CO_2 hydrogenation on Ruthenium: Comparative study of catalyst supports: Supplementary Information

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1. EXPERIMENTAL SETUP

The screening experiments are conducted in an automated setup, the P&ID flowsheet of which is shown in Fig.(S1).

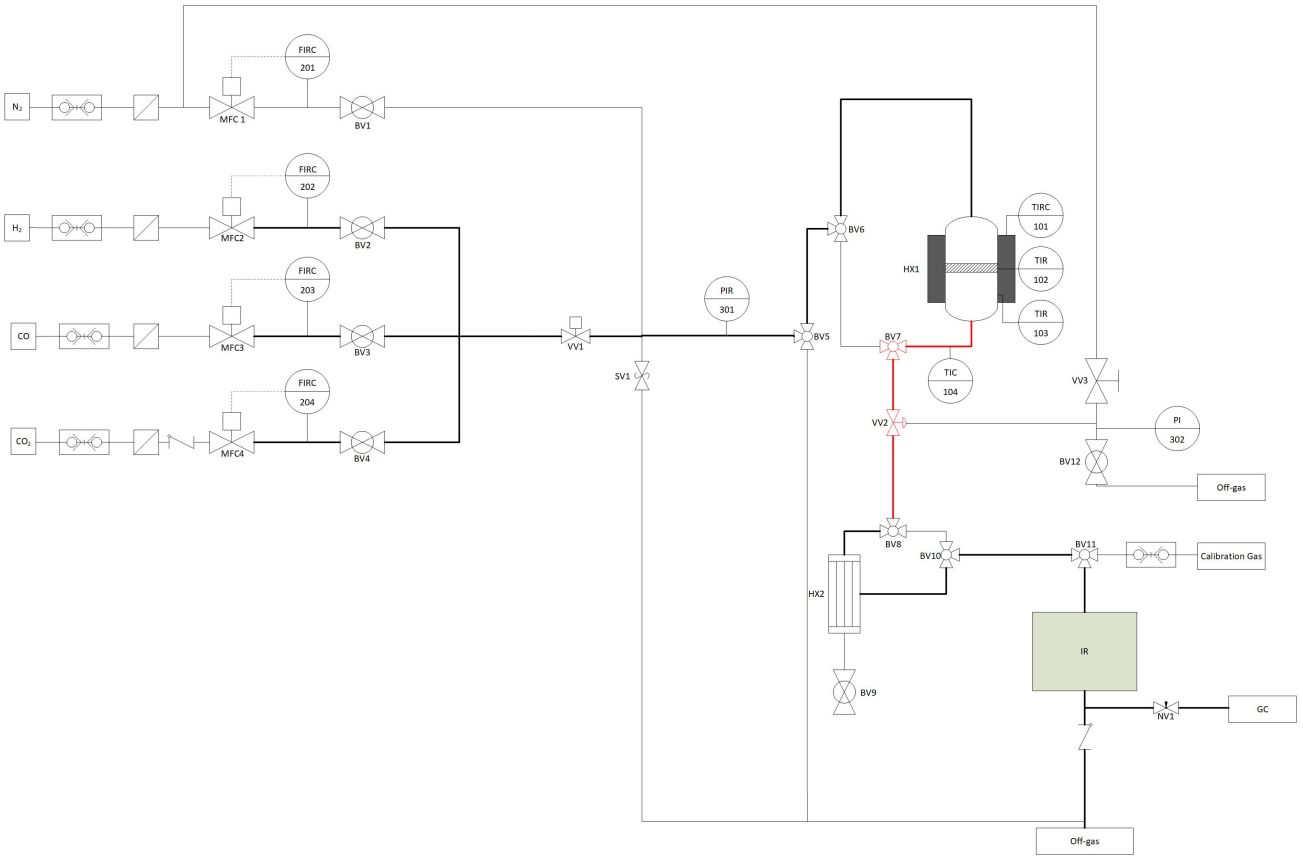

Fig. S1. P&ID flowsheet of the setup for screening experiments. Thicker lines indicate main process stream, red lines indicate pipes heated to 120°C.

The kinetic experiments are conducted in the same reactor in a different setup. The P&ID flowsheet for the setup in which the kinetic experiments are conducted is shown in Fig. (S2).

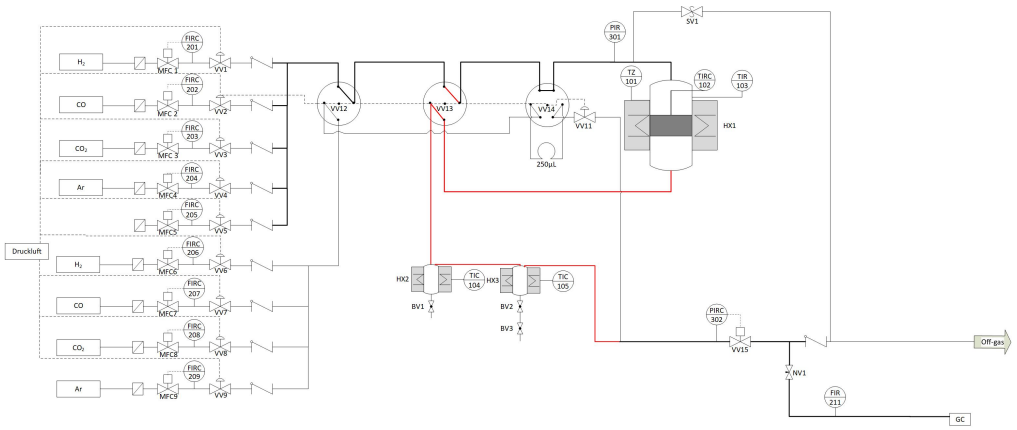

Fig. S2. P&ID flowsheet of plant for kinetic experiments. Thicker lines indicate main process stream, red lines indicate pipes heated to 120°C.

