CO_2 valorisation towards alcohols by Cu-based electrocatalysts: Challenges and perspectives

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Supporting Information

Summary

S1. CO_2-to-methanol via thermochemical route

Outstanding results following TC reactions for methanol production from our work1 with data taken from references2–[6]. Table S1 shows the best results following thermochemical reactions for methanol production.

Table S1. Outstanding results following TC reactions for methanol production from our work[1] with data taken from references[2–6].

Catalysts	CO_2 conversion, %	Selectivity Methanol, %	Temperature, °C	Pressure, MPa	Ref.
Cu/ZnO	5.5	50	240	2	3
Cu/ZrO_2	2.5	78	240	2	3
Cu/ZnO/Ga	6	88	270	2	5
Cu/ZrO_2/Ga	13.7	75.5	250	2	5
Cu/ZnO/ZrO_2	13	32	240	2	3
Cu/ZnO/ZrO_2/SiO_2	13.9	36	240	2	4
Cu/ZnO/ZrO_2/TiO_2	17.4	43.8	240	3	2
Cu/ZnO/ZrO_2/Al_2O_3/SiO_2	11.7	99.7	250	5	6

S2. CO_2-to-methanol via liquid phase electrochemical route

Table S2. State-of-the-art performance of the best catalysts to produce methanol from liquid-phase electrochemical CO_2 conversion.

Electrocatalysts	Faradaic efficiency to Methanol, %	Total current density, mA cm^{-2}	Cell configuration	Ref.
$Cu_{63,9}Au_{36,1}$/NCF	15.9	-	H-type cell (Nafion 117)	7
Anodiz. Cu foils	100.0	1.4	Traditional undivided 3 electrode cell	8
Electroch. Anodiz. Cu foils	20.0	5.0	Traditional undivided 3 electrode cell	
Cu_2O/stainless steel	38.0	5.0	Traditional undivided 3 electrode cell	
Cu\ $_{88}Sn_6Pb_6$ alloy foil	34.0	0.6	Two compartmentss (Nafion 117)	
Cu/Carbon paper	0.4	8.9	Two compartmentss (SPEEK)	
Electropolished Cu	0.1	10.0	Two compartmentss (AMV Selemion)	
Cu/ZnO	2.8	12.0	Two compartmentss (Nafion 117)	
Cu_2O /Carbon paper	20.0	2.4	Two compartmentss SPE (AMI-7001/ MEA)	
Cu/CuO	2.5	17.3	Two compartmentss (Nafion 117)	
Ru/Cu	42.0	0.1	Two compartmentss (agar bridge)	
Mo/Cu	84.0	0.8	Traditional undivided 3 electrode cell	
Cu_2O/ZnO	17.7	10.6	Two compartmentss (Nafion 117)	9
Cu-10-CNT/C	8.3	16.7	Two compartmentss (Nafion 117)	10
Cu_2O-MWCNTs	38.0	7.5	Two compartmentss (Nafion 117)	11
Oxide-der, Cu/ C (MOF)	18.0	1.0	Two compartmentss (Nafion 117)	12
CuO_x/ZnO	34.0	2.7	Traditional undivided 3 electrode cell	13
CuCNT-nanowires	47.4	0.9	Traditional undivided 3 electrode cell	14
CuCNT-Impregnation	23.3	0.9	Two compartmentss (Nafion 117)	14
Cu/Graphene	12.7	0.3	Two compartmentss (Nafion 117)	15
Cu/TiO_2/Graphene	19.5	0.3	Two compartmentss (Nafion 117)	15
Cu/Cu_2O	47.5	7.8	Two compartmentss (Nafion 117)	16
Cu-Y/CS:PVA MCE	68.0	0.3	Membrane coated electrode (MCE)	17
$Pd_{83}Cu_{17}$ Aerogels	80.0	31.8	H-type cell (Nafion 117)	18
$Cu_{1,63}Se_{1/3}$	77.6	41.5	H-type cell (Nafion 117)	19
CuSAs/TCNFs	44.0	93.0	H-type cell (Nafion 117)	20

S3. Faradaic efficiencies for different CO_2R products of the best liquid-phase electrocatalysts.

