Electronic Supplementary Information (ESI)

Synergistic effect between gold nanoparticles and metal-doped γ-MnO_2 toward enhanced aerobic selective oxidation of ethanol

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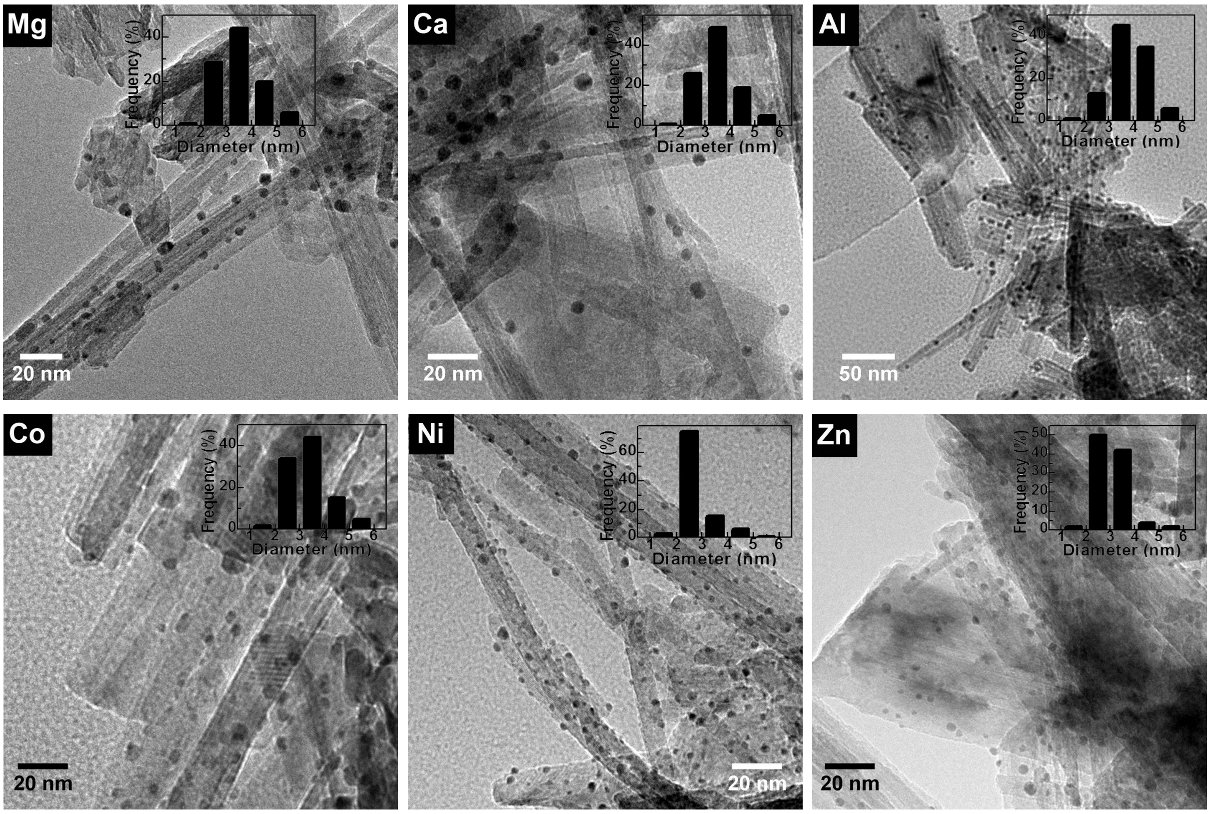

Fig. S1 TEM images and AuNP size distributions of various Au/M-γ-MnO_2 samples.

