

Supplementary Information

An Efficient Catalyst of CuPt/TiO₂ for Photocatalytic Direct Dehydrogenation of Methanol to Methyl Formate at Ambient Temperature

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Table S1. Catalytic performance of various catalysts in the oxidative dehydrogenation of methanol under thermal condition

Entry	Support	Loading	Temp. (°C)	Conv. MeOH (%)	Sel. MF (%)	by-products
1 ^[1]	SiO ₂	PdCu	160	65	92	CO ₂
2 ^[2]	VTiO	rGO	135	99.6	99.2	CO ₂
3 ^[3]	CeO ₂	ReOx	240	40	90	CO ₂ ,H ₂ CO,Methylal
4 ^[4]	Sn-Mo-O	--	225	50	35-50	CO ₂ ,H ₂ CO,H ₃ COCH ₃
5 ^[5]	Sn-Mo(7:3)	--	160	72	90	CO,CO ₂ ,H ₂ CO,HCOOH
6 ^[6]	Vanadia-titania -sulfate	--	145	98.7	98.6	H ₂ CO,Methylal,H ₃ COCH ₃
7 ^[7]	TiO ₂	AuPd	230	25	70	CO ₂
8 ^[8]	SiO ₂	Pd	80	88	72	CO ₂
9 ^[9]	CNT	RuO ₂	120	20	33	CO ₂ ,H ₂ CO,Methylal
10 ^[10]	TiO ₂	Pd	80	78	52	CO ₂
11 ^[11]	Fe ₂ O ₃	Pd	80	76	81	CO,CO ₂
12 ^[12]	Al-fiber	Au	140	50	90	CO ₂ ,H ₂ CO
13 ^[13]	Graphene	AuPd	70	90	100	--
14 ^[14]	TiO ₂	PdPt	50	78	67	CO ₂
15 ^[15]	Al-fiber	Porous Au	160	35	85	CO ₂ ,H ₂ CO
16 ^[16]	Porous Au	--	80	60	97	CO ₂
17 ^[17]	TiO ₂	V ₂ O ₅	100-150	85	82.5	CO,CO ₂ ,H ₂ CO,HCOOH, Methylal
18 ^[18]	SiO ₂	AuPd	130	57	72.7	CO ₂
19 ^[19]	ZrO ₂	RuOx	100	20	90.3	CO ₂ ,H ₂ CO
20 ^[20]	ZrO ₂	RuOx	100	15	96	CO ₂ ,H ₂ CO
21 ^[21]	ZrO ₂	RuOx	100	20	96	CO ₂ ,H ₂ CO
22 ^[22]	TS-1	VOx	170	56.7	16.2	COx,H ₂ CO,Methylal, H ₃ COCH ₃
23 ^[23]	TiO ₂	V ₂ O ₅	170	95	66	H ₂ CO,Methylal,H ₃ COCH ₃
24 ^[24]	TiO ₂	VOx	120	44	16.87	COx,H ₂ CO,Methylal, H ₃ COCH ₃
25 ^[25]	TiO ₂	V ₂ O ₅	120	33	14.47	COx,H ₂ CO,Methylal, H ₃ COCH ₃
26 ^[26]	ZrO ₂ -Al ₂ O ₃	V ₂ O ₅	215	66	30	H ₂ CO,Methylal,COx
27 ^[27]	TiO ₂ -SO ₄ ²⁻	V ₂ O ₅	170	92	79	COx,H ₂ CO,Methylal, H ₃ COCH ₃
28 ^[28]	TiO ₂	VOx	160	47	57	H ₂ CO,Methylal, H ₃ COCH ₃
29 ^[29]	TiO ₂	Hollow V ₂ O ₅	120-170	95	92	Methylal
30 ^[30]	SBA-15	AgPt	200	30	73	CO ₂ ,H ₂ CO,Methylal, H ₃ COCH ₃

Table S2. Catalytic performance of various catalysts in the direct dehydrogenation of methanol under thermal condition

