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Recyclable MFe_2O_4 ($\text{M} = \text{Mn}, \text{Zn}, \text{Cu}, \text{Ni}, \text{Co}$) coupled micro–nano bubbles for simultaneous catalytic oxidation to remove NO_x and SO_2 in flue gas

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NO_x can be efficiently removed by micro–nano bubbles coupling with Fe^{3+} and Mn^{2+} , but the catalyst cannot be reused and the adsorption wastewater should be treated. This work developed a new technology that uses micro–nano bubbles and recyclable MFe_2O_4 to simultaneously remove NO_x and SO_2 from flue gas, and clarified the effectiveness and reaction mechanism. MFe_2O_4 ($\text{M} = \text{Mn}, \text{Zn}, \text{Cu}, \text{Ni}$ and Co) prepared by a hydrothermal method was characterized. The results show that MFe_2O_4 can be activated to produce $\cdot\text{OH}$ which can accelerate the oxidation absorption of NO_x . Compared with no catalyst, the NO_x conversion rate increased from 32.85% to 83.88% in the NO_x – SO_2 – MFe_2O_4 –micro–nano bubble system, while the removal rate of SO_2 can reach 100% at room temperature. The catalytic activities of MFe_2O_4 showed the following trend: $\text{CuFe}_2\text{O}_4 > \text{ZnFe}_2\text{O}_4 > \text{MnFe}_2\text{O}_4 > \text{CoFe}_2\text{O}_4 > \text{NiFe}_2\text{O}_4$. The results provide a new idea for the application of advanced oxidation processes in flue gas treatment.

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1. Introduction

With the development of industry, nitrogen oxides (NO_x) and sulfur dioxide (SO_2) have become the most common atmospheric pollutants.^{1,2} The emission of these pollutants causes various environmentally harmful effects such as acid rain, photochemical smog, ozone depletion and climate warming.³ At present, the main methods to control NO_x in industry are dry denitration technology and wet denitration technology. Dry denitrification techniques include selective catalytic reduction (SCR) and selective non-catalytic reduction (SNCR).^{4–6} Wet denitrification techniques include oxidation, complexation absorption and acid–base absorption.^{7–9} There are many kinds of pollutants in the actual flue gas, which make it difficult to deal with. It is a new trend to study the oxidation and absorption of various pollutants in flue gas by simple devices.¹⁰ Flue gas desulfurization and denitrification integration refers to the process of simultaneous desulfurization and denitrification in the same equipment. Although this method can effectively improve the flue gas treatment efficiency and reduce the energy consumption, the main research is still in the research and development stage, there is still a long way to go before the large-scale industrialization. Micro–nano bubbles (MNB) coupled oxygen carrier (OCs) technology is a wet flue gas integrated removal technology, which can simplify the system,

reduce the cost, and ensure a high removal efficiency of NO_x and SO_2 ,^{11,12} and has a strong application potential. It is a new direction of the comprehensive removal of multi-pollutant flue gas.¹³

Micro–nano bubble technology refers to the bubble with the diameter between tens of microns to hundreds of nanometers when the bubble occurs.¹⁴ Compared with ordinary bubbles, it has the following characteristics: small size leads to large surface area, low rising speed, high internal pressure, large gas solubility, and free radicals formed when crushed.^{13,15} Hydroxyl radicals generated by the breakdown of micro–nano bubbles are an important reactive oxygen species with an oxidation potential of 2.8V.^{16–18} Xiao¹⁹ *et al.* used micro–nano bubbles to remove SO_2 and NO (1000 mg m^{-3}), and NO removal efficiency reached 87.7%. It is well known that Fe^{2+} ions can promote the interaction between NO_x and S(IV) in aqueous solution to form nitrosyl complexes, which lead to enhanced NO_x removal.^{20,21} Although the activation of transition metals can accelerate the oxidative absorption of NO_x , it is not suitable for recycling, and the product is heavy metal wastewater that causes secondary pollution. Therefore, it is necessary to use magnetic solid catalyst instead of ionic catalyst.

Previous studies have shown that spinel ferrite (chemical formula: $\text{M}^{2+}\text{Fe}_2^{3+}\text{O}_4$) has better mechanical stability, stronger mechanical strength, reoxidation ability and environmental friendliness than single metal oxide.^{22–24} In actual use, MFe_2O_4 have acted as an oxygen supply and a catalyst.^{25,26} The standard spinel structure is a lattice composed of 32 divalent oxygen ions that form a closed-pack, face-centered cubic arrangement with

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64 tetrahedral interstitial sites and 32 octahedral interstitial sites.²⁷ In the spinel structure, M^{2+} and Fe^{3+} are respectively located in the sites of tetrahedron or octahedron composed of oxygen and have metal synergistic effects which determine good oxygen transferability and catalysis properties.^{28,29} Therefore, spinel ferrites were attractive candidates because of their rich crystal chemistry, low cost, nontoxicity and environmentally friendly properties.^{30,31} Xu *et al.*³² found that a small quantity of palladium-doped ferrite spinel could achieve high NO conversion and the catalyst cost reduction. However, the simultaneous use of transition metal oxide and MNB for NO_x removal in a system has rarely been reported. Furthermore, the synergistic effects of the different metals in ferrites for NO and SO_2 removal have been rarely mentioned.