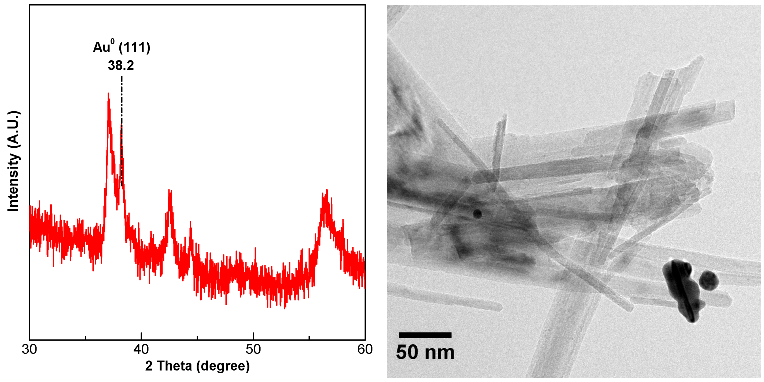

Fig. S2 XRD pattern and TEM image of Au/Cu-γ-MnO_2-DP sample.

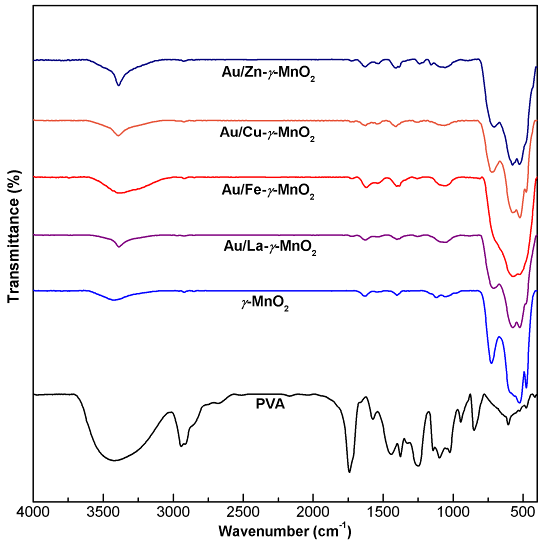

Fig. S3 FT-IR spectra of various samples.

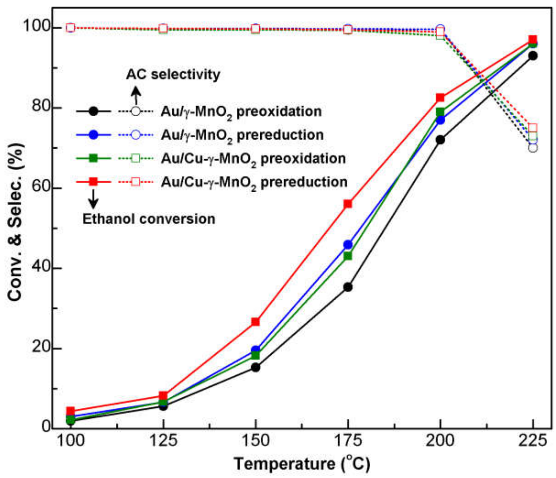

Fig. S4 Effect of catalyst pretreatment on the catalytic performance.

