Electronic Supporting Information – Structural dynamics in Ni-Fe catalysts during CO₂ methanation – role of iron oxide clusters

Marc-André Serrer, a,b Abhijeet Gaur a,b, Jelena Jelic b, Sebastian Weber a,b, Charlotte Fritsch a,b, Adam H. Clark c, Erisa Saraçi a,b, Felix Studt b, Jan-Dierk Grunwaldt* a,b

a Institute for Chemical Technology and Polymer Chemistry, Karlsruhe Institute of Technology (KIT), 76131 Karlsruhe, Germany
b Institute of Catalysis Research and Technology, Karlsruhe Institute of Technology (KIT), 76344 Eggenstein-Leopoldshafen, Germany
c SuperXAS beamline, Paul Scherrer Institut (PSI), 5232 Villigen, Switzerland
# 1 Table of Content

1 Table of Content .................................................................................................................. 1

2 Experimental ..................................................................................................................... 2

2.1 Experimental setup for operando synchrotron studies ..................................................... 2

2.2 Rietveld refinement of synchrotron-based powder XRD .................................................. 2

3 Additional results ............................................................................................................... 3

3.1 Catalyst activation and Ni$_3$Fe alloy formation ............................................................... 3

3.2 Active state of the Ni-Fe catalyst under steady state conditions ....................................... 4

3.2.1 EXAFS fitting details .................................................................................................. 5

3.2.2 Rietveld refinement of synchrotron-based powder XRD ............................................. 9

3.3 Development of a structural model .................................................................................. 16

3.4 Catalyst response to periodic CO$_2$ feed modulations (MES) .......................................... 17

3.4.1 Steady state of Ni/Al$_2$O$_3$ and Ni-Fe/Al$_2$O$_3$ before and after the MES experiment ..... 17

3.4.2 Ni K-edge XANES spectra of Ni/Al$_2$O$_3$ and Ni-Fe/Al$_2$O$_3$ before the MES experiment ..... 18

3.4.3 Fe K-edge XANES spectra of Ni/Al$_2$O$_3$ and Ni-Fe/Al$_2$O$_3$ before the MES experiment ..... 19

3.4.5 Time-resolved XANES spectra of the monometallic Ni/Al$_2$O$_3$ catalyst ....................... 20

3.4.6 Time-resolved XANES spectra of the bimetallic Ni-Fe/Al$_2$O$_3$ catalyst ....................... 21

3.4.7 Phase-resolved Ni K-edge MES spectra of Ni/Al$_2$O$_3$ and Ni-Fe/Al$_2$O$_3$ catalyst .......... 22

3.5 Calculations on the stability of the Ni-Fe alloy and formation of FeO$_x$ clusters .................. 25

3.5.1 Defining U value for GGA+U method ......................................................................... 25

3.5.2 Oxygen adsorption on Ni$_4$Fe(111) alloy ................................................................... 25

3.5.3 (FeO)$_x$/Ni$_4$Fe(111)* surface model ......................................................................... 27

3.5.4 Phase diagram ........................................................................................................... 28

3.5.5 Oxygen hydrogenation ............................................................................................... 30

3.5.5 Ni vs Ni$_4$Fe vs (FeO)$_x$/Ni$_4$Fe* .............................................................................. 30

4 References ......................................................................................................................... 32
2 Experimental

2.1 Experimental setup for operando synchrotron studies

![Operando setup used for the combined XAS & XRD measurements, as well as the MES experiments presented in this study.](Image)

2.2 Rietveld refinement of synchrotron-based powder XRD

FullProf software package was used for refinement of PXRD data. An instrumental resolution file was first obtained by profile fitting of a LaB₆ NIST 640b standard to correct for peak broadening based on the instrument. The nano-crystalline nature of the used γ-Al₂O₃ makes it difficult to refine this phase well, which can be especially seen in deviations of the measured and calculated patterns at 17.5 ° or 20.5 ° in all refinements shown in Figure S 11 - Figure S 15. However, reflections for Ni phase and overlapping reflections between both phases can be described well. Thermal displacement parameters and occupancies could not be stably refined and were fixed to meaningful or initial values from the structural models. The obtained fractions for both phases are shown in Figure S 8 and listed in Table S 2 - Table S 7 while the error for the γ-Al₂O₃ phase is quite high. Additionally, the values do not match the expected ones of 17 wt.% for Ni₃.₀Fe and 83 wt.% for γ-Al₂O₃ or as determined by elemental analysis. Reasons for this are that we are only considering the metal to be Ni and not the contribution of Fe, the γ-Al₂O₃ phase is not described well potentially overestimating the amount of γ-Al₂O₃ and only crystalline parts of the metal nanoparticles account to the phase fraction. Therefore, the obtained fractions should be rather considered qualitatively and not quantitatively.

2.3 Calculation of alloy composition using Vegard’s law

The calculation of the alloy composition was performed using Vegard’s law, i.e. the linear correlation of the lattice parameter a to the respective fraction of Ni (fcc, a=3.520 Å) and Ni₃Fe (fcc, a=3.553 Å)\(^3\). The lattice parameter of the alloy was determined based on the shifted Ni reflections obtained in the refined XRD results (cf. sections 2.2 and 3.2.2).
3 Additional results

3.1 Catalyst activation and Ni$_3$Fe alloy formation

Figure S2: Continuously recorded XRD data of (a) Ni/γ-Al$_2$O$_3$ and (b) Ni-Fe/γ-Al$_2$O$_3$ during H$_2$-TPR at 6 bar. (c) Fe K-edge XANES spectra of the Ni-Fe/γ-Al$_2$O$_3$ catalyst as prepared in comparison to references and (d) k$^2$-weighted FT-transformed EXAFS spectra obtained at the Fe K-edge of the Ni-Fe/γ-Al$_2$O$_3$ catalyst before and after H$_2$-TPR in comparison to a Ni and Fe metal foil.
3.2 Active state of the Ni-Fe catalyst under steady state conditions

To verify the formation of FeOₓ, the Fe K-edge XANES spectra were compared to their state during H₂-TPR (Figure S 3).

Figure S 3: Normalized XANES spectra at the Fe K-edge of the Ni-Fe/Al₂O₃ catalyst during methanation of CO₂ compared to the partially oxidized spectra during H₂-TPR.

A good comparability between the state of iron during CO₂ methanation (Figure S 3, green and orange dotted line) to the state during H₂-TPR (grey dotted line) was given. In case of carbide formation, a different shape of the pre-edge feature would be expected. Hence, it can be concluded that FeOₓ is formed.

Figure S 4: k²-weighted Fourier transformed EXAFS of the Ni (a) and Fe (b) K-edge spectra of the 17 wt.% Ni₃Fe/γ-Al₂O₃ catalyst at 50 °C after applying methanation conditions of 20 ml/min 50 vol% H₂:CO₂=4:1 in N₂ at atm and various temperatures for 1 h.