In this study, the recyclable catalyst MFe_2O_4 ($M = Mn, Co, Ni, Cu, Zn$) synthesized with hydrothermal method and MNB were used to form the NO_x - SO_2 - MFe_2O_4 -MNB system for simultaneous removal of NO_x and SO_2 from flue gas. The structural, physical, and chemical properties of the as-prepared MFe_2O_4 before and after the reaction were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), the Brunauer-Emmett-Teller (BET) method and X-ray photoelectron spectroscopy (XPS). The removal rates of NO and SO_2 were monitored with the flue gas analyzer and ion chromatography to explore the actions of MNB and the effects of various divalent cations contained in the ferrite. The goal of this study was to evaluate the simultaneous NO and SO_2 removal efficiencies, and elucidate the chemistry and reaction pathways of the NO_x - SO_2 - MFe_2O_4 -MNB system.

2. Experimental

2.1. Materials

All the materials used for synthesizing catalysts, including ethylene glycol, poly(ethylene glycol) (PEG), sodium acetate (CH_3COONa), ferric chloride ($FeCl_3 \cdot 6H_2O$), manganese chloride ($MnCl_2 \cdot H_2O$), zinc chloride ($ZnCl_2$), cupric chloride ($CuCl_2 \cdot 2H_2O$), nickel chloride ($NiCl_2 \cdot 6H_2O$), cobalt chloride ($CoCl_2 \cdot 6H_2O$), ethyl alcohol (C_2H_5OH), 5,5-dimethyl-1-pyrroline N-oxide (DMPO), were purchased from Sinopharm Chemical Reagent Co., Ltd. All chemicals were used without further purification.

2.2. Synthesis of MFe_2O_4 ($M = Mn, Co, Ni, Cu$ and Zn) by the hydrothermal method

The MFe_2O_4 ($M = Mn, Co, Ni, Cu$ and Zn) microspheres were synthesized based on the hydrothermal method. Briefly, polyethylene glycol and sodium acetate were added into ethylene glycol under vigorous stirring conditions. Then partial chloride was added to reach the metal cation (Fe^{3+} and M^{2+}) molar ratio of 2 : 1. The resultant homogeneous solution was obtained and then placed into the 500 mL Teflon-lined autoclave, reacted at 200 °C for 10 h. The black product was collected with a magnet, washed several times by ethanol and distilled water, and then dried at 80 °C for 6 h under vacuum. Finally, the resulting product was sufficiently grinded to obtain fresh MFe_2O_4 ($M = Mn, Co, Ni, Cu$ and Zn).

2.3. Characterization

A scanning electron microscope (SEM, Hitachi S4800) was adopted to observe the morphologies. Energy dispersive spectrometer (EDS) with Horiba 7593-H was used to confirm the proportion of each element in the catalysts. Powder X-ray diffraction meter (XRD, D/max 2550 PC, Japan Rigaku) operation was completed with $Cu K\alpha$ radiation in a 2θ angle between 10° and 80° at a rate of 2° min^{-1} to monitor crystal structure. The surface properties and valence state of the catalysts were determined through X-ray photoelectron spectroscopy (XPS) experiments by using the Escalab 250Xi spectrometer with an Al- $K\alpha$ radiation source at an energy step size of 1 eV to obtain high-resolution XPS spectra. The spectra were calibrated with respect to C 1s at a binding energy of 284.8 eV. The specific surface area of the samples was determined by using the Brunauer-Emmett-Teller (BET) method on an automated area and pore size analyzer (Autosorb-iQ) based on nitrogen adsorption desorption isotherm. The samples were outgassed at 200 °C for 2 h to remove remaining moisture and then analyzed with N_2 gas as an adsorbent at the temperature of liquid nitrogen. $\cdot OH$ and $\cdot O_2^-$ in the NO_x - SO_2 - MFe_2O_4 -MNB system were detected *via* electron paramagnetic resonance spectroscopy (EPR, JEOL-FA200), and DMPO was used for capturing $\cdot OH$ and $\cdot O_2^-$.

2.4. Reactivity measurement in the NO_x - SO_2 - MFe_2O_4 -MNB system

Fig. 1 shows the NO_x - SO_2 - MFe_2O_4 -MNB system installation diagram. Firstly, NO_x and SO_2 in the cylinder are fed into the mixer in a certain proportion to mix evenly. Gas flow rate is controlled by the rotameter. The flue gas analyzer (Testo350) was adopted to observe the intake gas concentration. Then a certain amount of MFe_2O_4 is uniformly dispersed in the absorption solution by ultrasonic oscillation. Finally, the configured gas and absorption solution are passed through the micro-nano bubble generator together to form the NO_x - SO_2 - MFe_2O_4 -MNB system in the reaction tower, so as to complete the catalytic oxidation and absorption process of NO_x and SO_2 . The removal efficiency of NO_x was calculated by the concentrations of NO_2^- and NO_3^- in the absorption liquid measured with ion chromatography (ICS-1100 AS11-HC, Thermo Fisher Scientific).

The rated parameters of the micro-nano bubble generator were set as follows: the effluent pressure (0.5 MPa), the inlet water flow (300 $mL min^{-1}$) and the intake air amount (48 $mL min^{-1}$). The volume of the oxidation absorption reactor is 1.5 L. MFe_2O_4 was uniformly dispersed in a tubular reactor as a catalyst. A gas mixture containing 5113 $mg m^{-3}$ NO_x and 3371 $mg m^{-3}$ SO_2 was used as the intake gas. NO_x is mainly composed of 3795 $mg m^{-3}$ NO and 2021 $mg m^{-3}$ NO_2 . In order to explore the practical application performance of the NO_x - SO_2 - MFe_2O_4 -MNB system, the effects of the addition of different recyclable MFe_2O_4 catalysts on the integrated desulfurization and denitrification efficiency were discussed by analyzing the IC test results of the absorption solution.



