Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Electronic Supplementary Information for the manuscript entitled

Na-promoted Ni/ZrO_2 dry reforming catalyst with high efficiency: details of Na_2O-ZrO_2-Ni interaction controlling activity and coke formation

by

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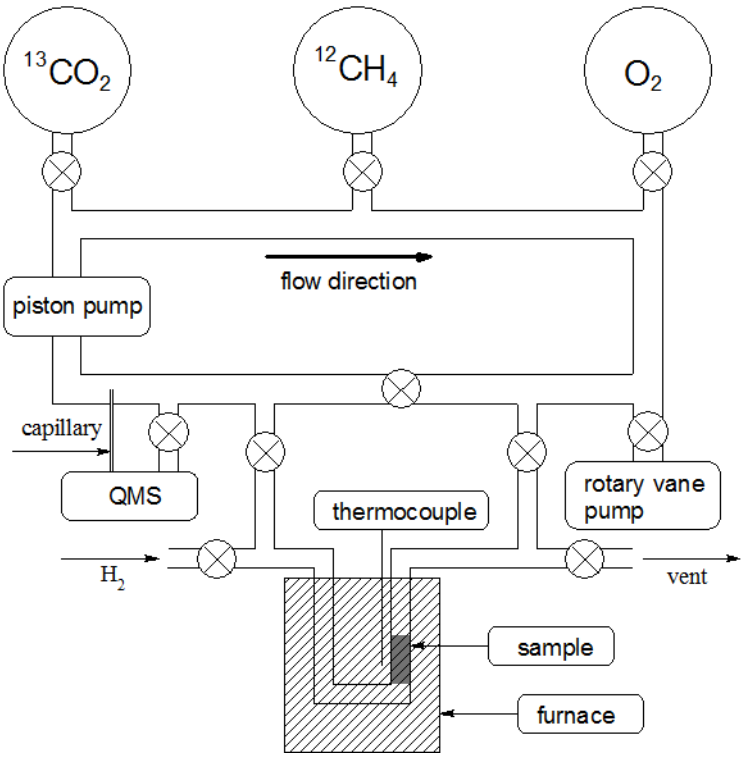


Figure S1 Schematic diagram of the closed loop circulation system used in $^{13}CO_2$-labeled dry reforming experiments at sub-atmospheric pressure