The reactor setup is identical in both plants. The 30 cm tubular reactor made of stainless steel is evenly heated by two aluminium half-jackets of 20 cm length with an inner diameter of 1/4 inch and an outer diameter of 6 cm. Four heating cartridges are built into the aluminium jacket, one of which is manufactured with a built-in K-type thermocouple. On the inner side of one of the half-jackets a 1 mm kerf is used to place a 1 mm K-type thermocouple at the interface between the heating jacket and the outer reactor wall. The two heating jackets are clamped together and insulated by aluminium laminated mineral wool.
The upstream end of the reactor tube consists of a T-piece. The end connected to the reactor tube and the perpendicular end are 1/4 inch iso-threads tightened with ferrules. The and axial to the reactor tube is a 1/4 inch female NPT-threading into which a straight 1/4 inch male-NPT to 1/16 inch iso-thread connector is set. The 1/16 inch is-thread is used to lead a sealed tube through the whole length of the reactor to be able to place a K-type thermocouple in the center of the catalyst bed.

2. ADDITIONAL CHARACTERIZATION

A. Physisorption Isotherms

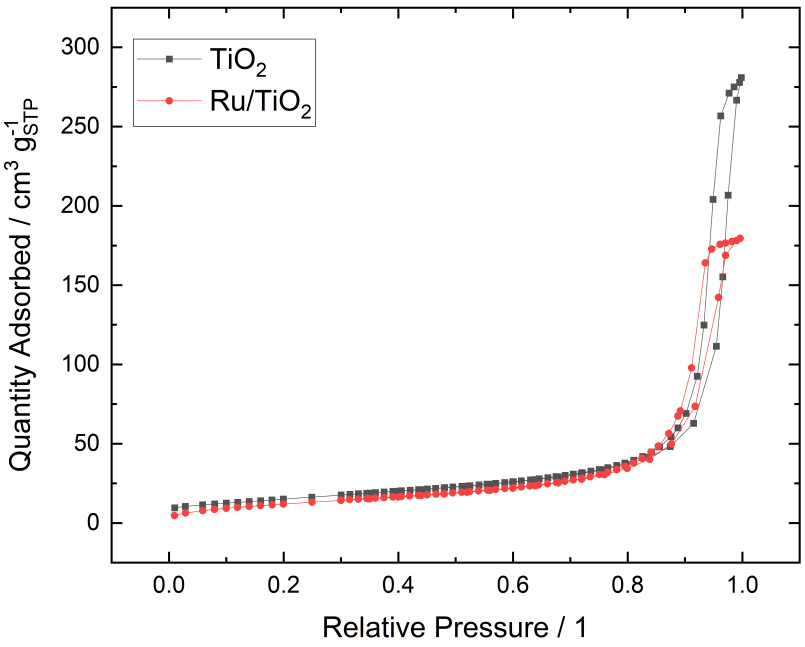

Fig. S3. Physisorption isotherms of fresh TiO_2 support and Ru/TiO_2 catalyst.

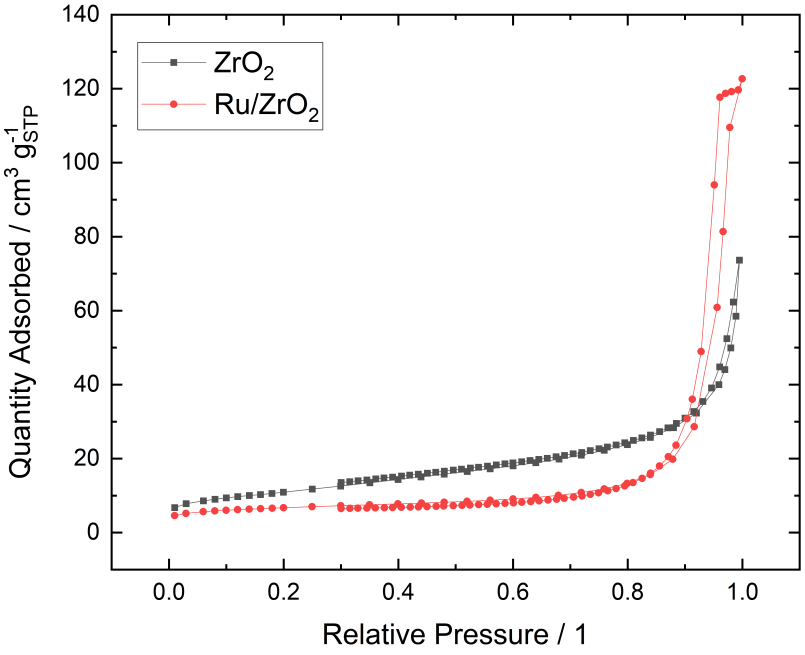

Fig. S4. Physisorption isotherms of fresh ZrO_2 support and Ru/ZrO_2 catalyst.

