

Available online at www.sciencedirect.com

ScienceDirect

www.elsevier.com/locate/jes

JES
JOURNAL OF
ENVIRONMENTAL
SCIENCES
www.jesc.ac.cn

Review

A critical review on the technique and mechanism of microwave-based denitrification in flue gas

Bo Yuan^{1,2}, Zhen Qian¹, Zili Zhang³, Le Fu¹, Shihang Pan¹,
Runlong Hao^{1,2,*}, Yi Zhao^{1,2}

¹Hebei Key Lab of Power Plant Flue Gas Multi-Pollutants Control, Department of Environmental Science and Engineering, North China Electric Power University, Baoding 071003, China

²MOE Key Laboratory of Resources and Environmental Systems Optimization, College of Environmental Science and Engineering, North China Electric Power University, Beijing 102206, China

³Fujian Special Equipment Inspection and Research Institute, Fuzhou, Fujian 350008, China

ARTICLE INFO

Article history:

Received 25 December 2020

Revised 31 May 2021

Accepted 20 June 2021

Available online 2 February 2022

Keywords:

Microwave

Denitrification

Reduction

Oxidation

Radical

ABSTRACT

Microwave radiation has received extensive attention due to its significant thermal and non-thermal effects, and the development of MW-based denitrification in flue gas has become one of the most promising methods to avoid the defects of ammonia escape, high temperature and cost in traditional SCR. This review introduces the thermal and non-thermal effects of microwaves and divides MW-based denitrification methods into MW reduction and oxidation denitrification, systematically summarizes these denitrification methods, including MW discharge reduction, MW-induced catalytic reduction using active carbon, molecular sieves, metal oxides (transition metals, perovskites, etc.), MW-induced oxidation denitrification with and without additional oxidant, and discusses their removal pathway and mechanism. Finally, several research prospects and directions regarding the development of microwave-based denitrification methods are provided.

© 2022 The Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences. Published by Elsevier B.V.

Introduction

Nitrogen oxides (NO_x) are the main gaseous pollutants produced by the combustion of fuels from stationary and mobile sources, causing a series of health and environmental problems; for example, eye and throat irritation, chest tightness, acid rain, ozone depletion and photochemical smog (Hao et al., 2019b; Yuan et al., 2020a; Yuan et al., 2020b; Zhao et al., 2017). The existing forms of NO_x are diverse, such as NO, NO₂, NO₃,

N₂O, N₂O₃ and N₂O₄. Since NO accounts for nearly 95% of fossil fuel flue gas, the key to NO_x control is to remove NO effectively (Hao et al., 2020a; Hao et al., 2019a; Hao and Zhao, 2016). At present, NO emissions are usually controlled by two mature technologies, namely, selective catalytic reduction (SCR) and selective non-catalytic reduction (SNCR). However, their disadvantages include high reaction temperature, ammonia escape, catalyst poisoning and disposal issues, high investment and operating costs, etc. (Hao et al., 2020b; Hao et al., 2018; Hao et al., 2017; Javed et al., 2007; Zhao et al., 2020). More importantly, these technologies have poor versatility and are not suitable for denitrification at low temperature, under large flow fluctuations or complex working conditions (Liu et al.,

* Corresponding author.

E-mail: hrl_ncepu@hotmail.com (R. Hao).

2017; Zhao et al., 2014; Zhao et al., 2019). Therefore, developing novel and efficient denitrification methods has always been an important research hotspot in the field of flue gas purification.

Owing to its merits such as prominent thermal effects, ability to reduce activation energy and generation of selective hotspots (State et al., 2019; Wei et al., 2020b), microwave (MW) radiation has been widely used in synthesis (Liu et al., 2020b; Trombi et al., 2020), pyrolysis (Liu et al., 2020c; Milh et al., 2018), extraction (Srogi, 2006), soil remediation (Lin et al., 2010), sewage sludge treatment (Pang et al., 2018; Wei et al., 2020a; Yin et al., 2016) and catalysis (Chen et al., 2019). Apart from this, it has also been successfully utilized to remove gaseous pollutants from flue gas (Cheng et al., 2020; Wei et al., 2009a; Xia et al., 2020). For MW-based denitrification methods, researchers have proposed various techniques, and catalytic materials such as active carbon, molecular sieve and metal oxides, etc. have been proven to be valid, with removal efficiencies of 70%–90%. To the best of our knowledge, there is no comprehensive review on the process and mechanism of these MW-based denitrification methods.

In this article, the thermal and non-thermal effects of MW are depicted in detail, the MW reduction and oxidation denitrification methods are summarized to outline the MW-based denitrification methods, and their reaction pathways and removal mechanism are also discussed systematically. Finally, several prospects and suggestions for the development of novel MW-based denitrification methods are proposed.

1. Overview of microwaves

As a kind of low-energy electromagnetic wave, the microwave frequency range is 0.3–300 GHz; the wavelength range is 0.001–1 m, located between infrared radiation and radio waves in the electromagnetic spectrum, with the characteristics of wide working frequency, easy control, selectivity and fast heating (Chen et al., 2020; Hu et al., 2020; Wang et al., 2016; Wei et al., 2020b). Since the discovery that MW can play significant roles in polymerization and organic synthesis, the function of MW in promoting chemical reactions has also been discovered and widely used (Jie et al., 2020; Nüchter M et al., 2003). Scholars have always held two different views on the promotion mechanism, namely thermal effects and non-thermal effects (Bulhoes Bezerra Cavalcante et al., 2020; Herrero et al., 2008; Horikoshi et al., 2014; Zhang et al., 2020).

1.1. Thermal effects

Most scientists believe that the increase in reaction rate under irradiation by microwaves is due to thermodynamic factors, that is, the promotion is caused by microwave heating (thermal effect). Microwave heating is generally regarded as a kind of "internal heating", since it is mainly generated by the rotation of molecules with dipole moments (Obermayer et al., 2009; Xue et al., 2019; Zhang et al., 2019). Interestingly, when MW interacts with different substances, the amount of heat generated varies. As shown in Fig. 1, three interaction forms between substances and microwaves are recognized. For conductors represented by metals, microwaves

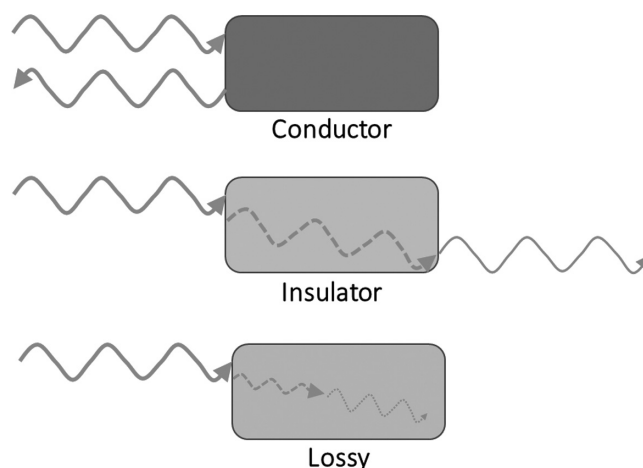


Fig. 1 – Interactions between MW and different substances.

are reflected rather than transmitted. As for insulators including Teflon, glass, ceramics and plastics, microwaves can easily pass through. Only for lossy media such as water, activated carbon, transition metal oxides, etc., will microwaves be quickly absorbed and converted into thermal energy (heat) (Robinson et al., 2010; Xue et al., 2019). The lossy media and insulators are used together; the lossy media absorb MW first and then the generated heat will be transferred to the insulators by conduction and convection, realizing selective heating of active sites and further inducing chemical reactions that do not easily occur under conventional heating (Li et al., 2018; Remya et al., 2011; Verma et al., 2018; Wang et al., 2016). This is the basis for the microwave-induced catalytic process that can guide the synthesis and design of catalysts, so it is extensively favored by scientists in the field of chemical catalysis.

Taking the common microwave-absorbing transition metal oxide catalytic materials as an example, based on the above principles, they can be divided into three categories: oxides with high microwave loss and rapid heating (MnO_2 , Ni_2O_3 , etc.), oxides with microwave loss that heat up after a period of time (V_2O_5 , Fe_2O_3 , etc.), and oxides with low microwave loss that heat up slowly (Al_2O_3 , TiO_2 , etc.). When choosing a suitable microwave-induced catalyst, MnO_2 or Ni_2O_3 can be used as the active components, and Al_2O_3 or TiO_2 can be used as the carriers to generate more hot spots on the catalyst surface to accelerate or catalyze the chemical reactions. Certainly, it should be pointed out that several researchers believe that this thermal effect is just a heating method, which is not essentially different from conventional heating, although it has the advantages of selective, rapid and uniform heating, and energy-saving (Obermayer et al., 2009). The kinetics will not change, and the increase in reaction rate and product selectivity is only due to the outstanding thermal effect of microwaves.

1.2. Non-thermal effects

Other researchers believe that there may be other reasons to explain the acceleration of chemical reactions by microwaves, not just the increase in temperature, but also changes in magnetic, electrical and chemical factors, which are called "non-

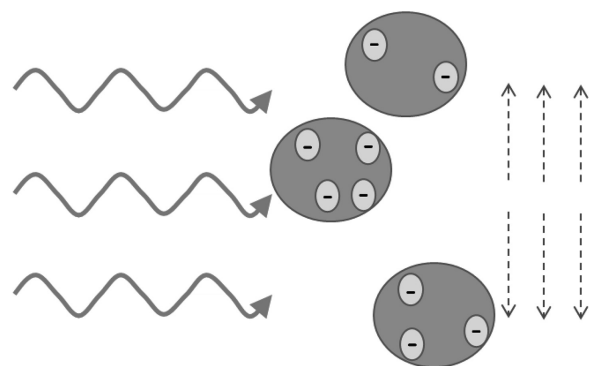


Fig. 2 – Irregular movements under the action of MW.

thermal effects” of MW. For chemical reactions under MW, the reaction progress will be affected by the non-thermal effects; the reactant molecules may be promoted to higher energy levels, and the chemical bond would also be weakened (Horikoshi et al., 2007; Hu et al., 2018; Hoz et al., 2007). Taking Fig. 2 as an example, MW energy is absorbed by reactant molecules, which increases the internal energy of molecules and aggravates the disordered motion of molecules, resulting in the increase of entropy. On the other hand, polar molecules would be forced to move as the electromagnetic field (microwave) changed, leading to a decrease in entropy (Binner et al., 2008; Hoz et al., 2007). Which of these two effects is more powerful mainly depends on the working mode and operating parameters of the electromagnetic waves. It can be considered that the role of microwaves is very complicated, and the non-thermal effects of MW will also vary with differences in conditions.

