Supplementary Information

1. Catalyst Synthesis:

Prices for the two precursors:

$RuCl_3 \cdot xH_2O$: 10 g, 518 €, last checked 02.02.2023 (Alfa Aeser)

$N_4O_{10}Ru$: 5 g, 412 €, last checked 02.02.2023 (Alfa Aeser)

In preparation:

A 4.7 wt% solutions of $RuCl_3 \cdot xH_2O$ was prepared, by dissolving the appropriate amount of the precursor in hot water. The 4.7 wt% solution of $Ru(NO)(NO_3)$ was used as received from the purchaser. γ-Al_2O_3 was heated under a static air environment to 500 °C in 1 h and the temperature was hold for 4 h. After cooling down the so received γ-Al_2O_3 was used in wet impregnation step.

Wet Impregnation:

The appropriate amount of γ-Al_2O_3 was suspended in 70 g of distilled Water. The round bottom flask was put in a pre heated oil bath at 70 °C. The appropriate amount of the 4.7 wt% solutions of the precursors in Water ($RuCl3 \cdot xH_2O$) and dilute nitric acid ($Ru(NO)(NO_3)$) were added. The so received dark coloured suspension was stirred at 70 °C over night. The hot solution was put into a rotary evaporator and the water was removed under reduced pressure (200 RPM, 42 mbar, 50 °C Water bath temperature). For complete dryness the so received pre-catalyst lumps where dried in a pre-heated oven at 120 °C. The lumps received where finely grounded. The so received powders (**-i.** ending) where halved. First half of the batches was directly reduced under a dilute H_2 (7-10% H_2 in N_2) flow (**-ir.** ending). The temperature program was put at 450 °C, this temperature was reached after 1 h of heating. The second half of the batches was calcined in static air at 600 °C, this temperature (**-ic.** ending) was reached with a heating rate of 10K/min. The so received powders where further reduced under same conditions as described before.

2. Correlation between H_2 uptake and metal loading (Temperature-programmed reduction)

Table S1: Comparison of H_2 uptake and metal loading.

Catalyst	H_2 uptake	loading of metal responsible for H_2 uptake
Ru-NO-1-ic.	70	0.283 (Ru)
Ru-NO-3-ic.	150	1.05 (Ru)
Ru-NO-5-ic.	290	1.604 (Ru)
RuNi-NO-ic. (LT)	230	2.129 (Ru)
RuNi-NO-ic. (HT)	500	10.34 (Ni)
Ru-Cl-1-ic.	70	0.43 (Ru)
Ru-Cl-3-ic.	210	1.443 (Ru)
Ru-Cl-5-ic.	320	2.576 (Ru)
RuNi-Cl-ic. (LT)	170	1.19 (Ru)
RuNi-Cl-ic. (HT)	500	10.78 (Ni)

3. Calculations of H_2 uptakes:

Altamira AMI300After measuring the thermograms the measurement systems calibrates itself with the injection of a specific amount of analyte gas. The integration of this 5 calibration signals gives an average area and therefore a correlation between amount of gas and area. With this correlation the area of the Thermograms can be multiplied to get the reactant gas uptake.

$$V = \frac{V_L \cdot \left(\frac{\%\frac{\mathrm{V}}{\mathrm{V}}}{100\%}\right)}{A_{Kal}} \cdot A_T \quad (1)$$

$$U = \frac{\mathrm{V} \cdot \mathrm{p}}{R \cdot \mathrm{T} \cdot m_{cat}} \quad (2)$$

Adsorbed analytical gas [µl]: V

H_2 uptake [µmol·g^{-1}] : U

Volume of analyte gas (Loop Volume) [µl]: V_L

Average of all 5 calibration signals: A_{Kal}

Area of the thermogram: A_T

Amount of catalyst to be analyzed [g]: m_{cat}

Loop Temperature [K]: T

Universal gas constant [L·atm·K^{-1}·mol^{-1}] : R

Pressure [atm]: p

Analytical Gas [%]: %v/v

4. Calculations of the productivities

After calibrating the different products within the appropriate concentration ranges, the samples from the reactors where filtrated and measured undiluted in the GC. This gave us the concentration of the compounds in that sample C_X x being the product.

