

Electronic Supporting Information

**Spinel ZnMn_2O_4 hollow nanospheres as efficient catalyst
for imine synthesis at near room temperature**

1. Experimental details

Materials and reagents

All the chemicals were purchased commercially and used directly. $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (99.99%), Ethylene glycol (EG, >99.5%) and toluene (AR) were purchased from Aladdin. Polyvinylpyrrolidone (PVP, >98%, M.W.= 58,000) was obtained from Tokyo Chemical Industry Co. Ltd. $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (98%), benzyl alcohol (99%), aniline (>99%), benzaldehyde (99%) and *N*-benzylideneaniline (99%) were obtained from Acros Organics.

Catalyst preparation

In a typical synthesis of hollow ZnMn_2O_4 microspheres, 0.3 g of PVP was firstly added into 200 mL of ethylene glycol and stirred at 80 °C until completely dissolved. Then, 2 mmol of $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ and 4 mmol of $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ were added into the above solution and continue stirring until dissolved. Subsequently, the solution was heated to 180 °C in an oil bath and refluxed for 6 h under stirring. After cooling to room temperature, the obtained solids (ZnMn-glycolate precursor) were collected by centrifugation and washed with hot (>90 °C) distilled water and ethanol for several times, respectively. Finally, the solids were dried at 80 °C for 12 h in vacuum and then calcined in air at 500 °C (1 °C min⁻¹) for 8 h.

In addition, the hollow Mn_5O_8 catalyst was synthesized by the same protocol.

Catalytic reaction

Catalytic experiments were conducted using a WP-TEC-1020HC parallel reactor supplied by WATTCASTM (<https://www.wattcas.com>). In a typical procedure, toluene (5 mL), benzyl alcohol (1.0 mmol), aniline (1.0 mmol), and the catalyst (50 mg) and were added to and mixed in the reactor. Then, the reaction was performed at 30 °C under open air for 18 h with magnetic stirring (800 rpm). It can be confirmed that internal and external diffusion limitations were excluded. Afterwards, the

clear liquid after filtration was identified by a gas chromatograph (TRACE 1310, Thermo Scientific) equipped with a TR-5 column (30 m, 0.32 mm, 0.25 μm) and a FID detector. The external standard method was employed for quantitative analysis. The external standard method was used to quantify the conversion of benzyl alcohol, the selectivity and yield of imine using the following equations on the basis of carbon balance. Notably, carbon balance measured for each reaction was almost 100%. During the following kinetic studies, the conversion of benzyl alcohol was maintained at below 20%. For recycling test, the used and separated catalyst was thoroughly washed with ethanol and water several times and then dried at 60 $^{\circ}\text{C}$ under vacuum overnight for the consecutive tests.

Equations for quantifying catalytic performances.

$$\text{Conv.}(\%) = \frac{n_{\text{alcohol,initial}} - n_{\text{alcohol,final}}}{n_{\text{alcohol,initial}}} \times 100\% \quad (\text{Eq. S1})$$

$$\text{Select.}(\%) = \frac{n_{\text{imine}}}{n_{\text{alcohol,initial}} - n_{\text{alcohol,final}}} \times 100\% \quad (\text{Eq. S2})$$

$$\text{Yield}(\%) = \frac{n_{\text{imine}}}{n_{\text{alcohol,initial}}} \times 100\% \quad (\text{Eq. S3})$$

$$r_{\text{initial}} (\text{mmol } g_{\text{Mn}}^{-1} \text{ h}^{-1}) = \frac{n_{\text{alcohol,initial}} - n_{\text{alcohol,final}}}{W_{\text{Mn}} \times \text{time}} \quad (\text{Eq. S4})$$

$$\text{Prod.} (\text{mmol } g_{\text{catal.}}^{-1} \text{ h}^{-1}) = \frac{n_{\text{imine}}}{W_{\text{catal.}} \times \text{time}} \quad (\text{Eq. S5})$$

