SUPPLEMENTARY INFORMATION

to the article «Synthesis and thermal properties of the heterometallic complex $[RuNO(NO_2)_4OHNi(En)_2]$ – the potential precursor for nanosized Ni-Ru alloy»

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Table S1. Crystal data and structure refinement for $[RuNO(NO_2)_4OHNi(En)_2]$

Identification code	bor538
Empirical formula	$C_4H_{17}N_9NiO_{10}Ru$
Formula weight	511.04
Temperature/K	100
Crystal system	triclinic
Space group	P-1
a/Å	6.63260(10)
b/Å	14.9677(3)
c/Å	17.3854(3)
α/°	77.0890(10)
β/°	83.0430(10)
γ/°	88.8190(10)
Volume/Å^3	1669.87(5)
Z	4
ρ_{calc}g/cm^3	2.033
μ/mm^{-1}	2.100
F(000)	1024.0
Crystal size/mm^3	0.1 × 0.05 × 0.02
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.42 to 55.226
Index ranges	$-7 \le h \le 8$, $-19 \le k \le 19$, $-22 \le l \le 22$
Reflections collected	14998
Independent reflections	7691 [R_{int} = 0.0313, R_{sigma} = 0.0478]
Data/restraints/parameters	7691/3/459
Goodness-of-fit on F^2	1.082
Final R indexes [I>=2σ (I)]	R_1 = 0.0360, wR_2 = 0.0821
Final R indexes [all data]	R_1 = 0.0500, wR_2 = 0.0990
Largest diff. peak/hole / e Å^{-3}	0.98/-0.75

Table S2. Bond Lengths for $[RuNO(NO_2)_4OHNi(En)_2]$

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Ru1	O6	1.950(3)	N8	O17	1.240(5)
Ru1	N7	2.087(4)	N1	O2	1.258(5)
Ru1	N3	2.127(4)	N1	O1	1.222(5)
Ru1	N11	2.067(4)	N3	O23	1.167(6)
Ru1	N13	2.072(4)	N3	O18	1.216(6)
Ru1	N14	1.752(4)	N6	O13	1.202(5)
Ru2	O5	1.954(3)	N6	O15	1.198(5)
Ru2	N8	2.060(4)	N2	C12	1.476(6)
Ru2	N1	2.091(3)	N9	O19	1.135(5)
Ru2	N6	2.108(3)	N10	C19	1.462(7)
Ru2	N9	1.760(4)	N11	O9	1.288(6)
Ru2	N4	2.114(4)	N11	O10	1.170(6)
Ni2	O5	2.051(3)	N13	O21	1.226(5)
Ni2	O2	2.138(3)	N13	O14	1.222(5)
Ni2	N2	2.102(4)	N14	O8	1.133(5)
Ni2	N10	2.109(3)	N18	C17	1.468(6)
Ni2	N18	2.090(3)	N20	C2	1.451(6)
Ni2	N20	2.106(4)	N5	C3	1.426(7)
Ni1	O6	2.072(3)	N12	C1	1.498(6)
Ni1	O4	2.182(3)	N15	C20	1.467(7)
Ni1	N5	2.074(4)	N4	O20	1.218(5)
Ni1	N12	2.088(3)	N4	O11	1.211(5)
Ni1	N15	2.086(4)	N22	C4	1.428(8)
Ni1	N22	2.083(4)	C12	C17	1.507(7)
N7	O4	1.249(4)	C19	C2	1.445(8)
N7	O16	1.223(4)	C20	C1	1.476(8)
N8	O7	1.221(5)	C3	C4	1.402(7)

