Insights on a methanation catalyst aging process: Aging characterization and kinetic study

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Supporting information

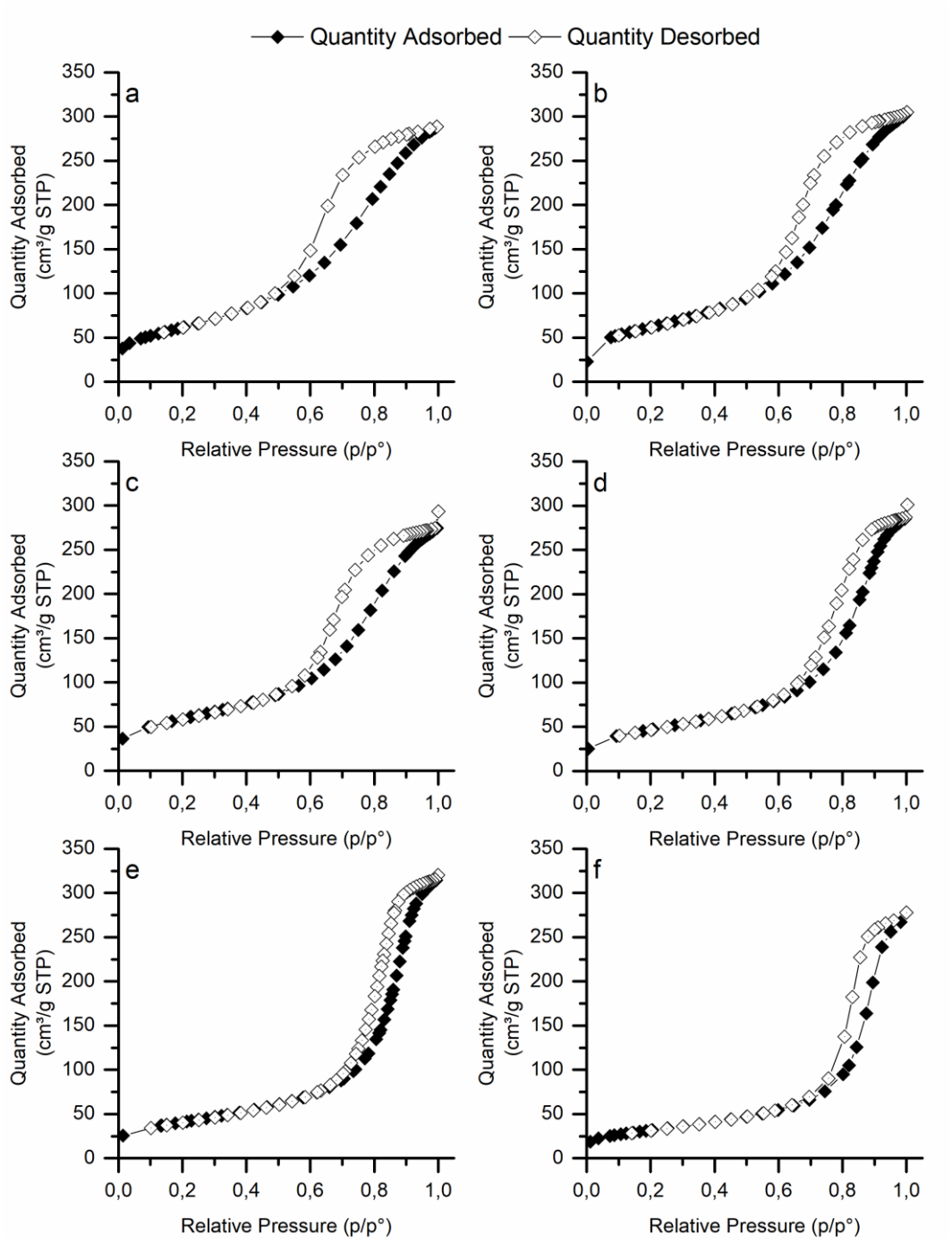

Figure S-1: Nitrogen adsorption isotherms for the a) fresh sample, b) fresh reduced, c) aged @270°C, d) aged @ 380°C, e) aged @ 425°C and f) aged @ 500°C

