

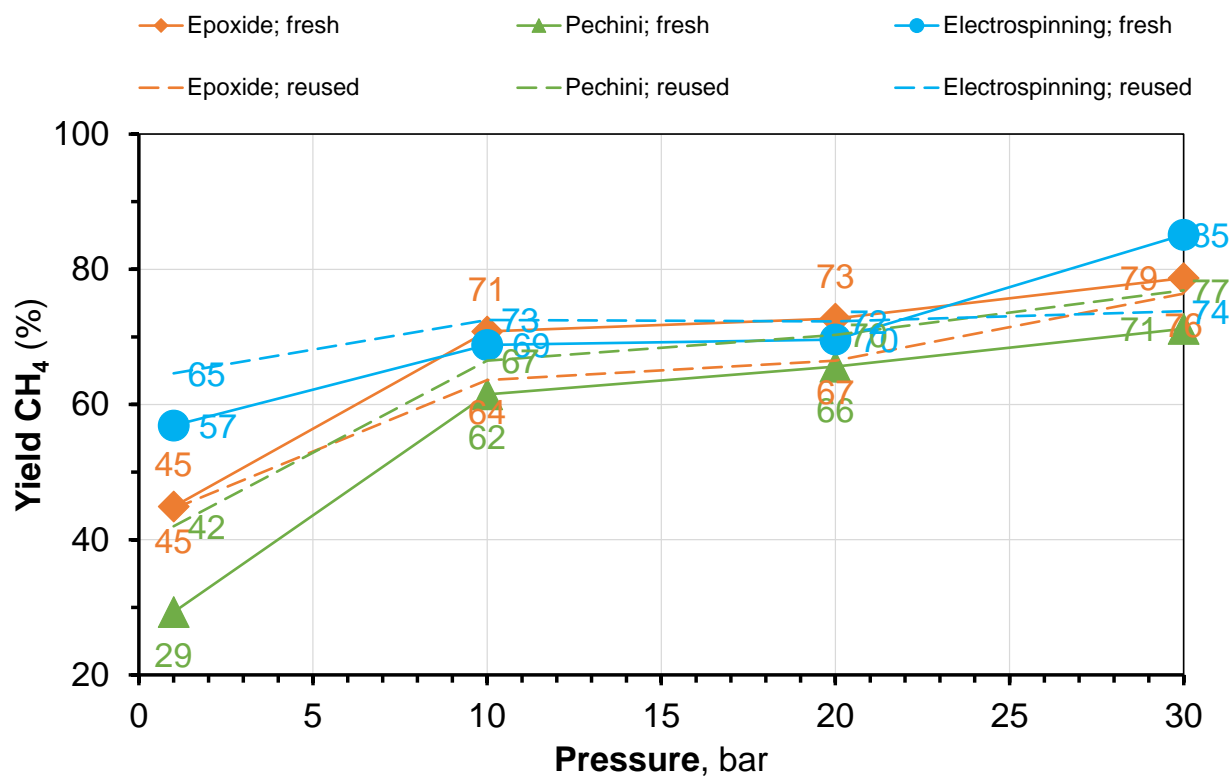
## **Supplementary Materials**

### **Cerium-Based Bimetallic Oxides as Catalysts for the Methanation of CO<sub>2</sub>: Pressure Effect**

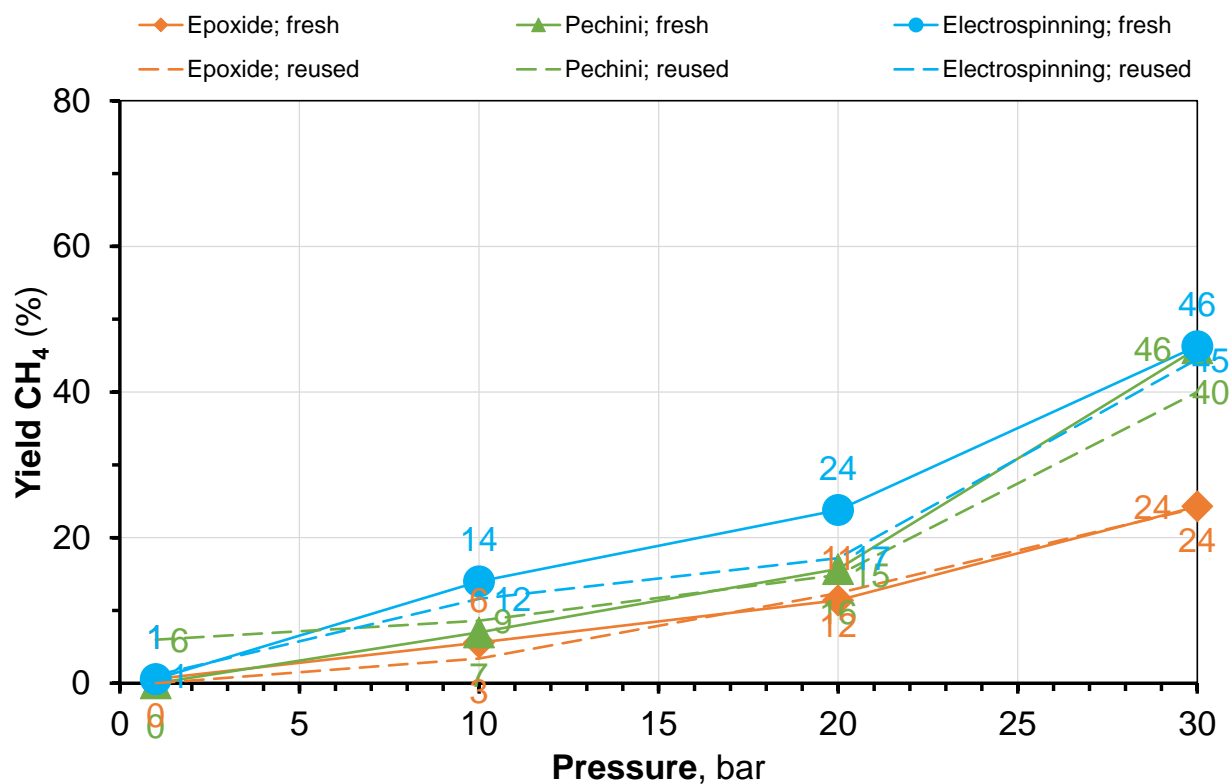
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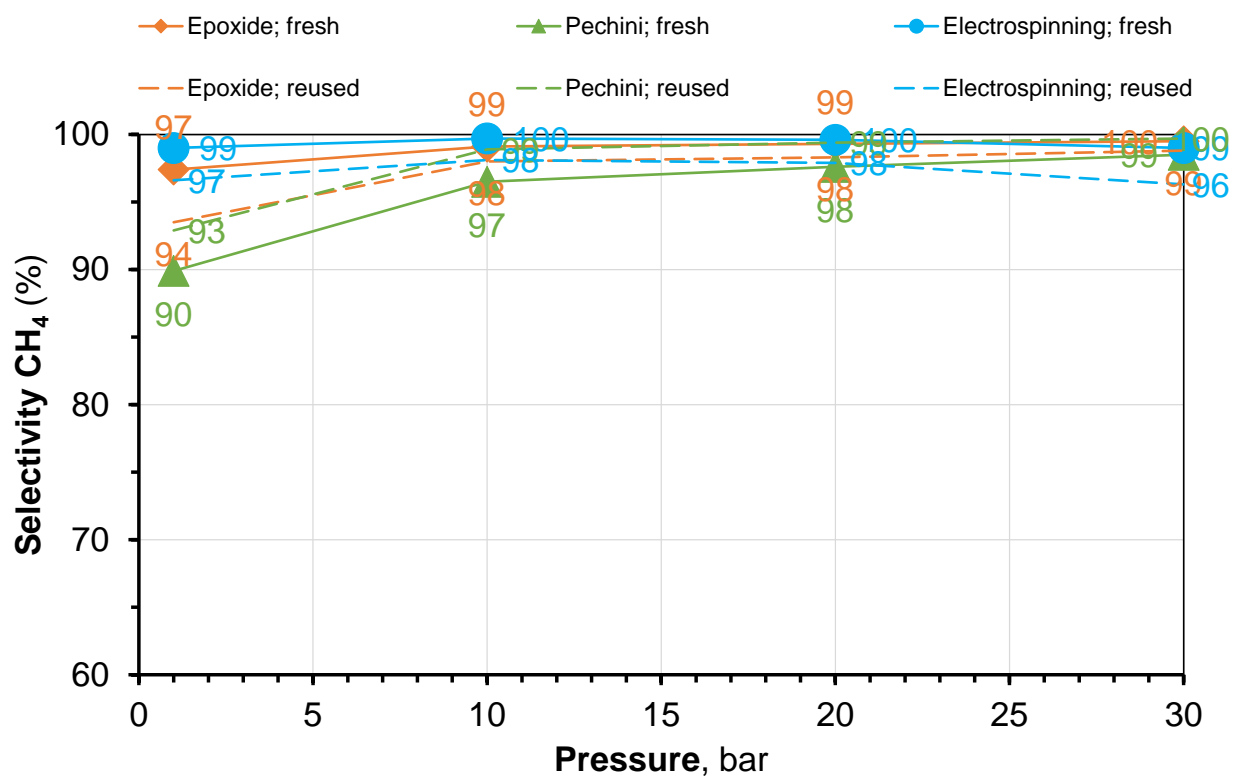
The catalytic behavior is very similar over the nickel- and cobalt- cerium bimetallic oxide catalysts pre-reduced under hydrogen fresh and reused. Minor variations on CO<sub>2</sub> methanation activity and selectivity could be observed, mostly over the catalysts obtained by the Pechini and Epoxide addition method (Figures S1 – S4).