Table S3 Bond Angles for $[RuNO(NO_2)_4OHNi(En)_2]$

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O6	Ru1	N7	87.22(13)	N5	Ni1	N22	82.98(16)
O6	Ru1	N3	88.40(13)	N12	Ni1	O4	175.46(15)
O6	Ru1	N11	89.60(15)	N15	Ni1	O4	93.78(14)
O6	Ru1	N13	87.22(14)	N15	Ni1	N12	82.65(16)
N7	Ru1	N3	87.38(16)	N22	Ni1	O4	87.15(13)
N11	Ru1	N7	92.27(15)	N22	Ni1	N12	96.00(16)
N11	Ru1	N3	177.99(16)	N22	Ni1	N15	96.13(16)
N11	Ru1	N13	91.01(16)	Ru2	O5	Ni2	123.55(15)
N13	Ru1	N7	173.52(14)	Ru1	O6	Ni1	124.64(15)
N13	Ru1	N3	89.15(17)	O4	N7	Ru1	121.0(3)
N14	Ru1	O6	176.78(15)	O16	N7	Ru1	120.7(3)
N14	Ru1	N7	94.84(16)	O16	N7	O4	118.0(4)
N14	Ru1	N3	94.15(16)	O7	N8	Ru2	119.5(3)
N14	Ru1	N11	87.85(18)	O7	N8	O17	120.0(4)
N14	Ru1	N13	90.87(17)	O17	N8	Ru2	120.4(3)
O5	Ru2	N8	88.82(14)	O2	N1	Ru2	122.7(3)
O5	Ru2	N1	86.78(13)	O1	N1	Ru2	119.4(3)
O5	Ru2	N6	86.74(13)	O1	N1	O2	117.7(4)
O5	Ru2	N4	86.82(14)	N1	O2	Ni2	121.8(2)
N8	Ru2	N1	174.50(15)	O23	N3	Ru1	119.8(4)
N8	Ru2	N6	90.88(13)	O23	N3	O18	121.4(5)
N8	Ru2	N4	89.63(15)	O18	N3	Ru1	118.6(4)
N1	Ru2	N6	92.16(13)	N7	O4	Ni1	123.8(3)
N1	Ru2	N4	86.83(15)	O13	N6	Ru2	119.8(3)
N6	Ru2	N4	173.53(14)	O15	N6	Ru2	121.7(3)
N9	Ru2	O5	179.23(15)	O15	N6	O13	118.4(4)
N9	Ru2	N8	91.94(16)	C12	N2	Ni2	108.2(3)
N9	Ru2	N1	92.45(16)	O19	N9	Ru2	178.7(4)
N9	Ru2	N6	93.40(15)	C19	N10	Ni2	107.4(3)
N9	Ru2	N4	93.03(16)	O9	N11	Ru1	118.5(3)
O5	Ni2	O2	84.44(11)	O10	N11	Ru1	122.0(4)
O5	Ni2	N2	168.44(14)	O10	N11	O9	118.8(4)
O5	Ni2	N10	89.77(13)	O21	N13	Ru1	120.9(3)
O5	Ni2	N18	92.02(13)	O14	N13	Ru1	120.1(3)
O5	Ni2	N20	92.93(14)	O14	N13	O21	118.9(4)
N2	Ni2	O2	85.40(13)	O8	N14	Ru1	172.4(4)
N2	Ni2	N10	96.30(14)	C17	N18	Ni2	108.3(3)
N2	Ni2	N20	97.64(16)	C2	N20	Ni2	108.5(3)
N10	Ni2	O2	93.18(14)	C3	N5	Ni1	109.3(3)

N18	Ni2	O2	88.93(14)	C1	N12	Ni1	108.3(3)
N18	Ni2	N2	82.28(14)	C20	N15	Ni1	106.7(3)
N18	Ni2	N10	177.36(15)	O20	N4	Ru2	119.6(4)
N18	Ni2	N20	95.88(15)	O11	N4	Ru2	119.5(3)
N20	Ni2	O2	174.61(14)	O11	N4	O20	120.8(4)
N20	Ni2	N10	82.08(15)	C4	N22	Ni1	108.7(3)
O6	Ni1	O4	82.03(11)	N2	C12	C17	108.5(4)
O6	Ni1	N5	92.59(13)	N18	C17	C12	108.1(4)
O6	Ni1	N12	95.04(13)	C2	C19	N10	110.9(5)
O6	Ni1	N15	88.75(14)	N15	C20	C1	108.3(4)
O6	Ni1	N22	168.41(13)	C20	C1	N12	110.0(4)
N5	Ni1	O4	88.68(14)	C19	C2	N20	112.8(5)
N5	Ni1	N12	94.94(16)	C4	C3	N5	118.0(5)
N5	Ni1	N15	177.34(15)	C3	C4	N22	116.1(6)

Table S4 Torsion Angles for $[RuNO(NO_2)_4OHNi(En)_2]$.

