

Electronic Supplementary Information

Copper-Alloy Catalysts: Structural Characterizations and Catalytic Synergies

Shanghong Zeng,^{*ab} Shiyao Shan,^b Aolin Lu,^b Shan Wang,^b Dominic T Caracciolo,^b Richard J Robinson,^b Guojun Shang,^b Lei Xue,^a Yuansong Zhao,^a Aiai Zhang,^a Yang Liu,^a Shangpeng Liu,^a Ze Liu,^a Fenghua Bai,^a Jinfang Wu,^a Hong Wang,^c and Chuan-Jian Zhong^{*b}

a. Inner Mongolia Key Laboratory of Chemistry and Physics of Rare Earth Materials, School of Chemistry and Chemical Engineering, Inner Mongolia University, Hohhot, Inner Mongolia 010021, P.R. China. E-mail: zengshanghong@imu.edu.cn

b. Department of Chemistry, State University of New York at Binghamton, Binghamton, NY 13902, USA. E-mail: cjzhong@binghamton.edu

c. School of Chemical Engineering, Inner Mongolia University of Technology, Hohhot, Inner Mongolia, 010051, P.R. China.

Table 1 Summary of Selected Examples of Copper-Alloy Catalysts in Terms of Methods, Structures and Reactions

Catalyst	Method	Morphology & Surface Composition	Catalytic reaction/mechanism	ref.
Au _n Cu _{100-n}	Wet chemical reduction	Nanocubes (AuCu nanoparticles)	CO oxid/ Melting-resolidification	1
AuCu	Co-deposition	Metallic films (AuCu alloy)	CO ₂ RR/ D-band center shifts	2
Fcc-AuCu	Seed-mediated	Nanoparticles (Fcc-AuCu alloy→ CuO)	CO oxid/ Mars-van Krevelen	3
Fct-AuCu	Seed-mediated	Nanoparticles (Fct-AuCu alloy→ CuO)	CO oxid/ Mars-van Krevelen	3
AuCu	Wet chemical	Nanoparticles (Cu, Au)	CO ₂ RR/ Three atomic gold layers	4
Au thin layer on Cu	Galvanic displacement	Lamella structure (Au-Cu alloy, Cu)	CO ₂ RR/ Au thin layer	5
Pt ₃₂ Cu ₆₈	Wet chemical	Nanowires (PtCu alloy)	CH ₃ OH Oxid/ PtCu nanowires site	6
Pt-Cu single - atom	Galvanic replacement	Nanoparticles (Pt, Cu)	CO oxid/ Pt-Cu single-atom alloy	7
Pt-Ni-Cu	Wet chemical	Nanoparticles (Pt, Ni, Cu)	ORR/ Extra bi-functional	8
Pd _n Cu _{100-n}	Wet chemical	Spherical particles (Pd-Cu alloy, Cu _x O)	CO oxid/ Catalytic synergy	9
PdCu/C	Wet chemical	Nanoparticles (Cu ⁰ , Cu ²⁺ , Pd ⁰ , Pd ²⁺)	ORR/ Nanostructural tuning	10
Pd _n Cu _{100-n}	Wet chemical reduction	Nanoparticles (PdCu alloy)	CO oxid/ Langmuir-Hinshelwood	11
Pd-Cu	Co-impregnation	Nanoparticles (PdCu alloy phase)	CO ₂ to CH ₃ OH/ H-shuttled DOM/ Isolated Pd in Cu surface	12
Pd/Cu(111)	--	Layer (Pd, Cu)	CO ₂ to CH ₄ / Paired Cu-Pd sites	13
Pd _x Cu _{1-y} -TiO ₂	Wet chemical	PdCu nanocrystal (Pd ⁰ , Cu ⁰)	CO ₂ RR/ Alloying Cu with Pd	14
Cu-Pd	Colloidal synthesis	Spherical (Cu-Pd nanoparticles)	CO oxid/ Langmuir-Hinshelwood	15
Ru _{0.5} Cu _{0.5}	Solution-phase co- reduction	Nanoparticles (RuCu alloy and bulk Cu)	CO oxid/ Langmuir-Hinshelwood	16
CuAg	Electro-deposition	Wire-like (Cu)	CO ₂ RR/ Cu ₂ O overlayer and Ag	17
CoCu/SiO ₂	Wetness co- impregnation	CoCu nanoalloy	FTS / CoCu covered by Cu	18
CuCo	Deposition	2D islands (Co substituting Cu clusters)	CO adsorption/ Bimetallic CuCo	19
CuIn	Wet chemical	Nanowires (In, In ³⁺ , Cu, Cu ²⁺)	CO ₂ RR/ Cu-In interface	20
Cu-In	Deposition	Large irregularly shaped grains (In, Cu)	CO ₂ RR/ In located on the edge sites	21
Cu atom-pair	Wet chemical	Nanowires (Cu ₁ ⁰ -Cu ₁ ^{x+} pair)	CO ₂ RR/ Biatomic activating	22
CuSn	Co-deposition	Nanoparticles (CuSn alloy)	CO ₂ RR/ Alloying Cu and Sn	23
Cu _{2-x} Se(y)	Solvothermal synthesis	Nanoparticles (Cu, Cu(I), Cu(II), Se)	CO ₂ RR/ Cu active sites	24

