

Supplementary information - Impact of small promoter amounts on coke structure in dry reforming over Ni/ ZrO₂

Robert Franz^{a,b}, Tobias Kühlewind^b, Genrikh Shterk^c, Edy Abou-Hamad^d, Alexander Parastaev^e, Evgeny Uslamin^a, Emiel Hensen^e, Freek Kapteijn^b, Jorge Gascon^c, Evgeny Pidko^{*a}

^a Inorganic Systems Engineering Group, Department of Chemical Engineering, Delft University of Technology, Van der Maasweg 9, 2629 HZ Delft, The Netherlands
Email: e.a.pidko@tudelft.nl

^b Catalysis Engineering, Department of Chemical Engineering, Delft University of Technology, Van der Maasweg 9, 2629 HZ Delft, The Netherlands

^c Advanced Catalytic Materials, KAUST Catalysis Center, King Abdullah University of Science and Technology, Thuwal 23955, Saudi Arabia

^d Core Labs, King Abdullah University of Science and Technology, Thuwal 23955, Saudi Arabia

^e Inorganic Materials & Catalysis group, Eindhoven University of Technology, PO Box 513, 5600 MB Eindhoven, The Netherlands

Content

S1 TPR analysis.....	2
S2 TEM images	3
S3 HRTEM images	5
S4 Catalytic activity	7
S5 TGA-MS results	8
S6 XRD patterns	9

S1 TPR analysis

Table S1: Reduction peaks observed during TPR profile deconvolution.

Sample	Peak 1 [°C]	Peak 2 [°C]	Peak 3 [°C]
REF	350 °C	460 °C	510 °C
1K	350 °C	420 °C	520 °C
2K	340 °C	400 °C	490 °C
1Na	320 °C	390 °C	490 °C
1Cs	340 °C	410 °C	510 °C
2Cs	370 °C	440 °C	530 °C
1Mn	330 °C	380 °C	470 °C

S2 TEM images

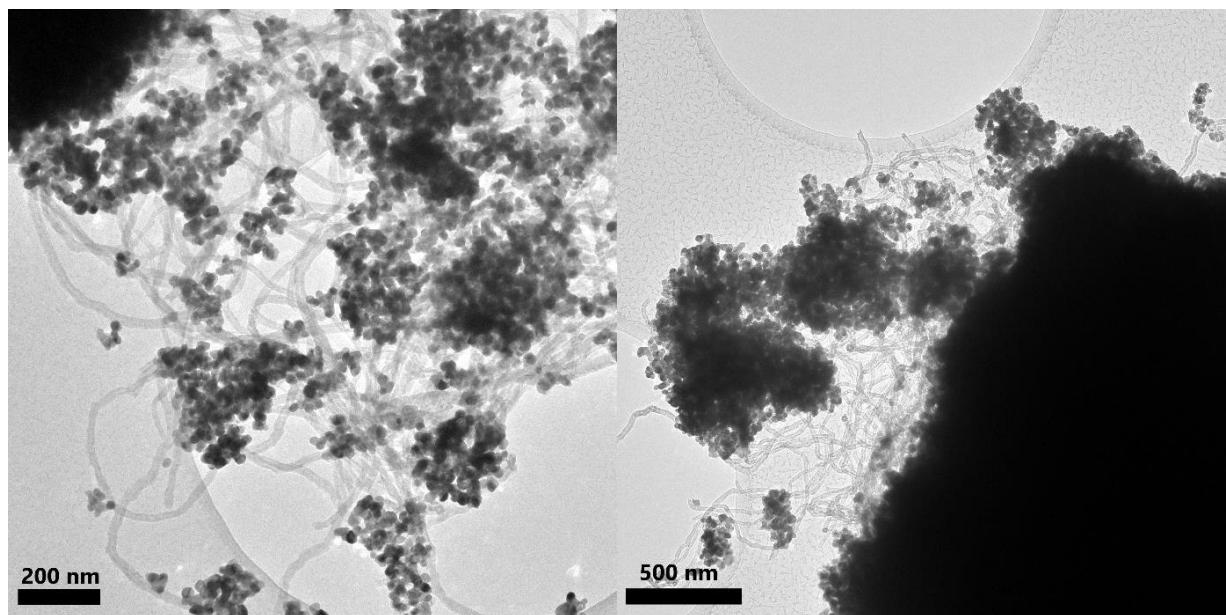


Fig. S1: Carbon fibres visible after 12 h of coking treatment (left - REF, right - 1Mn).