Entry	Support	Loading	Temp. (°C)	Conv. MeOH (%)	Sel. MF (%)
31 ^[31]	hectorite	Cu	220	12	19
32 ^[32]	TSM	Cu	400	82.1	31.8
33 ^[33]	SiO ₂	Cu	220	31.1	81.4
34 ^[34]	Mo ₂ C	--	200	20	41
	W ₂ C	--	220	20	17
	WC	--	200	20	81
35 ^[35]	TSM	Cu(II)	240	44.8	100
	TSM	Cu(I)	240	4.3	100
36 ^[36]	SiO ₂	Cu(0)	300	7.1	45
	SiO ₂	Cu	180	24	90
37 ^[37]	SiO ₂	Cu	250	62	25
	TiO ₂	Cu	250	21	91
38 ^[38]	ZrO ₂	Cu	250	30	63
	Cr ₂ O ₃ :SiO ₂	Cu	200-270	41	35
39 ^[39]	MO _x (M=Si,Zr,Mg,Zn,Cr and graphite)	Cu	220	41	58
40 ^[40]	ZnO	Pd	200	20.5	80
41 ^[41]	LaM _{1-x} Cu _x O ₃	--	200-260	40	65
42 ^[42]	ZnO	Cu	200	20	35
43 ^[43]	SiO ₂	Cu-PAN	250	45.4	97.4
	Clay (Lapo)	Cu	200	35.8	82.2
44 ^[44]	Clay (Sapo)	Cu	200	9.9	12.1
	TSM	Cu	200	19.7	89.3
45 ^[45]	CuAl ₂ O ₄	--	310	63.6	57.0
46 ^[46]	Cr ₂ O ₃	Cu	207	48	99
47 ^[47]	SiO ₂	Cu	230	50	75-80
	copper chromite				
48 ^[48]	copper hydroxysilicate	--	150-270	10	100
	copper-zinc hydroxysilicate				
49 ^[49]	Zeolite	Cu	280	27.9	72.4
50 ^[50]	mSiO ₂	Cu	230	40	80
51 ^[51]	CuMgO	Pd	250	16.7	88.1

