

CO2 valorisation towards alcohols by Cu-based electrocatalysts: challenges and perspectives

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CO2 valorisation towards alcohols by Cu-based electrocatalysts: challenges and perspectives / Hilmar, Guzman; Russo, Nunzio; Simelys, Hernandez. - In: GREEN CHEMISTRY. - ISSN 1463-9262. - ELETTRONICO. - 23:5(2021), pp. 1896-1920. [10.1039/d0gc03334k]

*Availability:*

This version is available at: 11583/2875982 since: 2021-03-23T16:43:06Z

*Publisher:*

RSC

*Published*

DOI:10.1039/d0gc03334k

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# CO<sub>2</sub> valorisation towards alcohols by Cu-based electrocatalysts: Challenges and perspectives

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## Supporting Information

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### ***S1. CO<sub>2</sub>-to-methanol via thermochemical route***

Outstanding results following TC reactions for methanol production from our work<sup>1</sup> with data taken from references<sup>2–6</sup>. 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<sup>1</sup> with data taken from references<sup>2–6</sup>.

Catalysts	CO <sub>2</sub> conversion, %	Selectivity Methanol, %	Temperature, °C	Pressure, MPa	Ref.
Cu/ZnO	5.5	50	240	2	3
Cu/ZrO <sub>2</sub>	2.5	78	240	2	3
Cu/ZnO/Ga	6	88	270	2	5
Cu/ZrO <sub>2</sub> /Ga	13.7	75.5	250	2	5
Cu/ZnO/ZrO <sub>2</sub>	13	32	240	2	3
Cu/ZnO/ZrO <sub>2</sub> /SiO <sub>2</sub>	13.9	36	240	2	4
Cu/ZnO/ZrO <sub>2</sub> /TiO <sub>2</sub>	17.4	43.8	240	3	2
Cu/ZnO/ZrO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> /SiO <sub>2</sub>	11.7	99.7	250	5	6

## S2. CO<sub>2</sub>-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<sub>2</sub> conversion.

Electrocatalysts	Faradaic efficiency to Methanol, %	Total current density, mA cm <sup>-2</sup>	Cell configuration	Ref.
Cu <sub>63.9</sub> Au <sub>36.1</sub> /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 <sub>2</sub> O/stainless steel	38.0	5.0	Traditional undivided 3 electrode cell	
Cu <sub>88</sub> Sn <sub>6</sub> Pb <sub>6</sub> 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 <sub>2</sub> O /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 <sub>2</sub> O/ZnO	17.7	10.6	Two compartmentss (Nafion 117)	
Cu-10-CNT/C	8.3	16.7	Two compartmentss (Nafion 117)	10
Cu <sub>2</sub> O-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 <sub>x</sub> /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 <sub>2</sub> /Graphene	19.5	0.3	Two compartmentss (Nafion 117)	15
Cu/Cu <sub>2</sub> O	47.5	7.8	Two compartmentss (Nafion 117)	16
Cu-Y/CS:PVA MCE	68.0	0.3	Membrane coated electrode (MCE)	17
Pd <sub>83</sub> Cu <sub>17</sub> Aerogels	80.0	31.8	H-type cell (Nafion 117)	18
Cu <sub>1.63</sub> Se <sub>1/3</sub>	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<sub>2</sub>R products of the best liquid-phase electrocatalysts.**

