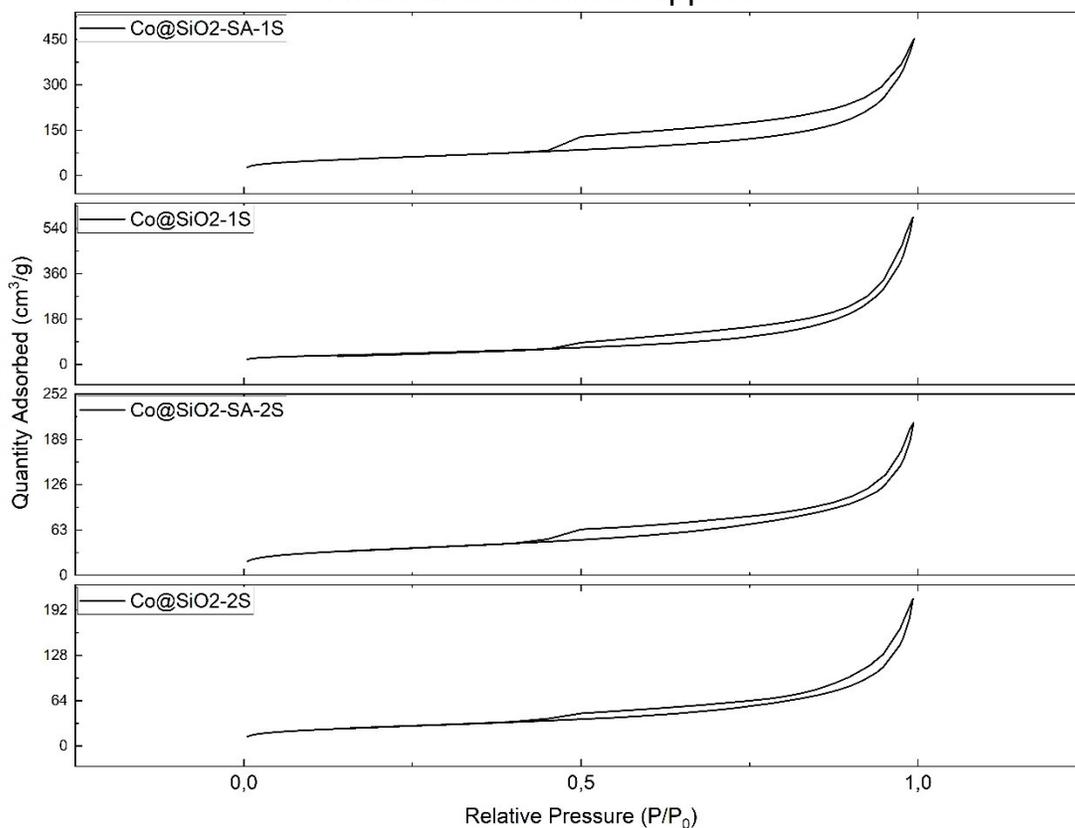
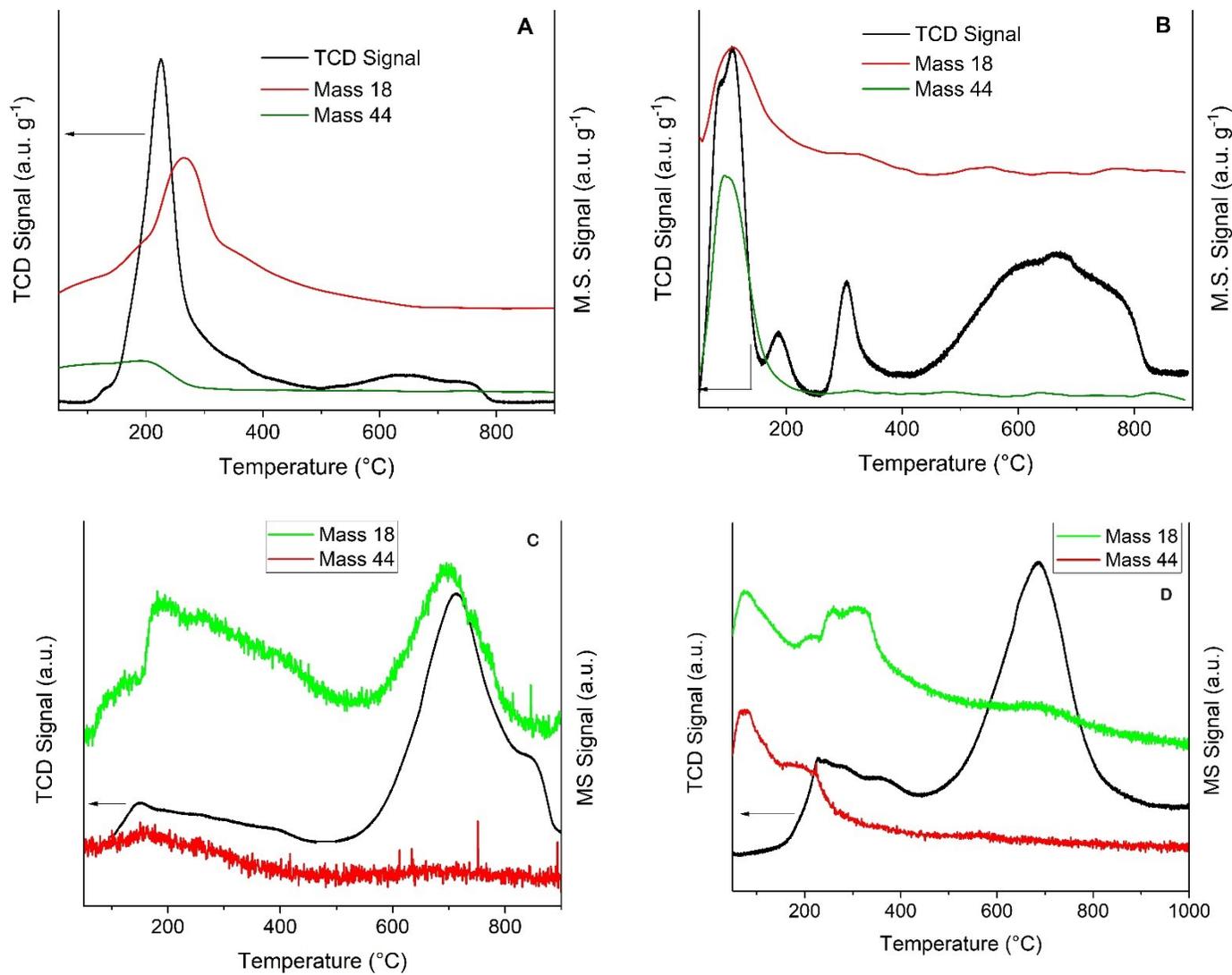


