

Electronic Supplementary Information

Tuning effect of amorphous Fe₂O₃ on Mn₃O₄ for efficiently atomic economic synthesis of imines at low temperature: Improving [O] transfer cycle of Mn³⁺/Mn²⁺ in Mn₃O₄

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EXPERIMENTAL SECTION

Materials

Ferric nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 99% w/w), Manganese acetate tetrahydrate ($\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, 99% w/w), ammonia solution (25%), and various reaction reagents were purchased from Macklin Biochemical Co., Ltd. Deionized water was used throughout the experiments. All chemicals were of analytical grade and used as received without further purification.

Sample preparation

A series of amorphous Fe_2O_3 modified Mn_3O_4 with different Mn molar content was synthesized by a simple co-precipitation method. In a typical synthesis procedure, 50 mmol $\text{Mn}(\text{CH}_3\text{COO})_2$ and 50 mmol $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were dissolved in 500ml water and stirred for 1h at room temperature. Then ammonia solution was added drop-wise to the mixed solution until pH value reached to 9. After stirring for another 5h, the resulting precipitate was filtered and thoroughly washed 5 times with deionized water until free from anion impurities. The sample was dried at 373K for 24h. The products were abbreviated as FeXMnY-T , in which X and Y represents the molar ratio of Fe and Mn, T represents the calcination temperature. Meanwhile, pure Fe_2O_3 -100 and Mn_3O_4 -100 were also prepared using the similar method.

Characterization

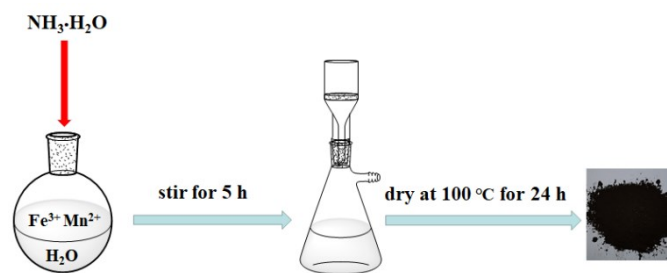
Fe and Mn content of the prepared catalysts were obtained by inductively coupled plasma atomic emission spectroscopy (ICP–AES). The amounts of Fe and Mn in all catalysts were calculated as atomic percentages (at.%) considering the moles of both cations. The Fe at.% calculation is presented in as followed eq: $\text{Fe (at.\%)} = \text{Fe (mol)} \times 100 / (\text{Fe (mol)} + \text{Mn (mol)})$. The crystallographic structure of the solid samples was investigated at room temperature using powder X-ray diffraction (XRD, Rigaku D/max-2400 diffractometer, Cu-K α radiation,) at a scanning rate of $5^\circ \cdot \text{min}^{-1}$. The dimension and morphology of the solid samples are examined using transmission electron microscopy (TEM, Tecnai G2 F30, 300 kV), and high-resolution transmission