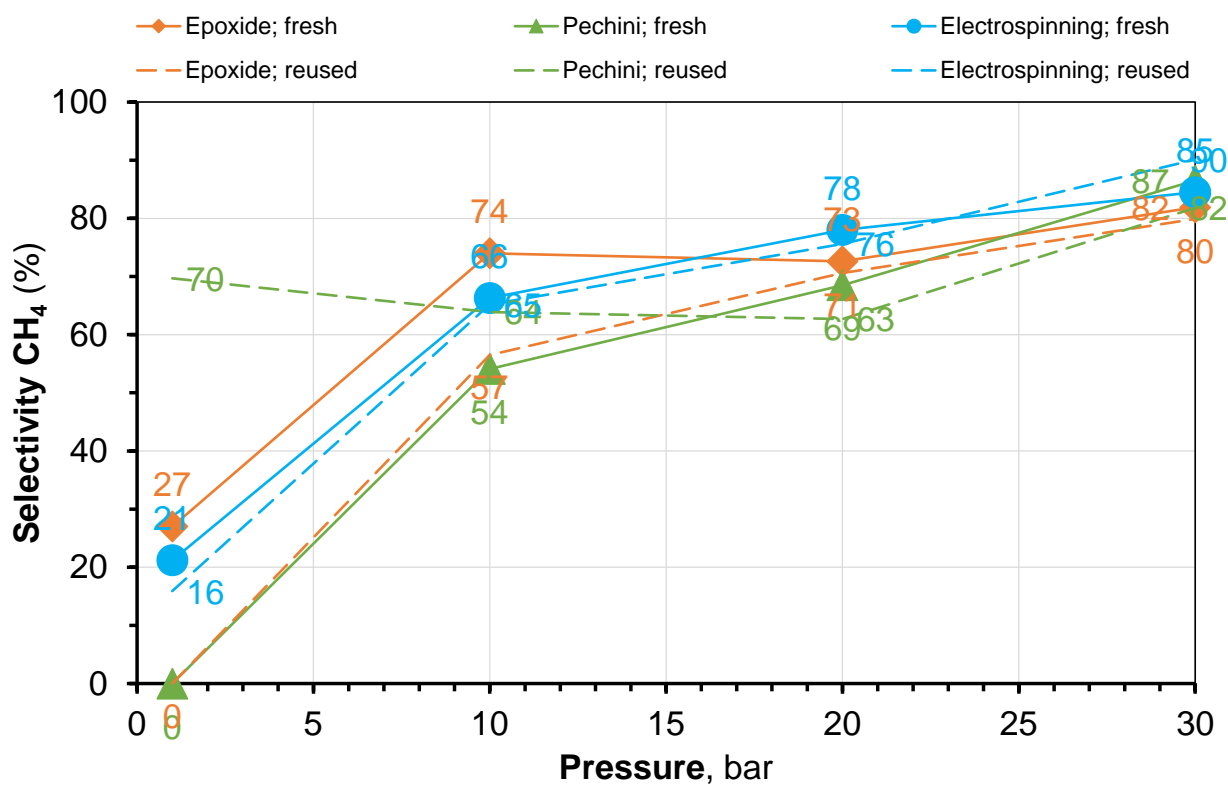
**Figure S1.** Methanation of CO<sub>2</sub> over reused nickel- cerium bimetallic oxides at 300 °C with pre-treatment under hydrogen: effect of preparation method and pressure on CH<sub>4</sub> yield.