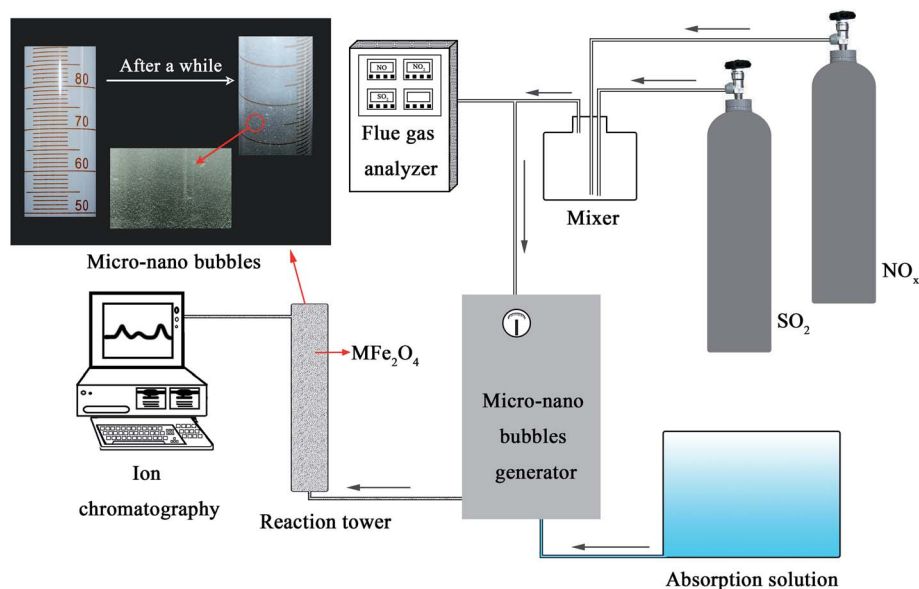


Fig. 1 The NO_x - SO_2 - MFe_2O_4 -MNB system installation diagram.

2.5. Analysis methods

The removal efficiency of NO_x can be calculated as

$$\eta_{\text{NO}_x} = \frac{N_{\text{out}}}{N_{\text{in}}} \times 100\% \quad (1)$$

$$N_{\text{in}} = \frac{c_{\text{NO}} \times q \times t}{M_{\text{NO}}} + \frac{c_{\text{NO}_2} \times q \times t}{M_{\text{NO}_2}} \quad (2)$$

$$N_{\text{out}} = \frac{c_{\text{NO}_2^-} \times V}{M_{\text{NO}_2^-}} + \frac{c_{\text{NO}_3^-} \times V}{M_{\text{NO}_3^-}} \quad (3)$$

where η_{NO_x} represents the removal efficiency of NO_x , N_{out} is the amount of NO_2^- and NO_3^- in the absorption liquid, N_{in} is the amount of NO_x entering the system, c_{NO} and c_{NO_2} are the concentrations of NO and NO_2 in the intake air respectively, $c_{\text{NO}_2^-}$ and $c_{\text{NO}_3^-}$ are the concentrations of NO_2^- and NO_3^- in the absorption liquid respectively, q is the air inflow, V is the volume of water in the reaction tower, M is the molecular weight, t is the system running time.

The removal efficiency of SO_2 can be calculated as

$$\eta_{\text{SO}_2} = \frac{N'_{\text{out}}}{N'_{\text{in}}} \times 100\% \quad (4)$$

$$N'_{\text{in}} = \frac{c_{\text{SO}_2} \times q \times t}{M_{\text{SO}_2}} \quad (5)$$

$$N'_{\text{out}} = \frac{c_{\text{SO}_4^{2-}} \times V}{M_{\text{SO}_4^{2-}}} \quad (6)$$

where η_{SO_2} represents the removal efficiency of SO_2 , N'_{out} is the amount of SO_4^{2-} in the absorption liquid, N'_{in} is the amount of SO_2 entering the system, c_{SO_2} are the concentrations of SO_2 in the intake air, $c_{\text{SO}_4^{2-}}$ are the concentrations of SO_4^{2-} in the absorption liquid.

3. Results and discussion

3.1. Physicochemical characterization

The SEM images of MFe_2O_4 ($M = \text{Mn}, \text{Zn}, \text{Cu}, \text{Ni}$ and Co) are shown in Fig. 2. The five spinel ferrites are similar to each other, exhibiting a spherical structure with a dense surface and abundant fine particles. Among the five OCs, CuFe_2O_4 and CoFe_2O_4 exhibited more agglomeration and sintering, possibly due to high temperature calcination and the small-dimension effect. Compared with CuFe_2O_4 and CoFe_2O_4 , MnFe_2O_4 , NiFe_2O_4 and ZnFe_2O_4 are spherical with the uniform shape and distribution. Fig. 2 gives a detailed description of MFe_2O_4 . MFe_2O_4 with the grain diameter of 100–350 nm. Among them, CoFe_2O_4 and CuFe_2O_4 had the smallest average particle sizes (127 nm for CoFe_2O_4 and 151 nm for CuFe_2O_4), which might be the cause for their relatively serious agglomeration. The particle sizes of various MFe_2O_4 showed the following decreasing sequence: $\text{MnFe}_2\text{O}_4 > \text{ZnFe}_2\text{O}_4 > \text{NiFe}_2\text{O}_4 > \text{CuFe}_2\text{O}_4 > \text{CoFe}_2\text{O}_4$.

EDS analysis results (shown in Table 1) confirmed that the component contents of the samples are in reasonable agreement with the atomic percentages deduced from their molecular formulas. The elemental composition in Table 1 indicates that there are only three elements (O, M and Fe) in the composite. Furthermore, the M/Fe molar ratios of samples were approximately 0.5. The contents of the three elements in each complex MFe_2O_4 were $10.48 \pm 0.99\%$ (M, at%) and $22.18 \pm 0.42\%$ (Fe, at%), respectively.

