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Journal of Chemical and Pharmaceutical Research, 2014, 6(6):1412-1417

Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

Microwave catalytic reduction of nitric oxide in activated carbon bed with a new microwave catalytic reactor system

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ABSTRACT

A new microwave catalytic reactor system was developed. By coupling the catalytic effect of microwave irradiation with the reducing activity of activated carbon, the microwave catalytic reduction of nitric oxide (NO) was studied in activated carbon bed. Novel results were observed under microwave irradiation. The conversion of NO to N_2 under microwave irradiation remarkably increased compared to conventional heating, which indicates that the microwave irradiation has microwave catalysis effect besides thermal effect. The exhaust gas temperature under microwave irradiation was much lower compared to that of conventional heating; there are different adsorption mechanisms of activated carbon under different heating modes. The effects of a series of reaction parameters, including reaction temperature, microwave power, NO concentration, O_2 concentration and gas hourly space velocity(GHSV) on the productivity of N_2 with a new microwave catalytic reactor system were investigated. The results show that NO is converted predominantly to N_2 under all reaction conditions and the highest conversion of NO to N_2 is up to 99.8% under optimized conditions.

Key words: microwave; microwave catalytic reactor; catalysis; activated carbon; nitrogen oxide

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INTRODUCTION

Nitrogen oxides (NO_x) are major factors of air pollutants that cause photochemical smog and acid rain. There is a worldwide effort to discover improved solutions for the removal of NO_x emissions [1-8]. At present, the selective catalytic reduction (SCR) technology has been widely used in industry. However, the consumption of ammonia (NH_3) in the SCR processes is high and the stoichiometric ratio of NH_3 must be strictly controlled. The use of NH_3 concerns the corrosion and the leakage in the transport and storage process, and moreover, excessive NH_3 used in SCR may also cause secondary pollution [9-11]. All of these urge us to find an efficient, environmentally friendly, and feasible substitute process.

Presently, the microwave technique is applied in many areas of chemistry, from the organic synthesis to the processing of inorganic [12-16]. It has been proved that microwave irradiation could greatly accelerate many chemical reactions and promote many chemical reactions which cannot occur under conventional conditions. It has been demonstrated that microwave irradiation has non-thermal effect besides thermal effect. This unique principle of microwave irradiation has been focused on widely by various domains researcher [17-20]. The microwave technique is applied in environment protection as well. Especially in the past decade, it attracted much attention [21-23]. Tang et al. [24] had studied microwave discharge-assisted NO reduction by CH_4 over Co/HZSM-5 and Ni/HZSM-5 under O_2 excess. And they found that, by comparing the activities of the catalysts in the microwave discharge mode with that in the conventional reaction mode, microwave discharge enhanced greatly the conversion of NO to N_2. Chang et al. [25] found that microwaves applied to a pyrolytic carbon matrix enhance the chemical reactions of nitric oxide (NO) and sulfur dioxide (SO_2) with carbon to produce nitrogen, sulfur and carbon dioxide.

In this work, a new microwave catalytic reactor system was developed. Using microwave energy and microwave field, microwave catalytic reduction of NO was studied in activated carbon bed by coupling the catalytic effect of microwave irradiation with the reducing action of activated carbon. Furthermore, the effects of reaction temperature, microwave power, NO concentration, O_2 concentration and GHSV on the productivity of N_2 were also investigated.

EXPERIMENTAL SECTION

MICROWAVE REACTION SYSTEM

A new microwave catalytic reactor system was developed, which can be applied to researching the role of the microwave field and the special effects of microwave energy in a continuous flow of gas-solid, liquid-solid and gas-liquid-solid catalytic reaction systems. The experimental diagram is shown in Fig.1. The microwave reaction system consisted of a microwave generator system and a reaction system. The microwave energy was supplied by a 2.45 GHz microwave generator, the power of which could be varied continuously in the range of 0-1000 W. The magnetron microwave source connected through a rectangular waveguide to a single-mode resonant cavity which was terminated with a tuning plunger. The microwave reactor consisted of quartz tube (Diameter 12 mm and 500 mm in length) at the center of the cavity. The activated carbons were filled in the middle of the reactor tube, with asbestos at both ends. The temperature of reaction bed of the new microwave catalytic reactor system was provided by microwave thermal effect, so the reaction bed has a minimum volume of catalyst. The temperature of reaction bed was controlled in the range of 0-1000 ˚C by adjusting the frequency of microwave power and the velocity of flow of cooling water. An infrared pyrometer (Shanghai Institute of Technical Physics, PR China) with temperature range of 30-1600 ˚C was used to measure the temperature of the catalyst bed.

