

Yolk-Shell Zeolite Nanoreactors Enable Multi-Poison Resistance for NO_x Reduction

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Abstract

The practical application of ammonia selective catalytic reduction (NH_3 -SCR) for stationary NO_x abatement is severely restricted by rapid catalyst deactivation in flue gases containing SO_2 and alkali metal. Although coupling zeolites with transition-metal oxides improves poisoning tolerance, most adopted loading or confining strategies cannot simultaneously ensure high redox-site content and effective protection. Herein, we realize a zeolite-confined nanoreactor concept by constructing a yolk-shell catalyst, in which high-content (>10 wt.%) MnFeO_x nanoparticles are confined within a hollow ZSM-5 single-crystal shell, with the zeolite framework fully preserved. *In situ* X-ray absorption fine structure (XAFS) and diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS), together with density functional theory (DFT) calculations, reveal a synergistic dual-shielding mechanism: the ZSM-5 shell physically hinders SO_2 from attacking the active oxide core, while external Brønsted acid sites chemically suppress SO_2 adsorption and intercept alkali metal. Consequently, the catalyst maintains $>90\%$ NO_x conversion with high N_2 selectivity under co-poisoning by SO_2 and K. This work establishes hollow zeolite-confined nanoreactors as a versatile platform for designing durable emission-control catalysts, enabling stable long-term operation under industrially relevant multi-poisoning conditions.

Introduction

The abatement of nitrogen oxides (NO_x) from industrial stationary sources (coal-fired power plants and waste incinerators, etc.) remains a critical environmental challenge due to their severe impact on air quality and human health¹⁻⁴. Ammonia selective catalytic reduction (NH_3 -SCR) is currently one of the most efficient industrial technologies for NO_x removal⁵⁻⁷. However, the practical longevity of SCR catalysts is severely compromised in real-world flue gas environments, where NO_x coexists with potent poisons such as sulfur dioxide (SO_2) and alkali metal (e.g., K_2O)^{8,9}. These poisons cause rapid and serious deactivation, making the development of catalysts with simultaneous resistance to SO_2 and alkali poisoning a paramount challenge for sustainable industrial operation¹⁰⁻¹³.

Coupling zeolites with transition-metal oxides has emerged as a promising approach because these components offer complementary functionalities¹⁴⁻¹⁷. Zeolites, such as ZSM-5, provide high surface area and Brønsted acidity capable of neutralizing alkali metal, whereas metal oxides (e.g., MnO_x , FeO_x , CeO_x) supply the redox activity required for SCR¹⁸⁻²⁰. Yet conventional integration strategies (e.g., simple mixing, deposition, or impregnation)^{16,17,21,22} leave oxide nanoparticles exposed on the external surface of the zeolite, making them vulnerable to sulfation and alkali poisoning, even when the oxide loading is increased^{23,24}.

To overcome this limitation, we envisioned a different architectural strategy: constructing a zeolite nanoreactor in which a high-content redox-active oxide core is encapsulated inside a porous acidic shell. In such a configuration, the zeolite shell would not merely confine the catalyst but actively regulate its

interaction with the environment, allowing reactants to diffuse inward while intercepting poisons before they reach the active phase. This confined architecture could enable simultaneous preservation of high redox-site content and strong resistance to multi-component poisoning. We realize this concept by synthesizing a yolk-shell $\text{MnFeO}_x\text{@YS-ZSM-5}$ catalyst through an impregnation-dissolution-recrystallization (IDR) strategy. The resulting nanoreactor consists of MnFeO_x nanoparticles confined within a hollow single-crystalline ZSM-5 shell. Structural characterization, operando spectroscopy, and theory collectively reveal a dual-shielding mechanism combining physical isolation and chemical adsorption control. This architecture delivers outstanding SCR activity and stability under simultaneous SO_2 and alkali exposure and can be generalized to other mixed-metal oxides, establishing hollow zeolite nanoreactors as a new platform for durable NO_x emission-control catalysis.

Results

Formation of the yolk-shell nanoreactor. The yolk-shell $\text{MnFeO}_x\text{@YS-ZSM-5}$ nanoreactor was synthesized via an IDR strategy (**Fig. 1A**). In this architecture, crystalline ZSM-5 forms a hollow shell, while MnFeO_x nanoparticles are confined as an internal yolk. Bulk ZSM-5 is first impregnated with Mn and Fe precursors and calcined to generate $\text{MnFeO}_x/\text{ZSM-5}$, in which metal oxide are dispersed on the zeolite external surface. Subsequent hydrothermal treatment in tetrapropylammonium hydroxide (TPAOH) induces selective internal dissolution of the zeolite and simultaneous recrystallization at the exterior, ultimately yielding a hollow ZSM-5 shell that fully encapsulates the MnFeO_x nanoparticles.

Electron microscopy reveals a clear structural evolution during this process. Pristine ZSM-5 consists of well-defined blocky crystals with sharp edges and an average particle size of ~ 145 nm (**Figs. S1** and **S2**). After impregnation, $\text{MnFeO}_x/\text{ZSM-5}$ retains the original morphology (**Fig. S3**), but transmission electron microscopy (TEM) and energy-dispersive X-ray spectroscopy (EDS; **Fig. S4**) mapping confirm that Mn and Fe species are distributed on the external surface. In contrast, the final $\text{MnFeO}_x\text{@YS-ZSM-5}$ nanoreactor exhibits a distinct yolk-shell architecture. Scanning electron microscopy (SEM) shows hollow cubic particles (**Fig. S5**), while TEM (**Figs. 1B, 1C, and S6**) and high-angle annular dark-field scanning TEM (HAADF-STEM) image (**Fig. 1D**) unambiguously demonstrate that MnFeO_x nanoparticles are confined within the internal cavity of hollow ZSM-5, with no detectable species on the outer surface. The nanoreactors maintain an average size of ~ 145 nm, with shell thicknesses ranging from ~ 10 to ~ 30 nm. Notably, the MnFeO_x nanoparticles are preferentially located near the inner shell surface rather than at the geometric center. EDS elemental mappings (**Figs. 1E and 1F**) and line-scan profiles (**Fig. S7**) confirm that Mn and Fe are spatially confined inside the zeolite shell rather than on the external surface. Integrated differential phase-contrast STEM (iDPC-STEM) (**Figs. 1G and S8**) directly resolves the atomic-scale MFI framework of the ZSM-5 shell while simultaneously visualizing the encapsulated MnFeO_x yolk. The corresponding Fourier transform pattern (**Fig. S8F**) reveals a well-ordered diffraction spot array, confirming the single-crystalline nature of the zeolite shell. Given that the zeolite micropores (~ 0.54

nm, **Fig. 1H**) are much smaller than the MnFeO_x nanoparticles (~ 8.73 nm), migration of the active phase into the zeolite channels is effectively prohibited.