Table 1 shows the specific surface areas of the five spinel catalysts. The five ferrites exhibited different specific surface areas due to their different metal compositions. Among the five OCs, CoFe_2O_4 had the largest specific surface area ($121.352 \text{ m}^2 \text{ g}^{-1}$), followed by NiFe_2O_4 ($72.727 \text{ m}^2 \text{ g}^{-1}$). The ferrites of MnFe_2O_4 , CuFe_2O_4 and ZnFe_2O_4 had the smallest specific surface areas (less than $30 \text{ m}^2 \text{ g}^{-1}$). The smaller the diameter of



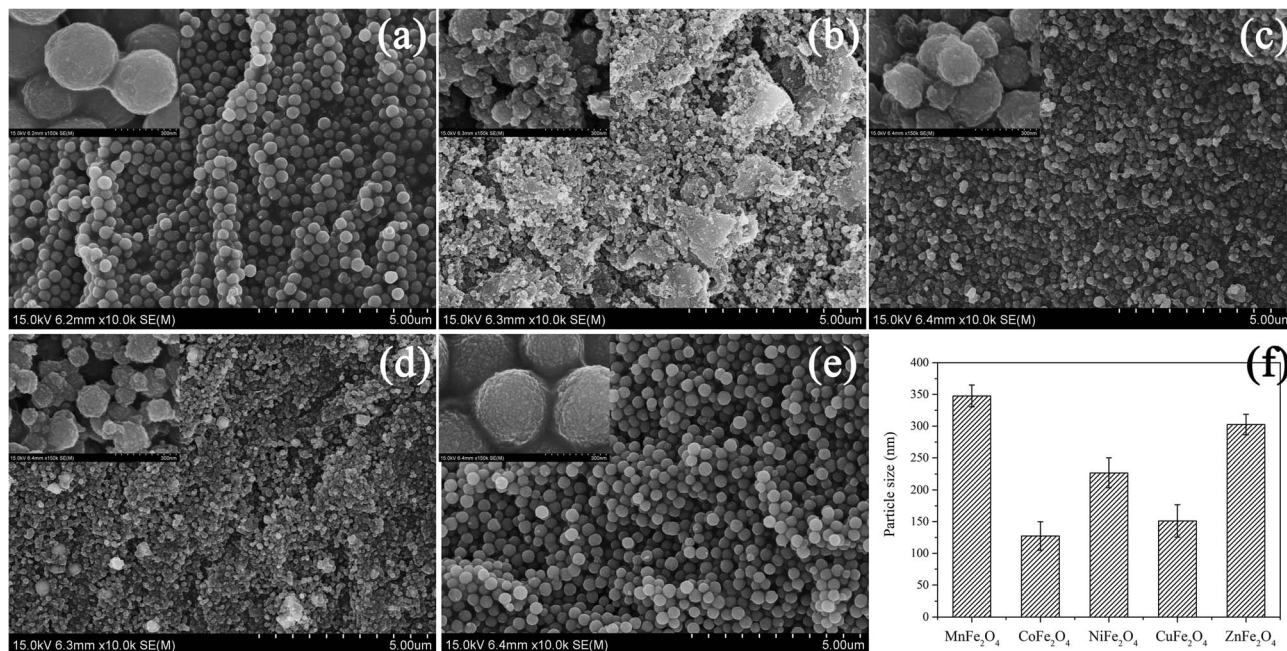


Fig. 2 SEM images of MFe₂O₄: (a) MnFe₂O₄, (b) CoFe₂O₄, (c) NiFe₂O₄, (d) CuFe₂O₄ and (e) ZnFe₂O₄ (f) size distributions of MFe₂O₄ nanoparticles.

MFe₂O₄ nanoparticles was, the larger the specific surface area was (Fig. 2f and Table 1).

XRD measurements were conducted to identify the crystal structures of the samples. The XRD patterns of MFe₂O₄ (M = Mn, Zn, Cu, Ni and Co) are shown in Fig. 3. X-ray powder diffraction patterns of MnFe₂O₄, CoFe₂O₄, NiFe₂O₄ and ZnFe₂O₄ samples were quite similar to those of cubic spinel-type structures belonging to the *Fd3m* (227) space group. The main diffraction reflection peaks included (220), (311), (400), (422), (511) and (440) crystal planes, which well matched with the standard XRD pattern representing the cubic spinel structure (JCPDS no. 38-0430, 22-1086, 10-0325, 34-0425 and 10-1108), indicating the good crystallinity of these MFe₂O₄.³³ Unlike these samples, however, CuFe₂O₄ exhibited a well-defined spinel ferrite structure with a strongest peak reflection peak at the plane (211) that matched well with the standard XRD pattern (JCPDS no. 34-0425) representing a tetragonal system (space group: *I4₁/amd*).³⁴

The crystallite size *D* for each sample was estimated according to the most intense reflection peak (311) with Scherrer's equation (eqn (7)).³⁵

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (7)$$

where *D* is the average crystallite size; *K* is Scherrer constant, 0.89; corresponds to the wavelength of Cu-K α radiation, 0.154 nm; β is the full width at half maximum intensity for a reflection maximum; θ is the diffraction angle.

With Scherrer's Equation, crystallite sizes of MFe₂O₄ nanocomposites were calculated to be 13 nm (Table 1). The crystallite sizes of these OCs ranged from 10.07 to 15.94 nm. The crystallite sizes of the five MFe₂O₄ showed the following decreasing sequence: MnFe₂O₄ > ZnFe₂O₄ > CuFe₂O₄ > CoFe₂O₄ > NiFe₂O₄. As the crystal grains of OCs increased, the crystallinity became better, but the probability of agglomeration also increased. CoFe₂O₄ and NiFe₂O₄ were most prone to agglomerate because of their smallest grain sizes, which were consistent with the SEM results (Fig. 2).