**Figure S2.** Methanation of CO<sub>2</sub> over reused cobalt- cerium bimetallic oxides at 300 °C with pre-treatment under hydrogen: effect of preparation method and pressure on CH<sub>4</sub> yield.

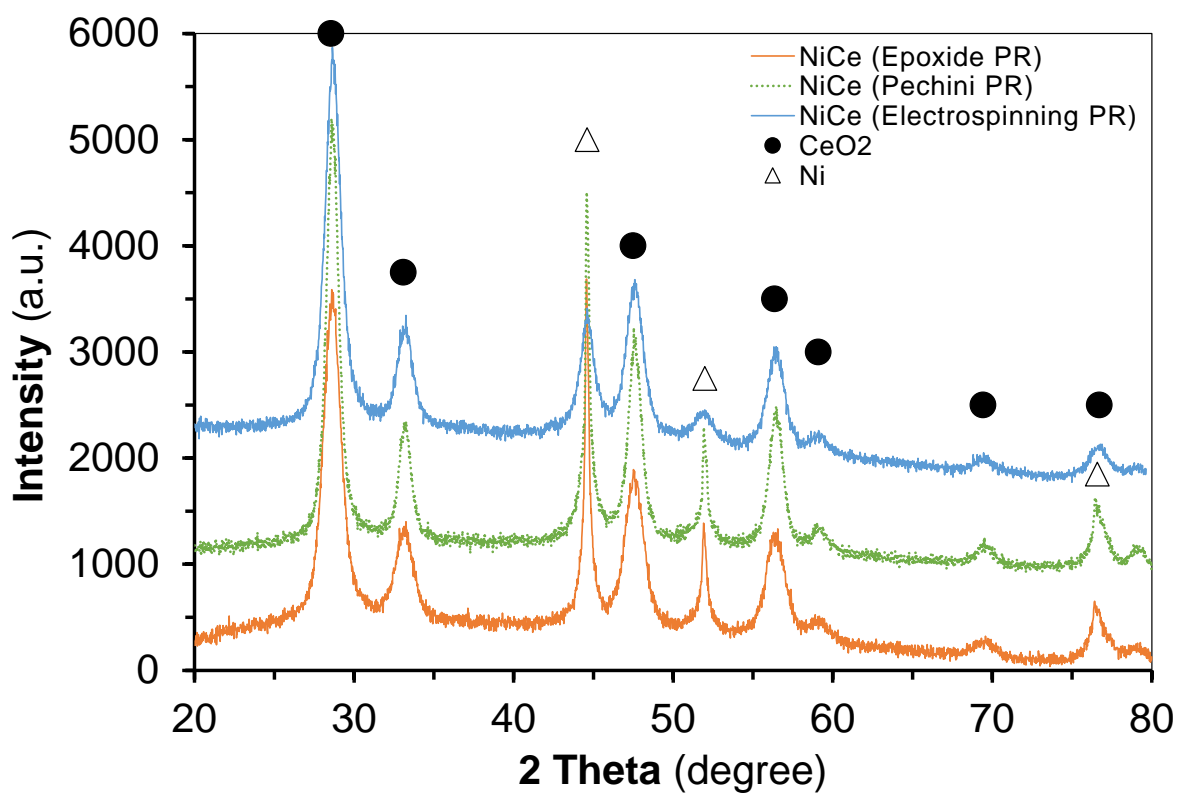


**Figure S3.** Methanation of CO<sub>2</sub> over reused nickel- cerium bimetallic oxides at 300 °C with pre-treatment under hydrogen: effect of preparation method and pressure on CH<sub>4</sub> selectivity.