electron microscopy (HRTEM/EDX, Tecnai G2 F30, 300 kV). Chemical bonding information of the samples was acquired with Fourier transform infrared spectroscopy (FT-IR, Nicolet NEXUS 670) using the potassium bromide (KBr) pellet technique. To make the KBr pellets, about 1 mg of sample was diluted with 100 mg of KBr powders. Each FTIR spectrum was collected after 32 scans with a resolution of 4 cm^{-1} from 400 to 4000 cm^{-1} . Surface and texture properties of the samples were studied by N_2 adsorption–desorption isotherms (ASAP2020) at the liquid nitrogen temperature (77 K). Before the measurement, all samples were degassed under vacuum for 6 h at 373 K. Specific surface areas of the samples were determined using the Brunauer–Emmett–Teller (BET) method. Then the pore size distribution was also calculated using nonlocal density function theory (NLDFT) from adsorption curve. X-ray photoelectron spectroscopy (XPS) was performed on the PHI-5702 instruments with an Mg anode ($\text{Mg K}\alpha$ $h\nu = 1253.6\text{ eV}$) at a base pressure of 5×10^{-8} mbar. The revision of the binding energies (BE) was implemented with the C1s peak of extraneous C at 284.6 eV. Temperature-programmed reduction (TPR) and temperature-programmed oxidation (TPO) experiments were performed on the Auto Chem II 2920 chemical adsorber produced by Micromeritics, USA with a TCD (thermal conductivity detector). In a typical H_2 -TPR process, 50 mg sample powders were outgassed at 373 K for 30 min under an Argon flow ($25\text{ mL}\cdot\text{min}^{-1}$) and subsequently cooled down to 303 K. Then the temperature was raised to 1173 K with a heating rate of $10\text{ K}\cdot\text{min}^{-1}$ under a hydrogen flow (10% in Argon, $50\text{ mL}\cdot\text{min}^{-1}$) and the consumption of H_2 was recorded. For the O_2 -TPO process, 50 mg sample powders were outgassed at 373 K for 30 min under an Argon flow ($25\text{ mL}\cdot\text{min}^{-1}$) and subsequently cooled down to 303 K. Then the temperature was raised to 1173 K with a heating rate of $10\text{ K}\cdot\text{min}^{-1}$ under an oxygen flow (10% in Argon, $50\text{ mL}\cdot\text{min}^{-1}$) and the consumption of O_2 was recorded. As for the O_2 - and NH_3 -TPD experiments, the sample (50 mg) was also pretreated under Ar at 373 for 30 min. After cooling to 323K and being flushed in Ar flow for 30 min, the sample was exposed to repeated 10% O_2/Ar and 10% NH_3/Ar pluses until saturation. Subsequently, the sample was purged at $50\text{ }^\circ\text{C}$ with He for 1 h to remove the physical adsorbed O_2 and NH_3 species,

and then the temperature was brought up to 973k at a ramping rate of 10 °C·min⁻¹. The final TPD profile were obtained by applying subtraction treatment between the adsorbed curve (O₂ and NH₃ species) with blank curve without adsorbing any probe molecular.

Catalyst test

The generous procedure for imine formation from benzyl alcohol and aniline is as follows: a mixture of benzyl alcohol (1 mmol), aniline (1 mmol), catalyst (50 mg) and toluene (3 mL) was taken into a round bottom tube with a reflux condenser under air. The resulting mixture was allowed to stir at 60 °C for 3 h. After reaction, the reaction mixture was filtered and the product mixtures were identified by GC-MS (GC-MS, Agilent 5977E) with an HP-5 capillary column. The conversion was calculated using normalization method based on the benzyl alcohol to imine ratio. The yield of imine was calculated based on the benzyl alcohol conversion and imine selectivity. In the recycle experiment, Fe5Mn5-100 was collected by centrifugation, and the spent catalyst was taken into a round bottom tube with only 3 ml ethanol, which was allowed to stir at 60 °C for 3 h, the solid was collected by centrifugation and exhaustively washed ethanol. Then it was dried at 100 °C in a drying oven for 24 h. The spent catalyst was used for the next run under the same conditions. Other cycles were repeated with the same procedure. The hot filtration test was carried out as following: after 2 h reaction, the solid catalyst was separated by a Buchner funnel. The mixture of filtrate was put into the reactor and continuously reacted under the same condition (60 °C, air) without a solid catalyst.



Scheme S1 Synthesis process of the samples.

Table S1 Chemical composition of the as-prepared catalysts.^a

Catalyst	Mn (at.%)	Fe (at.%)
Fe ₂ O ₃ -100	0	100
Fe9Mn1-100	10.5	89.5
Fe8Mn2-100	20.3	79.7
Fe7Mn3-100	31.1	68.9
Fe6Mn4-100	43.4	56.6
Fe5Mn5-100	51.5	48.5
Fe4Mn6-100	61.7	38.3
Fe3Mn7-100	71.9	28.1
Fe2Mn8-100	78.8	21.2
Fe1Mn9-100	91.3	8.7
Mn ₃ O ₄ -100	100	0