A	**B**	**C**	**D**	**Angle/°**	**A**	**B**	**C**	**D**	**Angle/°**
Ru1	N7	O4	Ni1	-13.4(4)	Ni1	N15	C20	C1	-47.4(5)
Ru2	N1	O2	Ni2	-10.1(4)	Ni1	N22	C4	C3	23.7(10)
Ni2	N2	C12	C17	39.6(5)	O1	N1	O2	Ni2	175.3(3)
Ni2	N10	C19	C2	-39.3(6)	N2	C12	C17	N18	-55.4(5)
Ni2	N18	C17	C12	42.7(5)	N10	C19	C2	N20	49.1(8)
Ni2	N20	C2	C19	-32.2(7)	O16	N7	O4	Ni1	172.7(3)
Ni1	N5	C3	C4	11.8(11)	N5	C3	C4	N22	-24.7(13)
Ni1	N12	C1	C20	-31.9(5)	N15	C20	C1	N12	53.6(6)

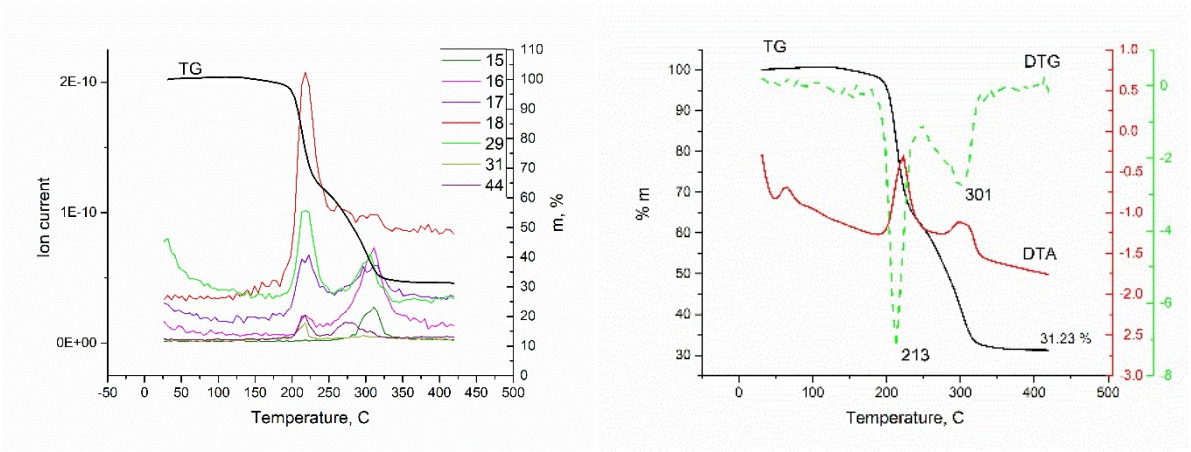

Figure S5. Synchronous TG-MS of $[RuNO(NO_2)_4OHNi(En)_2]$ in He-H_2 (TG and MS – left, TG, DTG and DTA – right).