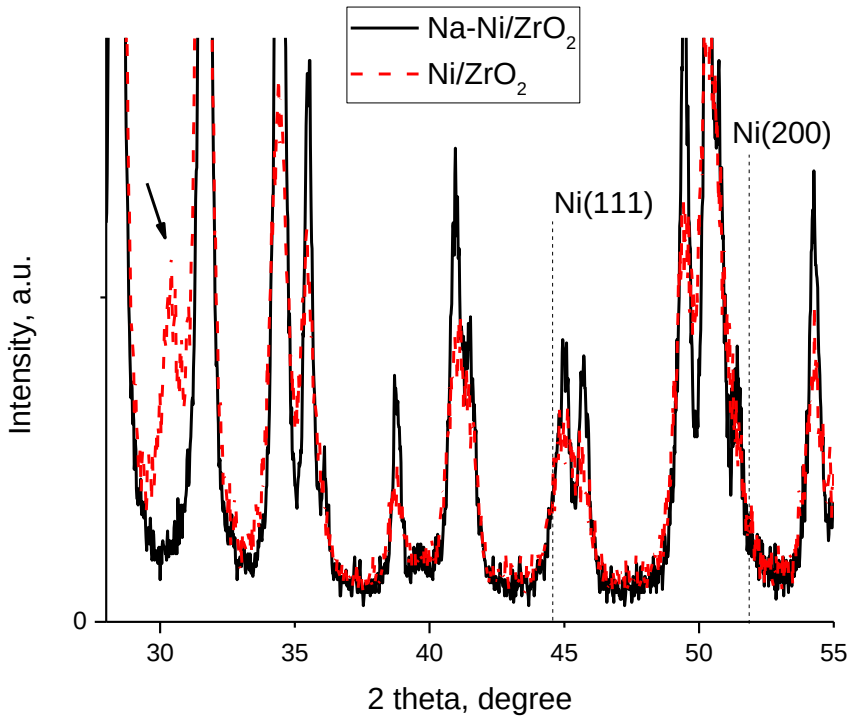
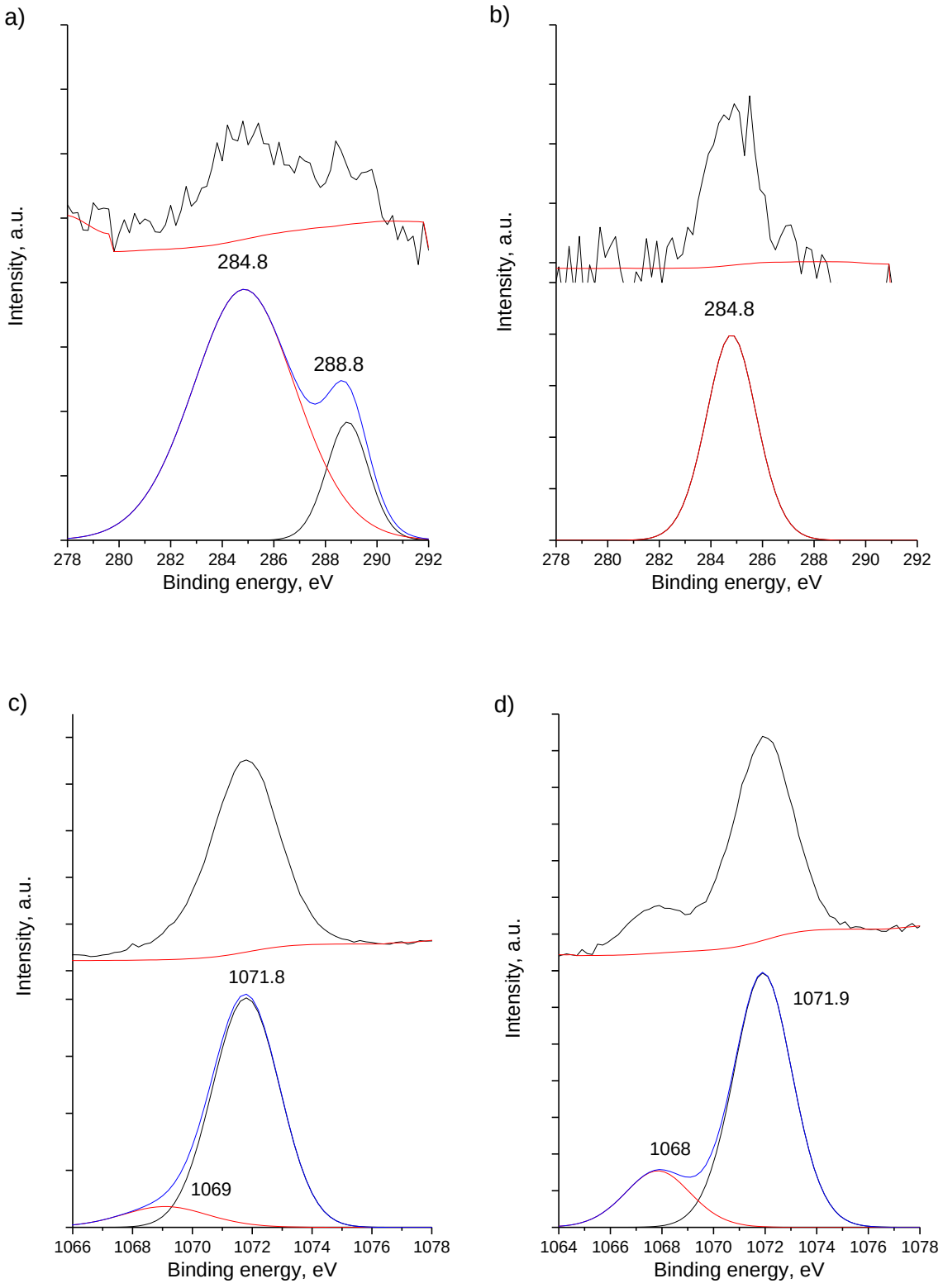