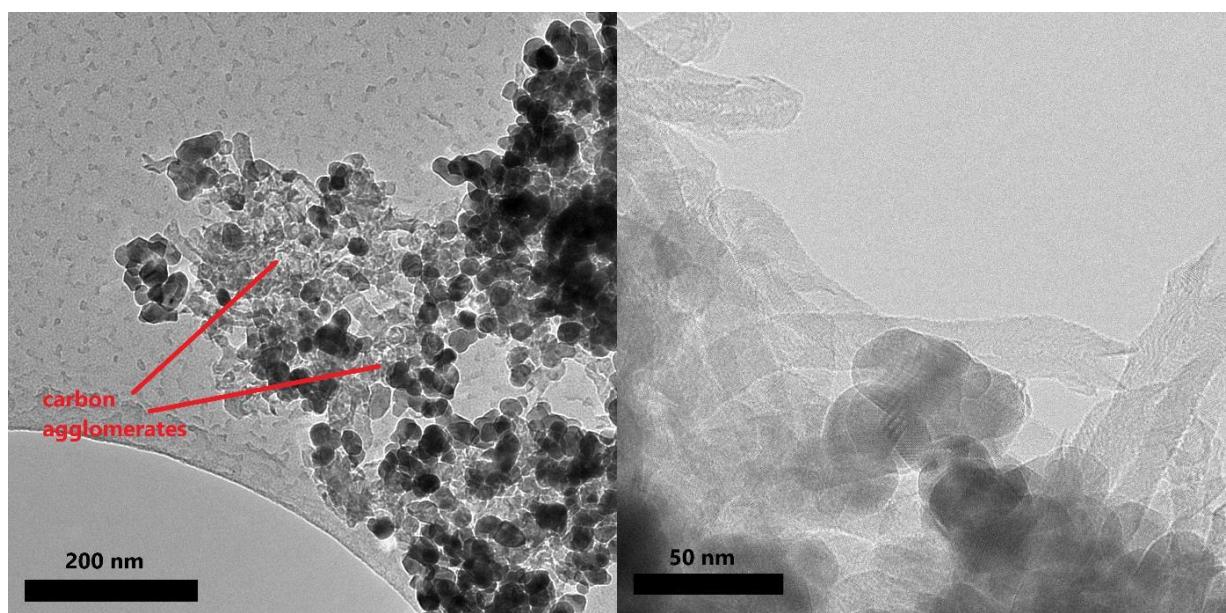


Fig. S2: Carbon clusters or agglomerates on sample REF in TEM (left) and HRTEM (right) after 12 h of coking treatment.