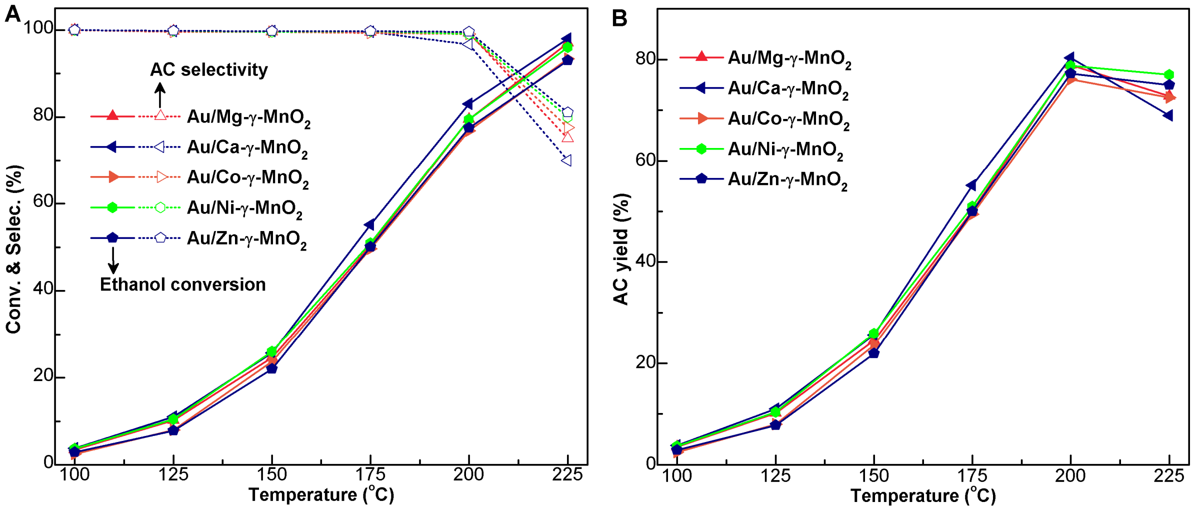

Fig. S5 Ethanol conversion & AC selectivity (A) and AC yield (B) as a function of the reaction temperature over various Au/M-γ-MnO_2 catalysts.

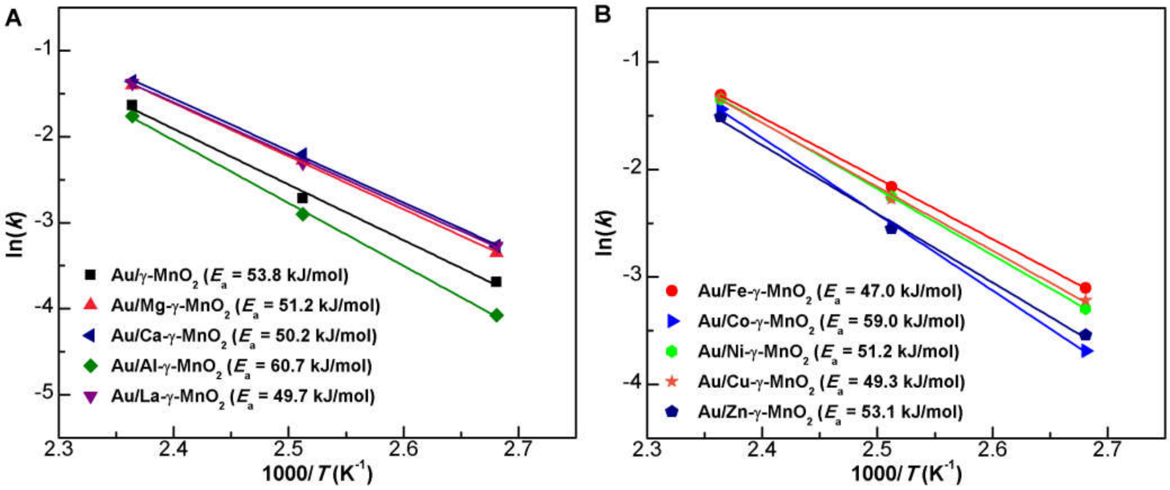

Fig. S6 Arrhenius plots and apparent activation energies for ethanol oxidation at 100-150 °C over various Au/M-γ-MnO_2 catalysts.

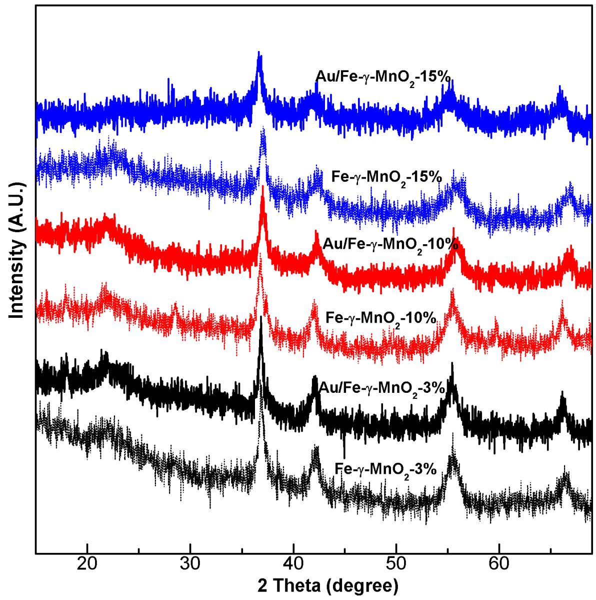

Fig. S7 XRD patterns of various Fe-γ-MnO_2 and Au/Fe-γ-MnO_2 samples.