Nitrogen adsorption-desorption results (**Figs. 1I** and **Fig. S9**) confirm the hollow structure of $\text{MnFeO}_x@YS\text{-ZSM-5}$, as evidenced by its distinctive H2-type hysteresis loop and increased total pore volume (**Table S1**)²⁵. XRD analysis (**Fig. S10**) verifies that the ZSM-5 zeolite retains its MFI crystal structure without loss of crystallinity after the encapsulation process. Meanwhile, the strong attenuation of Fe 2p and Mn 2p signals in the X-ray photoelectron spectroscopy (XPS) spectra (**Fig. 1J**) of $\text{MnFeO}_x@YS\text{-ZSM-5}$ provides further evidence consistent with the successful confinement of the MnFeO_x metal oxide core within the zeolite shell. Time-dependent hydrothermal treatments reveal the mechanism underlying yolk-shell formation. Progressive development of internal voids is observed with increasing treatment duration, as evidenced by microscopy (**Figs. S11-S17**) and N_2 adsorption-desorption results (**Fig. S18**), while XRD patterns (**Fig. S19**) confirm that the MFI framework is preserved throughout the process. XPS results (**Fig. S20**) show pronounced Si enrichment and Al depletion on the external surface after TPAOH hydrothermal treatment, indicative of preferential internal Si dissolution and outward recrystallization of silicate species (**Fig. S21**)²⁵. The universality of the IDR strategy is further demonstrated through the successful synthesis of hollow ZSM-5 zeolite encapsulating MnCoO_x or MnCeO_x (**Figs. S22** and **S23**). Both systems display well-defined yolk-shell architectures, as evidenced by adsorption-desorption profiles (**Figs. S24** and **S25**) and XRD patterns (**Fig. S26**), confirming that the zeolite crystallinity remains intact regardless of the metal oxide precursor.

NH_3 -SCR performance and multi-poison resistance. To clarify the catalytic advantages of the yolk-shell $\text{MnFeO}_x@YS\text{-ZSM-5}$ nanoreactor in NH_3 -SCR (**Fig. 2A**), comparative catalysts (MnFeO_x , $\text{MnFeO}_x/\text{ZSM-5}$, and $\text{MnFeO}_x/\text{S-1}$; the S-1 support is an aluminum-free zeolite with much weaker acidity than ZSM-5) were prepared (**Figs. S27-S32**; **Table S1**) and then evaluated. Pure MnFeO_x shows high activity only below 200 °C, followed by rapid deactivation due to excessive NH_3 oxidation (**Fig. S33**) and poor N_2 selectivity (**Fig. S34**). Coupling MnFeO_x with a zeolite broadens the operational window. Notably, $\text{MnFeO}_x@YS\text{-ZSM-5}$ delivers the most robust performance, maintaining $>80\%$ NO_x conversion across a wide temperature range of 220-500 °C, while $\text{MnFeO}_x/\text{S-1}$ and $\text{MnFeO}_x/\text{ZSM-5}$ display significantly compromised medium-high-temperature performance. Samples treated hydrothermally in TPAOH for different durations (**Fig. S35**) all retain similarly wide temperature windows. Compared with reported MnFeO_x -based catalysts (**Fig. S36** and **Table S2**), $\text{MnFeO}_x@YS\text{-ZSM-5}$ exhibits a remarkably broader operational range. Kinetic analysis (**Fig. S37** and **Tables S3-S5**) shows that all oxide-zeolite composites possess substantially lower apparent activation energies than pure MnFeO_x .

The SO_2 tolerance was evaluated at 246 °C with 50 ppm SO_2 (**Fig. 2B**). $\text{MnFeO}_x/\text{ZSM-5}$ undergoes rapid deactivation, with NO_x conversion dropping from 98% to 33% within 0.5 h and stabilizing below 39% after SO_2 was cut off. Pure MnFeO_x shows only transient resistance before severe deterioration. In striking contrast, $\text{MnFeO}_x@YS\text{-ZSM-5}$ stabilizes at $\sim 83\%$ conversion and rapidly recovers to $\sim 90\%$ once SO_2 is

removed, demonstrating largely reversible deactivation. Pre-sulfidation experiments (**Fig. S38**) further confirm the better SO₂ resistance of the yolk-shell nanoreactor. To decouple the effects of hollow morphology from encapsulation, a control catalyst consisting of MnFeO_x supported on hollow ZSM-5 (MnFeO_x/Hollow-ZSM-5) was synthesized (**Figs. S39-S40**). Although this catalyst exhibits comparable SCR activity (**Fig. S41**), its SO₂ tolerance is markedly inferior (**Fig. S42**), establishing that the superior durability of MnFeO_x@YS-ZSM-5 arises from the dual-shielding effect of the intact zeolite shell (physical protection of MnFeO_x from SO₂ and chemical regulation of surface adsorption) rather than from the hollow structure alone. Moreover, MnFeO_x@YS-ZSM-5 also shows outstanding alkali resistance. After K poisoning, MnFeO_x@YS-ZSM-5 maintains high NO_x conversion across the mid-temperature range with only minor losses at higher temperatures (**Fig. 2C**). In contrast, pure MnFeO_x suffers severe deactivation (**Fig. 2D**), consistent with alkali-induced neutralization of acid sites. MnFeO_x/ZSM-5 (**Fig. S43**) preserves moderate activity at intermediate temperatures but exhibits pronounced high-temperature deterioration, while MnFeO_x/S-1 undergoes deactivation over nearly the entire temperature range (**Fig. S44**), reflecting its limited acidity. Under simultaneous SO₂ and K poisoning, MnFeO_x@YS-ZSM-5 uniquely sustains >90% NO_x conversion at 231 °C (**Fig. S45**), underscoring its superior multi-poison resistance.

