Electronic Supporting Information

Efficient imine synthesis *via* oxidative coupling of alcohol with amine in air atmosphere using mesoporous manganese-zirconium solid solution catalyst

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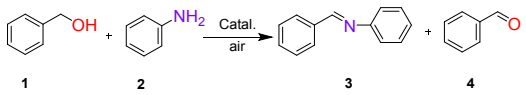
Table S1 Effect of stirring rate on imine formation



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Stirring rate (rpm)	Reaction rate (mmol g^{-1} h^{-1})[a]	Select. **3** (%)	Select. **4** (%)	Carbon balance (%)
300	2.81	> 99	< 1	100
500	4.16	> 99	< 1	100
700	6.16	> 99	< 1	100
800 (standard)	8.33	> 99	< 1	100
900	8.33	> 99	< 1	100
1000	8.33	> 99	< 1	100

Reaction conditions: benzyl alcohol, 1 mmol; aniline, 1.5 mmol; $Mn_1Zr_{0.5}O_y$, 60 mg; toluene, 5 mL; air, 1 atm; temperature, 80 °C; time, 1 h.

[a] Based on the conversion of benzyl alcohol.

The influence of stirring rate was explored and the results were listed in Table S1. With stirring rate increasing, the carbon balance remains stable at 100%, while initial reaction rate increases continuously and becomes almost constant when the stirring rate reaches 800 rpm. Therefore, the stirring rate of follow-up experiments is set at 800 rpm to make sure that all the reactions are conducted under chemical control. The absence of mass transport resistance is checked by Weisz-Prater Criterion (C_{WP}) for internal and external diffusion and it can be verified by changing the stirring rate. If $C_{WP} = \frac{\gamma_{obs}\rho_c R_P^2}{D_{eff}C_S} < 1$, then internal mass transfer effects can be neglected.

γ_{obs} = observed reaction rate, mol kg_{cat}^{-1} s^{-1}

R_P = catalyst particle radius, m

ρ_c = solid catalyst density, kg m^{-3}

D_{eff} = effective diffusivity, m^2 s^{-1}

$D_{eff} = \frac{D_{AB}\phi_P\sigma_c}{\tau}$

where D_{AB}= gas-phase diffusivity m^2 s^{-1}; $\emptyset_P$= pellet porosity;

σ_c= constriction factor; τ= tortuosity.

Cs = gas concentration of A at the external surface of the catalyst, mol m^{-3}

$C_{WP} = \frac{\gamma_{obs}\rho_c R_P^2}{D_{eff}C_S}$ = [(2.15 × 10^{-3} mol kg_{cat}^{-1} s^{-1}) × (5.06 × 10^3 kg m^{-3}) × (1.0 × 10^{-5} m)^2] / [(2.0 × 10^{-5} m^2 s^{-1}) × (7.30 mol m^{-3})] = 7.45×10^{-6} ≤ 1

So internal mass transfer effect can be neglected.

Table S2 XPS parameters of Mn 2p, Zr 3d and O 1s core level for MnO_y, $Mn_1Zr_xO_y$ and ZrO_2 catalysts

Catalyst	Bonding energy (eV)				$Mn^{3+}/(Mn^{3+}+Mn^{4+})$	$O_{surf.}/(O_{latt.}+O_{surf.})$
	Mn^{3+}	Mn^{4+}	Zr^{4+}	O 1s ($O_{latt.}$, $O_{surf.}$)	(%)	(%)
MnO_y	641.2, 652.7	642.8, 654.1	–	530.2, 531.6	34.9	33.1
$Mn_1Zr_{0.25}O_y$	641.7, 653.2	643.4, 654.4	181.9, 184.2	529.8, 531.2	39.1	45.8
$Mn_1Zr_{0.5}O_y$	641.8, 653.4	643.4, 654.7	181.8, 184.2	529.7, 531.2	45.4	52.5
$Mn_1Zr_1O_y$	641.8, 653.4	643.3, 654.6	181.7, 184.1	529.7, 531.2	41.3	47.2
ZrO_2	–	–	182.1, 184.5	529.7, 531.4	–	31.9

Table S3 Acidity and basicity measured by NH_3-TPD and CO_2-TPD for MnO_y, $Mn_1Zr_xO_y$ and ZrO_2 catalysts

Catalyst	Acidity (mmol g^{-1})			Basicity (mmol g^{-1})		
	Weak	Strong	Total	Weak	Strong	Total
MnO_y	0.04	0.26	0.30	0.13	0.22	0.35
$Mn_1Zr_{0.25}O_y$	0.39	0.50	0.89	0.17	0.23	0.40
$Mn_1Zr_{0.5}O_y$	0.50	0.55	1.05	0.28	0.20	0.48
$Mn_1Zr_1O_y$	0.53	0.33	0.86	0.23	0.20	0.43
ZrO_2	0.39	0.09	0.48	0.06	0.12	0.18