Some researchers believe that the non-thermal effects are reflected in changes in kinetics, activation energy and the pre-exponential factor (Hájek et al., 2004; Zhao et al., 2007), since the state of polar molecules is high-speed oscillation and is chaotic under the action of MW. There are also reports that microwaves can weaken chemical bonds, prompting the breaking and formation of bonds (Zhang et al., 2018). These effects are of great significance in inducing catalytic reactions. All in all, the non-thermal effects of MW are relatively diverse, and the academic community has not yet reached a consensus.

2. MW-based denitrification methods

Since MW has the advantages previously mentioned, scholars have long been trying to apply MW to NO removal. Based on the current status of MW-based denitrification methods, two categories are summarized: MW reduction denitrification and MW oxidation denitrification.

2.1. MW reduction denitrification

In this article, MW reduction denitrification is divided into MW discharge reduction and MW-induced catalytic reduction. Also, the MW-induced catalytic reduction method can be classified according to the different catalysts used: activated car-

bon, molecular sieves and metal oxides (transition metal oxides, perovskite-type oxides, etc.).

2.1.1. MW discharge reduction

MW energy can be converted into the internal energy of molecules by a high-frequency oscillating electromagnetic field, exciting and ionizing the reactants to generate electrons, positive/negative ions, free radicals and other active species, which can be widely used in pollutant control (Tang, 2001b; Yang, 2018). Taking MW discharge reduction denitrification as an example, the removal process is described as Fig. 3, in which several types of active species including radicals containing N and O are generated through the ionization, decomposition and excitation of NO molecules, and then the objective of removing NO is achieved by the reaction between these active particles and the residual NO (Tang, 2001b).

Tang et al., (2003) successfully applied MW discharge to flue gas denitrification and proved that the key for the decomposition of NO into N_2 was the active species produced by the MW discharge of gaseous reactants, which could induce selective reactions at lower temperatures (close to the average gas temperature). To promote the conversion of NO to N_2 , further studies adopted CH_4 , which broadened the reaction temperature, reduced the MW energy consumption, and achieved a maximum conversion rate of 88%. Interestingly, when 5 wt.% H_2O steam was added, the conversion of NO to N_2 decreased slightly, whereas the conversion from NO to NO_2 increased markedly. Besides, Tang et al. (2000, 2001a) conducted a series of NO removal experiments using MW discharge and CH_4 with the assistance of ZSM-5 zeolites, finding that NO was completely converted to N_2 at 325°C in the presence of CH_4 and Ni/HZSM-5. Similarly, Liu et al., (2020a) used MW discharge coupled with activated coke loaded with transition metal oxides (Fe, Mn, Cu) to remove NO, and found that the removal efficiency was increased by nearly 64.8% after the addition of Fe, and synergy between activated coke and MW was confirmed. Of course, the power of MW also has an obvious influence on the NO removal efficiency, because it can directly affect the reaction temperature and the yield of active species.

Overall, MW discharge can produce a large number of active species in the gas phase and significantly enhance the conversion from NO to N_2 within a wide active temperature range. Moreover, the metal oxides/catalysts and MW discharge have a synergistic effect in the decomposition of NO. However, since the non-thermal effects of MW are dominant in the generation of active species at lower gas/catalyst temperatures, this may cause problems such as high energy consumption, electrode corrosion and secondary environmental pollution.

2.1.2. MW-induced catalytic reduction using active carbon

Researchers have used activated carbon to replace NH_3 in the SCR system to avoid difficulties in NH_3 storage and escape (Li, 2013; Wang et al., 2019). But this will inevitably lead to consumption of the activated carbon by oxygen from flue gas, because this reduction reaction usually occurs above 500°C, and the activated carbon itself will start to burn above 300°C (Bueno-López et al., 2006; Chuang et al., 2011; Illan-Gomez et al., 1993). Finding a balance between the reduction reaction and the consumption of activated carbon has become

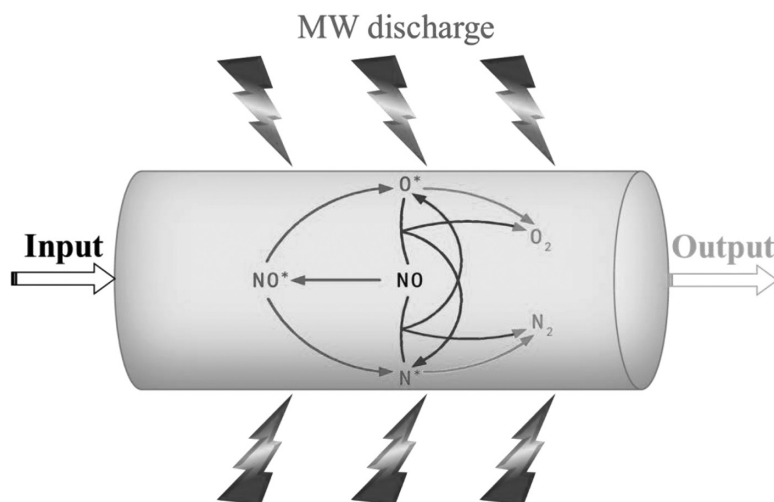


Fig. 3 – Mechanism of MW discharge reduction of NO

the key to developing carbon-based denitrification technologies. Considering the significant thermal effects and good selectivity of MW, it is possible for activated carbon to react selectively with polar NO instead of non-polar O_2 , which can reduce the consumption of activated carbon and decrease the reaction temperature at similar removal efficiency (Cha and Kong, 1995; Kong, 1995; Ma et al., 2011; Ma et al., 2013; Peng et al., 2017; Xu et al., 2014; Kong and Cha et al., 1996). As shown in Table 1, (Cha and Kong 1995; Kong, 1995; Kong and Cha et al., 1996) utilized several carbons (calcined char, char bed, and saturated char) to adsorb NO and explored the reduction of adsorbed NO by MW radiation. Although denitrification efficiencies of more than 90% were achieved in most situations, consumption of carbon was observed and NO_2 and HNO_3 were detected on the surface, and their contents were susceptible to the influence of moisture and oxygen in the feed gas.

Other researchers attempted to dope metal materials into activated carbon to form more functionalized active sites and help absorb MW, thereby reducing the loss of activated carbon and increasing the adsorption of NO by activated carbon. Ma et al. (2011, 2013) carried out desulfurization and denitrification experiments using MW and active carbons loaded with CuO , Mn_2O_3 and ZnO , finding that hot spots produced by the thermal effects of MW played an important role in the removal of SO_2 and NO, and that the different catalysts required different MW power (reaction temperature) to achieve similar removal efficiencies; namely, the catalytic activity of activated carbon loaded with CuO was significantly higher than that with Mn_2O_3 and ZnO , which also directly proved the selectivity of MW-induced catalysis. Taking the removal experiment over CuO -loaded activated carbon under microwave radiation as an example, the NO removal efficiency was still increased by about 25% at $350^\circ C$ in the presence of SO_2 , but the desulfurization efficiency was inhibited. On the other hand, Xu et al. (2014) prepared activated carbon loaded with Mn_2O_3 and adopted a MW-induced catalytic method to perform NO removal. The NO conversion efficiency reached 98.7% under the conditions of excess oxygen, 5 wt.% Mn_2O_3 and $300^\circ C$, and the removal mechanism is depicted in Fig. 4. It should also be

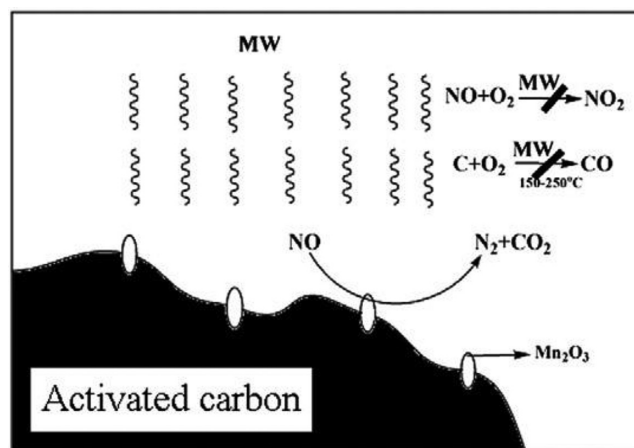


Fig. 4 – Mechanism of MW-induced reduction of NO by Mn_2O_3/AC (Xu et al., 2014).

noted that the consumption of activated carbon will also improve the surface characteristics of the activated carbon, creating porosity and increasing the specific surface area, which is conducive to the adsorption and reduction of NO_x .

In Zhou's study, the active sites of Mn_2O_3 under induction by MW effectively promoted the reaction between activated carbon and NO to generate N_2 and CO_2 , and O_2 did not react with activated carbon and NO due to the selectivity of polar molecules toward MW, thereby decreasing the consumption of activated carbon. Besides, the loading of Mn_2O_3 affected the NO conversion efficiency directly. When the loading of Mn_2O_3 was 5 wt.%, the efficiency was highest, because there were more active sites on the activated carbon surface. However, excessive Mn_2O_3 would block the surface pores of activated carbon and inhibit contact between activated carbon and NO, decreasing the catalytic activity and suppressing the reaction between activated carbon and NO. In subsequent research, activated carbon loaded with various metal oxides MeO_x ($Me = Ni, Mn, Fe, Ce$ etc.) was prepared (Peng et al.,

Table 1 – List of studies of MW-induced catalytic reductive denitrification.

