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Supporting Information

Re-Investigation of the Alleged Formation of CoSi Nanoparticles on Silica

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Experimental

All manipulations were carried out under an atmosphere of dry argon using Schlenk techniques or a glove box. Silica (Merck, particle size 0.015-0.040 nm) and activated charcoal (Fluka, particle size 75 % ≤ 40 μm) was used as received.

Nitrogen sorption measurements were performed on a Micromeritics ASAP 2010. The samples were degassed under vacuum at 50 °C for at least 5 h prior to measurements. X-Ray powder diffraction (XRD) measurements were performed on a Philipps X'Pert diffractometer using Cu K_α radiation (λ = 1.542 Å).

Energy-dispersive X-ray spectroscopy (EDX) was performed with the TECNAI F20. Line scan analyses were carried out in scanning transmission electron microscope (STEM) mode, using a real-time interactive imaging system using a high angle annular dark field (HAADF) detector.

TEM images were obtained using a TECNAI F20 analytical microscope equipped with a S-Twin objective lens and a field emission source operating at 200 kV and were recorded with a Gatan Orius SC600 CCD camera. The powders were deposited on a carbon grid for TEM analyses.

XPS spectra were recorded on a Perkin-Elmer Φ5600ci spectrometer using standard Al radiation (1486.6 eV) working at 350 W. The spectrometer was calibrated by assuming the binding energy (BE) of the $Au4f_{7/2}$ line at 83.9 eV with respect to the Fermi level. The

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standard deviation for the BE values was 0.15 eV. The reported BE were corrected for the charging effects, assigning, in the outer layers where contamination carbon is still present, to the C1s line of carbon the BE value of 284.6 eV.[1,2] Survey scans (187.85 pass energy, 1 eV/step, 25 ms per step) were obtained in the 0-1300 eV range. Detailed scans (58.7 eV pass energy, 0.1 eV/step, 100-150 ms per step) were recorded for the O1s, C1s, Co2p, CoLMM, Co3s, Co3p, Si2p, Si2s regions. The atomic composition, after a Shirley type background subtraction [3] was evaluated using sensivity factors supplied by Perkin-Elmer.[1] Samples were introduced directly, by a fast entry lock system, into the XPS analytical chamber. Peak assignments were carried out using values reported in the XPS Handbook, the NIST XPS Database and references given in the main text.[1]

Preparation of the nanocomposite

Preparation of the sample was performed as described in Ref. **Error! Bookmark not defined.**. $Co(CO)_4SiCl_3$ was prepared according to Ref. 4, and characterized by ^{29}Si and ^{13}C NMR spectroscopy. Silica was heated in air at 600 °C for 24 h to remove residual water (specific surface area after heating 467 m^2/g).

An amount of 0.5g (1.64 mmol) of $Co(CO)_4SiCl_3$ was thoroughly mixed with 0.7 g of SiO_2. Subsequently, the mixture was heated to 65 °C under argon for 160 min to adsorb $Co(CO)_4SiCl_3$ homogeneously in the SiO_2. Thermolysis under H_2/N_2 was performed in a split tube furnace (Carbolite HST 12/300) equipped with a gas flow control system. The $Co(CO)_4SiCl_3$-loaded silica was heated under a H_2/N_2 mixture (H_2 flow 20 mL/min, N_2 flow (190 mL/min) with a heating rate of 10 °C/min to 300 °C and held at this temperature for 120 min at atmospheric pressure. A grey powder was obtained (specific surface area 383 m^2/g). Part of the sample was additionally heated to 600 °C and 1000 °C under N_2 (200 mL/min)

with a heating rate of 10 °C/min. The samples were characterized after cooling to room temperature,.