### SUPPLEMENTARY INFORMATION FOR

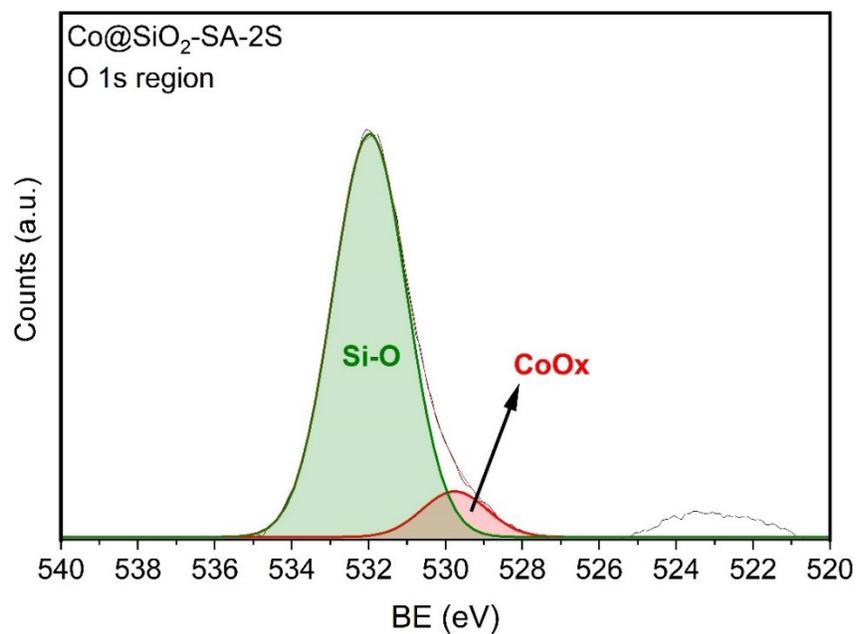
“Cobalt-based Core@Shell Catalysts for Guaiacol Hydro Conversion: use of Salicylic Acid as Sacrificial Modulator of the Interaction between the Metal Phase and the Silica Support”