Catalysts	Reductants	Optimal reaction conditions			NO _x removal efficiency (%)	SO ₂ removal efficiency (%)	Pros and cons	Reference
		Temperature (°C)	MW power (W)	O ₂ content (%)				
–	Calcined char	–	480	–	90	–	Char was consumed easily.	(Cha and Kong, 1995)
–	Char bed	–	480	–	98	–		(Kong, 1995)
–	Saturated char	–	480	–	90	–		(Kong and Cha et al., 1996)
CuO	AC	350	420	–	92.5	< 90	Desulfurization efficiency was not ideal which made it difficult to meet strict emission standards.	(Ma et al., 2013)
Mn ₂ O ₃	–	–	–	–	87.5	–		
ZnO	–	–	–	–	87.5	–		
CuO	AC	350	350	7.9	94.11	99.89	AC was inevitably consumed as an absorbent.	(Ma et al., 2011)
Mn ₂ O ₃	AC	300	400	5.8	98.7	–	AC reacted selectively under MW irradiation to reduce its consumption.	(Xu et al., 2014)
CeO ₂	AC	350	250	5	100	–	The consumption of reactant AC was inevitable.	(Peng et al., 2017)
NiO _x -CeO ₂	–	300	150	–	100	–		
MnO _x -CeO ₂	–	350	200	–	100	–		
FeO _x -CeO ₂	–	350	200	–	100	–		
Ga-A zeolites	NH ₄ HCO ₃	80–120	259–280	14–19	95.45	–	NH ₄ HCO ₃ easily decomposed and produced the by-product CO ₂ .	(Wei et al., 2007)
Zeolite	NH ₄ HCO ₃	200–250	211–280	–	86.5	99.1		(Wei et al., 2009a)
FeCu/zeolite	NH ₄ HCO ₃	–	280	–	95.8	93.4		(Wei et al., 2011)
FeCoCu/zeolite	NH ₄ HCO ₃	–	280	–	95.1	95.8		(Wei et al., 2010)
Co-NaZSM-5	CH ₄	269–402	200–300	0.4	72	–	NO _x removal efficiency was low, and it was difficult to meet strict emission standards.	(Chang et al., 1999)
Co-HZSM-5	CH ₄	395	100–120	0.4	85	–		
Fe ₂ O ₃ /HZSM-5	CH ₄	–	10–50	–	100	–	CH ₄ is neither economical nor safe.	(Wang et al., 2000)
Fe/NaZSM-5	–	300	16–18	2	70	–	The optimal Fe content was 20%.	(Tang et al., 2002)
Fe-ZSM-5	–	400–600	100	5	–	–	MW improved the thermal stability of the catalyst.	(Ohnishi et al., 2017)
Cu-ZSM-5	–	500–550	–	–	–	–		
MnO ₂ -Cu-ZSM-5	–	300	–	5	94.3	–	The stability of the catalyst was not good.	(Xu et al., 2015b)
Ni ₂ O ₃ -Cu-ZSM-5	–	350	–	–	92.3	–		
MeOx/Al ₂ O ₃ (Me=Cu, Mn, Fe)	–	250	100	10	94.8	–	Good catalytic activity and poor stability.	(Xu et al., 2016a)
BaMn _x Mg _{1-x} O ₃	–	250	< 150	10	99.8	–	MW significantly improved the denitrification efficiency, but the ratio of Mn to Mg was difficult to control.	(Xu et al., 2015a)
BaMnO ₃	–	300	< 150	10	93.7	–	The ratio of Ba to A sites was difficult to control, and the preparation was complicated.	(Xu et al., 2017)
Ba _{0.8} Ca _{0.2} MnO ₃	–	250	–	–	92.3	–		
Ba _{0.8} K _{0.2} MnO ₃	–	250	–	–	99.8	–		
Ba _{0.8} La _{0.2} MnO ₃	–	250	–	–	95.5	–		
BaMoO ₃	–	300	< 150	10	93.7	–	It was convenient to recycle, but the removal efficiency of NO _x was low.	(Xu et al., 2016b)
BaCoO ₃	–	250	< 150	–	99.8	–		
BaFeO ₃	–	250	1000	–	64.1	–		
MgCo ₂ O ₄	–	300	< 100	10	69.7	–		
MgCo ₂ O ₄ -BaCO ₃	–	250	–	–	99.69	–	Low NO _x resource utilization	(Xu et al., 2019)

2017), and the NO removal efficiency reached 100% at 300°C and 350°C over 5%(21%NiO_x)-CeO₂/AC and 5%CeO₂/AC catalysts, respectively.

In general, the consumption of activated carbon is inevitable no matter what kind of metal material is doped into it, because activated carbon participates in the reduction of NO as a reactant. The difference is that the stronger the catalytic activity in the MW-induced catalytic system, the lower the reaction temperature, and less activated carbon will be consumed by O₂ in the flue gas. In short, the superiority and selectivity of the MW thermal effects makes the MW-induced catalytic reduction method a promising method, although the problems of a short life cycle and the high cost of activated carbon have not been resolved.

2.1.3. MW-induced catalytic reduction using molecular sieves
Benefiting from advantages such as high adsorption, excellent catalytic activity and thermal stability, molecular sieves, especially ZSM-5 zeolite, have been widely used in MW-induced catalytic reduction denitrification (Wei et al., 2006; Zenkovets et al., 2020), and the related research is summarized as Table 1.

Studies found that when urea and a molecular sieve (type A) were used as the reducing agent and catalyst, respectively, the optimal NO removal efficiency reached 92% under MW radiation, higher than that of without microwaves or molecular sieves, in which the thermal effects of MW had a greater promotion effect. Wei et al. (2007) performed MW catalytic denitrification experiments using NH₄HCO₃ and Ga-A zeolite as the reducing agent and catalyst, achieving an optimal NO removal efficiency of 95.45%. Interestingly, suppression of the removal efficiency by the microwave power was discovered: the NO_x removal efficiency dropped from 89.3% to 86.7% when the power increased from 280 W to 331 W, and a similar SO₂ removal efficiency curve was observed. In addition, it was found that the SO₂ and NO_x concentrations had no significant impacts on the denitrification (or simultaneous desulfurization and denitrification) efficiency, indicating that the stability of MW catalytic reduction using NH₄HCO₃ and Ga-A zeolite was good. In this reaction system, when the MW power was 211–280 W, the authors adjusted the flow rate (from 0.54 to 0.2 m³/hr) and empty bed residence time (from 0.204 sec to 0.536 sec) to explore the influence of residence time on desulfurization and denitrification. The results indicated that with the rise in residence time, the SO₂ removal efficiency increased from 88.9% to 99.1%, and the conversion efficiency of NO_x increased from 77.8% to 86.5%, meaning that a long reaction residence time was beneficial to NO_x and SO₂ removal, as long as the flow rate did not exceed the maximum that the reaction system could withstand (Wei et al., 2009a). Further studies were carried out with Fe, Cu, and Co loaded on Ga-5A zeolite to improve the catalytic activity, and the removal efficiency of NO_x and SO₂ reached 95.8% and 93.4%, when FeCu/zeolite, MW and NH₄HCO₃ were used together (Wei et al., 2011). Meanwhile, when Co was supported on FeCu/zeolite, the NO_x removal efficiency remained unchanged and the desulfurization efficiency could be increased to 95.8% (Wei et al., 2010). Compared with liquid ammonia commonly used in the traditional SCR process, urea and NH₄HCO₃ have no transportation or leakage problems and can obtain higher removal efficiency.

However, they easy to decompose and produce the by-product CO₂.

The reducing agent CH₄ and ZSM-5 zeolite catalyst were also employed in MW catalytic reduction denitrification, and over 70% NO removal efficiency was achieved when Co-NaZSM-5 and Co-HZSM-5 were adopted at 250–400°C (Chang et al., 1999). Wang et al. (2000) synthesized a Fe₂O₃/HZSM-5 catalyst and utilized it to remove NO in the presence of MW and CH₄. It was found that MW could promote the activation of molecules and improve the water resistance of the catalyst. To reduce the risk of CH₄ in the MW catalytic system, Tang et al. (2002) investigated the removal of NO using MW and the Fe/NaZSM-5 catalyst without additional CH₄ or other reducing agents, and found that the removal efficiency with MW radiation reached 70%, while conventional heat had no effect on the removal of NO, indicating that the thermal effects of MW and the presence of Fe both had marked promotion effects on the reduction/decomposition of NO. Similar conclusions were also confirmed in the research of Ohnishi et al. (2017), in which NO was selectively decomposed into nitrogen and oxygen under the thermal effects of MW.

However, the water resistance of Fe/NaZSM-5 catalysts is poor, and the conversion from NO to N₂ was clearly affected by added H₂O. But, in Ohnishi's research, the NO removal efficiency was relatively stable even in the co-presence of oxygen and water when Cu- and Fe- exchanged ZSM-5 zeolites were heated by MW (Ohnishi et al., 2017). In the removal process illustrated in Fig. 5, the decomposition of NO was divided into low-temperature selective adsorption by zeolite with microporous structure and MW-induced decomposition of adsorbed NO. Although the thermal stability and oxygen resistance of Cu-ZSM-5 and Fe-ZSM-5 were verified, the NO removal efficiency was low, and could not meet strict emission standards.

Fortunately, in Xu's study (Xu et al., 2015a), more than 92% NO removal efficiency was obtained by doping MeO_x (Me = Mn, Ni, Cu) into ZSM-5, in which the concentration of oxygen had almost no influence on the activity of catalytic decomposition of NO, which was of great significance for the development of MW-induced catalytic denitrification technology. It should be noted that the development of MW-induced catalytic denitrification methods without additional reductant will be the main research direction in the future, in view of the cost of reducing agents and secondary environmental problems.

2.1.4. MW-induced catalytic reduction using metal oxides

To develop MW-induced catalytic denitrification technologies without additional reductant, metal oxides, including transition metal oxides and perovskites, were used as the catalysts (Xu et al., 2016a; Xu et al., 2016a; Xu et al., 2017; Xu et al., 2015a). Related research is summarized in Table 1, and the removal mechanism is shown in Fig 6.