Acidity-redox balance and structural stability. Given the central roles of surface acidity and redox properties in NH₃-SCR²⁶⁻²⁸, NH₃ temperature-programmed desorption (NH₃-TPD; **Figs. 3A, S46**, and **Table S6**) was performed. The results demonstrate that pure MnFeO_x possesses the weakest acidity, whereas all MnFeO_x-zeolite composites feature enhanced total acidity. MnFeO_x@YS-ZSM-5 delivers the highest acidity and the largest proportion of medium-strength acid sites. These medium-strength acid sites are critical for NH₃ adsorption and the dual SCR pathways involving both Eley-Rideal (E-R) and Langmuir-Hinshelwood (L-H) mechanisms,²⁰ and correlate well with the superior activity and broad operating window of MnFeO_x@YS-ZSM-5 as presented in **Fig. 2A**. Pyridine infrared (Py-IR; **Fig. S47**) experiment confirms abundant B/L acid sites in zeolite-containing samples and negligible acidity in pure MnFeO_x. After K poisoning (**Fig. S48** and **Table S6**), MnFeO_x@YS-ZSM-5 retains the highest total acidity, verifying that zeolite encapsulation buffers alkali attack. Hydrogen temperature-programmed reduction (H₂-TPR; **Fig. 3B**) further reveals how zeolite confinement modulates redox behavior. For MnFeO_x-zeolite composites, the low-temperature reduction peak (<500 °C, α region) corresponds to Mn⁴⁺ reduction²⁹, while the higher-temperature peak (β region) is attributed to Fe₂O₃ reduction³⁰. MnFeO_x@YS-ZSM-5 shows higher reduction temperatures in the α region, indicating weaker oxidative capacity. Pure MnFeO_x possesses the strongest redox capability, consistent with its highest low-temperature activity but narrow active temperature window (**Fig. 2A**). Zeolite coupling therefore mitigates NH₃ over-oxidation, and synergizes with enhanced acidity to improve high-temperature performance. After K poisoning (**Fig. S49**), pure MnFeO_x shows the most pronounced loss of reducibility, correlating with its severe deactivation (**Fig. 2D**). XPS analysis (**Fig. 3C** and **Table S7**) reveals that pure

MnFeO_x has the highest Mn⁴⁺ fraction (39.6%)³¹, which facilitates NO oxidation to NO₂ and promotes low-temperature fast SCR³². Zeolite coupling decreases the Mn⁴⁺ proportion, with MnFeO_x@YS-ZSM-5 showing the lowest (29.4%), consistent with its moderated redox behavior. After SO₂ exposure (**Fig. 2B**), the Mn⁴⁺ content of pure MnFeO_x (**Fig. S50**) decreases sharply, whereas MnFeO_x@YS-ZSM-5 (**Fig. 3C**) shows only a slight reduction (29.4%→28.3%). This decrease arises from electron transfer from SO₂ to Mn⁴⁺^{33,34}, leading to sulfate formation and site deactivation. Notably, MnFeO_x@YS-ZSM-5 exhibits the lowest surface sulfur content (**Table S7**), further corroborated by SO₂-TPD (**Fig. S51**). After K poisoning (**Fig. S52**), the Mn⁴⁺ fraction in pure MnFeO_x decreases markedly, while coupled catalysts remain largely unaffected, explaining their preserved low-temperature activity (**Figs. 2C** and **S43**).

Mn K-edge X-ray absorption near-edge structure (XANES) spectra (**Fig. 3D**) confirm that pure MnFeO_x has the highest Mn oxidation state. Zeolite coupling shifts the absorption edge to lower energies, with MnFeO_x/ZSM-5 exhibiting a higher Mn valence state than MnFeO_x@YS-ZSM-5, consistent with XPS results. After SO₂ poisoning (**Fig. 2B**), both MnFeO_x/ZSM-5 and MnFeO_x@YS-ZSM-5 exhibit decreased Mn valence (**Fig. 3E**), but the shift is substantially smaller for the yolk-shell catalyst, highlighting the protective role of the zeolite shell. Fourier-transformed (FT) *k*³-weighted extended X-ray absorption fine structure (EXAFS; **Fig. 3F**) shows shorter Mn-O bond distances in the composite catalysts than in pure MnFeO_x, indicative of stronger oxide-zeolite interactions. Wavelet transform analysis (**Figs. 3G-I**) identifies Mn-O and Mn-Mn/Mn-Fe coordination features³⁵, confirming the structural integrity of the encapsulated MnFeO_x phase.

Reaction pathway and dual-shielding mechanism. To elucidate the NH₃-SCR reaction pathways, *in situ* diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS) was conducted at 200 °C. For MnFeO_x@YS-ZSM-5, NH₃ adsorption (**Figs. 4A** and **4A₁**) revealed significantly stronger bands for both L acid-bound NH₃ (NH₃-L)³⁶ and B acid-bound NH₄⁺ species (NH₄⁺-B)^{37,38} compared to pure MnFeO_x (**Fig. S53**), confirming that zeolite encapsulation introduces abundant L and B acid sites, thereby enhancing NH₃ adsorption, consistent with the NH₃-TPD results. Upon introducing NO + O₂ to pre-adsorbed NH₃, the NH₃-L/NH₄⁺-B bands on MnFeO_x@YS-ZSM-5 decreased gradually without the formation of surface nitrate or nitrite intermediates over 40 min (**Figs. 4B** and **4B₁**). In contrast, pure MnFeO_x (**Fig. S54**) showed rapid consumption of NH₃-L species³⁹ and immediate accumulation of monodentate nitrate⁴⁰ and bridged nitrate⁴¹. Consistently, NO + O₂ adsorption experiments on MnFeO_x@YS-ZSM-5 (**Fig. 4C**) produced virtually no surface nitrogen species over 40 min, except for a weak transient NO₂ band⁴² that disappears upon N₂ purging, unlike pure MnFeO_x, which formed substantial nitrates/nitrites (**Fig. S55**). These results demonstrate that the NH₃-SCR reaction over MnFeO_x@YS-ZSM-5 predominantly follows the E-R mechanism, involving gaseous NO reacting directly with adsorbed NH₃ species. Conversely, pure MnFeO_x primarily proceeds via a L-H pathway involving surface nitrate intermediates (**Fig. S56**), and this mechanistic divergence is further supported by NO-TPD observations (**Fig. S57**). The substantially

