

## Electronic Supporting Information

### Low-temperature deep oxidation of N, N-dimethylformamide (DMF) over CeCu binary oxides

Cedric Karel Fonzeu Monguen<sup>a,b</sup>, Samuel Daniel<sup>a,b</sup>, Zhen-Yu Tian<sup>a,b,\*</sup>

<sup>a</sup> Institute of Engineering Thermophysics, Chinese Academy of Sciences, Beijing 100190, China

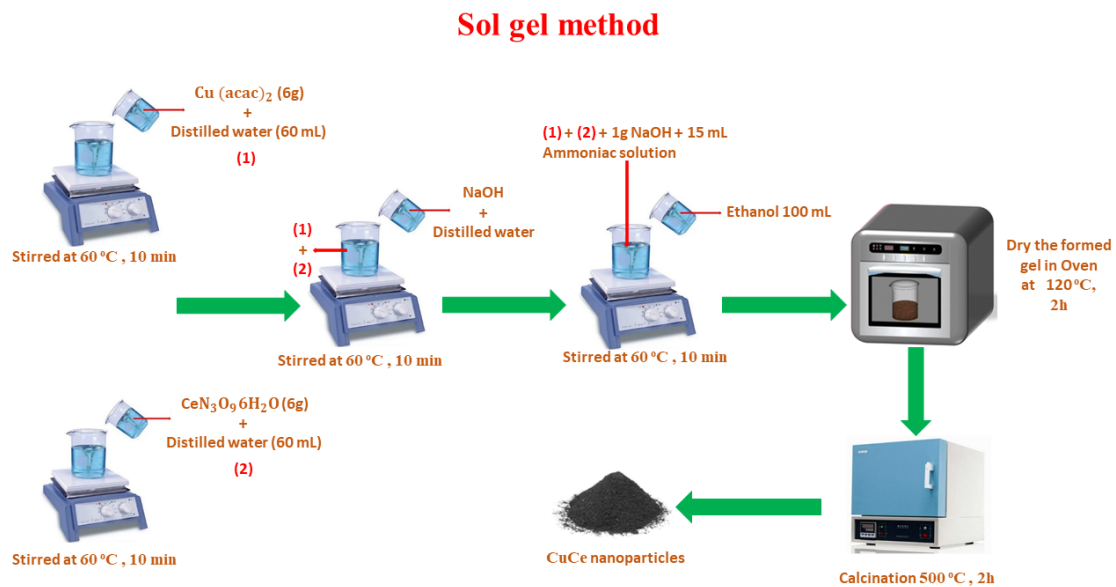
<sup>b</sup> University of Chinese Academy of Sciences, Beijing 100049, China

#### Table of Contents

<b>Section 1:</b> Preparation method .....	1
<b>Section 2:</b> Catalytic test experimental setup .....	2
<b>Section 3:</b> Structural properties .....	4
<b>Section 4:</b> Ionic states configuration .....	7
<b>Section 5:</b> Redox properties .....	11
<b>Section 6:</b> Catalytic activity .....	12
<b>References</b> .....	13