In order to give an insight into the elemental chemical valence and electronic properties on the surface layers of MFe₂O₄, XPS measurements of MFe₂O₄ before and after the reactions were conducted to examine the chemical compositions and electronic structures of the samples. Fig. 4 shows the

Table 1 Physical and chemical properties of the investigated spinel catalysts

Catalysts	<i>S</i> _{BET} (m ² g ^{−1})	Elemental composition (atomic percentage, %)			Crystallite size from XRD (nm)
		M cation (Mn/Zn/Cu/Ni/Co)	Fe	M/Fe	
MnFe ₂ O ₄	22.243	10.83	22.26	0.487	15.94
CoFe ₂ O ₄	121.352	11.94	22.72	0.458	11.61
NiFe ₂ O ₄	72.727	10.21	21.63	0.472	10.07
CuFe ₂ O ₄	30.009	9.24	21.92	0.422	12.78
ZnFe ₂ O ₄	20.326	10.20	22.37	0.456	14.11



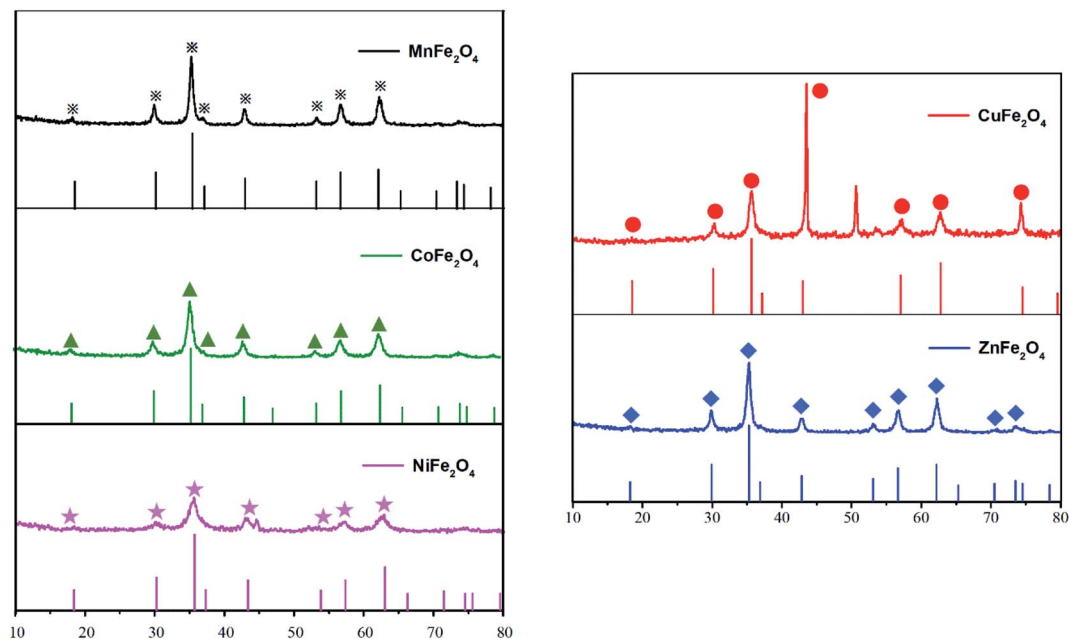


Fig. 3 XRD patterns of the investigated spinel catalysts MFe_2O_4 and their standard profiles.

XPS spectra of MFe_2O_4 , respectively. In full-scale XPS spectra (Fig. 4a), the apparent peaks of Fe 2p, C 1s, O 1s, Mn 2p, Co 2p, Ni 2p, Cu 2p and Zn 2p illustrated that iron, manganese, cobalt,

nickel, copper and zinc were the main elements of MFe_2O_4 . The comparison of the peak differentiation-imitating analysis results of the nano- MFe_2O_4 before and after the reaction

