Supporting Information for

TiH_2-supported Ru catalyst with unusual electron transfer behaviour for highly efficient carbon dioxide methanation at low temperature

Zhujie He,[†a] Huanfeng Huang,[†a] Zhuodi Chen,[a] Yuqian Liang,[a] Zhixiang Huang,[a] Shunnian Ning,[a] Lilin Tan,[b] Mihail Barboiu,[a,c] Dawei Wang *[a] and Cheng-Yong Su[a]

[a] Lehn Institute of Functional Materials, MOE Laboratory of Bioinorganic and Synthetic Chemistry, School of Chemistry, Sun Yat-Sen University, Guangzhou 510275, China

[b] Chemistry and Chemical Engineering Guangdong Laboratory, Shantou 515031, China

[c] Institut Europeen des Membranes, Adaptive Supramolecular Nanosystems Group, University of Montpellier, ENSCM-CNRS, Place E. Bataillon CC047, 34095 Montpellier, France

[†] These authors contributed equally to this work

Corresponding Author

E-mail: wdawei@mail.sysu.edu.cn

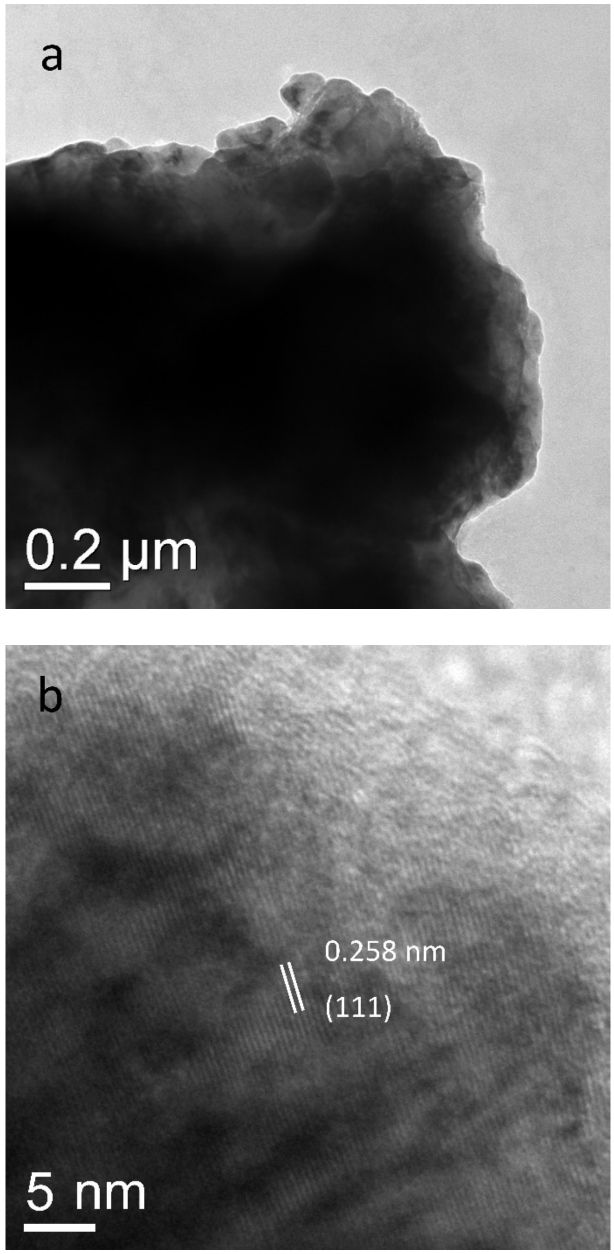

Fig. S1 TEM images of TiH_2 at different magnification.

