

SUPPORTING INFORMATION

**Nickel oxide supported on Porous Clay Heterostructures as selective
catalysts for the oxidative dehydrogenation of ethane**

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Experimental information

Surface coverage

5NiSi and 17NiPCH have similar NiO coverage of the support (ca. 3.10^{-4} g of NiO per m² of support).

5NiSi presents 5 wt.% of NiO and 95 wt.% of silica. Silica has a surface area of 181 m²/g. Therefore for 1 g of catalyst, 0.05 g of NiO are spread over 0.95 g of support, which corresponds to 171.95 m². Then, there are $2.91.10^{-4}$ g of NiO per m² of support.

17NiPCH presents 17 wt.% of NiO and 83 wt.% of PCH. PCH has a surface area of 644 m²/g. Therefore for 1 g of catalyst, 0.17 g of NiO are spread over 0.83 g of support, which corresponds to 534.52 m². Then, there are $3.18.10^{-4}$ g of NiO per m² of support.

Table S1. Physicochemical characteristics of the PCH supports.

Sample	S_{BET} (m²g⁻¹)	t-plot microp (m² g⁻¹)	V_P (cm³ g⁻¹)	V_P microp* (cm³ g⁻¹)	Pore size (nm)	Acidity μmolNH₃ g⁻¹	Acidity μmolNH₃ m⁻²
Montmorillonite	49	18	0.109	0.009	12.4	125	2.55
PCH	644	460	0.773	0.280	5.5	308	0.48
PCH-Ti	562	287	0.796	0.164	6.8	395	0.70

Table S2. Catalytic performance of pure supports in the oxidation of ethane at 450°C.^a

Catalyst	W/F ^b	Ethane Conversion,%	Selectivity, %	
			Ethylene	CO _x
Si	8	0.02	0	100
PCH	8	0.15	62	38
PCH-Ti	8	0.16	64	36

^a Reaction conditions detailed in the experimental part of the text; ^b Contact time in g_{cat} h (mol_{C2})⁻¹

Table S3. Temperature programmed $^{18}\text{O}_2$ isotopic exchange (TPIE) results.

Catalyst	$T_{\text{onset}}^{16}\text{O}_2$ (°C)	$T_{\text{onset}}^{16}\text{O}^{18}\text{O}$ (°C)	Area $^{16}\text{O}_2/^{16}\text{O}^{18}\text{O}$ ^a
10NiSi	Not observed	377	<0.1
10NiPCH	419	425	1.12
10NiPCH-Ti	419	450	1.32

^a relative amount of O-species released until 650°C.

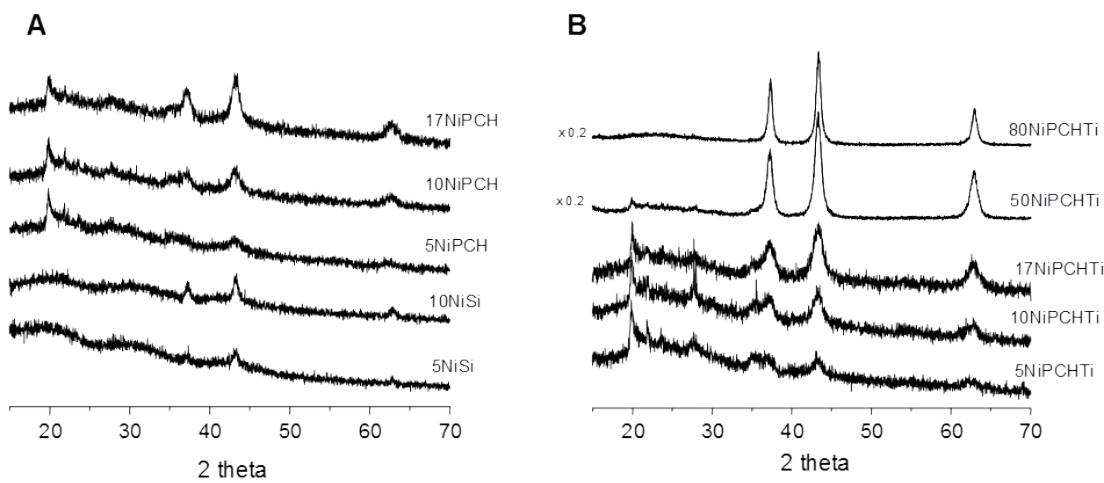


Figure S1. XRD patterns for NiO catalysts supported on conventional silica (NiSi-series) and pillared clays (both NiPCHSi- and NiPCH-Ti-series)