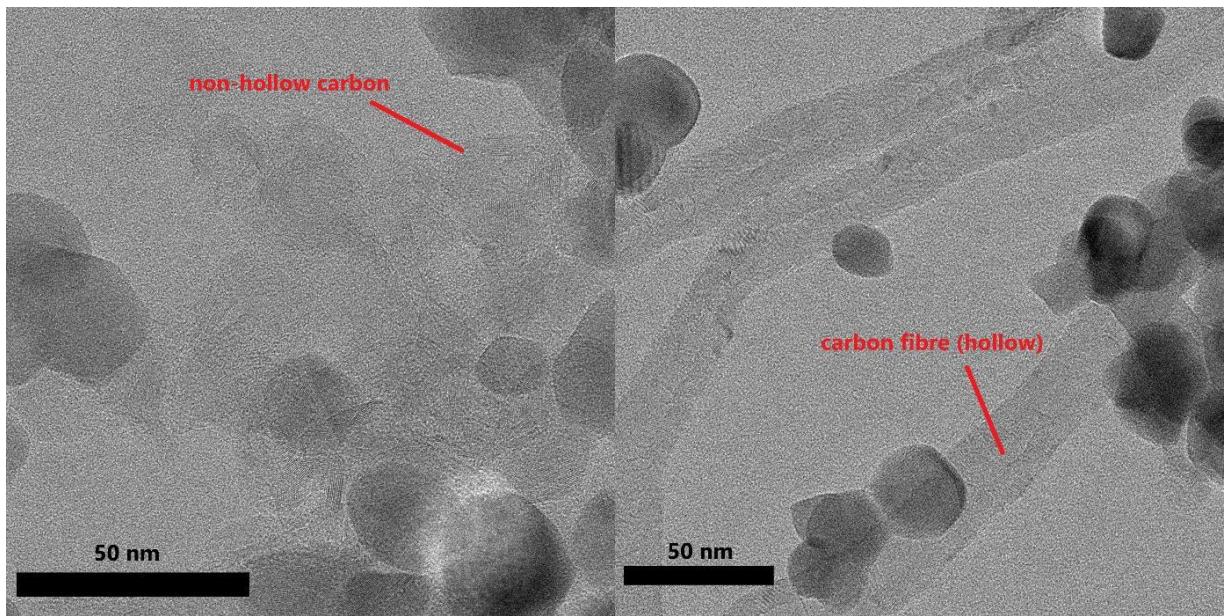


Fig. S3: Coke structure visible on sample 1Mn after 12 h of coking treatment.

S3 HRTEM images

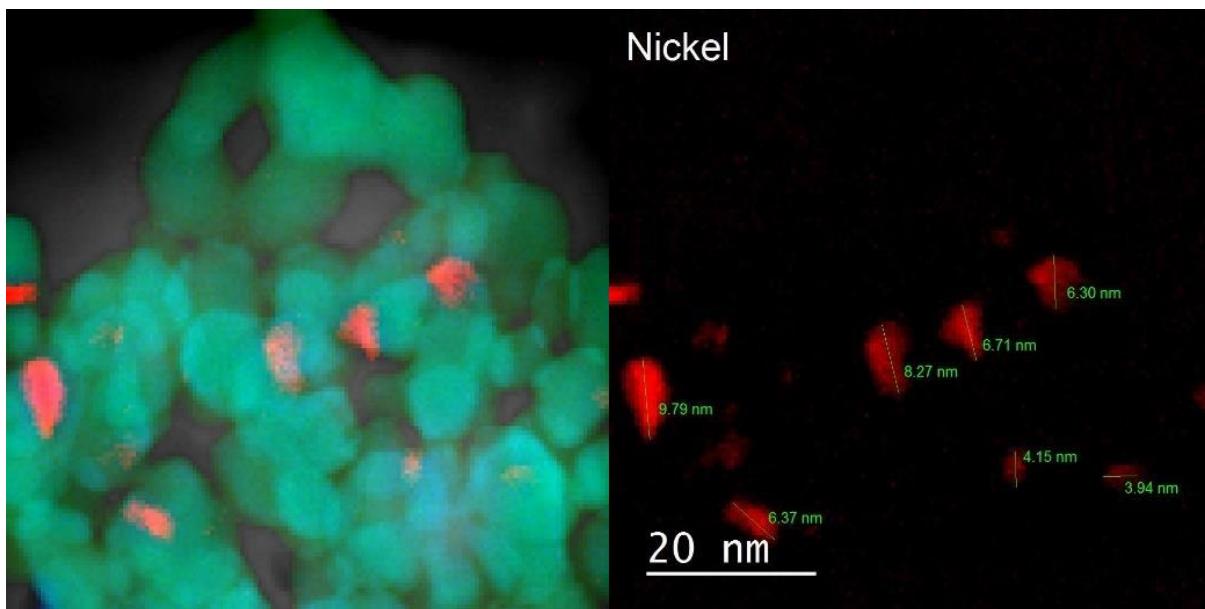


Fig. S4: Example of Ni particles visible on sample 2Cs.