Characterization methods

X-ray diffraction (XRD) was performed on a Bruker D8 Advance A25 Diffractometer with Cu $\text{K}\alpha$ radiation and the patterns were recorded in the 2θ domain (10–90 $^{\circ}$) with a measured rate of 0.02 $^{\circ}$ per 0.2 s. Inductively coupled plasma mass spectrometry (ICP-MS) was carried out on an Agilent 7500a apparatus. N_2 adsorption-desorption isotherms were obtained at 77 K on a Micromeritics TriStar II 3020 Analyzer. The specific surface area and pore size distribution were calculated using BET and BJH methods, respectively. Transmission electron microscopy (TEM)

and high-resolution transition electron microscopy (HRTEM) images were carried out on a Tecnai G2 F20 S-Twin microscope equipped with an element mapping technique (SDD, X-max 80 T, S3 OXFORD Instruments). X-ray photoelectron spectroscopy (XPS) was performed under ultra-high vacuum on a Thermo Scientific Escalab 250Xi system and the surface charging was adjusted using the C 1s line at 284.6 eV. Temperature-programmed reduction of H₂ (H₂-TPR) and temperature-programmed desorption of O₂ (O₂-TPD) were conducted on a Micromeritics AutoChem II 2920 Chemisorption Analyzer. For H₂-TPR, the catalyst (50 mg) was pretreated in He flow (30 mL min⁻¹) at 200 °C for 1 h. After cooling down to 50 °C, the gas was switched to 5 vol.% H₂-He (30 mL min⁻¹) till the baseline became stable and then the profile was recorded at 50-800 °C with a ramp of 10 °C min⁻¹. For O₂-TPD, the catalyst (50 mg) was pretreated in He flow (30 mL min⁻¹) at 200 °C for 1 h. After cooling down to 50 °C, the gas was switched to 5 vol.% O₂-He (30 mL min⁻¹) for 1 h, followed by a purging with He till the baseline became stable. The profile was recorded in He flow at 50-800 °C with a ramp of 10 °C min⁻¹. Low-temperature electron paramagnetic resonance (EPR) was carried out on an A300 Bruker EPR spectrometer with X-band frequencies of 9.4 GHz. A field modulation frequency at 100 kHz and standard modulation amplitude at 1.0-G were used. Quantitative analysis was based on the DPPH standard.

DFT Calculation Details

All calculations were carried out based on density functional theory (DFT) in Vienna ab-initio simulation package (VASP) program within the generalized gradient approximation (GGA) using the Perdew-Burke-Ernzerhof (PBE) formulation.^{1, 2} The (111) plane of Mn₅O₈ and (103) plane of ZnMn₂O₄ were used to build up the catalyst model. A grid of 1×1×1 Monkhorst–Pack k-points was used for the structural relaxation. A vacuum layer of 15 Å is adopted in the direction perpendicular to the monolayer surface to avoid the interactions between periodic slabs. The energy cutoff was set

to be 450 eV. The convergence criterion for the energy and maximum force for the optimization were set to 10^{-5} eV and 0.05 eV/Å, respectively.

The oxygen vacancy formation energy ($E_{V_{\text{O}}}$) is defined as :

$$E_{V_{\text{O}}} = E_{\text{defect}} + E_{\text{O}} - E_{\text{perfect}} \quad (\text{Eq. S6})$$

Where E_{defect} and E_{perfect} represent the total energy of the surface slab with and without oxygen vacancy, respectively. E_{O} represents the energy of O atom.

The adsorption energy ($E_{\text{ads.}}$) of an adsorbate A is defined as :

$$E_{\text{ads.}} = E(*\text{O}_2) - E(*) - E(\text{O}_2) \quad (\text{Eq. S7})$$

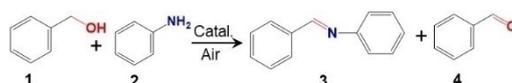
Where $E(*\text{O}_2)$ and $E(*)$ represent the total energy of surface systems with and without O_2 molecule, respectively; $E(\text{O}_2)$ represent the energy of an isolated O_2 molecule.