Temperature effects can be excluded in this FT-EXAFS data, as all spectra were recorded at 50 °C after the respective temperature step. The coordination number of Ni decreased slightly after switching to methanation conditions at 250 °C from 8.2 ± 1.2 to 8.0 ± 1.2 accompanied by decrease in the
coo
cordination number of Fe from 6.1 ± 1.2 to 4.4 ± 1.1. Furthermore, the Fe-Ni backscattering peak at 4 Å declined. The decreased Fe-Fe coordination might either be due to FeO formation or due to segregation of Fe to the surface of the alloyed particles. Due to insufficient data quality, the formation of Fe-O scatterings could not be additionally proven by EXAFS fitting at the Fe K-edge. As the Ni-Ni coordination peak in the FT-EXAFS spectra (Figure S 4) at 2.1 Å increased and the backscattering due to Fe-Fe contributions at 2.1 Å and Fe-Ni at 4.0 Å declined dealloying of the Ni-Fe particles under formation of an Fe/FeO rich surface was found (see next section and paper).

3.2.1 EXAFS fitting details

At the Ni K-edge EXAFS spectra were fitted in the range of R = 1.0-3.2 Å and k = 2.0-11.0 Å\(^{-1}\) for the as prepared catalyst and in range of R = 1.0-5.0 Å and k = 2.7-12.5 Å\(^{-1}\) for catalyst after TPR. The amplitude reduction factor (S\(_0^2\)), as determined from Ni foil, was fixed at 0.84 and one energy shift parameter (E\(_0\)) was defined for all scattering paths. Scattering paths Ni-O, and Ni-Ni obtained from reference models were used and parameters N, ΔR and σ\(^2\) were fitted.

At the Fe K-edge EXAFS spectra were fitted in the range of R = 1.0-5.0 Å and k = 2.7-10.5 Å\(^{-1}\). The amplitude reduction factor (S\(_0^2\)), as determined from Fe foil, was fixed at 0.82 and one energy shift parameter (E\(_0\)) was defined for all scattering paths. Scattering paths Fe-Fe (Fe bulk) and Fe-Fe (Ni-Fe alloy) obtained from reference models were used and parameters N, ΔR and σ\(^2\) were fitted.

Simulation of XANES spectra using FEFF9 code

For XANES simulations at Ni K- and Fe K-edges in FEFF9, the ab initio self-consistent real-space Green’s function (RSGF) approach was used including inelastic losses, core-hole effects, vibrational amplitudes, etc. The polarization dependence, core-hole effects, and local field corrections were based on self-consistent, spherical muffin-tin scattering potentials. In the present ab-initio calculations, the Hedin-Lundqvist potential was chosen and XANES, Absolute, SCF (self-consistent field), and FMS (full multiple scattering) cards were used. The self-consistent potential (SCF) parameters were as follows: rfms = 5.2, lfms1 = 0, nscmt = 100, ca = 0.2, nmix = 1. The XANES parameters were as follows: xkmax = 4, xkstep = 0.07, vixan = 0. The LDOS card was added for density of states calculation with an energy range of −20 to 30 eV with a Lorentzian broadening with half-width of 0.1 eV.
3.2.1.1 Ni K-edge EXAFS fitting of the Ni-Fe/Al₂O₃ catalyst

Figure S5: k²-weighted Fourier transformed EXAFS (black) and the fit result (red) at the Ni K-edge of the 17 wt.% Ni-Fe/γ-Al₂O₃ catalyst as prepared at 50 °C (a), after H₂-TPR (b), after applying for 1 h methanation conditions of 20 ml/min 50 vol% H₂:CO₂=4:1 in N₂ at atm and 250 °C (c), 350 °C (d), 400 °C (e) and 350 °C II (f). EXAFS fitting results in Table S1.
3.2.1.8 Fe K-edge EXAFS fitting of the Ni-Fe/Al₂O₃ catalyst after methanation of CO₂ at 250 °C

Figure S6: $k^2$-weighted Fourier transformed EXAFS (black) and the fitted spectrum (red) at the Fe K-edge of the 17 wt.% Ni-Fe/γ-Al₂O₃ catalyst after CO₂ methanation at 250 °C after applying for 1 h methanation conditions of 20 ml/min 50 vol% H₂:CO₂=4:1 in N₂ at atm and 250 °C (EXAFS fitting results in Table S1).
Table S1: Structural parameters of the 17 wt.% Ni-Fe/γ-Al₂O₃ catalyst determined of EXAFS spectra at the Ni K-edge, S₀² = 0.84, data fits are given in Figure S5.

| Ni-O | Ni-Ni |
|------|-------|
|      |       |       |       |       |       |       |       |
| R / Å| CN   | DW factor · 10⁻² / Å² | R / Å| CN   | DW factor · 10⁻² / Å² | R / Å| CN   | DW factor · 10⁻² / Å² | R / Å| CN   | DW factor · 10⁻² / Å² |   |   |
| As prepared | 2.05 | 5.6 ± 1.2 | 0.0077 ± 0.0023 | 2.97 | 7.6 ± 2.5 | 0.0117 ± 0.0027 |   |   |   |   |   |   | 753 | -3.7 ± 1.6 |
| After TPR | 2.50 | 8.2±1.2 | 0.0093 ± 0.0017 | 3.52 | 6.0¹ | 0.0168 ± 0.0024 | 4.36 | 24¹ | 0.0166 ± 0.0010 | 5.12 | 12¹ | 0.0088± 0.0013 | 77 | 6.9 ± 1.1 |
| Meth 250 °C | 2.49 | 8.0±1.2 | 0.0090 ± 0.0017 | 3.52 | 6.0f | 0.0168 ± 0.0021 | 4.35 | 24¹ | 0.0166 ± 0.0011 | 5.12 | 12¹ | 0.0096± 0.0014 | 104 | 6.6 ± 1.1 |
| Meth 350 °C | 2.49 | 7.2±1.8 | 0.0062 ± 0.0018 | 3.51 | 6.0f | 0.0173 ± 0.0060 | 4.33 | 24¹ | 0.0157 ± 0.0026 | 5.08 | 12¹ | 0.0102± 0.0027 | 619 | 4.8 ± 2.7 |
| Meth 450 °C | 2.50 | 8.4±1.2 | 0.0086 ± 0.0016 | 3.53 | 6.0f | 0.0154 ± 0.0023 | 4.36 | 24¹ | 0.0146 ± 0.0008 | 5.12 | 12¹ | 0.0069± 0.0011 | 136 | 8.4 ± 1.2 |
| Meth II 350 °C | 2.50 | 8.7±1.2 | 0.0093 ± 0.0016 | 3.52 | 6.0f | 0.0147 ± 0.0021 | 4.36 | 24¹ | 0.0147 ± 0.0010 | 5.12 | 12¹ | 0.0068± 0.0011 | 137 | 7.7 ± 1.2 |