stronger oxidative capability of pure MnFeO_x , as evidenced by H_2 -TPR, XPS, and XAFS analyses, facilitates NO oxidation to NO_2 and enables the “fast SCR” pathway at low temperatures, yet simultaneously promotes nitrate accumulation, NH_4NO_3 decomposition, and the formation of undesired N_2O . In contrast, zeolite encapsulation attenuates NO adsorption and oxidation, suppresses nitrate/nitrite formation, and thereby enhances N_2 selectivity across a broad temperature range. Density functional theory (DFT) calculations further support these findings. As shown in **Figs. 4D-G** and **S58-S59**, NO adsorption on Mn and Fe sites of pure MnFeO_x is strong, with adsorption energies (E_{ads}) of -2.607 eV (Mn, **Fig. 4D**) and -4.100 eV (Fe, **Fig. 4E**), respectively. In contrast, NO adsorption on $\text{MnFeO}_x@\text{YS-ZSM-5}$ is significantly weakened, with corresponding E_{ads} of -1.686 eV (Mn, **Fig. 4F**) and -2.971 eV (Fe, **Fig. 4G**), consistent with the experimentally observed suppression of surface nitrate formation.

The adsorption behavior of SO_2 was further examined by DFT calculations (**Figs. 5A-D**). Relative to pure MnFeO_x , SO_2 adsorption on $\text{MnFeO}_x@\text{YS-ZSM-5}$ is substantially weakened, accompanied by elongated S-Mn and S-Fe bond lengths. Remarkably, SO_2 adsorption on Fe sites becomes thermodynamically unfavorable ($E_{\text{ads}} = +0.383$ eV), indicating that the zeolite shell effectively suppresses SO_2 binding. Moreover, SO_2 adsorption on B acid sites of ZSM-5 is also unfavorable ($E_{\text{ads}} = +0.496$ eV; **Fig. S60**), reflecting electrostatic repulsion that further inhibits sulfur uptake. To directly probe the structural stability of active sites under SO_2 exposure, *in situ* EXAFS measurements were performed during transient $\text{SO}_2 + \text{O}_2$ treatment at 246°C (consistent with the temperature used in the SO_2 resistance test shown in Fig. 2B). As shown in **Fig. 5E**, the Mn *K*-edge XANES profiles of $\text{MnFeO}_x@\text{YS-ZSM-5}$ remain essentially unchanged after 2-3 h of $\text{SO}_2 + \text{O}_2$ exposure. Correspondingly, the Mn-O peak position in Fourier-transform EXAFS spectra (**Fig. S61**) and the Mn-O coordination number (~ 4.9), as well as the bond distance (~ 1.91 Å) (**Figs. 5F-H**) show negligible variation, confirming that SO_2 does not significantly interact with or perturb the encapsulated MnFeO_x active sites.

Collectively, these results establish a dual-shielding mechanism for SO_2 resistance in the yolk-shell $\text{MnFeO}_x@\text{YS-ZSM-5}$ nanoreactor (**Fig. 5I**). The crystalline ZSM-5 shell physically isolates the MnFeO_x core from direct sulfur attack, while its B acid sites electrostatically repel SO_2 and suppress its adsorption. This synergistic physical and chemical shielding not only preserves the structural integrity of the active phase but also enforces an E-R reaction pathway, thereby underpinning the remarkable activity, selectivity, and durability of the nanoreactor under harsh, multi-poisoning SCR conditions.

Discussion

In summary, we successfully realize the nanoreactor concept for NO_x reduction by constructing a yolk-shell $\text{MnFeO}_x@\text{YS-ZSM-5}$ catalyst that addresses the long-standing challenge of simultaneous SO_2 and alkali poisoning in NH_3 -SCR. While the synergistic coupling of zeolites and metal oxides has been extensively explored to mitigate deactivation, previous approaches, largely limited to simple mixing or impregnation, failed to achieve both high redox-site content and effective protection. We overcome this

limitation through an impregnation-dissolution-recrystallization strategy that enables the confinement of high-content (>10 wt.%) MnFeO_x nanoparticles within a hollow ZSM-5 single-crystal shell, yielding a robust yolk-shell nanoreactor with preserved zeolite framework integrity. This architecture reveals a synergistic dual-shielding mechanism governing its superior poisoning resistance: the ZSM-5 shell physically hinders the MnFeO_x core from being directly exposed to SO_2 , whereas its abundant external Brønsted acid sites provide chemical shielding by preferentially adsorbing alkali metal and suppressing SO_2 adsorption. This synergistic protection delivers >90% NO_x conversion with high N_2 selectivity under simultaneous SO_2 and K poisoning. The strategy further demonstrates broad versatility, extending successfully to other mixed metal oxides such as MnCoO_x and MnCeO_x . By establishing this yolk-shell architecture as a general platform, our work introduces a powerful paradigm for engineering durable SCR catalysts. More broadly, the hollow zeolite-confined nanoreactor concept opens new avenues for robust catalysts in emission control and other high-temperature environmental processes requiring long-term stability against complex poisons.

Methods

Catalyst synthesis

The yolk-shell MnFeO_x @YS-ZSM-5 catalyst was synthesized by an impregnation-dissolution-recrystallization (IDR) strategy. For comparison, MnFeO_x metal oxides supported on the outer surface of ZSM-5 was prepared by the conventional impregnation method. To reveal the formation mechanism of MnFeO_x @YS-ZSM-5, the samples crystallized at each step were collected. Furthermore, to verify the universality of the IDR method, ZSM-5 zeolite confining other metal active sites were also prepared. The detailed preparation procedures are discussed in the Supplementary Information.

