Supplementary Information for

Carbon-supported Ni nanoparticles in CO_2 methanation: role of a superficial NiO shell observed by *in situ* TEM

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METHODS

To obtain an oxygen-free surface with Lewis base sites, 3 g of NORIT GAC 1240 PLUS activated carbon (CABOT) was placed in a quartz tube reactor and heated to 900 °C at 10 °C/min under a N_2 flow rate of 100 cm^3/min. When 900 °C was reached, the flow rate was changed to 50 cm^3/min of H_2 and the system was maintained at 900 °C for 1 h. Ni-containing methanation catalyst was prepared by incipient wetness impregnation (IWI) method. 0.5 g of the as-synthesized reduced activated carbon (ACR) supporting material was placed under ultrasonic vibration and an aqueous solution of $Ni(NO_3)_2 \cdot 6H_2O$ was added to obtain a Ni^0 loading of 15%. The sample was left under ultrasonic vibration for other 90 min, and after that was dried at 120 °C overnight. Finally, the sample was annealed under N_2 (100 cm^3/min) for 1 h at 400 °C and reduced under H_2 (50 cm^3/min) for 3 h at 400 °C, with a heating rate of 10 °C/min, thus affording active and selective Ni/ACR methanation catalyst.[3]

The as-synthesized Ni/ACR catalyst powder was drop cast directly on the bottom MEMS chip into the center of the heating spiral for a DENSsolutions Climate gas and heating holder. The holder was then assembled in air and leak tested before loading into an image-corrected Titan-300 electron microscope (FEI), operating at 300 kV. Once inside the column, Ar gas was used to purge the system of any air. Three separated *in situ* experiments were performed: (*i*) a replication of external conditions with a pre-treatment under H_2 in Ar ratio 4:96 before observing the particles while mimicking CO_2 methanation conditions, (*ii*) we examined the particle behavior with the reduction treatment beforehand, and (*iii*) we examined the particle behavior in CO_2 alone. Heating was carried out at 400, 450 and 500 °C.