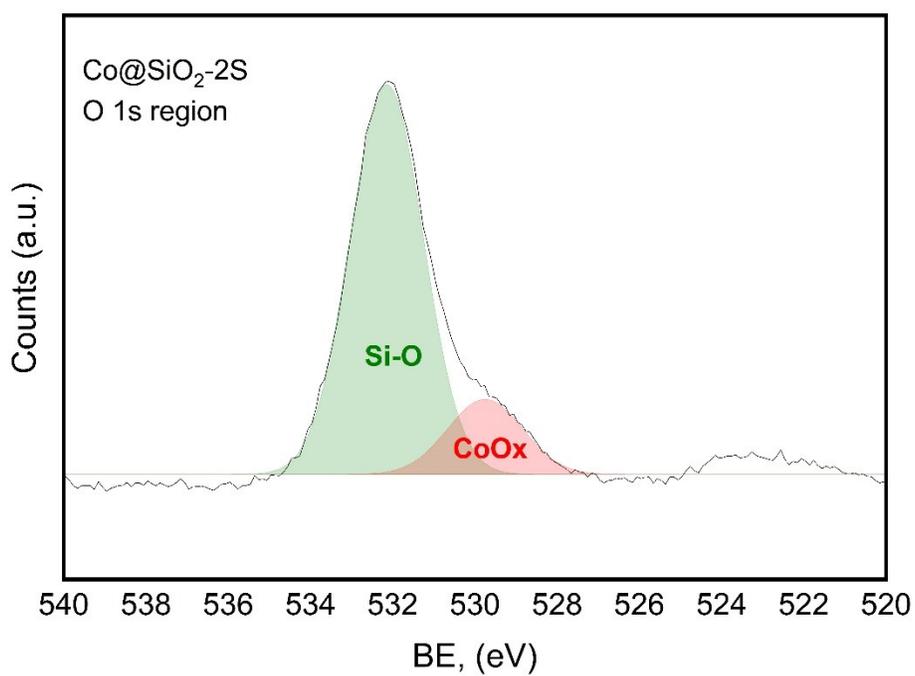
**Figure S1.** Nitrogen adsorption-desorption isotherms of the prepared catalysts. From top to bottom Co@SiO<sub>2</sub>-SA-1S, Co@SiO<sub>2</sub>-1S, Co@SiO<sub>2</sub>-SA-2S and Co@SiO<sub>2</sub>-2S



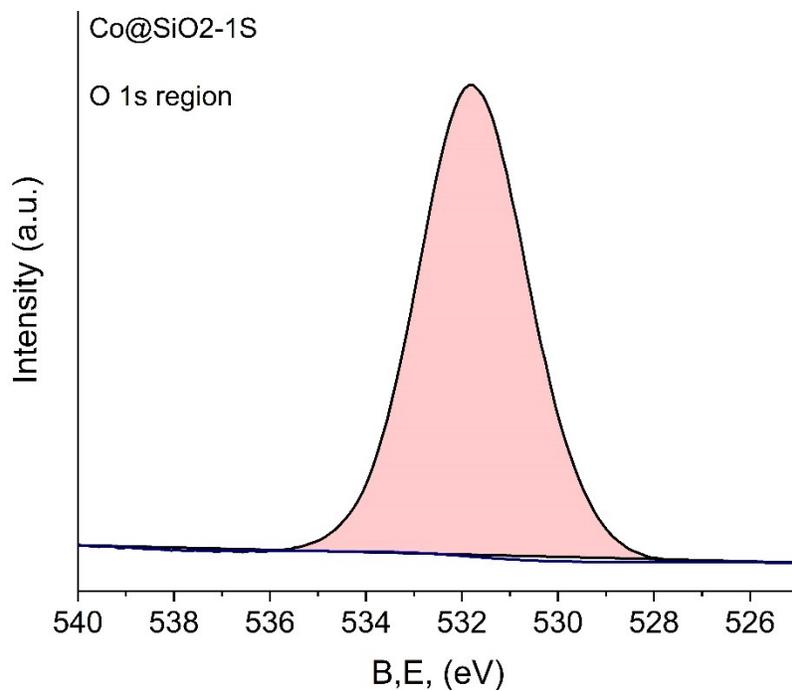
**Figure S2.** TPR-H<sub>2</sub> profiles of the prepared catalysts, with MS signals for H<sub>2</sub>O and CO<sub>2</sub>. A: Co@SiO<sub>2</sub>-2S; B: Co@SiO<sub>2</sub>-SA-2S; C: Co@SiO<sub>2</sub>-1S; D: Co@SiO<sub>2</sub>-SA-1S