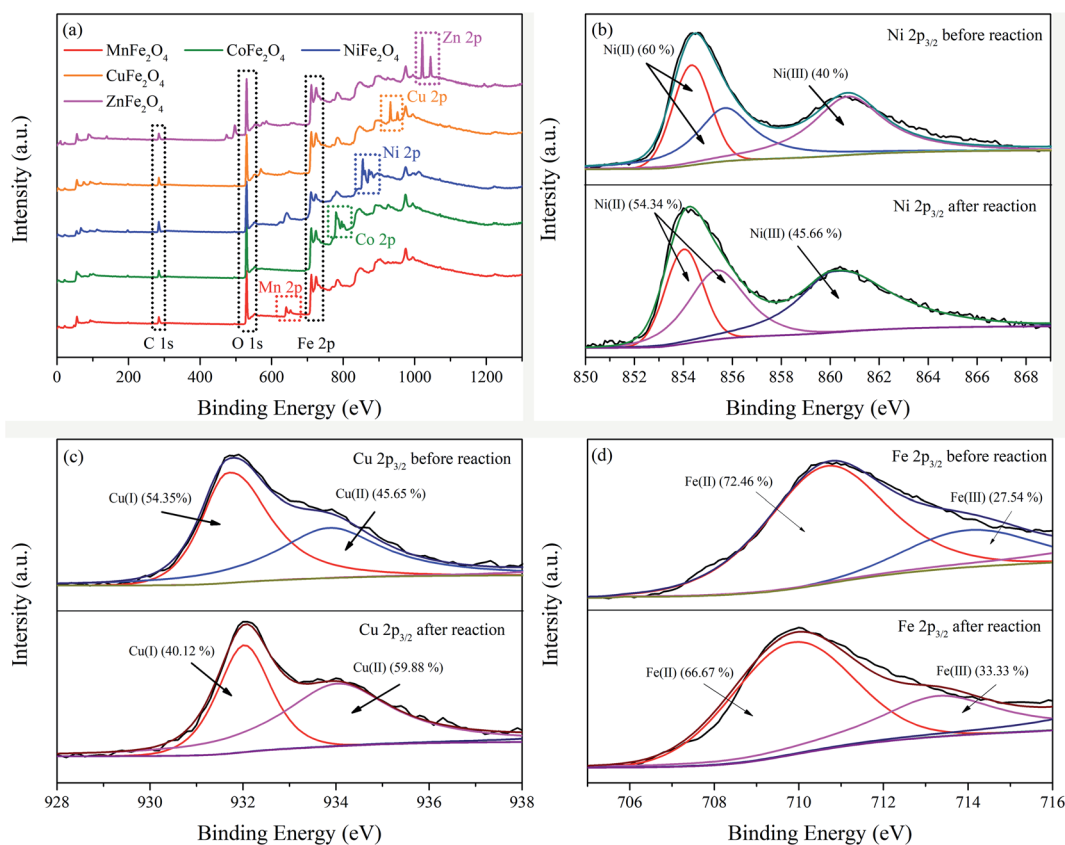


Fig. 4 XPS patterns of MFe_2O_4 in the NO_x - SO_2 - MFe_2O_4 -MNB system before and after reactions: full-range scan of the samples (a), Ni $2p_{3/2}$ (b), Cu $2p_{3/2}$ (c), and Fe $2p_{3/2}$ of ZnFe_2O_4 (d).

(Fig. 4b–e) indicated that the binding energy of $M 2p_{3/2}$ was slightly reduced. After the reaction, the $M(II)$ content in MFe_2O_4 decreased, whereas the $M(III)$ content increased with a variation range of $8.5 \pm 4.03\%$. $Fe 2p_{3/2}$ was found to have characteristic peaks of $Fe(II)$ and $Fe(III)$ before the reaction, and the contents $Fe(II)$ and $Fe(III)$ were 72.46% and 27.53%, respectively. After the reaction, the contents of $Fe(II)$ and $Fe(III)$ were changed to 66.67% and 33.33% (Fig. 4f). The chemical states of Fe were changed in the catalytic process, so the catalyst always maintained a certain activity.³⁶ These results demonstrated that Fe and M elements were chemically cyclically converted during the catalytic oxidation of NO_x , while generating active sites for free radicals.

3.2. Catalytic performance

The catalytic activities of the prepared samples of $ZnFe_2O_4$ nanocomposites against NO_x and SO_2 are shown in Fig. 5a. The $ZnFe_2O_4$ addition amount of 0.02 g promoted the removal of NO_x by the NO_x - SO_2 - MFe_2O_4 -MNB system, whereas the addition amount of 0.05 g inhibited the removal of NO_x . The addition of trace catalysts can promote the oxidation absorption of NO_x . However, excessive catalysts need to consume reactive oxygen species in the process of transformation to high price state, which forms a competitive relationship with the oxidation of NO_x and SO_2 , resulting in the reduction of NO_x removal rate. In addition, with the increase of the amount of additives, the particle catalyst and micro nano bubbles collide with each other, leading to a part of bubbles in advance rupture, unable to produce hydroxyl radicals, resulting in a reduction of NO_x removal rate. Therefore, 0.02 g of iron-based spinel samples were separately added to the NO_x - SO_2 - MFe_2O_4 -MNB system.

The NO_x removal efficiency is shown in Fig. 5b. The NO_x removal efficiency of the NO_x - SO_2 - MFe_2O_4 -MNB system was improved after the addition of MFe_2O_4 . The combined efficiency of MNB and MFe_2O_4 in removing NO_x reached $70.23 \pm 10.63\%$, while the efficiency of SO_2 removal reached 100% (eqn (17)–(21)). Oxidative absorption of NO_x involves two steps. NO_x is firstly oxidized into NO_2^- , which is then oxidized to NO_3^- (eqn (13)–(16)). $MnFe_2O_4$, $CuFe_2O_4$ and $ZnFe_2O_4$ significantly

improved the efficiency of the second step. After adding $CuFe_2O_4$, the efficiency of converting NO_x into NO_2^- increased by 10.16%, and the conversion into NO_3^- was 18.09%. Therefore, the comprehensive efficiency rate of NO_x treatment by the NO_x - SO_2 - $CuFe_2O_4$ -MNB system reaches 83.88%. The catalytic activities showed the following decreasing sequence: $CuFe_2O_4 > ZnFe_2O_4 > MnFe_2O_4 > CoFe_2O_4 > NiFe_2O_4$.

3.3. Free radical identification

EPR test was conducted to detect the radicals and analyze the oxygen species of the NO_x - SO_2 - MFe_2O_4 -MNB system. As shown in Fig. 6a, weak signals were observed in MNB solution alone, and an intensive symmetrical four-line peak was detected in the NO_x - SO_2 - MFe_2O_4 -MNB system. The four-line peak with the intensity ratio of 1 : 2 : 2 : 1 in the spectrum is the typical spectral shape of the DMPO- $\cdot OH$ adducts,³⁷ which indicates the existence of $\cdot OH$ in the system. However, the characteristic 1 : 1 : 1 triplet assigned to DMPO- $\cdot O_2^-$ adducts³⁸ formed by $\cdot O_2^-$ and DMPO in Fig. 6b was very weak, indicating that the system mainly removes NO_x through $\cdot OH$ instead of $\cdot O_2^-$. The intensity of the peak represents the concentration of $\cdot OH$ in the system, indicating that the concentration of $\cdot OH$ decreases in turn: $MNB/CuFe_2O_4 \gg MNB > H_2O$. This result was consistent with the removal rate of NO_x , which directly proved that $\cdot OH$ oxidized NO_x is the key to denitrification of flue gas. It can also be proved that MFe_2O_4 can be activated by MNB to produce $\cdot OH$, which is dominant in the process of NO_x removal.