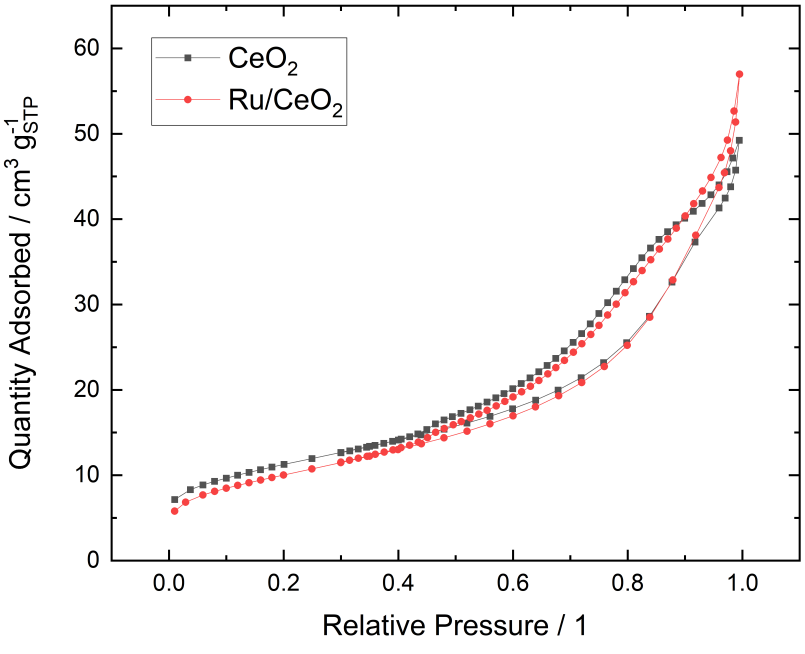

Fig. S5. Physisorption isotherms of fresh CeO_2 support and Ru/CeO_2 catalyst.

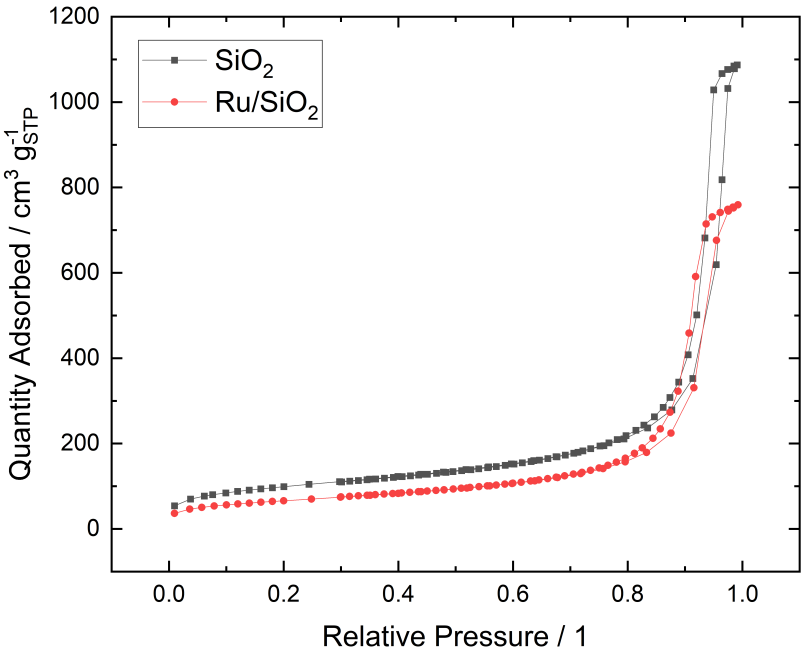

Fig. S6. Physisorption isotherms of fresh SiO_2 support and Ru/SiO_2 catalyst.

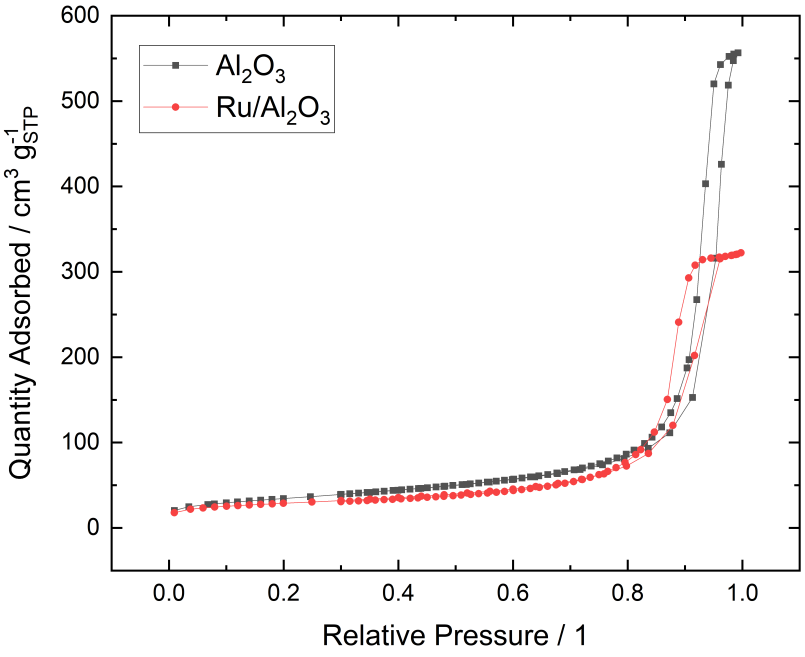

Fig. S7. Physisorption isotherms of fresh Al_2O_3 support and Ru/Al_2O_3 catalyst.