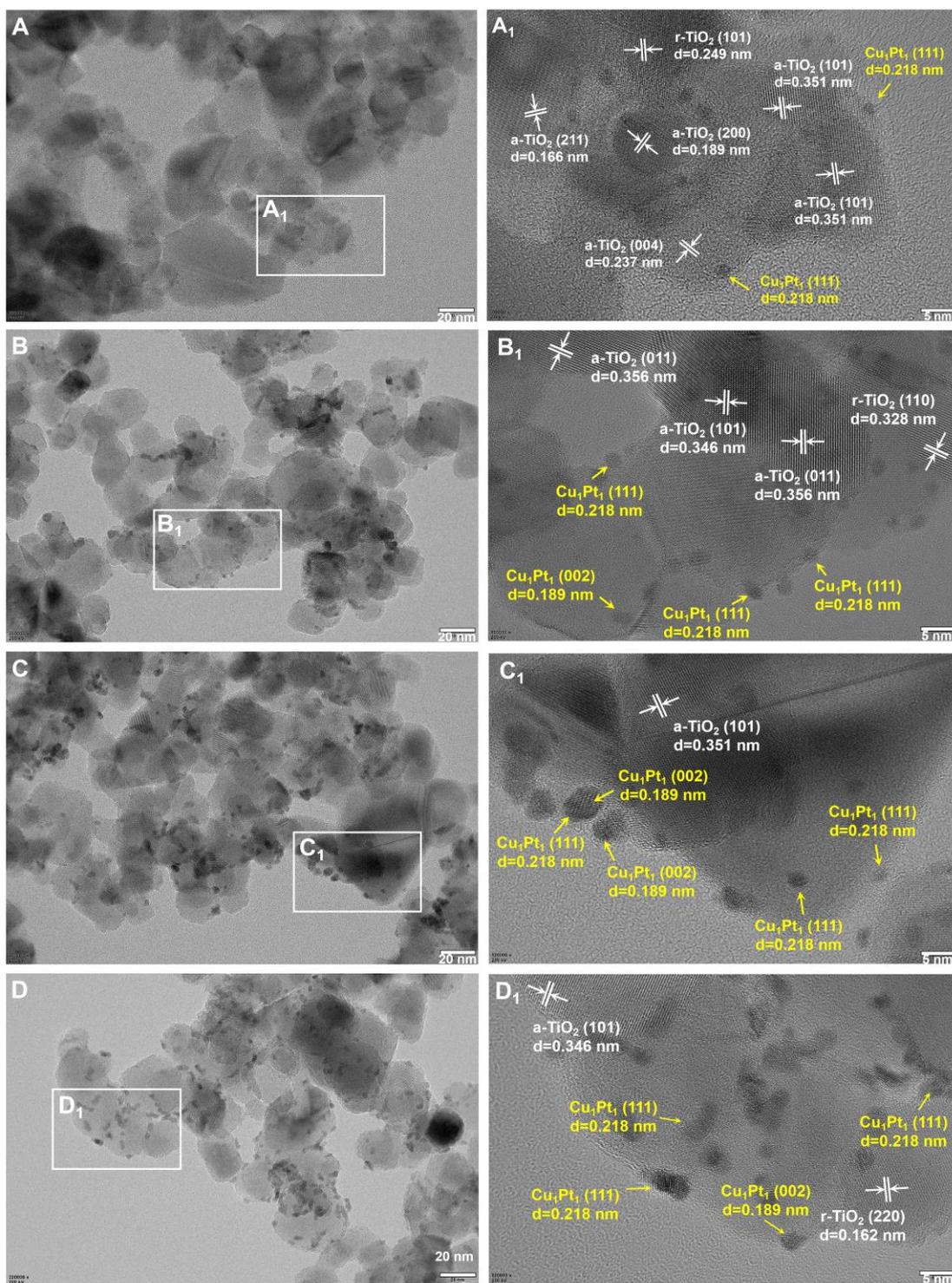


Figure S1. TEM and HR-TEM images of catalysts with different metal content. A. 1% CuPt (1:1)/TiO₂; B. 2% CuPt (1:1)/TiO₂; C. 4% CuPt (1:1)/TiO₂ and D. 6% CuPt (1:1)/TiO₂.

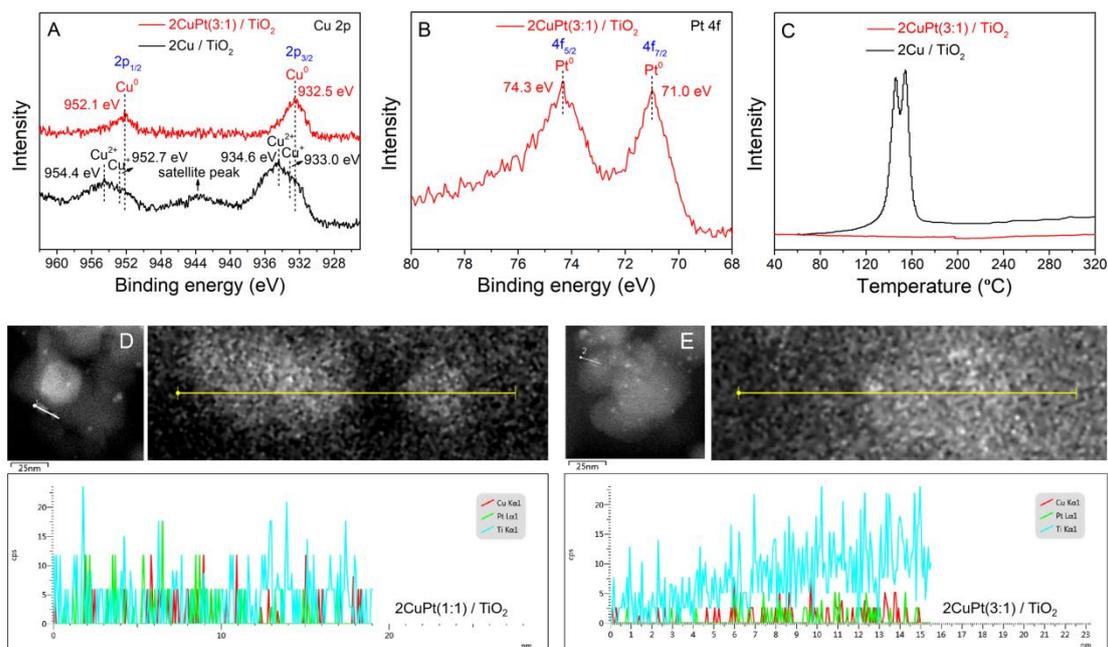


Figure S2. XPS (A, B), TPR (C) and line scan based on the HADDF-stem (D, E) of catalysts with different metal content.