Figure S2 XRD spectra of Ni/ZrO_2 and $Na\text{-}Ni/ZrO_2$ after TPR. The arrow signals the minor tetragonal ZrO_2 phase.


a)
Intensity, a.u.
284.8
288.8
278 280 282 284 286 288 290 292
Binding energy, eV
b)
Intensity, a.u.
284.8
278 280 282 284 286 288 290 292
Binding energy, eV
c)
Intensity, a.u.
1071.8
1069
1066 1068 1070 1072 1074 1076 1078
Binding energy, eV
d)
Intensity, a.u.
1071.9
1068
1064 1066 1068 1070 1072 1074 1076 1078
Binding energy, eV

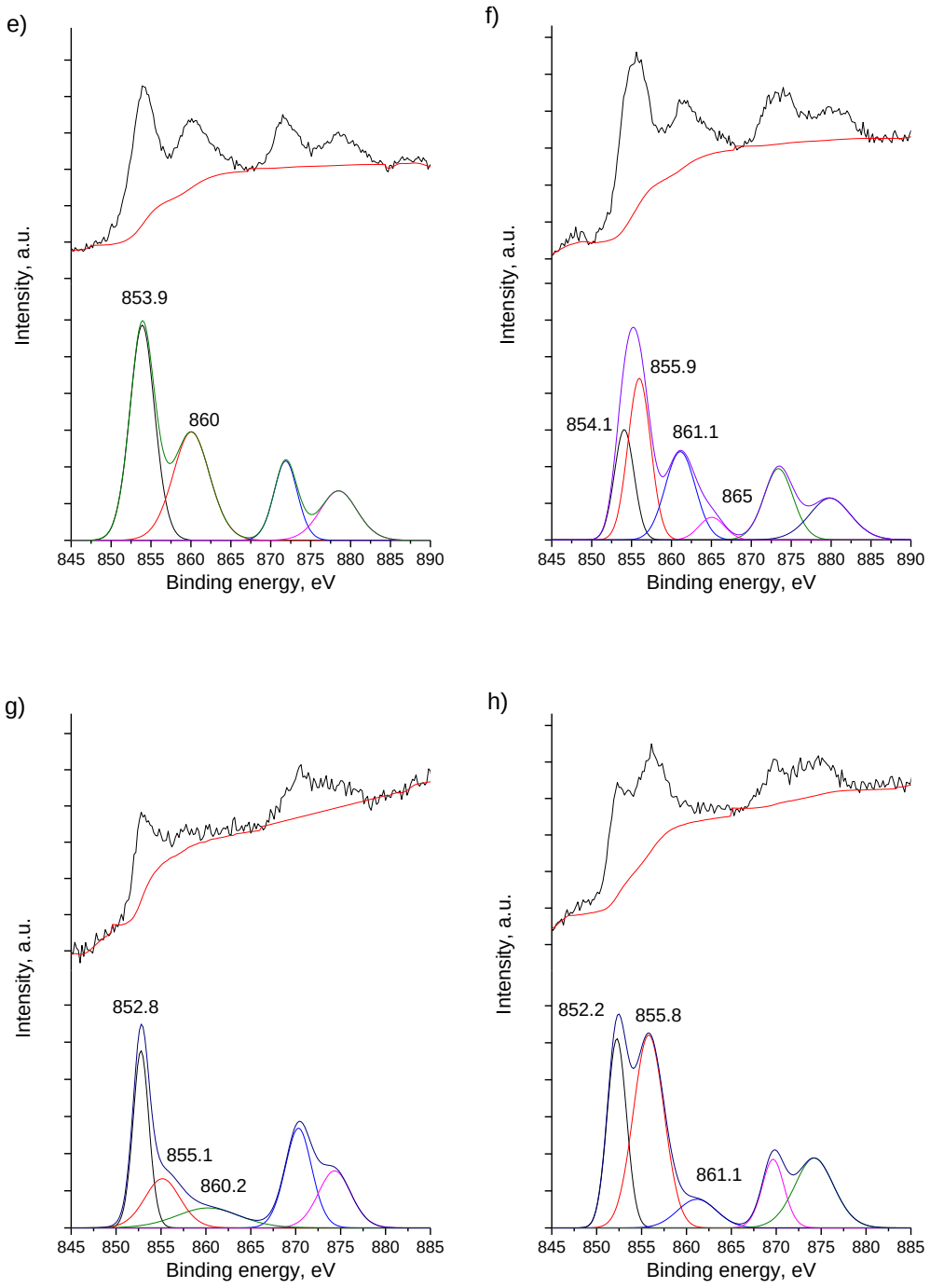


