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Journal of Environmental and Occupational Science

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Original Research

Plasma catalytic desulfurization and denitrification simultaneously over FeCo/zeolite

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Received: April 20, 2012

Accepted: May 01, 2012

Published: May 7, 2012

DOI : 10.5455/jeos.20120501110036

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Key words:

Simultaneous desulfurization and denitrification, Microwave catalytic, Microwave catalytic reduction, FeCo/zeolite, Kinetic

Abstract

Simultaneous desulfurization and denitrification has been investigated using FeCo/zeolite as catalyst. The reaction efficiency of microwave catalytic reduction of SO₂ and NO_x with ammonium bicarbonate (NH₄HCO₃) as a reducing agent could be up to 96 and 90.6%, respectively. A microwave reactor with FeCo/zeolite only could also be used to microwave catalytic radical oxidative 91% SO₂ to sulfate and 84.3% NO_x to nitrates. Microwave catalytic desulfurization and denitrification effect on FeCo/zeolite is slightly higher than that of catalytic reduction of SO₂ and NO_x using ammonium bicarbonate as reducing agent and FeCo/zeolite as catalyst. The mechanism for microwave-induced SO₂ and NO_x reduction can be described as the microwave induced catalytic reaction between SO₂, NO_x, and ammonium bicarbonate, with SO₂, NO_x, and ammonium bicarbonate, with FeCo/zeolite being the catalyst and microwave absorbent. Microwave catalytic removal of SO₂ and NO_x over FeCo/zeolite catalyst follows Langmuir—Hinshelwood (L-H) kinetics.

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INTRODUCTION

Acid rain control and public health considerations have led to worldwide action to reduce SO₂ and NO_x emissions from coal-fired boilers. Wet flue gas desulfurization (WFGD) and selective catalytic reduction (SCR) are most effective for SO₂ and NO_x removal respectively. Extensive research on selective catalytic reduction (SCR) of nitrogen oxides has been undertaken using hydrocarbons [1], ammonia [2] as reducing agent over various catalytic materials, such as, Fe-ZSM-5[3], Co- loaded zeolites[4], H-ZSM-5[5], CeO₂- zeolites [6]. Simultaneous desulfurization and denitrification is a promising technology at high efficiency and low cost. Simultaneous SO₂ and NO_x removal can be achieved with high efficiency using copper on alumina catalyst sorbents (CuO/Al₂O₃) [7], V₂O₅/AC [8] or by ozone injection [9].

Some research has been conducted in simultaneous

desulfurization and denitrification by plasma technologies such as calcium magnesium acetate [10], electron beam and electrical discharge induced nonthermal plasmas [11], pulsed corona discharge plasma [12] and nonthermal plasma [13]. Microwave was applied to a pyrolytic carbon such as activated carbon and char, enhancing the reaction of sulfur dioxide (SO₂) and nitrogen oxides (NO) with carbon [14]. The reaction efficiency of microwave reduction of NO_x could be up to 98% when microwave energy was applied continuously [15]. The simultaneous treatment with the accelerated electronic beams and the microwaves could increase the removal efficiency of NO_x and SO₂; about 80% of NO_x and more than 95% of SO₂ were removed by precipitation with ammonia [16].

The objective of this work is to study FeCo/zeolite as catalyst for microwave catalytic desulfurization and denitrification, and for microwave catalytic reduction

of SO₂ and NO_x with ammonium bicarbonate (NH₄HCO₃) as a reducing agent. The study evaluates the role of microwave and catalyst, the influence of microwave power, empty bed residence time (EBRT) on microwave catalytic reduction desulfurization and denitrification simultaneously, and the mechanistic and kinetic analysis of microwave-induced catalytic SO₂ and NO_x removal were elicited.

MATERIALS AND METHODS

Catalyst Preparation

The FeCo/zeolite catalyst was prepared by an incipient wetness impregnation using Fe(NO₃)₃, Co(NO₃)₂ as the metal precursors. After impregnation in Ca-5A zeolite for 24h in room temperature, the catalyst samples were dried in the drying oven at 32 °C for 36h, and placed in the middle of muffle furnace, calcined at 550 °C for 120 min. After cooling to room temperature, the samples were taken out for further investigations.