Xu et al. (2016a) utilized MeO_x/Al₂O₃ (Me = Cu, Mn, Ce) catalysts and MW to carry out denitrification experiments, and compared the removal efficiencies between MW-thermal catalysis and conventional thermal catalysis. Results indicated that under the action of MW-thermal catalysis, MeO_x/Al₂O₃ exhibited good catalytic activity and poor stability: the NO removal efficiency reached 94.8% at 250°C when CeCuMnO_x/Al₂O₃ was employed. But under conven-

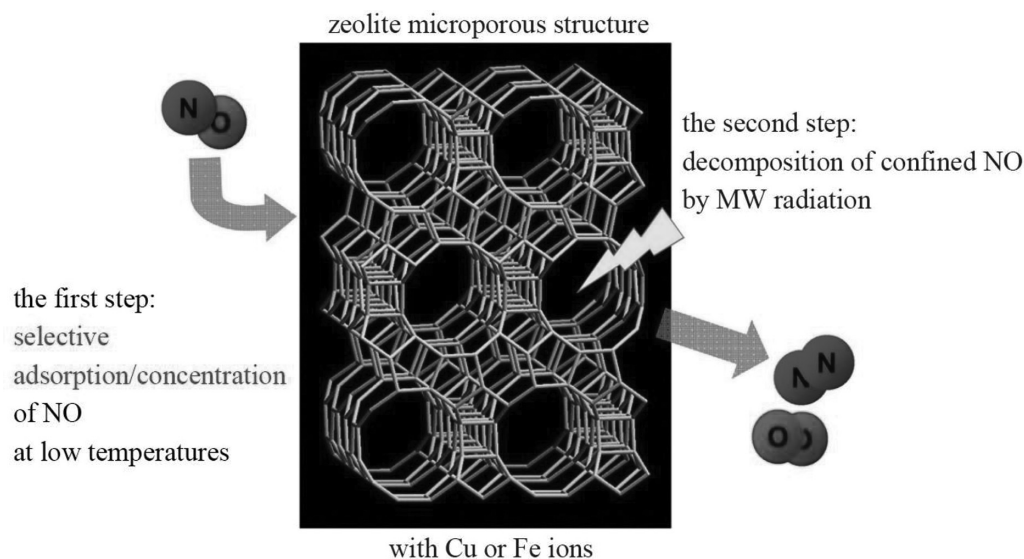


Fig. 5 – Removal process of MW catalytic reduction using zeolite doping with MeO_x ($\text{Me} = \text{Mn}, \text{Ni}, \text{Cu}$) (Ohnishi et al., 2017).

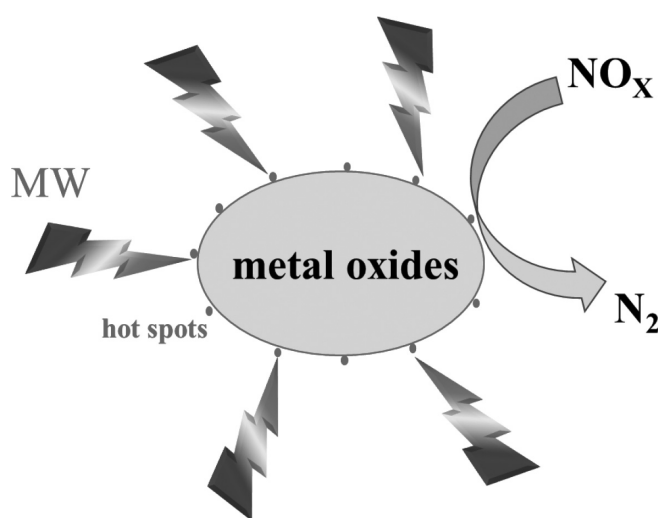


Fig. 6 – Removal mechanism of MW-induced catalytic denitrification technologies without additional reductant.

tional thermal catalysis with $\text{MeO}_x/\text{Al}_2\text{O}_3$, NO basically did not decompose unless the temperature exceeded 300°C. This study also found that the catalyst loading had a dual effect on NO removal: with the increase in the MeO_x content in Al_2O_3 , the removal efficiency was significantly improved, but the NO removal efficiency decreased once the loading of MeO_x exceeded 20%.

Perovskite-type oxides have also been employed in this kind of MW-induced catalytic denitrification method (Xu et al., 2016a; Xu et al., 2017; Xu et al., 2015a). Taking MW-induced $\text{BaMn}_x\text{Mg}_{1-x}\text{O}_3$ catalytic denitrification as an example, nearly 99.8% of NO could be directly decomposed under the conditions of 250°C and 10% O_2 over $\text{BaMn}_{0.9}\text{Mg}_{0.1}\text{O}_3$ (Xu et al., 2015a). Further study revealed that when BaMnO_3 , $\text{Ba}_{0.8}\text{Ca}_{0.2}\text{MnO}_3$, $\text{Ba}_{0.8}\text{K}_{0.2}\text{MnO}_3$ and $\text{Ba}_{0.8}\text{La}_{0.2}\text{MnO}_3$ were used separately, the proportions were 93.7%, 92.3%, 99.9% and

95.5%, respectively (Xu et al., 2017). The author also studied their catalytic activities and N_2 selectivity in the presence of water vapor, confirming that $\text{Ba}_{0.8}\text{K}_{0.2}\text{MnO}_3$ exhibited excellent water vapor resistance, which may be due to the strong polarity and good MW absorption capacity of H_2O , which can be quickly vaporized or desorbed from the catalyst; the N_2 selectivity was almost the same with and without the coexistence of 5% water vapor. Xu et al. (2016a) also investigated the catalytic activity of BaMeO_3 ($\text{Me} = \text{Mn}, \text{Co}, \text{Ba}$) in a MW-induced catalytic denitrification system, and the heating behavior of BaMO_3 with a MW power of 150 W was explored, finding that the Me site under MW thermal effects is the main reason for the higher removal efficiency. Additionally, BaFeO_3 , BaCoO_3 and BaMnO_3 were also prepared and explored. Under the conditions of 250°C and 10% O_2 , the NO removal efficiencies of BaCoO_3 and BaMnO_3 were 99.8% and 93.7%, respectively, while the NO removal efficiency of BaFeO_3 was only 64.1%, indicating that the catalytic activity of BaCoO_3 was higher. Moreover, BaCoO_3 also showed superior resistance to water vapor, which was closely related to its high reducibility, strong MW absorption and oxygen desorption capacity.

Researchers also found that the doping of carbonate in perovskite could increase the number of oxygen vacancies and promote the regeneration of oxygen vacancies, which was conducive to improving the utilization ratio of MW and the removal efficiency. For example, Xu et al., prepared the composite catalyst $\text{MgCo}_2\text{O}_4\text{-BaCO}_3$ by the co-precipitation method and realized high-efficiency catalytic decomposition of NO under MW radiation: the NO removal efficiency and N_2 selectivity over $\text{MgCo}_2\text{O}_4\text{-40%BaCO}_3$ at 250°C were 99.6% and 97.8%, respectively, while the NO removal efficiency of MgCo_2O_4 was only 69.7%. In contrast, under the conventional reaction mode and identical conditions, the highest NO removal and N_2 selectivity over $\text{MgCo}_2\text{O}_4\text{-40%BaCO}_3$ at 650°C were 29.5% and 15.1%, respectively (Xu et al., 2019). The reasons for the differences in efficiency were revealed through in-depth analysis of the catalyst: microwave radiation and the addition of carbonate could significantly reduce the apparent activation en-

ergy. In addition, the study also found that the concentrations of O_2 and water vapor had little effect on the NO conversion and N_2 selectivity in the presence of MW. Even when the concentrations of O_2 and H_2O were 10% and 5%, the NO removal efficiency and N_2 selectivity could reach 99.6% and 97.8%, respectively.

In summary, studies of MW-induced catalytic denitrification technology without additional reductant have achieved satisfactory results, and the removal efficiency can reach more than 90%, especially for perovskite catalysts, which meets the requirements of emission standards, making this a promising reduction denitrification technology. However, there are still several shortcomings, such as poor catalyst stability and low resource utilization of NO_x .

2.2. MW oxidation denitrification

At present, compared with MW reduction denitrification, there is little research on MW oxidation denitrification. The main technical route is to convert NO_x into nitrite or nitrate, which can be used as the main raw material of compound fertilizers, and then realize the resource value of the denitrification products. According to the presence or absence of additional oxidant, MW oxidation denitrification can be divided into denitrification with oxidant and without oxidant. The current research status is summarized and compared in Table 2.

2.2.1. MW-induced oxidation denitrification with oxidant

Wei et al., (2009a) performed simultaneous desulfurization and denitrification experiments using MW and zeolite loaded with $KMnO_4$, during which the zeolite absorbed MW and induced oxidation reactions between $KMnO_4$ and NO_x and SO_2 , achieving 96.8% desulfurization efficiency and 98.4% denitrification efficiency. Interestingly, the desulfurization efficiency increased with increasing SO_2 concentration, while the removal efficiency of NO_x decreased. Although MW played an important role, these high efficiencies were mainly due to the strong oxidizing properties of $KMnO_4$. In addition, (Qi et al., 2020) adopted H_2O_2 solution assisted with MW and an additive for simultaneous desulfurization and denitrification. Results showed that the NO removal efficiency showed a volcano-plot change trend with variation of temperature, pH, residence time, liquid-gas ratio, and the gas volume fractions of O_2 , NO as well as SO_2 . Additionally, when the amount of H_2O_2 or additives used was increased, the denitrification efficiency also increased. Moreover, MW could significantly reduce the activation energies of H_2O_2 decomposition and the oxidation of NO_x with an additive and accelerate the conversion from NO to NO_2 . In detail, in the absence of MW, 99% desulfurization efficiency and 73.4% denitrification efficiency were obtained under the optimal conditions. But when MW radiation was used, the SO_2 removal efficiency stabilized above 99.5%, and the NO removal efficiency increased to 87.74%. (Wang et al., 2020) proposed a novel MW-activated H_2O_2 /persulfate (PS) double-oxidant system to remove nitric oxide from flue gas, and several synergistic activation effects between MW, heat and oxidants were found. The removal mechanism is presented in Fig. 7, in which a variety of free radicals such as $\cdot OH$, $SO_4^{\cdot -}$ and $HO_2\cdot$ were generated under the dual catalysis of MW and heat at low temperature. $\cdot OH$ played a leading role,

and the maximum NO removal efficiency could reach 98.6%. The paper also explored the influence of various reaction parameters: increased MW power, oxidant and O_2 concentration could increase the removal efficiency of NO, and increases in the NO or SO_2 concentration, solution pH and flue gas flow rate weakened the removal of NO, whereas the reaction temperature and reagent flow rate showed dual effects on NO removal.

