nature catalysis

SUPPLEMENTARY INFORMATION

https://doi.org/10.1038/s41929-019-0244-4

In the format provided by the authors and unedited.

The renaissance of the Sabatier reaction and its applications on Earth and in space

Charlotte Vogt[1], Matteo Monai[1], Gert Jan Kramer[2] and Bert M. Weckhuysen[1*]

[1]Inorganic Chemistry and Catalysis Group, Debye Institute for Nanomaterials Science, Utrecht University, Utrecht, The Netherlands. [2]Copernicus Institute of Sustainable Development, Utrecht University, Utrecht, The Netherlands. *e-mail: B.M.Weckhuysen@uu.nl

Supplementary information to:

The Renaissance of the Sabatier Reaction and its Applications on Earth and in Space

Charlotte Vogt†, Matteo Monai†, Gert Jan Kramer¥ and Bert M. Weckhuysen†,*

†Inorganic Chemistry and Catalysis group, Debye Institute for Nanomaterials Science, Utrecht University, Universiteitsweg 99, 3584 CG Utrecht, the Netherlands

¥Copernicus Institute of Sustainable Development, Utrecht University, Heidelberglaan 2, 3584 CS Utrecht, the Netherlands

* B.M.Weckhuysen@uu.nl

Table S1: Turnover frequencies (TOFs) values against reaction temperature for the thermocatalytic CO_2 hydrogenation over different metal catalysts.

Nickel				
Catalyst	Main product	T (°C)	TOF (CO_2, s^{-1})	Reference
Ni/SiO_2	CH_4	280	$1,04 \times 10^{-1}$	[1]
Ni/Al_2O_3	CH_4	280	$3,35 \times 10^{-2}$	[1]
Ni(10 wt.%)/SiO_2	CH_4	350	$4,00 \times 10^{-2}$	[2]
Ni(3 wt.%)/SiO_2	CH_4	227	$8,10 \times 10^{-2}$	[3]
Ni(11.8 wt.%)/SiO_2	CH_4	200	$6,36 \times 10^{-4}$	[4]
Ni(11.8 wt.%)/SiO_2	CH_4	300	$2,01 \times 10^{-2}$	[4]
Ni(11.8 wt.%)/SiO_2	CH_4	400	$7,88 \times 10^{-2}$	[4]
Ni(6.7 wt.%)/SiO_2	CH_4	200	$6,76 \times 10^{-4}$	[4]
Ni(6.7 wt.%)/SiO_2	CH_4	300	$2,59 \times 10^{-2}$	[4]
Ni(6.7 wt.%)/SiO_2	CH_4	400	$1,14 \times 10^{-1}$	[4]
Ni(5 wt.%)/SiO_2	CH_4	200	$7,86 \times 10^{-4}$	[4]
Ni(5 wt.%)/SiO_2	CH_4	300	$2,45 \times 10^{-2}$	[4]
Ni(5 wt.%)/SiO_2	CH_4	400	$9,73 \times 10^{-2}$	[4]
Ni(19.5 wt.%)/SiO_2	CH_4	200	$1,38 \times 10^{-3}$	[4]
Ni(19.5 wt.%)/SiO_2	CH_4	300	$4,04 \times 10^{-2}$	[4]
Ni(19.5 wt.%)/SiO_2	CH_4	400	$1,05 \times 10^{-1}$	[4]
Ni(1 wt.%)/SiO_2	CH_4	200	$3,50 \times 10^{-4}$	[4]
Ni(1 wt.%)/SiO_2	CH_4	300	$1,54 \times 10^{-2}$	[4]
Ni(1 wt.%)/SiO_2	CH_4	400	$7,99 \times 10^{-2}$	[4]
Ni(60 wt.%)/SiO_2	CH_4	200	$3,68 \times 10^{-3}$	[4]
Ni(60 wt.%)/SiO_2	CH_4	300	$4,03 \times 10^{-2}$	[4]
Ni(60 wt.%)/SiO_2	CH_4	400	$4,68 \times 10^{-2}$	[4]
Ni/Al_2O_3	CH_4	250	$2,00 \times 10^{-2}$	[5]
Ni/Al_2O_3	CH_4	300	$8,00 \times 10^{-2}$	[5]
Ni/Ce-p	CH_4	300	$2,32 \times 10^{-2}$	[6]
Ni/Al-c	CH_4	300	$4,13 \times 10^{-2}$	[6]
Ni/Al-p	CH_4	300	$9,70 \times 10^{-2}$	[6]
Ni/Al_2O_3	CH_4	220	$5,00 \times 10^{-4}$	[7]
Ni/H-Al_2O_3 500	CH_4	220	$1,20 \times 10^{-3}$	[7]