Table S2: Structural parameters a of the 17 wt.% Ni-Fe/γ-Al₂O₃ catalyst determined of EXAFS spectra t the Fe K-edge spectra, S₀² = 0.82, data fit is given in Figure 2 and Figure S6.

| Fe-Fe1 | Fe-Fe2 | Fe-Fe4 | Fe-Fe3 (NiFe) |
|--------|--------|--------|--------------|
| R / Å  | CN     | DW factor · 10⁻² / Å² | R / Å  | CN     | DW factor · 10⁻² / Å² | R / Å  | CN     | DW factor · 10⁻² / Å² | R / Å  | CN     | DW factor · 10⁻² / Å² |   |   |   |
| After TPR | 2.50 | 6.1±1.2 | 0.0075 ± 0.0017 | 2.89 | 2.0¹ | 0.0075 ± 0.0017 | 4.79 | 4¹ | 0.0031 ± 0.0003 | 4.36 | 4¹ | 0.0128 ± 0.0124 | 237 | 4.4 ± 2.6 |
| Meth 250 °C | 2.48 | 4.4±1.1 | 0.0080 ± 0.0020 | 2.85 | 2.0¹ | 0.0080 ± 0.0020 | 4.72 | 3¹ | 0.0043 ± 0.0027 | 4.29 | 4¹ | 0.0122 ± 0.0093 | 95 | -2.9 ± 3.7 |

f – fixed during fitting
3.2.2 Rietveld refinement of synchrotron-based powder XRD

Figure S 7: Stacked diffraction patterns (λ = 0.4943 Å) for different stages of the catalysts used for Rietveld refinement over the whole measured angular scale. A 2θ range from 10 to 30 ° was used for Rietveld refinements. Broad reflections at 7 ° are caused by the quartz capillary. After H₂-TPR (purple); after 1 h methanation of CO₂ at 250 °C (orange), 350 °C (green), 450 °C (red) and a subsequent second step at 350 °C (blue).

Figure S 8: Fractions obtained from Rietveld refinement for γ-Al₂O₃ and Ni phases for different stages of the catalysts. Values should be only interpreted qualitatively, standard deviations for γ-Al₂O₃ phase are quite large.

Figure S 9: Lattice parameter a with standard deviation of γ-Al₂O₃ phase (left) and Ni phase (right) as obtained by Rietveld refinement for different stages of the catalysts.
Figure S 10: Crystallite sizes $D$ of γ-Al$_2$O$_3$ (left) and Ni phase (right) as obtained by Rietveld refinement for different stages of the catalysts.
3.2.2.1 Rietveld refinement of the XRD data obtained from the Ni-Fe catalyst after H$_2$-TPR

Figure S 11: Rietveld refinement after TPR; black crosses measured intensity, red calculated intensity and blue difference between measured and calculated intensity, green lines are Bragg marker. Bragg marker top: γ-Al$_2$O$_3$; Bragg marker bottom: Ni; $R_p$: 4.61; $R_p$: 3.72; $S$: 0.23.

Table S 3: Structural data obtained from Rietveld refinement after TPR.

| Phase   | Ni          | γ-Al$_2$O$_3$   |
|---------|-------------|-----------------|
| Space group | $Fm\overline{3}m$ (No. 225) | $Fd\overline{3}m$ (No. 227) |
| $a$ in pm  | 354.4(3) | 791.1(2) |
| $D$ in nm  | 2.69 | 2.49 |
| $\varepsilon$ in % | 5.76 | 0.31 |
| Fraction in wt.% | 5.9(9) | 94(9) |

| Phase | Ni | γ-Al$_2$O$_3$ |
|-------|----|--------------|
| atom  | $x$ | $y$ | $z$ | $B_{iso}$ | $occ$ |
| Ni    | 0  | 0  | 0  | 0.300 | 0.021 |

| Phase | Ni | γ-Al$_2$O$_3$ |
|-------|----|--------------|
| atom  | $x$ | $y$ | $z$ | $B_{iso}$ | $occ$ |
| O1    | 0.2583(18) | 0.2583(18) | 0.2583(18) | 1.000 | 0.167 |
| A11   | ½ | ½ | ½ | 0.500 | 0.048 |
| A12   | ¼ | ¼ | ½ | 0.500 | 0.035 |
| A13   | 0.014(6) | 0.014(6) | 0.014(6) | 0.500 | 0.028 |
3.2.2.2 Rietveld refinement of the XRD data obtained from the Ni-Fe catalyst after methanation at 250 °C

![Rietveld refinement of the XRD data obtained from the Ni-Fe catalyst after methanation at 250 °C](image)

Figure S 12: Rietveld refinement after the methanation step at 250 °C; black crosses measured intensity, red calculated intensity and blue difference between measured and calculated intensity, green lines are Bragg marker. Bragg marker top: γ-Al2O3; Bragg marker bottom: Ni; Rwp: 4.80; Rp: 3.88; S: 0.25.

Table S 4: Structural data obtained from Rietveld refinement after the methanation step at 250 °C.

| Phase  | Ni                         | γ-Al2O3              |
|--------|----------------------------|----------------------|
| Space  | Fm-3m (No. 225)            | Fd-3m (No. 227)      |
| group  |                            |                      |
| a in pm| 354.3(3)                   | 790.9(2)             |
| D in nm| 2.54                       | 2.56                 |
| ε in % | 3.06                       | 0.30                 |
| Fraction in wt.% | 5.4(9) | 95(9) |

| Phase | Ni | γ-Al2O3 |
|-------|----|---------|
| atom  | x  | y       | z     | B_{iso} | occ  |
| Ni    | 0  | 0       | 0     | 0.300   | 0.021|

| Phase | Ni | γ-Al2O3 |
|-------|----|---------|
| atom  | x  | y       | z     | B_{iso} | occ  |
| O1    | 0.2586(17) | 0.2586(17) | 0.2586(17) | 1.000 | 0.167|
| A11   | ½  | ½       | ½     | 0.500   | 0.048|
| A12   | ¼  | ¼       | ¼     | 0.500   | 0.035|
| A13   | 0.012(6) | 0.012(6) | 0.012(6) | 0.500 | 0.028|
3.2.2.3 Rietveld refinement of the XRD data obtained from the Ni-Fe catalyst after methanation at 350 °C