Researchers also developed a semi-dry MW-activated persulfate (PS) system for removing NO and SO_2 simultaneously, finding that with the increase in MW power, the concentrations of PS and O_2 enhanced the removals of NO and SO_2 . But when the concentration of NO or SO_2 increased, the removal efficiency decreased (Liu et al., 2020c). This may be because the increased pollutant concentrations can significantly enhance the competition between NO and SO_2 for the limited oxidants. The simultaneous removal efficiencies of NO and SO_2 increased from 18.2% and 23.9% to 92.4% and 98.8%, respectively, as the PS concentration increased from 0.1 mol/L to 1.2 mol/L. When the PS concentration was further increased, the removal efficiency of NO and SO_2 were no longer improved. Fig. 8 shows a schematic diagram of the removal mechanism, in which the leading role of MW-induced catalysis is presented, followed by thermal catalysis; $\cdot OH$ and $SO_4^{\cdot -}$ produced by MW activation of PS were the major active species for the oxidation of NO and SO_2 to NO_2 , SO_3 , sulfate and nitrate.

2.2.2. MW-induced oxidation denitrification without oxidant

Limited by the continuous consumption of oxidant and the corrosiveness or toxicity of strong oxidants, MW-induced oxidation denitrification with additional oxidant is not easy to implement widely. Hence, several researchers have attempted to combine MW with transition metal catalysts to replace the added oxidant, such as Fe, Cu and Co loaded on zeolite by impregnation to carry out flue gas purification (Wei et al., 2009c; Wei et al., 2010; Wei et al., 2011). When Fe was loaded on zeolite, the simultaneous desulfurization and denitrification efficiencies were 79.3% and 69.5%, respectively (Wei et al., 2009c); then the removal efficiencies increased to 91.7 and 79.6% as Fe and Cu were loaded together (Wei et al., 2011); when Fe-CoCu/zeolite was synthesized and exposed to MW, the SO_2 removal efficiency increased to 99.5%, while the NO removal efficiency slightly decreased to 86.1% (Wei et al., 2010). Subsequent studies revealed that the generation of active species including $\cdot OH$ and $HO_2\cdot$ radicals by MW-induced catalysis of transition metals/zeolite (Fe/zeolite, FeCu/zeolite, and Fe-CoCu/zeolite) was the main reason for the conversion of NO_x and SO_2 to nitrate and sulfate, and that the MW catalytic oxidation of SO_2 and NO_x follows Langmuir-Hinshelwood kinetics. Moreover, Gao et al. (2011) utilized MW plasma discharge to pretreat the CuO/TiO₂ catalyst, and found that this pretreatment promoted the formation of more active oxygen (O^*) on the catalyst surface, thereby improving the activity and selectivity of the catalyst, enabling low-temperature oxidation removal of NO to occur more easily.

In addition to denitrification methods that combine MW and a catalyst, Hao et al. (2020c) used MW and ultraviolet radiation to synergistically catalyze H_2O/O_2 to remove NO and Hg^0 in flue gas, and the removal mechanism is shown in Fig. 9. The results showed that ozone and $\cdot HO$ were the major active species for the oxidative removal, and the presence of SO_2

Table 2 – List of studies of MW-induced oxidation denitrification.

Catalysts	Oxidants	Optimal reaction conditions			NO _x removal efficiency (%)	SO ₂ removal efficiency (%)	Pros and cons	Reference
		Temperature (°C)	MW power (W)	O ₂ content (%)				
Zeolite	KMnO ₄	–	259	–	98.4	96.8	KMnO ₄ has high cost, corrosiveness and toxicity. Continuous consumption of H ₂ O ₂ and PS.	(Wei et al., 2009b)
–	H ₂ O ₂	60	450	3	73.4	> 99		(Qi et al., 2020)
–	H ₂ O ₂ /PS	150	320	12	98.6	–	Low removal efficiency cannot meet strict emission standards. Simultaneous removal efficiency was not ideal. NO and CO must exist at the same time. More UVEL lamps were required, meaning higher removal costs and energy consumption.	(Wang et al., 2020)
–	PS	160	320	9	>90	>95		(Liu et al., 2020c)
Fe/Ga-5A zeolite	–	90–110	280	–	79.3	69.5	Simultaneous removal efficiency was not ideal. NO and CO must exist at the same time. More UVEL lamps were required, meaning higher removal costs and energy consumption.	(Wei et al., 2009a)
FeCu/zeolite	–	–	280	–	91.7	79.6		(Wei et al., 2011)
FeCoCu/zeolite	–	–	280	–	86.1	99.5	NO and CO must exist at the same time. More UVEL lamps were required, meaning higher removal costs and energy consumption.	(Wei et al., 2010)
CuO/TiO ₂	–	300	–	–	92.0	–		(Gao et al., 2011)
–	H ₂ O/O ₂	80	260	2.8	89.3	97.0		(Hao et al., 2020c)

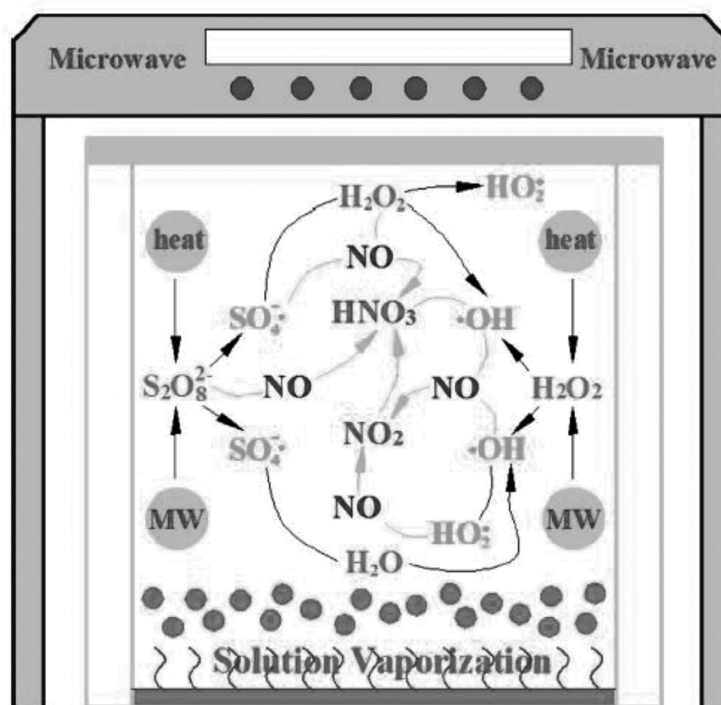


Fig. 7 – Removal mechanism of NO using microwave-induced $\text{H}_2\text{O}_2/\text{PS}$ removal system (Wang et al., 2020).

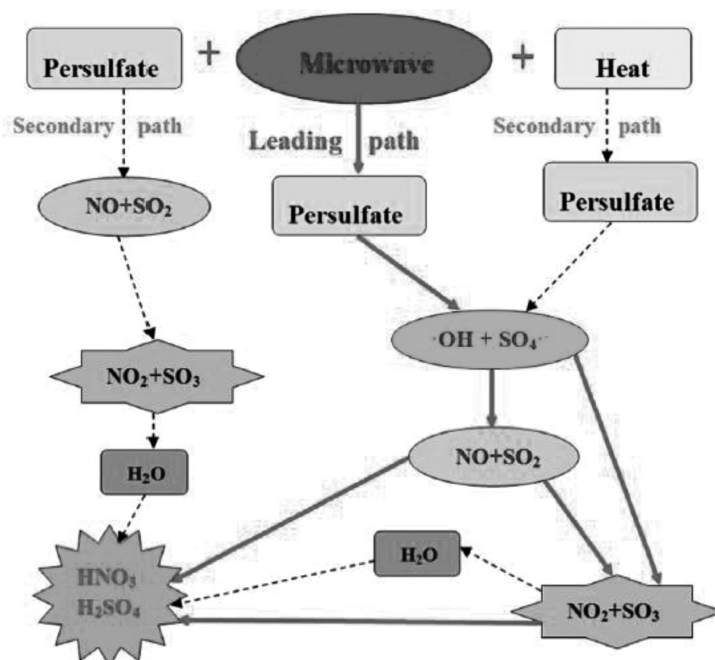


Fig. 8 – Removal mechanism of NO and SO_2 using MW-induced PS system (Liu et al., 2020c).

could generate $\text{SO}_3^{\cdot-}$ and $\text{SO}_4^{\cdot-}$ under the synergistic catalysis of MW and ultraviolet radiation, promoting the oxidative removal of NO and Hg^0 . The authors also investigated the influence of flue gas flow, MW power, reaction temperature, and the concentrations of NO, Hg^0 and SO_2 , and anion species on the removal efficiency, finding that high temperature facili-

tated NO removal but impaired Hg^0 removal; the presence of Cl^- and Br^- inhibited NO removal but promoted Hg^0 removal, because Cl^- and Br^- quenched $\cdot\text{HO}$ to produce Cl^- and Br^- radicals. Finally, NO removal efficiency of 89.3%, Hg^0 removal efficiency of 99.5%, and SO_2 removal efficiency of 97% were obtained. Although MW and UV co-catalysis of $\text{H}_2\text{O}/\text{O}_2$ can ef-