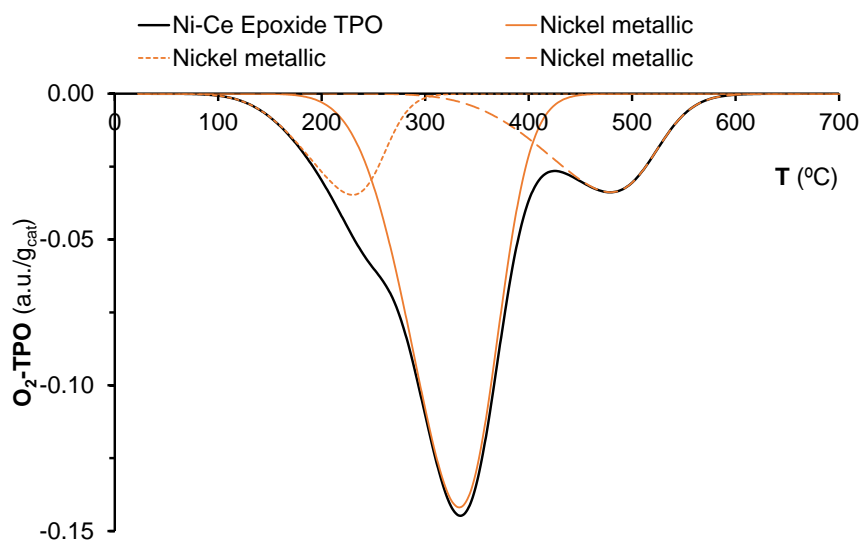
**Figure S4.** Methanation of CO<sub>2</sub> over reused cobalt- cerium bimetallic oxides at 300 °C with pre-treatment under hydrogen: effect of preparation method and pressure on CH<sub>4</sub> selectivity.

The analysis by XRD (powder) shows that after reaction under pressure over reused samples of nickel- cerium bimetallic oxides only the patterns of  $\text{CeO}_2$  and Ni could be observed (Figure S3). Regardless the preparation method or the pre-treatment, only weak variations observed over such catalysts pre-treatment under hydrogen.

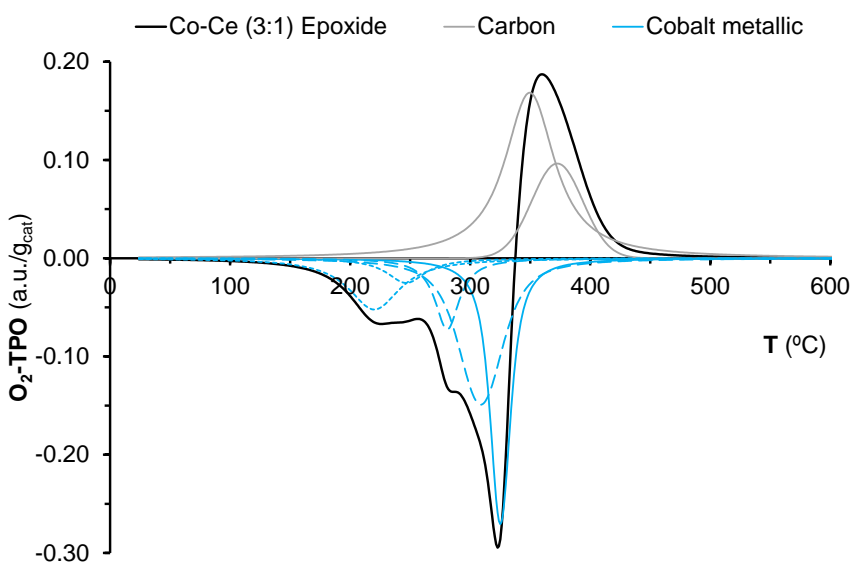


**Figure S5.** Nickel- cerium bimetallic oxides prepared by the different methods: XRD analysis (powder) after tests under pressure over reused samples.