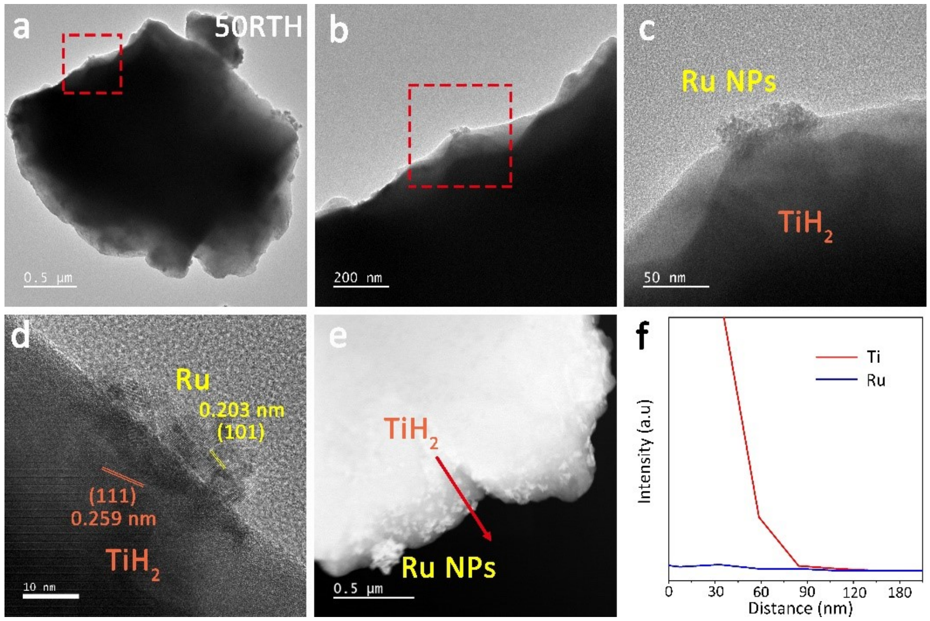

Fig. S2 Interfacial structure of 50RTH. (a–c) TEM images, (d) HRTEM image, (e) STEM image, and (d) EDS line scans.

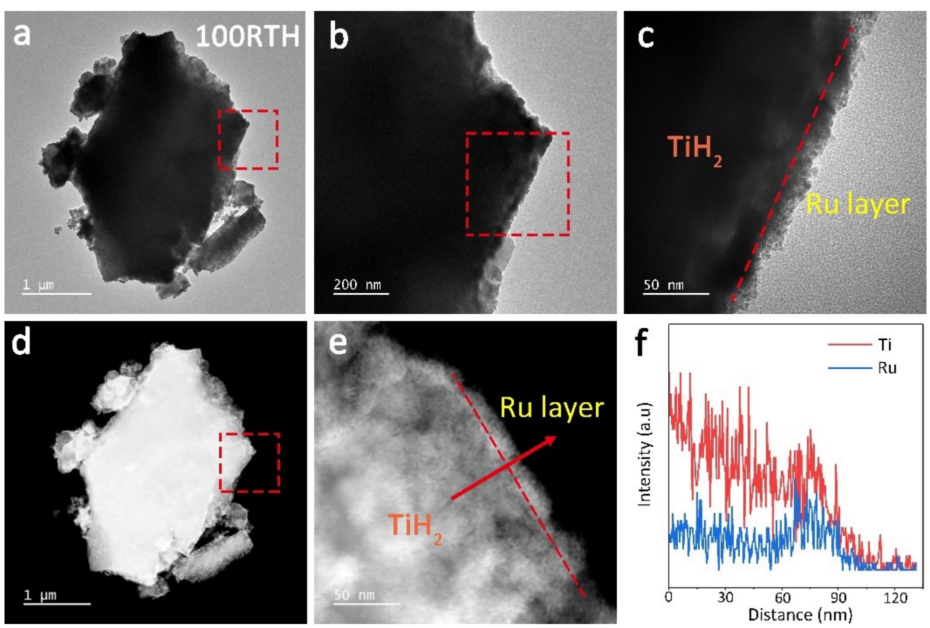

Fig. S3 Interfacial structure of 100RTH. (a–c) TEM images, (d) HRTEM image, (e) STEM image, and (d) EDS line scans.