2. Supplementary data

Table S1. XPS parameters of Mn 2p, O 1s and Zn 2p core levels for the Mn₅O₈, ZnMn₂O₄ and ZnO catalysts

Catalyst	Binding energy (eV)					
	Mn ⁴⁺	Mn ³⁺	Mn ²⁺	O 1s (O _{surf.})	O 1s (O _{latt.})	Zn ²⁺
Mn ₅ O ₈	642.8	641.7	640.6	531.5	529.7	–
ZnMn ₂ O ₄	643.1	642.0	640.9	531.4	529.7	1020.9
ZnO	–	–	–	–	–	1021.3

Table S2. Oxidative coupling of benzyl alcohol and aniline over ZnO, Mn₅O₈ and ZnMn₂O₄ catalysts



Catalyst	Conv. of 1 (%)	Select. of 3 (%)	Select. of 4 (%)	r_{initial} (mmol g _{Mn} ⁻¹ h ⁻¹)	CB (%)
ZnO	0	0	0	0	100
Mn ₅ O ₈	47	99	1.0	0.66	100
ZnMn ₂ O ₄	100	>99	<0.5	2.71	100

Reaction conditions: benzyl alcohol, 1.0 mmol; aniline, 1.0 mmol; catalyst: 50 mg; toluene, 5 mL; air, 1 atm; temperature, 30 °C; time, 18 h.

Table S3. Comparison of transition metal oxide catalysts for low-temperature oxidative coupling of benzyl alcohol and aniline

Entry	Catalyst	Temp. (°C)	Oxidant (1atm)	Time (h)	Yield (%)	Prod. (mmol g _{catal.} ⁻¹ h ⁻¹)	Reuse times	Stab.	Ref.
1	CeO ₂	30	air	24	75	0.31	<i>n.d.</i>	<i>n.d.</i>	3
2	CeO ₂ -5	30	air	36	≥99	0.55	4	no	4
3	MnZr _{0.50} O _y	30	air	24	99	0.68	5	yes	5
4	Fe ₅ Mn ₅ -100	30	air	16	94	1.18	4	no	6
5	ZnMn ₂ O ₄	30	air	18	99.1	1.10	8	yes	this work

References

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3. M. Tamura and K. Tomishige, *Angew. Chem. Int. Ed.*, 2015, **54**, 864.
4. H. Zhang, C. Wu, W. Wang, J. Bu, F. Zhou, B. Zhang and Q. Zhang, *Appl. Catal. B.*, 2018, **227**, 209.
5. S. Wu, H. Zhang, Q. Cao, Q. Zhao and W. Fang, *Catal. Sci. Technol.*, 2021, **11**, 810.
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Table S4. Oxidative coupling of aniline with different primary alcohols over the ZnMn₂O₄ catalyst

1	2	3
3a: 18 h, 99%, 98%	3b: 18 h, 99%, 98%	3c: 18 h, 96%, 95%
3d: 18 h, 95%, 94%	3e: 18 h, 95%, 94%	3f: 18 h, 90%, 89%
3g: 18 h, 89%, 88%	3h: 18 h, 85%, 84%	3i: 36 h, 20%, 19%
3j: 36 h, 50%, 49%	3k: 36 h, 41%, 40%	3l: 36 h, 22%, 21%

Reaction conditions: alcohol, 1.0 mmol; aniline, 1.0 mmol; catalyst, 50 mg; toluene, 5 mL; air, 1atm; temperature, 30 °C. Reaction time, conversion of alcohol and yield of imine were reported, respectively.

Table S5. Oxidative coupling of different primary amines with benzyl alcohol over the ZnMn₂O₄ catalyst

1	2	3
3m: 18 h, 98%, 97%	3n: 18 h, 99%, 98%	3o: 18 h, 98%, 97%
3p: 18 h, 96%, 95%	3q: 18 h, 91%, 90%	3r: 18 h, 93%, 92%
3s: 18 h, 90%, 89%	3t: 36 h, 65%, 64%	3u: 36 h, 52%, 51%
3v: 36 h, 18%, 17%		

Reaction conditions: alcohol, 1.0 mmol; aniline, 1.0 mmol; catalyst, 50 mg; toluene, 5 mL; air, 1atm; temperature, 30 °C. Reaction time, conversion of benzyl alcohol and yield of imine were reported, respectively.