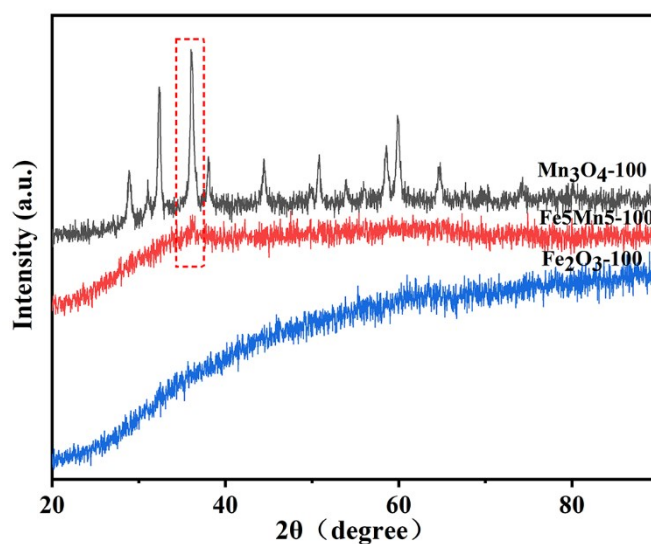
^a The amounts of Fe and Mn in all catalysts were calculated as atomic percentages (at.%) considering the moles of both cations.

Table S2 The properties of the as-prepared catalysts.

Catalyst	Surface area ($\text{m}^2\cdot\text{g}^{-1}$)	Pore volume ($\text{cm}^3\cdot\text{g}^{-1}$)	Mn ²⁺	Mn ³⁺	O _{sur}	O _{lat}
Fe ₂ O ₃ -100	224.8756	0.236	-	-	42%	58%
Fe ₈ Mn ₂ -100	266.9642	0.238	57%	43%	46%	54%
Fe ₅ Mn ₅ -100	289.7881	0.263	62%	38%	53%	47%
Fe ₂ Mn ₈ -100	101.8707	0.246	55%	45%	49%	51%
Mn ₃ O ₄ -100	72.9562	0.221	41%	59%	36%	64%

Table S3 The properties of fresh Fe₅Mn₅-100 and reused Fe₅Mn₅-100.

Catalyst	Surface area ($\text{m}^2\cdot\text{g}^{-1}$)	Pore volume ($\text{cm}^3\cdot\text{g}^{-1}$)	Mn ²⁺	Mn ³⁺	O _{sur}	O _{lat}
fresh Fe ₅ Mn ₅ - 100	289.7881	0.263	62%	38%	53%	47%
reused Fe ₅ Mn ₅ -100	249.7441	0.237	64%	36%	51%	49%

**Fig. S1** XRD patterns of Fe₂O₃-100, Fe₅Mn₅-100, Mn₃O₄-100.

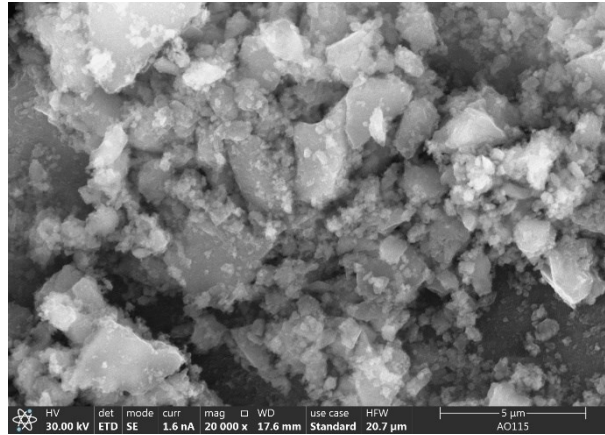


Fig. S2 SEM images of Fe5Mn5-100.

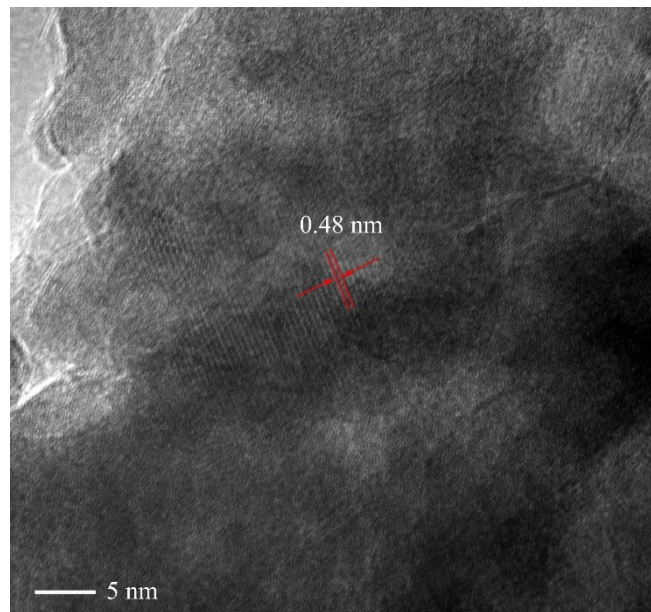


Fig. S3 HRTEM images of Fe5Mn5-100.