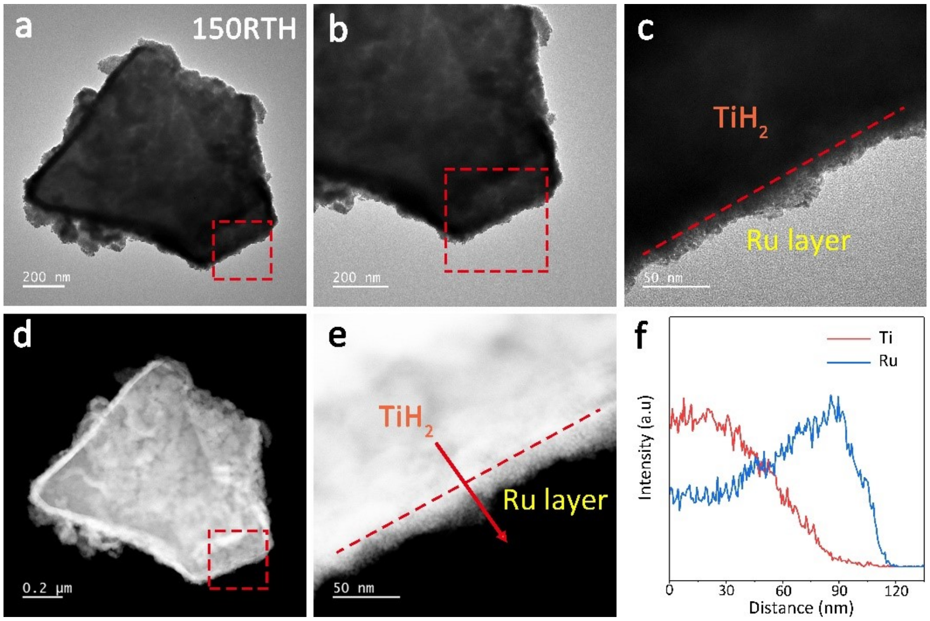

Fig. S4 Interfacial structure of 150RTH. (a–c) TEM images, (d) HRTEM image, (e) STEM image, and (d) EDS line scans.

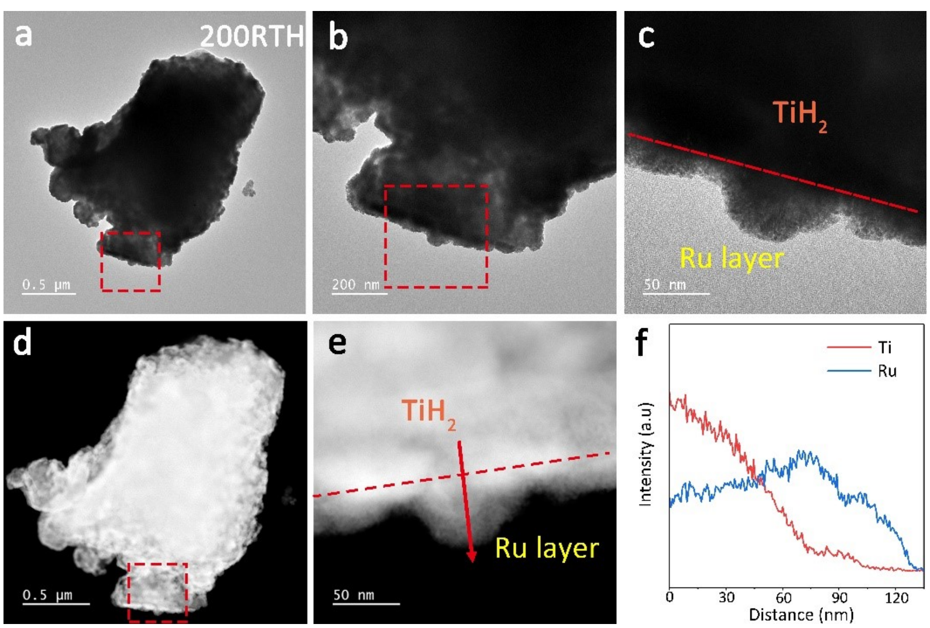

Fig. S5 Interfacial structure of 200RTH. (a–c) TEM images, (d) HRTEM image, (e) STEM image, and (d) EDS line scans.