Characterization methods

Various testing methods—including X-ray diffraction (XRD), N_2 adsorption/desorption analysis, X-ray photoelectron spectroscopy (XPS), pyridine infrared (Py-IR), NH_3 temperature-programmed desorption (NH_3 -TPD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), high resolution TEM (HRTEM), energy-dispersive X-ray spectroscopy (EDS) elemental mapping, aberration-corrected TEM (AC-TEM), AC-EDS elemental mapping, X-ray absorption near-edge structure (XANES), *in situ* extended X-ray absorption fine structure (*in situ* EXAFS), density functional theory (DFT) calculations, and the *in situ* diffuse reflectance infrared Fourier-transform spectroscopy (*in situ* DRIFTS)—were adopted to measure the physical and chemical properties and elucidate the plausible reaction mechanism over the yolk-shell MnFeO_x @YS-ZSM-5 and related samples. The detailed measuring processes are described in the Supplementary Information.

Activity and kinetic tests

The detailed NH_3 -SCR activity and kinetic tests are also presented in the Supplementary Information.

Declarations

Data availability

The additional data are provided in the Supplementary Information. All the data that support the findings of this study are available from the corresponding author upon reasonable request.

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Author contributions

H. Peng conceived the research idea, designed the experiments, and supervised this project, wrote-review & edited the manuscript. Y. Li performed the experiments, analyzed the data, and wrote the manuscript. G. Li performed the DFT calculations. R. Li took part in the synthesis of samples and characterizations. M. Liu commented on the manuscript and wrote-review & edited the manuscript. J. Ji, X. Hu, F. Yu, H. Li, and W. Liu discussed the results and commented on the manuscript.

Competing interests

The authors declare no competing financial interests.

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Figures

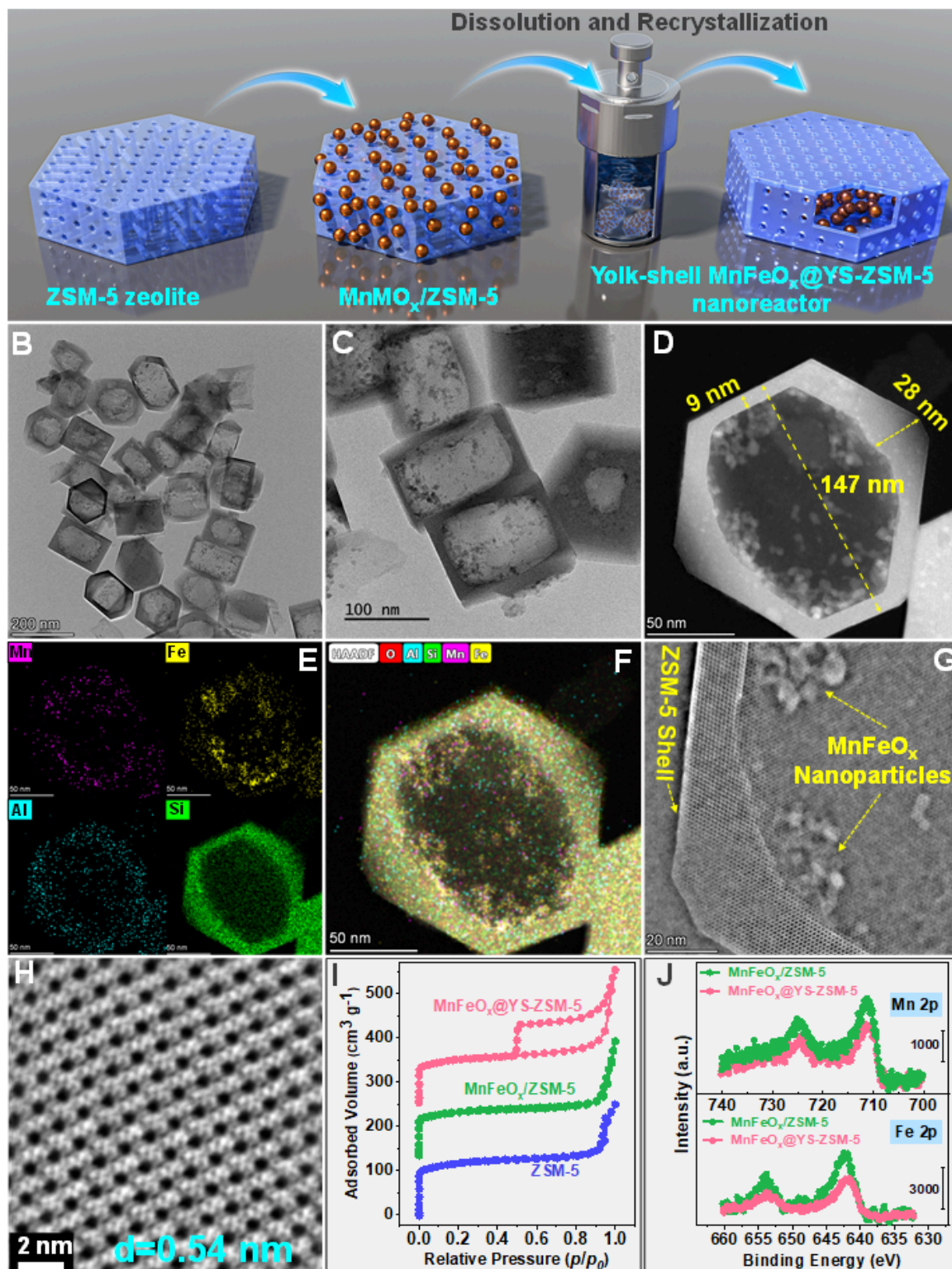


Figure 1

Morphological and structural characterizations. (A) Schematic illustration for the synthesis of the yolk-shell structured $\text{MnFeO}_x@\text{YS-ZSM-5}$ nanoreactor via the IDR method. (B, C) TEM images, (D) HAADF-STEM image, (E, F) EDS elemental mappings and (G, H) iDPC images of the yolk-shell structured $\text{MnFeO}_x@\text{YS-ZSM-5}$ nanoreactor. (I) N_2 adsorption-desorption isotherms of ZSM-5, $\text{MnFeO}_x/\text{ZSM-5}$, and $\text{MnFeO}_x@\text{YS-ZSM-5}$ nanoreactor. (J) XPS spectra of the yolk-shell structured $\text{MnFeO}_x@\text{YS-ZSM-5}$ nanoreactor.

MnFeO_x@YS-ZSM-5 samples. (J) Mn 2p and Fe 2p XPS spectra of the MnFeO_x/ZSM-5 and MnFeO_x@YS-ZSM-5 samples.