Figure S3 XPS results. C 1s spectrum on Na-Ni/ZrO_2 a) after calcination at 600 °C and b) subsequent reduction at 600 °C; and Na 1s spectrum on Na-Ni/ZrO_2 c) after calcination at 600 °C and d) subsequent reduction at 600 °C. The Ni 2p region after calcination at 600 °C on e) Ni/ZrO_2 and f) Na-Ni/ZrO_2; and after reduction at 600 °C on g) Ni/ZrO_2 and h) Na-Ni/ZrO_2. Measured data – upper curves, fitted spectra – lower curves

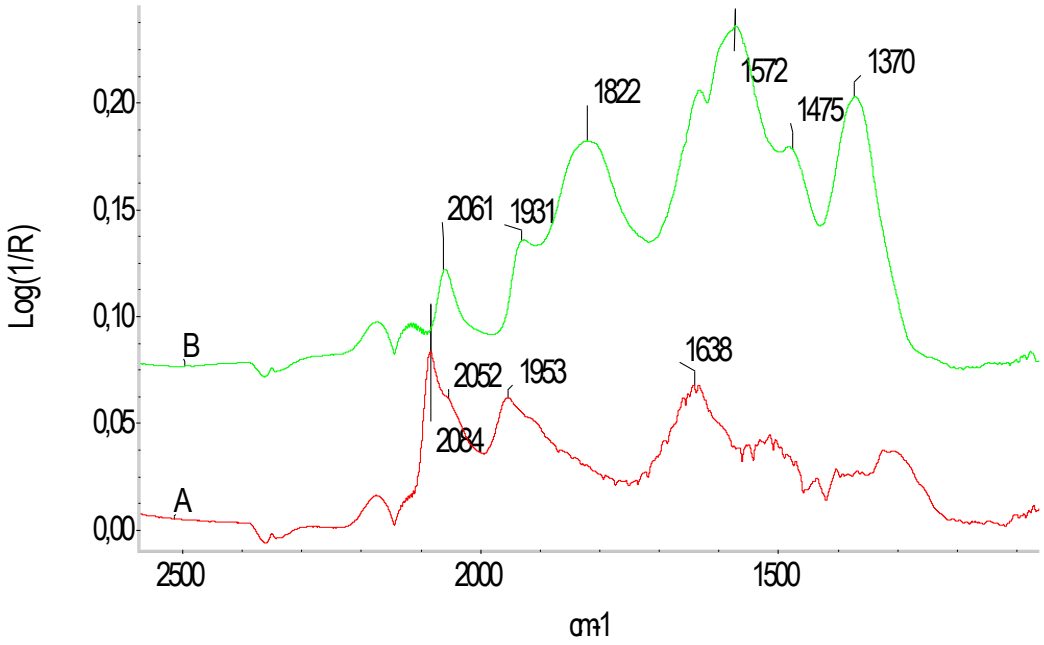


Figure S4 DRIFTS spectra in 1%CO/He stream at room temperature on A) Ni/ZrO_2 sample and B) $Na\text{-}Ni/ZrO_2$. Spectra are corrected with the one before CO chemisorption.