Ni/H-Al_2O_3 400	CH_4	220	2,40 x 10^{-3}	[7]
Ni/Al_2O_3	CH_4	260	6,57 x 10^{-3}	[8]
Ni/SiO_2	CH_4	260	4,36 x 10^{-3}	[8]
Ni/ZSM-5	CH_4	260	7,57 x 10^{-3}	[8]
Ni/SBA-15	CH_4	260	5,92 x 10^{-3}	[8]
Ni/MCM-41	CH_4	260	3,42 x 10^{-3}	[8]
Ni@UiO-66	CH_4	320	4,30 x 10^{-2}	[9]
10Ni/oxCNT	CH_4	240	1,40 x 10^{-3}	[10]
10Ni-1La/oxCNT	CH_4	240	3,84 x 10^{-2}	[10]
10Ni-2La/oxCNT	CH_4	240	5,18 x 10^{-2}	[10]
10Ni-4La/oxCNT	CH_4	240	5,46 x 10^{-2}	[10]
10Ni-6La/oxCNT	CH_4	240	3,23 x 10^{-2}	[10]
Cobalt				
Catalyst	main product	T (°C)	TOF (CO_2, s^{-1})	Reference
Co/MCF-17	CO/CH_4	250	2,02 x 10^{-2}	[11]
Co/MCF-17	CO/CH_4	300	1,20 x 10^{-1}	[11]
Co/MCF-17	CO/CH_4	250	6,17 x 10^{-2}	[11]
Co/MCF-17	CO/CH_4	300	1,83 x 10^{-1}	[11]
Co/MCF-17	CO/CH_4	250	1,00 x 10^{-1}	[11]
Co/MCF-17	CO/CH_4	300	2,80 x 10^{-1}	[11]
Co(3 wt.%)/SiO_2	CO/CH_4	227	7,60 x 10^{-3}	[3]
Co(3 wt.%)/SiO_2	CO/CH_4	252	1,10 x 10^{-2}	[3]
Co(3 wt.%)/SiO_2	CO/CH_4	277	2,48 x 10^{-2}	[3]
Co(15 wt.%)/SiO_2	CO/CH_4	227	3,00 x 10^{-2}	[3]
Co(3 wt.%)/SiO_2	CO/CH_4	227	7,90 x 10^{-2}	[3]
Co/SiO_2	CO/CH_4	250	7,00 x 10^{-3}	[12]
Co/TiO_2	CO/CH_4	250	2,00 x 10^{-2}	[12]
Co/Al_2O_3	CO/CH_4	300	1,05 x 10^{-2}	[13]
Co/Al_2O_3	CO/CH_4	325	2,12 x 10^{-2}	[13]
Co/Al_2O_3	CO/CH_4	350	2,67 x 10^{-2}	[13]
Co/$BaZrO_3$	CO/CH_4	250	3,38 x 10^{-3}	[13]
Co/$BaZrO_3$	CO/CH_4	275	1,55 x 10^{-2}	[13]
Co/$BaZrO_3$	CO/CH_4	300	3,12 x 10^{-2}	[13]
Co/$BaZrO_3$	CO/CH_4	325	5,00 x 10^{-2}	[13]
Co/$BaZrO_3$	CO/CH_4	350	5,71 x 10^{-2}	[13]
Iron				

Catalyst	Main product	T (°C)	TOF (CO_2, s^{-1})	Reference
Fe/SiO_2	CO/CH_4	253	3,30 x 10^{-3}	[3]
Fe/SiO_2	CO/CH_4	291	9,40 x 10^{-3}	[3]
Fe/SiO_2	CO/CH_4	227	7,90 x 10^{-4}	[3]
Fe/SiO_2	CO/CH_4	227	8,40 x 10^{-4}	[3]
Copper				
Catalyst	main product	T (°C)	TOF(CO2)	Reference
Cu(0.5% wt.%)/ZnO	CH_3OH	180	1,33 x 10^{-3}	[14]
Cu(1% wt.%)/ZnO	CH_3OH	180	1,25 x 10^{-3}	[14]
Cu(3% wt.%)/ZnO	CH_3OH	180	9,50 x 10^{-4}	[14]
Cu(5% wt.%)/ZnO	CH_3OH	180	9,10 x 10 x 10^{-4}	[14]
Cu(8% wt.%)/ZnO	CH_3OH	180	4,36 x 10^{-3}	[14]
Cu(15% wt.%)/ZnO	CH_3OH	180	4,03 x 10^{-3}	[14]
$Cu/ZnO/Al_2O_3$	CH_3OH	230	1,90 x 10^{-2}	[15]
Cu/MgO	CH_3OH	230	1,00 x 10^{-3}	[15]
Cu(5 wt.%)/SiO_2	CH_3OH	220	2,80 x 10^{-3}	[16]
Cu(5 wt.%)/Al_2O_3	CH_3OH	220	4,00 x 10^{-3}	[16]
Cu(5 wt.%)/TiO_2	CH_3OH	220	2,00 x 10^{-2}	[16]
Cu/SiO_2	CH_3OH	230	5,50 x 10^{-4}	[17]
Cu/ZrO_2	CH_3OH	230	1,60 x 10^{-3}	[17]
Cu/SiO_2	CO/CH_3OH	225	3,10 x 10^{-4}	[18]
Cu/SiO_2	CO/CH_3OH	250	6,00 x 10^{-4}	[18]
Cu/SiO_2	CO/CH_3OH	275	1,10 x 10^{-3}	[18]
Cu/SiO_2	CO	260	7,67 x 10^{-4}	[19]
Cu/SiO_2	CO	260	1,26 x 10^{-3}	[19]
Cu/SiO_2	CO	260	1,48 x 10^{-3}	[19]
Cu/SiO_2	CO	260	1,53 x 10^{-3}	[19]
Cu/SiO_2	CO	260	1,59 x 10^{-3}	[19]
Palladium				
Catalyst	Main product	T (°C)	TOF (CO_2, s^{-1})	Reference
Pd(0.5 wt.%)/Al_2O_3	CH_3OH /CH_4	300	3,00 x 10^{-2}	[20]
Pd(0.5 wt.%)/Al_2O_3	CH_3OH /CH_4	260	5,47 x 10^{-3}	[20]
Pd(0.5 wt.%)/Al_2O_3	CH_3OH /CH_4	280	8,21 x 10^{-3}	[20]
Pd(0.5 wt.%)/Al_2O_3	CH_3OH /CH_4	300	1,25 x 10^{-2}	[20]
Pd(0.5 wt.%)/Al_2O_3	CH_3OH /CH_4	320	1,73 x 10^{-2}	[20]
Pd(5 wt.%)/Al_2O_3	CH_3OH /CH_4	260	1,03 x 10^{-2}	[20]
Pd(5 wt.%)/Al_2O_3	CH_3OH /CH_4	280	1,48 x 10^{-2}	[20]
Pd(5 wt.%)/Al_2O_3	CH_3OH /CH_4	300	2,10 x 10^{-2}	[20]
Pd(5 wt.%)/Al_2O_3	CH_3OH /CH_4	320	2,72 x 10^{-2}	[20]
Pd(5 wt.%)/Al_2O_3	CH_3OH /CH_4	300	3,90 x 10^{-3}	[21]