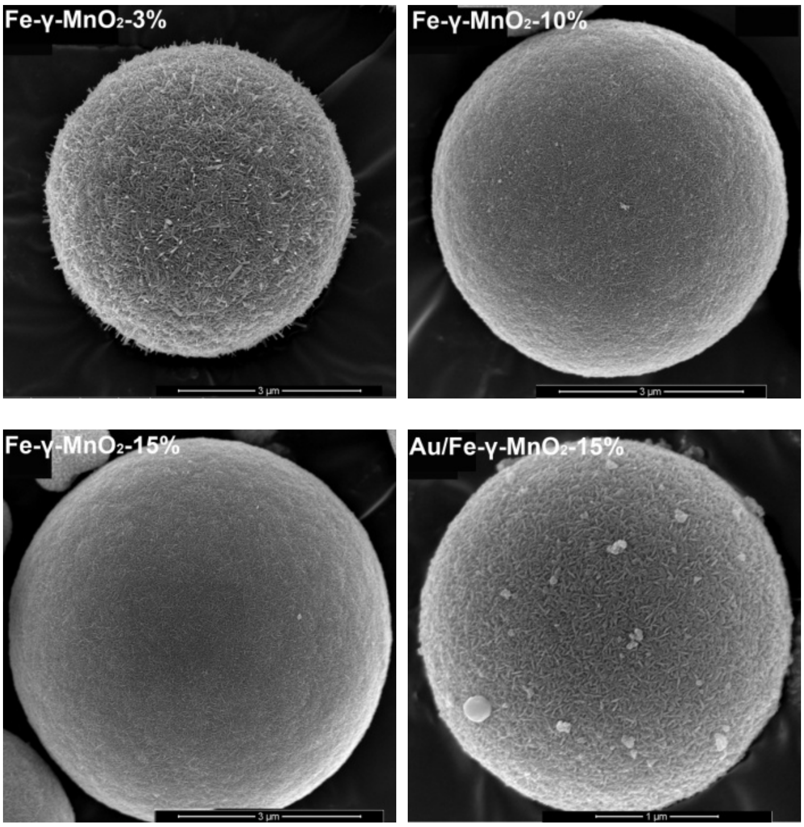

Fig. S8 SEM images of various Fe-γ-MnO_2 and Au/Fe-γ-MnO_2-15% samples.

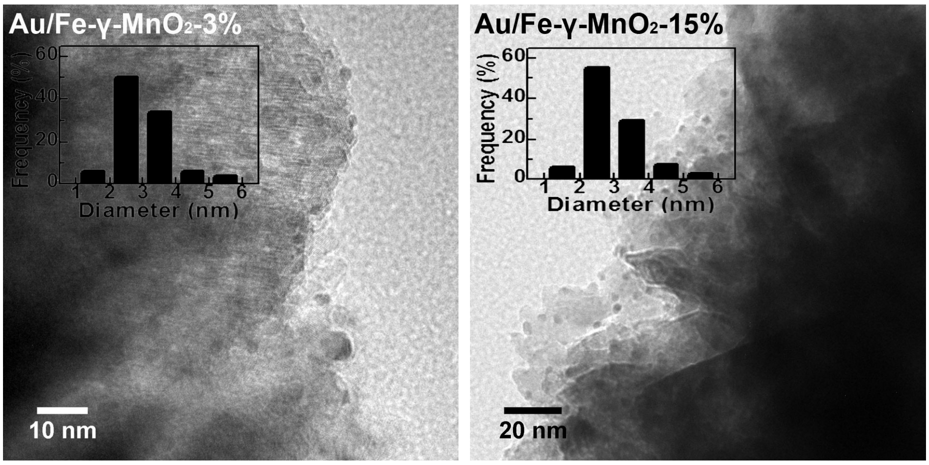

Fig. S9 TEM images of Au/Fe-γ-MnO_2-3% and Au/Fe-γ-MnO_2-15% catalysts.