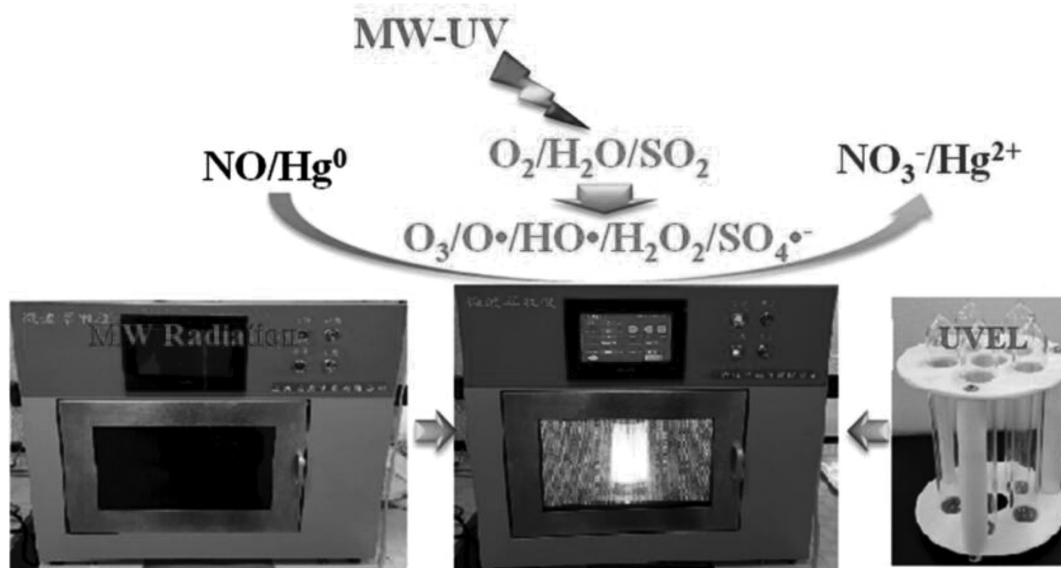


Fig. 9 – Removal mechanism of NO and Hg⁰ using microwave and ultraviolet co-catalysis system (Hao et al., 2020c).

fectively remove multiple gas pollutants simultaneously, the disadvantage is that more UVEL lamps are required, resulting in higher pollutant removal costs and excessive energy consumption.

Generally speaking, the removal efficiency by MW-induced oxidation denitrification methods using additional oxidant is always higher than those without additional oxidant; the former has the disadvantages of large oxidant consumption and high removal cost, while the latter faces bottlenecks such as weak catalyst activity or high energy consumption. The key to solving these problems is to develop novel MW-induced catalytic oxidation technologies, improving the catalytic ability and reducing the energy consumption.

3. Summary and perspectives

This article systematically reviewed the research status of MW-based denitrification methods, and the following conclusions can be drawn:

- (I) The acceleration of chemical reactions cannot be explained by thermal effects alone; there are also non-thermal effects including magnetic, electrical and chemical factors that may exist at the same time. For this reason, MW-based denitrification methods have great advantages over conventional catalytic denitrification, such as rapid heating, fast reaction speed, good selectivity, low activation energy, high removal efficiency and energy utilization, simple operation etc.
- (II) Compared with the catalytic reduction denitrification methods using NH₃, AC, urea, NH₄HCO₃, CH₄ etc., MW-induced catalytic denitrification methods without additional reductants have good application potential, and the removal efficiency can reach more than 90%, especially with perovskite catalysts, which can meet the requirements of emission standards.

- (III) The main advantage of MW-induced oxidation denitrification is its ability to oxidize NO to nitrite or nitrate, which can be used as the main raw material of compound fertilizers and realize resource utilization of removal products. However, the research on MW-induced oxidation denitrification is still in the development stage, and there are few related research studies.

On this basis, several prospects or suggestions are put forward for the further development of novel MW-based denitrification methods.

- (I) Research on the MW-induced catalytic denitrification mechanism is insufficient, and many studies are controversial. It is necessary to further reveal the MW-induced catalytic mechanism and explore the relationship between thermal effects and non-thermal effects.
- (II) It is recommended to synthesize and screen new materials with good MW-absorbing performance and catalytic ability, and further investigate the effects of flue gas components (dust, O₂, H₂O, CO₂, SO₂, CO, etc.) and microwave parameters on the denitrification efficiency to simulate actual flue gas.
- (III) It is necessary to strengthen the research on MW-induced catalytic oxidation denitrification methods, clarify the generation mechanism of oxidizing species and the removal pathways of NO_x, promote the effective conversion of intermediates to nitrate, and explore reasonable ways to utilize nitrate resources.

At present, MW-based denitrification methods are limited to bench scale. The feasibility of industrial experiments should be explored by designing and optimizing microwave catalytic devices. Meanwhile, radiation protection should be actively adopted to reduce the leakage of microwaves and avoid the adverse effects of microwaves on living things.

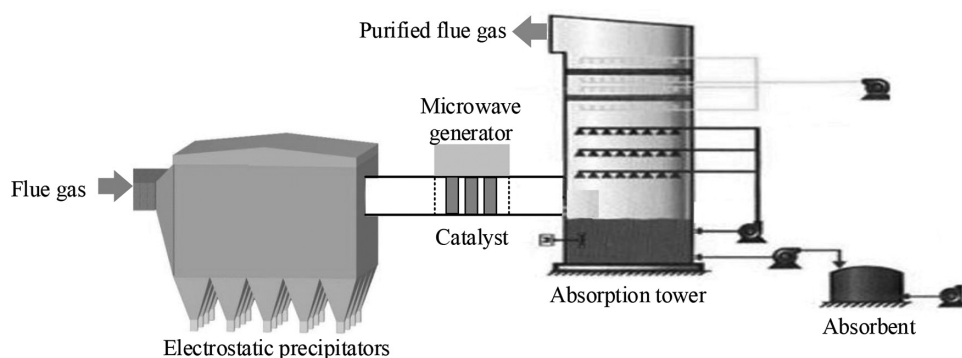


Fig. 10 – Conceptual diagram of MW-induced catalytic oxidation removal of multiple gas pollutants.

(I) On the basis of MW-induced catalytic oxidation denitrification, it is feasible to develop MW-induced catalytic oxidation methods without additional oxidant to synergistically remove multiple pollutants from flue gas. A possible reaction procedure is depicted in Fig. 10, in which the flue gas components such as H_2O , O_2 , HCl , et al. can be activated by MW-induced catalysis to produce abundant oxidizing species (OH , HO_2^\cdot , Cl^\cdot , ClO^\cdot , HOCl^\cdot –, etc.) that can convert NO and Hg^0 into soluble oxidation products (NO_2 , NO_2^- , Hg^{2+} , etc.), then these products and residual SO_2 can be simultaneously absorbed and removed in an absorption tower, realizing the integrated removal of multiple pollutants.

(VI) As long as the rapid generation of highly oxidizing species is achieved, MW-induced catalytic oxidation technology can also be used for the degradation of other gaseous pollutants, such as H_2S and volatile organic compounds (benzene, toluene, formaldehyde, halogenated hydrocarbons, etc.).

Acknowledgments

The authors appreciate the financial support by the Natural Science Foundation of China (Nos. 52000067, 51978262), the Natural Science Foundation of Hebei (No. E2020502033), the Fundamental Research Funds for the Central Universities (No. 2020MS127), the Central Guidance Special of China (No. 2019L3020), the Headquarters Science and Technology Project of China (No. 2019MK035).

REFERENCES

- Binner, J., Vaidhyathan, B., Wang, J., Price, D., Reading, M., 2008. Evidence for non-thermal microwave effects using single and multimode hybrid conventional/microwave systems. *J. Microw. Power EE* 42 (1), 47–63.
- Bueno-López, A., Soriano-Mora, J.M., García-García, A., 2006. Study of the temperature window for the selective reduction of NO_x in O_2 -rich gas mixtures by metal-loaded carbon. *Catal. Commun.* 7, 678–684.
- Bulhoes Bezerra Cavalcante, T.A., Santos Funcia, E.D., Wilhelms Gut, J.A., 2020. Inactivation of polyphenol oxidase by microwave and conventional heating: investigation of thermal and non-thermal effects of focused microwaves. *Food Chem.* 340, 127911.
- Cha, C.Y., Kong, Y., 1995. NO_x abatement with carbon adsorbents and microwave energy. *Energy Fuels* 9, 971–975.
- Chang, Y.F., Sanjurjo, A., Mccarty, J.G., Krishnan, G., Wachsman, W.E., 1999. Microwave-assisted NO reduction by methane over Co-ZSM-5 zeolites. *Catal. Lett.* 57 (4), 187–191.
- Chen, J., Xu, W., Zhu, J., Wang, X., Zhou, J., 2019. Highly effective microwave catalytic direct decomposition of H_2S over carbon encapsulated $\text{Mo}_2\text{C}-\text{Co}_2\text{C}/\text{SiC}$ composite. *Int. J. Hydrog. Energy* 44 (47), 25680–25694.
- Chen, J., Xu, W., Zhu, J., Wang, X., Zhou, J., 2020. Highly effective direct decomposition of H_2S by microwave catalysis on core-shell $\text{Mo}_2\text{N}-\text{MoC}/\text{SiO}_2$ microwave catalyst. *Appl. Catal. B* 268, 118454.
- Cheng, J., Song, L., Wu, R., Li, S., Sun, Y., Zhu, H., et al., 2020. Promoting effect of microwave irradiation on $\text{CeO}_2-\text{TiO}_2$ catalyst for selective catalytic reduction of NO by NH_3 . *J. Rare Earth* 38 (1), 59–69.
- Chuang, K.H., Lu, C.Y., Wey, M.Y., Huang, Y.N., 2011. NO removal by activated carbon-supported copper catalysts prepared by impregnation, polyol, and microwave heated polyol processes. *Appl. Catal. A Gen.* 397 (1–2), 234–240.
- Gao, F., Liu, B., Sun, W., Wu, Y., Dong, L., 2011. The influence of microwave plasma pretreated CuO/TiO_2 catalysts in $\text{NO} + \text{CO}$ reaction. *Catal. Today* 175, 34–39.
- Hájek, M., 2004. *Microwave Catalysis in Organic Synthesis*. Wiley-VCH Verlag GmbH & Co. KGaA.
- Hao, R., Ma, Z., Qian, Z., Gong, Y., Wang, Z., Luo, Y., et al., 2020a. New insight into the behavior and cost-effectiveness of different radicals in the removal of NO and Hg^0 . *Chem. Eng. J.* 385, 123885.
- Hao, R., Mao, X., Qian, Z., Zhao, Y., Wang, L., Yuan, B., et al., 2019a. Simultaneous removal of SO_2 and NO using a novel method of ultraviolet irradiating chlorite-ammonia complex. *Environ. Sci. Technol.* 53 (15), 9014–9023.
- Hao, R., Mao, X., Wang, Z., Zhao, Y., Wang, T., Sun, Z., et al., 2019b. A novel method of ultraviolet/ $\text{NaClO}_2-\text{NH}_4\text{OH}$ for NO removal: mechanism and kinetics. *J. Hazard. Mater.* 368, 234–242.
- Hao, R., Song, Y., Tian, Z., Li, Y., Zhao, Y., Wang, Z., et al., 2020b. Cooperative removal of SO_2 and NO using a cost-efficient triple-area control method. *Chem. Eng. J.* 383, 123164.
- Hao, R., Wang, X., Zhao, X., Xu, M., Zhao, Y., Mao, X., et al., 2018. A novel integrated method of vapor oxidation with dual absorption for simultaneous removal of SO_2 and NO : feasibility and prospect. *Chem. Eng. J.* 333, 583–593.
- Hao, R., Wang, Z., Gong, Y., Ma, Z., Qian, Z., Luo, Y., et al., 2020c. Photocatalytic removal of NO and Hg^0 using microwave