Productivity P_x was given in mmol·l^{-1}·g_{cat}^{-1} and therefore calculated: $P_x = C_x \cdot m^{-1}_{cat}$

5. Correlation between particle size and MeFo productivity for the different ruthenium catalysts

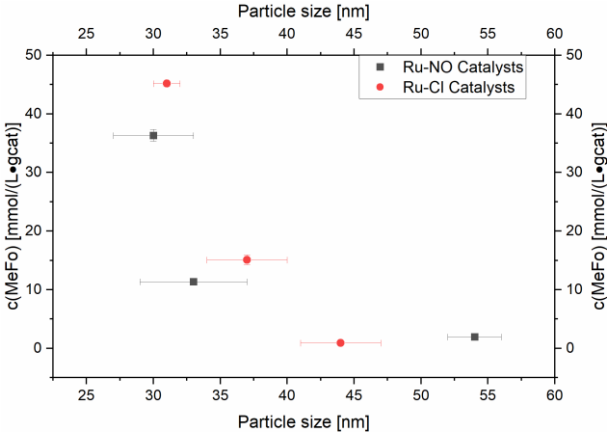

Figure S1: Comparison of particle size and MeFo productivity for the Ru-XX catalysts.

6. Scanning electron microscopy measurements coupled with energy dispersive x-rays

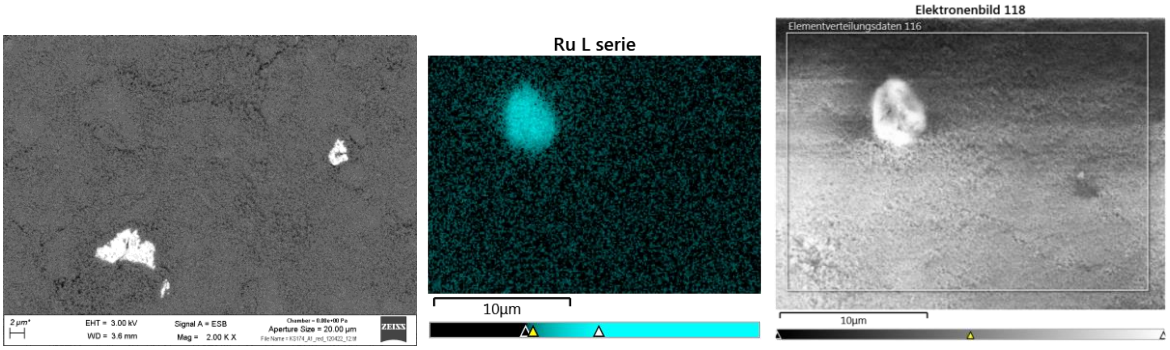

Figure S2: SEM-EDX pictures of Ru-NO-1-icr. catalyst.

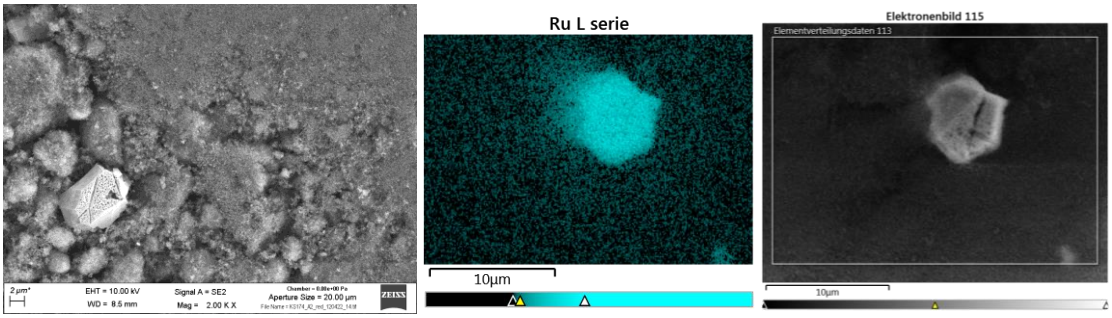

Figure S3: SEM-EDX pictures of Ru-NO-3-icr. catalyst.