Pd(5 wt.%)/Al_2O_3	CH_3OH /CH_4	300	3,75 x 10^{-3}	21
Pd(5 wt.%)/Al_2O_3	CH_3OH /CH_4	300	4,20 x 10^{-3}	21
Pd(1 wt.%)/Al_2O_3	CH_3OH /CH_4	300	4,01 x 10^{-2}	21
Pd(5 wt.%)/Al_2O_3	CH_3OH /CH_4	300	1,99 x 10^{-2}	21
Pd(5 wt.%)/Al_2O_3	CH_3OH /CH_4	300	3,23 x 10^{-2}	21
Pd(5 wt.%)/TiO_2	CH_3OH /CH_4	300	2,29 x 10^{-1}	21
Pd(5 wt.%)/SiO_2	CH_3OH /CH_4	300	1,32 x 10^{-3}	21
Pd(5 wt.%)/SiO_2	CH_3OH /CH_4	300	3,34 x 10^{-3}	21
Pd(5 wt.%)/MgO	CH_3OH /CH_4	300	4,30 x 10^{-3}	21
Pd-I/In_2O_3	CH_3OH /CH_4	200	1,35 x 10^{-3}	22
Pd-P/In_2O_3	CH_3OH /CH_4	200	1,55 x 10^{-3}	22
Pd-I/In_2O_3	CH_3OH /CH_4	225	5,39 x 10^{-3}	22
Pd-P/In_2O_3	CH_3OH /CH_4	225	6,34 x 10^{-3}	22
Platinum				
Catalyst	Main product	T (°C)	TOF (CO_2, s^{-1})	Reference
Pt/TiO_2	CO	280	1,82	23
Pt/TiO_2	CO	290	2,26	23
Pt/TiO_2	CO	300	2,76	23
Pt/TiO_2	CO	310	3,31	23
Pt/TiO_2	CO	320	3,98	23
Pt/TiO_2	CO	330	4,67	23
Pt/TiO_2	CO	340	5,45	23
Pt/TiO_2	CO	350	6,26	23
Pt/SiO_2	CO	280	0,35	23
Pt/SiO_2	CO	290	0,45	23
Pt/SiO_2	CO	300	0,58	23
Pt/SiO_2	CO	310	0,74	23
Pt/SiO_2	CO	320	0,91	23
Pt/SiO_2	CO	330	1,10	23
Pt/SiO_2	CO	340	1,32	23
Pt/SiO_2	CO	350	1,55	23
Ruthenium				
Catalyst	Main product	T (°C)	TOF (CO_2, s^{-1})	Reference
Ru(5 wt.%)/SiO_2	CH_4	227	7,50 x 10^{-3}	2
Ru(5 wt.%)/SiO_2	CH_4	227	7,32 x 10^{-2}	2
Ru(0.1 wt.%)/Al_2O_3	CH_4	300	3,00 x 10^{-2}	2
Ru(5 wt.%)/Al_2O_3	CH_4	320	5,26 x 10^{-1}	24
Ru(5 wt.%)/Al_2O_3	CH_4	310	4,45 x 10^{-1}	24
Ru(5 wt.%)/Al_2O_3	CH_4	300	3,55 x 10^{-1}	24
Ru(5 wt.%)/Al_2O_3	CH_4	390	2,84 x 10^{-1}	24
Ru(5 wt.%)/Al_2O_3	CH_4	280	2,27 x 10^{-1}	24
Ru(5 wt.%)/Al_2O_3	CH_4	270	1,81 x 10^{-1}	24

Ru(0.1 wt.%)/Al_2O_3	CH_4	350	1,13 x 10^{-1}	24
Ru(0.1 wt.%)/Al_2O_3	CH_4	340	8,72 x 10^{-2}	24
Ru(0.1 wt.%)/Al_2O_3	CH_4	330	7,54 x 10^{-2}	24
Ru(0.1 wt.%)/Al_2O_3	CH_4	320	5,89 x 10^{-2}	24
Ru(0.1 wt.%)/Al_2O_3	CH_4	310	3,85 x 10^{-2}	24
Ru(0.1 wt.%)/Al_2O_3	CH_4	300	3,40 x 10^{-2}	24
Ru(0.5 wt.%)/Al_2O_3	CH_4	320	1,76 x 10^{-1}	24
Ru(0.5 wt.%)/Al_2O_3	CH_4	310	1,26 x 10^{-1}	24
Ru(0.5 wt.%)/Al_2O_3	CH_4	300	9,40 x 10^{-2}	24
Ru(0.5 wt.%)/Al_2O_3	CH_4	290	7,18 x 10^{-2}	24
Ru(0.5 wt.%)/Al_2O_3	CH_4	280	5,37 x 10^{-2}	24
Ru(1 wt.%)/Al_2O_3	CH_4	330	5,21 x 10^{-1}	24
Ru(1 wt.%)/Al_2O_3	CH_4	320	4,35 x 10^{-1}	24
Ru(1 wt.%)/Al_2O_3	CH_4	310	3,08 x 10^{-1}	24
Ru(1 wt.%)/Al_2O_3	CH_4	300	2,51 x 10^{-1}	24
Ru(1 wt.%)/Al_2O_3	CH_4	290	1,92 x 10^{-1}	24
Ru(1 wt.%)/Al_2O_3	CH_4	280	1,48 x 10^{-1}	24
Ru(0.5 wt.%)/TiO_2	CH_4	200	1,50 x 10^{-2}	25
Ru(0.5 wt.%)/TiO_2	CH_4	225	3,27 x 10^{-2}	25
Ru(0.5 wt.%)/TiO_2	CH_4	225	3,68 x 10^{-2}	25
Ru(0.5 wt.%)/TiO_2	CH_4	250	5,90 x 10^{-2}	25
Ru(0.5 wt.%)/TiO_2	CH_4	250	6,57 x 10^{-2}	25
Ru(0.5 wt.%)/TiO_2	CH_4	270	9,71 x 10^{-2}	25
Ru(0.5 wt.%)/TiO_2	CH_4	290	1,42 x 10^{-1}	25
Ru(0.5 wt.%)/TiO_2	CH_4	320	2,58 x 10^{-1}	25
Ru(0.5 wt.%)/TiO_2	CH_4	350	4,26 x 10^{-1}	25
Iridium				
Catalyst	Main product	T (°C)	TOF (CO_2, s^{-1})	Reference
Ir(0.7 wt.%)/CeO_2	CH_4/CO	300	2,00 x 10^{-2}	26
Ir(20 wt.%)/CeO_2	CH_4/CO	300	2,40 x 10^{-3}	26
Ir(10 wt.%)/CeO_2	CH_4/CO	300	2,50 x 10^{-3}	26
Ir(5 wt.%)/CeO_2	CH_4/CO	300	6,25 x 10^{-3}	26
Rhodium				
Catalyst	Main product	T (°C)	TOF (CO_2, s^{-1})	Reference
Rh(0.8 wt.%)/TiO_2	CH_4	100	4,54 x 10^{-5}	27
Rh(2 wt.%)/TiO_2	CH_4	100	2,02 x 10^{-4}	27
Rh(3 wt.%)/TiO_2	CH_4	100	4,27 x 10^{-4}	27
Rh(5 wt.%)/TiO_2	CH_4	100	3,87 x 10^{-4}	27
Rh(0.8 wt.%)/TiO_2	CH_4	120	1,82 x 10^{-4}	27