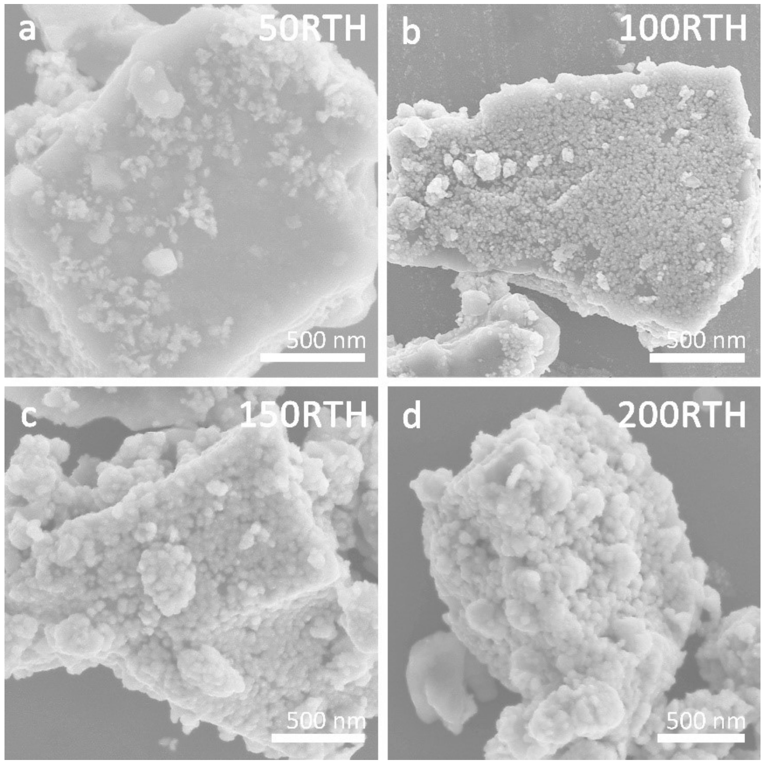

Fig. S6 SEM images of (a) 50RTH, (b) 100RTH, (c) 150RTH, and (d) 200RTH.

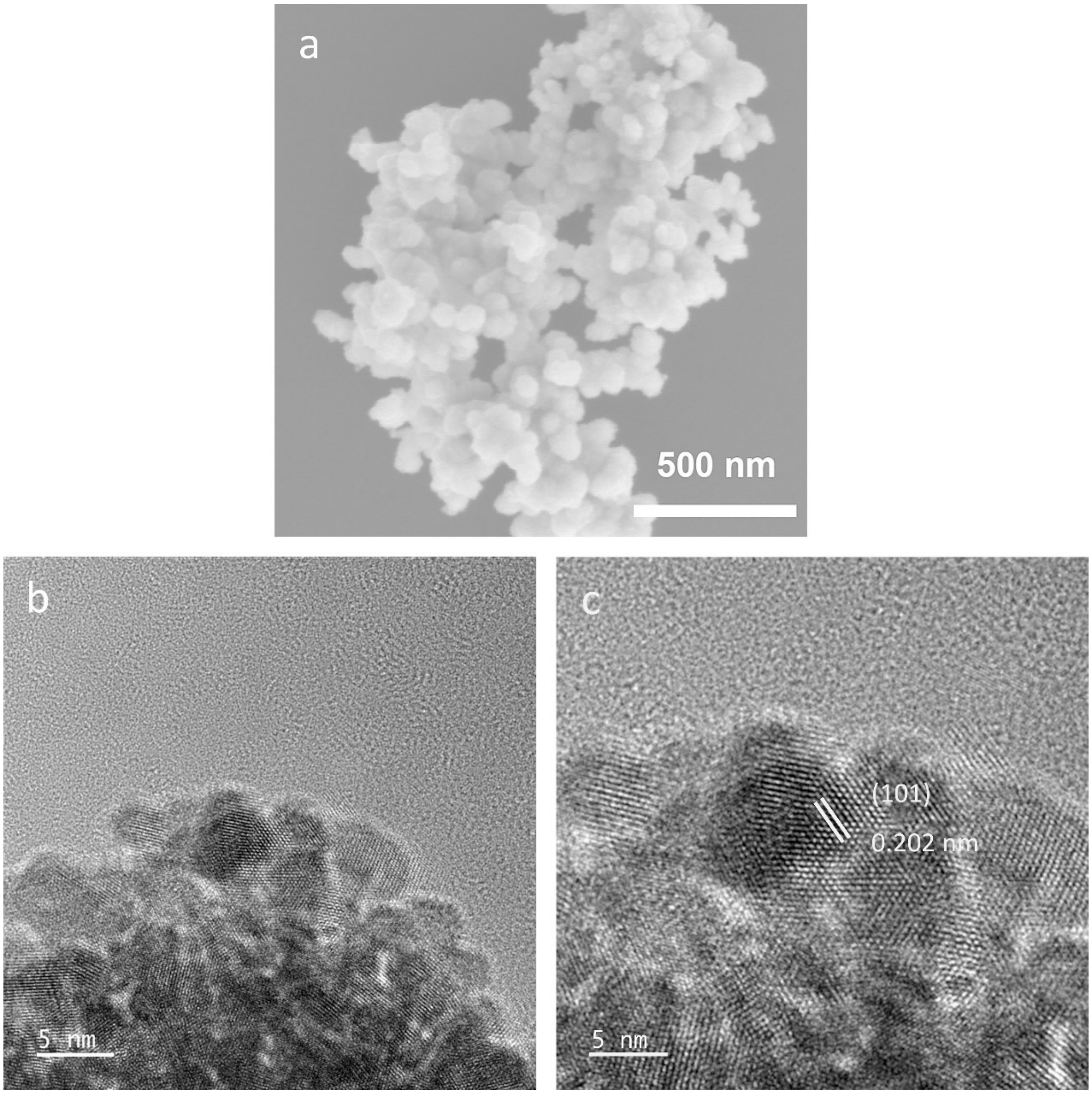

Fig. S7 (a) SEM, (b) TEM, and (c) HRTEM images of Ru NPs.

