

Nickel-silicide colloid prepared under mild conditions as a versatile Ni-precursor for more efficient CO₂ reforming of CH₄ catalysts.

David Baudouin,^{1,2,†} Kaï Chung Szeto,¹ Pierre Laurent,¹ Aimery De Mallmann,¹ Bernard Fenet,^{3,4} Laurent Veyre,¹ Uwe Rodemerck,⁵ Christophe Copéret,^{1,2,†,*} Chloé Thieuleux^{1,*}.

1- Université de Lyon, ICL, C2P2 UMR 5265, CPE Lyon, 43 Bd du 11 Novembre 1918, F-69616, Villeurbanne, France

2- Institute for Inorganic Chemistry, ETH Zürich, HCI H 206, Wolfgang-Pauli-Strasse 10, CH-8093 Zürich, Switzerland

3- Centre Commun de RMN, Université de Lyon, 69003 Lyon, France

4- Université Lyon 1 Claude Bernard, ESCPE Lyon, 43, Bd du 11 Novembre 1918, 69616 Villeurbanne Cedex, France

5- Leibniz Institute for Catalysis at University Rostock, Albert-Einstein-Straße 29a D-18059 Rostock, Germany.

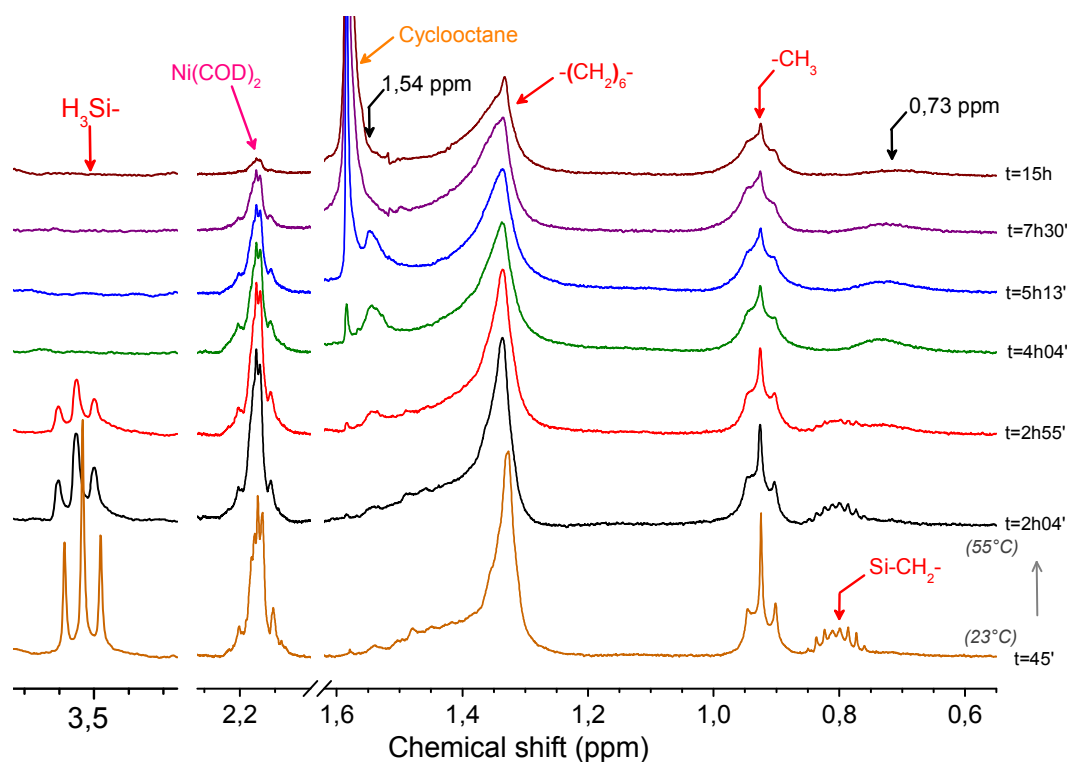


Figure S1. In situ liquid ¹H NMR study of colloid formation in THF at 55°C, normalized to THF-d₈ signal. To limit the influence T₁ and T₂ relaxation variations with reaction time, a 60s dead time was used prior to single scan spectra measurement.