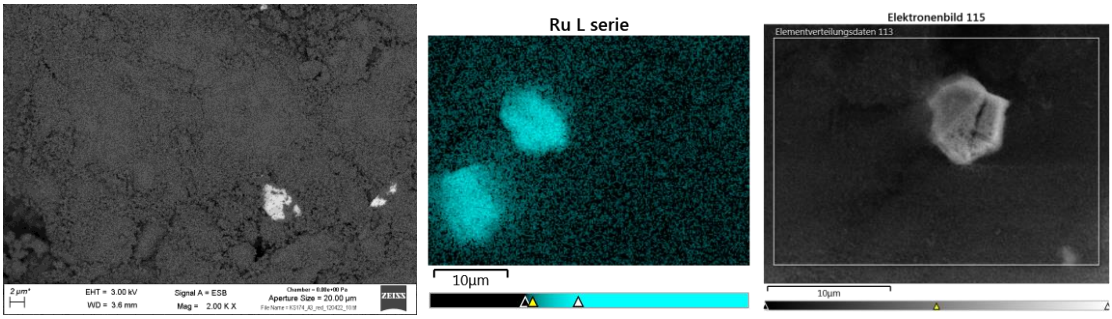

Figure S4: SEM-EDX pictures of Ru-NO-5-icr. catalyst.

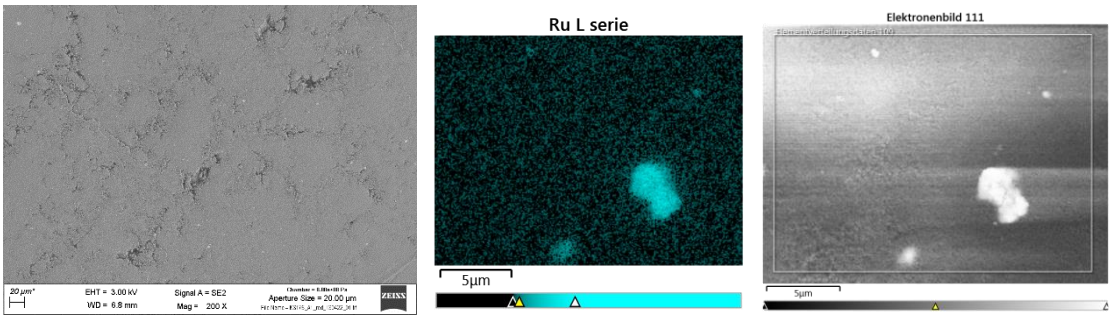

Figure S5: SEM-EDX pictures of Ru-Cl-1-icr. catalyst.

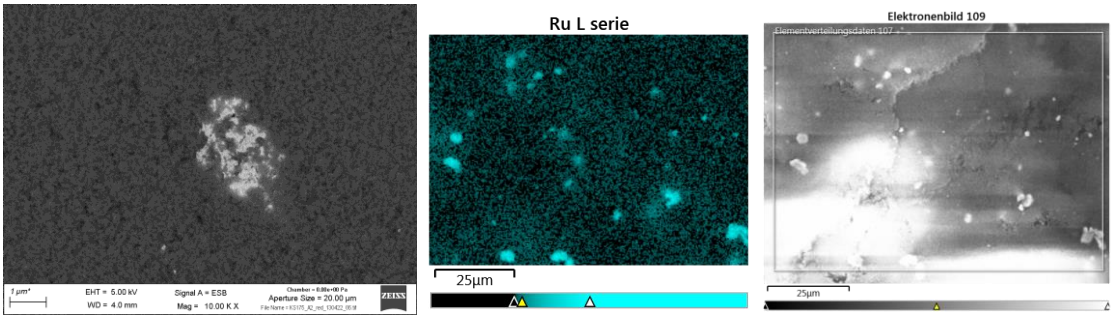

Figure S6: SEM-EDX pictures of Ru-Cl-3-icr. catalyst.

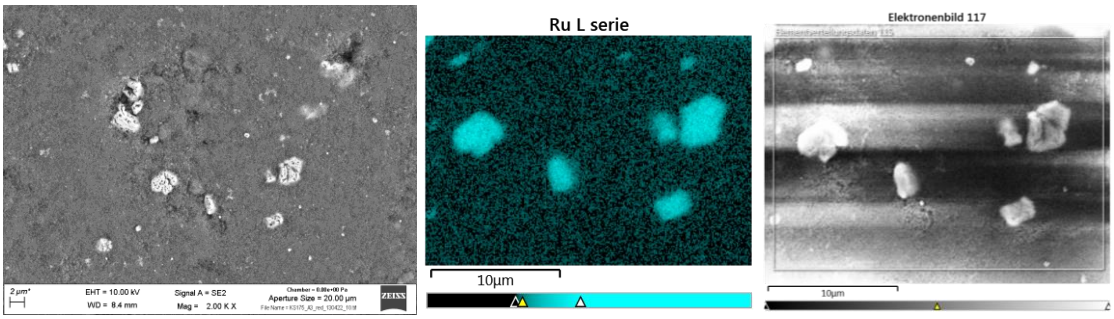

Figure S7: SEM-EDX pictures of Ru-Cl-5-icr. catalyst.