Zn/Cu	Deposition	Layer (ZnO _x , ZnCu alloy)	CO ₂ RR/ Zn/Cu(997) step sites	25
Ni-Cu/CeO ₂	Wet chemical	Nanoparticles (Cu ²⁺ , Cu ⁺ /Cu ⁰ , Ni ⁰ , Ni ²⁺)	HT-WGS/ One-site carboxyl	26
CH ₃ OH oxid	oxidation of methanol;	CO oxid	oxidation of carbon monoxide;	CO-PROX
	preferential oxidation of carbon monoxide;	CO ₂ RR	reduction reaction of carbon dioxide;	ORR
	oxygen reduction reaction; Oxid	oxidation.		

References:

1. Yin, J.; Shan, S.; Yang, L.; Mott, D.; Malis, O.; Petkov, V.; Cai, F.; Shan Ng, M.; Luo, J.; Chen, B. H.; Engelhard, M.; Zhong, C.-J. Gold-Copper Nanoparticles: Nanostructural Evolution and Bifunctional Catalytic Sites. *Chem. Mater.* **2012**, *24*, 4662-4674.
2. Liu, K.; Ma, M.; Wu, L.; Valenti, M.; Cardenas-Morcoso, D.; Hofmann, J. P.; Bisquert, J.; Gimenez, S.; Smith, W. A. Electronic Effects Determine the Selectivity of Planar Au-Cu Bimetallic Thin Films for Electrochemical CO₂ Reduction. *ACS Appl. Mater. Inter.* **2019**, *11*, 16546-16555.
3. Zhan, W.; Wang, J.; Wang, H.; Zhang, J.; Liu, X.; Zhang, P.; Chi, M.; Guo, Y.; Guo, Y.; Lu, G.; Sun, S.; Dai, S.; Zhu, H.; Crystal Structural Effect of AuCu Alloy Nanoparticles on Catalytic CO Oxidation. *J. Am. Chem. Soc.* **2017**, *139*, 8846-8854.
4. Kim, D.; Xie, C.; Becknell, N.; Yu, Y.; Karamad, M.; Chan, K.; Crumlin, E. J.; Nørskov, J. K.; Yang, P. Electrochemical Activation of CO₂ through Atomic Ordering Transformations of AuCu Nanoparticles. *J. Am. Chem. Soc.* **2017**, *139*, 8329-8336.
5. Kim, J.-H.; Woo, H.; Yun, S.-W.; Jung, H.-W.; Back, S.; Jung, Y.; Kim, Y.-T. Highly Active and Selective Au Thin Layer on Cu Polycrystalline Surface Prepared by Galvanic Displacement for the Electrochemical Reduction of CO₂ to CO. *Appl. Catal., B: Environ.* **2017**, *213*, 211-215.
6. Liao, Y.; Yu, G.; Zhang, Y.; Guo, T.; Chang, F.; Zhong, C.-J.; Composition-Tunable PtCu Alloy Nanowires and Electrocatalytic Synergy for Methanol Oxidation Reaction. *J. Phys. Chem. C* **2016**, *120*, 10476-10484.
7. Liu, J.; Lucci, F. R.; Yang, M.; Lee, S.; Marcinkowski, M. D.; Therrien, A. J.; Williams, C. T.; Sykes, E. C. H.; Flytzani-Stephanopoulos, M. Tackling CO Poisoning with Single-Atom Alloy Catalysts. *J. Am. Chem. Soc.* **2016**, *138*, 6396-6399.
8. Petkov, V.; Maswadeh, Y.; Zhao, Y.; Lu, A.; Cronk, H.; Chang, F.; Shan, S.; Kareem, H.; Luo, J.; Zhong, C.-J.; Shastri, S.; Kenesei, P. Nanoalloy Catalysts Inside Fuel Cells: An Atomic-Level Perspective on the Functionality by Combined in Operando X-ray Spectroscopy and Total Scattering. *Nano Energy* **2018**, *49*, 209-220.