FIGURES

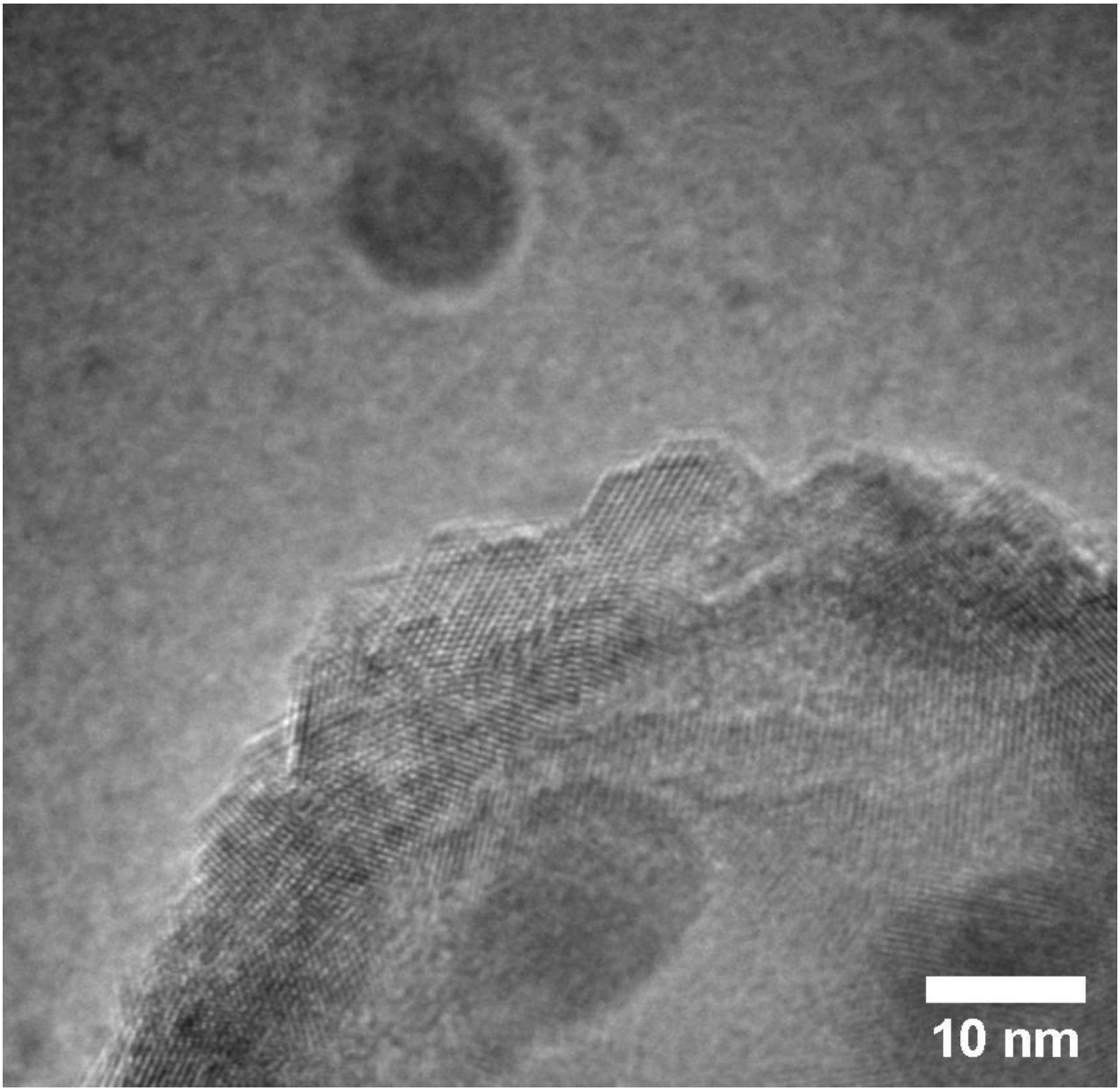

Figure S1. High resolution *in situ* TEM image evidencing the polycrystalline NiO shell formation around Ni nanoparticle catalyst during CO_2 methanation.