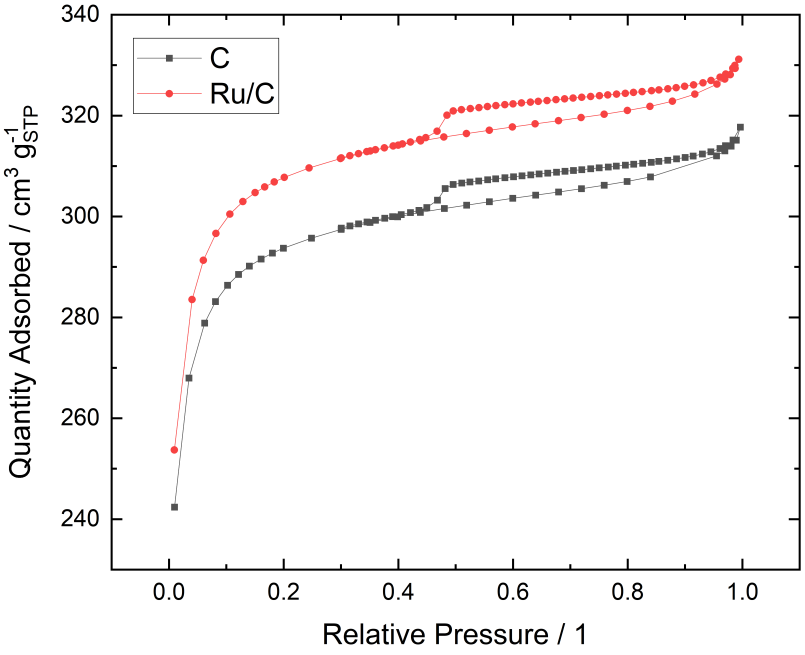

Fig. S8. Physisorption isotherms of fresh C support and Ru/C catalyst.

B. TEM Images

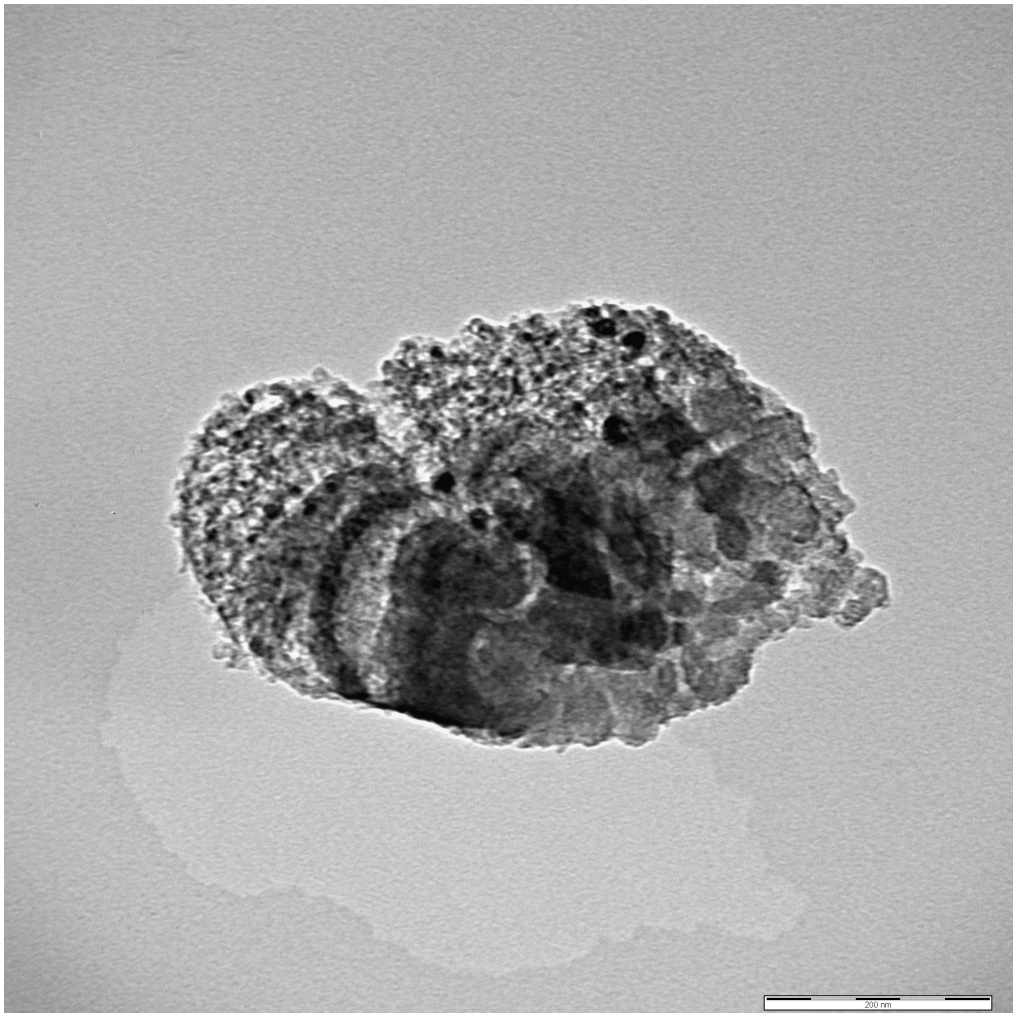

Fig. S9. Representative TEM image of Ru/TiO_2 catalyst.