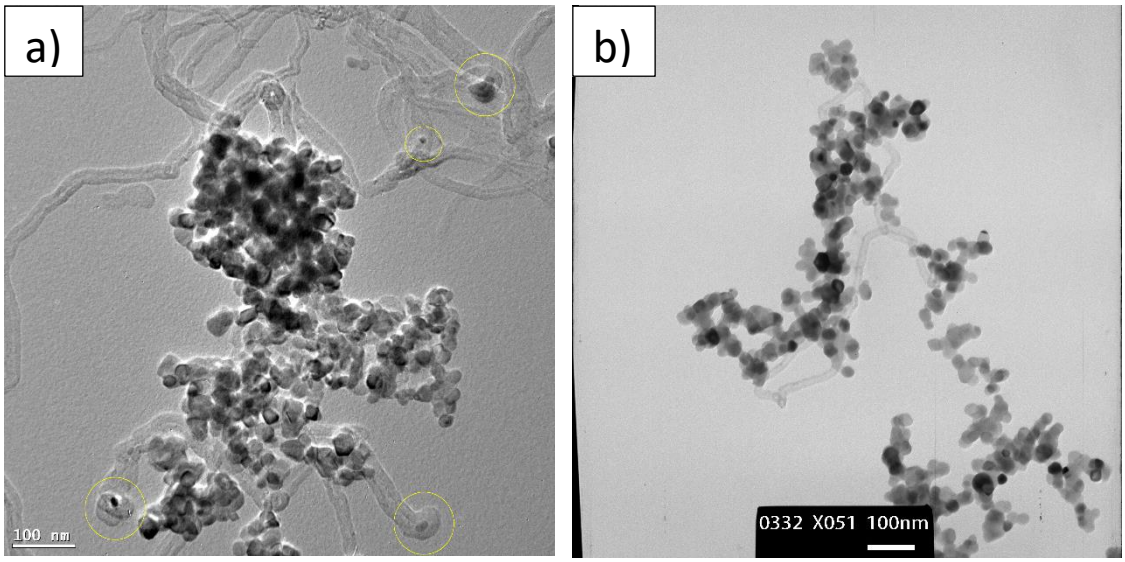


Figure S5 TEM images taken after long term stability tests on a) Ni/ZrO_2 and b) $Na\text{-}Ni/ZrO_2$.