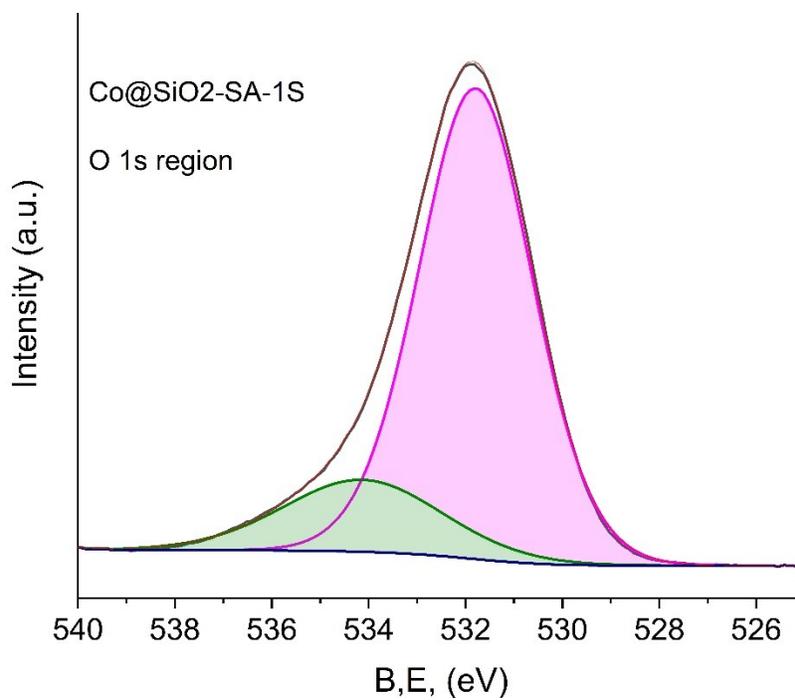
**Figure S3.** Fitted XPS spectrum for the O 1s region for the Co@SiO<sub>2</sub>-SA-2S catalyst.



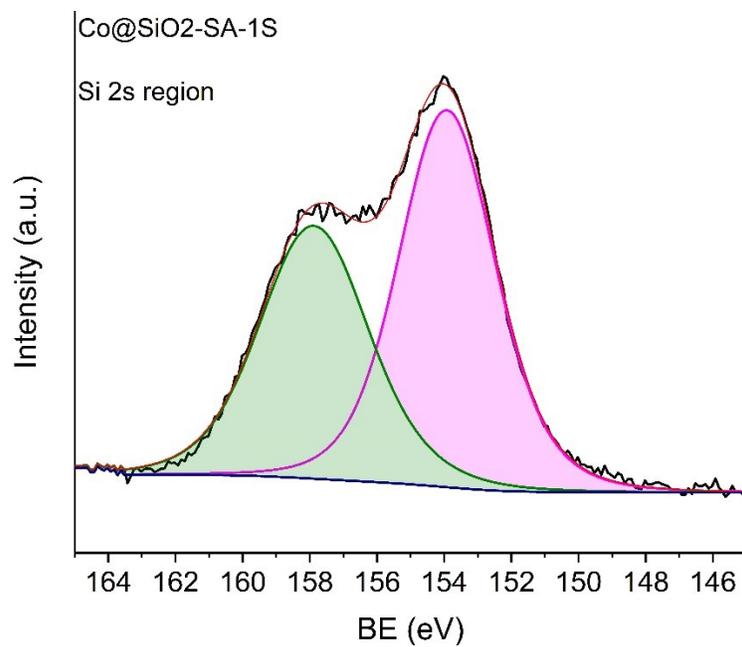
**Figure S4.** Fitted XPS spectrum for the O 1s region for the Co@SiO<sub>2</sub>-2S catalyst.



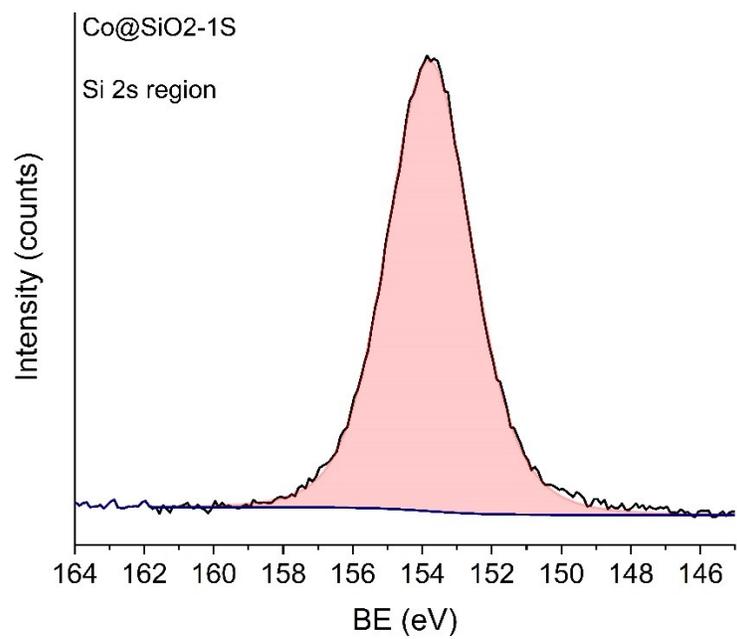
**Figure S5.** Fitted XPS spectrum for the O 1S region for the Co@SiO<sub>2</sub>-1S catalyst.