Microwave catalytic experiments

The experimental flow loop used in the study is shown schematically in Fig.1. The microwave reactor consisted of a quartz tube (i.d. 10 mm and 250 mm long) with FeCo/zeolite and ammonium bicarbonate

(NH₄HCO₃) or FeCo/zeolite only was set up to study removal of SO₂ and NO_x (NO, NO₂) from stimulated waste gas. A constant input microwave power of 164~331 W was used, and the microwave frequency was 2450 MHz. SO₂ and NO_x supplied from the gas cylinders, were first diluted with the compressed air, passed through an air mixture bottle and flowed upwards through the microwave reactor. The flow meter and the valve were used to monitor the gas flow through the reactor. SO₂ and NO_x (NO, NO₂) concentrations were analyzed by the device of S2000 flue gas, and gas flow rate was monitored by the rotameter and the mass flow controllers. In the process of the experiments, the simulated SO₂ and NO_x-containing flue gas were supplied to the microwave reactor, at a flow rate of 150~350 L.h⁻¹ (EBRT, 0.153~0.358 s).

Analytical Methods

The periodic measurements of the gas concentration from sampling ports and the gas flow of the quartz tube in the microwave reaction system were carried out by using the following devices. S2000 flue gas device was used for the analysis of sulfur dioxide (SO₂) and nitrogen oxides NO_x (NO, NO₂).

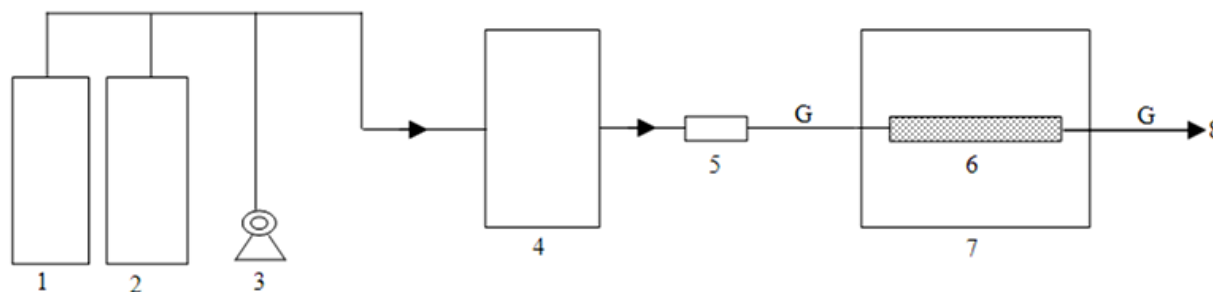


Fig.1 Experimental flow loop of simultaneous desulfurization and denitrification over FeCo/zeolite. (1) SO₂ gas cylinder; (2) NO_x gas cylinder; (3) air compressor; (4) the bottle of gas mixture; (5) flow meter; (6) quartz tube; (7) microwave reactor; (8) outlet port; (G) sampling port.

RESULTS

Microwave catalytic desulfurization and denitrification simultaneously

The influence of concentration of SO₂ and NO_x in inlet on desulfurization and denitrification is shown in Figs. 2 and 3, under the conditions of gas flow of 0.15 m³.h⁻¹ and microwave power (280 W). The MWFeCo/zeolite and ABFeCo/zeolite profile are represented by FeCo/zeolite under microwave and ammonium bicarbonate over FeCo/zeolite separately. SO₂ removal

efficiency decreases from 91 to 78.3% when the concentration of SO₂ is increased; while NO_x removal efficiency changes from 84.3 to 56.1% with increasing concentration of NO_x. This illustrates that FeCo/zeolite catalyst has good performance of microwave catalytic desulfurization and denitrification under no reducing agent, and microwave catalytic desulfurization and denitrification effect on FeCo/zeolite is slightly higher than that of catalytic reduction of SO₂ and NO_x using ammonium bicarbonate as reducing agent and FeCo/zeolite as catalyst.

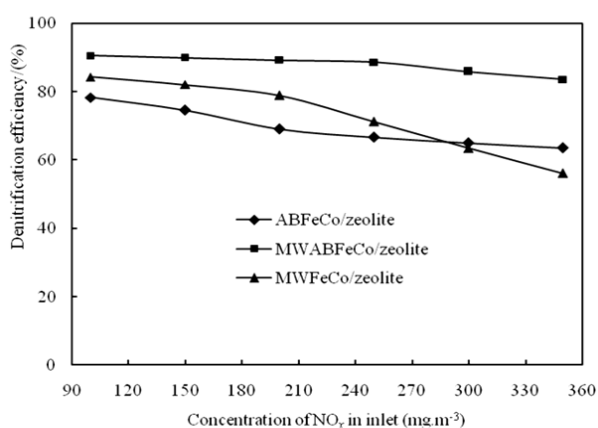


Fig.2 Influence of concentration of NO_x in inlet on denitrification (reaction conditions: gas flow = 0.15 m³.h⁻¹; EBRT = 0.358s; inlet concentration of SO₂ = 1000 mg.m⁻³; microwave power = 280 W)