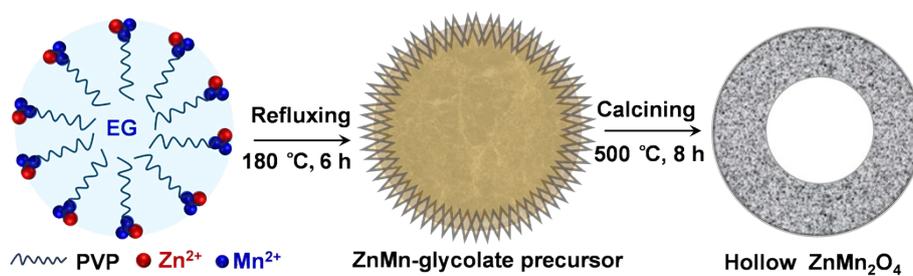


Fig. S1 Schematic illustration for the synthesis of hollow ZnMn_2O_4 nanospheres.

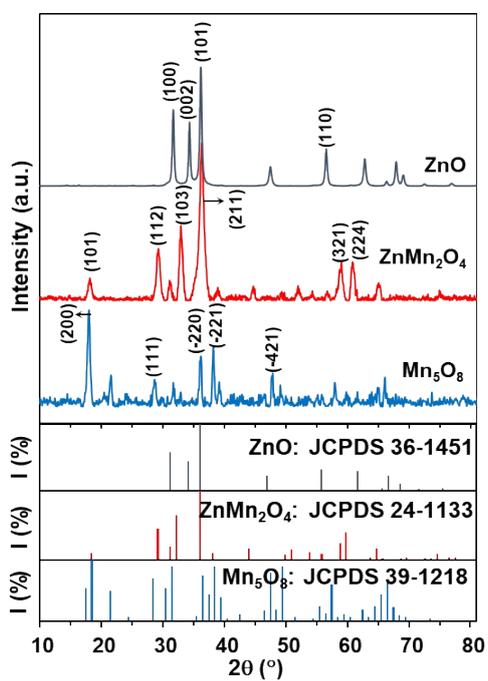


Fig. S2 XRD patterns of Mn_5O_8 , ZnMn_2O_4 and ZnO catalyst

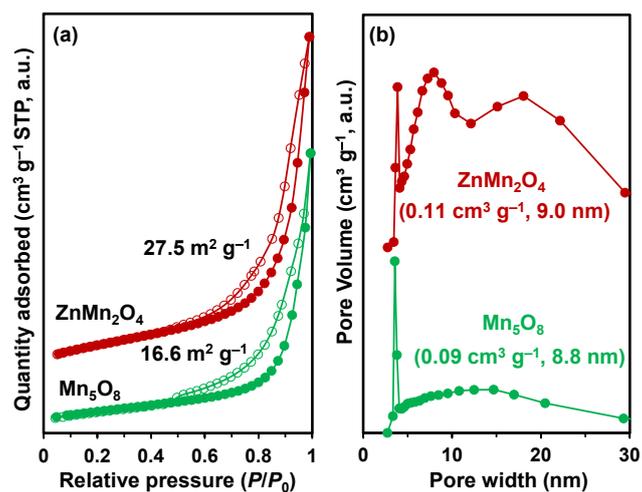


Fig. S3 (a) N₂ adsorption-desorption isotherm and (b) pore size distribution of Mn₅O₈ and ZnMn₂O₄ catalysts.