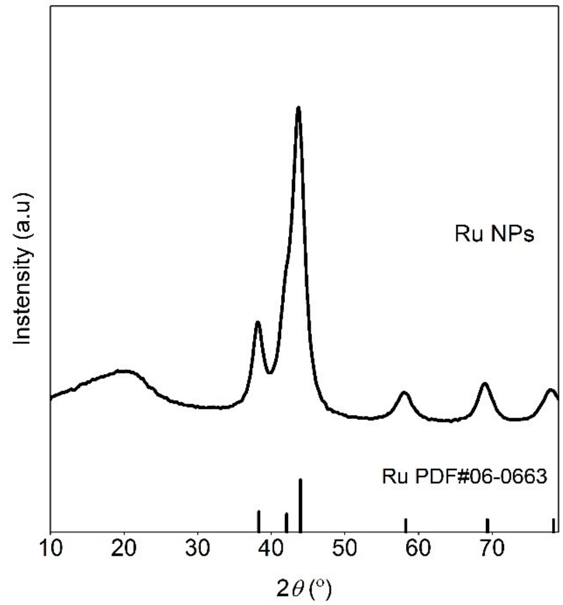

Fig. S8 XRD patterns of Ru NPs.

Diffraction peaks at 2θ = 38.4, 42.2, 44.0, 58.3, 69.4 and 78.4° are indexed to the (100), (002), (101), (102), (110), and (103) lattice planes of hexagonal ruthenium, respectively.

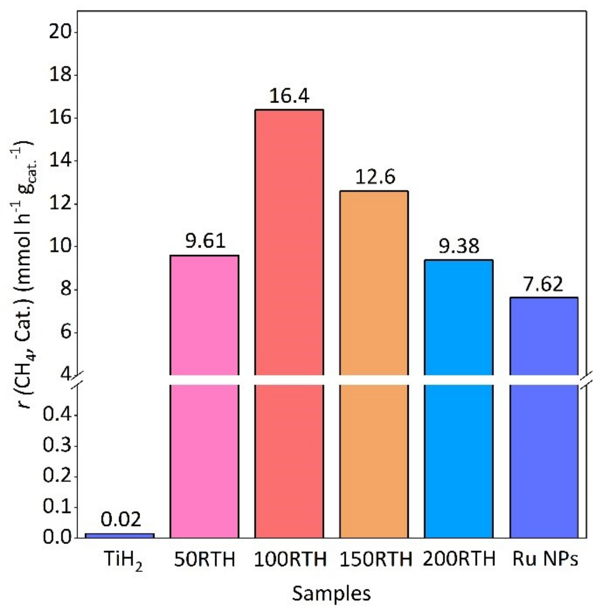

Fig. S9 Production rate of CH_4 based on the total mass of catalysts.

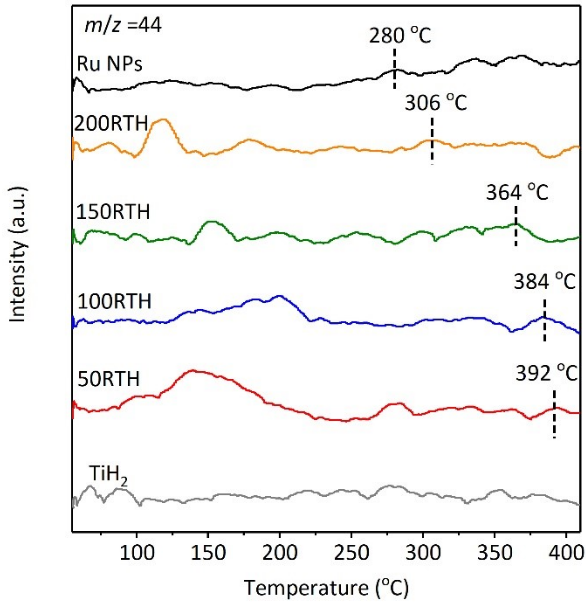

Fig. S10 Mass spectrometer signals for CO_2 (m/z = 44) during temperature-programmed desorption measurement for *m*RTH and control catalysts.