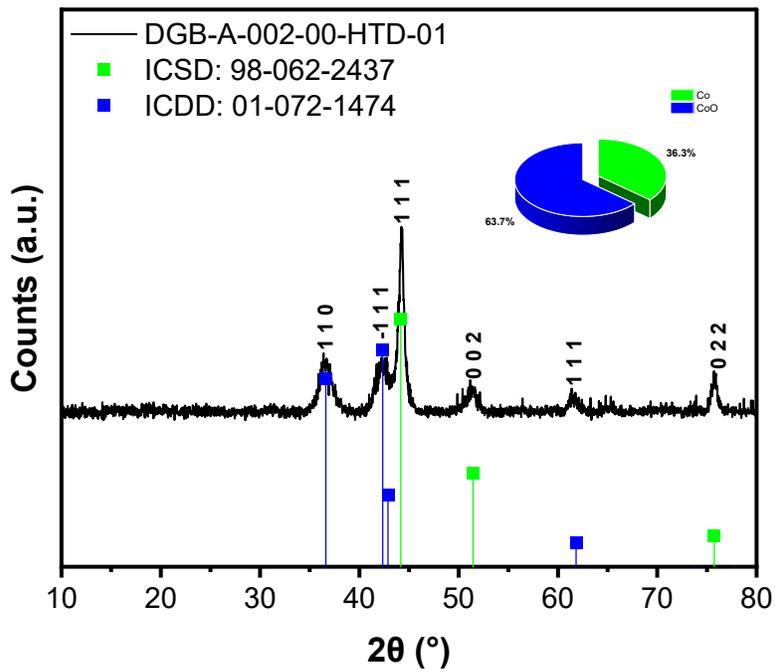
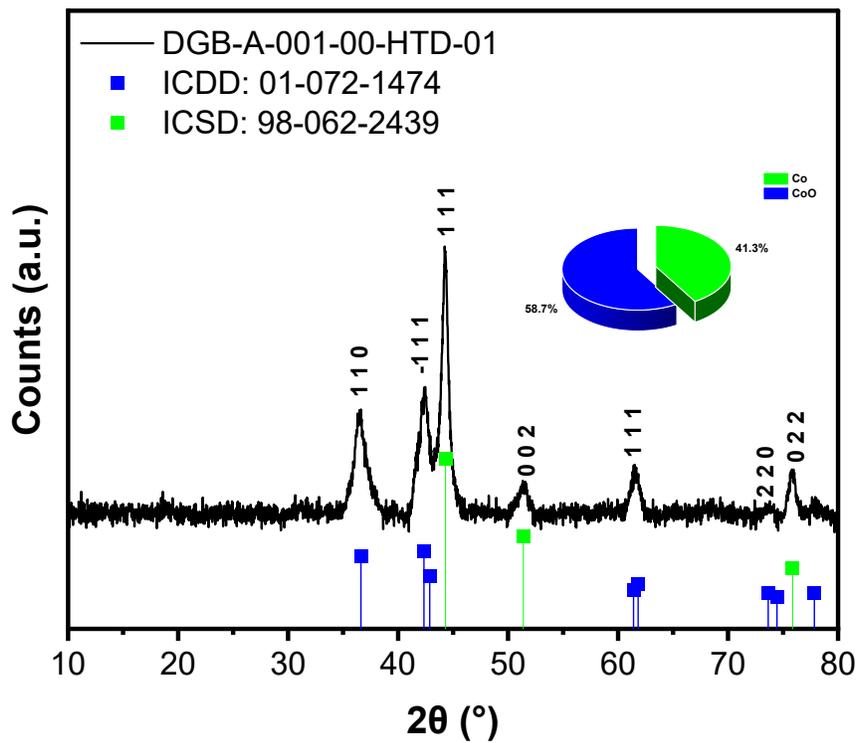
**Figure S6.** Fitted XPS spectrum for the O 1S region for the Co@SiO<sub>2</sub>-SA-1S catalyst.