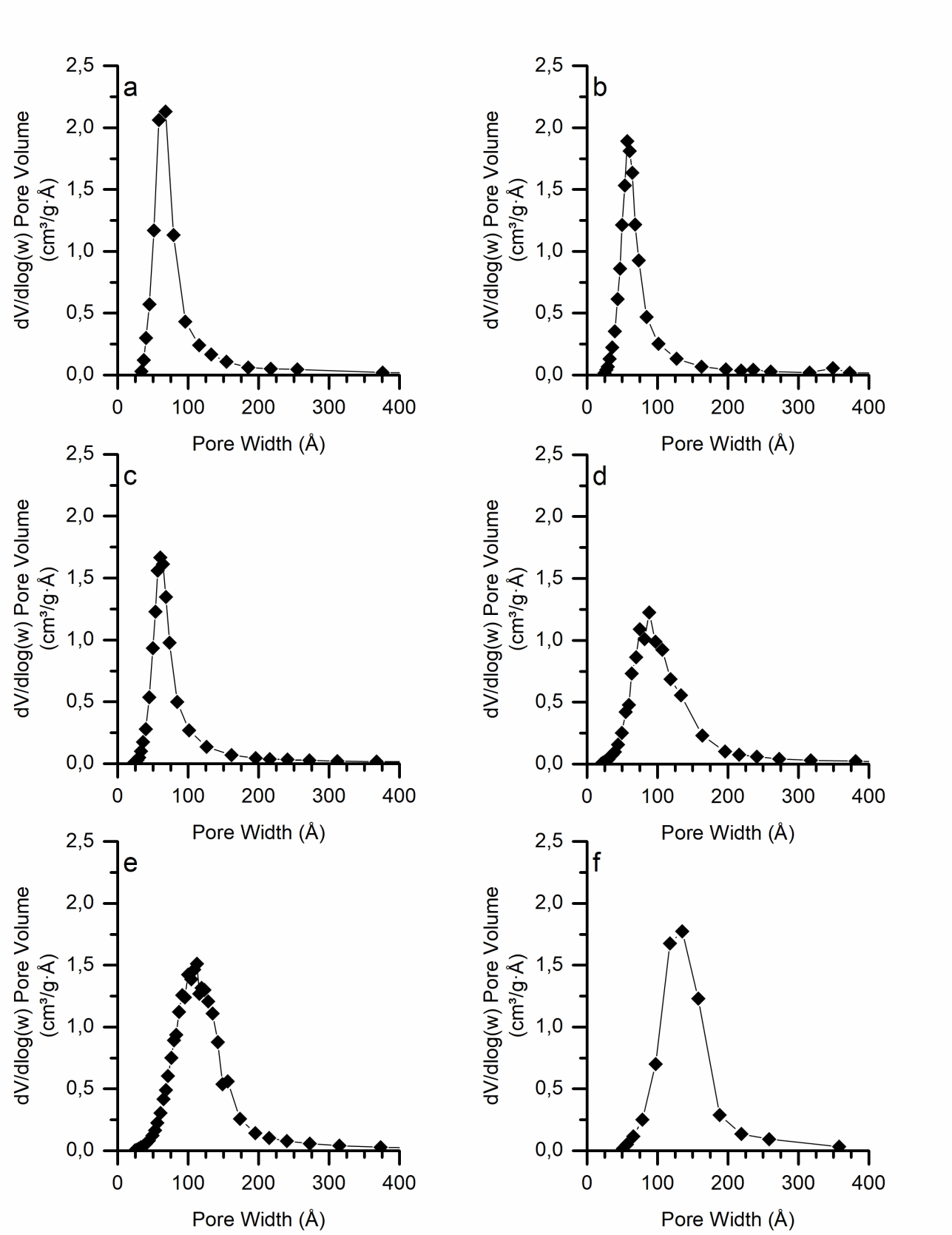

Figure S-2: BJH desorption pore-size distribution curves for the a) fresh sample, b) fresh reduced, c) aged @ 270°C, d) aged @ 380°C, e) aged @ 425°C and f) aged @ 500°C

The reducibility of the catalyst was investigated using a hydrogen temperature programmed reduction technique (H_2-TPR). The tests were performed in a homemade setup. A 200 mg fresh catalyst sample was loaded into a U-shaped quartz tube reactor with an internal diameter of 4 mm. The reactor was then placed into temperature-controlled oven. The H_2-TPR was performed with a 200 ml/min gas mixture containing 5% of H_2 in N_2 and with a heating rate of 5°C/min up to 800°C. Hydrogen consumption was monitored using a multi-channel Emerson X-Stream gas analyser equipped with non-dispersive infrared (NDIR) sensors for CO, CO_2 and CH_4, a thermal conductivity (TCD) detector for H_2 and a paramagnetic sensor for O_2 measurement. The temperature was recorded using a thermocouple placed within the catalyst bed.