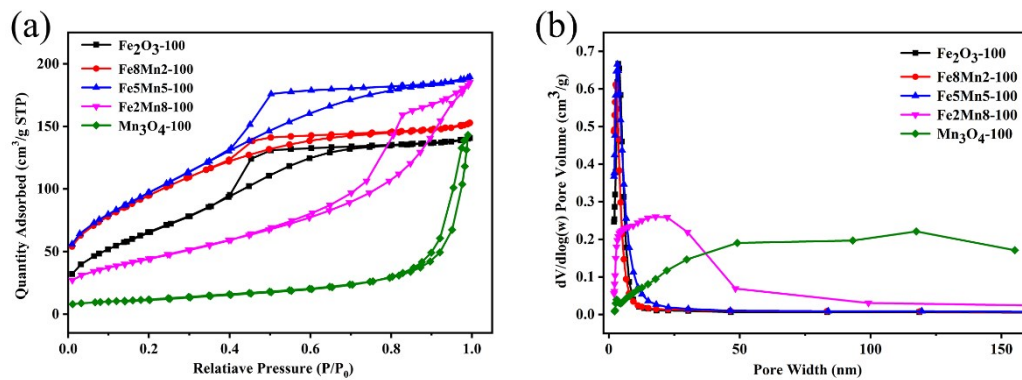


Fig. S4 (a) N₂ adsorption-desorption isothermal curves of the as-prepared samples, (b) pore size distribution curves of the as-prepared samples.

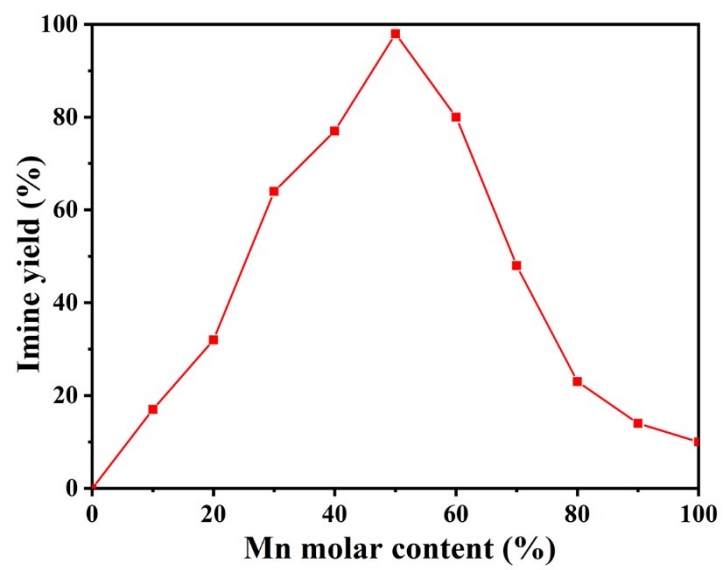


Fig. S5 Catalytic activity of different Mn molar content of the as-prepared catalysts.