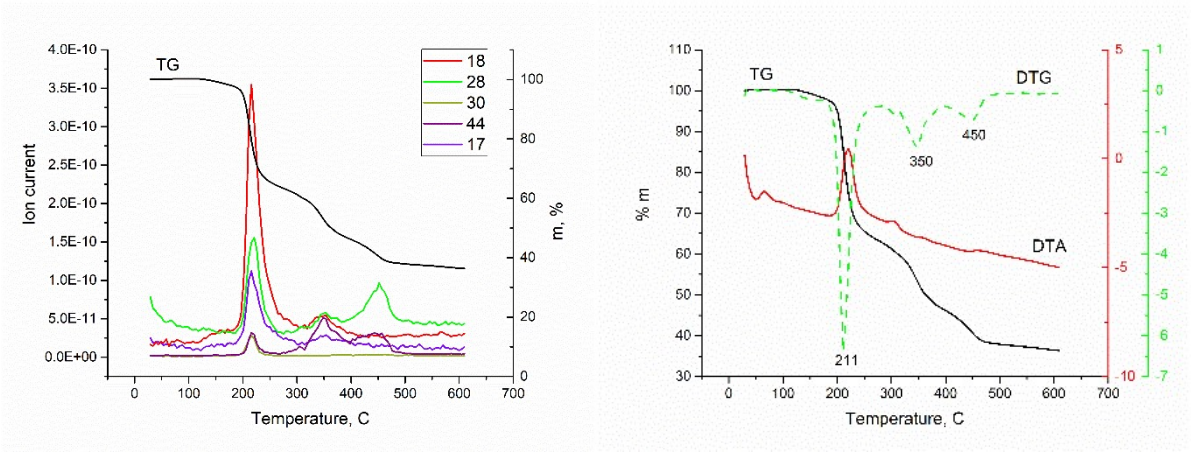

Figure S6. Synchronous TG-MS of $[RuNO(NO_2)_4OHNi(En)_2]$ in He (TG and MS – left, TG, DTG and DTA – right).