Rh(1 wt.%)/TiO_2	CH_4	120	2,85 x 10^{-4}	[27]
Rh(2 wt.%)/TiO_2	CH_4	120	5,16 x 10^{-4}	[27]
Rh(3 wt.%)/TiO_2	CH_4	120	1,09 x 10^{-3}	[27]
Rh(5 wt.%)/TiO_2	CH_4	120	8,61 x 10^{-4}	[27]
Rh(0.5 wt.%)/TiO_2	CH_4	165	6,48 x 10^{-4}	[27]
Rh(0.8 wt.%)/TiO_2	CH_4	165	1,65 x 10^{-3}	[27]
Rh(1 wt.%)/TiO_2	CH_4	165	2,01 x 10^{-3}	[27]
Rh(2 wt.%)/TiO_2	CH_4	165	2,83 x 10^{-3}	[27]
Rh(3 wt.%)/TiO_2	CH_4	165	5,31 x 10^{-3}	[27]
Rh(5 wt.%)/TiO_2	CH_4	165	4,36 x 10^{-3}	[27]
Rh(0.5 wt.%)/TiO_2	CH_4	150	2,39 x 10^{-4}	[27]
Rh(0.8 wt.%)/TiO_2	CH_4	150	7,87 x 10^{-4}	[27]
Rh(1 wt.%)/TiO_2	CH_4	150	1,01 x 10^{-3}	[27]
Rh(2 wt.%)/TiO_2	CH_4	150	1,59 x 10^{-3}	[27]
Rh(3 wt.%)/TiO_2	CH_4	150	3,29 x 10^{-3}	[27]
Rh(5 wt.%)/TiO_2	CH_4	150	2,52 x 10^{-3}	[27]
Rh(0.5 wt.%)/TiO_2	CH_4	135	1,00 x 10^{-4}	[27]
Rh(0.8 wt.%)/TiO_2	CH_4	135	3,86 x 10^{-4}	[27]
Rh(1 wt.%)/TiO_2	CH_4	135	5,75 x 10^{-4}	[27]
Rh(2 wt.%)/TiO_2	CH_4	135	9,28 x 10^{-4}	[27]
Rh(3 wt.%)/TiO_2	CH_4	135	1,83 x 10^{-3}	[27]
Rh(5 wt.%)/TiO_2	CH_4	135	1,52 x 10^{-3}	[27]
Rh/TiO_2	CH_4/CO	200	9,50 x 10^{-3}	[28]

Table S2: Turnover frequencies (TOFs) values against overpotential for the electrocatalytic CO_2 reduction over different metal catalysts.

Nickel						
Catalyst	Main Product	Overpotential (V)	TOF (CO_2, s^{-1})	Electrolyte	FE to main product (%)	Ref
Ni/N-graphene/glassy carbon	CO	0,61	4,11	$KHCO_3$ 0,5 M pH 7,3	97	29
Ni/N-graphene/carbon paper	CO	0,61	8,20 x 10^{-1}	$KHCO_3$ 0,5 M pH 7,3	94	29
Ni/graphene	CO	0,61	2,22	$KHCO_3$ 0,5 M pH 7,3	97	29
SE-Ni SAs@PNC	CO	0,8	7,75	$KHCO_3$ 0,5 M pH 7,3	98	30
SE-Ni SAs@PNC	CO	0,9	13,3	$KHCO_3$ 0,5 M pH 7,3	90	30
SE-Ni SAs@PNC	CO	1	13,6	$KHCO_3$ 0,5 M pH 7,3	88	30
Ni/graphene/polished glassy carbon	CO	0,7	8,00	$KHCO_3$ 0,5 M pH 7,3	93	31
Ni SAs/N-C	CO	0,59	2,23 x 10^{-1}	$KHCO_3$ 0,5 M pH 7,3	72	32
Ni SAs/N-C	CO	0,64	3,73 x 10^{-1}	$KHCO_3$ 0,5 M pH 7,3		32
Ni SAs/N-C	CO	0,69	5,61 x 10^{-1}	$KHCO_3$ 0,5 M pH 7,3		32
Ni SAs/N-C	CO	0,74	5,69 x 10^{-1}	$KHCO_3$ 0,5 M pH 7,3		32
Ni SAs/N-C	CO	0,79	1,07	$KHCO_3$ 0,5 M pH 7,3		32
Ni SAs/N-C	CO	0,84	1,26	$KHCO_3$ 0,5 M pH 7,3		32
Ni SAs/N-C	CO	0,89	1,46	$KHCO_3$ 0,5 M pH 7,3		32
Ni SAs/N-C	CO	0,94	1,40	$KHCO_3$ 0,5 M pH 7,3		32
Ni SAs/N-C	CO	0,99	1,24	$KHCO_3$ 0,5 M pH 7,3		32
Ni SAs/N-C	CO	1,04	1,11	$KHCO_3$ 0,5 M pH 7,3		32
Ni SAs/N-C	CO	1,09	9,53 x 10^{-1}	$KHCO_3$ 0,5 M pH 7,3		32
Ni NPs/N-C	CO	0,59	7,63 x 10^{-2}	$KHCO_3$ 0,5 M pH 7,3		32
Ni NPs/N-C	CO	0,64	8,79E-02	$KHCO_3$ 0,5 M pH 7,3		32
Ni NPs/N-C	CO	0,69	1,25 x 10^{-1}	$KHCO_3$ 0,5 M pH 7,3		32