With no reducing agent such as ammonium bicarbonate, about 91% sulfur dioxide or 71.2% nitric oxides are converted in the microwave reactor with FeCo/zeolite only under the conditions of gas flow of 0.15 m³.h⁻¹, microwave power (280 W), inlet concentration of 1000 mg.m⁻³ of SO₂ and inlet concentration of NO_x 250 mg.m⁻³. The possible reason for this could be that a fast inducement over the surface of the FeCo/zeolite catalyst by microwave, includes the produce of hydroxyl radicals; which not only induces SO₂ oxidation catalyst reaction to sulfate, but also induces NO_x oxidation to nitrates. This illustrates that microwave catalytic generated hydroxyl radicals play an important role in the oxidation of SO₂ to sulfate and NO to nitrate [17]. Two main classes of catalysts, zeolites and metal oxides, have been reported to be highly effective for NO_x removal in combination with non-thermal plasma [18]. Microwave heating has been used to promote desulfurization with methane over MoS₂ catalysts [19]. However, until today non-thermal plasma and more recent hybrid plasma catalyst technology has not matured yet to meet 2007 regulations [20]. Microwave catalytic simultaneous SO₂ and NO_x removal could be achieved with high efficiency using FeCo/zeolite as catalyst only.

Microwave catalytic reduction performance

Microwave catalytic reduction of SO₂ and NO_x simultaneously

The MWABFeCo/zeolite profile is represented by ammonium bicarbonate and FeCo/zeolite under microwave. As are shown in Figs. 2 and 3, the additional use of microwave to the ammonium bicarbonate over FeCo/zeolite leads to the enhancement of SO₂ removal efficiency from 8.4 to 11.4%, and NO_x removal efficiency from 12.3 to 21.9%, this illustrates synergetic interactions in a one-stage plasma-over catalyst reactor between microwave and FeCo zeolite

catalyst during NH₄HCO₃ reduction of SO₂ and NO_x. For comparison, in the presence of microwave irradiation and FeCo/zeolite, with/without ammonium bicarbonate (NH₄HCO₃) in flue gas treatment process, SO₂ removal efficiency increases from 5 to 9.1% and the denitrification efficiency increases from 6.3 to 27.5%. Microwave catalytic reduction of SO₂ and NO_x effect simultaneously are much higher than that of catalytic reduction or microwave catalytic desulfurization and denitrification, which are generally in the order:

Desulfurization: (MWABFeCo/zeolite) > (MWFeCo/zeolite) > (ABFeCo/zeolite)

Denitrification: (MWABFeCo/zeolite) > (MWFeCo/zeolite) ≈ (ABFeCo/zeolite)

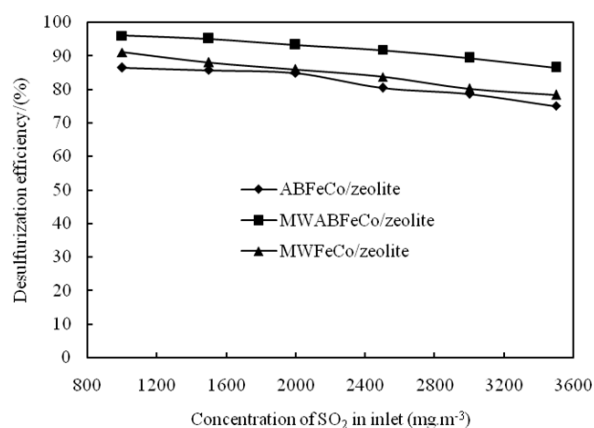


Fig.3 Influence of concentration of SO₂ in inlet on desulfurization (reaction conditions: gas flow = 0.15 m³.h⁻¹; EBRT = 0.35 8s; inlet concentration of NO_x = 250 mg.m⁻³; microwave power = 280 W)