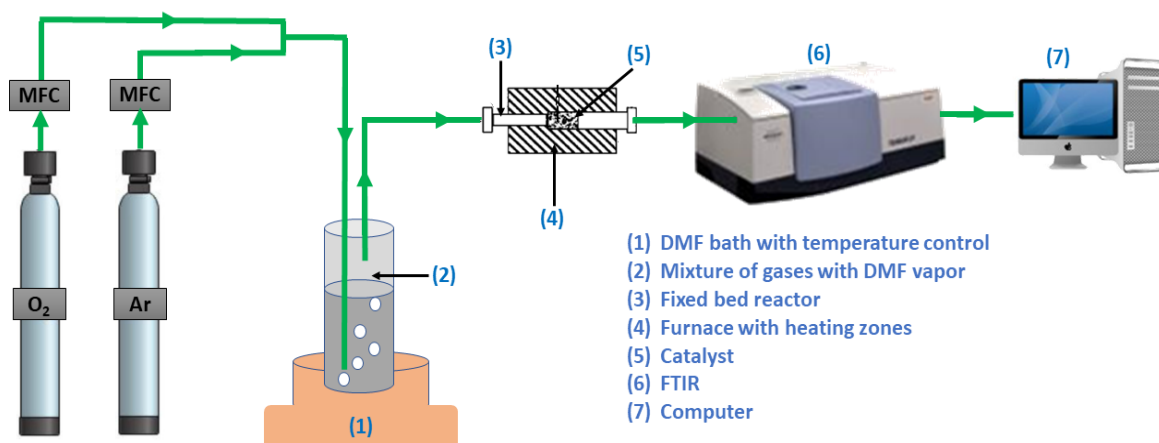
## Section 1: Preparation method

The powders were fabricated by Sol-gel method.



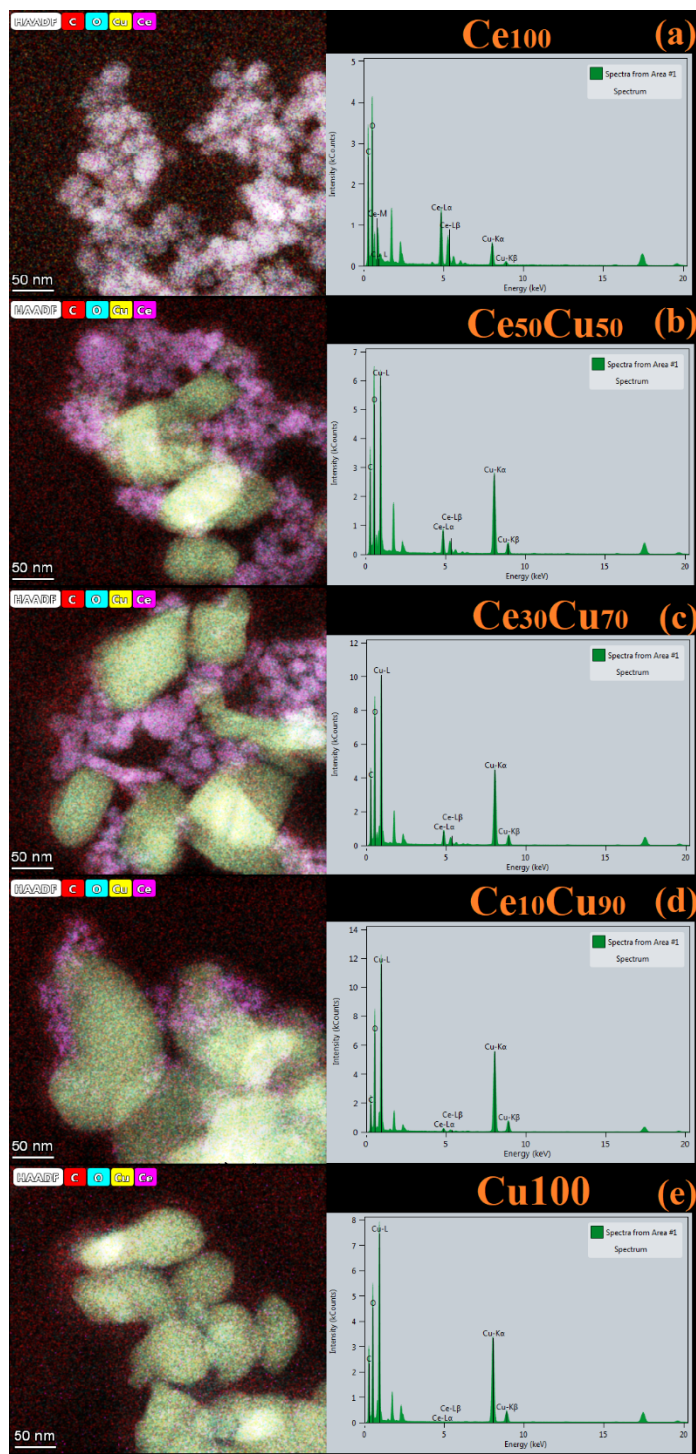
**Figure S1.** Sol-gel setup for the nanoparticles catalyst preparation <sup>1,2</sup>.