Ni NPs/N-C	CO	0,74	$1,18 \times 10^{-1}$	$KHCO_3$ 0,5 M pH 7,3		32
Ni NPs/N-C	CO	0,79	$1,22 \times 10^{-1}$	$KHCO_3$ 0,5 M pH 7,3		32
Ni NPs/N-C	CO	0,84	$9,80 \times 10^{-2}$	$KHCO_3$ 0,5 M pH 7,3		32
Ni NPs/N-C	CO	0,89	$7,71 \times 10^{-2}$	$KHCO_3$ 0,5 M pH 7,3		32
Ni NPs/N-C	CO	0,94	$6,70 \times 10^{-2}$	$KHCO_3$ 0,5 M pH 7,3		32
Ni NPs/N-C	CO	0,99	$6,05 \times 10^{-2}$	$KHCO_3$ 0,5 M pH 7,3		32
Ni NPs/N-C	CO	1,04	$5,76 \times 10^{-2}$	$KHCO_3$ 0,5 M pH 7,3		32
Ni NPs/N-C	CO	1,09	$5,83 \times 10^{-2}$	$KHCO_3$ 0,5 M pH 7,3		32
Ni-N-MEGO	CO	0,29	$4,00 \times 10^{-2}$	$KHCO_3$ 0,5 M pH 7,3		33
Ni-N-MEGO	CO	0,44	$1,40 \times 10^{-2}$	$KHCO_3$ 0,5 M pH 7,3		33
Ni-N-MEGO	CO	0,59	$2,40 \times 10^{-2}$	$KHCO_3$ 0,5 M pH 7,3		33
Cobalt						
Catalyst	Main Product	Overpotential (V)	TOF (CO_2, s^{-1})	Electrolyte	FE to main product (%)	Ref
COF-366-Co/carbon fabric	CO	0,67	$6,9 \times 10^{-1}$	$KHCO_3$ 0,5 M pH 7,3	90	34
COF-366-Co/glassy carbon	CO	0,67	4,7	$KHCO_3$ 0,5 M pH 7,3	86	34
COF-367-Co	CO	0,67	$5,30 \times 10^{-1}$	$KHCO_3$ 0,5 M pH 7,3		34
COF-367-Co(1%)	CO	0,67	2,6	$KHCO_3$ 0,5 M pH 7,3	40	34
COF-367-Co(10%)	CO	0,67	1,2	$KHCO_3$ 0,5 M pH 7,3	70	34
Co-N2	CO	0,73	7,69	$KHCO_3$ 0,5 M pH 7,3	66	35
Co-N2	CO	0,68	9,15	$KHCO_3$ 0,5 M pH 7,3	93	35
Co-N2	CO	0,63	7,11	$KHCO_3$ 0,5 M pH 7,3	85	35
Co-N2	CO	0,58	6,45	$KHCO_3$ 0,5 M pH 7,3	95	35
Co-N2	CO	0,53	5,03	$KHCO_3$ 0,5 M pH 7,3	94	35
Co-N2	CO	0,48	3,83	$KHCO_3$ 0,5 M pH 7,3	94	35
Co-N2	CO	0,43	2,00	$KHCO_3$ 0,5 M pH 7,3	69	35

Co-N2	CO	0,38	1,59	$KHCO_3$ 0,5 M pH 7,3	75	35
immobilized 5,10,15,20-tetrakis(4-aminophenyl)porphinato]cobalt [Co(TAP)]	CO	0,67	$1,0 \times 10^{-1}$	$KHCO_3$ 0,5 M pH 7,3	-	34
Co protoporphyrin/pyrolytic graphite electrode	CO/HCOOH	0,5	$2,0 \times 10^{-1}$	1mM $HClO_4$, 99 mM $NaClO_4$	60	36
Co protoporphyrin/pyrolytic graphite electrode	CO/HCOOH	0,7	$8,0 \times 10^{-1}$	1mM $HClO_4$, 99 mM $NaClO_4$	40	36
cobalt phthalocyanine (CoPc)/CNTs	CO	0,52	2,70	$KHCO_3$ 0,1 M pH 6,8	92	37
CoPc-CN/CNT (cyano groups)	CO	0,52	4,10	$KHCO_3$ 0,1 M pH 6,8	95	37
CoPC/RGO	CO	0,52	$9,3 \times 10^{-1}$	$KHCO_3$ 0,1 M pH 6,8		37
CoPc/CB	CO	0,52	$5,6 \times 10^{-1}$	$KHCO_3$ 0,1 M pH 6,8		37
Iron						
Catalyst	Main Product	Overpotential (V)	TOF (CO_2, s^{-1})	Electrolyte	FE to main product (%)	Ref
Fe_MOF-525	CO	0,71	$1,87 \times 10^{-2}$	1 M TBAPF6 in DMF		38
Fe_MOF-525	CO	0,61	$1,52 \times 10^{-2}$	1 M TBAPF6 in DMF		38
Fe_MOF-525	CO	0,51	$1,24 \times 10^{-2}$	1 M TBAPF6 in DMF		38
Fe_MOF-525	CO	0,41	$1,09 \times 10^{-2}$	1 M TBAPF6 in DMF		38
Fe_MOF-525	CO	0,31	$9,68 \times 10^{-3}$	1 M TBAPF6 in DMF		38
Fe_MOF-525	CO	0,21	$8,57 \times 10^{-3}$	1 M TBAPF6 in DMF		38
Fe_MOF-525	CO	0,11	$6,95 \times 10^{-3}$	1 M TBAPF6 in DMF		38
Fe_MOF-525	CO	0,70	$1,30 \times 10^{-1}$	1 M TBAPF6 in DMF + TFE		38
PCN-222(Fe)	CO	0,49	$3,66 \times 10^{-1}$	$KHCO_3$ 0,5 M pH 7,3	91	39