![Rietveld refinement after the methanation step 350 °C; black crosses measured intensity, red calculated intensity and blue difference between measured and calculated intensity, green lines are Bragg marker. Bragg marker top: γ-Al₂O₃; Bragg marker bottom: Ni; Rwp: 5.02; Rp: 3.96; S: 0.26.](image)

Table S 5: Structural data obtained from Rietveld refinement after the methanation step at 350 °C.

| Phase    | Ni          | γ-Al₂O₃       |
|----------|-------------|---------------|
| Space group | Fm-3m (No. 225) | Fd-3m (No. 227) |
| a in pm  | 353.9(2)   | 791.0(2)     |
| D in nm  | 2.73       | 2.52         |
| ε in %   | 1.80       | 0.30         |
| Fraction in wt.% | 5.1(8) | 95(8) |

| Phase | Ni          |
|-------|-------------|
| atom  | x           | y           | z          | Biso | occ |
| Ni    | 0           | 0           | 0          | 0.300 | 0.021 |

| Phase | γ-Al₂O₃       |
|-------|---------------|
| atom  | x           | y           | z          | Biso | occ |
| O1    | 0.2587(17)   | 0.2587(17)  | 0.2587(17) | 1.000 | 0.167 |
| A11   | ½           | ½           | ½          | 0.500 | 0.048 |
| A12   | ¼           | ¼           | ¼          | 0.500 | 0.035 |
| A13   | 0.013(5)    | 0.013(5)    | 0.013(5)   | 0.500 | 0.028 |
3.2.2.4 Rietveld refinement of the XRD data obtained from the Ni-Fe catalyst after methanation at 450 °C

Figure S 14: Rietveld refinement after the methanation step at 450 °C; black crosses measured intensity, red calculated intensity and blue difference between measured and calculated intensity, green lines are Bragg marker. Bragg marker top: γ-Al₂O₃; Bragg marker bottom: Ni; Rwp: 5.14; Rp: 4.03; S: 0.27.

Table S 6: Structural data obtained from Rietveld refinement after the methanation step at 450°C.

| Phase                  | Ni       | γ-Al₂O₃  |
|------------------------|----------|----------|
| Space group            | Fm-3m (No. 225) | Fd-3m (No. 227) |
| a in pm                | 353.61(17) | 791.1(2)   |
| D in nm                | 3.21     | 2.55     |
| ε in %                 | 2.17     | 0.30     |
| Fraction in wt. %      | 5.3(7)   | 95(8)    |

| Phase | Ni      |          |          |
|-------|---------|----------|----------|
| atom  | x       | y        | z        | Biso    | occ   |
| Ni    | 0       | 0        | 0        | 0.300   | 0.021 |

| Phase | γ-Al₂O₃ |          |          |
|-------|---------|----------|----------|
| atom  | x       | y        | z        | Biso    | occ   |
| O1    | 0.2585(17) | 0.2585(17) | 0.2585(17) | 1.000   | 0.167 |
| A11   | ½       | ½        | ½        | 0.500   | 0.048 |
| A12   | ¼       | ¼        | ¼        | 0.500   | 0.035 |
| A13   | 0.015(5) | 0.015(5) | 0.015(5) | 0.500   | 0.028 |
3.2.2.5 Rietveld refinement of the XRD data obtained from Ni-Fe catalyst after methanation at 350 °C

Figure S 15: Rietveld refinement after the methanation step at 350 °C subsequent to 450 °C; black crosses measured intensity, red calculated intensity and blue difference between measured and calculated intensity, green lines are Bragg marker. Bragg marker top: γ-Al₂O₃; Bragg marker bottom: Ni; Rwp: 5.13 %, Rp: 4.00 %, Σ: 0.26.

Table S 7: Structural data obtained from Rietveld refinement of after the methanation step at 350 °C subsequent to 450 °C.

| Phase   | Ni            | γ-Al₂O₃         |
|---------|---------------|-----------------|
| Space group | *Fm-3m* (No. 225) | *Fd-3m* (No. 227) |
| a in pm  | 353.57(18)    | 791.1(2)        |
| D in nm  | 3.31          | 2.53            |
| ε in %   | 2.97          | 3.02            |
| Fraction in wt.% | 5.2(7) | 95(8) |

| Phase | Ni | | γ-Al₂O₃ |
|-------|----|---|--------|
| atom  | x  | y | z     | Biso  | occ |
| Ni    | 0  | 0 | 0     | 0.300 | 0.021 |

| Phase | γ-Al₂O₃         |
|-------|-----------------|
| atom  | γ-Al₂O₃         |
| O1    | 0.258(17)       | 0.258(17) | 0.258(17) | 1.000 | 0.167 |
| Al1   | ½              | ½           | ½           | 0.500 | 0.048 |
| Al2   | ¼              | ¼           | ¼           | 0.500 | 0.035 |
| Al3   | 0.015(5)       | 0.015(5)    | 0.015(5)    | 0.500 | 0.028 |
3.3 Development of a structural model

To develop the structural model, it is important to understand how the surface composition changes. The number and composition of nickel and iron atoms in the particle and on the surface was estimated (Table S 8).

Table S 8: Calculation of atoms and surface atoms of the Ni-Fe catalyst after TPR and at various temperatures during CO₂ methanation.

| Number Atoms | ATPR   | 250 °C | 350 °C | 450 °C | 350 °C II |
|--------------|--------|--------|--------|--------|-----------|
| Total Ni+Fe  | 1660 ± 1000 | 1400 ± 850 | 1730 ± 1050 | 2800 ± 1660 | 3060 ± 1810 |
| Total Ni     | 1380 ± 860  | 1180 ± 740  | 1500 ± 920  | 2480 ± 1490  | 2710 ± 1620  |
| Total Fe     | 320 ± 210   | 270 ± 180   | 270 ± 180   | 350 ± 230   | 390 ± 250   |
| Surface      | 390 ± 170   | 350 ± 150   | 400 ± 170   | 550 ± 230   | 590 ± 250   |
| Surface Ni   | 320 ± 150   | 280 ± 120   | 290 ± 130   | 350 ± 150   | 370 ± 160   |
| Surface Fe   | 70 ± 40     | 70 ± 30     | 130 ± 80    | 220 ± 130   | 240 ± 150   |
| Oxidized Fe  | -           | 50 ± 40     | 120 ± 80    | 180 ± 120   | 190 ± 120   |

The error margin in the obtained numbers of atoms is quite high due to the error of ± 0.9 in the particle size of 3.9. However, the numbers give a good trend how surface and particle composition change. Based on the estimation, the amount of iron at the surface strongly increases with temperature. The iron on the surface is nearly fully oxidized as soon as CO₂ methanation conditions were applied.
3.4 Catalyst response to periodic CO$_2$ feed modulations (MES)