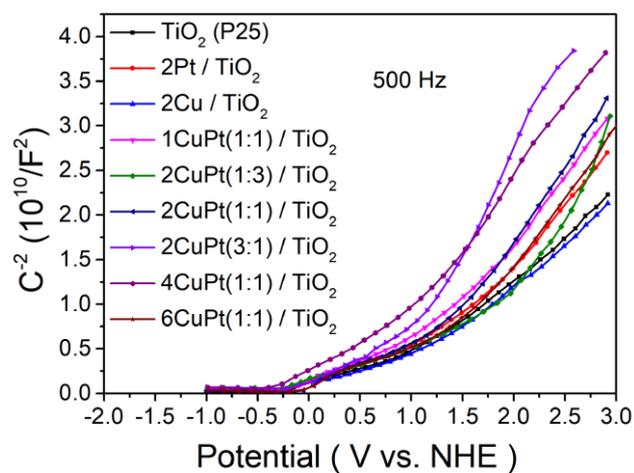


Figure S3. Mott-Schottky diagram of the catalyst at 500 Hz in 0.2 M Na_2SO_4 solution.

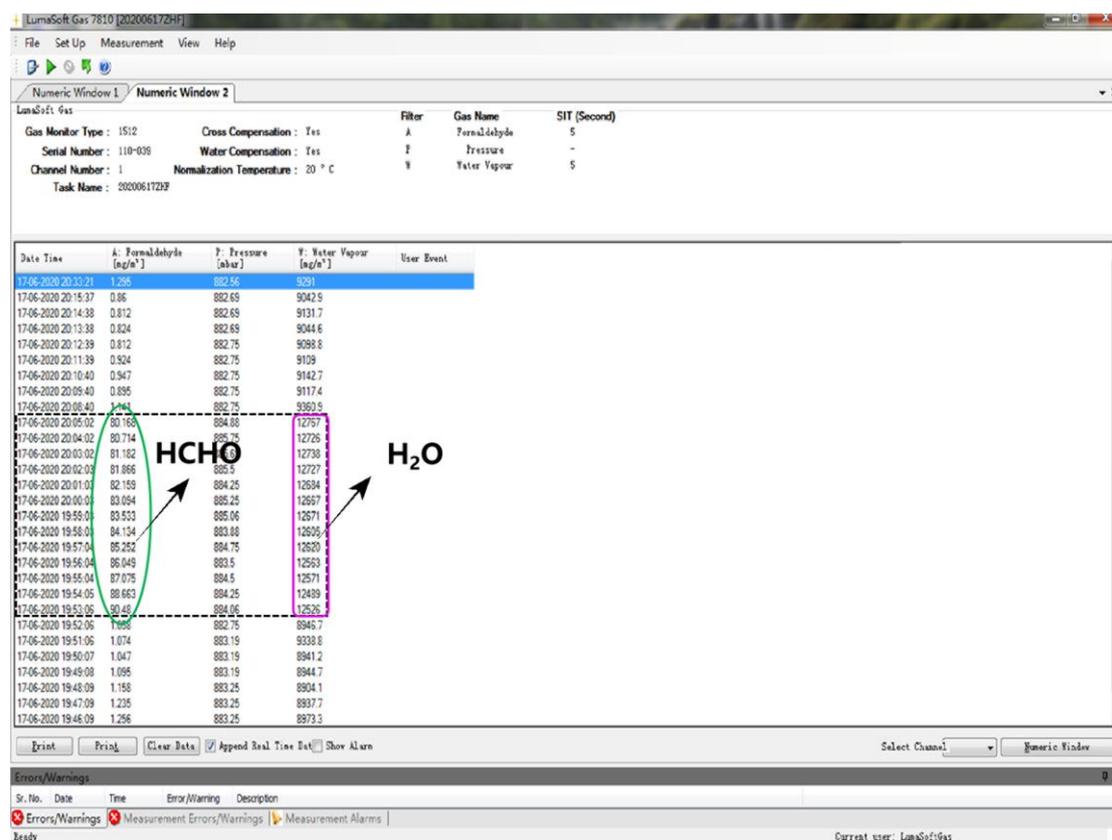


Figure S4. The HCHO and H₂O were detected in the reaction by Photoacoustic Gas Monitor- Innova 1512 installed by LumaSense Technologies.

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