## Section 2: Catalytic test experimental setup

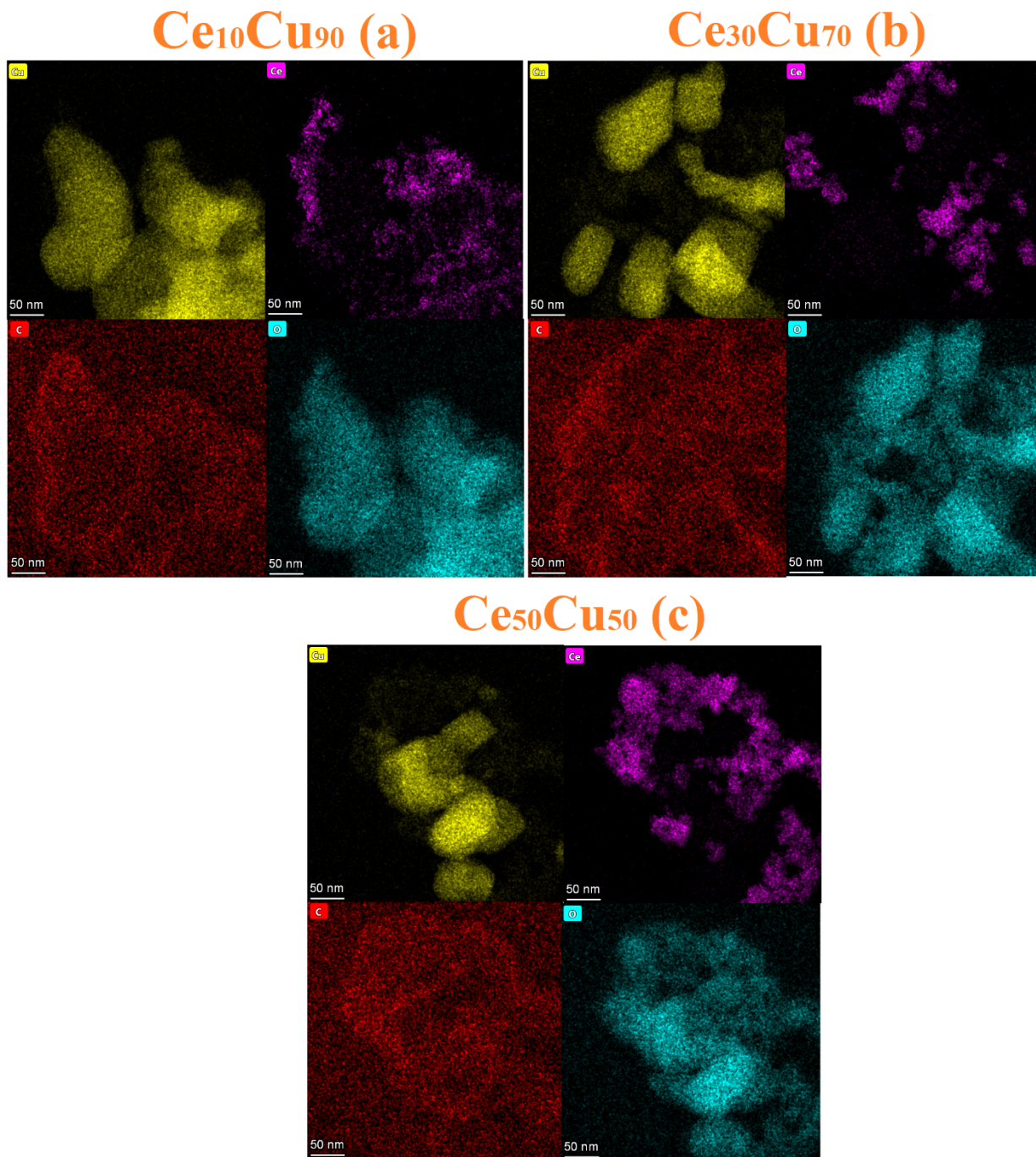


**Figure S2.** The catalytic test system connected to the FTIR equipment.

### Section 3: Structural properties



**Figure S3.** EDS-HAADF images of CuCe samples; Ce<sub>100</sub>(a), Ce<sub>50</sub>Cu<sub>50</sub>(b), Ce<sub>30</sub>Cu<sub>70</sub>(c), Ce<sub>10</sub>Cu<sub>90</sub>(d), Cu<sub>100</sub>.