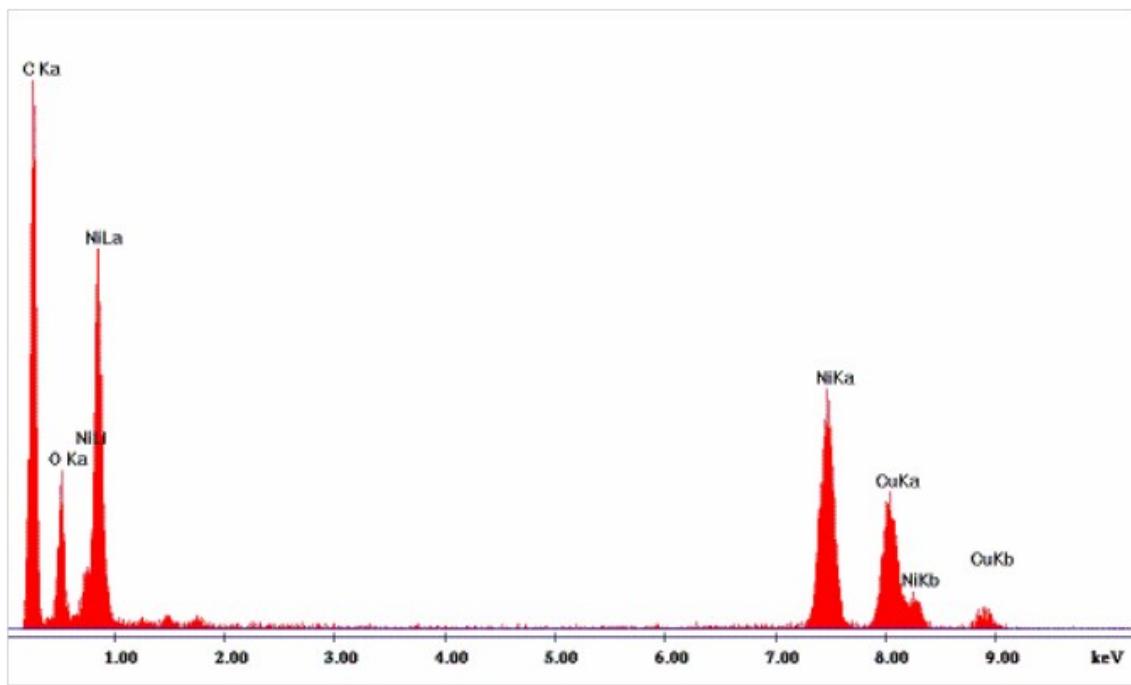


Figure S2. Local EDX spectrum of a single NiO nanoparticle in **17NiPCH-Ti**.

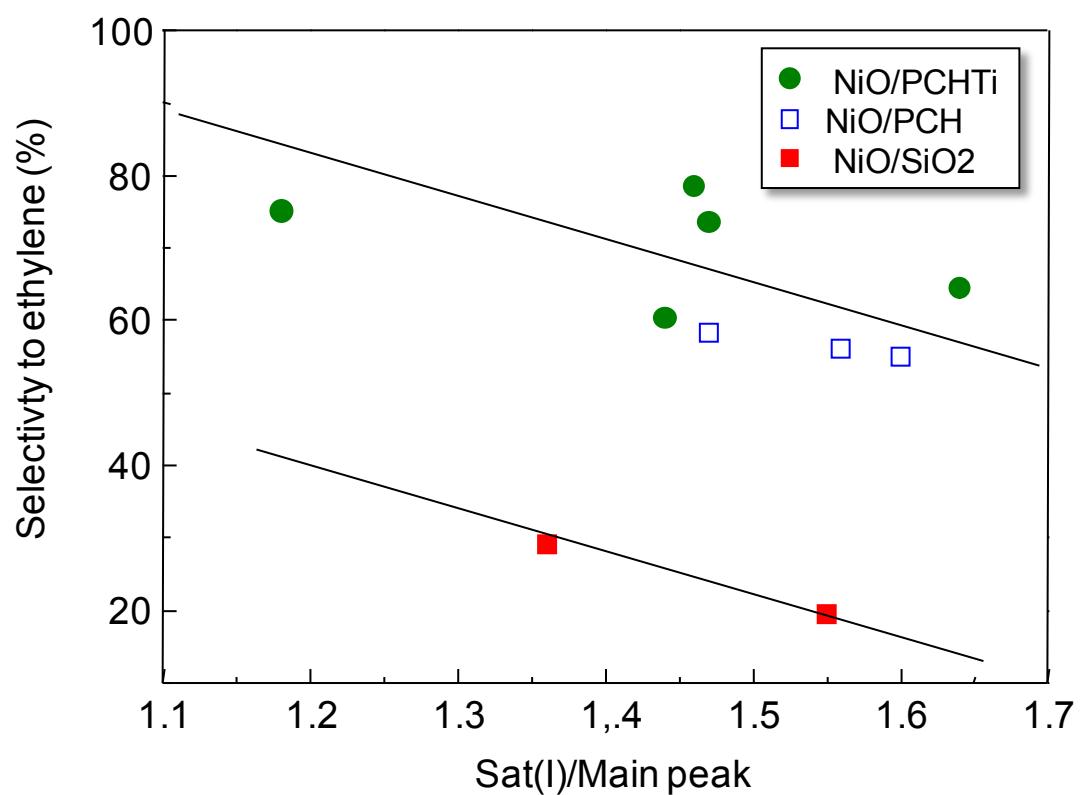


Figure S3. Relationship between selectivity to ethylene and the Sat(I)/Main peak ratio determined by XPS. Note: Selectivity to ethylene as in Figure 6.