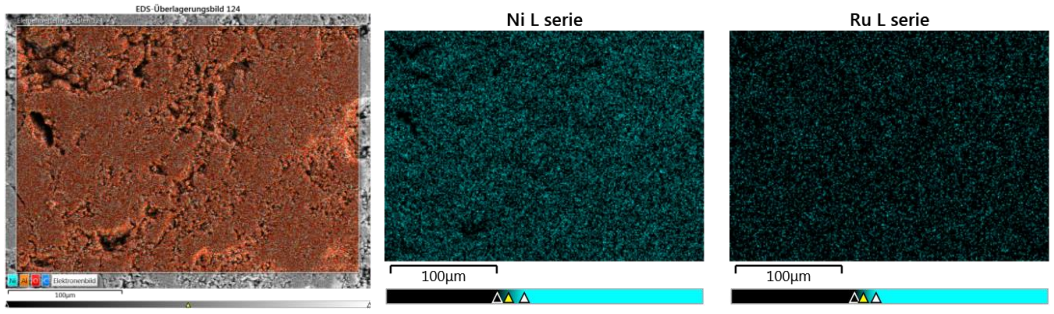

Figure S8: SEM-EDX pictures of RuNi-NO-ir. catalyst.

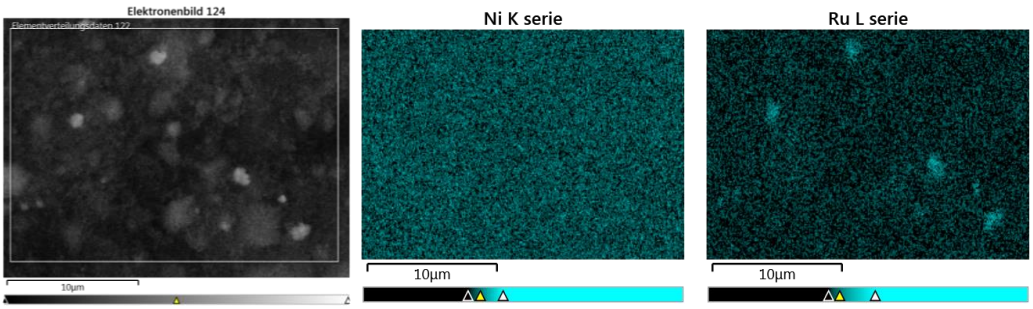

Figure S9: SEM-EDX pictures of RuNi-NO-icr. catalyst.