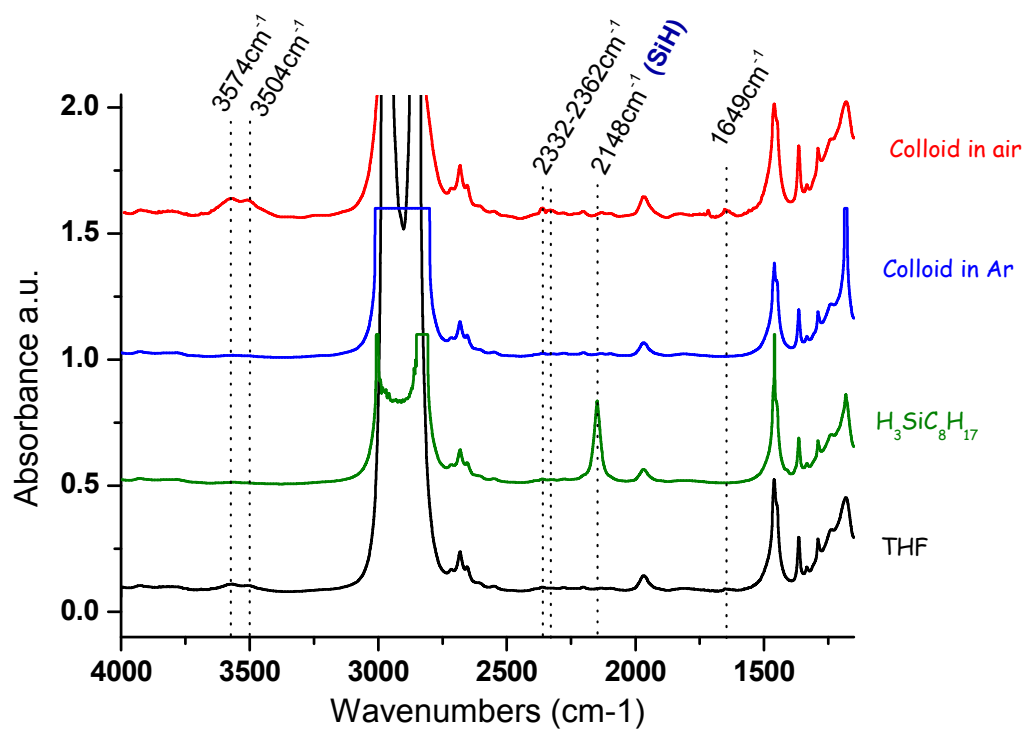


Figure S2. FT-IR of THF, octylsilane, concentrated colloid under Ar and exposed to air. The concentration of Ni and Si in the concentrated colloid is approximately 0.3 mole.L⁻¹.

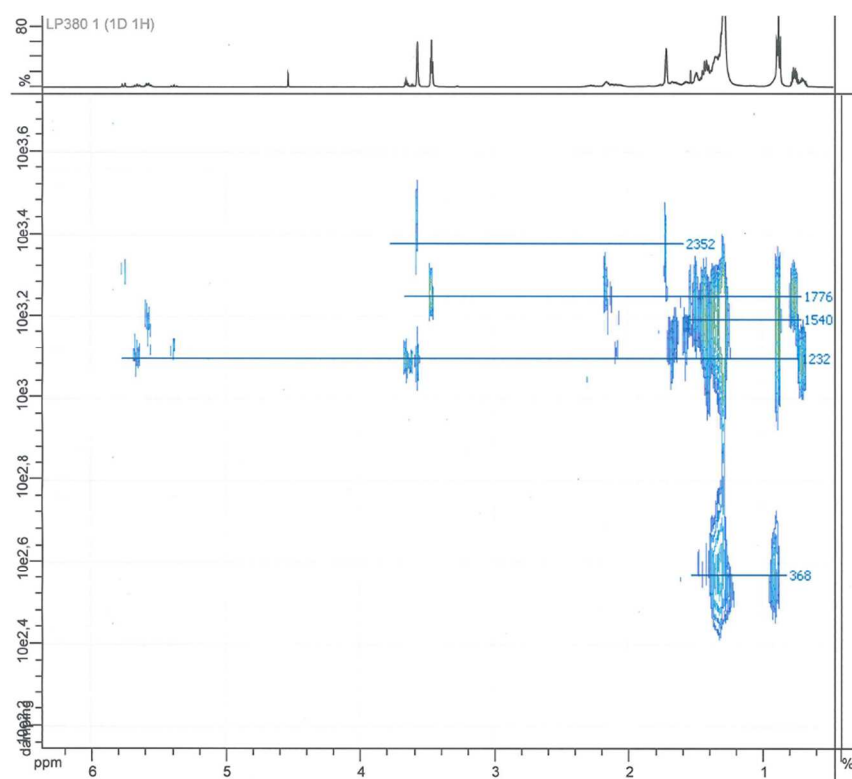


Figure S3. Diffusion-ordered NMR spectroscopy (DOSY) study of colloid formed with an excess of silane at 60°C performed at 298K on a 500 MHz spectrometer.