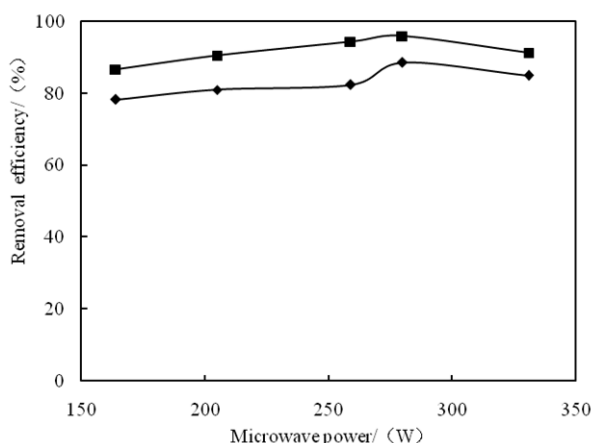


Fig.4 Influence of microwave powers on microwave catalytic reduction desulfurization and denitrification using ammonium bicarbonate and FeCo/zeolite (reaction conditions: gas flow = 0.15 m³.h⁻¹; inlet concentration of SO₂ = 1000 mg.m⁻³; inlet concentration of NO_x = 250 mg.m⁻³)

Table 1. Kinetic parameters for desulfurization and denitrification according to the L-H rate expression

Reaction	$k(\text{DS}\#)$ $\text{mg.m}^{-3}.\text{s}^{-1}$	$k(\text{DN}^*)$ $\text{mg.m}^{-3}.\text{s}^{-1}$	$K(\text{DS})$ $(\text{mg.m}^{-3})^{-1}$	$K(\text{DN})$ $(\text{mg.m}^{-3})^{-1}$
MWFeCo /zeolite	15771.2	1012.4	0.0005	0.007
MWABFeCo/zeolite	18330.7	3610.3	0.00057	0.002

#desulfurization, * denitrification

This result is in accordance with Niu’s [21] research. Niu et al reported that NO_x conversion by a catalyst-filled dielectric barrier discharge with methane additive was much higher than with plasma alone. The NO_x conversion for pure plasma induced, pure catalyst induced and plasma-catalyst induced reactions was 24, 25 and 65%, respectively. Plasma assisted and e-beam assisted catalysis for NO_x and SO_x control only for electron beam irradiation 63-80% for SO_2 and 0-63% for NO_x ; for combined electron beam-microwave treatment 68-95% for SO_2 and 0-70% for NO_x by electron beam and combined electron beam-microwave irradiation [22]. Studies [23] proved that these in a one-stage plasma-over catalyst reactor between DBD plasma and Cu-ZSM-5 catalyst during C_2H_4 selective reduction of NO_x behave similarly to those with the catalyst positioned post plasma. This implicates that the catalytic mechanism does not involve effects such as electric field enhancement or electron impact excitation of the catalyst surface. It can be concluded that microwave-induce catalytic reduction of SO_2 and NO_x over FeCo/zeolite is a promising technology for waste gas treatment.

The influence of microwave power

Fig. 5 shows the influence of microwave power on simultaneous desulfurization and denitrification using ammonium bicarbonate as reducing agent and FeCo/zeolite as catalyst. The conversion of desulfurization efficiency gradually increases from 86.7% with 164 W microwave power to 96% with 280 W, and then decreases to 91.3% with 331W; while the conversion of denitrification efficiency increases from 78.3% with 164 W to 88.6% with 280 W, decreases to 85% with 331W, showing excellent desulfurization and denitrification effect by microwave reactor with ammonium bicarbonate (NH_4HCO_3) and FeCo/zeolite. The experimental results show that the optimum microwave power for desulfurization and denitrification simultaneously is supposed to be 280 W.

The influence of empty bed residence time (EBRT)

The influence of empty bed residence time (EBRT) on microwave catalytic reduction desulfurization and denitrification simultaneously is presented in Fig.5, under the conditions of microwave power of 280 W, inlet concentration of $1000 \text{ mg.m}^{-3} \text{ SO}_2$, and inlet concentration of NO_x 250 mg.m^{-3} with ammonium bicarbonate and FeCo/zeolite. With increasing EBRT, SO_2 removal efficiency increases from 83.3 to 96%,

whereas NO_x removal efficiency changes from 75 to 88.6%. This indicates the longer EBRT is a benefit on the removal of SO_2 and NO_x , in the case where the EBRT is too short to reduce SO_2 and NO_x to sulfur and nitrogen before release. The type of FeCo/zeolite and the length of the quartz tube with catalyst and reducing agent are the key elements. SO_2 and NO_x are rapidly reduced, when ammonium bicarbonate and FeCo/zeolite are added under microwave simultaneously.