3.4. Proposed reaction pathways

It can be found that the NO_x - SO_2 - MFe_2O_4 -MNB system has a high catalytic efficiency as a heterogeneous catalytic system, based on characterizing the physical and chemical properties of MFe_2O_4 ($M = Mn, Zn, Cu, Ni$ and Co) before and after the reaction and analyzing the SO_2 and NO_x removal efficiency. Hydroxyl radical is the main oxidant during the chemical oxidation of SO_2 and NO_x in aqueous solution. In this system, the sources of hydroxyl radicals are divided into two parts. Some hydroxyl radicals are derived from the rupture of MNB,^{39,40} and the other part is derived from the activation of recyclable

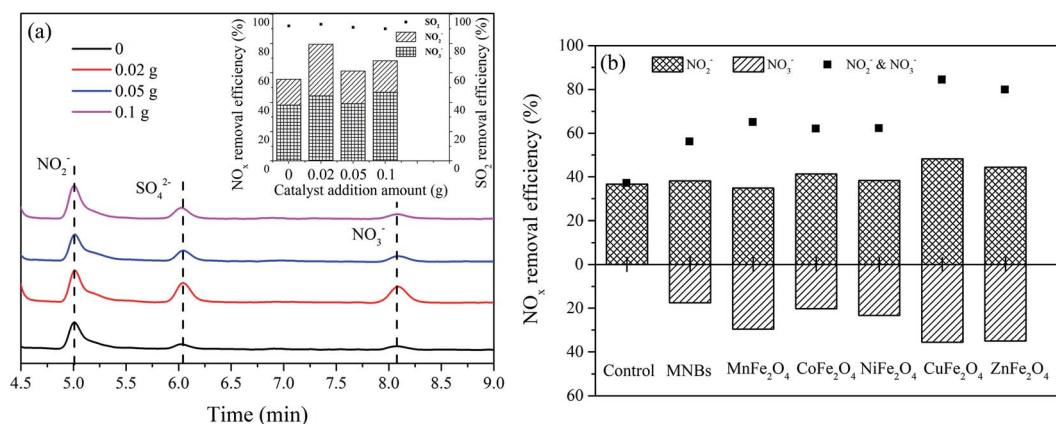


Fig. 5 Effect of spinel catalyst on NO_x and SO_2 removal rate: $ZnFe_2O_4$ (a), MFe_2O_4 (b).



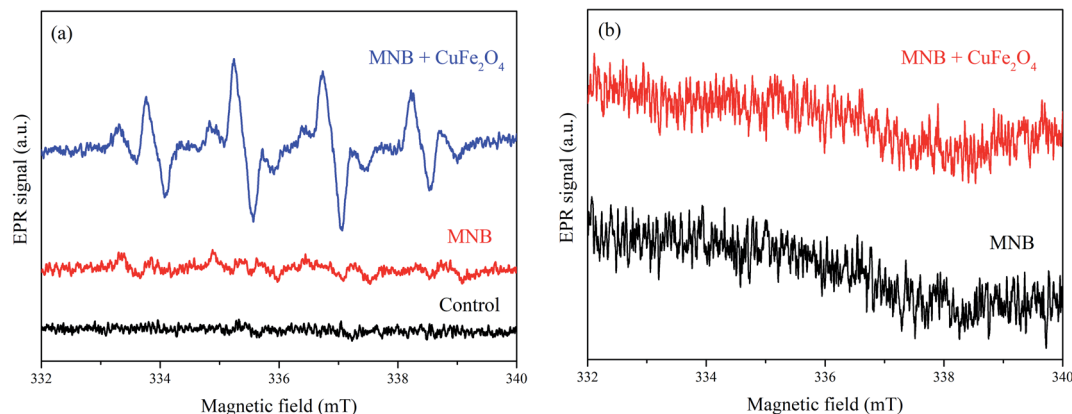


Fig. 6 EPR spectra of the $\text{NO}_x\text{-SO}_2\text{-MFe}_2\text{O}_4\text{-MNB}$ system: $\text{DMPO-}\cdot\text{OH}$ (a), and $\text{DMPO-}\cdot\text{O}_2^-$ (b).

MFe_2O_4 . The chemistry of simultaneous oxidation of NO_x and SO_2 by micro-nano bubbles breakdown and MFe_2O_4 activation is complex, since it takes place through electron transfer from the lattice oxygen, free radical oxidation reactions *via* $\cdot\text{OH}$ and $\cdot\text{O}_2^-$, and the direct reaction of the NO_x with HSO_3^- .^{41,42}