	Faradaic efficiency, % *											
Electrocatalysts	H_2	CO	C_2H_4	$HCOO^-$ /HCOOH	CH_3OH	C_2H_5OH	C_3H_8O	C_2H_6	CH_3COO^-	CH_4	J_{total}, mA cm^{-2}	Ref.
$Pd_{83}Cu_{17}$ Aerogels		<1.0			80.0						31.8	18
$Cu_{1.63}$Se1/3	<1.0	2.0	-	22.0	77.6	-	-	-	-	-	41.5	19
CuSAs/TCNFs	<1.0	54.0	-	-	44.0	-	-	-	-	-	93.0	20
Cu_2O					42.3	10.1	2.4				10.0	43
Cu_2O/ZnO					27.5	3.9	-				10.0	43
CuB_9 MOF	34.0	11.0	6.0	13.0	10.0	17.0	-	-	-	-	20.0	33
$CuBi_{12}$ MOF	30.0	9.0	7.0	16.0	9.0	28.0	-	-	-	-	20.0	33
B-OD-Cu	45.0	<1.0	20.0	5.0	-	20.0	-	8.0	-	-	33.4	44
Cu 25nm thickness	5.0	5.0	70.0	1.0	-	11.0	-	-	5.0	-	275.0	35
$Ag_{0.14}/Cu_{0.86}$ /PTFE	10.0	3.0	31.0	-	-	41.0	-	-	10.0	5.0	250.0	36
Electrodeposited CuAg alloy	9.8	6.5	55.2	3.0	-	25.9	2.4	-	1.6	1.6	300.0	37
Nanoporous Cu	7.6	14.7	38.6	1.9	-	16.6	4.5	-	2.2	-	653.0	34
Cu Nps/Carbon paper	10.6	38.9	35.0	7.6	-	11.2	2.1	-	0.4	-	430.0	38
Cu_2S–Cu-V	12.6	5.5	21.2	15.4	-	25.0	7.0	-	3.0	1.1	400.0	39
Ce(OH)x/Cu/PTFE	14.2	0.5	33.8	1.1	-	42.6	0.6	-	3.3	2.9	300.0	45
NGQ/Cu-nr	10.0	5.0	23.0	5.0	-	45.0	7.0	-	4.0	-	282.0	46
34% N-C/Cu/PTFE	7.4	0.3	37.5	1.7	-	52.3	1.4	-	2.3	1.2	300.0	40
$La_{1.8}SrO_{0.2}CuO_4$					2.0	30.5	10.0				180.0	41
Porous copper foam	69.2	4.6	4.0	5.9	-	3.2	4.9	2.8	0.7	-	37.5	42

Empty cells: no information available. (-) These products were not detected. * All values were approximated from the reported literature data.

S4. Ethanol and n-propanol production from CO_2 via liquid-phase electrochemical route

Table S3. State-of-the-art performance of the production of ethanol and n-propanol from liquid-phase electrochemical CO_2 conversion.

Electrocatalysts	Faradaic efficiency to Ethanol, %	Faradaic efficiency to n-Propanol, %	Total current density, mA cm^{-2}	Cell configuration	Ref.
Graphene/Cu_2O/Cufoil	9.9	-	5.3	Two compartments 3-electrodes cell separated by a glass frit	21
Cu(100)	9.7	1.5	5.0	Traditional undivided 3 electrode cell	22
Polycrystalline Cu	21.9	-	5.0	Two compartments separated by Selemion	23
3,6 µm film of Cu_2O	16.4	-	35.0	Two compartments separated by Selemion	24
CuO/TiO_2	37.5	5.6	8.3	H-type cell (Nafion 117)	25
$Cu_{63,9}Au_{36,1}$/NCF	12.0	-	-	H-type cell (Nafion 117)	7
Cu/N-Graphene	63.0	-	2.8	Two compartments separated by Selemion	26
Graphene/ZnO/Cu_2O/Cufoil	-	30.0	8.0	Two compartments cell separated by a glass frit	27
Cu nanocrystals	-	10.6	16.4	Two compartments separated by Selemion	28
Cu Nps/ Carbon paper x22.5 loading	13.3	5.9	12.7	Two compartments separated by Selemion	29
Cu/Graphene	24.1	3.1	1.3	Gas Diffusion electrode (Nafion 117)	30
CuO/TiO_2/Graphene	43.6	3.3	1.4	Gas Diffusion electrode (Nafion 117)	30
Cu_{1ML}/THH Pd NCs	20.4	-	0.6	H-type cell (Nafion 115)	31
Electrodeposited Cu onto Cu mesh	10.0	13.0	10.0 (normalized to the ECSA)	H-type cell (Nafion 117)	32
$CuBi_9$ MOF	17.0	-	20.0	Two compartmentss (Nafion 117)	33

$CuBi_{12}$ MOF	28.0	-	20.0	Two compartmentss (Nafion 117)	33
Nanoporous Cu	16.6	4.5	653.0	Gas Diffusion electrode	34
Cu 25nm thickness	11.0	-	275.0	Flow cell reactor	35
$Ag_{0,14}/Cu_{0,86}$ /PTFE	41.0	-	250.0	Gas Diffusion electrode	36
Electrodeposited CuAg alloy	25.0	-	300.0	Flow cell reactor	37
Cu Nps/Carbon paper	11.0	2.1	430.0	Flow cell reactor	38
Cu_2S–Cu-V	25.0	7.0	400.0	Gas Diffusion electrode	39
34% N-C/Cu/PTFE	52.0	1.0	300.0	Gas Diffusion electrode	40
$La_{1,8}Sr_{0,2}CuO_4$	30.5	10.0	180.0	H-cell	41
Porous copper foam	-	4.93	37.5	H-cell	42

S5. CO_2-to-alcohols via catholyte-free electrochemical route.

