

Heterogeneous & Homogeneous & Bio- & Nano-

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CATALYSIS

Supporting Information

A Seed-Mediated Approach for the Preparation of Modified Heterogeneous Catalysts

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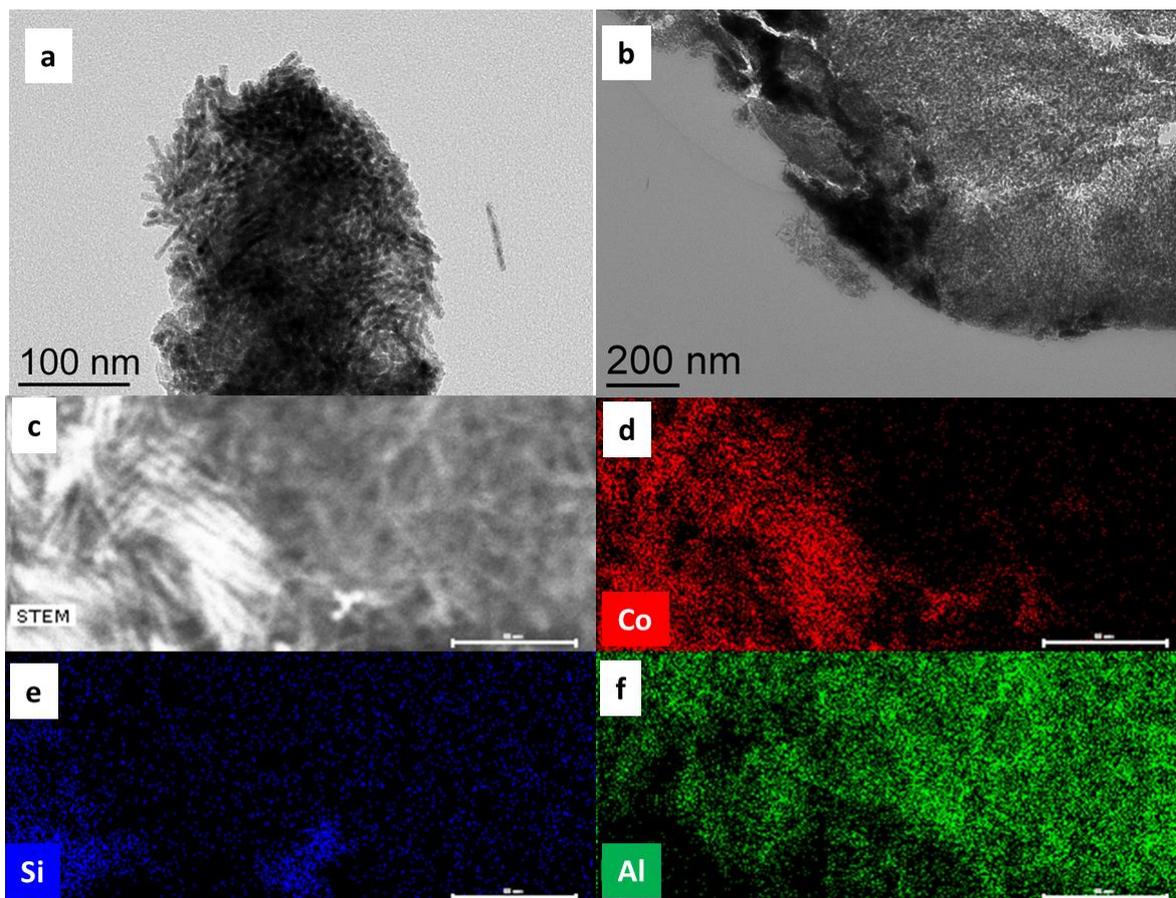


Figure SI-1. Impregnation of $\text{Al}_2\text{O}_3\text{-SiO}_2$ with preformed Co NRs. a) TEM, b) TEM of a slice obtained by ultramicrotomy c) f) STEM and EDX element distribution on a slice obtained by microtomy Co (red), Si (blue), Al (green). Scale bars a): 100 nm; b): 200 nm; c-f): 60 nm.