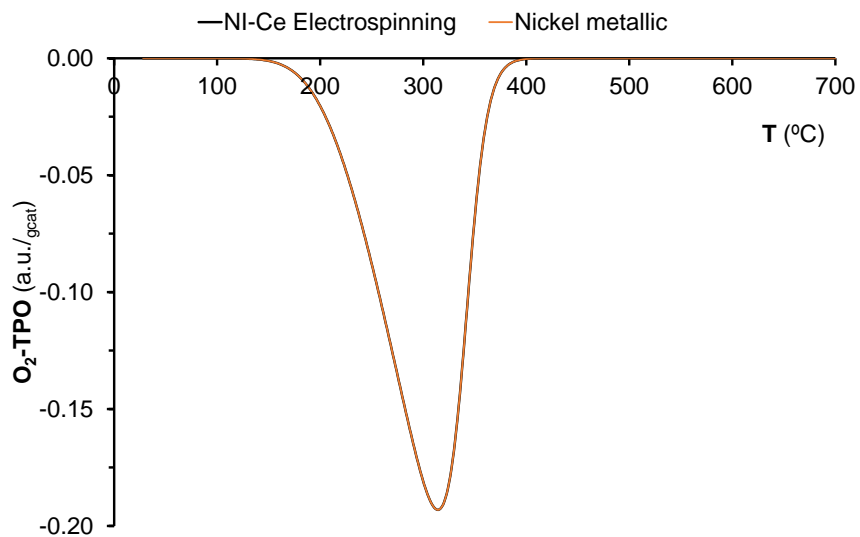
Temperature-programmed oxidation ( $O_2$ -TPO) studies performed after reaction show that the amount of carbon is below detection limit over the nickel-based catalysts and over the 5%Rh catalyst supported on alumina ( $<0.01$  wt. %;  $0.0001$  g / g<sub>cat</sub>), whereas over the cobalt-based catalysts high and measurable amounts of carbon were detected (Figure S4 a and c), which seems to correlate the preparation method: lower over the nanoparticles (Epoxide and Pechini methods) and higher over the nanofibers (Electrospinning technique) (S4 b and d; respectively).



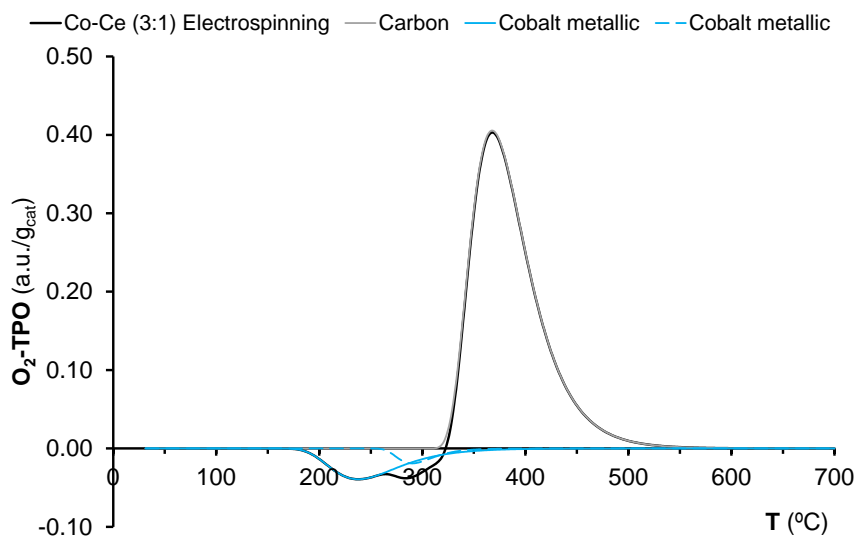
a)



b)