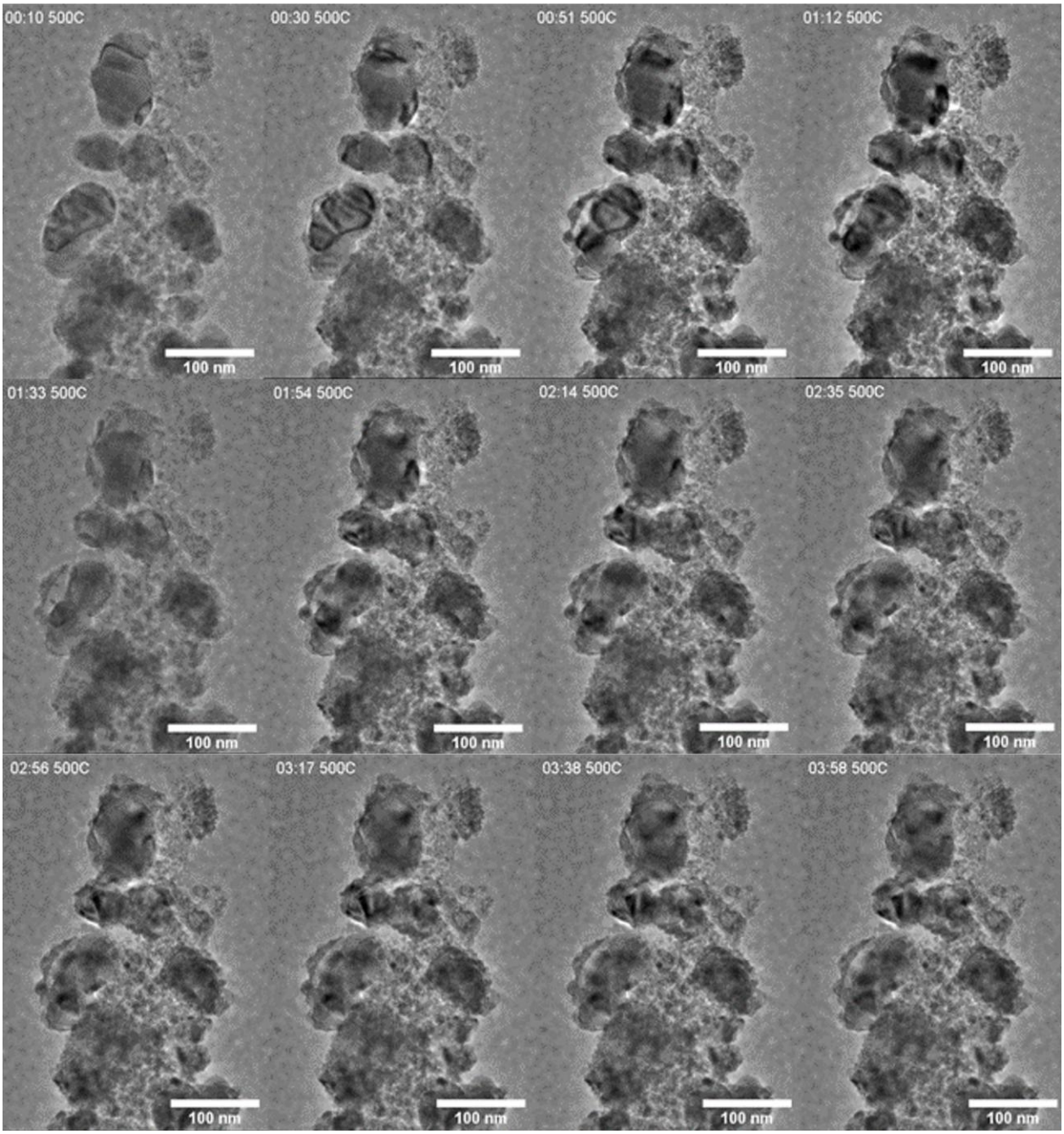

Figure S2. Sequence of *in situ* TEM images of Ni nanoparticles oxidising under a CO_2 environment at 500 °C – the images depict the transformations at 500 °C instead of 450 °C, since the modifications were more apparent at this temperature. In sharp contrast to the formation of Ni@NiO core@shell catalyst nanoparticles under methanation reaction conditions (*i.e.*, $CO_2 + H_2$), the entire oxidation of Ni catalyst nanoparticle into NiO is evidenced in the presence of CO_2 alone, *i.e.*, without H_2.

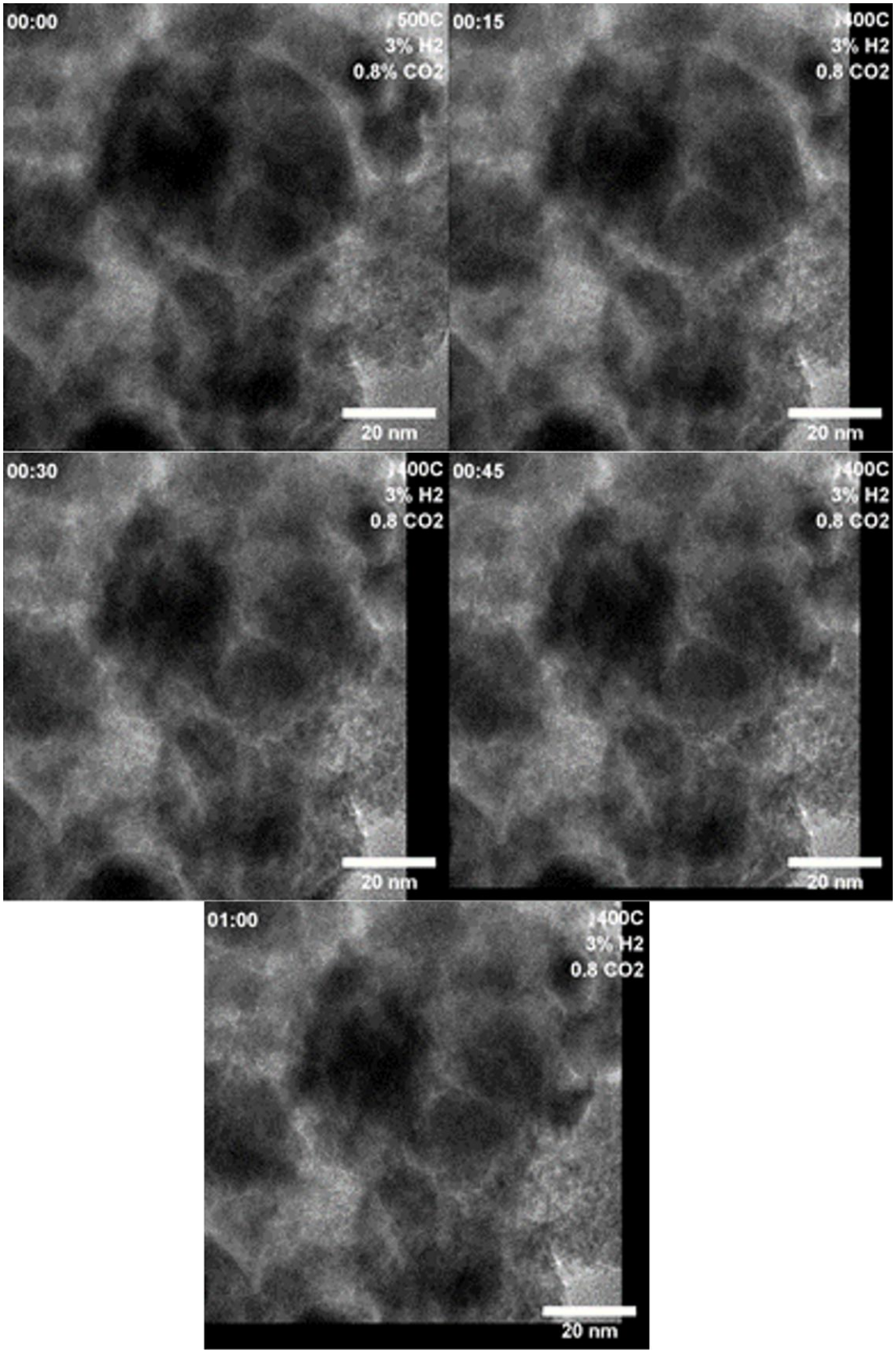

Figure S3. Sequence of *in situ* TEM images of the catalyst during the temperature decrease.