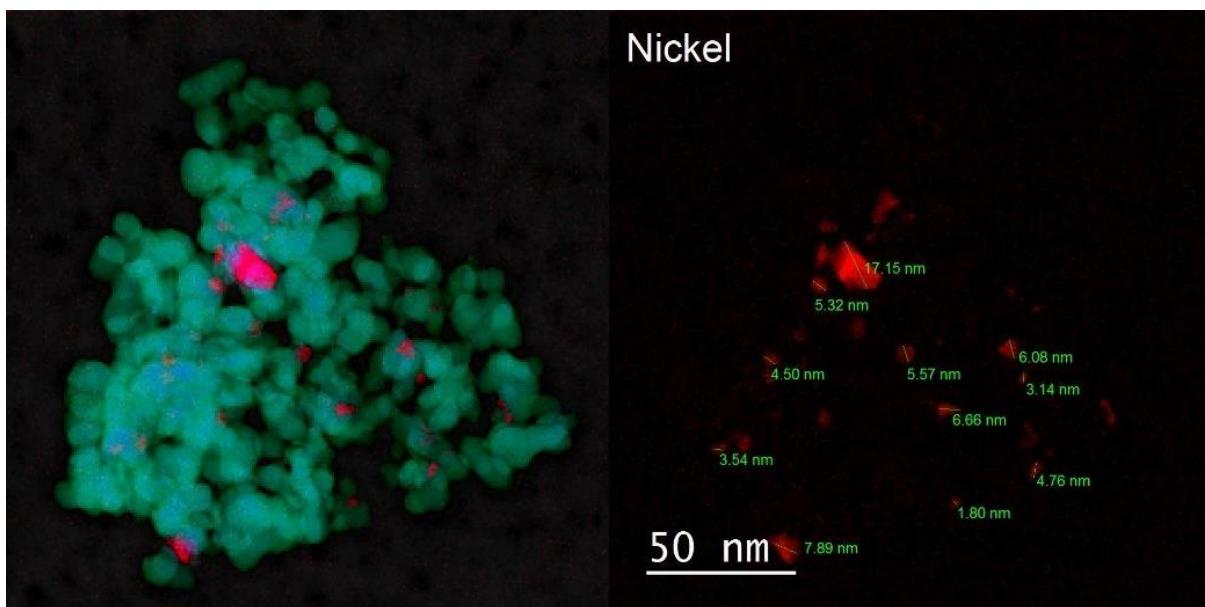


Fig. S5: Example of Ni particles visible on 1K.

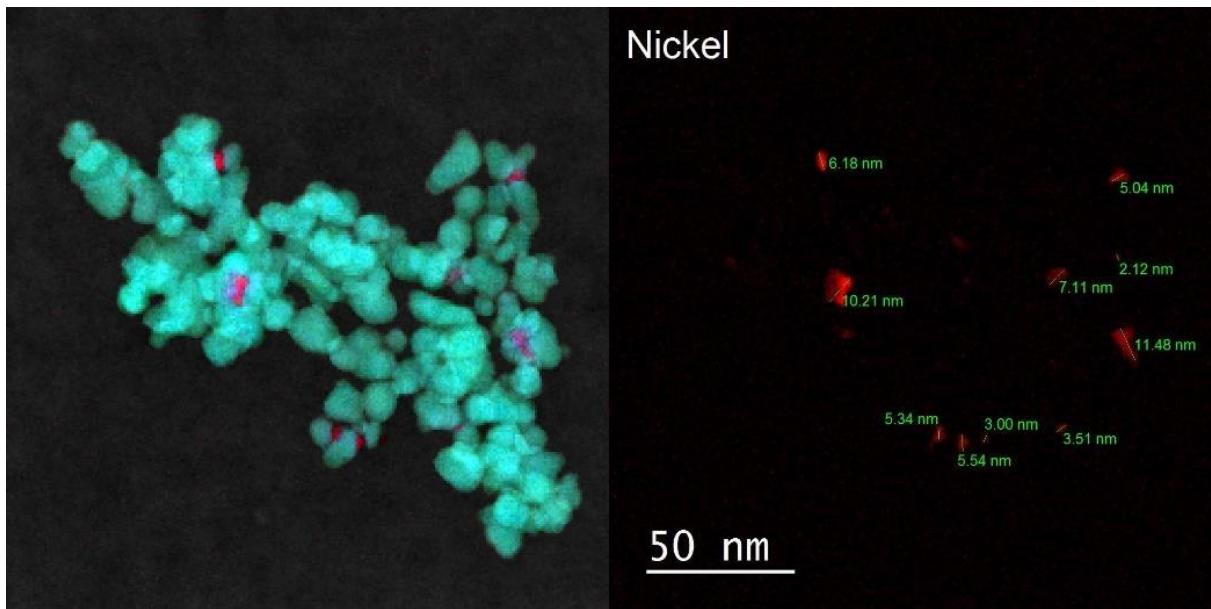


Fig. S6: Example of Ni particles visible on 1Mn.