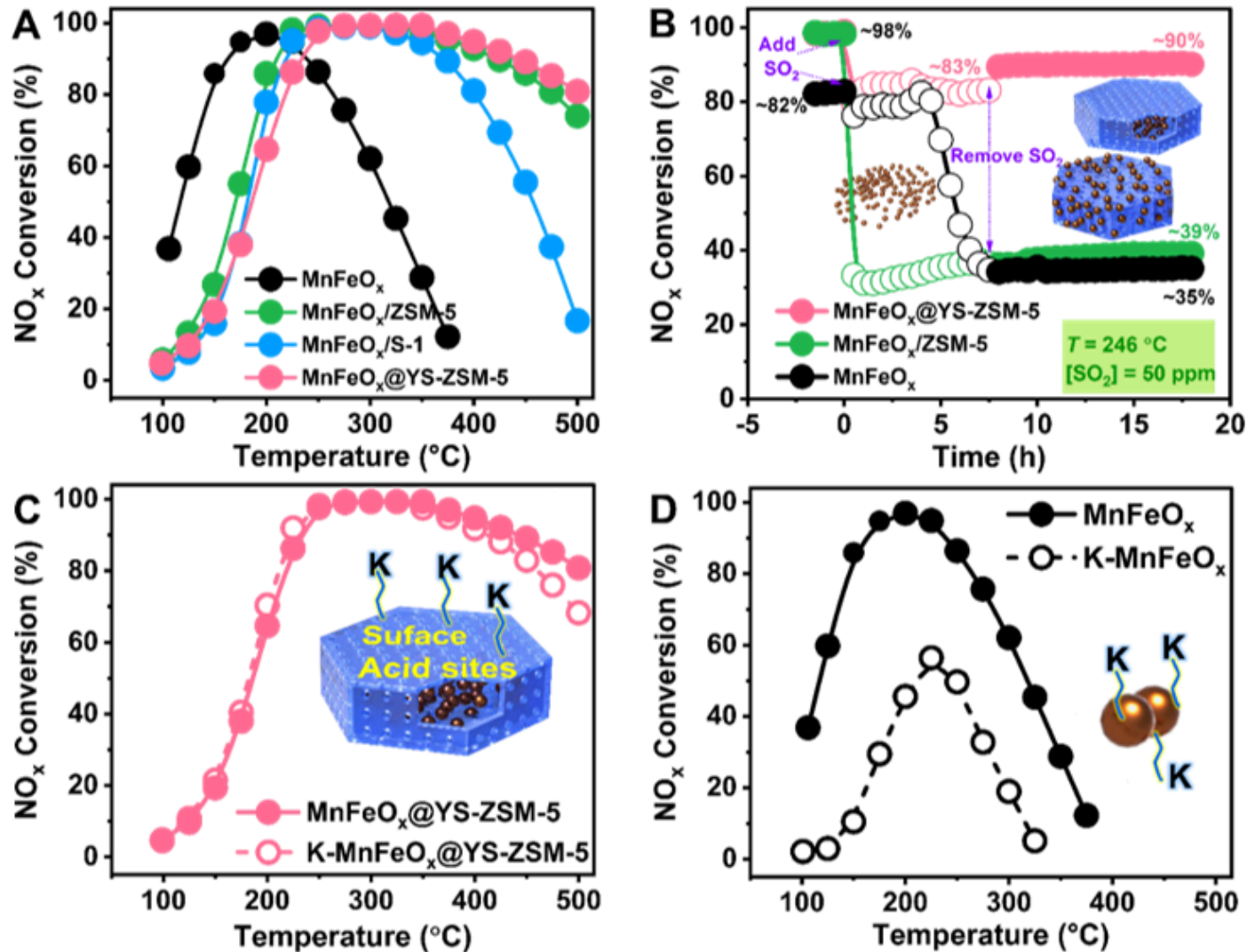


Figure 2

NH₃-SCR catalytic performance. (A) NO_x conversion as a function of temperature in NH₃-SCR reaction over the MnFeO_x, MnFeO_x/ZSM-5, MnFeO_x/S-1, and MnFeO_x@YS-ZSM-5 catalysts. (B) SO₂ resistance performance over the MnFeO_x, MnFeO_x/ZSM-5, and MnFeO_x@YS-ZSM-5 catalysts at 246 °C. (C and D) NO_x conversion as a function of temperature in NH₃-SCR reaction over the K-poisoned and fresh catalysts. Reaction conditions: 500 ppm NO, 500 ppm NH₃, 5 vol.% O₂, 5 vol.% H₂O, 50 ppm SO₂ (when used), balance N₂, WHSV = 60000 mL g_{cat.}⁻¹ h⁻¹.

