

Supporting Information

Engineering yolk-shell MnFe@CeO_x@TiO_x nanocages as a highly efficient catalyst for selective catalytic reduction of NO with NH₃ at low temperature

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Table S1 The number of acid sites on the surface of MnFeO_x, MnFe@TiO_x, MnFe@CeO_x, MnFe@CeO_x@TiO_x-20, MnFe@CeO_x@TiO_x-40 and MnFe@CeO_x@TiO_x-90.

Samples	Weak acid	Medium acid	Strong acid	Total acid
	peak area	peak area	peak area	peak area
MnFeO _x	83.4	88.1	-	171.5
MnFe@TiO _x	72.1	163.2	29.7	265.0
MnFe@CeO _x	45.6	94.4	5.7	145.7
MnFe@CeO _x @TiO _x -20	89.2	189.0	40.1	318.3
MnFe@CeO _x @TiO _x -40	62.3	118.0	74.0	254.3
MnFe@CeO _x @TiO _x -90	89.5	74.0	43.8	207.3

Table S2 MnFe@CeO_x@TiO_x-40 fresh and after enduring H₂O test at 160 °C catalyst

surface element content and Mn 2p, Fe 2p, Ce 3d, and O1s spectra fitting result.

Sample	Surface composition (at.%)					Mn ⁴⁺ /Mn _{total}	Fe ³⁺ /Fe _{total}	Ce ³⁺ /Ce _{total}	O _{ads} /O _{total}	O _{sur} /O _{total}
	Mn	Fe	Ce	O	Ti	(%)	(%)	(%)	(%)	(%)
Fresh	2.4	4.0	2.2	70.9	20.5	43.5	68.8	22.5	61.2	20.9
160°C	3.4	3.3	2.7	72.1	18.5	34.6	63.9	18.0	47.5	28.4

We prepared MnFe@TiO_x-40@CeO_x catalyst sample. Take 0.20 g of the previously prepared precursor Mn₃[Fe(CN)₆]₂ • nH₂O nanocubes and disperse them in 40 ml of absolute ethanol by ultrasonic (30 min). After stirring for 30 min, 5 ml of deionized water was added dropwise and recorded as solution A. Dissolve 0.50 g of butyl titanate in 20 ml of absolute ethanol and call it solution B. Then, under vigorous stirring, the B solution was slowly dropped into the A solution. After aging in a 25 °C water bath for 2 h, the product was collected by centrifugation. After washing with absolute ethanol for 3 times, the obtained product was dried at 80 °C for 12 h to obtain MnFe@TiO_x-40 precursor. Take 0.10 g of the previously prepared precursor MnFe@TiO_x-40 and disperse it in a mixed solution of 40 ml of absolute ethanol and 40 ml of deionized water. Under magnetic stirring, 0.30 g of Ce(NO₃) • 6H₂O and 0.40 g of C₆H₁₂N₄ were added to the above solution in turn. Heat further to 70 °C in a water bath and maintain reflux for 2 h. After naturally cooling to room temperature, the product was collected by centrifugation and washed twice with deionized water. The obtained product was dried at 60 °C for 12 h and calcined at 400 °C for 3 h (the heating rate was 1 °C/min) to obtain the MnFe@TiO_x-40@CeO_x catalyst.

We prepared CeO_x@TiO_x-40 catalyst. Under magnetic stirring, 0.30 g of Ce(NO₃) • 6H₂O and 0.40 g of C₆H₁₂N₄ were dispersed in a mixed solution of 40 ml of absolute ethanol and 40 ml of deionized water. Stir in a water bath at 70 °C for 2 h, a CeO_x precursor is obtained. Take 0.20 g CeO_x precursor ultrasonically (30min) and disperse it in 40 ml absolute ethanol, after stirring for 30min, add 5ml deionized water dropwise and record as solution A. Dissolve 0.50 g of butyl titanate in 20 ml of

absolute ethanol and call it solution B. Then, under vigorous stirring, the B solution was slowly dropped into the A solution. After aging in a 25 °C water bath for 2 h, the product was collected by centrifugation. After washing three times with absolute ethanol, the obtained product was dried at 80 °C for 12 h, and calcined at 400 °C for 3 h (the heating rate was 1 °C/min) to obtain the CeO_x@TiO_x-40 catalyst.