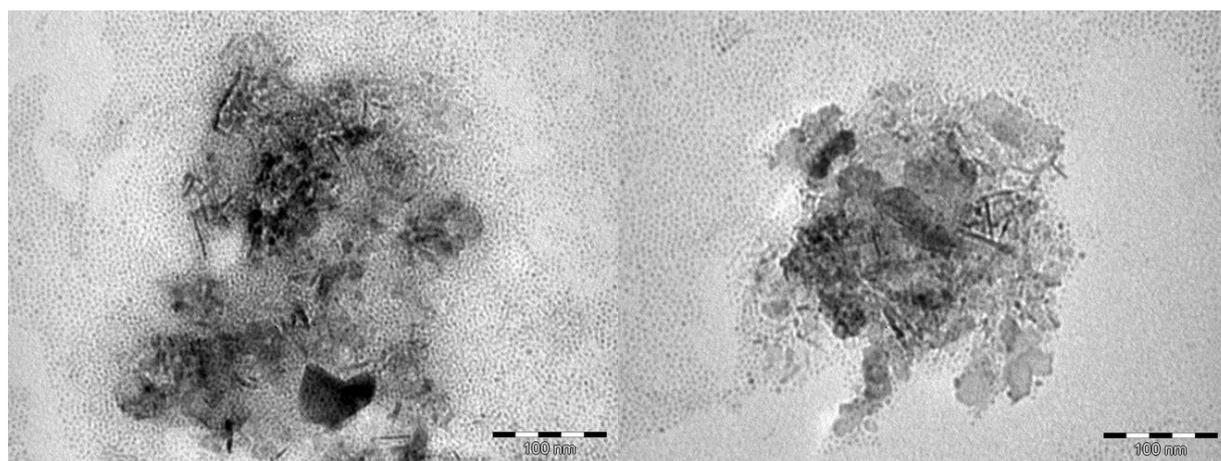


Figure SI-2. In situ reduction of Co NRs in the presence of $\text{Al}_2\text{O}_3\text{-SiO}_2$. TEM of a crude sample: nanorods and nanoparticles are formed in solution as well as on the support. Ill shaped nano-objects are also present on the support (scale bars = 100 nm).

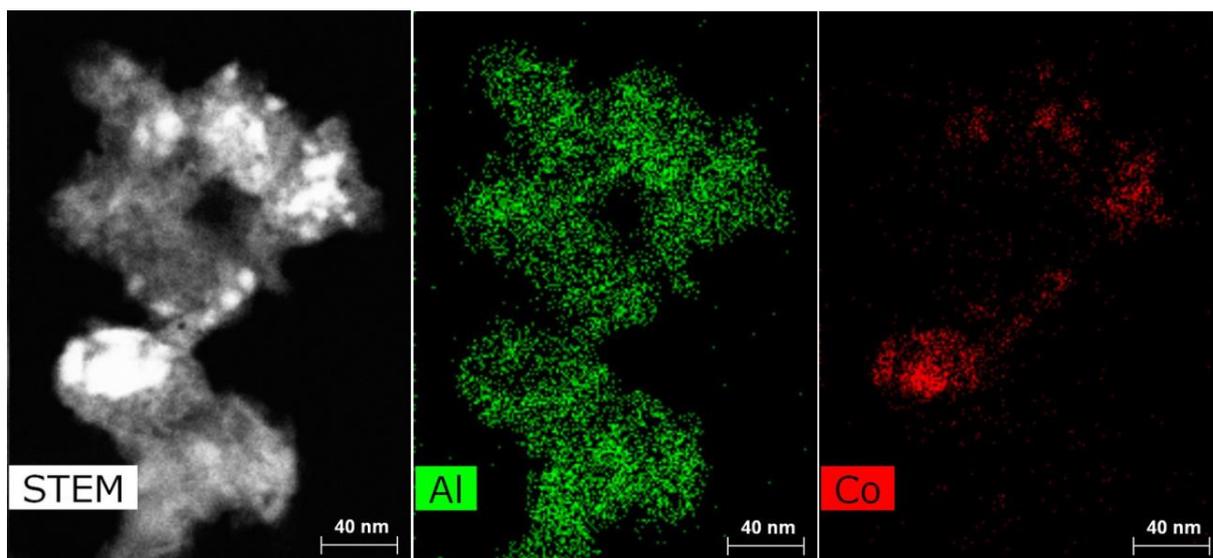


Figure SI-3. STEM-EDX of the 15% Co/Al₂O₃-SiO₂ catalyst (scale bars 40 nm).