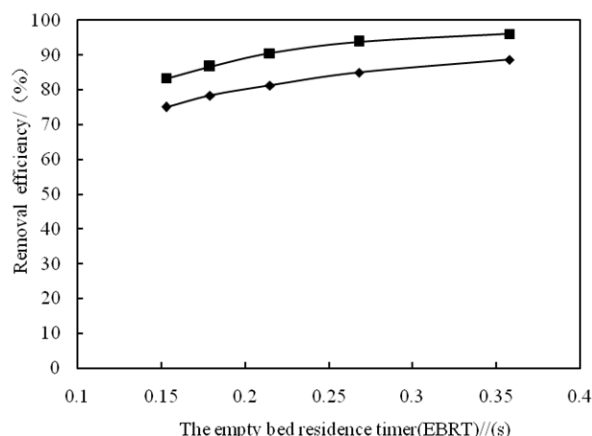


Fig.5 Influence of empty bed residence time (EBRT) on desulfurization and denitrification (reaction conditions: the microwave power = 280 W; inlet concentration of SO_2 =1000 mg.m^{-3} ; inlet concentration of NO_x = 250 mg.m^{-3})

Kinetic analysis

The Langmuir-Hinshelwood (L-H) rate expression has been widely used to describe the gas-solid phase reaction for heterogeneous catalysis [24]. The reaction rate in a microwave reactor can be expressed linearly as:

$$\ln \left(\frac{C_{in}}{C_{out}} \right) = \frac{kK}{k_{in} - C_{out}} \left(\frac{1}{Q} \right) \quad (1)$$

where C_{in} and C_{out} are the inlet and outlet concentrations of SO_2 and NO_x , respectively; V is the volume of the microwave reactor (14.92 ml); and Q is the flow rate through the reactor (150 L.h^{-1}).

The values of L-H reaction rate constant k of the desulfurization is more than that of the denitrification (Table 1), the possible reason for this could be that concentrations of SO_2 in inlet are more than concentrations of NO_x in inlet under our experimental conditions. This demonstrates that desulfurization capacity is higher than that of denitrification. The values of L-H reaction rate constant K suggests that reaction occurs on the FeCo/zeolite catalyst surface through L-H mechanism and not in the gas phase. The microwave catalytic removal of SO_2 and NO_x rate matches Langmuir–Hinshelwood model in the microwave reactor with FeCo/zeolite and ammonium bicarbonate or FeCo/zeolite only.

DISCUSSION

The combination of microwave and heterogeneous catalyst allows an efficient removal of SO_2 and NO_x . Microwave-catalytic -generated free radicals with a high oxidation contribute to removal of SO_2 and NO_x , and play an important role in the oxidation of SO_2 to sulfate and NO_x to nitrate.

FeCo/zeolite does absorb microwave energy but require the reducing agent such as ammonium bicarbonate. The use of both FeCo/zeolite and ammonium bicarbonate combined with microwave energy would induce SO_2 and NO_x catalytic reduction reaction significantly [25]. The microwave induced catalytic reduction reaction among SO_2 , NO_x and ammonia (NH_3) decomposed by ammonium bicarbonate can also proceed in a different way, giving rise to the product S, N_2 and H_2O over FeCo/zeolite acting as catalyst when ammonium bicarbonate and FeCo/zeolite are used together under microwave, which is critical to microwave catalytic reduction desulfurization and denitrification simultaneously. FeCo/zeolite could adsorptive SO_2 and NO_x , ammonium bicarbonate could reduce SO_2 and NO_x to sulfur and nitrogen. Microwave could induce SO_2 and NO_x reduction catalyst reaction using ammonium bicarbonate over FeCo/zeolite with being the catalyst and microwave absorbent. Microwave accentuates catalyst reduction of SO_2 and NO_x , and increases the desulfurization and denitrification efficiency. Thus, a major mechanism for microwave-induced SO_2 and NO_x reduction can be described as the microwave induced reduction catalyst reaction between SO_2 and NO_x and ammonium bicarbonate with FeCo/zeolite being the catalyst and microwave absorbent.

CONCLUSIONS

The paper revealed that the microwave reactor with ammonium bicarbonate and FeCo/zeolite or the microwave reactor with FeCo/zeolite only can be used

for simultaneous desulfurization and denitrification, and Langmuir–Hinshelwood kinetic model was successfully applied to describe this process on microwave catalytic reduction of SO_2 and NO_x . Microwave catalytic desulfurization and denitrification effect of the experiment using a microwave reactor with FeCo/zeolite only is slightly higher than that of catalytic reduction of SO_2 and NO_x using ammonium bicarbonate and FeCo/zeolite together.

ACKNOWLEDGEMENTS.

The authors gratefully acknowledge the financial support from the Research Fund Program of Guangdong Provincial Key Laboratory of Environmental Pollution Control and Remediation Technology (2006K0013)

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