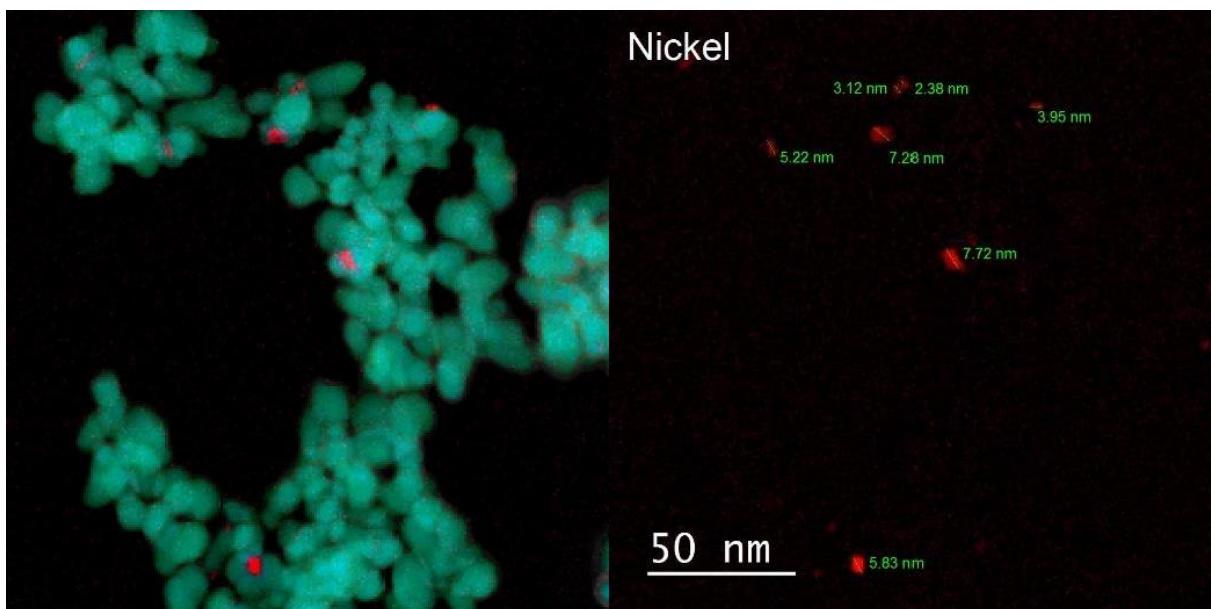


Fig. S7: Example of Ni particles visible on REF.

S4 Catalytic activity

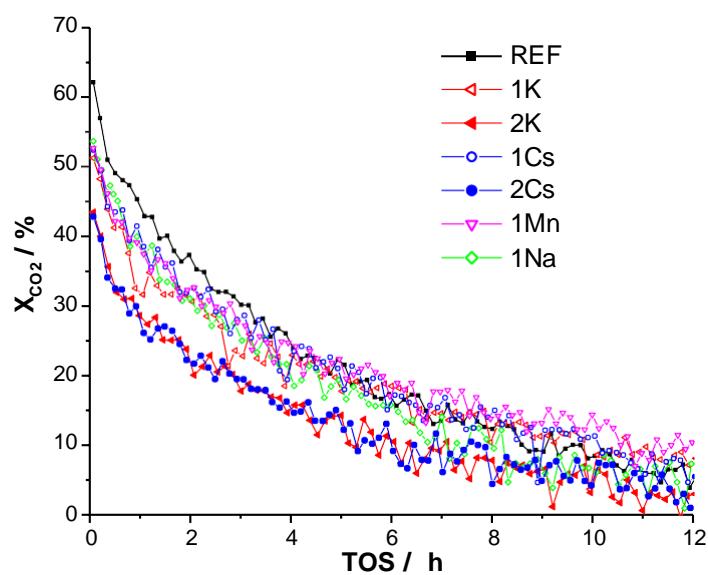


Fig. S8: CO₂ conversion over promoted and non-promoted Ni/ ZrO₂ as a function of time-on-stream; 650 °C, 1 bar, 30 mg catalyst, 80 mL min⁻¹ (20 %CH₄, 20 % CO₂ in N₂).