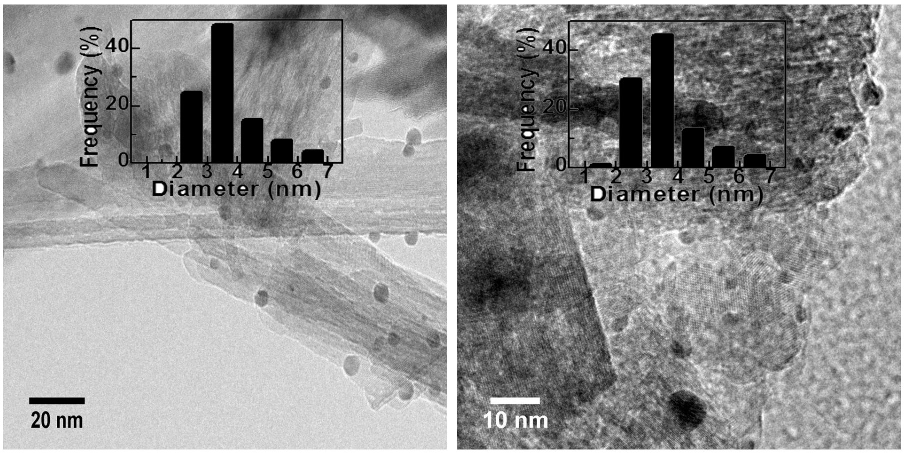

Fig. S10 TEM images and AuNP size distributions of the spent Au/γ-MnO_2 and Au/Fe-γ-MnO_2 catalysts.

Table S1 H_2-TPR results of various Au/M-γ-MnO_2 catalysts and M-γ-MnO_2 supports

Sample	H_2 uptake (mmol/g)	H_2 uptake of support (mmol/g)
Au/γ-MnO_2	8.6	10.7
Au/Mg-γ-MnO_2	9.3	9.6
Au/Ca-γ-MnO_2	9.0	10.1
Au/Al-γ-MnO_2	7.2	8.3
Au/La-γ-MnO_2	8.8	10.3
Au/Fe-γ-MnO_2	6.8	7.7
Au/Co-γ-MnO_2	8.2	9.7
Au/Ni-γ-MnO_2	7.9	9.2
Au/Cu-γ-MnO_2	8.1	9.5
Au/Zn-γ-MnO_2	8.5	9.8

Table S2 Comparison of representative supported gold catalysts from the literature and the present work for gas-phase aerobic oxidation of ethanol at 200 °C.

Catalyst	**[ethanol] (vol.%)**	**O_2/ethanol**	**Conv. (%)**	**Selec. (%)**	**Yield (%)**	**STY ($g_{aldehyde}$ g_{cat}^{-1} h^{-1})**	**Ref.**
2wt% Au/TiO_2	2.0	9	65	60	39	0.06	[1]
1wt% Au/MoO_3	0.77	3	65.5	99	65	0.19	[2]
1wt% Au/MnO_2	0.77	3	100	0	0	0	[2]
1wt% Au/Recryst-S1	2.0	1	50	98	49	1.38	[3]
1wt% Au/$CuSiO_3$	1.5	3	30	94	28.2	0.64	[4]
1.4wt% AuCu/BN	1.5	3	92	87	80	2.4	[5]
0.9wt% Au/$MgCuCr_2O_4$	1.5	3	73	99	72	2.1	[6]
1wt% Au/Cu-OMS	2.5	1	92	87	80	3.0	[7]
1wt% Au/γ-MnO_2	2.5	1	77	99.6	77	2.9	**This**
0.7wt% Au/Fe-γ-MnO_2	**2.5**	**1**	**89**	**96**	**85**	**3.2**	**work**

Table S3 Kinetic isotope effects for ethanol oxidation on Au/Fe-γ-MnO_2 at 125 °C.[a]

Reactant	Conv. (%)	Selec. (%)	Activity (mmol g_{cat}^{-1} h^{-1})	KIE (k_H/k_D)
C_2H_5OH	11.5	99.8	9.8	-
C_2H_5OD	8.4	99.7	7.2	1.37
C_2D_5OD	5.6	99.6	4.8	2.05

[a] Ethanol conversion and acetaldehyde selectivity at 125 °C (catalyst 0.06 g, ethanol/O_2/N_2 = 1/1/38, GHSV = 100,000 mL g_{cat}^{-1} h^{-1}).

Reference

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