Fe porphyrin/MWCNTs	CO	0,51	4,90 x 10^{-2}	$NaHCO_3$ 0,5 M pH 7,3		[40]
Copper						
Catalyst	Main Product	Overpotential (V)	TOF (CO_2, s^{-1})	Electrolyte	FE to main product (%)	Ref
Cu immobilized	CH_4/C_2H_4	0,86	6,1	$KHCO_3$ 0,5 M pH 7,3		[41]
Cu foil	$HCOOH/CH_4/C_2H_4$	0,57	9,17 x 10^{-2}	$KHCO_3$ 0,1 M pH 6,8		[42]
Cu foil	$HCOOH/CH_4/C_2H_4$	0,64	1,45 x 10^{-1}	$KHCO_3$ 0,1 M pH 6,8		[42]
Cu foil	$HCOOH/CH_4/C_2H_4$	0,71	2,32 x 10^{-1}	$KHCO_3$ 0,1 M pH 6,8		[42]
Cu foil	$HCOOH/CH_4/C_2H_4$	0,78	3,86 x 10^{-1}	$KHCO_3$ 0,1 M pH 6,8		[42]
Cu foil	$HCOOH/CH_4/C_2H_4$	0,85	5,70 x 10^{-1}	$KHCO_3$ 0,1 M pH 6,8		[42]
Cu foil	$HCOOH/CH_4/C_2H_4$	0,91	8,19 x 10^{-1}	$KHCO_3$ 0,1 M pH 6,8		[42]
Cu foil	$HCOOH/CH_4/C_2H_4$	0,95	8,03 x 10^{-1}	$KHCO_3$ 0,1 M pH 6,8		[42]
Cu foil	$HCOOH/CH_4/C_2H_4$	0,99	1,10	$KHCO_3$ 0,1 M pH 6,8		[42]
Cu foil	$HCOOH/CH_4/C_2H_4$	1,04	1,51	$KHCO_3$ 0,1 M pH 6,8		[42]
Cu foil	$HCOOH/CH_4/C_2H_4$	1,07	1,89	$KHCO_3$ 0,1 M pH 6,8		[42]
Cu-SIM NU-1000 thin film	Formate/CO	0,71	2,80 x 10^{-2}	$NaClO_4$ 0,1 M, pH of 4,6		[43]
Palladium						
Catalyst	Main Product	Overpotential (V)	TOF (CO_2, s^{-1})	Electrolyte	FE to main product (%)	Ref
Pd NPs/C black/Carbon paper	CO	0,78	5,89 x 10^{-2}	$KHCO_3$ 0,1 M pH 6,8		[44]
Pd NPs/C black/Carbon paper	CO	0,78	1,25 x 10^{-1}	$KHCO_3$ 0,1 M pH 6,8		[44]
Pd NPs/C black/Carbon paper	CO	0,78	1,64 x 10^{-1}	$KHCO_3$ 0,1 M pH 6,8		[44]
Pd NPs/C black/Carbon paper	CO	0,78	1,48 x 10^{-1}	$KHCO_3$ 0,1 M pH 6,8		[44]
Pd NPs/C black/Carbon paper	CO	0,78	1,18 x 10^{-1}	$KHCO_3$ 0,1 M pH 6,8		[44]

Pd NPs/C black/Carbon paper	CO	0,78	$3,43 \times 10^{-2}$	$KHCO_3$ 0,1 M pH 6,8		44
Pd NPs/C black/Carbon paper	CO	0,68	$4,16 \times 10^{-2}$	$KHCO_3$ 0,1 M pH 6,8		44
Pd NPs/C black/Carbon paper	CO	0,68	$8,61 \times 10^{-2}$	$KHCO_3$ 0,1 M pH 6,8		44
Pd NPs/C black/Carbon paper	CO	0,68	$1,08 \times 10^{-1}$	$KHCO_3$ 0,1 M pH 6,8		44
Pd NPs/C black/Carbon paper	CO	0,68	$9,16 \times 10^{-2}$	$KHCO_3$ 0,1 M pH 6,8		44
Pd NPs/C black/Carbon paper	CO	0,68	$7,09 \times 10^{-2}$	$KHCO_3$ 0,1 M pH 6,8		44
Pd NPs/C black/Carbon paper	CO	0,68	$1,82 \times 10^{-2}$	$KHCO_3$ 0,1 M pH 6,8		44
Pd NPs/C black/Carbon paper	CO	0,58	$2,57 \times 10^{-2}$	$KHCO_3$ 0,1 M pH 6,8		44
Pd NPs/C black/Carbon paper	CO	0,58	$5,12 \times 10^{-2}$	$KHCO_3$ 0,1 M pH 6,8		44
Pd NPs/C black/Carbon paper	CO	0,58	$5,80 \times 10^{-2}$	$KHCO_3$ 0,1 M pH 6,8		44
Pd NPs/C black/Carbon paper	CO	0,58	$4,30 \times 10^{-2}$	$KHCO_3$ 0,1 M pH 6,8		44
Pd NPs/C black/Carbon paper	CO	0,58	$3,94 \times 10^{-2}$	$KHCO_3$ 0,1 M pH 6,8		44
Pd NPs/C black/Carbon paper	CO	0,58	$8,6 \times 10^{-3}$	$KHCO_3$ 0,1 M pH 6,8		44
Pd NPs/C black/Carbon paper	CO	0,48	$1,02 \times 10^{-2}$	$KHCO_3$ 0,1 M pH 6,8		44
Pd NPs/C black/Carbon paper	CO	0,48	$2,09 \times 10^{-2}$	$KHCO_3$ 0,1 M pH 6,8		44
Pd NPs/C black/Carbon paper	CO	0,48	$2,01 \times 10^{-2}$	$KHCO_3$ 0,1 M pH 6,8		44
Pd NPs/C black/Carbon paper	CO	0,48	$1,26 \times 10^{-2}$	$KHCO_3$ 0,1 M pH 6,8		44
Pd NPs/C black/Carbon paper	CO	0,48	$7,5 \times 10^{-3}$	$KHCO_3$ 0,1 M pH 6,8		44
Pd NPs/C black/Carbon paper	CO	0,48	$2,85 \times 10^{-3}$	$KHCO_3$ 0,1 M pH 6,8		44
Silver						
Catalyst	Main Product	Overpotential (V)	TOF (CO_2, s^{-1})	Electrolyte	FE to main product (%)	Ref
Ag (bulk)	CO	0,17	$8,0 \times 10^{-1}$	18 mol % EMIM-BF_4 in water	99	45
Ag (bulk)	CO	0,67	1,19	18 mol % EMIM-BF_4 in water	99	45
Ag (bulk)	CO	0,92	1,32	18 mol % EMIM-BF_4 in water	97	45