Table S4 Comparison of the initial conversion rates of benzyl alcohol in oxidative coupling with aniline and aerobic oxidation without aniline

Catalyst	Initial conversion rate (mmol $g_{cat.}^{-1}$ h^{-1})	
	With aniline	Without aniline
MnO_y	4.17	1.83
$Mn_1Zr_{0.25}O_y$	6.33	2.83
$Mn_1Zr_{0.5}O_y$	8.33	3.67
$Mn_1Zr_1O_y$	7.00	3.17
ZrO_2	0.40	0.22

Reaction conditions: benzyl alcohol, 1 mmol; aniline, 1.5 mmol; catalyst, 60 mg; toluene, 5 mL; air, 1 atm; temperature, 80 °C; time, 1 h.

Table S5 Kinetic data of oxidative coupling of benzyl alcohol withaniline over $Mn_1Zr_xO_y$ catalysts

T (K)	Conv. (%)			k (s^{-1})			1000/T	ln(k×10^5)		
	$Mn_1Zr_{0.25}O_y$	$Mn_1Zr_{0.5}O_y$	$Mn_1Zr_1O_y$	$Mn_1Zr_{0.25}O_y$	$Mn_1Zr_{0.5}O_y$	$Mn_1Zr_1O_y$	(K^{-1})	$Mn_1Zr_{0.25}O_y$	$Mn_1Zr_{0.5}O_y$	$Mn_1Zr_1O_y$
333.15	24	37	19	5.08E-05	8.56E-05	3.90E-05	3.00	1.63	2.15	1.36
343.15	41	55	36	9.77E-05	1.48E-04	8.26E-05	2.91	2.28	2.69	2.11
353.15	61	72	55	1.74E-04	2.36E-04	1.48E-04	2.83	2.86	3.16	2.69
363.15	78	86	71	2.80E-04	3.64E-04	2.29E-04	2.75	3.33	3.59	3.13

Reaction conditions: benzyl alcohol, 1 mmol; aniline, 1.5 mmol; catalyst, 60 mg; toluene, 5mL; air, 1atm; time, 1.5 h. The rate constant (k) was calculated by $\ln C_0/\ln C_t = kt$. The apparent activation energy (E_a) was calculated based on the arrangement of Arrhenius equation, $E_a = -R d\ln k/d\ln(1/K)$.

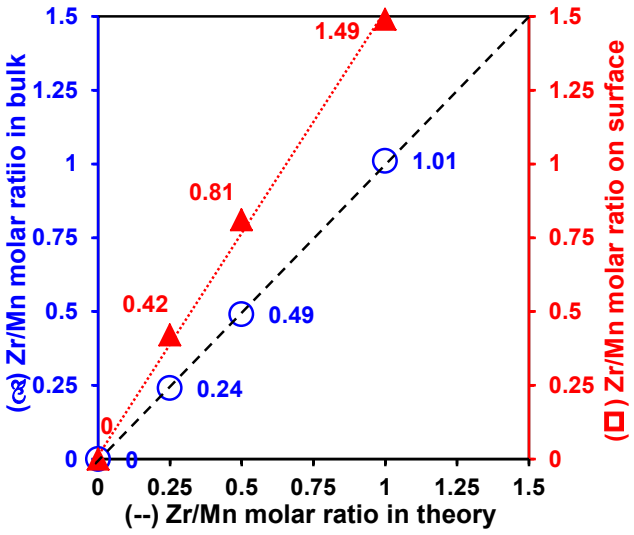

Fig. S1 Zr/Mn molar ratio of the $Mn_1Zr_xO_y$ catalysts obtained from bulk by ICP-MS and from surface by XPS as a function of the theoretical ratio.

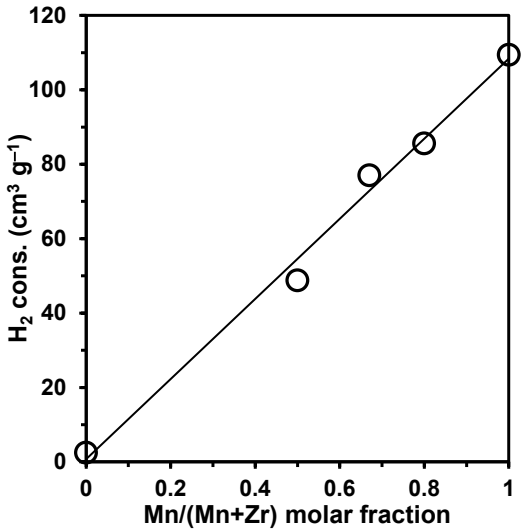

Fig. S2 H_2 consumption during TPR *versus* the molar fraction of Mn in the $Mn_1Zr_xO_y$ catalysts.