9. Shan, S.; Petkov, V.; Prasai, B.; Wu, J.; Joseph, P.; Skeete, Z.; Kim, E.; Mott, D.; Malis, O.; Luo, J.; Zhong, C.-J. Catalytic Activity of Bimetallic Catalysts Highly Sensitive to the Atomic Composition and Phase Structure at the Nanoscale. *Nanoscale* **2015**, *7*, 18936-18948.
10. Wu, Z.-P.; Shan, S.; Xie, Z.-H.; Kang, N.; Park, K.; Hopkins, E.; Yan, S.; Sharma, A.; Luo, J.; Wang, J.; Petkov, V.; Wang, L.; Zhong, C.-J. Revealing the Role of Phase Structures of Bimetallic Nanocatalysts in the Oxygen Reduction Reaction. *ACS Catal.* **2018**, *8*, 11302-11313.
11. Zhang, W.; Shan, S.; Luo, J.; Fisher, A.; Chen, J.-F.; Zhong, C.-J.; Zhu, J.; Cheng, D. Origin of Enhanced Activities for CO Oxidation and O₂ Reaction over Composition-Optimized Pd₅₀Cu₅₀ Nanoalloy Catalysts. *J. Phys. Chem. C* **2017**, *121*, 11010-11020.
12. Nie, X.; Jiang, X.; Wang, H.; Luo, W.; Janik, M. J.; Chen, Y.; Guo, X.; Song, C. Mechanistic Understanding of Alloy Effect and Water Promotion for Pd-Cu Bimetallic Catalysts in CO₂ Hydrogenation to Methanol. *ACS Catal.* **2018**, *8*, 4873-4892.
13. Boucher, M. B.; Marcinkowski, M. D.; Liriano, M. L.; Murphy, C. J.; Lewis, E. A.; Jewell, A. D.; Mattera, M. F. G.; Kyriakou, G.; Flytzani-Stephanopoulos, M.; Sykes, E. C. H. Molecular-Scale Perspective of Water-Catalyzed Methanol Dehydrogenation to Formaldehyde. *ACS Nano* **2013**, *7*, 6181-6187.
14. Long, R.; Li, Y.; Liu, Y.; Chen, S.; Zheng, X.; Gao, C.; He, C.; Chen, N.; Qi, Z.; Song, L.; Jiang, J.; Zhu, J.; Xiong, Y. Isolation of Cu Atoms in Pd Lattice: Forming Highly Selective Sites for Photocatalytic Conversion of CO₂ to CH₄. *J. Am. Chem. Soc.* **2017**, *139*, 4486-4492.
15. Mun, Y.; Lee, S.; Cho, A.; Kim, S.; Han, J. W.; Lee, J. Cu-Pd Alloy Nanoparticles as Highly Selective Catalysts for Efficient Electrochemical Reduction of CO₂ to CO. *Appl. Catal., B: Environ.* **2019**, *246*, 82-88.
16. Huang, B.; Kobayashi, H.; Yamamoto, T.; Matsumura, S.; Nishida, Y.; Sato, K.; Nagaoka, K.; Kawaguchi, S.; Kubota, Y.; Kitagawa, H. Solid-Solution Alloying of Immiscible Ru and Cu with Enhanced CO Oxidation Activity. *J. Am. Chem. Soc.* **2017**, *139*, 4643-4646.
17. Hoang, T. T. H.; Verma, S.; Ma, S.; Fister, T. T.; Timoshenko, J.; Frenkel, A. I.; Kenis, P. J. A.; Gewirth, A. A. Nanoporous Copper-Silver Alloys by Additive-Controlled Electrodeposition for the