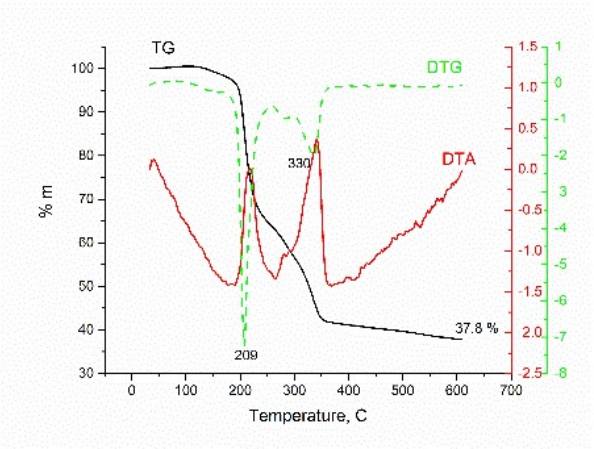

Figure S7. TG-DTA of $[RuNO(NO_2)_4OHNi(En)_2]$ in Ar-O_2

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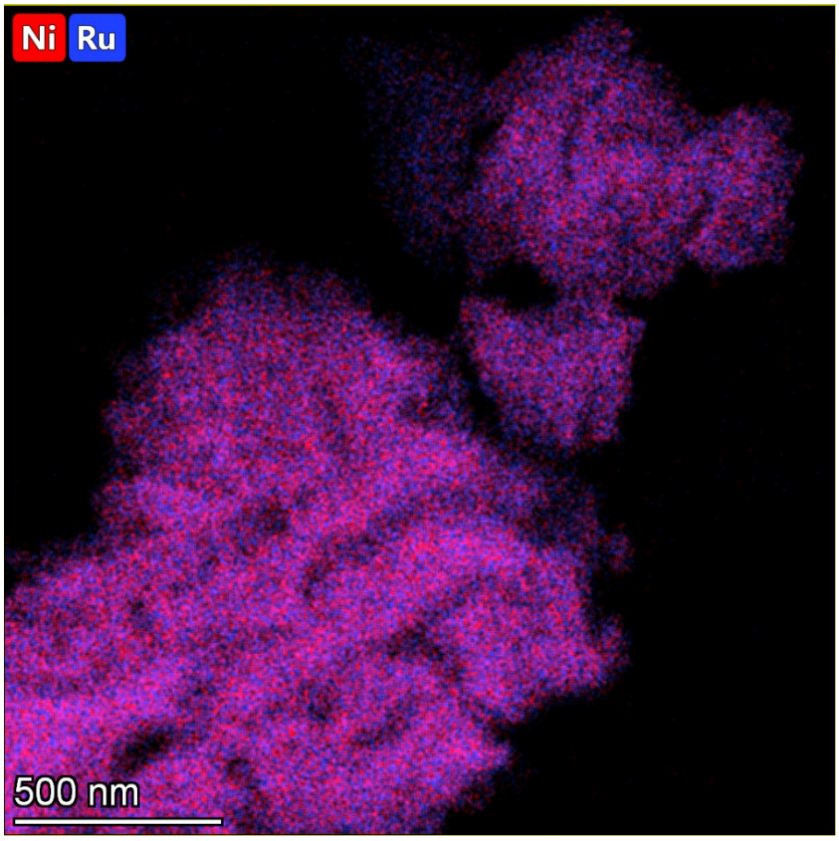
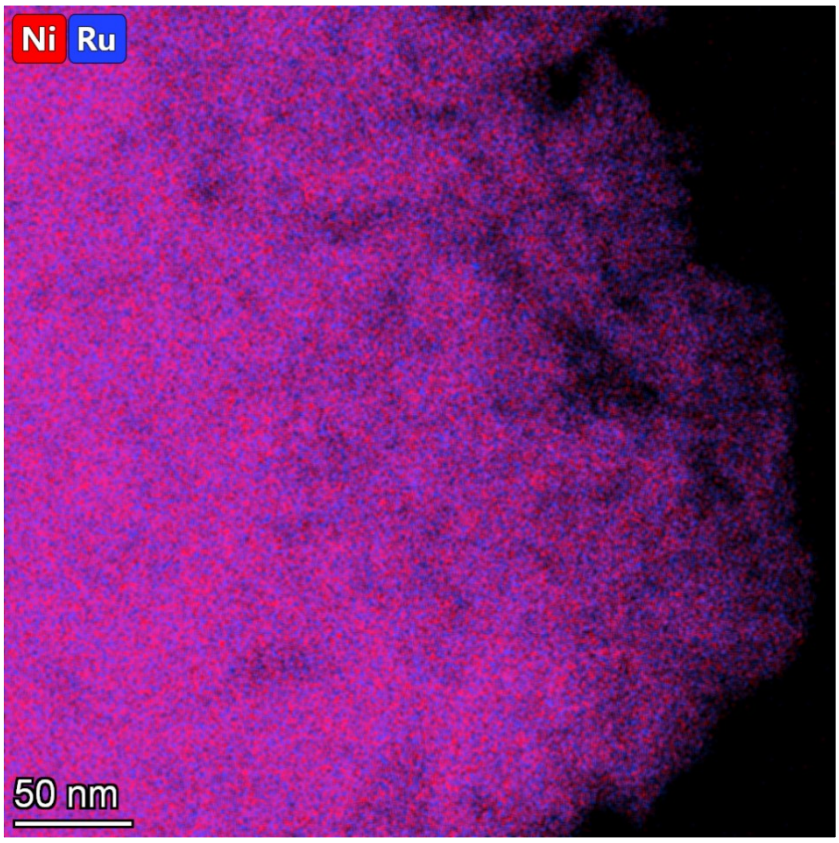
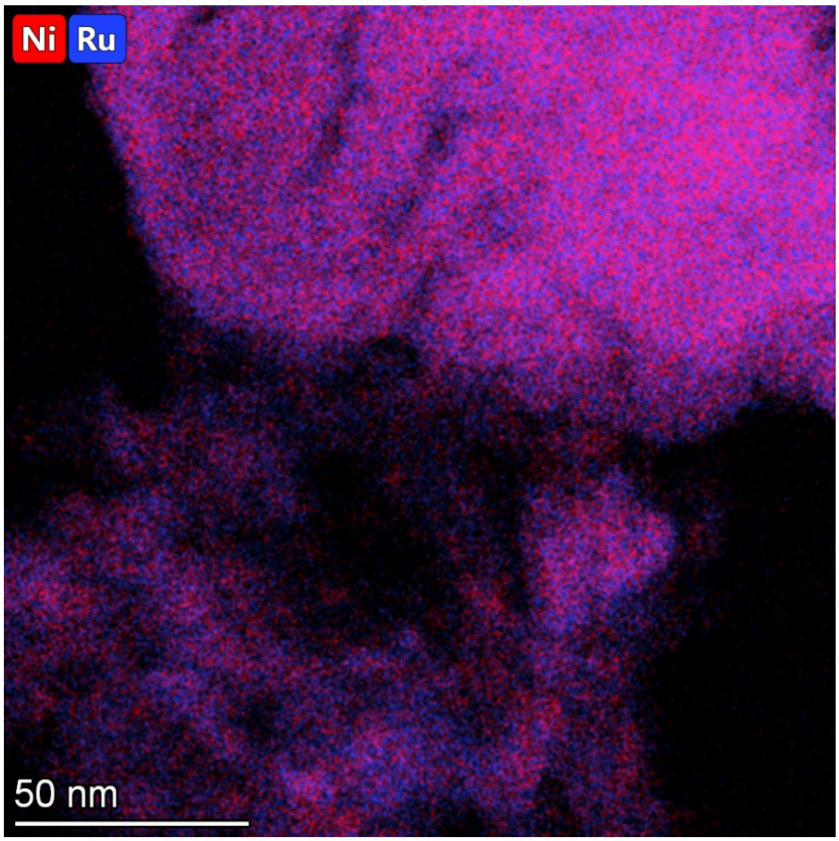
Figure S8. Nickel and ruthenium distribution (atomic percent) in the product of thermal decomposition of $[RuNO(NO_2)_4OHNi(En)_2]$ in He-H_2.