S5 TGA-MS results

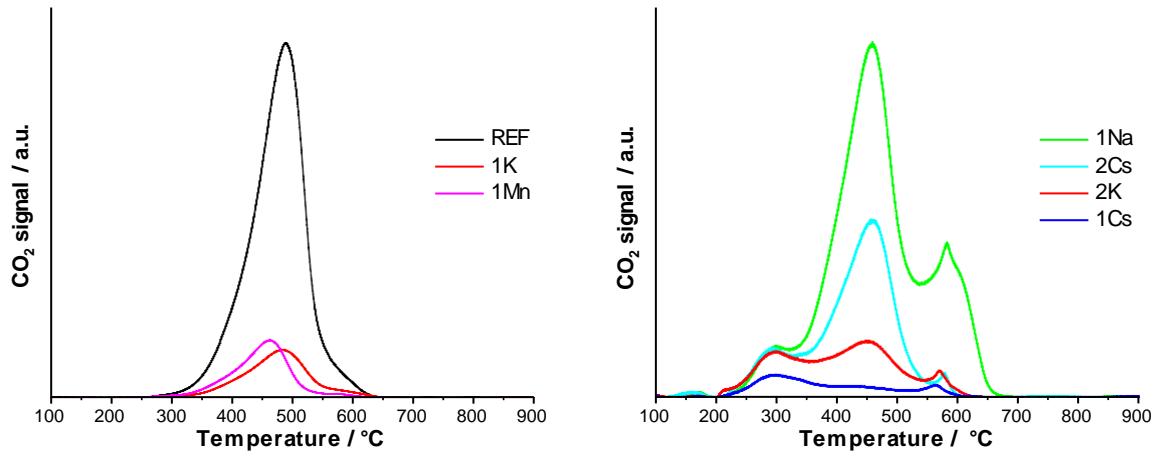


Fig. S9: CO₂ signals measured during the TGA-MS analyses as a function of the sample temperature.

The CO₂ signals obtained during TGA-MS analysis did not allow for further insight into the carbons structure. For samples with more than 5 mg_C g⁻¹_{cat}, the TPO profile is dominated by a peak at 450-500 °C. On the other samples, the development of this peak is already partially observable. We attribute this to the use of undiluted synthetic air during TGA, which prevents sufficient separation of the oxidation temperatures of the different carbon species.

S6 XRD patterns

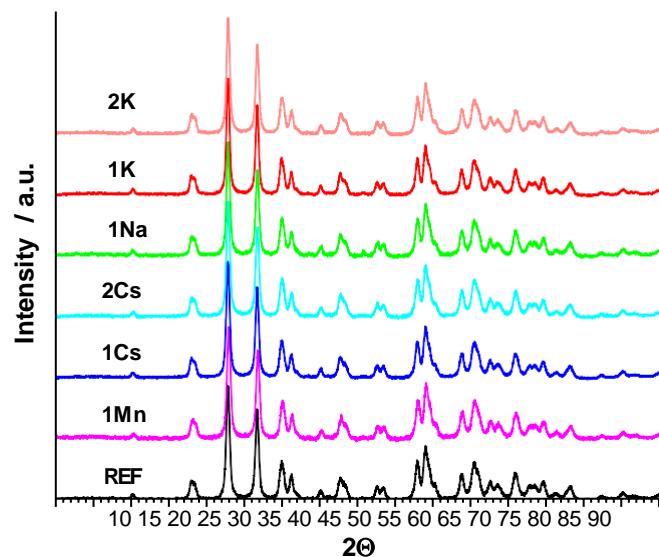


Fig. S10: XRD patterns of the freshly calcined samples.