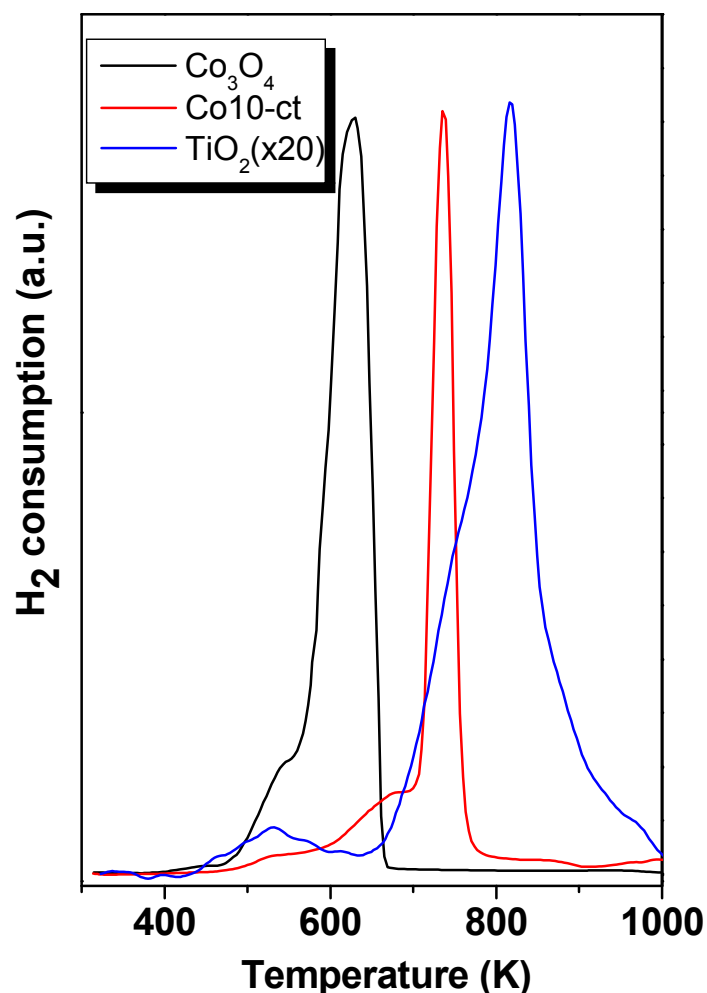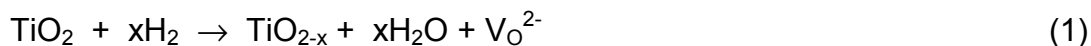

Figure S4. Temperature reduction profiles under H_2 atmosphere for: TiO_2 anatase sample and a spinel cobalt oxide (Co_3O_4) as reference, and Co10-ct.

TPR profile corresponding to TiO_2 reduction (multiplied by a factor of 20) shows (figure S4) a small uptake of H_2 which indicates the reduction of the TiO_2 as follows [3]:

$$TiO_2 + xH_2 \rightarrow TiO_{2-x} + xH_2O + V_O^{2-} \tag{1}$$

The Co_3O_4 profile points to a two-step reduction process: a first one involving a low H_2-consumption starts at ca. 475 K and overlaps with the more intense second one whose maximum is placed at about 630 K [4, 5]

$$Co_3O_4 + H_2 \rightarrow 3CoO + H_2O \tag{2}$$

$$3CoO + 3H_2 \rightarrow 3Co + 3H_2O \tag{3}$$

The reduction profile of Co10-ct catalyst shows a main and well defined reduction peak centered at ca. 750 K and a shoulder at lower temperature (lower than 700 K). If compared with Co_3O_4 reduction profile, a shift toward higher temperatures is observed, indicating the development of metal-support interactions. The wide shoulder that appears between 475 and 700 K is attributed to the reduction of cobalt spinel to CoO. The broadening of this peak indicates the difficulty of the first reduction step, due to a strong metal-support interaction [6, 7].

3. Rekoske, J. E, Barteau M. A., J. Chem. Phys. B 1997, 101 1113-1124.

4. V.A. de la Peña O'Shea, N.N. Menendez, J.D. Tornero, J.L.G. Fierro, Catal. Lett., 88 (2003) 123.

5. P. Arnoldy, J.A. Moulijn, J. Catal., 93 (1985) 38.

6. S.W. Ho, J.M. Cruz, M. Houalla, D.M. Hercules J. Catal., 135 (1992) 173.

7. B. Jongsomjit, C. Sakdamnuson, P. Praserthdam, Mat. Chem. Phys., 89 (2005) 395.

4. Chemisorption Analysis

H_2 and CO uptake measurements were performed in a pulse mode using He as carrier gas (30 STP cm^3 min^{-1}). Before measurements, catalyst samples were reduced under a 10% H_2/N_2 flow (100 cm^3 min^{-1}) for 1 h at 773 K and then flushed at the same temperature (20 min) in the He carrier flow. After cooling to room temperature, H_2 or CO pulses (0.5 µmol) were injected onto the sample until saturation was reached. Reduced sample shows a nearly total suppression of CO and H_2 chemisorptions