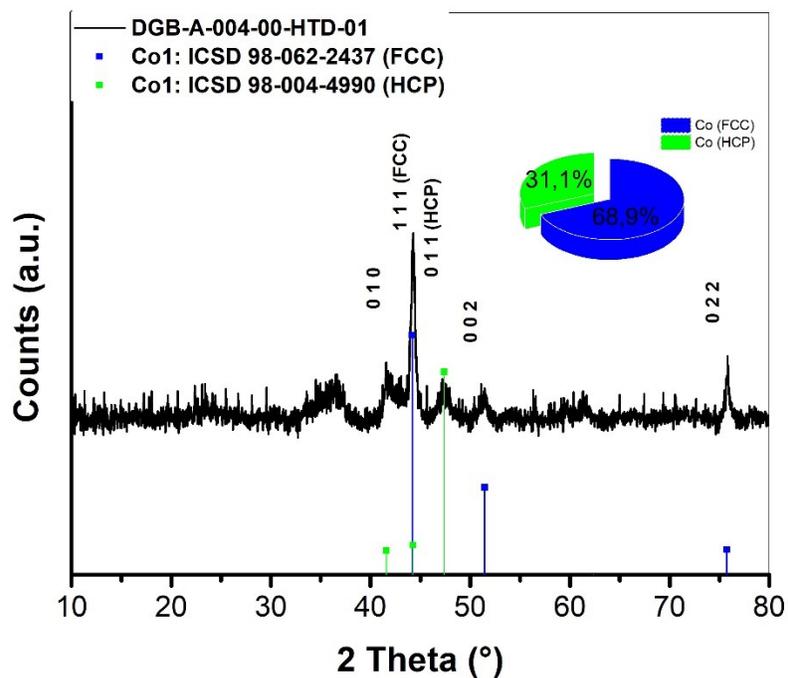
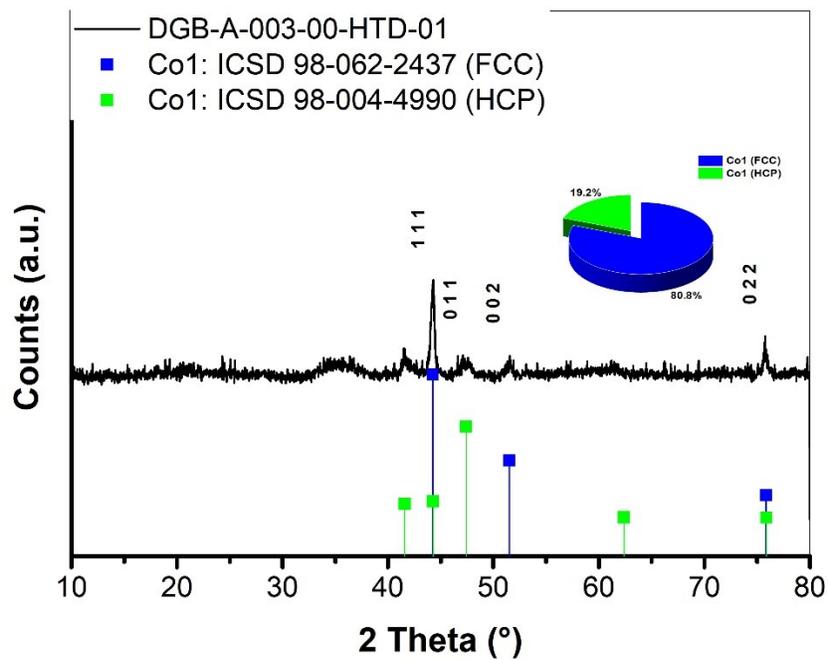