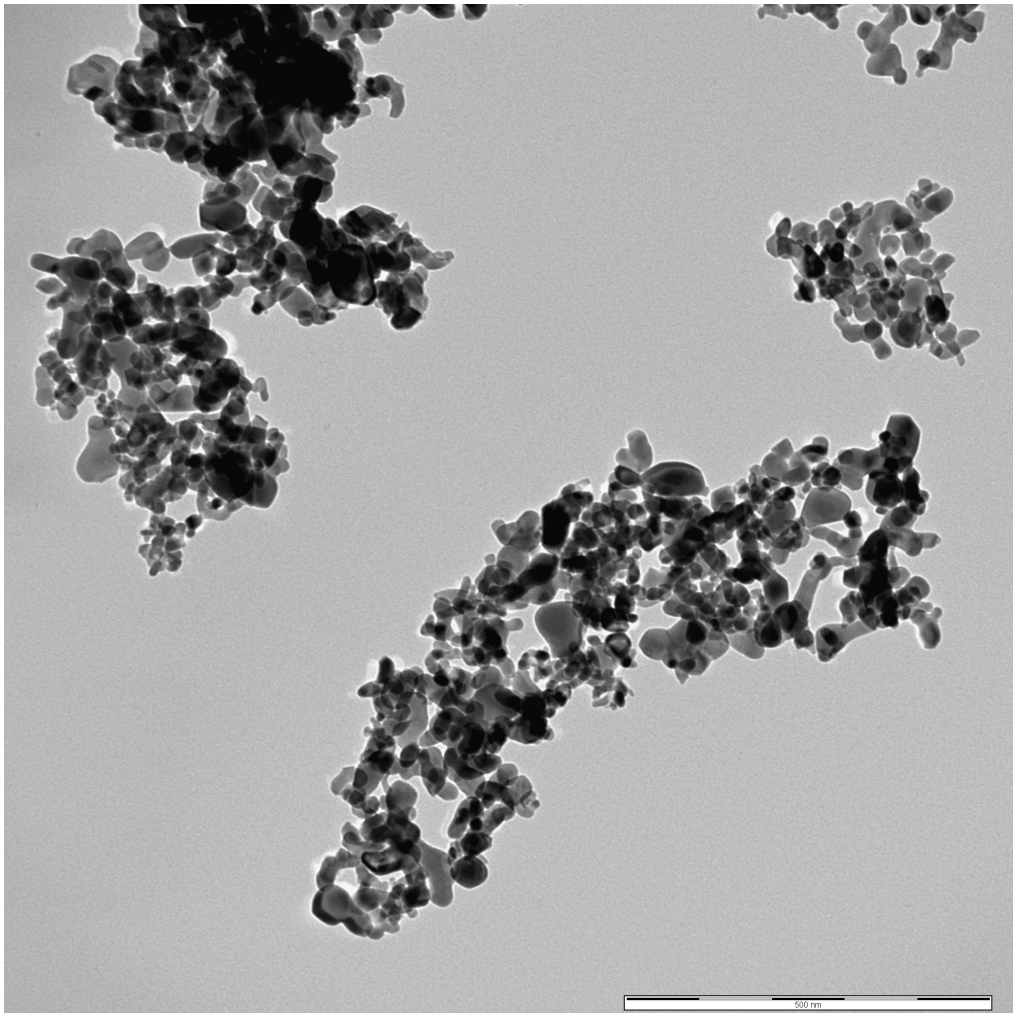

Fig. S10. Representative TEM image of Ru/ZrO_2 catalyst.