3.4.1 Steady state of Ni/Al$_2$O$_3$ and Ni-Fe/Al$_2$O$_3$ before and after the MES experiment

The overall catalyst performance (Table S 9) reflected the trends observed in previous studies with comparison between Ni and Ni-Fe catalysts.[11-13]

Table S 9: Conversion and yields of the Ni/Al$_2$O$_3$ and the Ni-Fe/Al$_2$O$_3$ catalyst at 250 °C and 450 °C before and after the MES experiments. The conversions were normalized to the average catalyst mass of 4.4 mg obtained from our capillary reactor with a catalyst bed of 1 cm length and 1.5 mm diameter.

|          | Ni               | Ni-Fe              |
|----------|------------------|--------------------|
|          | 250 °C           | 350 °C             | 450 °C             |
|          | Before MES       | After MES          | Before MES         | After MES         | Before MES | After MES |
| X(CO$_2$) | 2 %              | 2 %                | 33 %               | 33 %              | 49 %       | 49 %      |
| S(CH$_4$) | 69 %             | 69 %               | 54 %               | 53 %              | 78 %       | 76 %      |

At 250 °C, a slightly higher CO$_2$ conversion of 3 % was observed for the Ni-Fe catalyst compared to 2 % of the unpromoted Ni catalyst. However, the selectivity was better for the unpromoted sample reaching 69 % compared to 53 % of the Ni-Fe catalyst. When the temperature was increased to 450 °C, both catalysts provided a CO$_2$ conversion of 49 % and a selectivity to CH$_4$ of ~ 78 %. Note, that the CO formation was much more pronounced in this experiment compared to the literature and our previous studies under stationary conditions, as we applied in this case a WHSV$_{\text{total}} = 684000$ ml/(g$_{\text{cat}}$*h) to ensure fast changes of the reactant gases in the catalyst bed during the MES experiments. The conversion profiles provided evidence that there was no major catalyst deactivation after the MES experiments suggesting that possible changes during the modulations were reversible.
3.4.2 Ni K-edge XANES spectra of Ni/Al₂O₃ and Ni-Fe/Al₂O₃ before the MES experiment

The normalized XANES spectra at the Ni K-edge after reaching the steady state of the catalyst during methanation of CO₂ at various temperatures are shown in Figure S 16 for Ni and Ni-Fe, respectively.

For the unpromoted Ni catalyst, at 250 °C (Figure S 16a, grey), Ni was mostly in reduced metal phase with some partial oxidation during the methanation of CO₂. The corresponding FT EXAFS spectra shown in the inset further substantiated that Ni remained in its reduced state. A coordination number (CN) of 7.6 ± 1.0 for Ni-Ni scattering was estimated and no Ni-O contribution was observed.

At 350 °C, an increase in the intensity of white line and a slight shift of the edge towards higher energy were found indicating a higher amount of oxidized Ni species (Figure S 16a, orange). Note, that this might partially be due to an experimental error during the reduction procedure (different H₂:N₂ ratio). A contribution from Ni-O was found in the FT EXAFS spectra (Figure S 16a, inset). The CN of Ni-Ni remained unchanged at 7.6 ± 1.2 compared to the steady state at 250 °C.

In the steady state at 450 °C, the intensity of the white line was also slightly increased, and the edge shifted to higher energy compared to the state at 250 °C. The EXFAS fitting results at 450 °C, with a CN of 8.8 ± 1.3 for Ni-Ni scattering at 2.45 Å and weak contribution from Ni-O at 2.02 Å (fixed CN =1) points towards contribution from Ni-O species which may be due to some Ni species in oxidized phase.

The steady state of the Ni-Fe catalyst (Figure S 16b) was already discussed in the main article. The states before MES are displayed here to confirm the previous results. It should be mentioned, that in contrast to the unpromoted sample, Ni remained in its reduced state during all temperature steps. The EXAFS analysis demonstrated that the CN of Ni-Ni scattering at 2.45 Å in the bimetallic Ni-Fe catalyst were 8.8 ± 1.4, 8.8 ± 1.2 and 8.5 ± 0.8 at 450 °C, 350 °C and 250 °C, respectively. This was in a good
agreement with the results provided in the main article. In comparison to the unpromoted Ni catalyst, the addition of Fe resulted in a weaker contribution from Ni-O at 350 °C and 450 °C. Hence, Ni was comparatively more reduced in presence of Fe and more stable during the methanation of CO$_2$ at different temperatures.

3.4.3 Fe K-edge XANES spectra of Ni/Al$_2$O$_3$ and Ni-Fe/Al$_2$O$_3$ before the MES experiment

The changes occurring during MES can depend on the steady state of the catalyst before MES. Figure S 17a shows the normalized XANES spectra at Fe K-edge for the steady state of the catalyst before MES experiment at different temperatures.

Figure S 17: XANES spectra recorded in transmission mode (a) and $k^2$-weighted Fourier transformed EXAFS (b) at the Fe K-edge of the 17 wt.% Ni$_x$Fe$_{y}$/γ-Al$_2$O$_3$ catalyst at 250 °C (black), 350 °C (orange) and 450 °C (red) during methanation of CO$_2$ in 50 ml/min 25 vol% H$_2$:CO$_2$=4:1 in N$_2$ at atm prior to the MES experiment.

At 250 °C, Fe was mostly in reduced metal phase with some partial oxidation, however at 350 °C the increase in the intensity of white line and shift of the edge towards higher energy indicate that more Fe species are present in oxidized phase, i.e., FeO. The degree of oxidation increases further at 450 °C showing effect of temperature on oxidation state of Fe. The changes in the XANES spectra can be further confirmed in the corresponding FT EXAFS spectra shown in Figure S 17b where contribution from of Fe-O scattering at ~ 1.6 Å observed as shoulder to the first scattering peak Fe-Fe grows with increasing temperature indicating high oxidation of Fe species. From EXAFS fitting, the CN of Fe-O scattering at 1.96 Å were found to be 1.2 ± 0.3, 1.7 ± 0.6 and 3.5 ± 1.2 at 250 °C, 350 °C and 450 °C, respectively. Hence, at higher temperatures Fe is more oxidized in its steady state before MES.
3.4.5 Time-resolved XANES spectra of the monometallic Ni/Al₂O₃ catalyst

Time-resolved XANES spectra obtained from 30 periods averaged into one period (a total of 24 spectra) and the corresponding phase-resolved spectra obtained during the experiment performed at 450 °C are given in Figure S 18.