5. Surface Analysis

X-ray photoelectron spectroscopy (XPS) were acquired with a VG Escalab 200R spectrometer equipped with a hemispherical electron analyser and an Al $K\alpha_1$ (hν=1486.6 eV) 120 W X-ray source. The powder samples were pressed into small Inox cylinders and then mounted on a sample rod, placed in the pre-treatment chamber and degassed at 373 K for 1 h. In the case of reduction studies the *in-situ* sample reduction (under H_2 at 773K for 1 h) was performed into the XPS pre-chamber. The C 1s core-level of adventitious carbon at a binding energy of 284.9 eV was taken as an internal standard. Atomic ratios were calculated from the integrated area ratios after background subtraction and corrected by the atomic sensitivity factors [8].

8. C.D. Wagner, L.E. Davis, M.V. Zeller, J.A. Taylor, R.H. Raymond, L.H. Gale, Surf. Interface Anal., 3 (1981) 211.

6. Transmission Electron Microscopy studies

Transmission electron micrographs were taken with a Philips CM30 microscope. The acceleration voltage was set at 300 kV. The powdered sample was first suspended in acetone, after which a drop of the suspension was deposited on a copper grid covered by a fine carbon film evaporated under a vacuum.

7. Catalytic Tests

Activity tests were carried out using an autoclave high pressure (Autoclave Engineers, Ltd.) catalytic reactor. The catalysts (0.5 g) were activated in a mixture of N_2/H_2(10%) at 773 K for 10 h under atmospheric pressure. The reaction was conducted at 503 K and at 40 bar. The composition of the feed stream— CO (30%), H_2 (60%) and N_2 (10%)—with a total flow of 100 ml(STP)/min. Gas product analysis was carried out by Gas Chromatography using a Hewlett–Packard 6890 gas chromatograph equipped with an HP-1 capillary column and a Haysep Q packed column for on-line product separation Liquid hydrocarbons were analysed in a Hewlett–Packard 5890 gas chromatograph equipped with a HP-1 column. In both cases a thermal conductivity (TCD) and flame ionisation (FID) detectors were used

Table S4. Influence of support on products selectivity in Co10-c and Co10-ct catalysts. Experimental Conditions: T = 503 K, P= 4Mpa, H_2/CO = 2/1, 100 mLN/min

Catalyst	% Selectivity to[a]					C_2-C_4 Olefinity[b]
	C_1	C_2	C_3	C_4	C_{5+}	
Co10-c	25	3	5	4	63	0.57
Co10-ct	98	2	-	-	-	-

[a] Selectivity = mol CO to product/mol CO total consumed
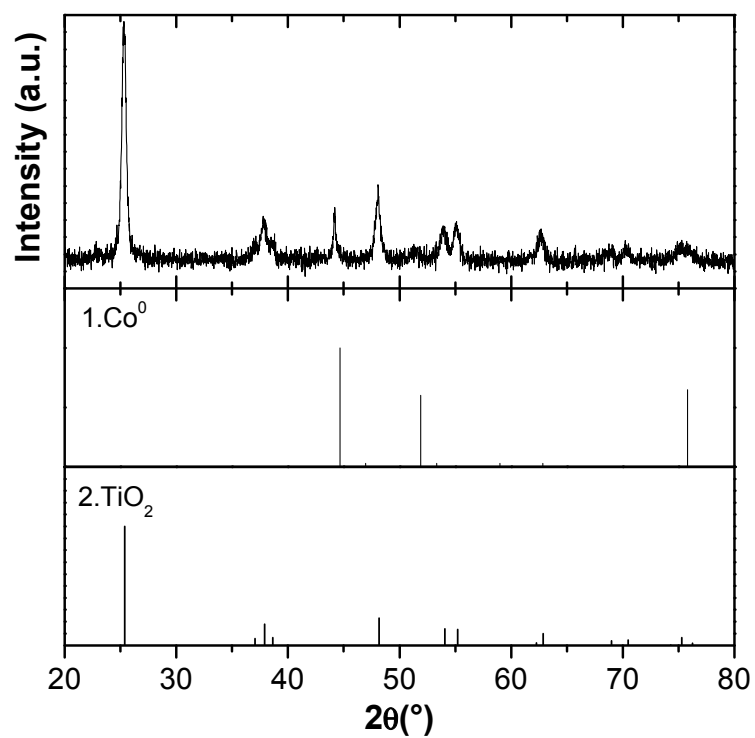[b] Olefinity = mol alkenes formed/mol alkanes formed

Figure S5 XRD profiles and diffraction patterns of Co10-ct after reaction.