In Figure S-3 the hydrogen concentration variation is reported. The reduction peaks characterize the metal-support interaction[27,28]. The deconvolution of the TPR profile has allowed to identify the presence of three reduction peaks ($R^2 \geq 0.99$). A big reduction peak was observed at around 290°C. This peak can be assigned to the reduction of surface amorphous NiO and bulk NiO. Two more peaks were identified at 445 °C and 492 °C that can be assigned to NiO weakly and strongly interacting with the Al_2O_3 support. The activation temperature of 260°C that is used in the real plant will only reduce part of the NiO. About 22% of the total hydrogen uptake takes place during the activation procedure. This corresponds to the same fraction of reduced nickel.

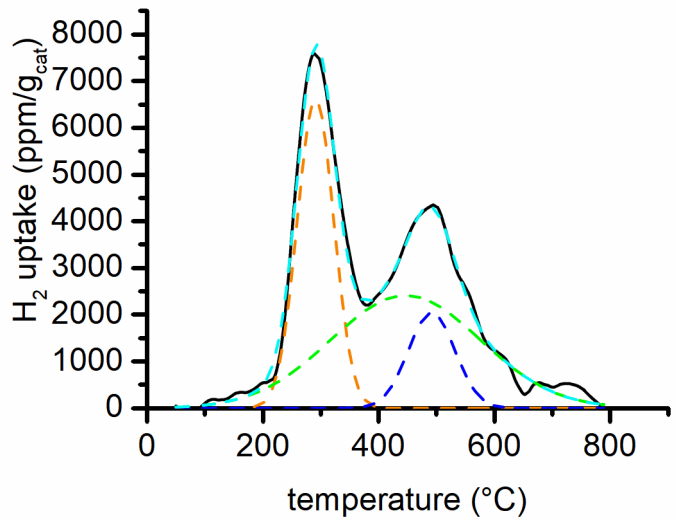

Figure S-3: H_2-TPR with peak deconvolution

The CO_2 adsorption capacity of the catalyst was investigated by performing a CO_2-TPD. The same apparatus used for the TPR analysis was employed also for the TPD. A 200 mg sample of catalyst was reduced in situ at 400°C prior to the analysis. The sample was then saturated with carbon dioxide at room temperature under continuous flow (100 ml/min, 10% CO_2 in nitrogen) for one hour. After cleaning the sample for 30 minutes under nitrogen flow the desorption was started. A heating rate of 10°C/min and a 200 ml/min of N_2 were used during the desorption.

In Figure S-4 the CO_2 concentration evolution is reported. Most of the adsorbed CO_2 is released at temperature below 350°C. This result was useful for the identification of the catalyst samples pre-treatment procedure before the TPO analysis. The TPO procedure is illustrated in Figure S-5.