![Figure S 18: Normalized time-resolved Ni K-edge XANES (top) and corresponding demodulated spectra (bottom), at selected values of phase angle (Δϕ) consisting of a total of 24 spectra covering 5 seconds each for the 17 wt.% Ni/γ-Al₂O₃ catalyst during CO₂/H₂/N₂ (0-60 s) vs. H₂/N₂ (60-120 s) cycling and 30 periods average (bottom).]
3.4.6 Time-resolved XANES spectra of the bimetallic Ni-Fe/Al₂O₃ catalyst

Figure S 19: Normalized time-resolved Ni K-edge XANES (top) and corresponding demodulated spectra (bottom) at selected values of phase angle ($\Delta\phi$) consisting of a total of 24 spectra covering 5 seconds each for the 17 wt.% Ni-Fe/γ-Al₂O₃ catalyst during CO₂/H₂/N₂ (0-60 s) vs. H₂/N₂ (60-120 s) cycling and 30 periods average (bottom).
3.4.7 Phase-resolved Ni K-edge MES spectra of Ni/Al₂O₃ and Ni-Fe/Al₂O₃ catalyst

First, the monometallic Ni/Al₂O₃ catalyst was investigated. No distinct changes were visible in the characteristic features of the conventional time-resolved Ni K-edge XANES spectra (Figure S 18b).

![Comparison of the difference spectrum obtained at the Ni K-edge during H₂-TPR with the demodulated spectra of maximum amplitude at 250 °C, 350 °C and 450 °C.](image)

The demodulated spectra obtained at 250 °C, 350 °C and 450 °C in comparison to the difference spectra collected during H₂-TPR (Ni-NiO) are displayed in Figure S 20. The comparison did not result in a good match. This demonstrates that complex structural changes are occurring at the Ni K-edge of the monometallic Ni catalyst.

![Simulated Ni K-edge XANES spectra for the DFT simulated structure for C (red), CO (blue), HCOO (orange) and HOCOO (green, dotted) substitution on the reduced Ni structure. Comparison of the obtained difference spectrum from these theoretical XANES spectra with simulated pure Ni metal spectrum to the experimentally obtained demodulated spectrum at 450 °C, 300°.](image)

One representative curve of the changes after the demodulation of the Ni/Al₂O₃ catalyst at 450 °C and a phase angle of 300° recorded at the Ni K-edge is displayed in Figure S 21.
In order to interpret the features of the demodulated spectrum, XANES spectra for DFT calculated structures of Ni surface with different species, i.e., Ni-C, Ni-CO, Ni-HCOO and Ni-HOCOO have been simulated using FEFF9 as shown in Figure S 21a along with simulated Ni metal spectrum. Their corresponding difference spectra with the simulated Ni metal spectrum were calculated and compared to our experimental demodulated spectrum (Figure S 18b, black curve). Four features were observed in the experimental spectrum, and denoted as $P$, $S$, $A$ and $B$, respectively. Feature $P$ at $\sim$ 8334 eV (pre-edge region) correlated well to the difference spectra of Ni-NiC and Ni-NiCO, although shifted to slightly higher energy. The shoulder $S$ at around 8345 eV was found in all references. However, the shoulder feature was not intense in the experimental data indicating the contribution of Ni-HCOO/Ni-HOCOO species, as the shoulder was less intense for these species compared to Ni-C / Ni-CO. The formation of Ni-HCOO/Ni-HOCOO species would be in a good agreement to DRIFTS studies$^{[14-16]}$ on Ni based catalysts. After the white line region, feature $A$ at 8355 eV in the post edge region further substantiated the formation of Ni-C / Ni-CO species, as already suggested by feature $P$. However, feature $B$ at 8368 eV correlated rather more to Ni-C than Ni-CO. Hence, the dissociative pathway of CO$_2$ activation seems to be preferred on the monometallic Ni/γ-Al$_2$O$_3$ catalyst at 450 °C.

![Figure S 22: Demodulated Ni K-edge spectra of the 17 wt.% Ni/γ-Al$_2$O$_3$ (a) and the 17 wt.% Ni-Fe/γ-Al$_2$O$_3$ (b) catalyst at 250 °C (black), 350 °C (orange) and 450 °C (red) during CO$_2$/H$_2$N$_2$ (0-60 s) vs. H$_2$/N$_2$ (60-120 s) cycling with 30 periods average.](image)

The demodulated spectra of both catalysts with the highest amplitude at the Ni K-edge at 250 °C, 350 °C and 450 °C have been plotted in Figure S 22. On the monometallic Ni catalyst in Figure S 22a an increase in temperature resulted in a sharpening of the pre-edge feature $P$. This indicated a preferred formation of Ni-C or Ni-CO species during CO$_2$ modulations at higher temperatures. However, feature $B$ only is formed, when the amount of Ni-CO species is decreased (see Figure S 21b) due to a higher fraction of Ni-C or Ni-HCOO / Ni-HOCOO species. Hence, the formation of feature $B$ in addition to the increasing feature $P$ demonstrated that the intermediates shifted from Ni-CO to Ni-C at elevated reaction temperatures on the monometallic Ni/γ-Al$_2$O$_3$ catalyst. The fact that feature $A$ did not flatten with the formation of feature $B$ further substantiated the formation of Ni-C, especially at 450 °C (Figure S 22a).
As feature \textit{S} did decrease, although more Ni-C species were formed at higher temperatures, Ni-HCOO / Ni-HOCOO species must be present and formed with an increasing ratio. Hence, we can conclude that in the investigated temperature regime all mentioned species were present during the methanation of CO$_2$ on the monometallic Ni catalyst. The following relative trends were observed: At 250 °C, preferably Ni-CO was formed. At 350 °C, the amount of Ni-CO was decreased accompanied by an increase in the amount of Ni-HCOO / Ni-HOCOO and Ni-C. By further increasing the temperature to 450 °C the amount of Ni-CO further decreased and a distinct formation of Ni-HCOO / Ni-HOCOO and Ni-C was observed.

The same experiment was performed on the bimetallic Ni-Fe sample (Figure S 19). The demodulated spectra of the Ni K-edge with the highest amplitude at 250 °C, 350 °C and 450 °C are displayed in Figure S 22b (overview on all phase angles is given in Figure S 23).

At 250 °C, the shape of the demodulated spectrum was similar to the unpromoted sample. This demonstrates that the origin in the difference in catalytic activity at 250 °C can be traced back to reactions on iron sites. With increasing reaction temperature, the feature intensity of \textit{P} and \textit{A} increased while shoulder \textit{S} was declined (Figure S 22b). As discussed for the monometallic Ni sample, a higher intensity of feature \textit{P} and \textit{B} correlates to the formation of Ni-CO and/or Ni-C. In the demodulated spectra of the Ni-Fe catalyst at 350 °C and 450 °C feature \textit{A} was more pronounced compared to the Ni catalyst without pronounced changes in feature \textit{B}. This suggests a higher ratio of Ni-CO species on the bimetallic Ni-Fe catalyst. Feature \textit{S} was distinctly hampered already at 350 °C suggesting the formation of Ni-HCOO / Ni-HOCOO. As this was not observed at 350 °C on the monometallic Ni catalyst (Figure S 22a), where we determined a lower catalytic activity (see Table S 9), these might be crucial intermediates in the methanation of CO$_2$.