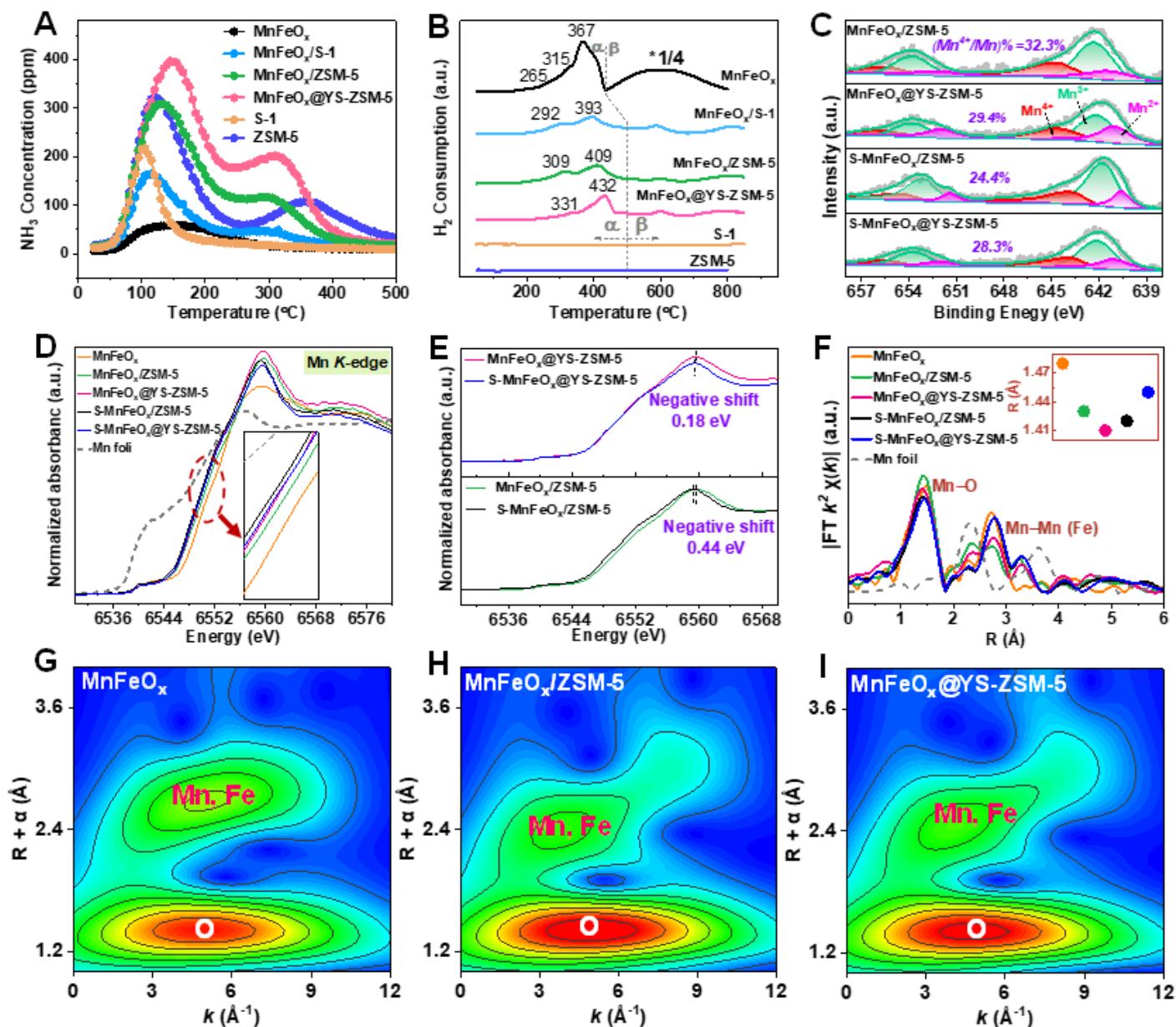


Figure 3

Physicochemical characterizations and analysis. (A) NH₃-TPD curves and (B) H₂-TPR profiles over the MnFeO_x@YS-ZSM-5 and related samples. (C) Mn 2p XPS spectra over the fresh and related SO₂-poisoned samples. (D and E) Mn K-edge XANES spectra and (F) FTs of Mn K-edge EXAFS oscillations for fresh and corresponding SO₂-poisoning samples. (G-I) WT plots for EXAFS spectra over the MnFeO_x, MnFeO_x/ZSM-5, and MnFeO_x@YS-ZSM-5.