**Figure S4.** Fine-Element mapping images of CuCe samples; Ce<sub>10</sub>Cu<sub>90</sub> (a), Ce<sub>30</sub>Cu<sub>70</sub> (b), and Ce<sub>50</sub>Cu<sub>50</sub>(c).

**Table S1** Crystallite size and micro-strain of thin-films samples.

Samples	hkl	FWHM ( $\beta$ ) ( $^{\circ}$ )	$2\theta$ ( $^{\circ}$ )	Crystallite size D (nm)	D average (nm)	Micro-strain $\epsilon$ (%)	$\epsilon$ average (%)
<b>Ce<sub>100</sub></b>	110	0.41	35.47	20.34	20.20	0.11	0.12
	111	0.42	38.69	20.05		0.13	
<b>Ce<sub>50</sub>Cu<sub>50</sub></b>	110	0.46	35.47	18.13	18.42	0.13	0.13
	111	0.45	38.69	18.71		0.14	
<b>Ce<sub>30</sub>Cu<sub>70</sub></b>	110	0.49	35.47	17.02	17.28	0.14	0.14
	111	0.48	38.69	17.54		0.15	
<b>Ce<sub>10</sub>Cu<sub>90</sub></b>	110	0.59	35.47	14.14	14.87	0.16	0.16
	111	0.54	38.69	15.59		0.16	
<b>Cu<sub>100</sub></b>	110	0.63	35.47	13.24	13.52	0.17	0.18
	111	0.61	38.69	13.80		0.19	

**Note:** hkl refers to Miller indices,  $\theta$  refers to Bragg's angle, and FWHM refers to the full width at half maximum of the peak.

**Table S2** CeCu materials specific surface area.

Samples	Surface area ( $\text{m}^2/\text{g}$ )	Pore volume ( $\text{cm}^3/\text{g}$ )	Pore size (nm)
<b>Ce<sub>100</sub><sup>3</sup></b>	3.775	0.009	25.703
<b>Ce<sub>50</sub>Cu<sub>50</sub></b>	4.962	0.027	28.660
<b>Ce<sub>30</sub>Cu<sub>70</sub></b>	5.319	0.031	39.382
<b>Ce<sub>10</sub>Cu<sub>90</sub></b>	6.146	0.034	41.689
<b>Cu<sub>100</sub></b>	7.739	0.044	42.645

## Section 4: Ionic states configuration

**Table S3** Comparison of the relative contents of CeCu binary oxides using EDS and XPS.

Samples	Type	Ce	Cu	C	O	Ce/O	Cu/O	Cu/Ce
<b>Ce<sub>100</sub></b>	XPS	5.77	0.00	29.11	65.12	0.09	0.00	0.00
	EDS	12.50	0.00	35.70	51.80	0.24	0.00	0.00
<b>Ce<sub>50</sub>Cu<sub>50</sub></b>	XPS	4.05	5.86	36.47	53.62	0.08	0.11	1.45
	EDS	3.40	17.30	39.40	39.90	0.08	0.43	5.09
<b>Ce<sub>30</sub>Cu<sub>70</sub></b>	XPS	3.34	6.87	39.66	50.13	0.07	0.14	2.06
	EDS	2.50	19.40	40.70	39.40	0.06	0.49	7.76
<b>Ce<sub>10</sub>Cu<sub>90</sub></b>	XPS	1.05	8.83	40.45	49.67	0.02	0.18	8.41
	EDS	0.20	22.80	46.00	30.50	0.01	0.75	114
<b>Cu<sub>100</sub></b>	XPS	0.00	9.03	52.21	38.76	0.00	0.23	-
	EDS	0.00	23.90	49.90	26.20	0.00	0.91	-

**Table S4** Results of curve-fitting on the Ce 3*d* binding energies and relative atomic percentage for the five sets of catalysts.