However, none of the simulated references fitted precisely to experimentally obtained data. Although we can get clues on the intermediate species forming on the active sites during CO$_2$ methanation, the interpretation of the MES signals is still fragile to draw conclusive statements. Nevertheless, we can conclude with certainty that we have no indication of Ni-O species formed and the complex MES analysis demonstrate that processes on Ni are complex with response signal consisting of several C-containing intermediates/structures that give hints on the reaction mechanism.
3.5 Calculations on the stability of the Ni-Fe alloy and formation of FeO\textsubscript{x} clusters

3.5.1 Defining U value for GGA+U method

We applied the GGA+U method in order to better describe delocalized iron d orbitals and obtain more accurate energies. Based on the value of the FeO heat of formation compared to metallic Fe\textsuperscript{17}, we have applied different U values to find the best fit for the experimental data and found a U of 2.7 eV to be optimal.

![Graph showing calculated heat of FeO formation as a function of U value.](image)

Figure S23: Calculated heat of FeO formation as a function of U value

3.5.2 Oxygen adsorption on Ni\textsubscript{4}Fe(111) alloy

To address the segregation of Fe in the Ni\textsubscript{3}Fe alloy during the CO\textsubscript{2} hydrogenation process we constructed a Ni\textsubscript{4}Fe(111) slab with the dimension 5x2 in x and y direction. We also take this slab to study FeO ontop of the Ni-Fe alloy. The orthogonal orientation of this unit cell provides close to perfect lattice match in the y direction (4.366 Å) with the FeO lattice parameter (4.363 Å).
Figure S 24 shows the phase diagram of the Ni-Fe alloy as a function of the oxygen chemical potential expressed as through the H$_2$O/H$_2$ ratio. As can be seen in Figure S 24 oxygen adsorption is favorable at higher H$_2$O/H$_2$ ratios and leads to the segregation of Fe to the surface of the NiFe alloy.

### 3.5.3 Carbon monoxide adsorption on Ni$_3$Fe(111) alloy and Ni$^{\text{top layer}}$/Ni$_3$Fe(111)

We tested the effect of Fe on the CO adsorption energy using a stoichiometric Ni-Fe alloy (Ni$_3$Fe(111)) as well as Fe in the sublayers (Ni$^{\text{top layer}}$/Ni$_3$Fe(111)). Our calculations indicate that this does not affect the CO or H binding strength (see Table A). However, the presence of oxygen at the surface will reduce the CO binding energy through repulsive adsorbate-adsorbate interactions (see Table A).

![Phase diagram](image)

Table S 10: Zero point energy corrected binding energy at (2x2) large unit cells of Ni(111), Ni(111) surface layer over Ni$_3$Fe(111) three sublayers and Ni$_3$Fe(111), of: 0.25 ML atomic hydrogen, 0.25 ML CO, CO differential binding energy at 0.50 ML CO, CO referenced to CO+O.

| eV         | H    | CO    | 2CO-differential | CO (CO+O)$_{\text{ref}}$ |
|------------|------|-------|------------------|--------------------------|
| Ni(111)    | -0.31| -1.54 | -1.33            | -1.03                    |
| Ni$^{\text{top layer}}$/Ni$_3$Fe(111) | -0.30| -1.52 | -1.42            | -1.13                    |
| Ni$_3$Fe(111) | -0.37| -1.59 | -1.41            | -0.94                    |
3.5.4 \((\text{FeO})x/\text{Ni}_4\text{Fe}(111)^*\) surface model

We further investigated oxidation of metallic Fe to FeO that segregates to the surface of the Ni$_4$Fe(111) alloy. Such particles are modeled as nanowires with different numbers of FeO units in x direction, infinitely repeated in y direction (see also above).

In this model, the oxidation is modeled through segregation of Fe from the alloy to the surface where the alloy is correspondingly depleted of Fe, this is referred to as Ni$_4$Fe(111)*. We choose such a model because it is assumed that the bulk of the alloy will mostly remain the same and that near surface Fe will segregate to the surface and form FeO nanoparticles. Due to the stronger Fe interaction with oxygen compared to Ni, surface Fe atoms are placed underneath the (FeO)$_x$ nanowire.

(FeO)$_2$/Ni$_4$Fe(111)* is the smallest studied nanowire. Such a nanowire is less stable than 0.2 and 0.3 ML O/Ni$_4$Fe(111). Slightly larger (FeO)$_3$/Ni$_4$Fe(111)* is already more stable than any oxygen adsorbed on Ni$_4$Fe(111) alloy structure. (FeO)$_4$/Ni$_4$Fe(111)* and (FeO)$_6$/Ni$_4$Fe(111)* were additionally constructed. The reason behind the increase of the size of the nanowire is to look not only at the “flat” single layer nanowires (FeO)$_2,4$ but few layers thick (FeO)$_6$ as well, so that different parts of the particle could be analyzed.

![Figure S25: (FeO)$_n$/Ni$_4$Fe(111)* surface model, side and top view.](image)

(FeO)$_6$/Ni$_4$Fe(111)* model is shown in Figure S 25. Few types of Fe species are present and their Bader Charges are given in Table S 11.

Table S 11: Bader charge of different Fe species in (FeO)$_n$/Ni$_4$Fe* surface model.

| Bader charge | Ni$_4$Fe-I | Ni$_4$Fe-II | Cl-I | Cl-II | Cl-III | Cl-IV | FeO |
|--------------|------------|------------|------|-------|--------|-------|-----|
Table S10 shows a Bader charge analysis of the Fe in the various structures. Ni₄Fe-I denotes bulk Fe, whereas Ni₄Fe-II denotes Fe located at the surface of the Ni₄Fe(111)* alloy. Figure S 26 shows the location of the other Fe atoms at the FeO clusters.

| (FeO)₆/Ni₄Fe(111) | 7.41 | 7.2 | 6.87 | 6.78 | 6.57 | 6.6 | 6.61 |

Table S 12 shows the Bader charge analysis of a structure with an additional oxygen at the perimeter between FeO and the NiFe alloys.