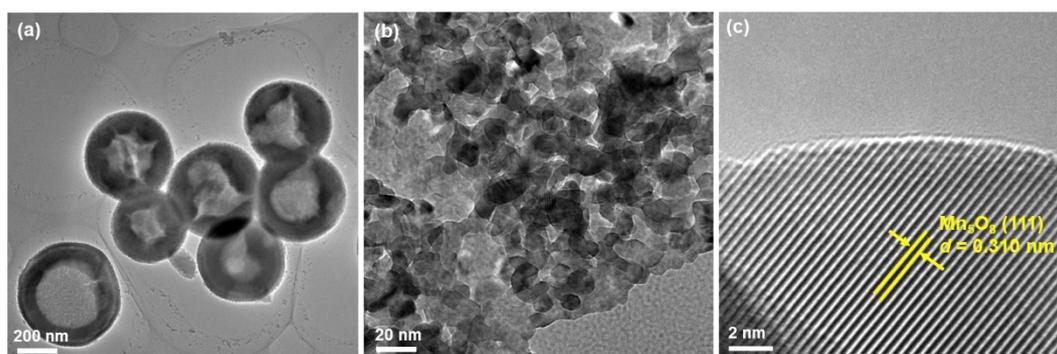


Fig. S4 (a, b) TEM and (c) HR-TEM images of Mn₅O₈ catalyst

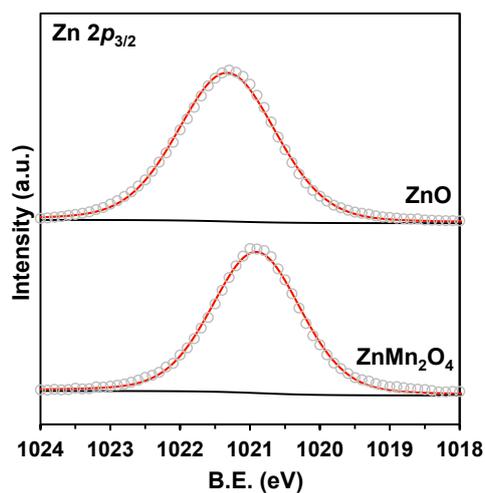


Fig. S5 XPS spectra of the Zn $2p_{3/2}$ core levels of ZnO and ZnMn₂O₄ catalysts.

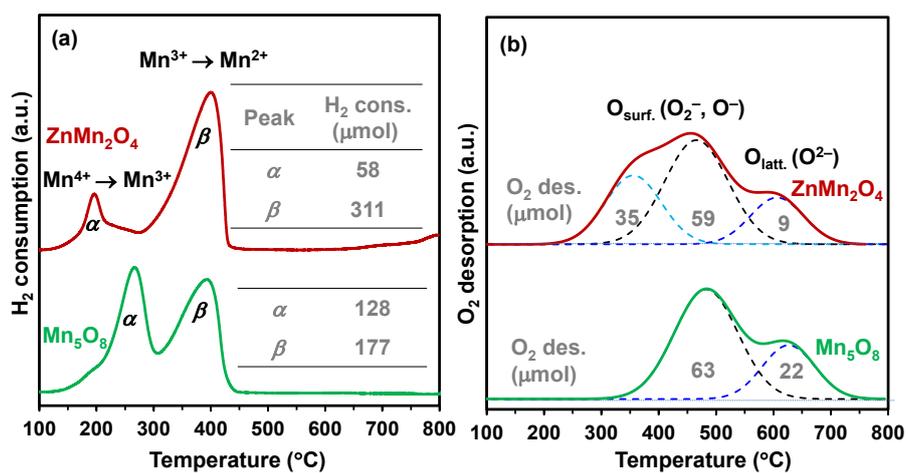


Fig. S6 (a) H₂-TPR and (b) O₂-TPD profiles of Mn₅O₈ and ZnMn₂O₄ catalysts.