Catalysts	Parameters	Ce 3 <i>d</i> 5/2			Ce 3 <i>d</i> 3/2		
		Ce <sup>3+</sup>	Ce <sup>4+</sup>	Ce <sup>3+</sup> /Ce <sup>4+</sup>	Ce <sup>3+</sup>	Ce <sup>4+</sup>	Ce <sup>3+</sup> /Ce <sup>4+</sup>
<b>Ce<sub>100</sub></b>	Species	Ce <sup>3+</sup>	Ce <sup>4+</sup>	Ce <sup>3+</sup> /Ce <sup>4+</sup>	Ce <sup>3+</sup>	Ce <sup>4+</sup>	Ce <sup>3+</sup> /Ce <sup>4+</sup>
	BE (eV)	884.04	882.23	0.34	900.70	898.14	0.36
	RA (%)	25.36	74.64		26.46	73.54	
<b>Ce<sub>50</sub>Cu<sub>50</sub></b>	Species	Ce <sup>3+</sup>	Ce <sup>4+</sup>	Ce <sup>3+</sup> /Ce <sup>4+</sup>	Ce <sup>3+</sup>	Ce <sup>4+</sup>	Ce <sup>3+</sup> /Ce <sup>4+</sup>
	BE (eV)	884.33	882.16	0.39	900.61	898.06	0.40
	RA (%)	27.84	72.16		28.35	71.65	
<b>Ce<sub>30</sub>Cu<sub>70</sub></b>	Species	Ce <sup>3+</sup>	Ce <sup>4+</sup>	Ce <sup>3+</sup> /Ce <sup>4+</sup>	Ce <sup>3+</sup>	Ce <sup>4+</sup>	Ce <sup>3+</sup> /Ce <sup>4+</sup>
	BE (eV)	883.76	882.29	0.79	900.95	898.24	0.70
	RA (%)	44.24	55.76		41.30	58.70	
<b>Ce<sub>10</sub>Cu<sub>90</sub></b>	Species	Ce <sup>3+</sup>	Ce <sup>4+</sup>	Ce <sup>3+</sup> /Ce <sup>4+</sup>	Ce <sup>3+</sup>	Ce <sup>4+</sup>	Ce <sup>3+</sup> /Ce <sup>4+</sup>
	BE (eV)	883.79	882.30	1.13	900.92	898.26	0.93
	RA (%)	53.07	46.93		48.27	51.73	
<b>Cu<sub>100</sub></b>	-	-	-	-	-	-	-

**Note:** BE refers to binding energy, and RA refers to the relative area of the peak.



**Table S5** Results of curve-fittings on the O 1s binding energies and relative atomic percentage for the four sets of catalysts

Catalysts	Parameters	O 1s					
		Species	O <sup>2-</sup>	CO <sub>3</sub> <sup>2-</sup>	OH <sup>-</sup>	H <sub>2</sub> O	O <sub>Lat</sub> /O <sub>Ads</sub>
Ce <sub>100</sub>	BE (eV)	529.20	531.17	532.74	535.86	0.22	0.32
	RA (%)	17.88	16.27	50.60	15.20		
Ce <sub>50</sub> Cu <sub>50</sub>	BE (eV)	529.43	531.13	532.32	535.13	0.32	1.90
	RA (%)	24.51	42.16	22.23	11.10		
Ce <sub>30</sub> Cu <sub>70</sub>	BE (eV)	529.35	531.22	532.61	535.38	0.34	2.60
	RA (%)	25.92	45.72	17.56	10.80		
Ce <sub>10</sub> Cu <sub>90</sub>	BE (eV)	529.58	531.17	533.01	535.51	0.38	3.24
	RA (%)	27.63	48.75	15.05	8.57		
Cu <sub>100</sub>	BE (eV)	529.57	531.36	532.65	535.37	0.43	3.40
	RA (%)	29.92	49.13	14.44	6.51		

**Note:** BE refers to the binding energy; O<sub>Lat</sub> refers to the lattice oxygen; O<sub>Ads</sub> refers to the adsorption oxygen; RA refers to the relative area of the peak.