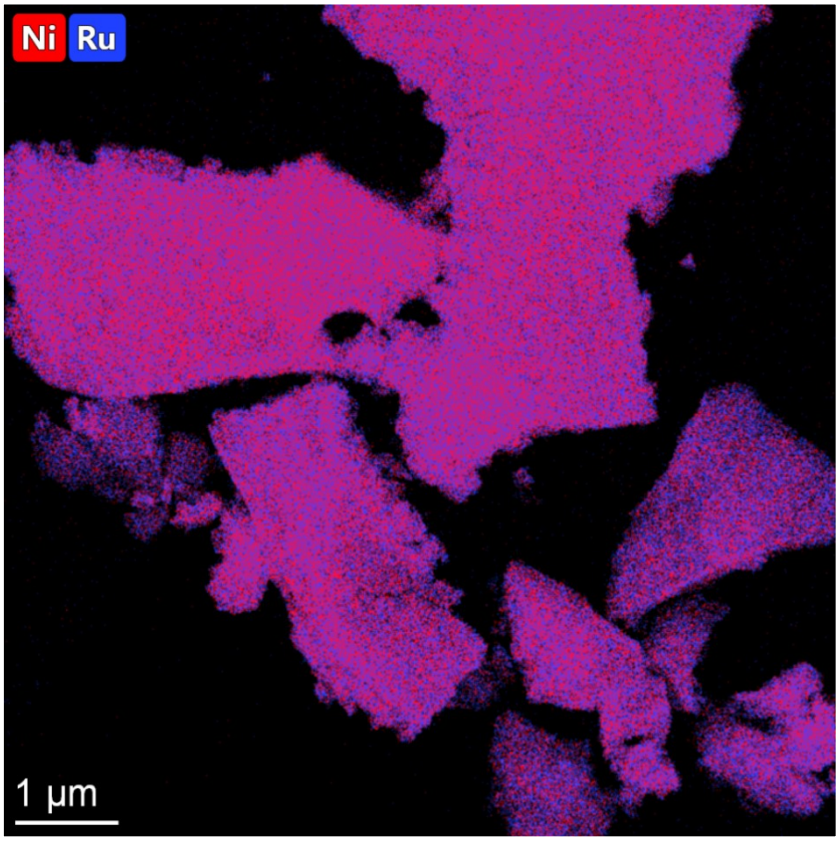
a) Ni (49.36) – Ru (50.64).



b) Ni (51.67) – Ru (48.33).