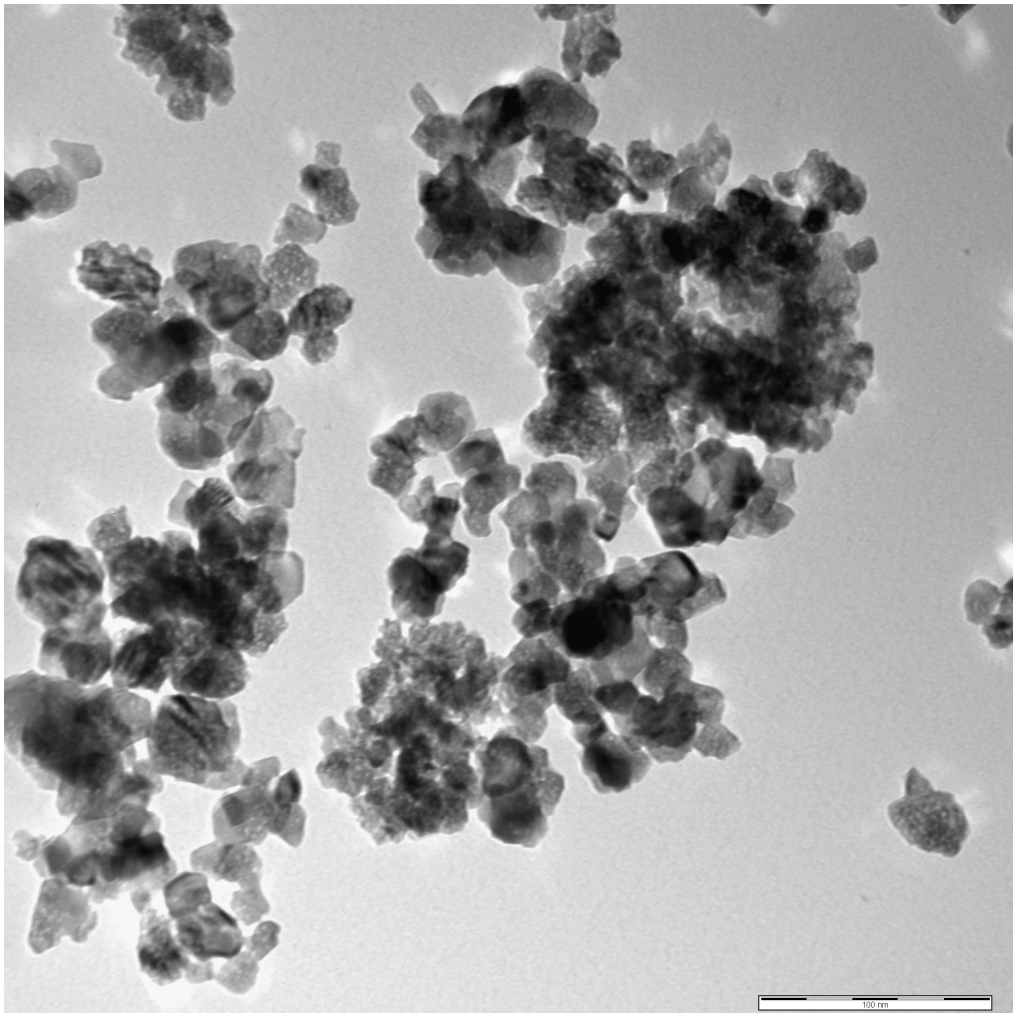

Fig. S11. Representative TEM image of Ru/CeO_2 catalyst.

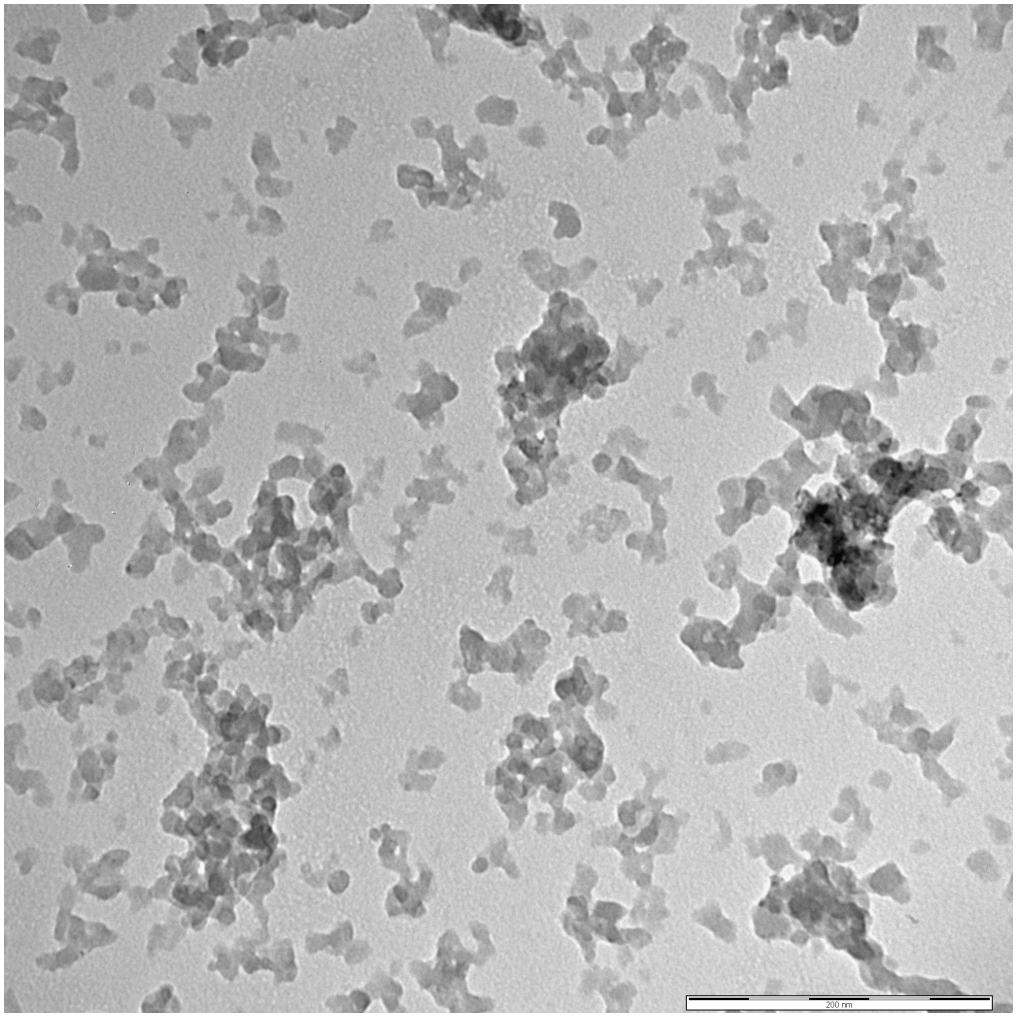

Fig. S12. Representative TEM image of Ru/SiO_2 catalyst.