- induced ultraviolet irradiating $\text{H}_2\text{O}/\text{O}_2$ mixture. *J. Hazard. Mater.* 383, 121135.
- Hao, R., Yang, S., Yuan, B., Zhao, Y., 2017. Simultaneous desulfurization and denitrification through an integrative process utilizing $\text{NaClO}_2/\text{Na}_2\text{S}_2\text{O}_8$. *Fuel Process. Technol.* 159, 145–152.
- Hao, R., Zhao, Y., 2016. Macrokinetics of NO oxidation by vaporized H_2O_2 association with ultraviolet light. *Energy Fuel* 30 (3), 2365–2372.
- Herrero, M.A., Kremsner, J.M., Kappe, C.O., 2008. Nonthermal microwave effects revisited: on the importance of internal temperature monitoring and agitation in microwave chemistry. *J. Org. Chem.* 73 (1), 36–47.
- Horikoshi, S., Kajitani, M., Serpone, N., 2007. The microwave-/photo-assisted degradation of bisphenol-A in aqueous TiO_2 dispersions revisited. *J. Photoch. Photobiol. A* 188 (1), 1–4.
- Horikoshi, S., Serpone, N., 2014. On the influence of the microwaves' thermal and non-thermal effects in titania photoassisted reactions. *Catal. Today* 224, 225–235.
- Hoz, A.L., Diaz-Ortiz, A., Moreno, A., 2007. Review on non-thermal effects of microwave irradiation in organic synthesis. *J. Microw. Power EE* 41, 44–64.
- Hoz, A.L., A, D-O., Moreno, A., 2007. Review on non-thermal effects of microwave irradiation in organic synthesis. *J. Microw. Power EE* 41 (1), 45–66.
- Hu, L., Wang, P., Shen, T., Wang, Q., Wang, X., Xu, P., et al., 2020. The application of microwaves in sulfate radical-based advanced oxidation processes for environmental remediation: a review. *Sci. Total Environ.* 722, 137831.
- Hu, Y., He, Y., Cheng, H., 2018. Microwave-induced degradation of N-nitrosodimethylamine (NDMA) sorbed in zeolites: Effect of mineral surface chemistry and non-thermal effect of microwave. *J. Clean Prod.* 174, 1224–1233.
- Illan-Gomez, M.J., Linares-Solano, A., Salinas-Martinez, dL.C., Calo, J.M., 1993. Nitrogen oxide (NO) reduction by activated carbons. 1. the role of carbon porosity and surface area. *Energy Fuels* 7 (1), 146–154.
- Javed, M.T., Irfan, N., Gibbs, B.M., 2007. Control of combustion-generated nitrogen oxides by selective non-catalytic reduction. *J. Environ. Manag.* 83 (3), 251–289.
- Jie, X., Li, W., Slocombe, D., Gao, Y., Banerjee, I., Gonzalez-Cortes, S., et al., 2020. Microwave-initiated catalytic deconstruction of plastic waste into hydrogen and high-value carbons. *Nat. Catal.* 3 (11), 902–912.
- Kong, C.Y., 1995. Enhancement of NOx adsorption capacity and rate of char by microwaves. *Carbon* 33 (8), 1141–1146.
- Kong, Y., Cy, C., 1996. Reduction of NOx adsorbed on char with microwave energy. *Carbon* 34 (8), 1035–1040.
- Li, H., 2013. Study on Microwave Selective Catalytic Reduction of NO Over Microwave Catalysts $\text{Mn}_2\text{O}_3/\text{AC}$. Xiangtan University, Hu Nan, China.
- Li, Z., Liu, F., Zhang, B., Ding, Y., You, H., Jin, C., 2018. Mineralization of quinoline in aqueous solution by microwave-assisted catalytic wet peroxide oxidation system: process optimization, products analysis and degradation route research. *Water Sci. Technol.* 78 (5–6), 1324–1335.
- Lin, L., Yuan, S., Chen, J., Wang, L., Wan, J., Lu, X., 2010. Treatment of chloramphenicol-contaminated soil by microwave radiation. *Chemosphere* 78 (1), 66–71.
- Liu, H., Yang, J., Qiao, X., Jin, Y., Fan, B.G., 2020. Microwave plasma-assisted catalytic reduction of NO by active coke over transition-metal oxides. *Energy Fuels* 34, 4384–4392.
- Liu, Y., Guo, X., Chen, Z., Zhang, W.J., Wang, Y.X., et al., 2020. Microwave-synthesis of g- C_3N_4 nanoribbons assembled seaweed-like architecture with enhanced photocatalytic property. *Appl. Catal. B* 266, 118624.
- Liu, Y., Shan, Y., Wang, Y., 2020. Novel simultaneous removal technology of NO and SO_2 using a semi-dry microwave activation persulfate system. *Environ. Sci. Technol.* 54 (3), 2031–2042.
- Liu, Y., Zhang, J., 2017. Removal of NO from flue gas using $\text{UV}/\text{S}_2\text{O}_8^{2-}$ process in a novel photochemical impinging stream reactor. *AIChE J.* 63 (7), 2968–2980.
- Ma, S.C., Jin, X., Wang, M.X., Jin, Y.J., Yao, J.J., Liu, W., 2011. Experimental study on removing NO from flue gas using microwave irradiation over activated carbon carried catalyst. *Sci. China. Technol. Sci.* 54, 3431–3436.
- Ma, S.C., Yao, J., Ma, X., Gao, L., Guo, M., 2013. Removal of SO_2 and NOx using microwave swing adsorption over activated carbon carried catalyst. *Chem. Eng. Technol.* 36 (7), 1217–1224.
- Nüchter, M., Müller, U., Ondruschka, B., Tied, A., Lautenschlager, W., 2003. Microwave-assisted chemical reactions. *Chem. Eng. Technol.* 26 (12), 1207–1216.
- Obermayer, D., Gutmann, B., Kappe, C.O., 2009. Microwave chemistry in silicon carbide reaction vials: separating thermal from nonthermal effects. *Angew. Chem. Int. Ed.* 121 (44), 8471–8474.
- Ohnishi, T., Kawakami, K., Nishioka, M., Ogura, M., 2017. Direct decomposition of NO on metal-loaded zeolites with coexistence of oxygen and water vapor under unsteady-state conditions by NO concentration and microwave rapid heating. *Catal. Today* 281, 566–574.
- Pang, Y., Kong, L., Chen, D., Yuvaraja, G., 2018. Rapid Cr(VI) reduction in aqueous solution using a novel microwave-based treatment with $\text{MoS}_2\text{-MnFe}_2\text{O}_4$ composite. *Appl. Surf. Sci.* 471, 408–416.
- Peng, K., Zhou, J., Xu, W., You, Z., Long, W., Xiang, M., et al., 2017. Microwave irradiation-selective catalytic reduction of NO to N_2 by activated carbon at low temperature. *Energy Fuels* 31 (7), 7344–7351.
- Qi, Y., Ge, P., Wang, M., Shan, X., Ma, R., Huang, J., et al., 2020. Experimental investigation and numerical simulation of simultaneous desulfurization and denitrification by H_2O_2 solution assisted with microwave and additive. *Chem. Eng. J.* 391, 123559.
- Remya, N., Lin, J.G., 2011. Current status of microwave application in wastewater treatment-a review. *Chem. Eng. J.* 166 (3), 797–813.
- Robinson, J., Kingman, S., Irvine, D., Licence, P., Smith, A., Dimitrakakis, G., et al., 2010. Understanding microwave heating effects in single mode type cavities-theory and experiment. *Phys. Chem. Chem. Phys.* 12 (18), 4750–4755.
- Srogi, K., 2006. A review: application of microwave techniques for environmental analytical chemistry. *Anal. Lett.* 39, 1261–1288.
- State, R.N., Volceanov, A., Muley, P., Boldor, D., 2019. A review of catalysts used in microwave assisted pyrolysis and gasification. *Bioresour. Technol.* 277, 179–194.
- Tang, J., Tao, Z., Liang, D., Yang, H., Li, N., Lin, L., 2002. Direct decomposition of NO by microwave heating over $\text{Fe}/\text{NaZSM-5}$. *Appl. Catal. B* 36 (1), 1–7.
- Tang, J., Zhang, T., Liang, D., Xu, C., Sun, X., Lin, L., 2000. Microwave discharge-assisted catalytic conversion of NO to N_2 . *Chem. Commun.* 19 (19), 1861–1862.
- Tang, J.W., Zhang, T., Ma, L., Li, L., Zhao, J.F., Zheng, M.Y., Lin, L.W., et al., 2001a. Microwave discharge-assisted NO reduction by CH_4 over $\text{Co}/\text{HZSM-5}$ and $\text{Ni}/\text{HZSM-5}$ under O_2 excess. *Catal. Lett.* 73, 2–4.
- Tang J.W., 2001b. Conversion of NO with microwave irradiation. Dalian Institute of Chemical Physics Chinese Academy of Sciences (in chinese).
- Tang, J., Zhang, T., Ma, L., Li, N., 2003. Direct decomposition of NO activated by microwave discharge. *Ind. Eng. Chem. Res.* 42 (24), 5993–5999.