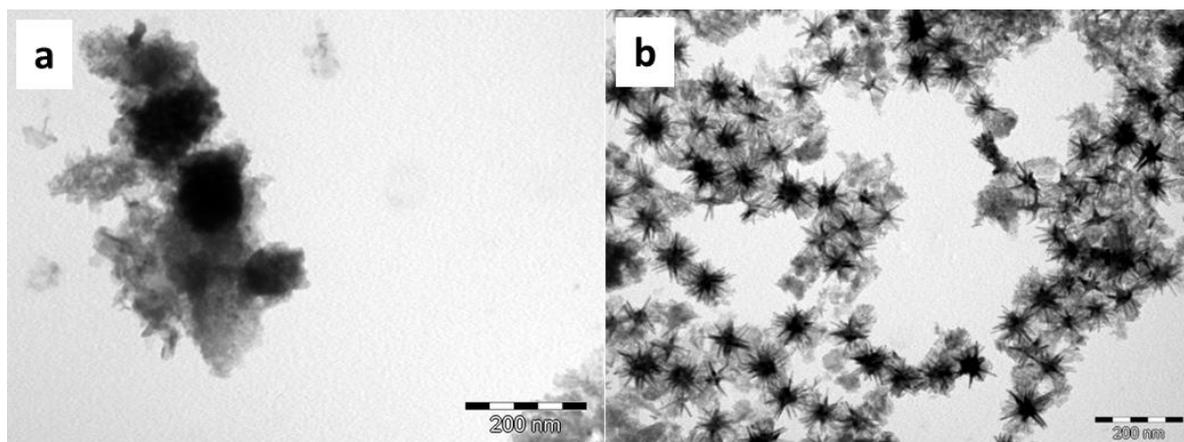


Figure SI-4. TEM of catalysts obtained by decomposition of [Co{N(SiMe₃)₂}₂(thf)] on: a) 15% Co₃O₄/Al₂O₃-SiO₂; and b) 15% CoO/Al₂O₃-SiO₂. (scale bars 200 nm).

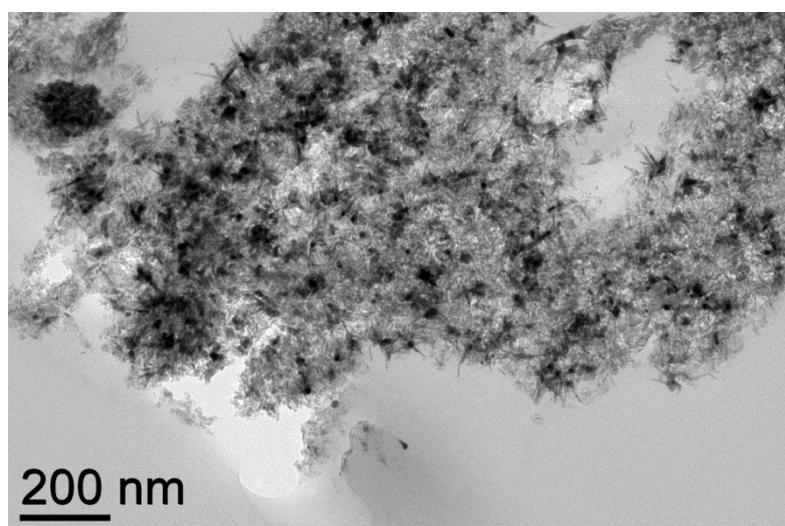
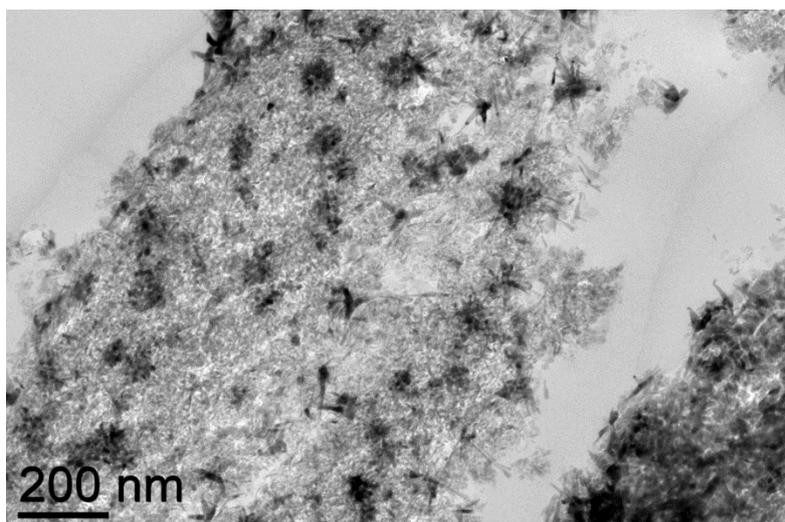