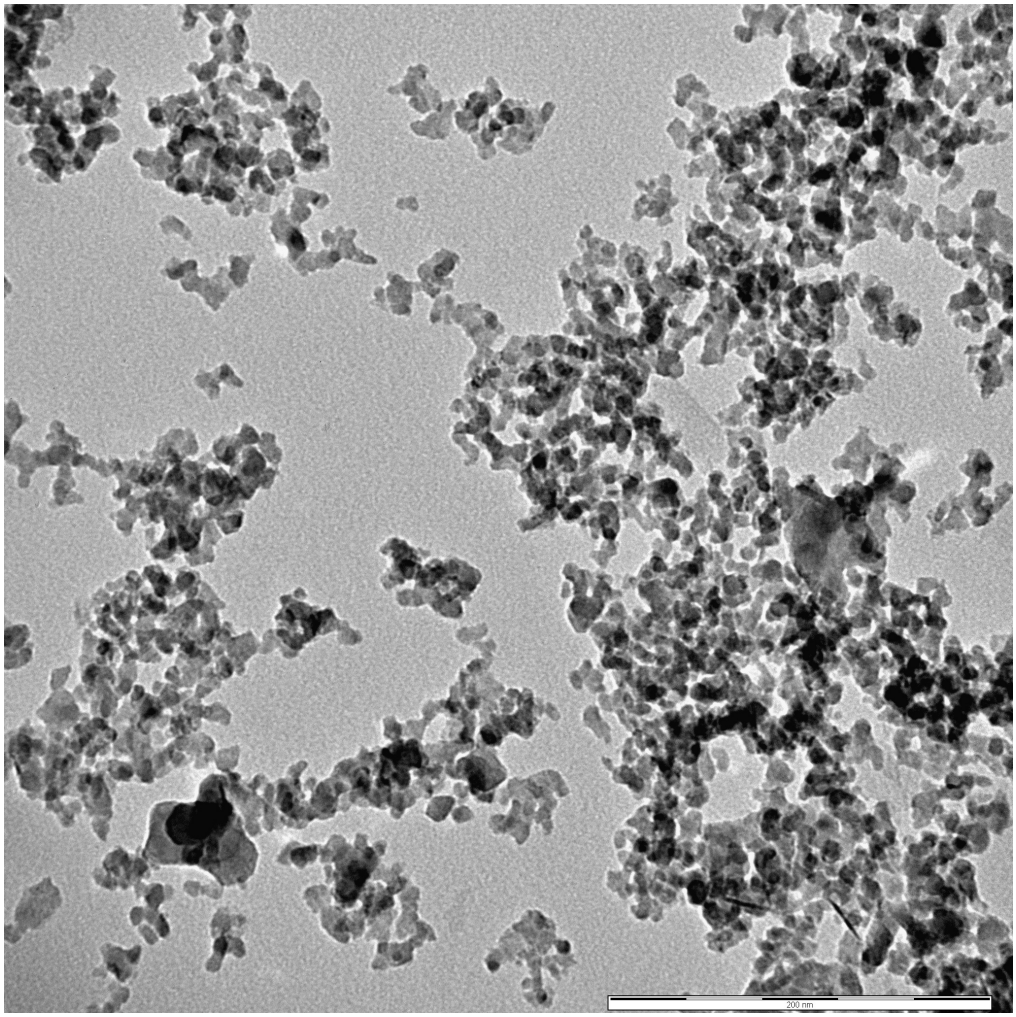

Fig. S13. Representative TEM image of Ru/Al_2O_3 catalyst.

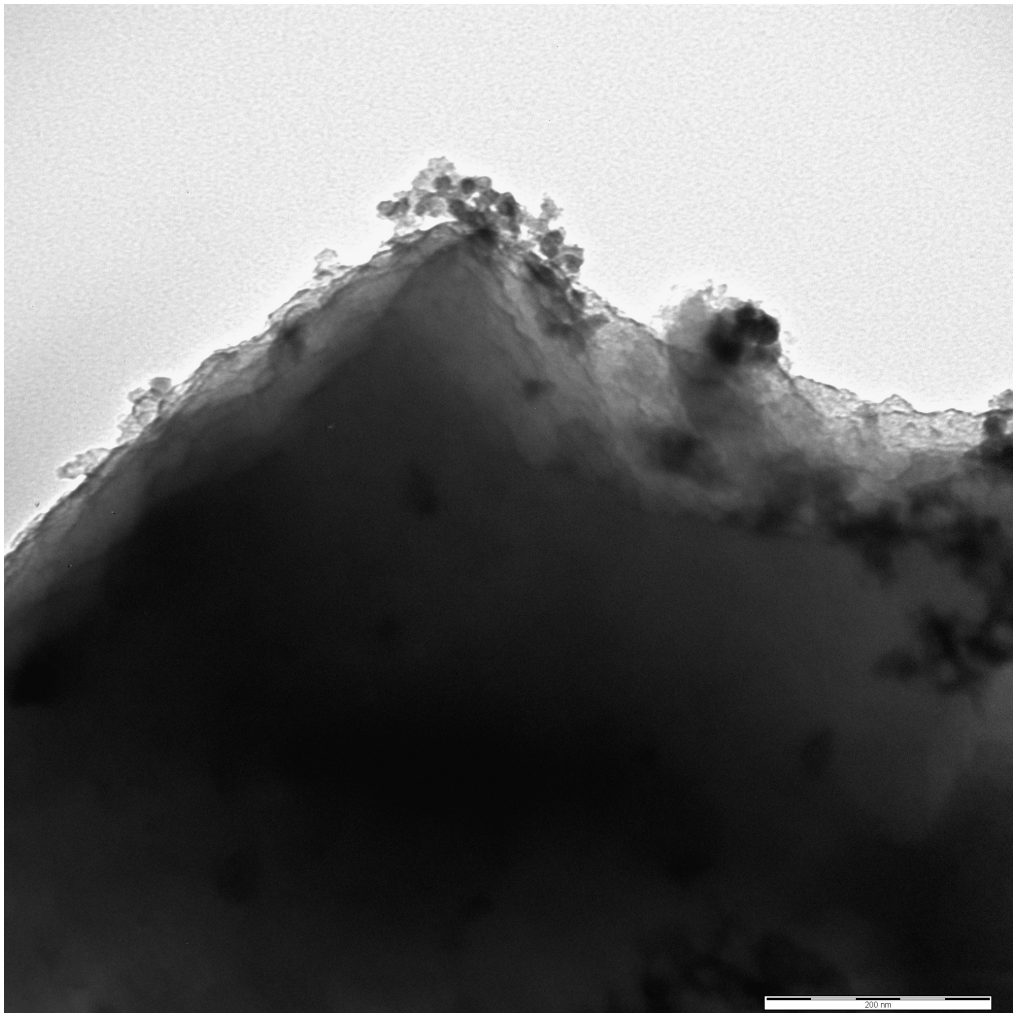

Fig. S14. Representative TEM image of Ru/C catalyst.