**Table S6** Results of curve-fitting on the Cu 2*p* binding energies and relative atomic percentage for the five sets of catalysts.

Catalysts	Parameters	Cu 2 <i>p</i> 3/2			Cu 2 <i>p</i> 1/2		
<b>Ce<sub>100</sub></b>	-	-	-	-	-	-	-
	Species	Cu <sup>2+</sup>	Cu <sup>+</sup>	<b>Cu<sup>2+</sup>/Cu<sup>+</sup></b>	Cu <sup>2+</sup>	Cu <sup>+</sup>	<b>Cu<sup>2+</sup>/Cu<sup>+</sup></b>
<b>Ce<sub>50</sub>Cu<sub>50</sub></b>	BE (eV)	934.74	933.52	0.60	954.45	952.98	0.56
	RA (%)	37.42	62.58		35.98	64.02	
	Species	Cu <sup>2+</sup>	Cu <sup>+</sup>	<b>Cu<sup>2+</sup>/Cu<sup>+</sup></b>	Cu <sup>2+</sup>	Cu <sup>+</sup>	<b>Cu<sup>2+</sup>/Cu<sup>+</sup></b>
<b>Ce<sub>30</sub>Cu<sub>70</sub></b>	BE (eV)	934.67	933.10	0.66	954.43	952.84	0.66
	RA (%)	39.69	60.31		39.72	60.28	
	Species	Cu <sup>2+</sup>	Cu <sup>+</sup>	<b>Cu<sup>2+</sup>/Cu<sup>+</sup></b>	Cu <sup>2+</sup>	Cu <sup>+</sup>	<b>Cu<sup>2+</sup>/Cu<sup>+</sup></b>
<b>Ce<sub>10</sub>Cu<sub>90</sub></b>	BE (eV)	935.03	933.26	0.80	954.86	953.09	0.80
	RA (%)	44.42	55.58		43.80	56.20	
	Species	Cu <sup>2+</sup>	Cu <sup>+</sup>	<b>Cu<sup>2+</sup>/Cu<sup>+</sup></b>	Cu <sup>2+</sup>	Cu <sup>+</sup>	<b>Cu<sup>2+</sup>/Cu<sup>+</sup></b>
<b>Cu<sub>100</sub></b>	BE (eV)	935.08	933.57	0.92	954.88	953.03	0.87
	RA (%)	47.94	52.06		46.50	53.50	

**Note:** BE refers to binding energy, and RA refers to the relative area of the peak.

## Section 5: Redox properties

**Table S7** Results of the H<sub>2</sub>-TPR analysis for the CeCu catalysts.

Cat.	H <sub>2</sub> consumptions (mmol/g)			
		Peak 1	Peak 2	Peak 3
Ce <sub>100</sub>	Temperature (°C)	575.60	589.94	641.77
	Area	4.03	1.31	6.52
Ce <sub>50</sub> Cu <sub>50</sub>	Temperature (°C)	339.58	392.46	520.55
	Area	1.74	1.68	0.38
Ce <sub>30</sub> Cu <sub>70</sub>	Temperature (°C)	305.51	0.00	0.00
	Area	6.65	0.00	0.00
Ce <sub>10</sub> Cu <sub>90</sub>	Temperature (°C)	255.39	0.00	0.00
	Area	5.59	0.00	0.00
Cu <sub>100</sub>	Temperature (°C)	249.28	0.00	0.00
	Area	5.02	0.00	0.00