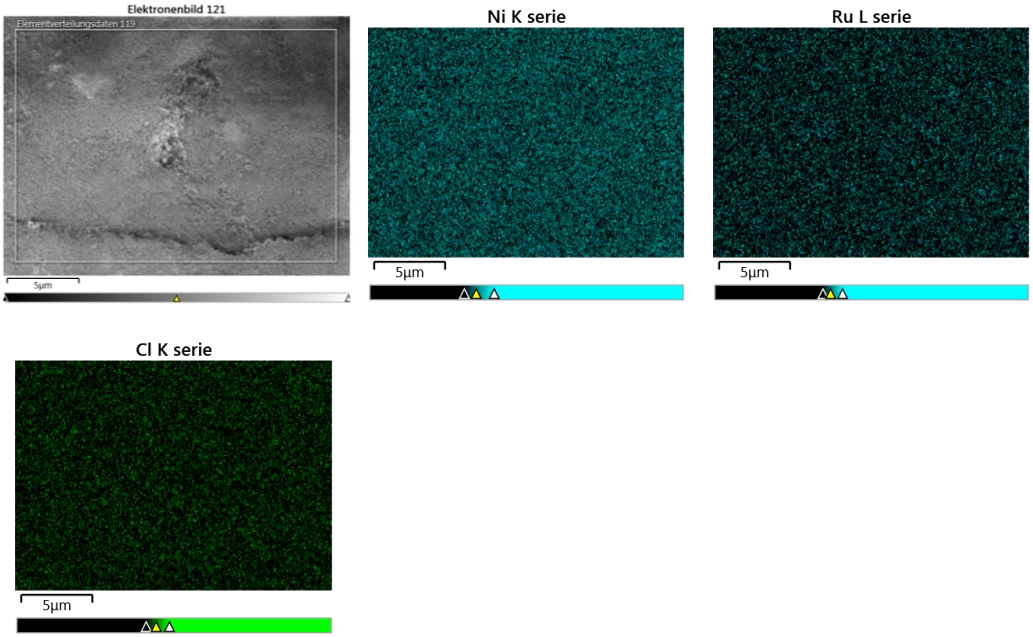

Figure S10: SEM-EDX pictures of RuNi-Cl-ir. catalyst.

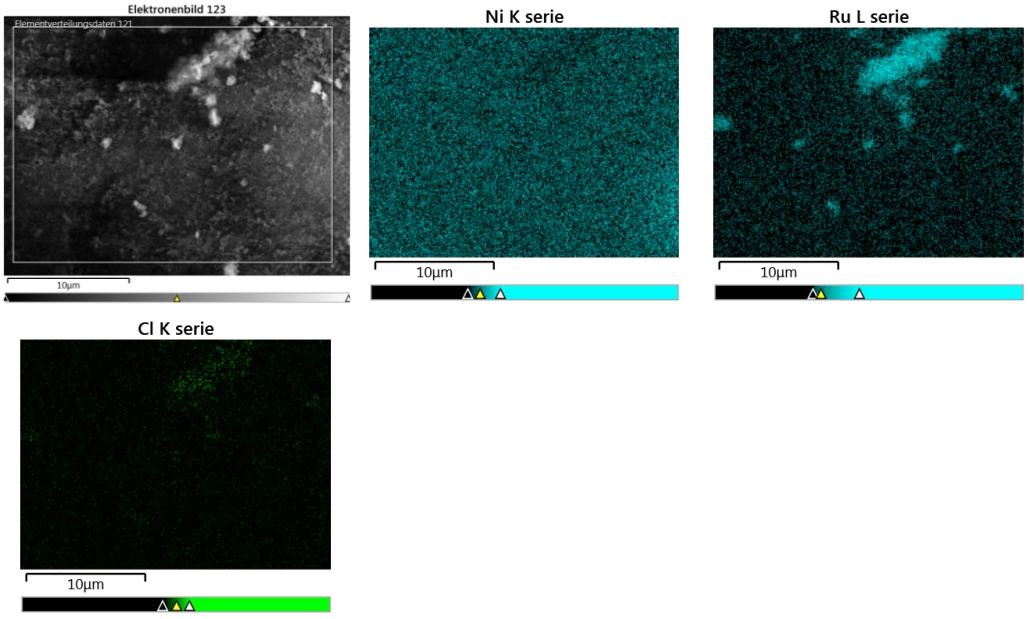

Figure S11: SEM-EDX pictures of RuNi-Cl-icr. catalyst.

7. Catalyst testing & analytics

Figure S12: Pictures of the PASCAR plant used for all catalyst screening experiments and for parameter studies.

Figure S13: Picture of the gas chromatograph used for the off-line analysis of samples.

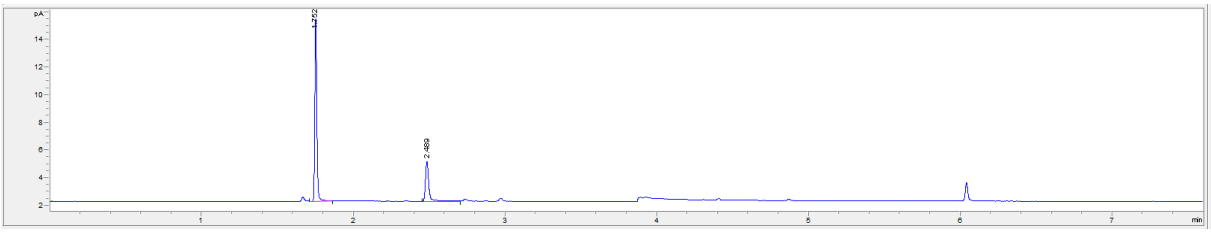

Figure S14: Exemplary chromatogram of a measurement of the CO-Hydrogenation in methanolic media after 24 h with the use of a Ru-NO-3 catalyst. The signal at the retention time of 1.752 min corresponds to Dimethylether, the signal at 2.489 min to Methylformate. The methanol signal is cut out by the use of a Deans Switch during 3.3 to 3.8 min.

