Supporting Information

Ag substituted Au clusters supported on Mg-Al-hydrotalcite for highly efficient base-free aerobic oxidation of 5-hydroxymethylfurfural to 2,5-furandicarboxylic acid

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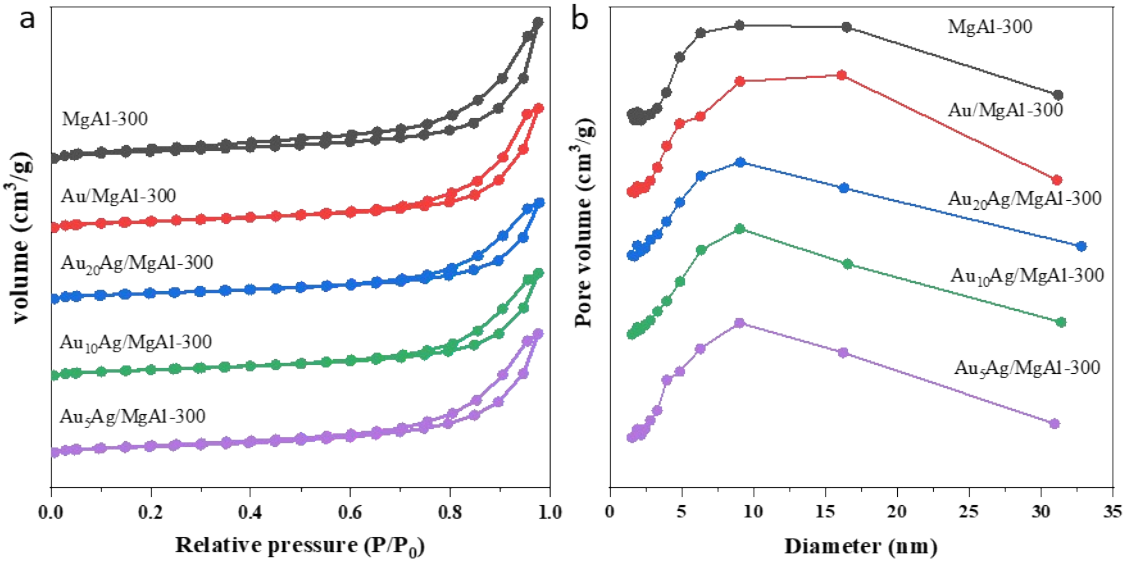

Figure S1. (a) N_2 physisorption isotherms and (b) BJH-pore size distributions of supported Au and Au-Ag bimetallic catalysts.

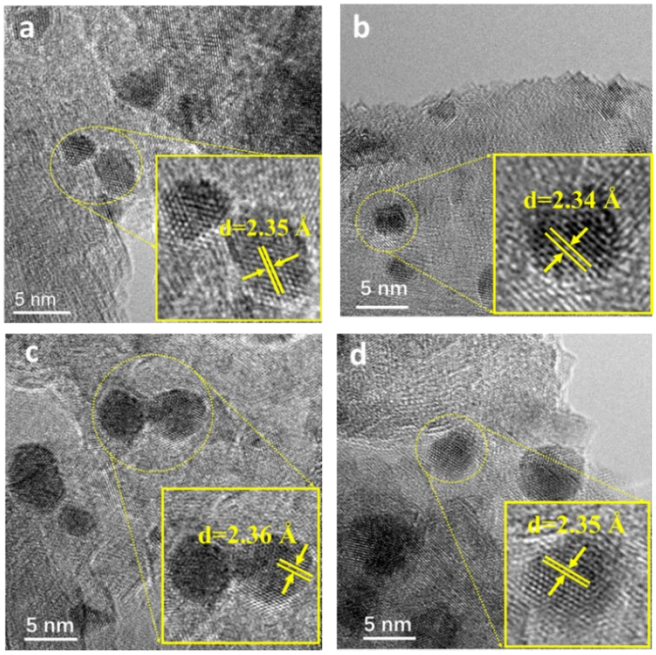

Figure S2. HRTEM images of supported Au and Au-Ag bimetallic catalysts: (a) Au/MgAl-300; (b) $Au_{20}Ag$/MgAl-300; (c) $Au_{10}Ag$/MgAl-300; (d) Au_5Ag/MgAl-300.