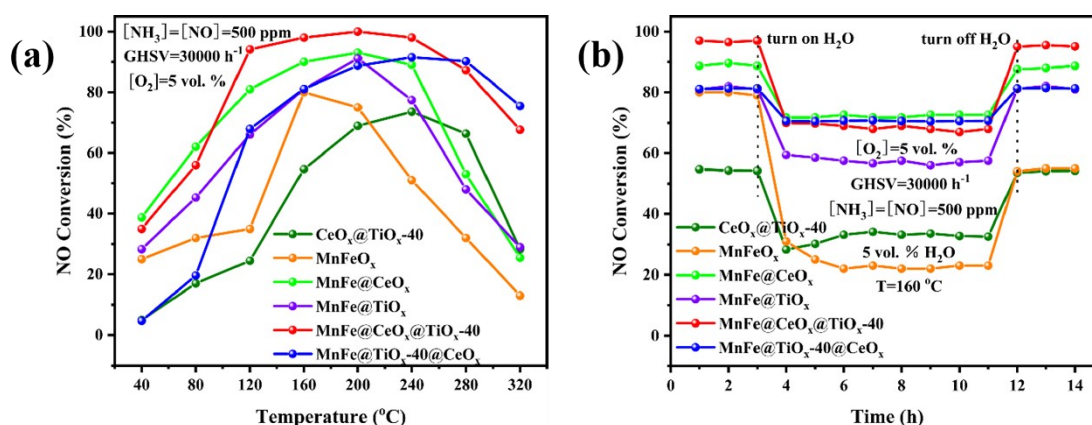


Fig. S1. NO conversion rate of the catalysts under $\text{GHSV}=30,000 \text{ h}^{-1}$ (a, b). H₂O-resistance and stability test of the catalysts (c, d). Testing conditions: 500 ppm NH₃, 500 ppm NO, and 5 vol. % O₂ balanced with N₂ and 5 vol. % H₂O (when needed).