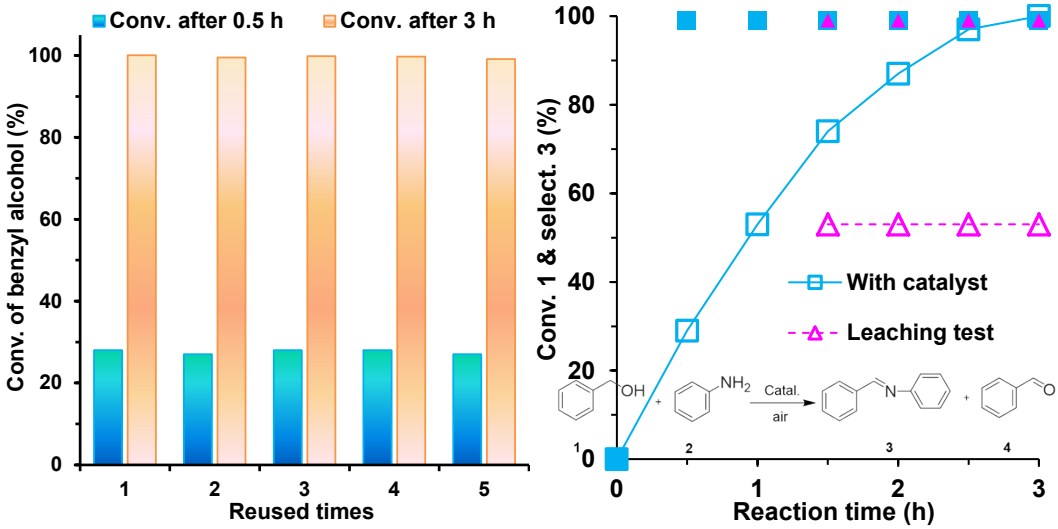

Fig. S3 (left) Recycling test of the $Mn_1Zr_{0.5}O_y$ catalyst for oxidative coupling of benzyl alcohol with aniline within the kinetic-controlled region and under the optimized conditions. (right) Leaching test of metals in the $Mn_1Zr_{0.5}O_y$ catalyst during oxidative coupling of benzyl alcohol with aniline. Reaction conditions: benzyl alcohol, 1 mmol; aniline, 1.5 mmol; catalyst, 60 mg; toluene, 5 mL; air, 1 atm; temperature, 80 °C.

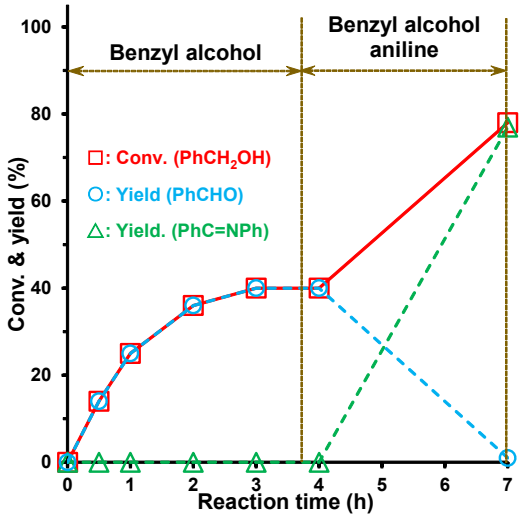

Fig. S4 Time course for aerobic oxidation of benzyl alcohol with or without aniline. Reaction conditions: benzyl alcohol, 1 mmol; aniline, 1.5 mmol; $Mn_1Zr_{0.5}O_y$, 60 mg; toluene, 5 mL; air, 1 atm; temperature, 80 °C.

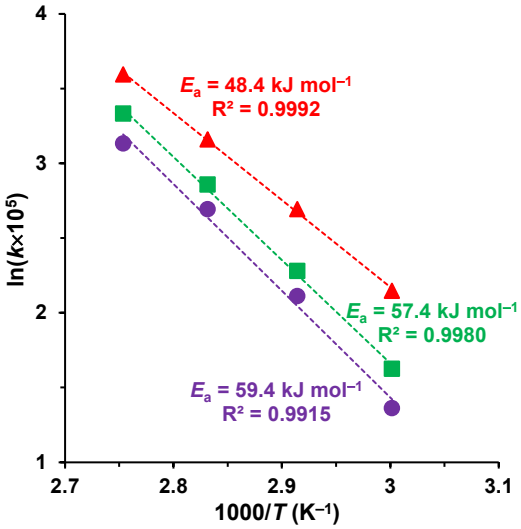

Fig. S5 Arrhenius plot for conversion of benzyl alcohol during oxidative coupling of benzyl alcohol with aniline over the (○) $Mn_1Zr_{0.25}O_y$ (□) $Mn_1Zr_{0.5}O_y$ and (ᔓ) $Mn_1Zr_1O_y$ catalysts. Reaction conditions: benzyl alcohol, 1 mmol; aniline, 1.5 mmol; catalyst, 60 mg; toluene, 5 mL; air, 1 atm; temperature, 60–90 °C; time, 1.5 h.