Ag (bulk)	CO	1,17	1,37	18 mol % EMIM-BF_4 in water	98	45
Nanoporous Ag	CO	0,39	$2,0 \times 10^{-3}$	$KHCO_3$ 0,5 M pH 7,3	92	46
Gold						
Catalyst	Main Product	Overpotential (V)	TOF (CO_2, s^{-1})	Electrolyte	FE to main product (%)	Ref
Au nanowires	CO	0,24	$2,0 \times 10^{-2}$	$KHCO_3$ 0,5 M pH 7,3	91	47

1. Campbell, T. K. & Falconer, J. L. Carbon dioxide hydrogenation on potassium-promoted nickel catalysts. *Appl. Catal.* **50**, 189–197 (1989).

2. Kattel, S., Liu, P. & Chen, J. G. Tuning Selectivity of CO_2 Hydrogenation Reactions at the Metal/Oxide Interface. *J. Am. Chem. Soc.* **139**, 9739–9754 (2017).

3. Weatherbee, G. D. & Bartholomew, C. H. Hydrogenation of CO_2 on group VIII metals: IV. Specific activities and selectivities of silica-supported Co, Fe, and Ru. *J. Catal.* **87**, 352–362 (1984).

4. Vogt, C. *et al.* Unravelling structure sensitivity in CO_2 hydrogenation over nickel. *Nat. Catal.* **1**, 127–134 (2018).

5. Mutz, B. *et al.* Surface Oxidation of Supported Ni Particles and Its Impact on the Catalytic Performance during Dynamically Operated Methanation of CO_2. *Catalysts* **7**, 279 (2017).

6. Bian, L., Zhang, L., Xia, R. & Li, Z. Enhanced low-temperature CO_2 methanation activity on plasma-prepared Ni-based catalyst. *J. Nat. Gas Sci. Eng.* **27**, 1189–1194 (2015).

7. He, S. *et al.* A Surface Defect-Promoted Ni Nanocatalyst with Simultaneously Enhanced Activity and Stability. *Chem. Mater.* **25**, 1040–1046 (2013).

8. Guo, X. *et al.* Carbon Dioxide Methanation over Nickel-Based Catalysts Supported on Various Mesoporous Material. *Energy & Fuels* **32**, 3681–3689 (2018).

9. Zhao, Z.-W. *et al.* Ultrasmall Ni nanoparticles embedded in Zr-based MOFs provide high selectivity for CO_2 hydrogenation to methane at low temperatures. *Catal. Sci. Technol.* **8**, 3160–3165 (2018).

10. Gao, J. *et al.* Probing the enhanced catalytic activity of carbon nanotube supported Ni-LaO x hybrids for the CO_2 reduction reaction. *Nanoscale* **10**, 14207–14219 (2018).

11. Iablokov, V. *et al.* Size-controlled model Co nanoparticle catalysts for CO_2 hydrogenation: synthesis, characterization, and catalytic reactions. *Nano Lett.* **12**, 3091–3096 (2012).

12. Melaet, G. *et al.* Evidence of Highly Active Cobalt Oxide Catalyst for the Fischer–Tropsch Synthesis and CO_2 Hydrogenation. *J. Am. Chem. Soc.* **136**, 2260–2263 (2014).

13. Shin, H. H., Lu, L., Yang, Z., Kiely, C. J. & McIntosh, S. Cobalt Catalysts Decorated with Platinum Atoms Supported on Barium Zirconate Provide Enhanced Activity and Selectivity for CO_2 Methanation. *ACS Catal.* **6**, 2811–2818 (2016).

14. Karelovic, A. & Ruiz, P. The role of copper particle size in low pressure methanol synthesis via CO_2 hydrogenation over Cu/ZnO catalysts. *Catal. Sci. Technol.* **5**, 869–881 (2015).

15. Felix, S. *et al.* The Mechanism of CO and CO_2 Hydrogenation to Methanol over Cu-Based Catalysts. *ChemCatChem* **7**, 1105–1111 (2015).

16. Bando, K. K., Sayama, K., Kusama, H., Okabe, K. & Arakawa, H. In-situ FT-IR study on CO_2 hydrogenation over Cu catalysts supported on SiO_2, Al_2O_3, and TiO_2. *Appl. Catal. A Gen.* **165**, 391–409 (1997).

17. Larmier, K. *et al.* CO_2-to-Methanol Hydrogenation on Zirconia-Supported Copper Nanoparticles: Reaction Intermediates and the Role of the Metal-Support Interface. *Angew. Chem. Int. Ed.* **56**, 2318–2323 (2017).

18. Clarke, D. B. & Bell, A. T. An Infrared Study of Methanol Synthesis from CO_2 on Clean and Potassium-Promoted Cu/SiO_2. *J. Catal.* **154**, 314–328 (1995).

19. Karelovic, A. *et al.* Mechanism and structure sensitivity of methanol synthesis from CO_2 over SiO_2-supported Cu nanoparticles. *J. Catal.* **369**, 415–426 (2019).

20. Wang, X., Shi, H., Kwak, J. H. & Szanyi, J. Mechanism of CO_2 Hydrogenation on Pd/Al_2O_3 Catalysts: Kinetics and Transient DRIFTS-MS Studies. *ACS Catal.* **5**, 6337–6349 (2015).