Electrocatalysts	Faradaic efficiency, % *										J <sub>total</sub> , mA cm <sup>-2</sup>	Ref.
	H <sub>2</sub>	CO	C <sub>2</sub> H <sub>4</sub>	HCOO <sup>-</sup> / HCOOH	CH <sub>3</sub> OH	C <sub>2</sub> H <sub>5</sub> OH	C <sub>3</sub> H <sub>8</sub> O	C <sub>2</sub> H <sub>6</sub>	CH <sub>3</sub> COO <sup>-</sup>	CH <sub>4</sub>		
Pd <sub>83</sub> Cu <sub>17</sub> Aerogels		<1.0			80.0						31.8	18
Cu <sub>1.63</sub> 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 <sub>2</sub> O					42.3	10.1	2.4				10.0	43
Cu <sub>2</sub> O/ZnO					27.5	3.9	-				10.0	43
CuB <sub>9</sub> MOF	34.0	11.0	6.0	13.0	10.0	17.0	-	-	-	-	20.0	33
CuBi <sub>12</sub> 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 <sub>0.14</sub> /Cu <sub>0.86</sub> /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 <sub>2</sub> S–Cu–V	12.6	5.5	21.2	15.4	-	25.0	7.0	-	3.0	1.1	400.0	39
Ce(OH) <sub>x</sub> /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 <sub>1.8</sub> SrO <sub>0.2</sub> CuO <sub>4</sub>					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<sub>2</sub> 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<sub>2</sub> conversion.

Electrocatalysts	Faradaic efficiency to Ethanol, %	Faradaic efficiency to n-Propanol, %	Total current density, mA cm <sup>-2</sup>	Cell configuration	Ref.
Graphene/Cu <sub>2</sub> O/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 <sub>2</sub> O	16.4	-	35.0	Two compartments separated by Selemion	24
CuO/TiO <sub>2</sub>	37.5	5.6	8.3	H-type cell (Nafion 117)	25
Cu <sub>63,9</sub> Au <sub>36,1</sub> /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 <sub>2</sub> O/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 <sub>2</sub> /Graphene	43.6	3.3	1.4	Gas Diffusion electrode (Nafion 117)	30
Cu <sub>1ML</sub> /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 <sub>9</sub> MOF	17.0	-	20.0	Two compartments (Nafion 117)	33

CuBi <sub>12</sub> MOF	28.0	-	20.0	Two compartments (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 <sub>0.14</sub> /Cu <sub>0.86</sub> /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 <sub>2</sub> S-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 <sub>1.8</sub> Sr <sub>0.2</sub> CuO <sub>4</sub>	30.5	10.0	180.0	H-cell	41
Porous copper foam	-	4.93	37.5	H-cell	42

**S5. CO<sub>2</sub>-to-alcohols via catholyte-free electrochemical route.**

Table S4. State-of-the-art performance of the production of alcohols from solvent-less electrochemical CO<sub>2</sub> conversion .

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



					CO <sub>2</sub> electroreduction. MEA Configuration.	
Cu(250nm)-C-G/PTFE	-	20.3	5.4	150.0	Continuous gas-phase CO <sub>2</sub> electroreduction. MEA Configuration.	53
Cu/TiO <sub>2</sub> 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 <sub>2</sub> electroreduction. MEA Configuration.	40
Commercial Cu <sub>2</sub> O (solid-state electrolyte)	-	7.0	7.0	90.0	CO <sub>2</sub> electroreduction. MEA Configuration.	55

**S6. Total Faradaic efficiencies of the best catholyte-free EC CO<sub>2</sub>R electrocatalysts**

Electrocatalysts	Relative Faradaic efficiency, %											J <sub>total</sub> , mA cm <sup>-2</sup>	Ref .
	CH <sub>3</sub> OH	C <sub>2</sub> H <sub>4</sub> O	C <sub>2</sub> H <sub>5</sub> OH	C <sub>3</sub> H <sub>6</sub> O	C <sub>3</sub> H <sub>8</sub> O	CH <sub>3</sub> COOH	CH <sub>4</sub>	C <sub>2</sub> H <sub>4</sub> O <sub>2</sub>	CO	C <sub>2</sub> H <sub>4</sub>	HCOO <sup>-</sup> / HCOOH		
Fe <sub>10</sub> - CNTox/GDL	21.7	2.0	70.5	0.1	3.3	2.53	-	-	-	-	-	1.4	47
Pt <sub>10</sub> - 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 <sub>2</sub> 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 <sub>2</sub> O (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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