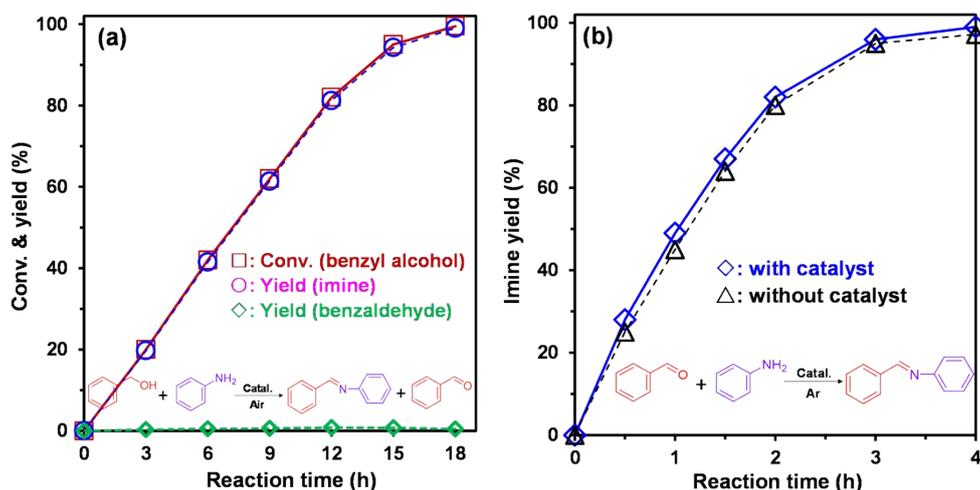


Fig. S7 Time-course curves for (a) oxidation of benzyl alcohol with aniline over the ZnMn_2O_4 catalyst, (b) condensation of benzaldehyde and aniline in Ar with or without the ZnMn_2O_4 catalyst. Reaction conditions: benzyl alcohol, 1.0 mmol; aniline, 1.0 mmol; benzaldehyde, 1.0 mmol; catalyst, 50 mg; toluene, 5 mL; air or Ar, 1 atm; temperature, 30 °C.

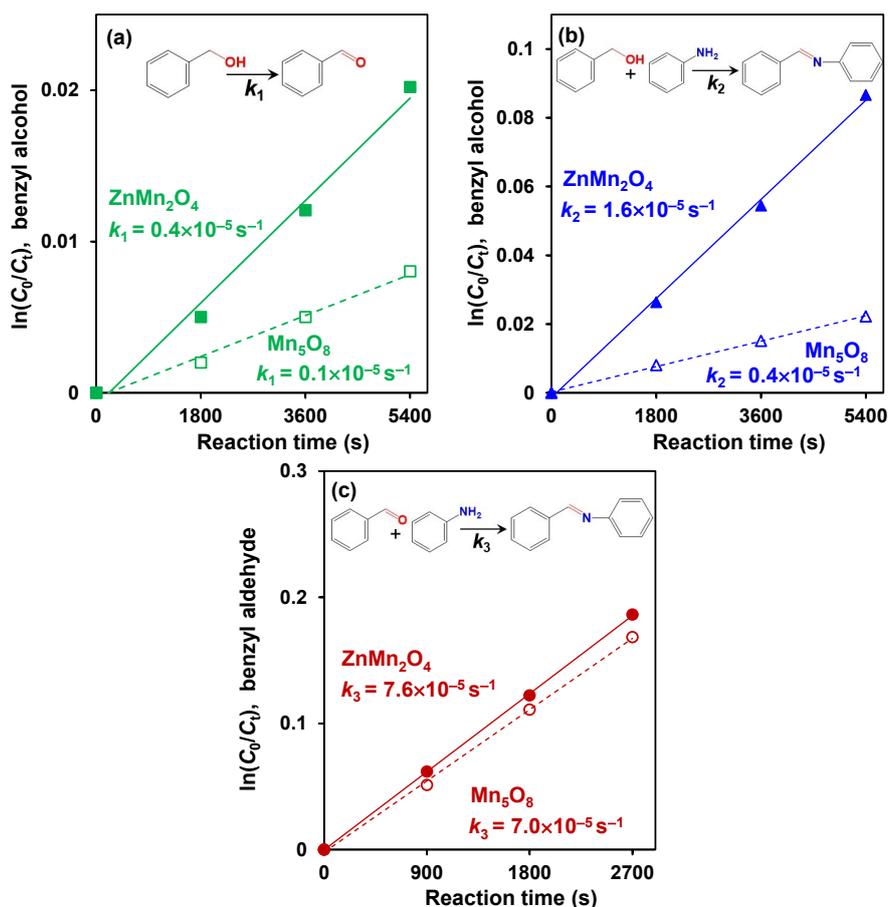


Fig. S8 Kinetic profiles for (a) oxidation of benzyl alcohol, (b) oxidative coupling of benzyl alcohol and aniline and (c) condensation of benzaldehyde with aniline over ZnMn_2O_4 and Mn_5O_8 catalysts. Reaction conditions: benzyl alcohol, 1.0 mmol; aniline, 1.0 mmol; benzaldehyde, 1.0 mmol; catalyst, 50 mg; temperature, 30 °C; toluene, 5 mL; air, 1 atm.

