Experimental data:
Comparing single pulse and pulse series experiments
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Catalyst
Nickel nitrate hexahydrate (Alpha Aeser, 98 wt.-%) was heated in a closed glass flask to dissolve it in its own crystal water. The liquid volume was adjusted with additional water (fully demineralized water, ion exchanger, conductivity < 4 \times 10^{-6} \text{ S/m} ) match with the pore volume of the used support material. As support material Puralox® Al₂O₃-Spheres 0.8/160 (Sasol Germany) with 800 µm diameter and a specific surface area of 160 m² g⁻¹ was used. The support material was dried and kept at 80 °C in ambient air prior to use. Support material and precursor solution were mixed and homogenized at 80 °C in a closed glass flask for 12 h. The water was evaporated slowly at 65 °C in order to fixate the salt inside the pores of the support. The catalyst precursor was decomposed by defined calcination at 300 °C in N₂-flow (99.999 vol%, Linde) for 36 h.

Setup
The experiments were conducted in a catalyst analyzer (BelCat-M, Bel Japan) equipped with two different gas feed lines, as well as a mass spectrometer (GAM200, InProcess Instruments) for transient effluent analysis (Fig. 1a). One feed line (carrier/pretreatment gas) is providing the carrier gas, being either He (99.999 %, Linde) or a mixture of H₂/Ar (Varigon H10, 10 % H₂ in Ar, Linde). The second feed line (pulse gas) allows to choose between three different gases: 1. pure H₂ (99.999 %, Linde), 2. CO in He (9.95 % CO, rest 99.999 % He, Linde), and 3. CH₄ in He (9.96 % CH₄ in 99.999 % He, Linde). The gas flow path through the setup can be controlled by two 6-port valves, which were actuated manually. One valve (valve 1) is used to inject pulses via a 1.012 mL sample loop. The second valve (valve 2) can be used to change the gas line subjected to the catalyst sample. In measurement position the carrier gas is passing the sample, while in pretreatment position the pretreatment gas is in contact to the sample.

Figure 1: a) Schematic of the experimental setup; gas dosing section (left side), two switching valves (grey) to modify the flow path (indicated with colors); b) Sample positioning in the reactor: photograph of the inner tube equipped with a sample and glass wool and depiction of the flow path (left), schematic of the reactor and flow path (right).

The reactor, consisting of two concentric quartz glass tubes (see Fig. 1b), is placed inside an electrical furnace controlled using a thermocouple (type R). The outer tube has an inner diameter of 8 mm and a wall thickness of 1 mm and is closed at the bottom. The catalyst sample is fixed in the inner tube (inner diameter: 5 mm, wall thickness: 1 mm), which is closed at the bottom, too. Gas is supplied via the concentric space between the outer and the inner tube. Therefore, four holes in the wall of the inner tube close to the bottom are introduced to provide the gas flow to pass the sample. The catalyst sample is mounted in between two layers of quartz wool to provide a homogeneous flow distribution. A thermocouple (type K) is placed close to the catalyst through the upper quartz wool layer for temperature measurement of the sample. The mass spectrometer is attached to the reactor ca. 15 cm downstream the sample via a fused silica capillary (50 µm inner diameter) as transfer line heated to 200 °C.

Mass spectrometer configuration
The mass spectrometer operates with a tungsten ion source and with a cathode voltage of 70 V. A secondary electron multiplier, operated at 1200 V, was used to increase sensitivity by a gain of 360. The measurements were done in the mass-ion-detection mode with an overall measurement duration of 1 s for each time step. Six different ion masses were observed. Main masses were used for H₂ (2 amu), He (4 amu), H₂O (18 amu), CO (28 amu) and CO₂ (44 amu). For CH₄ the fragment at 15 amu was used. Since the mass ion detection mode is not a quantitative measurement, CO and CH₂ were calibrated with respect to the internal standard He by using named test gas mixtures.
**Experimental method:**

All experiments were performed at atmospheric pressure. For activation the calcined catalyst was reduced in a 40 mL min$^{-1}$ pure H$_2$-flow (99.999 %, Linde) at 350 °C for 12 h. After reduction the samples were degassed at 400 °C in He for one hour. Afterward, the catalyst was flushed the carrier gas H$_2$/Ar (33 mL$_{STP}$ min$^{-1}$) for 10 min. After stabilization of the MS signal the pulse reaction experiments were started.

Pulse reaction experiments were performed with an equilibration time ($dT / dt < 0.1$ K min$^{-1}$) at the desired temperature of the sample, which was monitored by the thermocouple in the reactor. The sample loop with CO/He pulse gas containing 4 µmol CO was injected in 33 mL$_{STP}$ min$^{-1}$ H$_2$/Ar carrier gas stream after 70 s. 15 minutes after the first injection, a pulse series of 20 pulses was injected with an injection interval of 60 s. The signals of the MS and the thermocouple were recorded for 45 min in total.
Data set:
The data sets are given as csv-data file. The name of the data set contains the following information: '[temperature in °C]_[catalyst mass in mg]', where the temperature is the equilibrated temperature. The measurements of the data set were conducted with a 5 wt.-% catalyst. No temperature change was monitored during the experiments.
The data points are given with the following columns (divided in primary and secondary data):

**Primary data**
RelTime / s: relative time in s, since the beginning of the measurement
H2 (2): ion current in A for mass 2
He (4): ion current in A for mass 4
CH4 (15): ion current in A for mass 15
H2O (18): ion current in A for mass 18
CO (28): ion current in A for mass 28
CO2 (44): ion current in A for mass 44

**Secondary data**
E_He: Residence time distribution of He in s⁻¹
Y_CH4 E_CH4: Normalized residence time distribution of CH4 in s⁻¹, normalized by the yield with reference to the injected amount of CO
E_H2O: Residence time distribution of H2O in s⁻¹
(1-X) E_CO: Normalized residence time distribution of CO in s⁻¹, normalized by the residual fraction, being: \( f = 1 - X \), with the conversion X
E_CO2: Residence time distribution of CO2 in s⁻¹
E_H2: Virtual residence time distribution of H2 in s⁻¹, actually the time distribution of the H2 replacement and consumption induced by the pulse
C-balance/%: carbon balance based on CO and CH4 in 1, value is calculated from \( Y_{CH_4} + X_{CO} \)
O-balance/%: oxygen balance based on CO and H2O in 1, value is calculated from \( Y_{H_2O} + X_{CO} \)