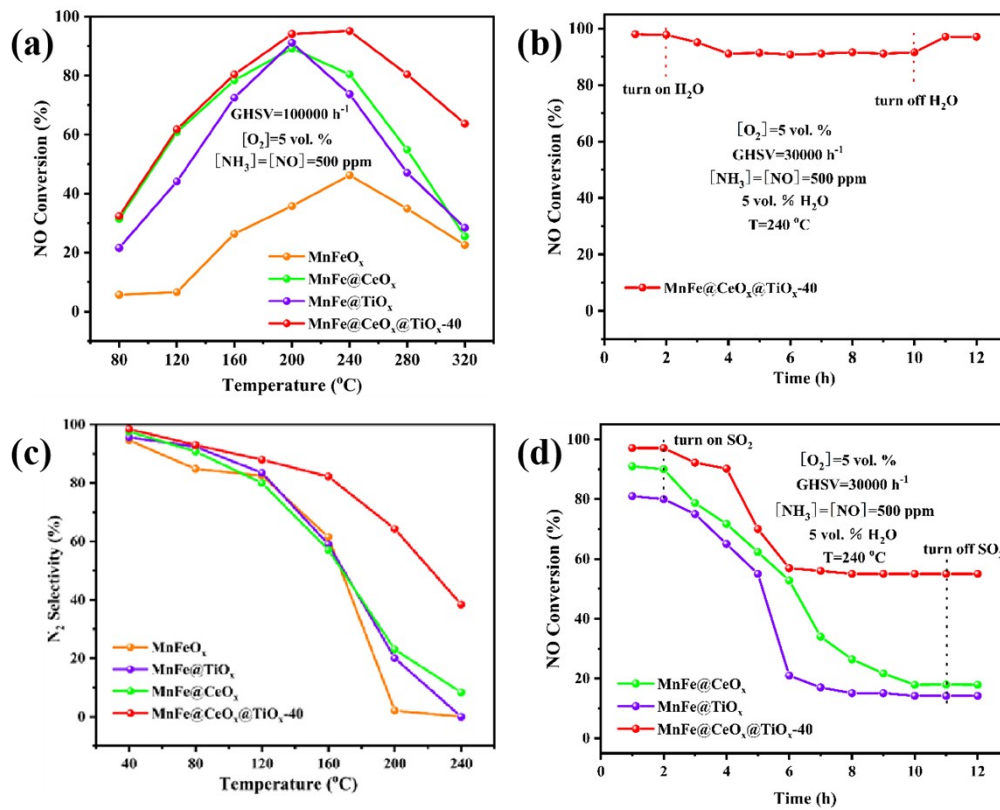


Fig. S2. NO conversion rate of the catalysts under GHSV=100000 h⁻¹ (a). The H₂O resistance test of MnFe@CeO_x@TiO_x-40 catalyst at 240 °C (b), N₂ selectivity of catalysts (c), The SO₂ resistance test of catalysts (d).

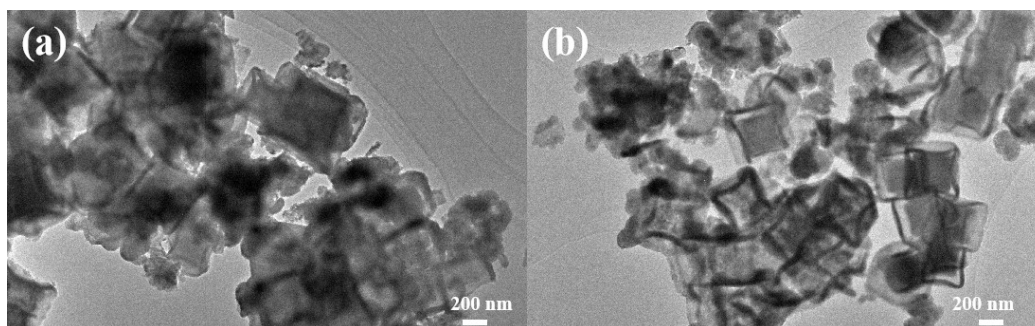


Fig. S3. TEM images of the MnFe@TiO_x catalyst.