Figure SI-5. Co nano-objects obtained by decomposition of $[\text{Co}\{\text{N}(\text{SiMe}_3)_2\}_2(\text{thf})]$ on a 8% $\text{Co}/\text{Al}_2\text{O}_3\text{-SiO}_2$ catalyst: TEM micrographs of samples obtained after ultra-microtomy.

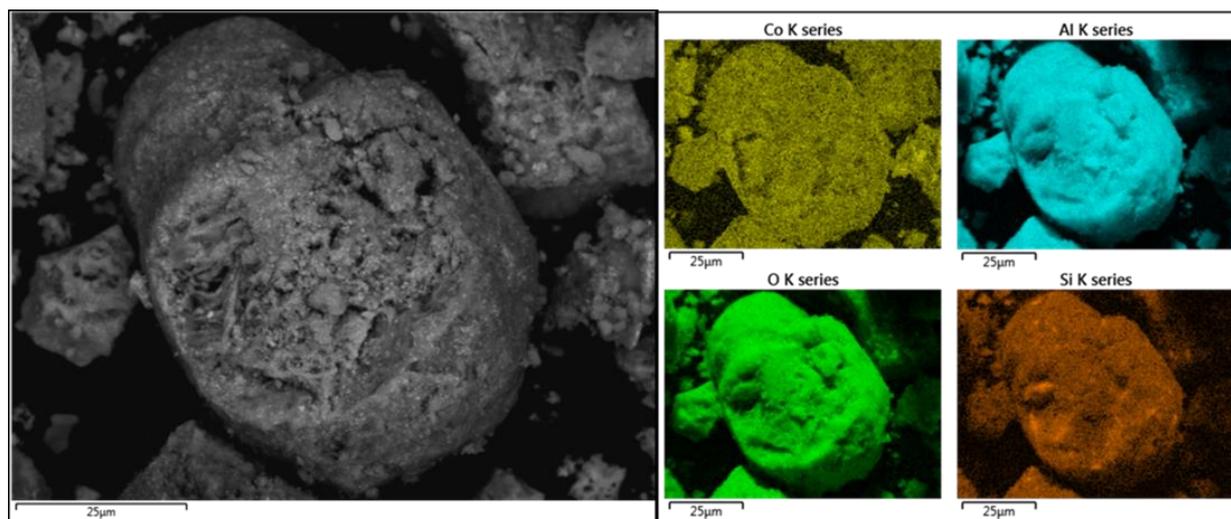


Figure SI-6. SEM-EDX of a 7%Co/8%Co/SiO₂-Al₂O₃ modified catalyst. The Co (yellow) is homogeneously distributed on the catalyst grain (scale bars 25 μm).