The catalytic oxidation mechanism of $\text{NO}_x\text{-SO}_2\text{-MFe}_2\text{O}_4\text{-MNB}$ system is described visually in the reaction scheme shown in Fig. 7. As the MNB slowly rise and shrink in the water, the charge ions (H^+ , OH^-) rapidly concentrate at the very narrow gas-liquid interface. At the moment of MNB explosion, due to the drastic changes caused by the disappearance of the gas-liquid interface, the concentrated ions on the interface will immediately release the stored chemical energy, thus producing a large number of $\cdot\text{OH}$. MFe_2O_4 is a magnetic semiconductor material with spinel structure. Oxygen in molecular state (O_2) is adsorbed on the metal surface and then dissociated into

adsorbed atoms (O_{ad}) because MFe_2O_4 is magnetic.⁴³ The type I adsorbed oxygen atom ($\text{O}_{\text{ad}}(\text{I})$) is first formed during dissociation, which is equivalent to a locally adsorbed oxygen atom on the metal surface. The oxygen atom in this state has extremely high reactivity to NO_x . In addition, as a semiconductor material, MFe_2O_4 consists of a low energy valence band full of electrons and an empty high energy conduction band. In the excited state, the valence band electron jumps to the conduction band, which is called the conduction band electron (e_{CB}^-). At the same time, a highly active hole in the valence band is generated, which is called the valence band electron hole (h_{VB}^+). The electron hole pair produces a large number of reactive oxygen species such as hydroxyl free radicals and hydrogen peroxide free radicals on the material surface, as shown in eqn (8)–(12). Reactive oxygen species is the main oxidant in the process of removing NO_x and SO_2 . According to the double reduction oxidation mechanism,

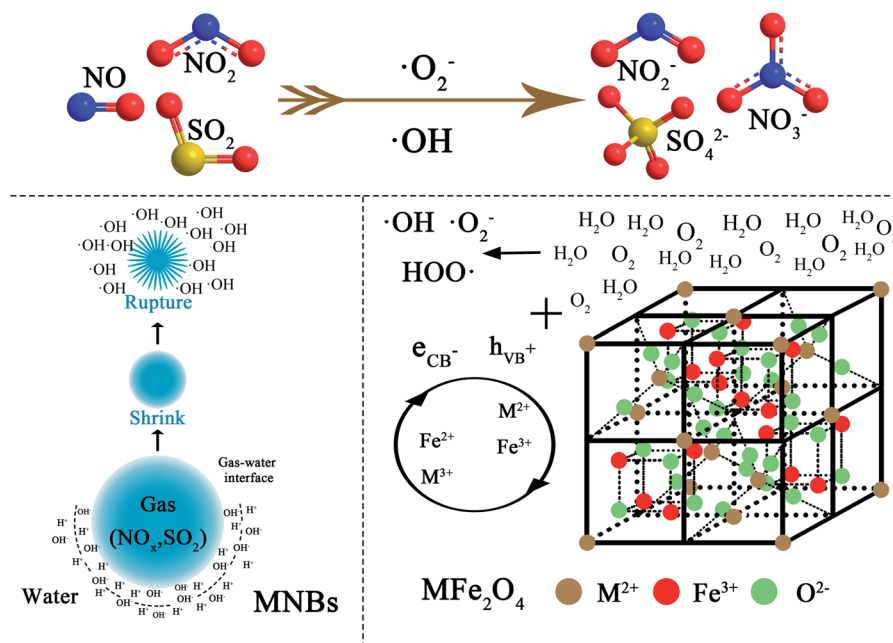
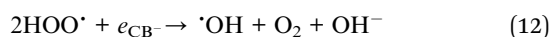
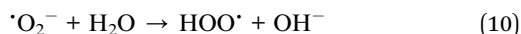
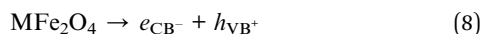


Fig. 7 Schematic diagram of the $\text{NO}_x\text{-SO}_2\text{-MFe}_2\text{O}_4\text{-MNB}$ reacting system.

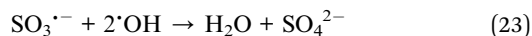
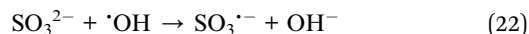
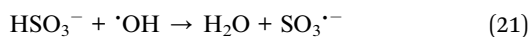
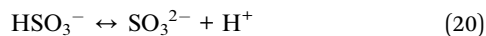
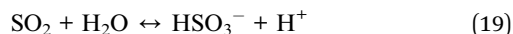
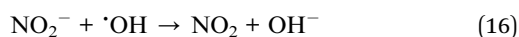
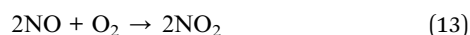


a kind of cations (Fe^{3+}) perform the function of activating and oxidizing NO_x and SO_2 , and their reoxidation depends on the lattice oxygen (O^{2-}) transferred along the lattice. Another metal cation (M^{2+} ($\text{M} = \text{Mn}, \text{Co}, \text{Ni}, \text{Cu}$ and Zn)) in the reduced state assumes the role of accepting gas-phase oxygen.

The main reactions involved in spinel catalytic oxidation are:



The main reactions involved in the simultaneous oxidation of NO_x and SO_2 are:



producing a large number of hydroxyl radicals. Recyclable MFe_2O_4 ($\text{M} = \text{Mn}, \text{Zn}, \text{Cu}, \text{Ni}$ and Co) can produce $\cdot\text{OH}$ and $\cdot\text{O}_2^-$ by being activated, thus accelerating the oxidation and absorption process of NO_x and SO_2 . However, this research also points out many areas that require further research, such as using the system for organic gas and wastewater treatment, which is beyond the scope of current research, but is still the subject of future research.

Conflicts of interest

There are no conflicts to declare.

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4. Conclusion

This work developed a new technology that uses micro-nano bubbles and MFe_2O_4 to simultaneously remove NO_x and SO_2 from flue gas. The physicochemical properties of MFe_2O_4 prepared by the hydrothermal method were characterized. The results indicated that both micro-nano bubbles and MFe_2O_4 improved NO_x removal, while the removal rate of SO_2 can reach 100% at room temperature. NO_x removal rate reached 83.88% in NO_x - SO_2 - CuFe_2O_4 -MNB system. At the moment when the MNB burst, the concentrated ions on the gas-water interface will release the stored chemical energy at once, thus



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