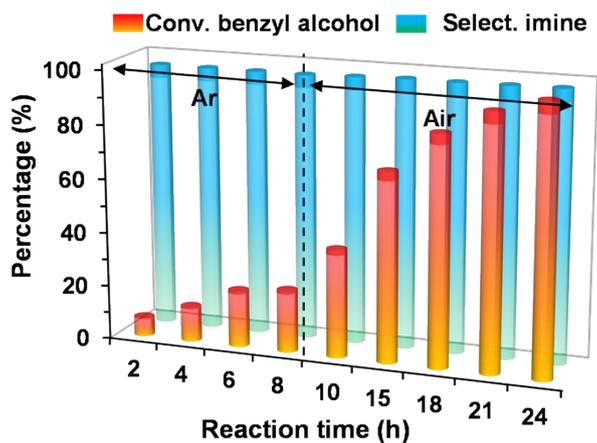


Fig. S9 Time-course experiment for oxidative coupling of aniline and benzyl alcohol over the $ZnMn_2O_4$ catalyst under Ar or air atmosphere. Reaction conditions: benzyl alcohol, 1.0 mmol; aniline, 1.0 mmol; catalyst, 50 mg; temperature, 30 °C; toluene, 5 mL; Ar or air, 1 atm.

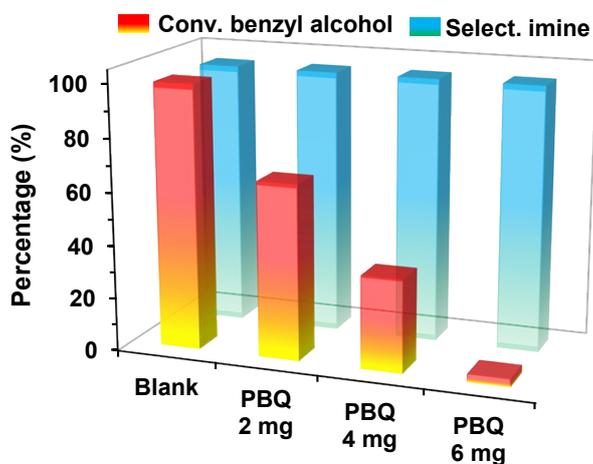


Fig. S10 Oxidative coupling of benzyl alcohol and aniline over $ZnMn_2O_4$ catalyst with addition of p-benzoquinone as a scavenger. Reaction conditions: benzyl alcohol, 1.0 mmol; aniline, 1.0 mmol; catalyst, 50 mg; temperature, 30 °C; toluene, 5 mL; air, 1 atm; time 18 h.

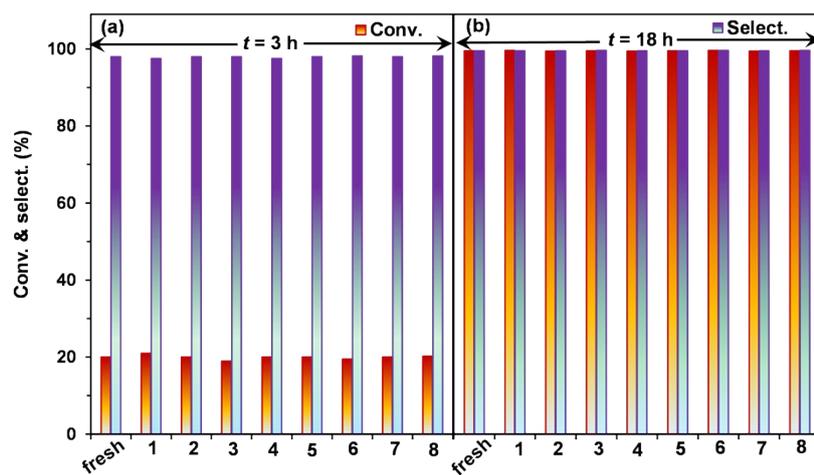


Fig. S11 Recycling test of the ZnMn_2O_4 catalyst within the (a) kinetic-controlled stage and (b) under optimized conditions. Reaction conditions: benzyl alcohol, 1.0 mmol; aniline, 1.0 mmol; catalyst, 50 mg; temperature, 30 °C; toluene, 5 mL; air, 1 atm.