21. Erdöhelyi, A., Pásztor, M. & Solymosi, F. Catalytic hydrogenation of CO_2 over supported palladium. *J. Catal.* **98**, 166–177 (1986).

22. Rui, N. *et al.* CO_2 hydrogenation to methanol over Pd/In_2O_3: effects of Pd and oxygen vacancy. *Appl. Catal. B Environ.* **218**, 488–497 (2017).

23. Kattel, S., Yan, B., Chen, J. G. & Liu, P. CO_2 hydrogenation on Pt, Pt/SiO_2 and Pt/TiO_2: Importance of synergy between Pt and oxide support. *J. Catal.* **343**, 115–126 (2016).

24. Kwak, J. H., Kovarik, L. & Szanyi, J. CO_2 Reduction on Supported Ru/Al_2O_3 Catalysts: Cluster Size Dependence of Product Selectivity. *ACS Catal.* **3**, 2449–2455 (2013).

25. Petala, A. & Panagiotopoulou, P. Methanation of CO_2 over alkali-promoted Ru/TiO_2 catalysts: I. Effect of alkali additives on catalytic activity and selectivity. *Appl. Catal. B Environ.* **224**, 919–927 (2018).

26. Li, S. *et al.* Tuning the Selectivity of Catalytic Carbon Dioxide Hydrogenation over Iridium/Cerium Oxide Catalysts with a Strong Metal–Support Interaction. *Angew. Chem. Int. Ed.* **56**, 10761–10765 (2017).

27. Karelovic, A. & Ruiz, P. Mechanistic study of low temperature CO_2 methanation over Rh/TiO_2 catalysts. *J. Catal.* **301**, 141–153 (2013).

28. Matsubu, J. C., Yang, V. N. & Christopher, P. Isolated Metal Active Site Concentration and Stability Control Catalytic CO_2 Reduction Selectivity. *J. Am. Chem. Soc.* **137**, 3076–3084 (2015).

29. Yang, H. Bin *et al.* Atomically dispersed Ni(i) as the active site for electrochemical CO_2 reduction. *Nat. Energy* **3**, 140–147 (2018).

30. Yang, J. *et al.* In Situ Thermal Atomization To Convert Supported Nickel Nanoparticles into Surface-Bound Nickel Single-Atom Catalysts. *Angew. Chem. Int. Ed.* **130**, 14291–14296 (2018).

31. Jiang, K. *et al.* Transition-Metal Single Atoms in a Graphene Shell as Active Centers for Highly Efficient Artificial Photosynthesis. *Chem* **3**, 950–960 (2017).

32. Zhao, C. *et al.* Ionic Exchange of Metal–Organic Frameworks to Access Single Nickel Sites for Efficient Electroreduction of CO_2. *J. Am. Chem. Soc.* **139**, 8078–8081 (2017).

33. Cheng, Y. *et al.* Unsaturated edge-anchored Ni single atoms on porous microwave exfoliated

graphene oxide for electrochemical CO_2. *Appl. Catal. B Environ.* **243**, 294–303 (2019).

34. Lin, S. *et al.* Covalent organic frameworks comprising cobalt porphyrins for catalytic CO_2 reduction in water. *Science* **349**, 1208–1213 (2015).

35. Wang, X. *et al.* Regulation of Coordination Number over Single Co Sites: Triggering the Efficient Electroreduction of CO_2. *Angew. Chem. Int. Ed.* **57**, 1944–1948 (2018).

36. Shen, J. *et al.* Electrocatalytic reduction of carbon dioxide to carbon monoxide and methane at an immobilized cobalt protoporphyrin. *Nat. Commun.* **6**, 8177 (2015).

37. Zhang, X. *et al.* Highly selective and active CO_2 reduction electrocatalysts based on cobalt phthalocyanine/carbon nanotube hybrid structures. *Nat. Commun.* **8**, 14675 (2017).

38. Hod, I. *et al.* Fe-Porphyrin-Based Metal–Organic Framework Films as High-Surface Concentration, Heterogeneous Catalysts for Electrochemical Reduction of CO_2. *ACS Catal.* **5**, 6302–6309 (2015).

39. Dong, B.-X. *et al.* Electrochemical Reduction of CO_2 to CO by a Heterogeneous Catalyst of Fe–Porphyrin-Based Metal–Organic Framework. *ACS Appl. Energy Mater.* **1**, 4662–4669 (2018).

40. Maurin, A. & Robert, M. Catalytic CO_2-to-CO conversion in water by covalently functionalized carbon nanotubes with a molecular iron catalyst. *Chem. Commun.* **52**, 12084–12087 (2016).

41. Weng, Z. *et al.* Electrochemical CO_2 Reduction to Hydrocarbons on a Heterogeneous Molecular Cu Catalyst in Aqueous Solution. *J. Am. Chem. Soc.* **138**, 8076–8079 (2016).

42. Kuhl, K. P., Cave, E. R., Abram, D. N. & Jaramillo, T. F. New insights into the electrochemical reduction of carbon dioxide on metallic copper surfaces. *Energy Environ. Sci.* **5**, 7050 (2012).

43. Kung, C.-W. *et al.* Copper Nanoparticles Installed in Metal–Organic Framework Thin Films are Electrocatalytically Competent for CO_2 Reduction. *ACS Energy Lett.* **2**, 2394–2401 (2017).

44. Gao, D. *et al.* Size-Dependent Electrocatalytic Reduction of CO_2 over Pd Nanoparticles. *J. Am. Chem. Soc.* **137**, 4288–4291 (2015).

45. Rosen, B. A. *et al.* Ionic Liquid-Mediated Selective Conversion of CO_2 to CO at Low Overpotentials. *Science* **334**, 643–644 (2011).

46. Lu, Q. *et al.* A selective and efficient electrocatalyst for carbon dioxide reduction. *Nat. Commun.* **5**, 3242 (2014).

47. Zhu, W. *et al.* Active and selective conversion of CO_2 to CO on ultrathin Au nanowires. *J. Am. Chem. Soc.* **136**, 16132–16135 (2014).