- Trombi, L., Cugini, F., Rosa, R., Amadè, N.S., Chicco, S., Solzi, M., et al., 2020. Rapid microwave synthesis of magnetocaloric Ni-Mn-Sn Heusler compounds. *Scr. Mater.* 176, 63–66.
- Verma, P., Samanta, Kumar, S., 2018. Microwave-enhanced advanced oxidation processes for the degradation of dyes in water. *Environ. Chem. Lett.* 16 (3), 969–1007.
- Wang, H., Yuan, B., Hao, R., Zhao, Y., Wang, X., 2019. A critical review on the method of simultaneous removal of multi-air-pollutant in flue gas. *Chem. Eng. J.* 378, 122155.
- Wang, N., Wang, P., 2016. Study and application status of microwave in organic wastewater treatment-a review. *Chem. Eng. J.* 283, 193–214.
- Wang, X., Zhang, T., Xu, C., Sun, X., Liang, D., Lin, L., 2000. Microwave effects on the selective reduction of NO by CH₄ over an In-Fe₂O₃/HZSM-5 catalyst. *Chem. Commun.* 4 (4), 279–280.
- Wang, Y., Liu, Y., Shi, S., 2020. Removal of nitric oxide from flue gas using novel microwave-activated double oxidants system. *Chem. Eng. J.* 393, 124754.
- Wei, R., Wang, P., Zhang, G., Wang, N., Zheng, T., 2020b. Microwave-responsive catalysts for wastewater treatment: a review. *Chem. Eng. J.* 382, 122781.
- Wei, W., Shao, Z., Qiao, R., Chen, W., Zhou, H., Yuan, Y., 2020a. Recent development of microwave applications for concrete treatment. *Constr. Build. Mater.* 269, 121224.
- Wei, Z.S., Niu, H.J., Ji, Y.F., 2009a. Simultaneous removal of SO₂ and NO_x by microwave with potassium permanganate over zeolite. *Fuel. Process. Technol.* 90 (2), 324–329.
- Wei, Z., Lin, Z., Niu, H., He, H., Ji, Y., 2009b. Simultaneous desulfurization and denitrification by microwave reactor with ammonium bicarbonate and zeolite. *J. Hazard. Mater.* 162 (2–3), 837–841.
- Wei, Z., Zeng, G., Xie, Z., 2009c. Microwave catalytic desulfurization and denitrification simultaneously on Fe/Ca-5A zeolite catalyst. *Energy Fuels* 23 (3), 2947–2951.
- Wei, Z.S., Lin, Z.H., Qiu, R.L., He, H.M., 2006. Catalytic reduction of NO_x with microwave urea over catalyst Ga-A zeolites. *Acta Sci. Nat. Univ. Sunyatseni* 45, 103–106.
- Wei, Z., Zeng, G., Xie, Z., Sun, J., 2010. Simultaneous desulfurization and denitrification by microwave catalytic over FeCoCu/Zeolite 5A catalyst. *J. Environ. Eng.* 136 (12), 1403–1408.
- Wei, Z.S., Du, Z.Y., Lin, Z.H., He, H.M., Qiu, R.L., 2007. Removal of NO_x by microwave reactor with ammonium bicarbonate and Ga-A zeolites at low temperature. *Energy* 32 (8), 1455–1459.
- Wei, Z.S., Zeng, G.H., Xie, Z.R., Ma, C.Y., Liu, X.H., Sun, J.L., et al., 2011. Microwave catalytic NO_x and SO₂ removal using FeCu/zeolite as catalyst. *Fuel* 90, 1599–1603.
- Xia, X., Zhao, X., Zhou, P., Feng, T., Ma, C., Song, Z., 2020. Reduction of SO₂ to elemental sulfur with carbon materials through electrical and microwave heating methods. *Chem. Eng. Process.* 150, 107877.
- Xu, W., Cai, J., Zhou, J., Ou, Y., Long, W., You, Z., et al., 2016a. Highly effective direct decomposition of nitric oxide by microwave catalysis over BaMeO₃ (Me=Mn, Co, Fe) mixed oxides at low temperature under excess oxygen. *ChemCatChem* 8 (2), 417–425.
- Xu, W., Cai, J., Zhou, J., You, Z., Su, Z., Shi, N., et al., 2016b. Microwave irradiation coupled with MeOx/Al₂O₃ (Me=Cu, Mn, Ce) catalysts for nitrogen monoxide removal from flue gas at low temperatures. *Energy Technol.* 4, 856–863.
- Xu, W., Shi, N., You, Z., Cai, J., Peng, K., Su, Z., et al., 2017. Low-temperature NO decomposition through microwave catalysis on BaMnO₃-based catalysts under excess oxygen: effect of A-site substitution by Ca, K and La. *Fuel Process. Technol.* 167, 205–214.
- Xu, W., Wang, Q., Peng, K., Chen, F., Han, X., Wang, X., et al., 2019. Development of MgCo₂O₄-BaCO₃ composites as microwave catalysts for the highly effective direct decomposition of NO under excess O₂ at a low temperature. *Catal. Sci. Technol.* 9 (16), 4276–4285.
- Xu, W., Zhou, J., Li, H., Yang, P., You, Z., Luo, Y., 2014. Microwave-assisted catalytic reduction of NO into N₂ by activated carbon supported Mn₂O₃ at low temperature under O₂ excess. *Fuel Process. Technol.* 127, 1–6.
- Xu, W., Zhou, J., You, Z., Luo, Y., Ou, Y., 2015a. Microwave Irradiation coupled with physically mixed MeOx (Me=Mn, Ni) and Cu-ZSM-5 catalysts for the direct decomposition of nitric oxide under excess oxygen. *ChemCatChem* 7 (3), 450–458.
- Xu, W., Zhou, J., Ou, Y., Luo, Y., You, Z., 2015b. Microwave selective effect: a new approach towards oxygen inhibition removal for highly-effective NO decomposition by microwave catalysis over BaMn_(x)Mg_(1-x)O₃ mixed oxides at low temperature under excess oxygen. *Chem. Commun.* 51 (19), 4073–4076.
- Xue, C., Mao, Y., Wang, W., Song, Z., Zhao, X., Sun, J., et al., 2019. Current status of applying microwave-associated catalysis for the degradation of organics in aqueous phase-a review. *J. Environ. Sci.* 81, 119–135.
- Yang, L.M., 2018. Study on the effect of microwave discharge on the process of activated carbon desulfurization and denitrification. Taiyuan University of Technology (in chinese).
- Yin, J., Cai, J., Yin, C., Gao, L., Zhou, J., 2016. Degradation performance of crystal violet over CuO@AC and CeO₂-CuO@AC catalysts using microwave catalytic oxidation degradation method. *J. Environ. Chem. Eng.* 4 (1), 958–964.
- Yuan, B., Mao, X., Wang, Z., Hao, R., Zhao, Y., 2020a. Radical-induced oxidation removal of multi-air-pollutant: a critical review. *J. Hazard. Mater.* 383, 121162.
- Yuan, B., Zhao, Y., Mao, X., Zheng, Z., Hao, R., 2020b. Simultaneous removal of SO₂, NO and Hg⁰ from flue gas using vaporized oxidant catalyzed by Fe/ZSM-5. *Fuel* 262, 116567.
- Zenkovets, G.A., Shutilov, R.A., Sobolev, V.I., Gavrillov, V.Y., 2020. Catalysts Cu/ZSM-5 for N₂O decomposition obtained with copper complexes of various structures. *Catal. Commun.* 144, 106072.
- Zhao, J., Chen, J., Zhang, M., Lin, Y., 2007. Non-thermal effect during microwave heating at low temperature. *Int. Mater. Rev.* 21, 4–6.
- Zhang, B., Li, L., 2018. Investigation of chemical bonds in the ordered Ba₃Zn(Nb_{2-x}Mo_x)O_{9+x/2} ceramics and its effects on the microwave performance. *J. Eur. Ceram. Soc.* 38, 4446–4452.
- Zhang, J.W., Chen, W.Y., Gaidau, C., 2020. The thermal and non-thermal effects of microwave in the chrome tanning process. *J. Soc. Leather Tech. Chem.* 104, 98–104.
- Zhang, X., Kou, J., Sun, C., 2019. A comparative study of the thermal decomposition of pyrite under microwave and conventional heating with different temperatures. *J. Anal. Appl. Pyrol.* 138, 41–53.
- Zhao, J., Wei, X., Li, T., Li, S., 2020. Effect of HCl and CO on nitrogen oxide formation mechanisms within the temperature window of SNCR. *Fuel* 267, 117231.
- Zhao, Y., Hao, R., Peng, Z., Zhou, S., 2014. Integrative process for simultaneous removal of SO₂ and NO utilizing a vaporized H₂O₂/Na₂S₂O₈. *Energy Fuels* 28 (10), 6502–6510.
- Zhao, Y., Yuan, B., Hao, R., Tao, Z., 2017. Low-temperature conversion of NO in flue gas by vaporized H₂O₂ and nanoscale zerovalent iron. *Energy Fuels* 31 (7), 7282–7289.
- Zhao, Y., Yuan, B., Zheng, Z., Hao, R., 2019. Removal of multi-pollutant from flue gas utilizing ammonium persulfate solution catalyzed by Fe/ZSM-5. *J. Hazard. Mater.* 362, 266–274.