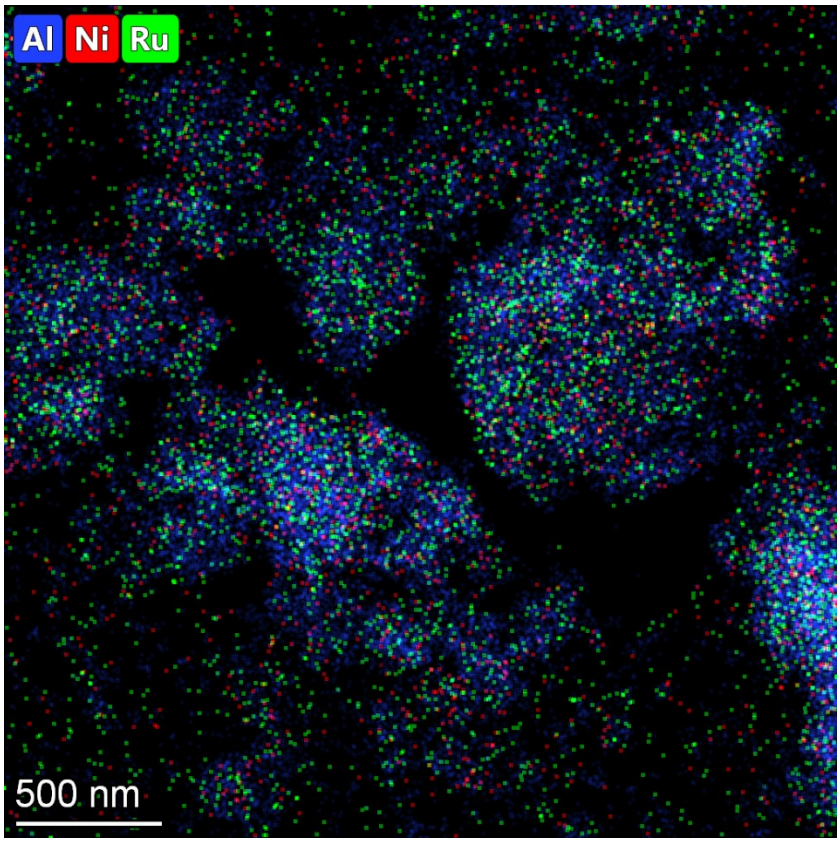


c) Ni (49.9) – Ru (50.01).

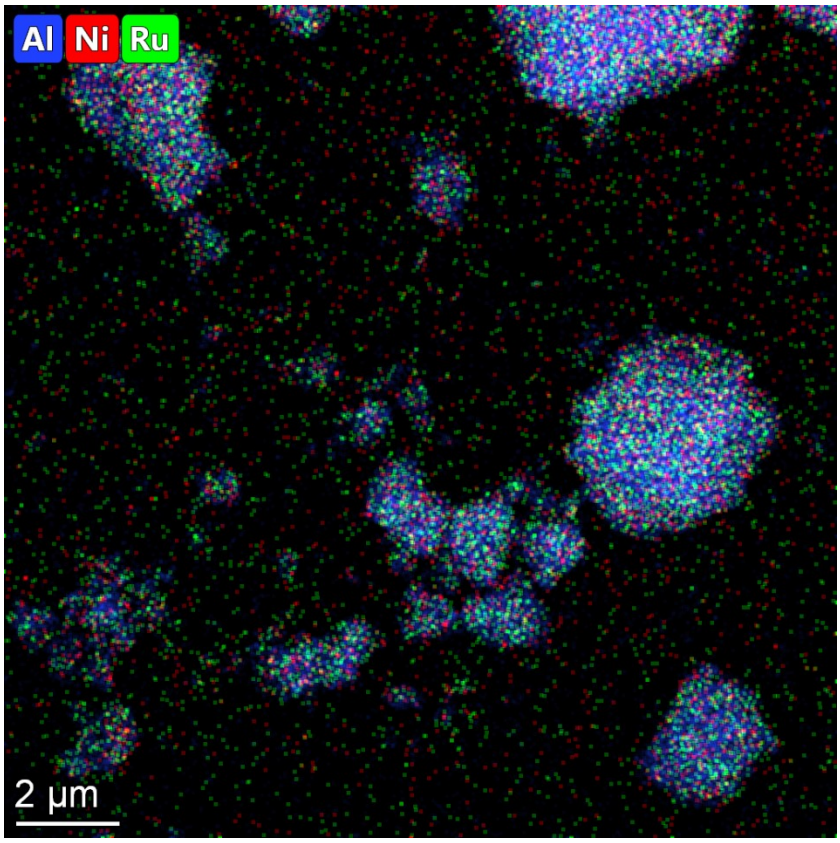


d) Ni (54.02) – Ru (45.98).

Figure S9. Nickel, ruthenium and alumina distribution (atomic percent) for the 5 % (weight) NiRu on the Al_2O_3. Theoretical atomic percent of Ni and Ru according to the weight load is 1.61 %.



a) Ni (0.89) – Ru (1.16) – Al (97.96).



b) Ni (1.05) – Ru (1.21) – Al (97.75).

Figure S10. Temperature dependences of CO_2 for CO methanation over supported catalysts. Reaction mixture (vol. %): 1 CO + 99 H_2. WHSV: 80 $L \cdot g^{-1} \cdot h^{-1}$ (STP).