Table S4. EXAFS fitting parameters for $[(\text{Ni}_x\text{Si}-\text{C}_8\text{H}_{17})/\text{SiO}_2]$, $[(\text{Ni}_x\text{Si})/\text{SiO}_2]^{\text{H}2}_{500}$, $[(\text{Ni}_x\text{Si})/\text{SiO}_2]^{\text{H}2}_{1000}$ and commercial $\delta\text{-Ni}_2\text{Si}$, as well as the parameters of two amorphous nickel silicide extrapolated from reference [19].

Sample	Atom	Coordination number (N)	Neighbour distance (R) $\text{\AA}$	Debye-Waller factor (σ^2) $10^{-3}\text{\AA}^2$
$[(\text{Ni}_x\text{Si}-\text{C}_8\text{H}_{17})/\text{SiO}_2]$	Si	4.4(9)	2.25(2)	15(3)
	Ni	2.8(10)	2.45(2)	11(3)
$[(\text{Ni}_x\text{Si})/\text{SiO}_2]_{500^\circ\text{C}}$	Si	2.1(5)	2.25(2)	8(3)
	Ni	3.1(8)	2.46(1)	11(2)
$[(\text{Ni}_x\text{Si})/\text{SiO}_2]_{1000^\circ\text{C}}$	Si	2.6(11)	2.32(4)	12(8)
	Ni	4.5(11)	2.46(1)	9(2)
$\delta\text{-Ni}_2\text{Si}$	Si	4	2.30(1)	7(1)
	Ni	8	2.56(1)	8.6(6)
	Si	1	2.60(5)	10(3)
Amorphous $\text{Ni}_3\text{Si}_2^{\text{a}}$	Si	4.6(10)	2.30(5)	8(3)
	Ni	3.1(10)	2.45(3)	8(3)
Amorphous $\text{Ni}_2\text{Si}^{\text{a}}$	Si	2.8(10)	2.27(5)	8(2)
	Ni	4.6(13)	2.46(2)	7(2)
$\text{Ni}^{(0)}$ foil	Ni	12	2.47(1)	6.0(4)
	Ni	6	3.49(2)	9.6(6)
	Ni	24	4.32(1)	9.6*
	Ni	12	4.97(1)	9.6*

a- Extrapolated from reference (19) (cf. publication).

Numbers between parentheses correspond to the error on the last digit

X-Ray Absorption Spectroscopy:

Transmission data were obtained at the Ni-K edge at HASYLAB (DESY) on DORIS III beam-line X1 (RÖMO II). The data reduction was performed by standard procedures using the program Athena. The background was removed by fitting a polynomial to the pre-edge of the data such that the post-edge spectrum followed a Victoreen function. The spectra were calibrated with a Ni foil located behind the sample, energies are measured at the inflexion point(s) of the absorption signal, using the derivative curve, precision on the energy of the edge is ± 0.5 eV in the (8303-8373 eV) area.

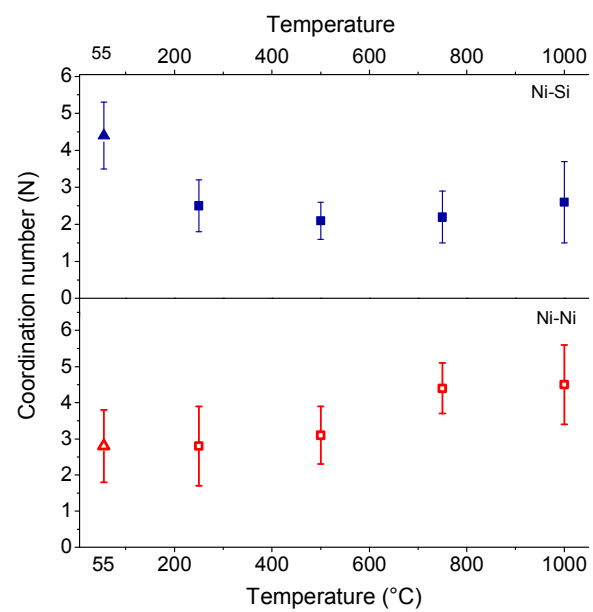


Figure S5. Average first-shell Ni coordination numbers obtained from Ni K-edge data for $[(\text{Ni}_x\text{Si-C}_8\text{H}_{17})/\text{SiO}_2]$ as prepared and after heating under hydrogen at various temperature.