Table S1. Element analysis of *m*RTH based on ICP measurements.

Samples	Ti (wt. %)	Ru (wt. %)
50RTH	85.17	5.72
100RTH	82.38	9.76
150RTH	74.96	15.54
200RTH	72.89	17.35

Table S2. Contact potentials from KPFM measurements shown in Figure 3.

Samples	Absolute contact potential (mV)		
	E_{sample} (mV)	$E_{substrate}$ (mV)	ΔCPD (mV)
TiH_2	-415	-407	-8.0
50RTH	-110	-112	2.0
100RTH	-93.6	-120	26.4
150RTH	-46.6	-84.0	37.4
200RTH	-92.2	-161	68.8

Table S3. Binding energies of XPS peaks shown in Figure 4a-b.

Samples	Binding energy (eV)			
	Ti^{4+} $2p_{3/2}$	TiO_{2-x} $2p_{3/2}$	Ru^{4+} $3d_{5/2}$	Ru^{0} $3d_{3/2}$
TiH_2	458.22	457.92	/	/
50RTH	458.34	457.93	280.30	279.52
100RTH	458.82	458.35	280.33	279.73
150RTH	458.83	458.42	280.45	279.77
200RTH	459.38	458.63	280.50	279.83
Ru NPs	/	/	280.63	279.90

Table S4. Performance comparison between *m*RTH and others Ru-based catalysts reported in literature.

Catalysts	**Temperature** °C	**Pressure**	**CO_2 conversion** %	**CO_2 Selectivity** %	**CH_4 Production Rate**	**References**
100RTH	**200**	**4 bars** **$CO_2:H_2$ = 1:4**	**86.4**	**99.8**	**168.7** **(mmol g_{Ru}^{-1} h^{-1})**	**This work**
5%Ru/TiO_2-P25-450	200	1 atm $CO_2:H_2$ = 1:4 20 mL/min	27.4	100	9.25 (mmol g_{Ru}^{-1} h^{-1})	*Catal. Sci. Technol.*, 2016, 6, 8117
Ru/TiO_2	400	1 atm 10%CO_2/40% H_2/50%Ar 40 mL/min	75	~97	78.48 (mmol $g_{cat.}^{-1}$ h^{-1})	*Appl. Surf. Sci.*, 2022, 587, 152856
Ru/TiO_2-200Air-300R	200	0.1 MPa $H_2/CO_2/N_2$ = 70/20/10 GHSV = 60 000 mL h^{-1} g_{cat}^{-1}	4.05	100	3.47 $mmol_{CO2}$ g_{Ru}^{-1} h^{-1}	*ACS Catal.* 2022, 12, 1697

Ru/CeO_2	250	CO_2 (15%,v/v) H_2 (60%, v/v) Ar (25%, v/v) 40 mL/min	92.7		4.032 mmol $g_{cat.}^{-1}$ h^{-1}	*J. Am. Chem. Soc*. 2016, 138, 6298
Ru(3%)/CeO_2-NCs	150	CO_2 (15%, v/v) H_2 (60%, v/v) Ar (25%, v/v) 40 mL/min	<10	>99	0.17 mmol $g_{cat.}^{-1}$ h^{-1}	*J. Catal*., 2015, 329, 177
5%Ru/N-CNF	370	5%CO_2 15%H_2/Ar 60 mL min^{-1}	~60	~61	1900 mmol g_{Ru}^{-1} h^{-1}	*ChemCatChem*，2015,7,1347
Ru/TiO_2	200	1 atm CO_2/H_2 = 1:3 GHSV = 20000 mL g_{cat}^{-1} h^{-1}	~1		3.51 mmol g_{Ru}^{-1} h^{-1}	*J. Mater. Chem. A*, 2020, 8, 7390
Ru/ZrO_2@C(MIL)	300	40 bar H_2/CO_2 = 3:1 70 mL/min	64	100	2340 mmol $g_{cat.}^{-1}$ h^{-1}	*Catal. Today*, 2021, 371, 120

Ru/pBN-1.13%F	400	10 bar H_2:CO_2 = 4:1 GHSV = 18000 h^{-1}	61.6%	96.5	7380	*ACS Catal.* 2019, 9, 10077
Ru/TiO_2(001)	200	1 atm 10% CO_2 40% H_2 50%N_2 20 mL/min	~10%	100	~2.16	*J. CO_2 Util.*, 2019, 33, 242