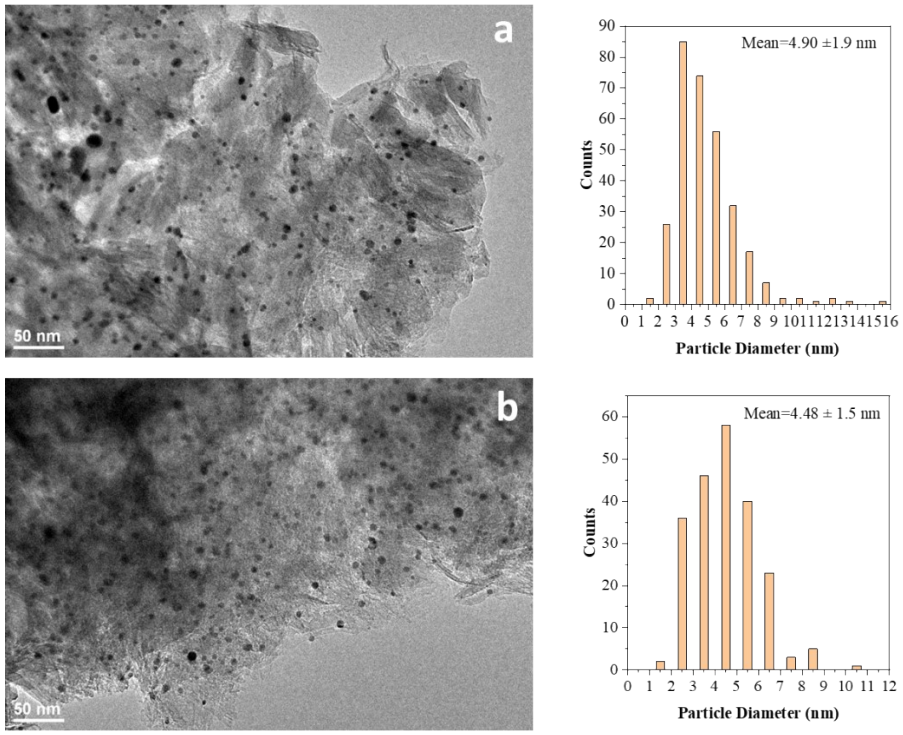

Figure S3. TEM images and histogram of size distributions of (a) Au/MgAl-300 and (b) $Au_{20}Ag$/MgAl-300 catalysts after recycle for three times.

Table S1. Representative Au-based heterogeneous catalysts for aerobic oxidation of HMF to FDCA.

Entry	Catalyst	HMF/Metal molar ratio	Base additive	T/ °C	P_{O2}/ atm	Time/ h	HMF Conv. / %	FDCA Sel. / %	Specific reaction rates ($mol_{HMF}·mol_{Au}^{-1}·h^{-1}$)	Catalytic productivity ($mol_{FDCA}·mol_{Au}^{-1}·h^{-1}$)	Ref.
1	Au/MgAl-300	70	no	90	5	2	100	95.5	704.9	17	This work
2	$Au_{20}Ag_1$/MgAl-300	70	no	90	5	2	100	95.5	748.6	33.3	This work
3	Au/HT	40	no	95	1	7	>99	>99	36	5.7	1
4	Au/MgO	50	no	110	5.5	2	99	91	25	22.5	2
5	Au/nNiO	100	no	90	10	6	71	25	19	3	3
6	Au/HT-AC	100	no	100	5	24	100	>99	38	8.3	4
7	Pd/HT-5	20	no	100	1	8	100	>99	18.8	2.5	5
8	$Pd_{20}Pt_{80}$-PVP/HT	75	no	95	1	11.5	100	>99	27	6.5	6
9	Pt/NC-CeO_2	163	no	150	4	2	100	99	114	81.4	7
10	Pt/NiO	200	no	100	10	12	100	100	124	22.2	8
11	AuPd/La-CaMgAl-LDH	53	no	120	5	2	96	91	64	23	9
12	AuPd/CNT	100	no	100	5	12	100	94	80	7.8	10
13	AuPd/nNiO	100	no	90	10	6	95	70	82	11.1	3
14	Au/SiO_2	72	$NaHCO_3$	90	10	5	>99	74	14	10.7	11
15	Au/CeO_2	78	Na_2CO_3	140	5	15	>99.9	91	64	4.7	12
16	Au/TiO_2	100	NaOH	30	20	18	100	71	5.6	3.9	13
17	Au/MZ-600	143	NaOH	95	1	4	100	95	72	34	14
18	Au/HSAG-N	160	$NaHCO_3$	90	10	12	>99	75	1195	10	15
19	Au/ZrO_2	373	NaOH	125	10.5	5	100	89	75	67	16
20	Au_1Pd_3/pBN_2C-800	35	Na_2CO_3	100	30	24	100	97.6	29	2	17
21	Ag_3Au_7/ZrO_2	100	NaOH	125	2.1	5	100	95	20	19	18
22	Au_1Pd_1/PECN	100	K_2CO_3	90	1	12	99.7	99	190	8.3	19
23	AuPd/IRA-743	100	Na_2CO_3	100	10	4	100	93	60	23	20

24	AuPd/ZOC	100	$NaHCO_3$	80	3	4	>99	>99	74	25	21
25	$AuCu/TiO_2$	100	NaOH	95	10	4	>99	99	130	25	22
26	Au_8Pd_2/AC	200	NaOH	60	3	2	>99	99	100	99	23

Table S2. The original data for drawing the Arrhenius plots for HMF oxidation over the Au/MgAl-300 and $Au_{20}Ag$/MgAl-300 catalysts.