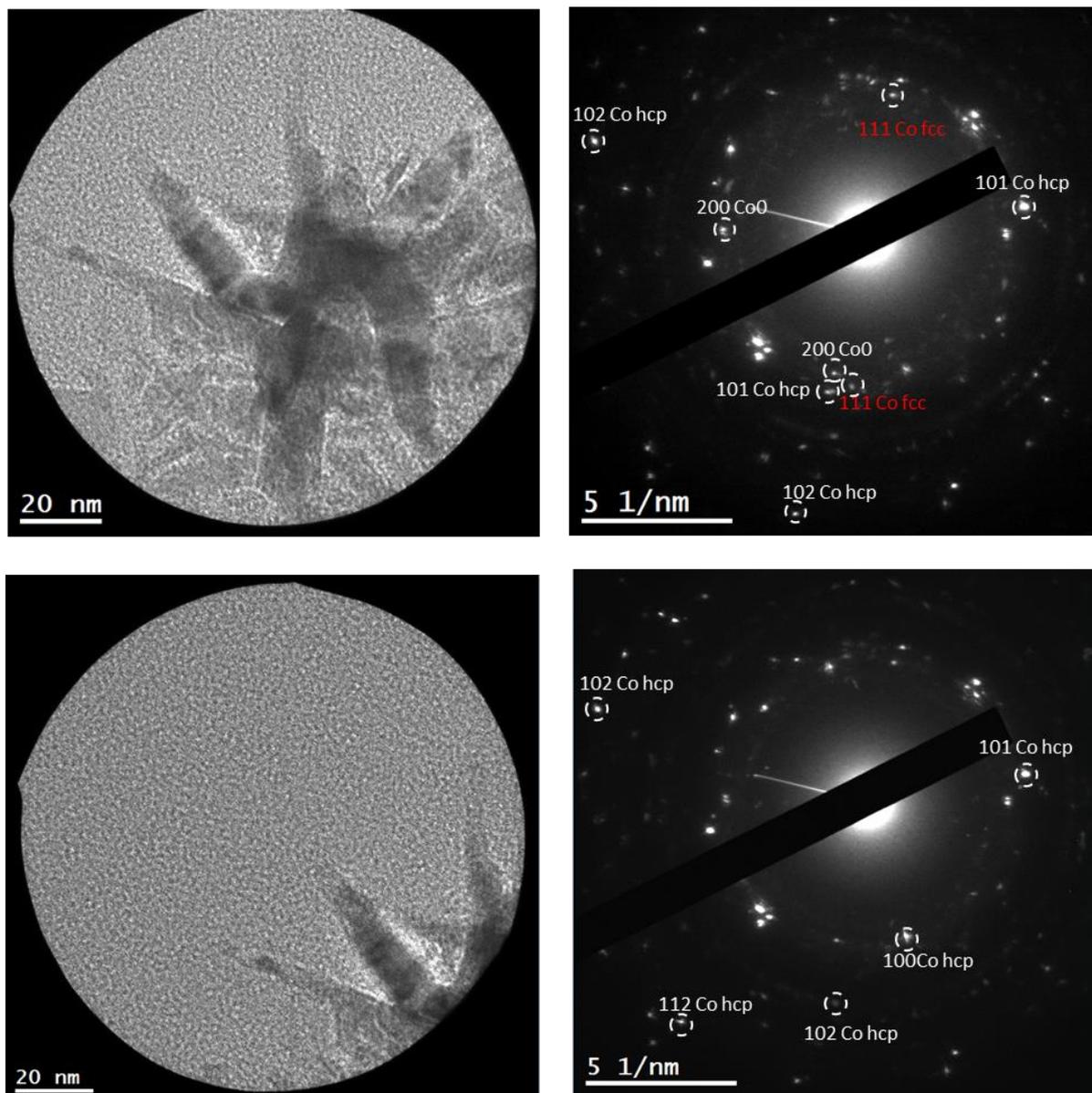


Figure SI-7. TEM of the 7%Co/8%Co/SiO₂-Al₂O₃.

Structural analysis of the Co nano-objects by selected area electron diffraction (SAED). Top: TEM image and corresponding diffraction pattern acquired on the whole individual nano-object (core and branches) showing the contribution of both hcp and fcc structures. Bottom: TEM image and corresponding diffraction pattern taken only on some branches of the same nano-object, illustrating in this case the predominant contribution of the hcp structure.