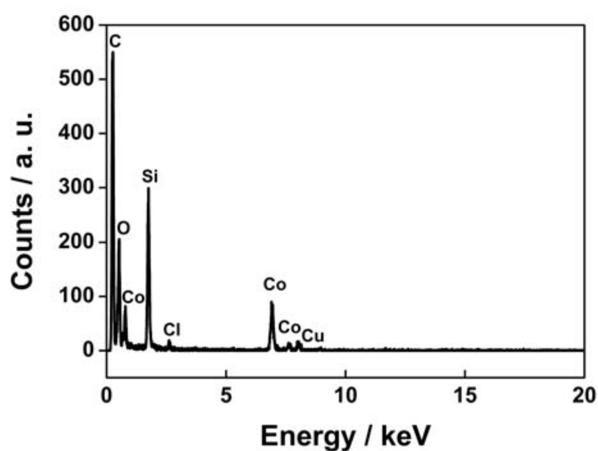

Fig. S1 EDX spectrum of a single nanoparticle in SiO_2

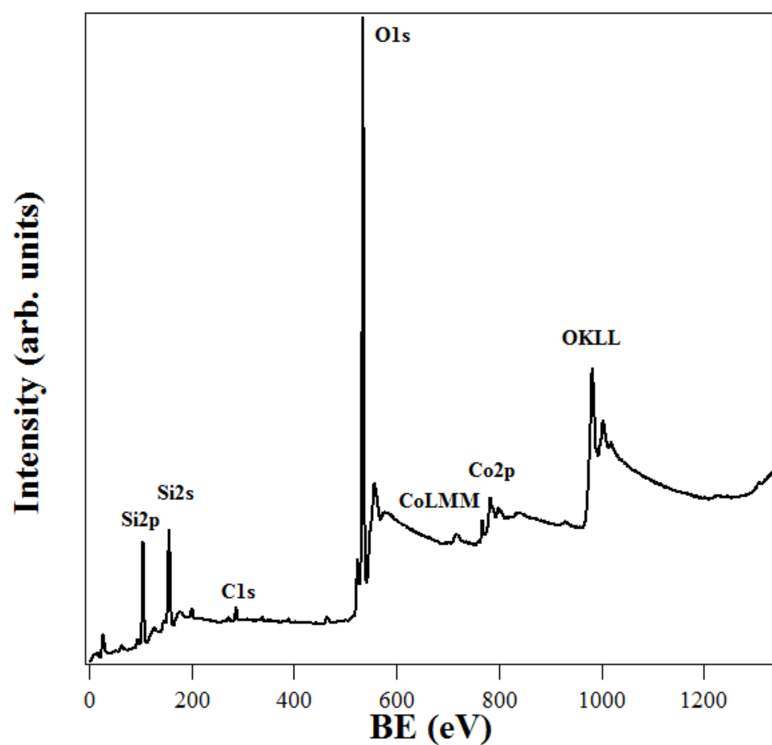

Fig. S2 XPS survey spectrum of the material obtained after treating the precursor loaded silica sample at 300 °C under H_2.

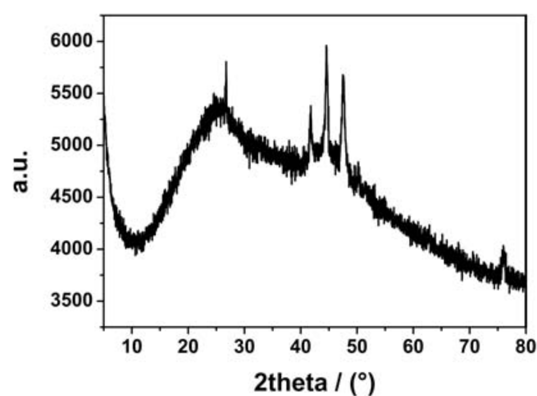

Fig. S3 Diffraction pattern of Co nanoparticles on charcoal after thermolysis at 300 °C under H_2.

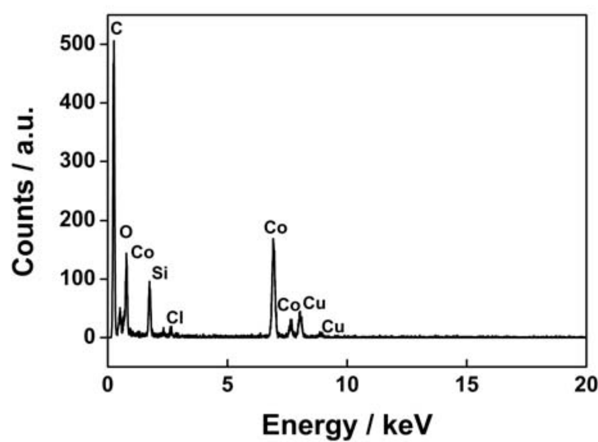

Fig. S4 EDX spectrum of a single particle (charcoal support)

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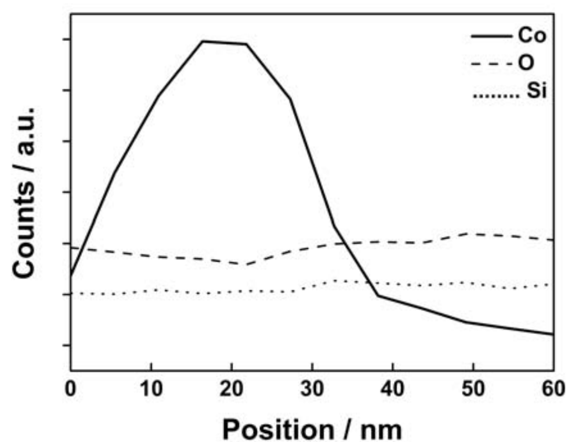

Fig. S5 EDX line scan profile of a single cobalt nanoparticle on charcoal

[1] J. F. Moulder, W. F. Stickle, P. E. Sobol and K. D. Bomben, *Handbook of X-Ray Photoelectron Spectroscopy*, ed. J. Chastain, Perkin Elmer Corp., Eden Prairie, MN, 1992

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[3] D.A. Shirley, *Phys. Rev.*, 1972**, 55**, 4709.

[4] C. Liang, A. Zhao, X. Zhang, Z. Maa and R. Prins, *Chem. Comm.*, 2009, 2047.