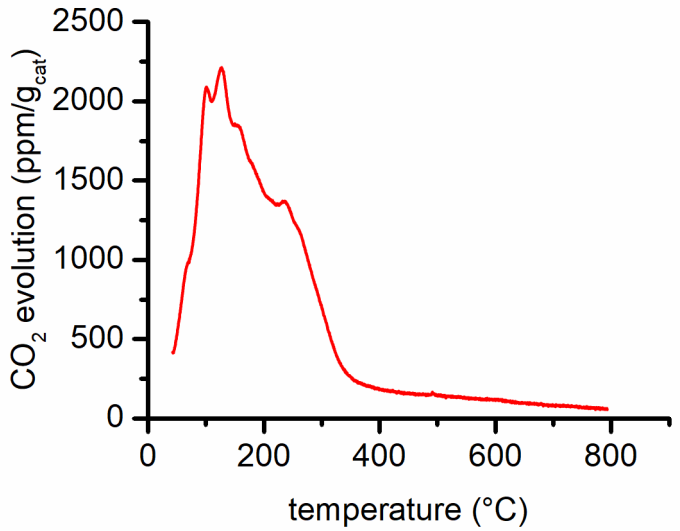

Figure S-4: CO_2 evolution during TPD analysis

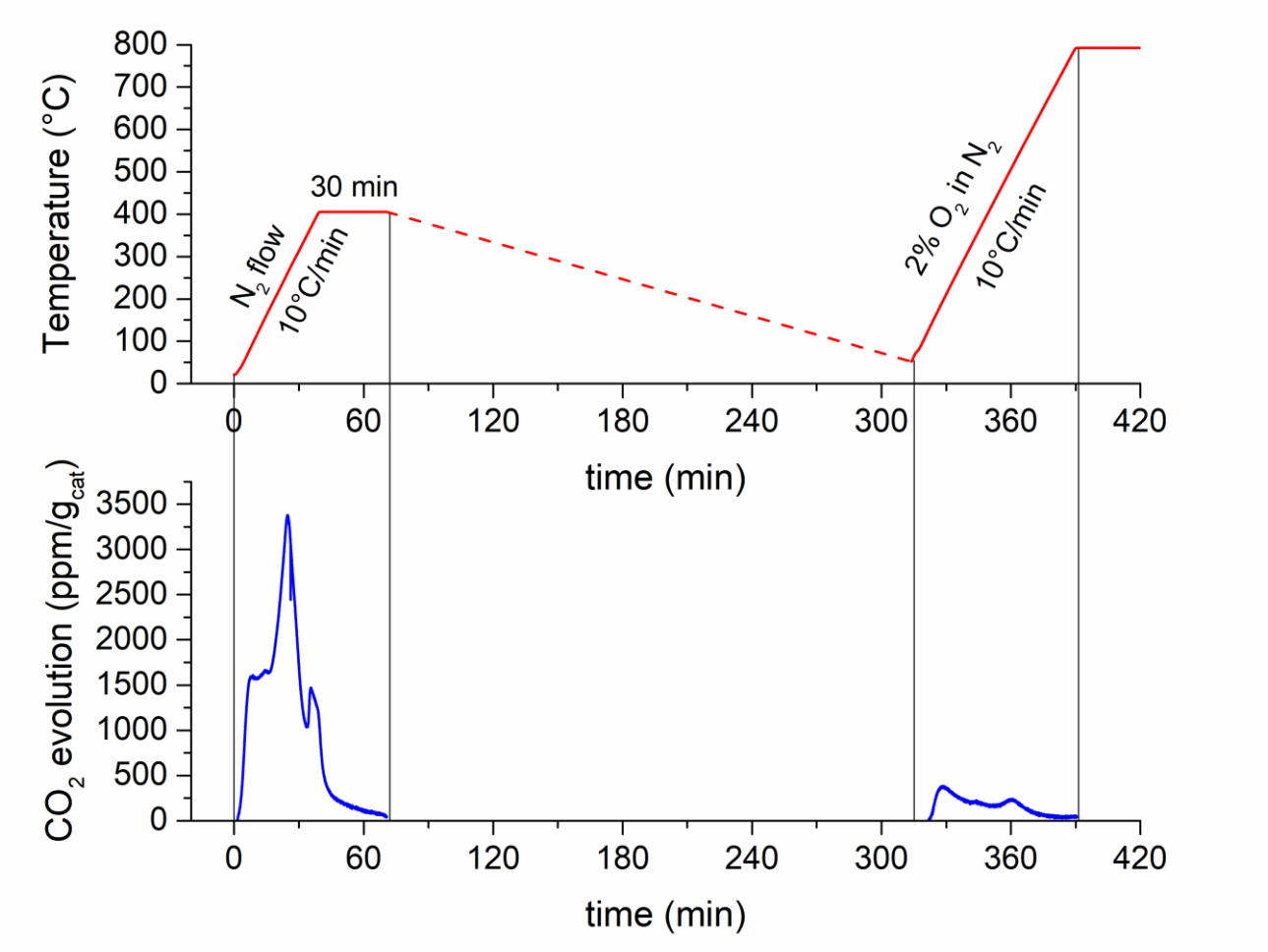

Figure S-5: CO_2 evolution during TPD analysis