**Figure S7.** Fitted XPS spectrum for the Si 2S region for the Co@SiO<sub>2</sub>-SA-1S catalyst.

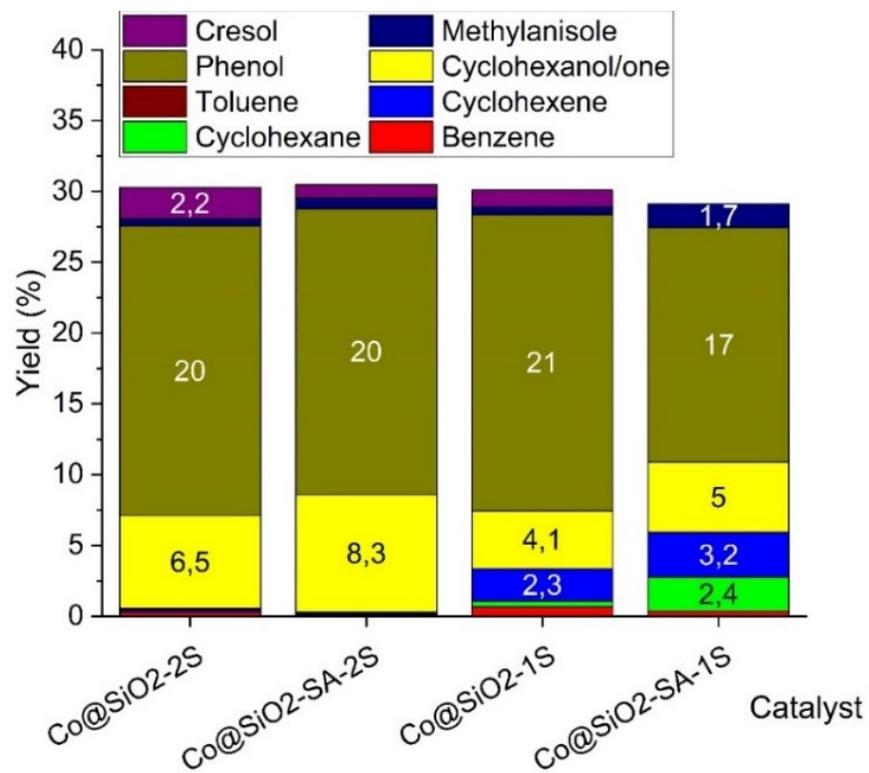


**Figure S8.** Fitted XPS spectrum for the Si 2s region for the Co@SiO<sub>2</sub>-1S catalyst.





**Figure S9.** Identification of phases present on the Co@SiO<sub>2</sub> catalysts, derived from Rietveld's analysis. The samples' identities are: DGB-A-001: Co@SiO<sub>2</sub>-SA-2S; DGB-A-002: Co@SiO<sub>2</sub>-2S; DGB-A-003: Co@SiO<sub>2</sub>-1S; DGB-A-004: CO@SiO<sub>2</sub>-SA-1S



**Figure S10.** Product distribution at 30% conversion for the catalysts reported in this paper.

### Reducibility Calculations

For this part, the analyzed signal was the TCD from the TPR-H<sub>2</sub> experiments in the range between 250 to 500 °C. The signal was integrated and then the H<sub>2</sub> consumption was determined using the following calibration curve:

$$TCD_{signal} = 1.20 \times mmolH_2 + 2.40 \times 10^{-2}$$

The obtained data are given in Table S4; a new sample of the Co@SiO<sub>2</sub>-2S material was measured to obtain a better signal, due to the loss of clarity of the TCD signal due to the overlapping of the H<sub>2</sub>O signal for the first experiment. The expected H<sub>2</sub> consumption was calculated from the Co and CoO percentages obtained by ICP and Rietveld's analysis, respectively.

**Table S1.** H<sub>2</sub> consumption and reducibility percentage for the CO@SiO<sub>2</sub>-2S and Co@SiO<sub>2</sub>-SA-2S samples

Sample	Mass, g	Expected H <sub>2</sub> consumption, mmol	TCD Signal, a.u.	Real H <sub>2</sub> consumption, mmol	Reducibility, %
Co@SiO <sub>2</sub> -2S	3,34 x 10 <sup>-2</sup>	2.45 x 10 <sup>-1</sup>	3.32 x 10 <sup>-2</sup>	2,57 x 10 <sup>-2</sup>	10.5
Co@SiO- SA- 2S	2,93 x 10 <sup>-2</sup>	1.74 x 10 <sup>-1</sup>	1.32 x 10 <sup>-1</sup>	1,08 x 10 <sup>-1</sup>	62.1

**Calculations of Weisz-Pratter criterion for the employed catalysts; it is assumed that the size of the particle is the mean value obtained by TEM.**

$$C_{WP} = \frac{r_{obs} \rho_{SiO_2} R_p^2}{D_{eff} C_{GUA}}$$

**Table S2.** Data for the calculation of the Weisz-Pratter criterion

Parameter	Value
Particle Radius, cm	Co@SiO <sub>2</sub> -2S = 2.0 x 10 <sup>-6</sup> Co@SiO <sub>2</sub> -SA-2S = 2.1 x 10 <sup>-6</sup> Co@SiO <sub>2</sub> -1S = 1.9 x 10 <sup>-6</sup> Co@SiO <sub>2</sub> -SA-1S = 3.0 x 10 <sup>-6</sup>
Silica Shell density, cm <sup>3</sup> g <sup>-1</sup> [1]	1.40
Effective Diffusivity, cm <sup>2</sup> s <sup>-1</sup> [2]	2.7 x 10 <sup>-8</sup>
Guaiacol Concentration, molcm <sup>-3</sup>	3.2 x 10 <sup>-4</sup>
Observed rate, mol <sub>GUA</sub> s <sup>-1</sup> g <sub>cat</sub> <sup>-1</sup>	Co@SiO <sub>2</sub> -2S = 6.38 x 10 <sup>-4</sup> Co@SiO <sub>2</sub> -SA-2S = 9.68 x 10 <sup>-4</sup>

Calculations were made only for the materials with a Core@shell structure, namely Co@SiO2-2S and Co@SiO2-SA-2S.