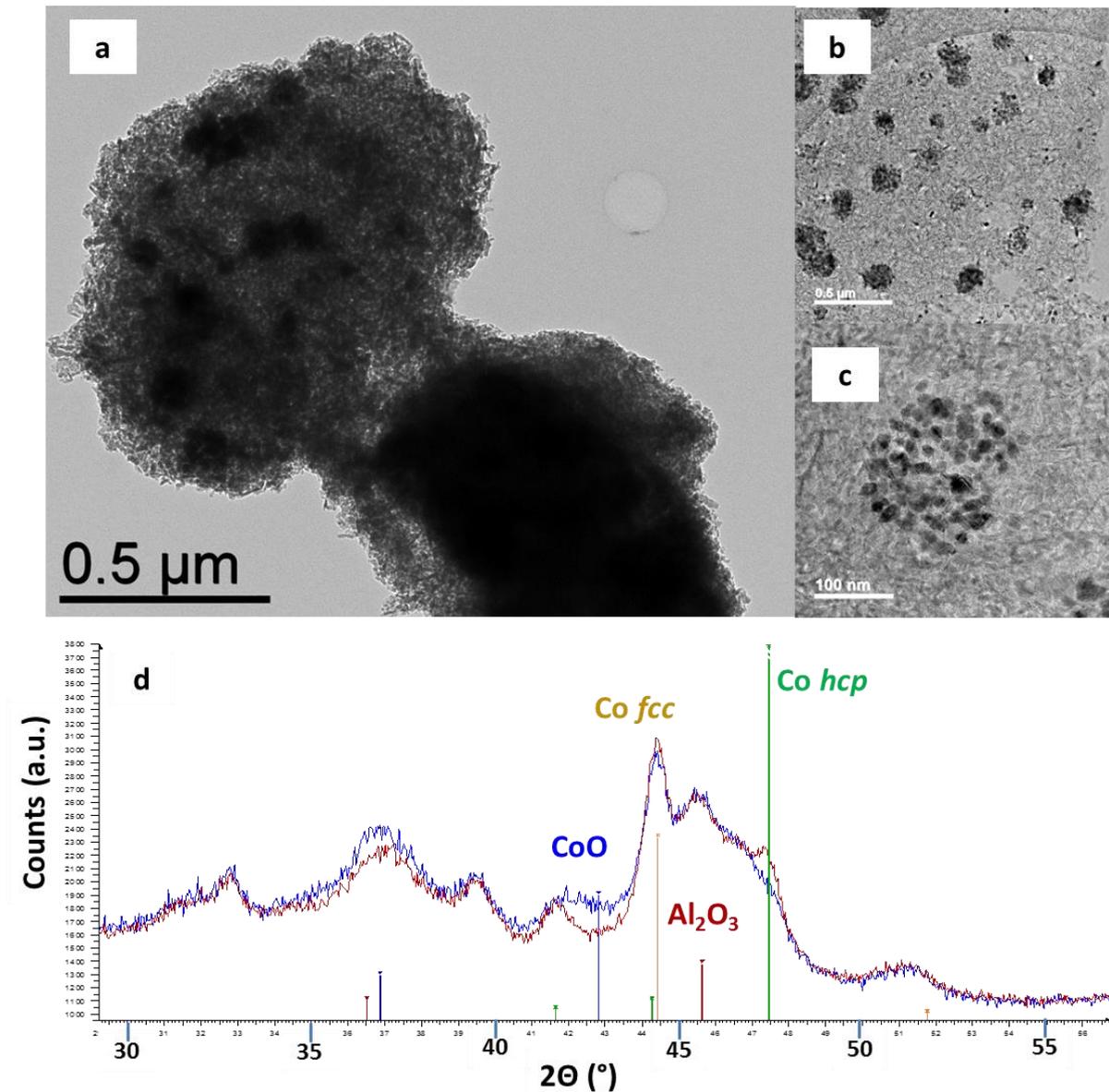


Figure SI-8. a) TEM of the 7%Co/8%Co/SiO₂-Al₂O₃ modified catalyst after 475 hours catalytic run, b-c) TEM of a sample obtained by ultramicrotomy in two magnifications (scale bars b: 500 nm, b: 100 nm). d) XRD: The blue diffractogram corresponds to the catalyst before use, the red to the used catalyst. The green lines correspond to the Co hcp, the yellow to the Co fcc the blue to CoO and the red to Al₂O₃.