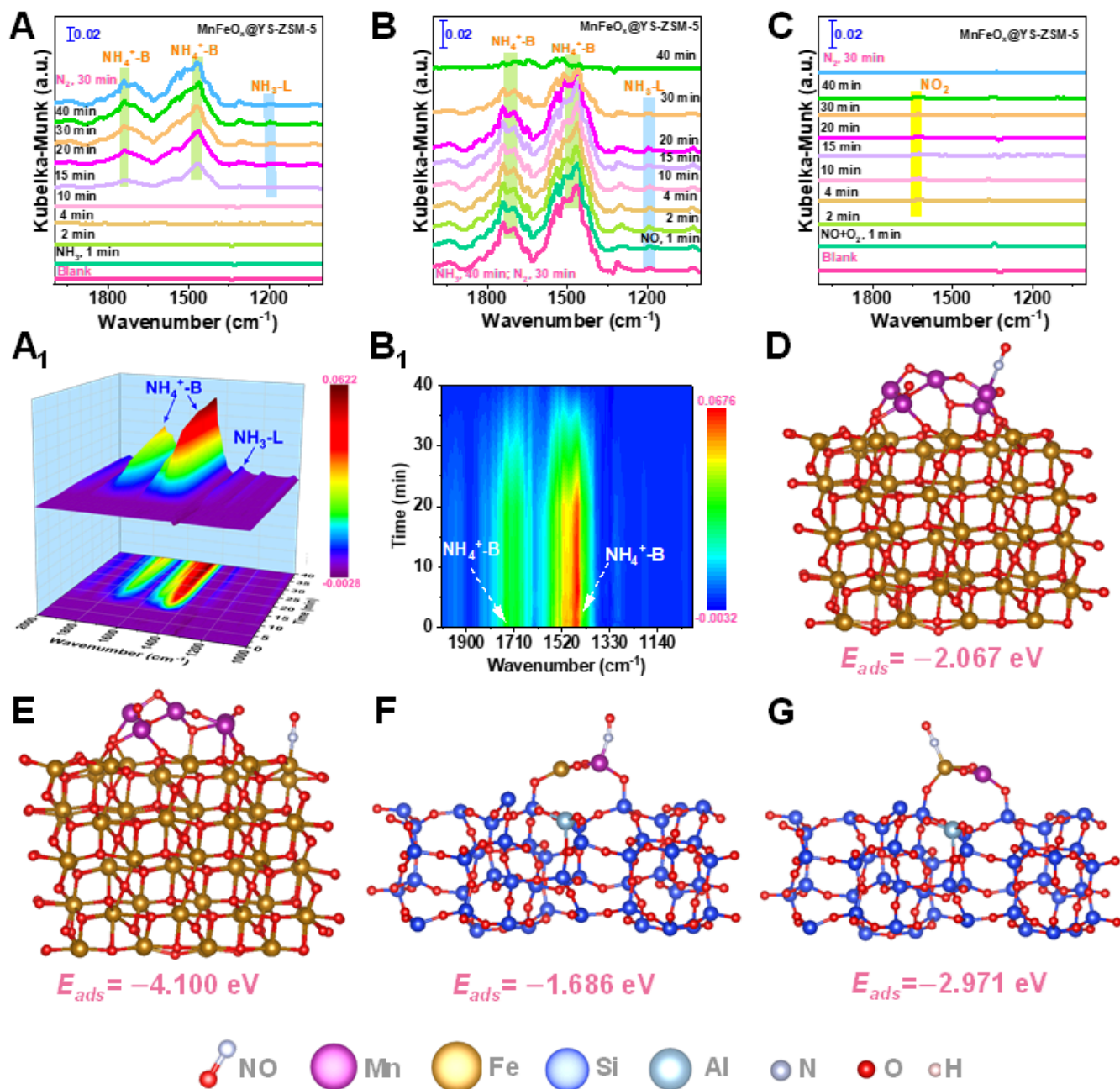


Figure 4

Study on the mechanism of catalytic reaction. (A and A₁) *In situ* DRIFT spectra of NH_3 adsorption on $\text{MnFeO}_x/\text{YS-ZSM-5}$ catalyst at 200 °C. (B and B₁) *In situ* DRIFT spectra of pre-adsorbed NH_3 species reacted with $\text{NO} + \text{O}_2$ on $\text{MnFeO}_x/\text{YS-ZSM-5}$ catalyst at 200 °C; (C) *In situ* DRIFT spectra of $\text{NO} + \text{O}_2$ adsorption on $\text{MnFeO}_x/\text{YS-ZSM-5}$ catalyst at 200 °C; Optimized adsorption configurations of NO gas molecules on (D and E) MnFeO_x and (F and G) $\text{MnFeO}_x/\text{YS-ZSM-5}$ samples.

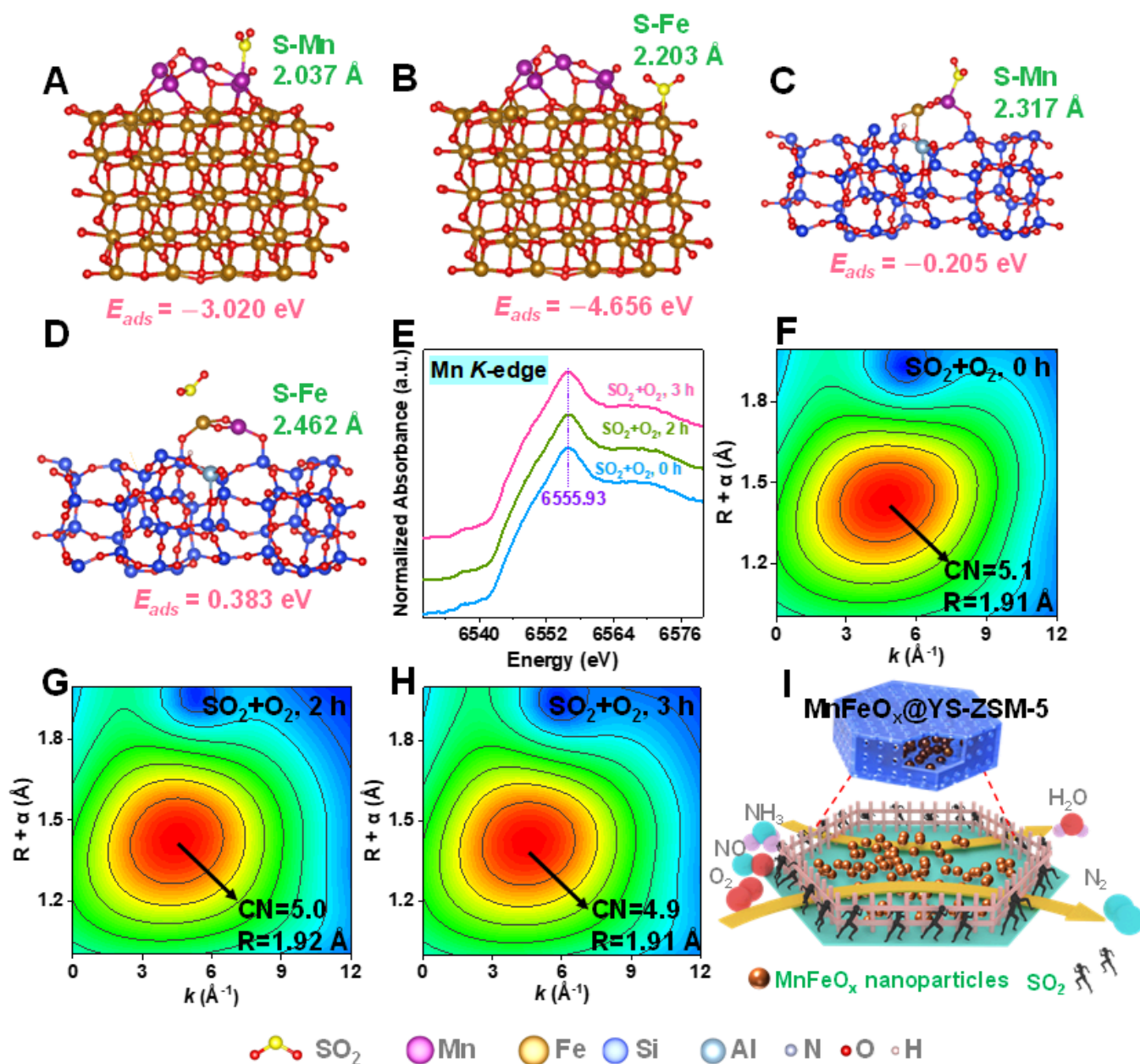


Figure 5

Structure-activity relationship analysis. Optimized adsorption configurations of SO_2 gas molecules on (A and B) MnFeO_x and (C and D) $\text{MnFeO}_x@YS\text{-ZSM-5}$ catalysts. (E) *In situ* Mn K-edge XANES spectra of the transient reaction on $\text{MnFeO}_x@YS\text{-ZSM-5}$ catalyst after 0, 2, and 3 h treatment at 246 °C in 250 ppm SO_2 + 5 vol.% O_2 atmosphere. WT plots for EXAFS spectra of $\text{MnFeO}_x@YS\text{-ZSM-5}$ catalyst after being treated at 246 °C in an atmosphere of 250 ppm SO_2 + 5 vol.% O_2 for (F) 0 h, (G) 2 h, and (H) 3 h (R and CN denote the average interatomic distances between Mn and the O atoms in the first coordination shell and the Mn-O coordination number, respectively). (I) Schematic diagram of enhanced SO_2 poisoning resistance of the catalyst through combined physical shielding and chemical repulsion effects.

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