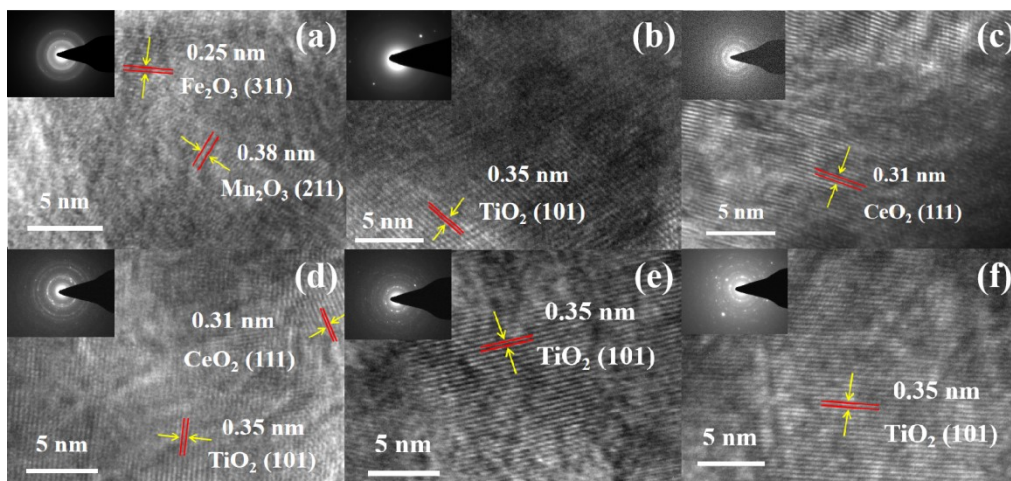


Fig. S4. HR-TEM image of the catalysts: MnFeO_x (a), MnFe@TiO_x (b), MnFe@CeO_x (c), $\text{MnFe@CeO}_x@TiO_x-20$ (d), $\text{MnFe@CeO}_x@TiO_x-40$ (e), $\text{MnFe@CeO}_x@TiO_x-90$ (f).

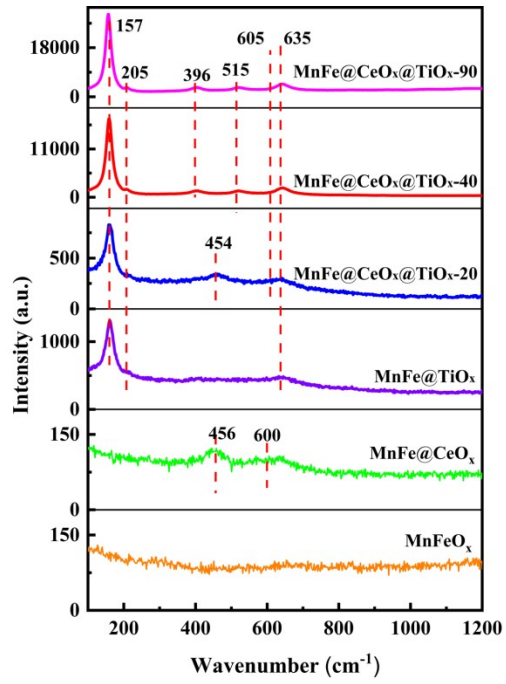


Fig. S5. Raman spectra of the catalysts.

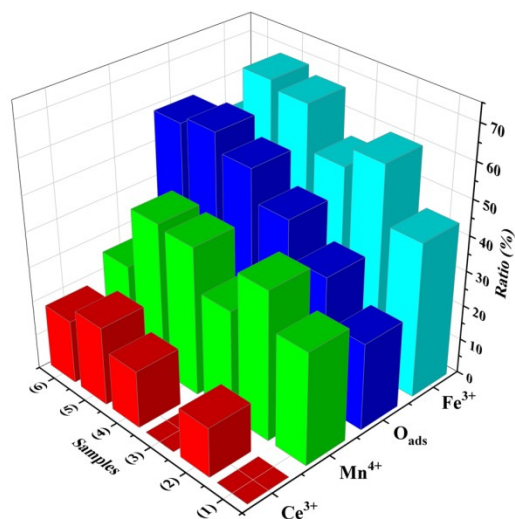


Fig. S6. The relative proportion of catalysts active species (MnFeO_x (1), MnFe@CeO_x (2), MnFe@TiO_x (3), MnFe@CeO_x@TiO_x-20 (4), MnFe@CeO_x@TiO_x-40 (5), MnFe@CeO_x@TiO_x-90 (6)).