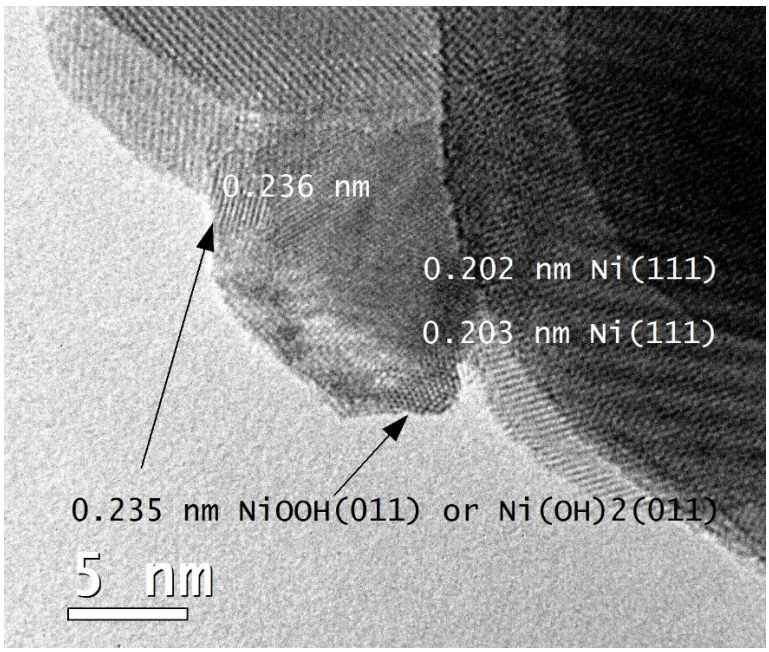


Figure S6 HRTEM image of a single Ni particle decorated by $Ni(OH)_2$/NiOOH domains after the ramp-hod experiments with $^{13}CO_2$

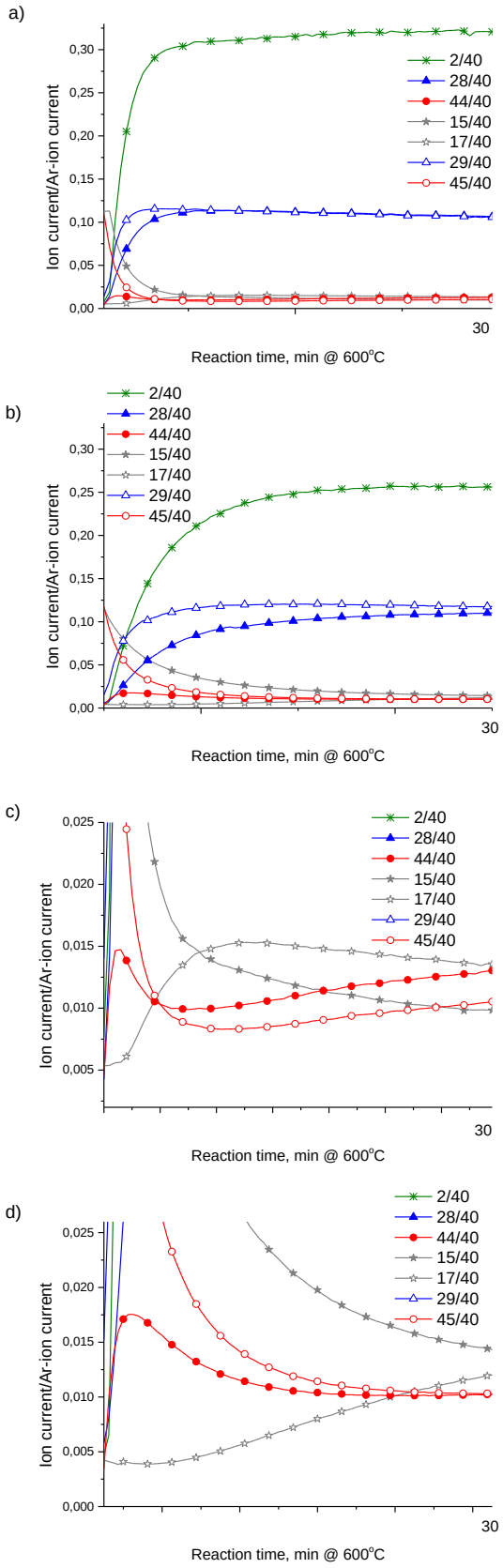


Figure S7 Isothermal type dry reforming reaction with $^{13}CO_2$:$^{12}CH_4$=1 mixture in the closed loop circulation system on a) Ni/ZrO_2; b) Na-Ni/ZrO_2; c) enlargement of low intensity signals of spectum „a" and d) enlargement of low intensity signals of spectrum „b". Conditions: introduction of a mixture of ~ 25 mbar of each reactant ($^{12}CH_4$ contains 2% Ar) onto the catalyst at 600 °C, then 30 min hold at 600 °C.