Au/MgAl-300				$Au_{20}Ag$/MgAl-300			
Temperature (°C)	Conversion (%)	10^4/RT	In(r)	Temperature (°C)	Conversion (%)	10^4/RT	In(r)
75	7.05	3.45	-2.88	75	10.94	3.45	-2.44
85	9.80	3.36	-2.55	85	12.06	3.36	-2.34
95	11.04	3.27	-2.43	95	13.51	3.27	-2.22
105	16.15	3.18	-2.05	105	16.62	3.18	-2.02
115	24.36	3.10	-1.64	115	22.67	3.10	-1.71

References

1. N. K. Gupta, S. Nishimura, A. Takagaki, K. Ebitani. *Green Chem.*, **2011**, *13*, 824-827.
2. C. P. Ferraz, M. Zielinski, M. Pietrowski, S. Heyte. *ACS Sustainable Chem. Eng.*, **2018**, *6*, 16332-16340.
3. D. Bonincontro, A. Lolli, A. Villa, L. Prati. *Green Chem.*, **2019**, *21*, 4090-4099.
4. T. Gao, T. Gao, W. Fang, Q. Cao. *Mol. Catal.,***2017**, *439*, 171-179.
5. Y. Wang, K. Yu, D. Lei, W. Si, Y. Feng, S. Liu. *ACS Sustain. Chem. Eng.*, **2016**, *4*, 4752–4761.
6. H. Choudhary, K. Ebitani. *Chem. Lett.*, **2016**, *45*, 613–615.
7. C. Ke, M. Li, G. Fan, L. Yang, F. Li. *Chemistry*, **2018**, *13*, 2714-2722.
8. H. Zhang, T. Gao, Q. Cao, W. Fang. *ACS Sustainable Chem. Eng.*, **2021**, *9*, 6056-6067.
9. Z. Gao, R. Xie, G. Fan, L. Yang. *ACS Sustainable Chem. Eng.*, **2017**, *5*, 5852-5861.
10. X. Wan, C. Zhou, J. Chen, W. Deng. *ACS Catal.*, **2014**, *4*, 2175-2185.
11. N. Masoud, B. Donoeva, P. E. Jongh. *Appl. Catal. A-Gen.*, **2018**, *561*, 150-157.
12. M. Kim, Y. Su, A. Fukuoka, E. J. M. Hensen. *Angew. Chem. Int. Ed.*, **2018**, *57*, 8235 - 8239.
13. Y. Y. Gorbanev, S. K. Klitgaard, J. M. Woodley, C. H. Christensen. *ChemSusChem*, **2009**, *2*, 672-675.
14. A. I. M. Rabee, S. D. Le, K. Higashimine, S. Nishimura. *ACS Sustainable Chem. Eng.*, **2020**, *8*, 7150-7161.
15. B. Donoeva, N. Masoud, P. E. Jongh. *ACS Catal.*, **2017**, *7*, 4581-4591.
16. O. R. Schade, K. F. Kalz, D. Neukum, W. Kleist. *Green Chem.*, **2018**, *20*, 3530-3541.
17. W. Guan, Y. Zhang, Y. Chen, J. Wu. *J. Catal.*, **2021**, *396*, 40-53.
18. O. R. Schade, F. Stein, S. Reichenberger, A. Gaur. *Adv. Synth. Catal.*, **2020**, *362*, 5681-5696.
19. Q. Wang, W. Hou, S. Li, J. Xie. *Green Chem.*, **2017**, *19*, 3820-3830.
20. C. A. Antonyraj, S. K. Parka, S. S, J. K. Cho. *Appl. Catal. A-Gen.*, **2017**, *547*, 230-236.
21. Z. Gui, W. Cao, S. Saravanamurugan, A. Riisager. *ChemCatChem*, **2016**, *8*, 3636-3643.

22. T. Pasini, M. Piccinini, M. Blosi, R. Bonelli. *Green Chem.*, **2011**, *13*, 2091-2099.

23. A. Villa, M. Schiavoni, S. Campisi , G. M. Veith. *ChemSusChem*, **2013**, *6*, 609-612.