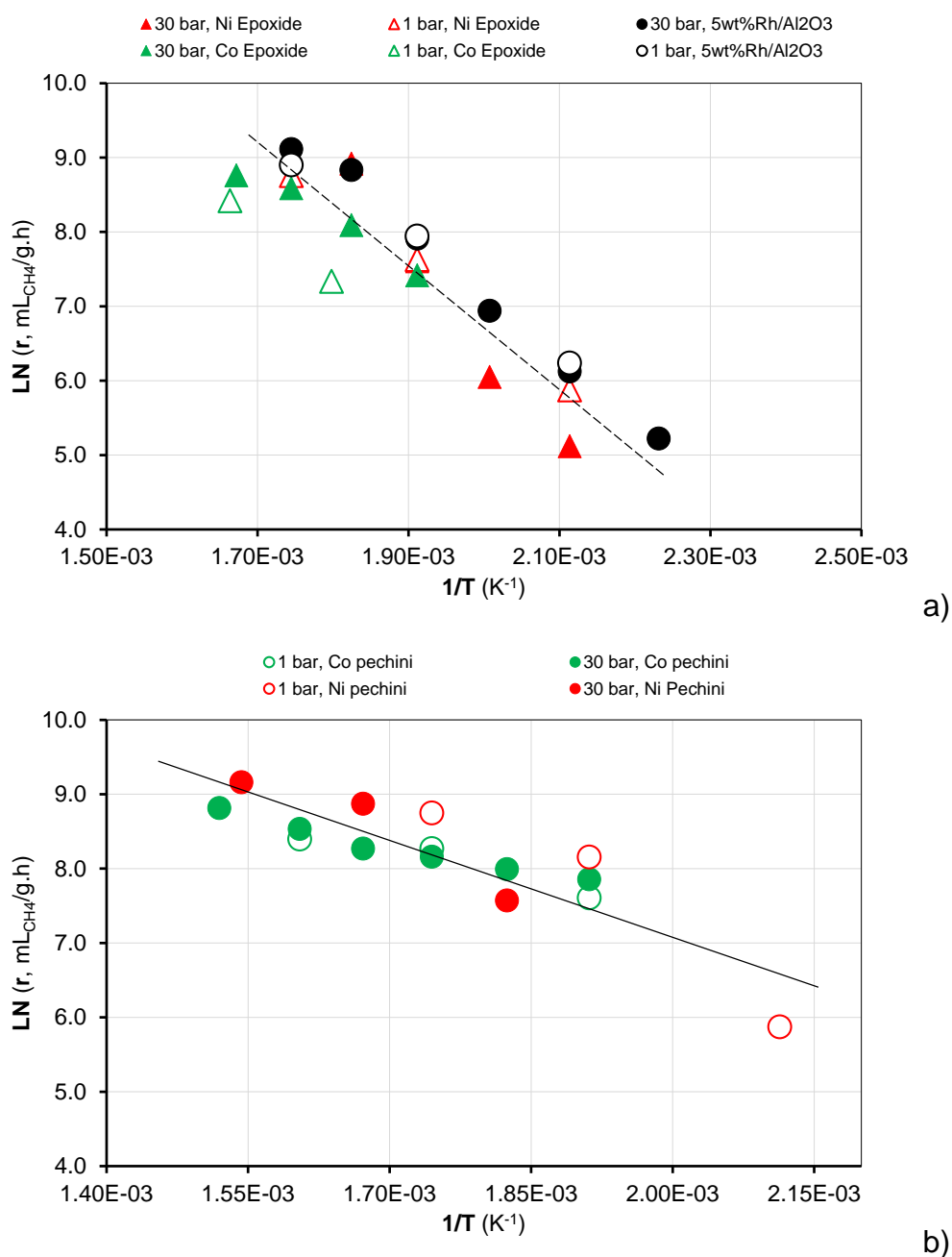
c)



d)

**Figure S6.**  $O_2$ -TPO obtained after reaction for nickel- and cobalt - cerium bimetallic oxides catalysts pre-treated under hydrogen and obtained by the Epoxide method (a, b) and Electrospinning technique (c, d).





**Figure S7.** Relationship between reaction rates to temperature linearized in coordinates of the Arrhenius equation obtained for the catalysts prepared by the Epoxide addition method and the commercial rhodium catalysts (5wt%Rh/Al<sub>2</sub>O<sub>3</sub>) (a) and by the pechini method (b).

**Table S1.** Kinetic data: activation energy ( $E_{\text{CH}_4}$ ) and methane rate of formation ( $k_{\text{CH}_4}$ ) at 300 °C under atmospheric and 30 bar pressure.

Catalyst	Method	$E_{\text{CH}_4}$ , kJ/mol		$K_{\text{CH}_4}$ , mL/g.h	
		1 bar	30bar	1 bar	30bar
Co-Ce	Pechini	10.1	10.9	3503	3905
Ni-Ce	Pechini	35.7	33.1	4485	6295
Co-Ce	Epoxide	33.7	29.5	4535	5373
Ni-Ce	Epoxide	32.8	39.5	6368	8160
Co-Ce	Electrospinning	33.8	-	6050	-
Ni-Ce	Electrospinning	41.0	-	9685	-
5%Rh/Al <sub>2</sub> O <sub>3</sub>	-	30.4	35.2	7339	9087