For the Co@SiO2-2S system:

$$C_{WP} = \frac{6.38 \times 10^{-4} \times 1.40 \times (2.0 \times 10^{-6})^2}{2.7 \times 10^{-8} \times 3.2 \times 10^{-4}} = 4.1 \times 10^{-4}$$

For the Co@SiO2-SA-2S system:

$$C_{WP} = \frac{9.68 \times 10^{-4} \times 1.40 \times (2.1 \times 10^{-6})^2}{2.7 \times 10^{-8} \times 3.2 \times 10^{-4}} = 6.9 \times 10^{-4}$$

The Mears' criterion ( $C_M$ ) was used to determine whether external mass transfer can be neglected:

$$C_M = \frac{(-r'_A) \cdot \rho_b \cdot R_p \cdot n}{k_c \cdot C_{Ab}} < 0.15$$

where  $r'_A$  is the initial reaction rate,  $\rho_b$  is the bulk density of the catalyst bed ( $0.68 \text{ g cm}^{-3}$ ), calculated by  $(1 - \phi) \cdot \rho_c$  where  $\phi$  is the porosity (0.57) [3] and  $\rho_c$  is the density of the catalyst;  $n$  is the reaction order (assumed to be 1),  $C_{Ab}$  is the guaiacol concentration ( $3.2 \times 10^{-4} \text{ mol cm}^{-3}$ ),  $k_c$  is the mass transfer coefficient ( $\text{cm s}^{-1}$ ).  $k_c$  is estimated from the modified Sherwood parameter  $N_{sh}$ :

Co@SiO2-2S:

$$k_c = \frac{N_{sh} \cdot D_{AB}}{2 \cdot R_p} = \frac{2 \cdot 2.7 \times 10^{-8}}{2 \cdot 2.0 \times 10^{-6}} = 0.0135$$

Co@SiO2-SA-2S:

$$k_c = \frac{N_{sh} \cdot D_{AB}}{2 \cdot R_p} = \frac{2 \cdot 2.7 \times 10^{-8}}{2 \cdot 2.1 \times 10^{-6}} = 0.0129$$

Assuming a Sherwood number of 2 to obtain a minimum value of  $k_c$ [4] the estimated  $C_M$  for each system are:

For the Co@SiO<sub>2</sub>-2S system:

$$C_M = \frac{(6.38 \times 10^{-4}) \times 1.14 \times 2.0 \times 10^{-6} \times 1}{0.0135 \times 3.2 \times 10^{-4}} = 3.4 \times 10^{-4}$$

For the Co@SiO<sub>2</sub>-SA-2S system:

$$C_{WP} = \frac{(9.68 \times 10^{-4}) \times 1.14 \times 2.1 \times 10^{-6} \times 1}{0.0129 \times 3.2 \times 10^{-4}} = 5.6 \times 10^{-4}$$

- [1] Takai C, Watanabe H, Asai T, Fuji M. Determine apparent shell density for evaluation of hollow silica nanoparticle. *Colloids Surfaces A Physicochem Eng Asp* 2012;404:101–5.
- [2] Perullini M, Jobbágy M, Japas ML, Bilmes SA. New method for the simultaneous determination of diffusion and adsorption of dyes in silica hydrogels. *J Colloid Interface Sci* 2014;425:91–5.
- [3] Pope EJA, Mackenzie JD. Sol-gel processing of silica. II. The role of the catalyst. *J Non Cryst Solids* 1986;87:185–98.
- [4] Dolce GM, Savage PE, Thompson LT. Hydrotreatment activities of supported molybdenum nitrides and carbides. *Energy and Fuels* 1997;11:668–74.

### Carbon Balance Calculations

The response factors for the analyzed compounds were obtained from calibration curves, using n-hexadecane as the internal standard, and normalizing the signal using the areas for each compound. The obtained factors are given below:

**Table S3.** Response factors for the compounds obtained during the hydro treatment of guaiacol.

Compound	Factor Response
Benzene	5.63
Cyclohexane	5.92
Cyclohexene	6.15
Methylcyclohexane	6.15
Toluene	6.84
Cyclohexanol	5.36
Anisole	5.83
Phenol	5.7
2-Methylanisole	6.1
<i>o</i> -Cresol	5.97
Catechol	5.1
Guaiacol	7.43

The carbon balance was determined by dividing the total concentrations of the compounds, including guaiacol, by the initial load of guaiacol. In the following table are given the carbon balances obtained with the corresponding conversion, for each of the samples analyzed.

**Table S4.** Carbon balance and conversion for the catalysts studied in this work.

Co@SiO <sub>2</sub> -2S		Co@SiO <sub>2</sub> -SA-2S		Co@SiO <sub>2</sub> -1S		Co@SiO <sub>2</sub> -SA-1S	
Conversion	C <sub>Balance</sub>	Conversion	C <sub>Balance</sub>	Conversion	C <sub>Balance</sub>	Conversion	C <sub>Balance</sub>
9.95%	97.1%	39.6%	94.1%	1.42%	98.8%	6.64%	82.3%
30.3%	93.2%			8.38%	95.6%	16.5%	81.7%
				16.6%	94.1%	29.1%	81.5%