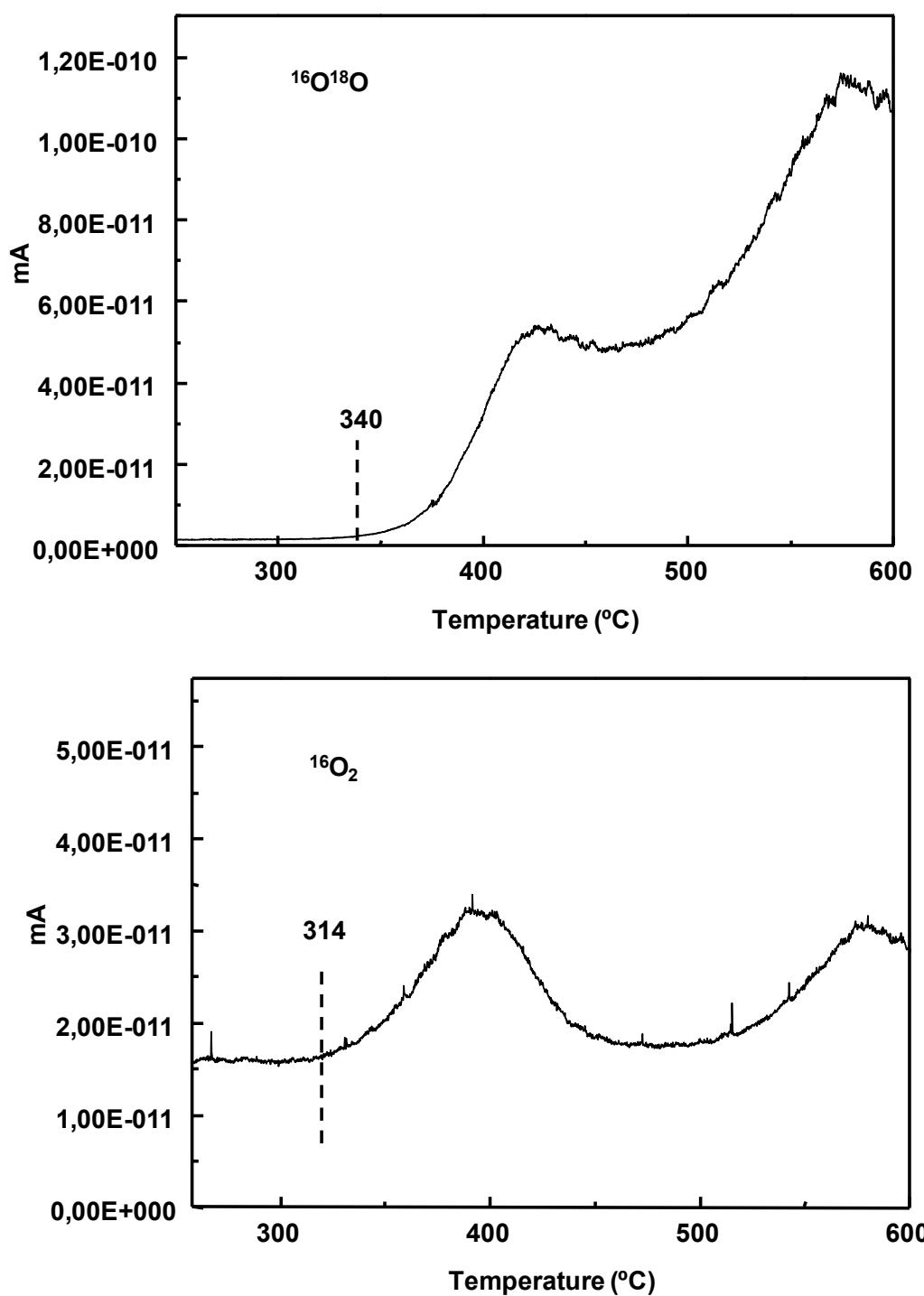


Figure S4. Evolution of the oxygen exchange ($^{16}\text{O}^{18}\text{O}$ and $^{16}\text{O}_2$) formation species per Ni atom during TPIE experiments versus temperature over NiO catalyst.