C. XRD Data

As no significant peaks associated with Ruthenium are detected, all XRD-Signals are normalized according to:

$$Y_{Norm}(x) = \frac{Y(x)}{Y_{max}} \tag{S1}$$

Thid allows an easy comparison of all materials.

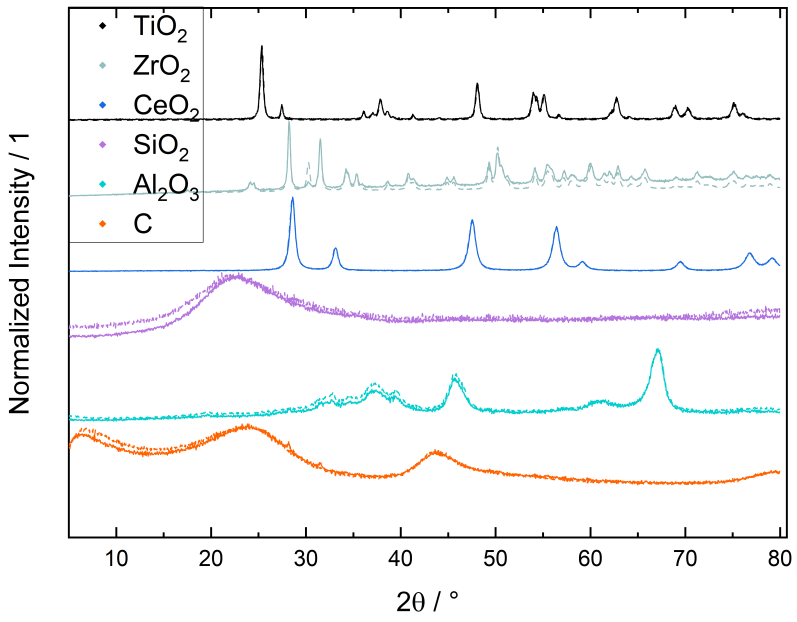

Fig. S15. Normalized Intensities of Diffraction of fresh supports (dashed lines) and catalysts (solid lines)

3. ADDITIONAL DATA

The following tables show additional data from the screening experiments. The CH_4 selectivity for all catalysts under all operating points is shown in Tab. (S1). The

Table S1. Methane selectivity in percent for all catalysts under all operating conditions

Catalyst	B	C	D	E	F	G	H	I	J	K
Ru/TiO_2	97	96	96	97	97	97	97	95	98	98
Ru/ZrO_2	97	96	96	97	97	97	97	94	98	97
Ru/CeO_2	44	32	37	43	53	42	47	45	57	53
Ru/Al_2O_3	97	93	97	98	98	98	96	97	97	96
Ru/SiO_2	99	98	99	99	99	99	99	99	99	99
Ru/C	83	87	95	73	67	62	77	54	85	73

selectivity to higher hydrocarbons for all catalysts under all operating points is shown in Tab. (S2). The CO selectivity for all catalysts under all operating points is shown in Tab. (S3). The CO_2 conversion for all catalysts under all operating points is shown in Tab. (S4).

Table S2. Selectivity to higher hydrocarbons in percent for all catalysts under all operating conditions

Catalyst	B	C	D	E	F	G	H	I	J	K
Ru/TiO_2	3	4	4	3	3	3	3	5	2	2
Ru/ZrO_2	3	4	4	3	3	3	3	6	2	3
Ru/CeO_2	6	9	7	5	4	5	8	6	10	9
Ru/Al_2O_3	3	7	3	2	2	2	4	3	3	4
Ru/SiO_2	1	2	1	1	1	1	1	1	1	1
Ru/C	3	13	5	4	2	4	3	4	4	3

Table S3. CO Selectivity in percent for all catalysts under all operating conditions

Catalyst	B	C	D	E	F	G	H	I	J	K
Ru/TiO_2	0	0	0	0	0	0	0	0	0	0
Ru/ZrO_2	0	0	0	0	0	0	0	0	0	0
Ru/CeO_2	50	59	56	52	43	53	45	49	33	38
Ru/Al_2O_3	0	0	0	0	0	0	0	0	0	0
Ru/SiO_2	0	0	0	0	0	0	0	0	0	0
Ru/C	14	0	0	23	31	34	20	42	11	24

Table S4. CO_2 conversion in percent for all catalysts under all operating conditions

Catalyst	B	C	D	E	F	G	H	I	J	K
Ru/TiO_2	7.39	1.48	3.47	7.10	13.71	6.77	8.97	3.90	13.08	8.64
Ru/ZrO_2	6.66	0.77	2.43	6.64	17.89	7.29	10.2	2.86	17.05	10.53
Ru/CeO_2	0.32	0.05	0.12	0.30	0.73	0.29	0.35	0.17	0.48	0.33
Ru/Al_2O_3	0.67	0.09	0.36	0.80	1.67	0.84	0.85	0.48	1.51	0.71
Ru/SiO_2	0.3	0.05	0.16	0.44	1.13	0.53	0.73	0.36	1.10	0.78
Ru/C	0.09	0.01	0.03	0.10	0.27	0.10	0.12	0.06	0.16	0.12