**Table S8** Results of the O<sub>2</sub>-TPO analysis for the CeCu catalysts.

Cat.	O <sub>2</sub> consumptions (mmol/g)			
		Peak 1	Peak 2	Peak 3
Ce <sub>100</sub>	Temperature (°C)	693.42	0.00	0.00
	Area	7.09	0.00	0.00
Ce <sub>50</sub> Cu <sub>50</sub>	Temperature (°C)	180.24	536.26	694.14
	Area	0.09	0.64	0.71
Ce <sub>30</sub> Cu <sub>70</sub>	Temperature (°C)	130.66	438.95	693.84
	Area	0.02	0.23	0.68
Ce <sub>10</sub> Cu <sub>90</sub>	Temperature (°C)	85.69	399.26	599.29
	Area	0.03	0.18	0.50
Cu <sub>100</sub>	Temperature (°C)	84.09	187.15	573.07
	Area	0.02	0.06	0.67

## Section 6: Catalytic activity

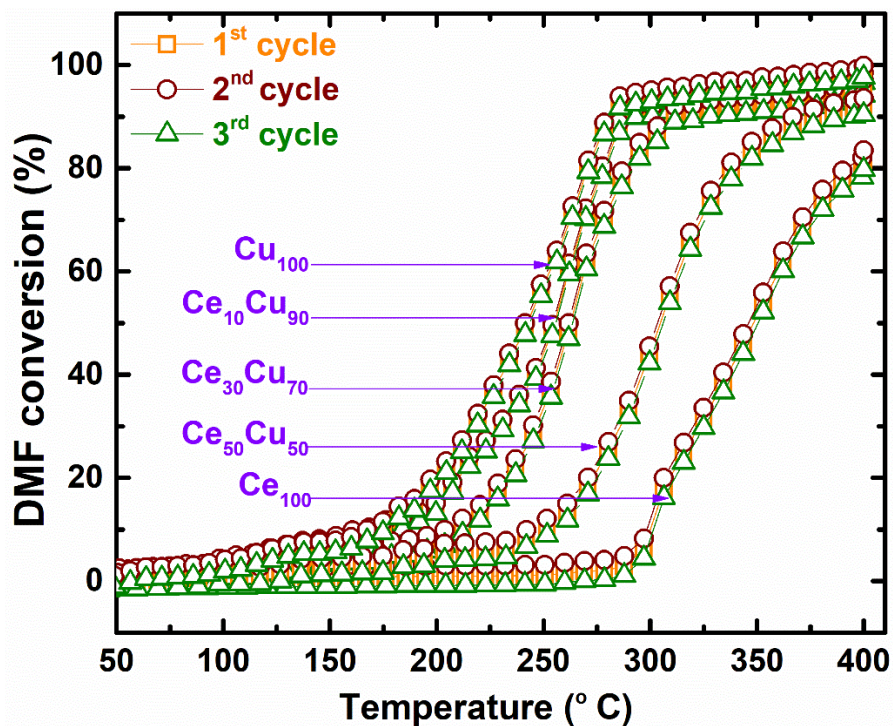


Figure S5. Reproducibility of DMF oxidation over CeCu binary oxides catalysts.

Table S9 Results of DMF conversion and selectivity of products obtained for CeCu binary oxides catalysts.

Catalysts	DMF	CO <sub>2</sub>	NO <sub>2</sub>
Ce <sub>100</sub>	81.48	66.29	33.71
Ce <sub>50</sub> Cu <sub>50</sub>	91.99	62.48	37.52
Ce <sub>30</sub> Cu <sub>70</sub>	95.61	56.81	43.19
Ce <sub>10</sub> Cu <sub>90</sub>	97.55	56.33	43.67
Cu <sub>100</sub>	98.72	56.27	43.73

## References

1. C. K. Fonzeu Monguen, A. El Kasmi, M. F. Arshad, P. M. Kouotou, S. Daniel and Z.-Y. Tian, *Ind. Eng. Chem. Res.*, 2022, **61**, 4546-4560.
2. S. Daniel, C. K. F. Monguen, A. El Kasmi, M. F. Arshad and Z.-Y. Tian, *Catal. Lett.*, 2022, DOI: 10.1007/s10562-022-03977-6.
3. C. K. Fonzeu Monguen, E.-J. Ding, S. Daniel, J.-Y. Jia, X.-H. Gui and Z.-Y. Tian, *Catalysts*, 2023, **16**, 865.