- Selective Electroreduction of CO₂ to Ethylene and Ethanol. *J. Am. Chem. Soc.* **2018**, *140*, 5791-5797.
18. Su, J.; Zhang, Z.; Fu, D.; Liu, D.; Xu, X.-C.; Shi, B.; Wang, X.; Si, R.; Jiang, Z.; Xu, J.; Han, Y.-F. Higher Alcohols Synthesis from Syngas over CoCu/SiO₂ Catalysts: Dynamic Structure and the role of Cu. *J. Catal.* **2016**, *336*, 94-106.
 19. Eren, B.; Torres, D.; Karshoğlu, O.; Liu, Z.; Wu, C. H.; Stacchiola, D.; Bluhm, H.; Somorjai, G. A.; Salmeron, M. Structure of Copper–Cobalt Surface Alloys in Equilibrium with Carbon Monoxide Gas. *J. Am. Chem. Soc.* **2018**, *140*, 6575-6581.
 20. Luo, W.; Xie, W.; Mutschler, R.; Oveisi, E.; De Gregorio, G. L.; Buonsanti, R.; Züttel, A. Selective and Stable Electroreduction of CO₂ to CO at the Copper/Indium Interface. *ACS Catal.* **2018**, *8*, 6571-6581.
 21. Rasul, S.; Anjum, D. H.; Jedidi, A.; Minenkov, Y.; Cavallo, L.; Takanebe, K. A Highly Selective Copper–Indium Bimetallic Electrocatalyst for the Electrochemical Reduction of Aqueous CO₂ to CO. *Angew. Chem. Int. Ed.* **2015**, *54*, 2146-2150.
 22. Jiao, J.; Lin, R.; Liu, S.; Cheong, W.-C.; Zhang, C.; Chen, Z.; Pan, Y.; Tang, J.; Wu, K.; Hung, S.-F.; Chen, H. M.; Zheng, L.; Lu, Q.; Yang, X.; Xu, B.; Xiao, H.; Li, J.; Wang, D.; Peng, Q.; Chen, C.; Li, Y.; Copper Atom-pair Catalyst Anchored on Alloy Nanowires for Selective and Efficient Electrochemical Reduction of CO₂. *Nat. Chem.* **2019**, *11*, 222-228.
 23. Zheng, X.; Ji, Y.; Tang, J.; Wang, J.; Liu, B.; Steinrück, H.-G.; Lim, K.; Li, Y.; Toney, M. F.; Chan, K.; Cui, Y. Theory-Guided Sn/Cu Alloying for Efficient CO₂ Electroreduction at Low Overpotentials. *Nat. Catal.* **2019**, *2*, 55-61.
 24. Yang, D.; Zhu, Q.; Chen, C.; Liu, H.; Liu, Z.; Zhao, Z.; Zhang, X.; Liu, S.; Han, B. Selective Electroreduction of Carbon Dioxide to Methanol on Copper Selenide Nanocatalysts. *Nat. Commun.* **2019**, *10*, 677.
 25. Koitaya, T.; Yamamoto, S.; Shiozawa, Y.; Yoshikura, Y.; Hasegawa, M.; Tang, J.; Takeuchi, K.; Mukai, K.; Yoshimoto, S.; Matsuda, I.; Yoshinobu, J. CO₂ Activation and Reaction on Zn-Deposited Cu Surfaces Studied by Ambient-Pressure X-ray Photoelectron Spectroscopy. *ACS Catal.* **2019**, *9*, 4539-4550.
 26. Saw, E. T.; Oemar, U.; Tan, X. R.; Du, Y.; Borgna, A.; Hidajat, K.; Kawi, S. Bimetallic Ni–Cu Catalyst Supported on CeO₂ for High-Temperature Water–Gas Shift Reaction: Methane Suppression via Enhanced CO Adsorption. *J. Catal.* **2014**, *314*, 32-46.