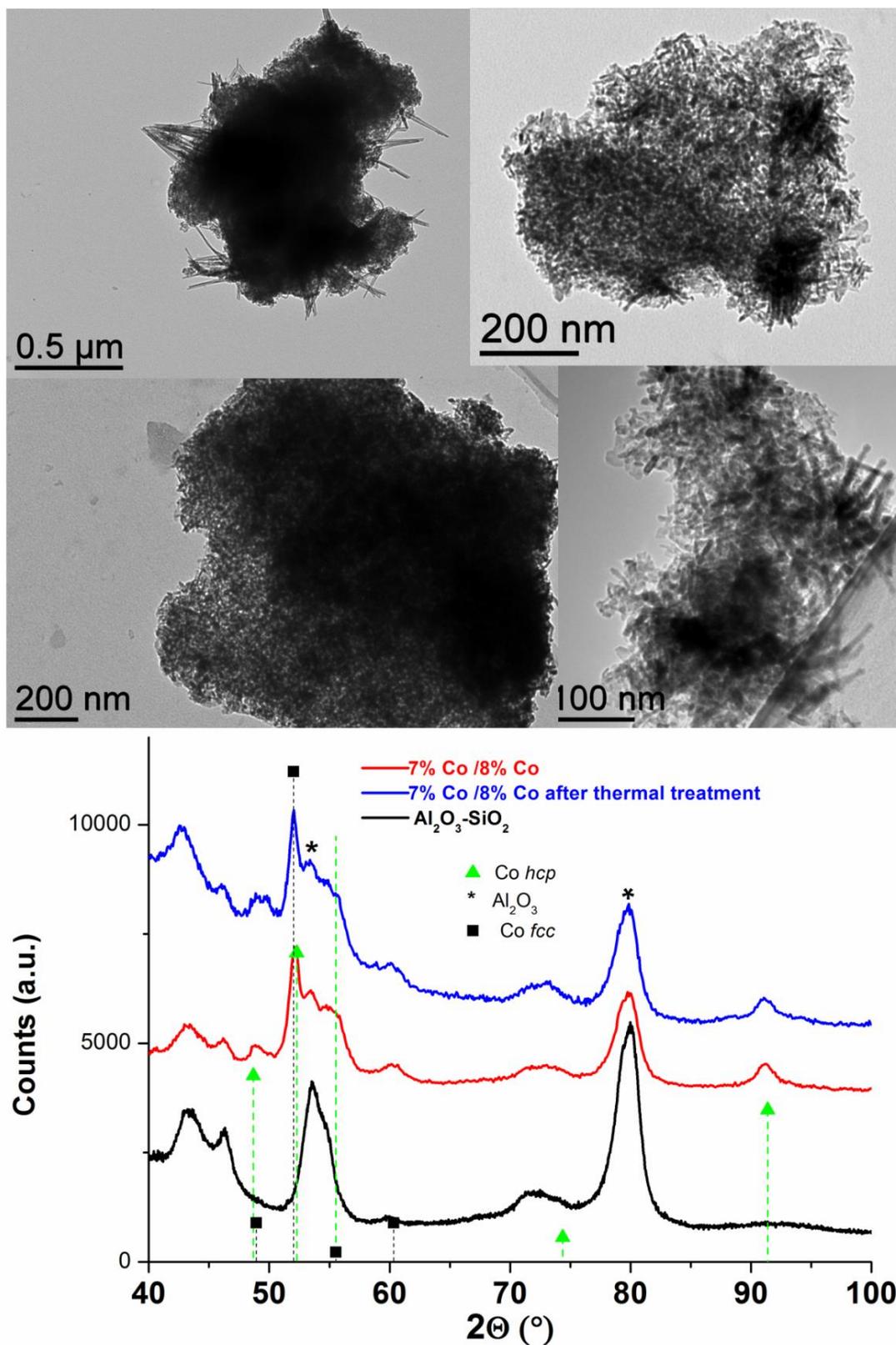


Figure SI-9. TEM micrographs after heat treatment of the 7%Co/8%Co/ $\text{SiO}_2\text{-Al}_2\text{O}_3$ modified catalyst and XRD diffractograms of the $\text{SiO}_2\text{-Al}_2\text{O}_3$ support (black), and the 7%Co/8%Co/ $\text{SiO}_2\text{-Al}_2\text{O}_3$ modified catalyst before (red) and after (blue) heat treatment.