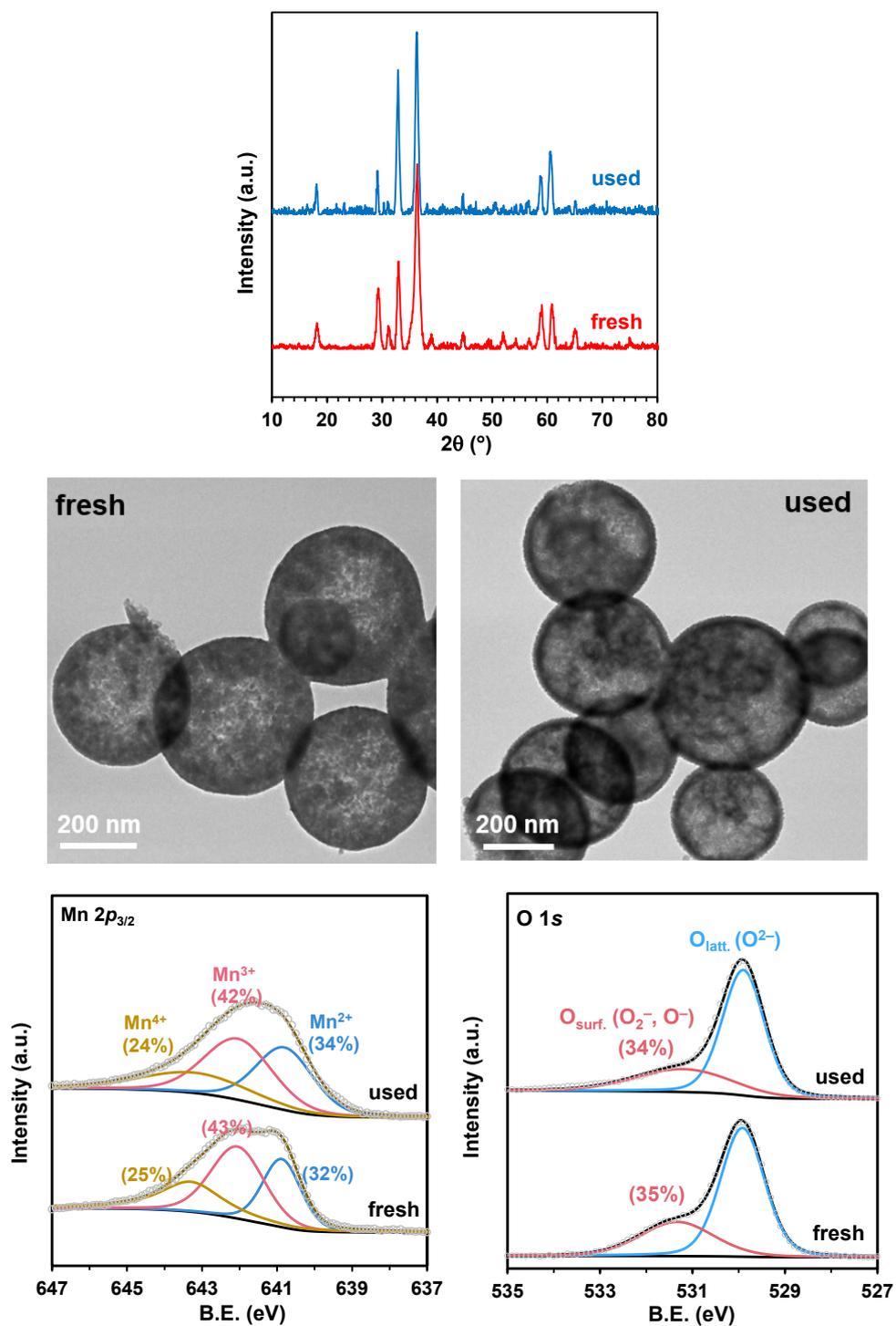


Fig. S12 XRD, TEM and XPS analysis of the ZnMn₂O₄ catalyst before and after catalytic reaction.