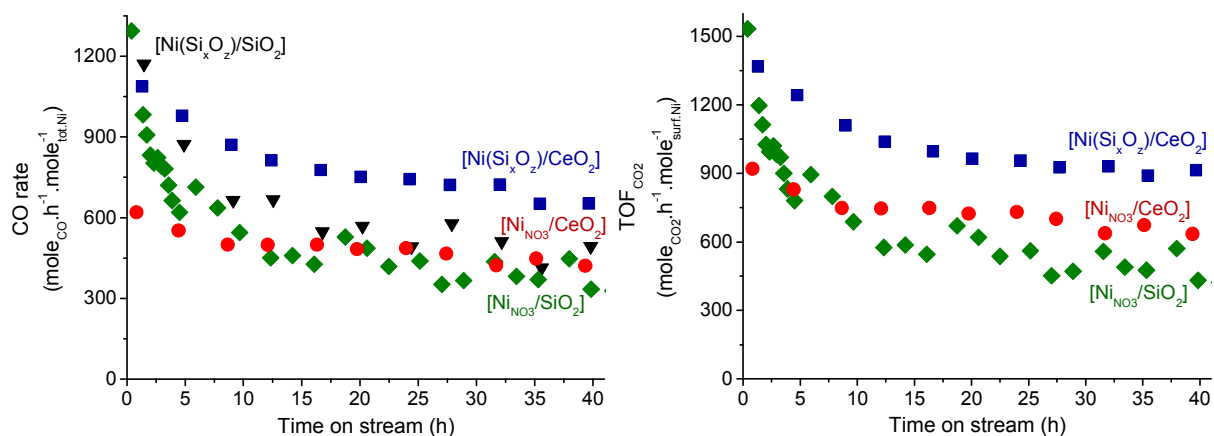


Figure S6. Variation of [Ni(Si_xO₂)/SiO₂], [Ni_{NO3}/SiO₂], [Ni(Si_xO₂)/CeO₂] and [Ni_{NO3}/CeO₂] CO rate (left) and TOF_{CO2} (right) in CO₂ reforming of CH₄ with time on stream. For the sake of clarity, the variation of [Ni(Si_xO₂)/SiO₂] TOF is not presented for its similarity with [Ni_{NO3}/SiO₂]. Test conditions: CH₄:CO₂:N₂ = 2.2:1.8:6 (v:v), i.e. CH₄/CO₂=1.3, with a specific flow of 16000 mole_{reactant}·h⁻¹·mole⁻¹_{surf. Ni}.

Table S7. The initial and steady state TOF_{CO_2} of various Ni_x/SiO_2 catalysts during dry reforming of methane at 773K and their variation of activity and dispersion.

Sample	Initial D_{Ni}^{b,c} %	TOF_{CO_2}^d $t = 5\text{min}$	TOF_{CO_2}^d $t = 43\text{h}$	Activity loss %
$[\text{Ni}^0(\text{Si}_y\text{O}_2)/\text{SiO}_2]$	71±5	2170	450	79
$[\text{Ni}_{\text{NO}_3}/\text{SiO}_2]$	50±3	2240	490	78
$[\text{Ni}(\text{Si}_x\text{O}_2)/\text{CeO}_2]$	54±3	2010	910	55
$[\text{Ni}_{\text{NO}_3}/\text{CeO}_2]$	47±4	1110	680	39

a - Air circulating oven used with a heating ramp of $2\text{K}.\text{min}^{-1}$;

b - $\text{Ni}^{(0)}$ dispersion from H_2 chemisorption – Blanks showed negligible adsorption;

c - “±” error ;

d - in $\text{mole}_{\text{CO}_2}.\text{h}^{-1}.\text{mole}^{-1}_{\text{surf. Ni}}$;