Table S4**.** State-of-the-art performance of the production of alcohols from solvent-less electrochemical CO_2 conversion .

Electrocatalysts	Relative FE to methanol, %	Relative FE to ethanol, %	Relative FE to n-Propanol, %	Total current density, mA cm^{-2}	Cell configuration	Ref.
Fe_{10}-CNTox/GDL	21.7	70.5	3.3	1.4	Continuous gas-phase CO_2 electroreduction. MEA Configuration.	47
Pt_{10}-CNTox/GDL	16.1	25.1	34.8	1.4	Continuous gas-phase CO_2 electroreduction. MEA Configuration.	47
Cu-Graphite/C	75.0	-	-	2.4	Continuous gas-phase CO_2 electroreduction. MEA Configuration.	48
Cu-AC/C	45.0	-	-	2.4	Continuous gas-phase CO_2 electroreduction. MEA Configuration.	48
Cu-CNF/C	2.5	2.0	2.5	2.4	Continuous gas-phase CO_2 electroreduction. MEA Configuration.	48
Cu-CNF/C (PBI)	5.0	2.0	0.2	1.6	Continuous gas-phase CO_2 electroreduction. MEA Configuration.	49
Cu powder	92.8	-	-	1.6	Continuous gas-phase CO_2 electroreduction. MEA Configuration.	50
Cu_C powder	14.1	-	-	1.6	Continuous gas-phase CO_2 electroreduction. MEA Configuration.	50
Cu Oxide/ZnO	0.2	0.2		7.5	Continuous gas-phase CO_2 electroreduction. MEA Configuration.	51
Pb/CNT	6.3	-	-	16.0	Continuous gas-phase	52

					CO_2 electroreduction. MEA Configuration.	
Cu(250nm)-C-G/PTFE	-	20.3	5.4	150.0	Continuous gas-phase CO_2 electroreduction. MEA Configuration.	53
Cu/TiO_2 NTs	23.5	-	-	120.0	Continuous Solid Polymer Electrolyte Membrane (SPE) Reactor	54
34% N-C/Cu/PTFE	-	56.5	2.7	160.0	Continuous gas-phase CO_2 electroreduction. MEA Configuration.	40
Commercial Cu_2O (solid-state electrolyte)	-	7.0	7.0	90.0	CO_2 electroreduction. MEA Configuration.	55

S6. Total Faradaic efficiencies of the best catholyte-free EC CO_2R electrocatalysts

	Relative Faradaic efficiency, %												
Electrocatalysts	CH_3OH	C_2H_4O	C_2H_5OH	C_3H_6O	C_3H_8O	CH_3COOH	CH_4	$C_2H_4O_2$	CO	C_2H_4	$HCOO^-$ /HCOOH	J_{total}, mA cm^{-2}	Ref .
Fe_{10}-CNTox/GDL	21.7	2.0	70.5	0.1	3.3	2.53	-	-	-	-	-	1.4	47
Pt_{10}-CNTox/GDL	16.1	19.8	25.1	0.2	34.8	4.1	-	-	-	-	-	1.4	47
Cu-Graphite/C	75.0	8.0	-	12.0	-	-	2.5	2.5	-	-	-	2.4	48
Cu-AC/C	45.0	48.0	-	5.0	-	-	1.0	1.0	-	-	-	2.4	48
Cu-CNF/C	2.5	70.0	2.0	-	2.5	-	5.0	12.0	10.0	-	-	2.4	48
Cu-CNF/C (PBI)	5.0	68.0	2.0	-	0.2	-	0.6	19.0	5.0	-	-	1.6	49
Cu_25nm powder	-	-	-	-	-	-	2.1	-	0.1	97.8	-	7.5	56
Cu powder	92.7	1.9	-	-	-	-	5.3	-	-	-	-	1.6	50
Cu_C powder	14.1	60.7	-	-	-	-	25.8	-	-	-	-	1.6	50
Cu Oxide/ZnO	0.2	-	0.2	0.2	-	-	0.5	-	0.3	98.5	-	7.5	51
Pb/CNT	6.3	-	-	-	-	-	34.4	-	9.4	-	50.0	16.0	52
Cu(250nm)-C-G/PTFE	-	-	20.3	-	5.4	6.7	-	-	13.5	54.1	-	150.0	53
Cu/TiO_2 NTs	23.5	-	-	-	-	-	17.6	-	58.8	-	-	120.0	54
34% N-C/Cu/PTFE	-	-	56.5	-	2.7	2.7	-	-	-	38.0	-	160.0	40
Commercial Cu_2O (solid-state electrolyte)	-	-	7.0	-	7.0	1.4	-	-	35.2	28.2	21.1	90.0	55

(-) These products were not detected.

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