Table S 12: Bader charge of different Fe species in O+(FeO)₆/Ni₄Fe* surface model.

| Bader charge                  | Ni₄Fe-I | Ni₄Fe-II | Cl-I | Cl-II | Cl-III | Cl-IV | FeO  |
|--------------------------------|---------|----------|------|-------|--------|-------|------|
| O+(FeO)₆/Ni₄Fe(111)            | 7.41    | 7.2      | 6.64 | 6.78  | 6.56   | 6.61  | 6.61 |

3.5.5 Phase diagram

For the construction of the final phase diagram, we have used all structures given in Section 3.5.2 and 3.5.3 of SI and we have calculated oxygen binding energies in following way:

For oxygen rich surface alloys:

\[ xO/Ni₄Fe(111) = E(2O/Ni₄Fe(111)) - E(Ni₄Fe(111)-x*μO) \]

for \( x = 2,3,4 \)
For nanowires:

\[(\text{FeO})_y/\text{Ni}_4\text{Fe}(111)^* = E((\text{FeO})_y/\text{Ni}_4\text{Fe}(111)^*) - E(\text{Ni}_4\text{Fe}(111)) - 2*E(\text{Ni}_{\text{bulk}}) - (y-2)*(\text{Fe}_{\text{bulk}}) - y^*\mu_O\]

\[O+(\text{FeO})_y/\text{Ni}_4\text{Fe}(111)^* = E((\text{FeO})_y/\text{Ni}_4\text{Fe}(111)^*) - E(\text{Ni}_4\text{Fe}(111)) - 2*E(\text{Ni}_{\text{bulk}}) - 4*(\text{Fe}_{\text{bulk}}) - 7^*\mu_O\]

For \(y = 2, 3, 4, 6\)

\(\mu_O = \mu_{\text{H}_2\text{O}} - \mu_{\text{H}_2}\) – Figure 8 in the main text.

\(\mu_O = \mu_{\text{CO}_2} - \mu_{\text{CO}}\) – Figure S 27.

Number of \((\text{Fe}_{\text{bulk}})\) is \(y-2\) because \(\text{Ni}_4\text{Fe}(111)^*\) and \(\text{Ni}_4\text{Fe}(111)\) differ in two sublayer Fe atoms.

Number of \(E(\text{Ni}_{\text{bulk}})\) is 2 because \(\text{Ni}_4\text{Fe}(111)^*\) and \(\text{Ni}_4\text{Fe}(111)\) differ in two sublayer Ni atoms.

Figure S 27: Phase diagram of \(\text{Ni}_4\text{Fe}(111)\) and \((\text{FeO})_y/\text{Ni}_4\text{Fe}(111)^*\) system as a function of the \(p_{\text{CO}_2} / p_{\text{CO}}\) ratio and for temperature range between 0 and 550 °C.
3.5.6 Oxygen hydrogenation

To compare the activity of the additional oxygen at the interface O+(FeO)/Ni4Fe(111)* we calculate the hydrogenation of this oxygen to form H2O. The results are given in Table S 13: Energy of the first and second hydrogenation steps of interface oxygen and stoichiometric oxygen.

Table S 13: Energy of the first and second hydrogenation steps of interface oxygen and stoichiometric oxygen.

| eV                     | First hydrogenation | Second hydrogenation |
|------------------------|---------------------|----------------------|
| O+(FeO)/Ni4Fe(111)*    | -0.34               | -0.35                |
| (FeO)/Ni4Fe(111)*      | -0.27               | +0.33                |

3.5.7 Ni vs Ni4Fe vs (FeO)6/Ni4Fe*

Binding energies of some important intermediates at Ni(111), Ni4Fe(111) and (FeO)6/Ni4Fe(111)* surfaces are given in Table S 14 the structures are shown in Figure S 28.

Table S 14: Binding energies of O, CO+O, CO3 and HCOO at Ni(111), Ni4Fe(111) and (FeO)6/Ni4Fe(111)*.

| eV | O      | CO+O | CO3  | HCOO  |
|----|--------|------|------|-------|
| Ni(111) | 0.47   | -0.52| 0.78 | -0.87 |
| Ni4Fe(111) | 0.16   | -0.94| 0.25 | -1.27 |
| (FeO)6/Ni4Fe(111)* | 0.15   | -1.02| -0.08| -1.12 |
Figure S 28: CO+O, CO$_3$ and HCOO binding geometries at (FeO)$_x$/Ni$_x$Fe(111)*.
4 References

[1] J. Rodríguez-Carvajal, *Physica B Condens. Matter* **1993**, *192*, 55-69.

[2] L. Vegard, Z. *Angew. Phys.* **1921**, *5*, 17-26.

[3] Z. Ahmed, J. C. Bevan, *Mineral. Mag.* **1981**, *44*, 225–230.

[4] S. Azadeh-Ranjbar, F. Karimzadeh, M. H. Enayati, *Int. J. Mod. Phys B* **2011**, *25*, 1013–1019.

[5] K. H. J. Buschow, P. G. van Engen, R. Jongebreur, *J. Magn. Magn. Mater.* **1983**, *38*, 1–22.

[6] A. Lutts, P. M. Gielen, *Phys. Status Solidi B* **1970**, *41*, K81–K84.

[7] E. A. Owen, E. L. Yates, *Proc. Phys. Soc.* **1937**, *49*, 17–28.

[8] Y. Tanaka, S. Ishida, S. Asano, *Mater. Trans.* **2005**, *46*, 355–360.

[9] R. J. Wakelin, E. L. Yates, *Proc. Phys. Soc. B* **1953**, *66*, 221–240.

[10] H. Zhao, Q. Zhu, Y. Gao, P. Zhai, D. Ma, *Appl. Catal., A* **2013**, *456*, 233–239.

[11] B. Mutz, M. Belimov, W. Wang, P. Sprenger, M.-A. Serrr, D. Wang, P. Pfeifer, W. Kleist, J.-D. Grunwaldt, *ACS Catal.* **2017**, *7*, 6802-6814.

[12] T. Burger, F. Koschany, O. Thomys, K. Köhler, O. Hinrichsen, *Appl. Catal., A* **2018**, *558*, 44-54.

[13] C. Mebrahtu, S. Abate, S. Chen, A. F. Sierra Salazar, S. Perathoner, F. Krebs, R. Palkovits, G. Centi, *Energy Technol.* **2018**, *6*, 1196-1207.

[14] J. Ren, X. Qin, J.-Z. Yang, Z.-F. Qin, H.-L. Guo, J.-Y. Lin, Z. Li, *Fuel Process. Technol.* **2015**, *137*, 204-211.

[15] D. Pandey, G. Deo, *J. Mol. Catal. A: Chem.* **2014**, *382*, 23-30.

[16] H. C. Wu, Y. C. Chang, J. H. Wu, J. H. Lin, I. K. Lin, C. S. Chen, *Catal. Sci. Technol.* **2015**, *5*, 4154-4163.

[17] *NIST Chemistry WebBook*, (available at [https://webbook.nist.gov/](https://webbook.nist.gov/), accessed on 01.06.2020).