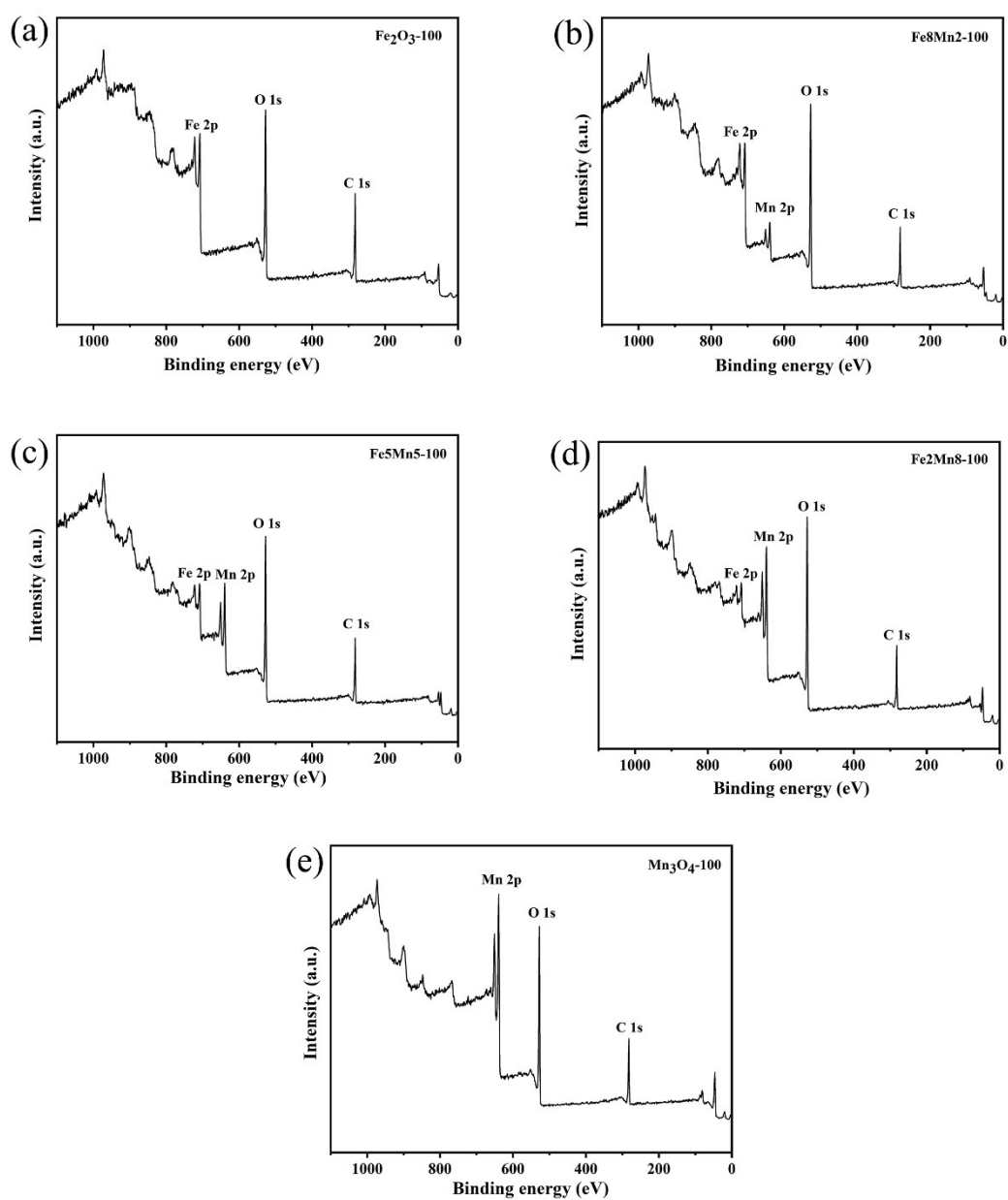


Fig. S6 Broad XPS spectra of the as-prepared (a) Fe_2O_3 -100, (b) Fe_8Mn_2 -100, (c) Fe_5Mn_5 -100, (d) Fe_2Mn_8 -100, (e) Mn_3O_4 -100.

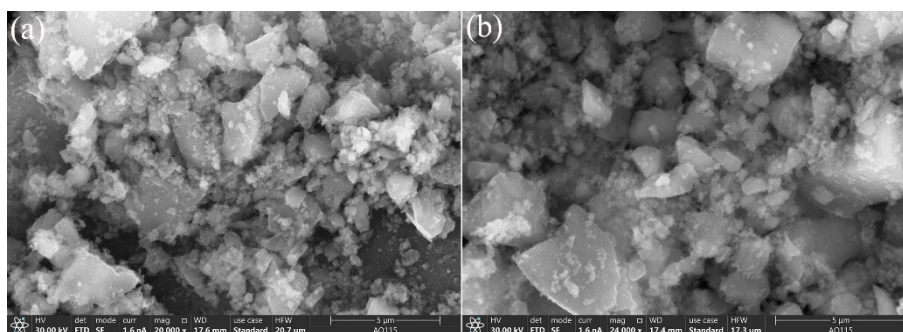


Fig. S7 SEM images of (a) fresh Fe5Mn5-100 and (b) reused Fe5Mn5-100.