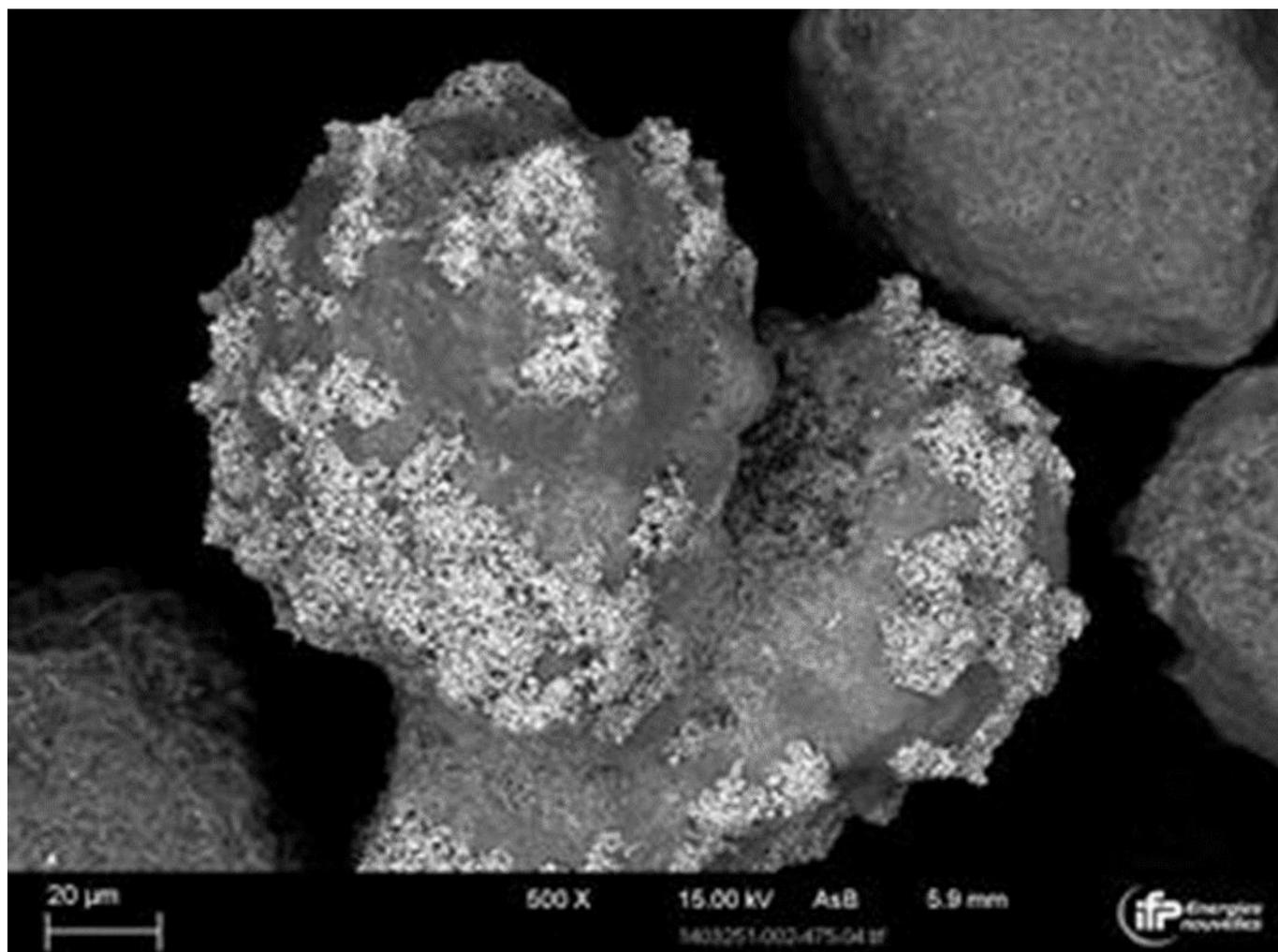


Figure SI-10. SEM micrograph of the used 15%Co- SiO₂-Al₂O₃ reference catalyst after 300 h TOS, where Co is visibly extracted and sintered on the support grains.