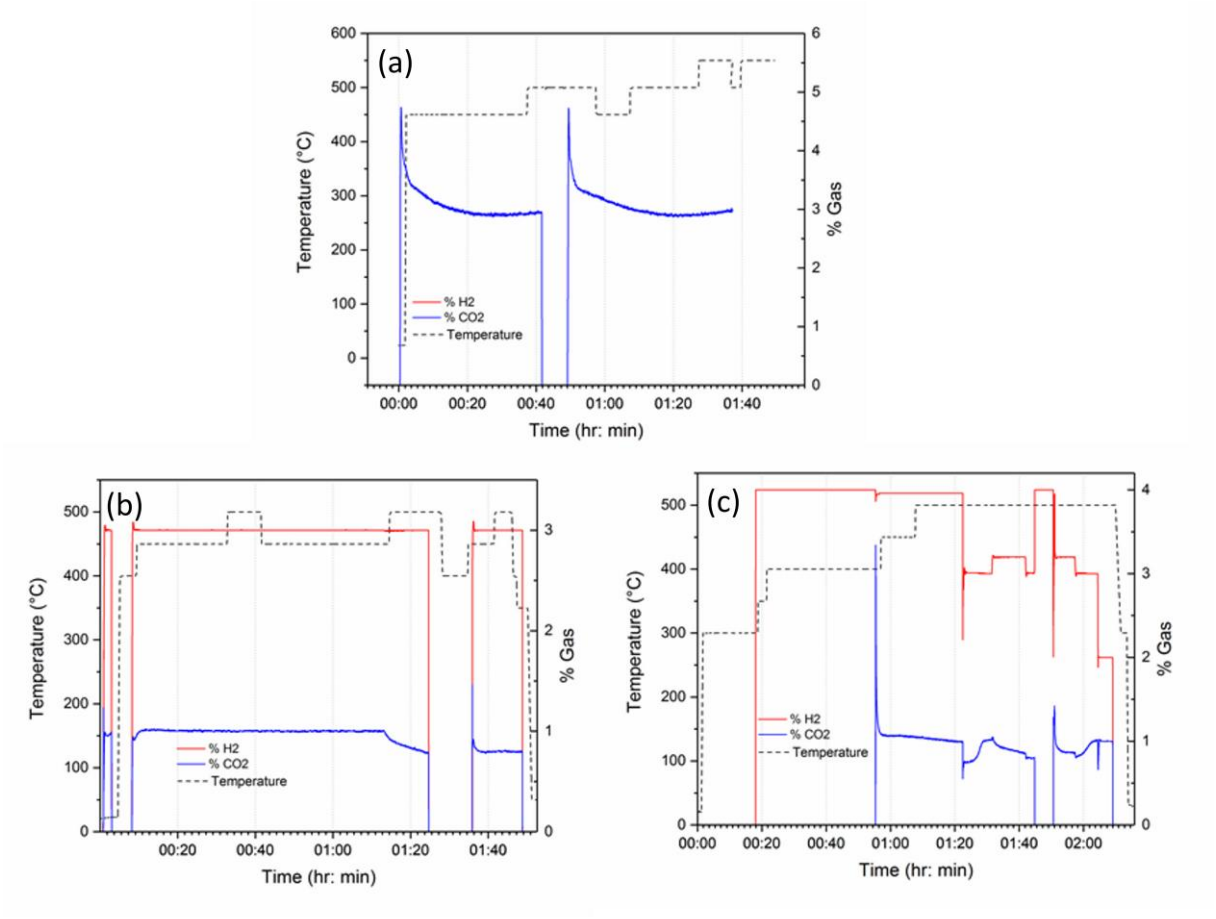

Figure S4. Experimental conditions (temperature, CO_2 and CH_4 concentration) in the different experiments: (a) in the experiment with a flow of only CO_2; (b) in the experiment under reaction conditions without H_2 pre-treatment; and (c) in the experiment under reaction conditions with H_2 pre-treatment.