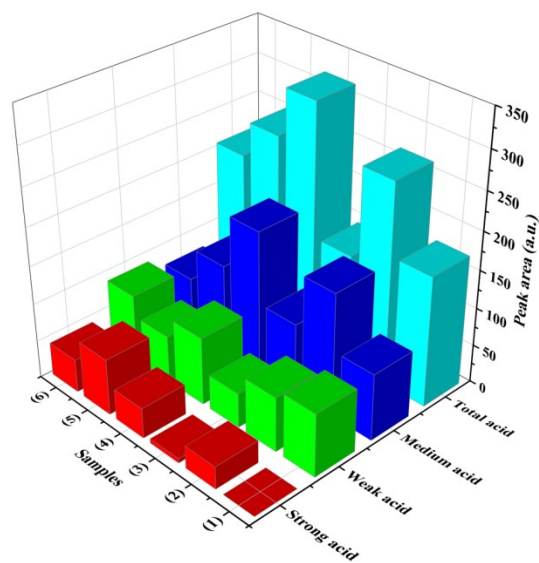


Fig. S7. Relative number of catalyst acid sites (MnFeO_x (1), MnFe@TiO_x (2), MnFe@CeO_x (3), $\text{MnFe@CeO}_x@\text{TiO}_x$ -20 (4), $\text{MnFe@CeO}_x@\text{TiO}_x$ -40 (5), $\text{MnFe@CeO}_x@\text{TiO}_x$ -90 (6)).

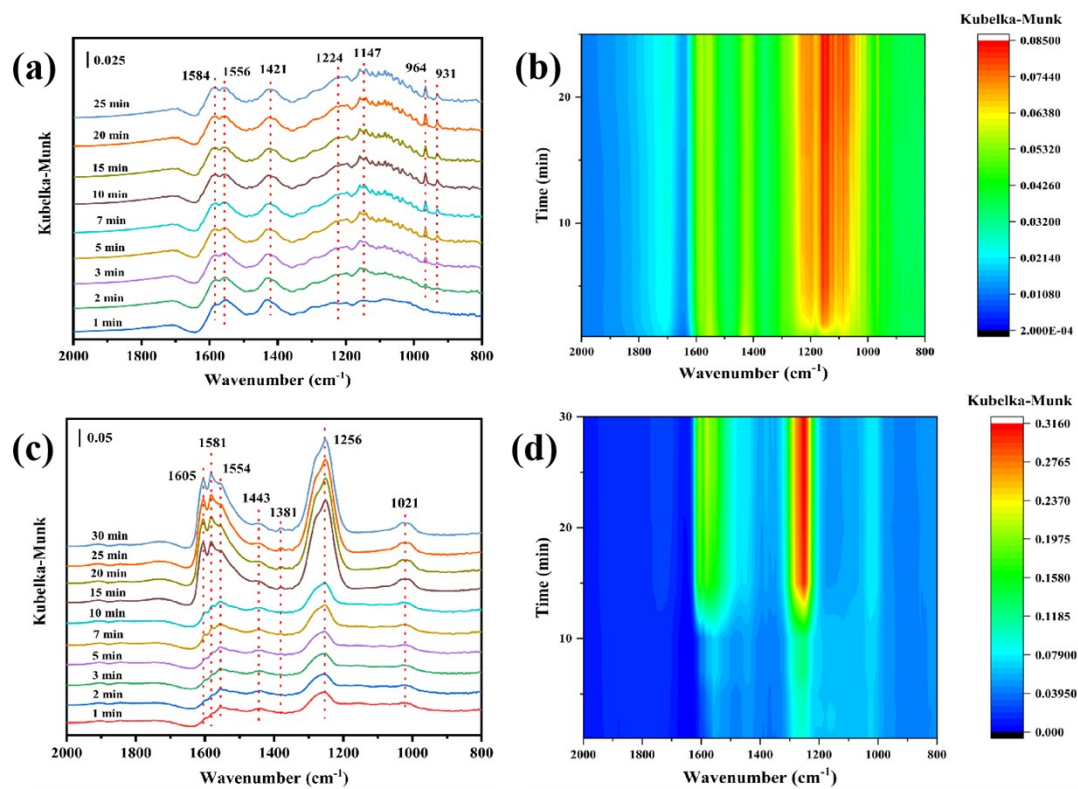


Fig. S8. MnFe@CeO_x@TiO_x-40 catalyst at 160 °C NH₃ in-situ DRIFT adsorption experiment (a-b) and NO+O₂ in-situ DRIFT adsorption experiment (c-d).