GC Method:

==========

Agilent 8890

==========

GC

GC Summary

Run Time 7.6 min

Post Run Time 0 min

Oven

Equilibration Time	0 min
Max Temperature	240 °C
(Initial)	40 °C
Hold Time	2 min
Post Run	110 °C
#1 Rate	25 °C/min
#1 Value	180 °C
#1 Hold Time	0 min

ALS

Front Injector	
Syringe Size	10 µL
Injection Volume	1 µL
Solvent A Washes (PreInj)	5
Solvent A Washes (PostInj)	5
Solvent A Volume	8 µL
Sample Washes	1
Sample Wash Volume	8 µL
Sample Pumps	3
Solvent Wash Draw Speed	150 µL/min
Solvent Wash Dispense Speed	6000 µL/min
Sample Wash Draw Speed	150 µL/min
Sample Wash Dispense Speed	6000 µL/min
Injection Dispense Speed	6000 µL/min
Viscosity Delay	0 sec
L1 Airgap	0.2 µL

Front SS Inlet He

Mode	Split
Heater	On 180 °C

Pressure	On 0
Total Flow	On 133.4 mL/min
Septum Purge Flow	On 3 mL/min
Pre-Run Flow Test	Off
Gas Saver	On 20 After 2 min mL/min
Split Ratio	50 :1
Split Flow	127.84 mL/min
Liner	Agilent 5190-3165: 870 µL (Split, taper, wool, low pressure drop)

PolyArc

Temperature	
Setpoint	On
(Initial)	450 °C

Column #1

Column Information	Agilent 123-7033UI DB-WAX Ultra I
Temperature Range	20 °C—240 °C (240 °C)
Dimensions	30 m x 320 µm x 0.5 µm
In	Front SS Inlet He
Out	Aux EPC 1
(Initial)	40 °C
Pressure	0
Flow	2.5568 mL/min
Average Velocity	33.826 cm/sec
Holdup Time	1.4781 min
Control Mode	Constant Flow
(Initial)	2.5568 mL/min
Post Run	1 mL/min

Column #2

Column Information	Agilent FS, Deactivate
Temperature Range	20 °C—240 °C (240 °C)
Dimensions	2.5 m x 250 µm x 0 µm
Out	Front Detector FID
(Initial)	40 °C
Pressure	0
Flow	4 mL/min
Average Velocity	122.56 cm/sec
Holdup Time	0.033996 min
Control Mode	Constant Flow
Setpoint	On
(Initial)	4 mL/min
Post Run	9.5407 mL/min

Front Detector FID

Makeup	He
Heater	On 250 °C
H2 Flow	On 1.5 mL/min
Air Flow	On 350 mL/min
Makeup Flow	On 25 mL/min
Carrier Gas Flow Correction	Constant Makeup and Fuel FlowFlame
Initial Baseline Minimum	2 pA
Initial Baseline Maximum	20 pA
Initial Baseline Noise	0.3 pA
Final Baseline Minimum	2 pA
Final Baseline Maximum	40 pA
Final Baseline Noise	0.6 pA
Total Peak Area	100 pA*sec
Maximum Peak Height	3 pA
Time Window Start	0 min
Time Window End	0.5333333333 min

==========

Column(s)

==========

Column Description : DB-WAX Ultra I

Inventory# : autoID-2

Model# : 123-7033UI

Manufacturer : Agilent

Diameter : 320.0 µm

Length : 30.0 m

Film thickness : 0.50 µm

Void time : 1.478 min

Maximum Temperature: 240.0 °C

Comment :

Column Description : FS, Deactivate

Inventory# : autoID-3

Model# :

Manufacturer : Agilent

Diameter : 250.0 µm

Length : 2.5 m

Film thickness : 0.00 µm

Void time : 0.034 min

Maximum Temperature: 240.0 °C

Comment :