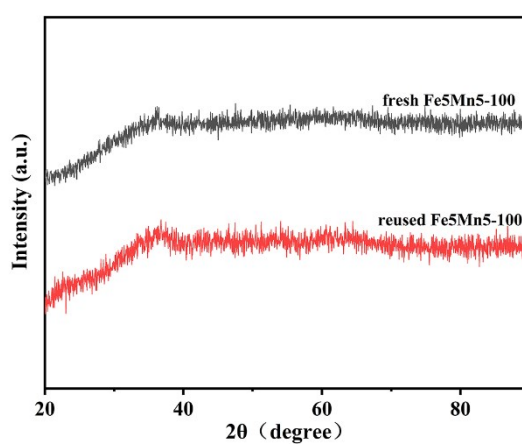


Fig. S8 XRD patterns of fresh Fe5Mn5-100 and reused Fe5Mn5-100.

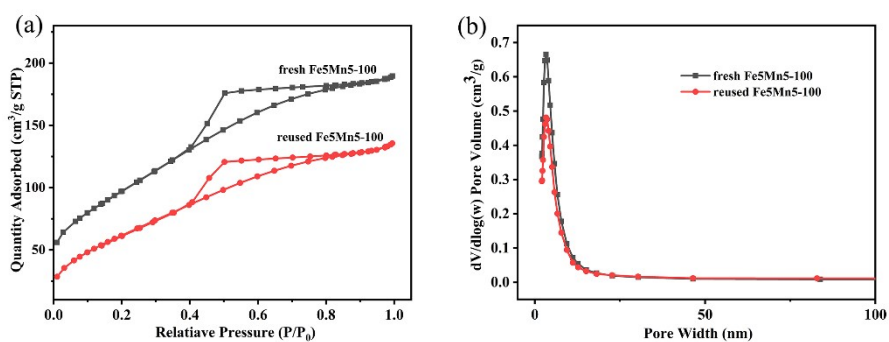


Fig. S9 (a) N₂ adsorption-desorption isothermal curves of fresh Fe5Mn5-100 and reused Fe5Mn5-100, (b) pore size distribution curves of fresh Fe5Mn5-100 and reused Fe5Mn5-100.

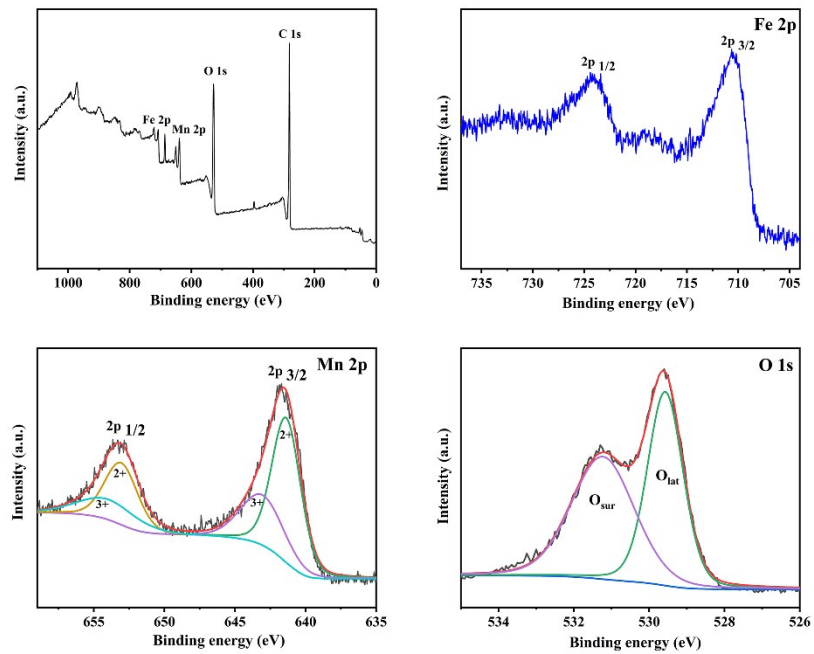


Fig. S10 (a) Broad, (b) Fe 2p, (c) Mn 2p, (d) O 1s XPS spectra of reused Fe₅Mn₅-100.