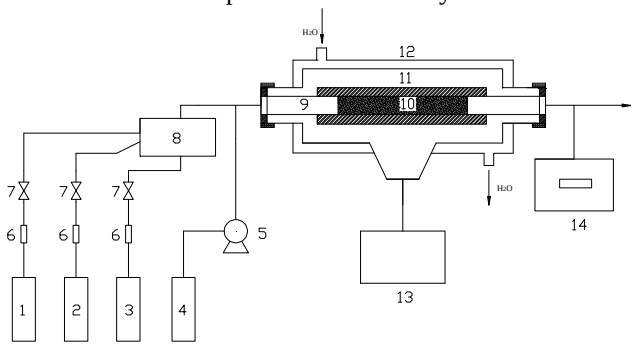

Fig. 1: Schematic diagram of microwave catalytic reactor

(1. NO; 2.O_2; 3.N_2; 4. Storage tank; 5. Metering pump; 6. Mass flowmeter; 7. Valve; 8. Premixer; 9. Quartz reactor; 10. Fixed bed; 11. Thermal insulation; 12. Resonant cavity; 13. Microwave generator; 14. NO_x analyzer)

PRETREATMENT OF ACTIVATED CARBON

The approach of microwave catalysis is based on the idea of selective heating of an active sensitizer supported on a porous carrier, therefore, the choice of the catalyst is of great importance. Evidently, such a catalyst has to be a good receptor of microwave energy, and yet cannot change its structure and properties under intense microwave radiation. The activated carbon is not only an excellent microwave absorber, but also an excellent adsorption material and catalyzed material. At the same time, it is also an excellent reducing agent for reducing NO. Therefore, the activated carbon was used as catalyst and reducing agent in our work.

The activated carbon is a commercial product from Jiangxi Taisheng charcoal industry. For preparing activated carbon beds, the activated carbon was sieved and boiled, washed with deionized water, and dried at 120 °C for 12 h. The sizes of activated carbon are 10–20 mesh, and other physical properties are shown in the table 1.

Table 1 physical properties of activated carbon

Specification (φ)	specific surface area (m^2/g)	micropore volume (cm^3/g)	packing density (kg/m)	Particle Size (mm)
3.0	1050±50	0.45	418	2.00-0.84

REACTION TESTS

The reactant gas are composed of O_2, N_2 and NO, which were prepared on line according to the proportion of simulated flue gas, and passed through a premixer before entering the reactor. The reactor was filled with 10 ml granular activated carbon for each run. The gas composition was analyzed by an online NO_x analyzer (42C, Thermo Environmental Instruments Co., Ltd., U.S.). For the sake of convenience in comparison, the microwave irradiation reaction and the conventional reaction were carried out in the same quartz reactor with the same amount of activated

carbon under identical conditions of gas composition, reaction temperature and space velocity. In conventional reactions, the reaction test was carried out using a micro device (MRT-6123; Beijing Xin Hang Shield Petrochemical Technology Co., Ltd.), the experimental diagram refer to Ref. 7 [7].

RESULTS AND DISCUSSION

THE COMPARISON OF NO CONVERSION UNDER DIFFERENT REACTOR SYSTEMS

Under different reactor systems, the conversions of NO to N_2 were investigated with the same reaction parameters, including reaction temperature, O_2 concentration, NO concentration, and GHSV, as presented in the table 2. It can be observed that the conversion of NO to N_2 under microwave irradiation remarkably increases compared to that of conventional heating, especially at low temperatures. For example, compared with that under conventional heating condition, the rate of increase of the conversion of NO under microwave irradiation were increased by 33.3%, 44.2%, 40.8%, 15.2% and 7.5% at 250 ˚C, 300 ˚C, 400 ˚C, 500 ˚C, and 600 ˚C, respectively. It has been demonstrated that microwave irradiation could greatly enhances the conversion of NO.

Table 2 the conversions of NO under different reactor systems

Reaction temperature (˚C)	The conversion of NO under microwave irradiation (%)	The conversion of NO under conventional heating (%)	The rate of increase (%)
250	62.9	47.2	33.3
300	75.7	52.5	44.2
400	92.5	65.7	40.8
500	99.7	86.6	15.2
600	99.8	92.8	7.5

Reaction conditions: molar fraction of O_2, 5.88%; molar fractions of NO, 1×10^{-3} and GHSV, 1920 h^{-1}; microwave power, 500 W

THE COMPARISON OF EXHAUST GAS TEMPERATURES UNDER DIFFERENT REACTOR SYSTEMS

Under the same reaction conditions (reaction temperature, O_2 concentration, NO concentration, and GHSV), the exhaust gas temperatures were compared in two different reactor systems, the microwave irradiation and the conventional heating. As shown in Fig. 2, it is interesting to observe that the exhaust gas temperature near the activated carbon bed remained stable around 34 ˚C under microwave irradiation, while it increased from 100 ˚C to 132 ˚C as the reaction temperature changed from 200 ˚C to 600 ˚C in conventional heating. These observations may be attributed to a different heating mechanism in the two heating modes, as well as a different adsorption mechanism of activated carbon.

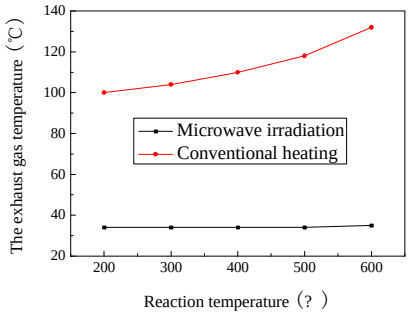

Fig.2 The comparison of exhaust gas temperatures under different reactor systems (Reaction conditions: molar fraction of O_2, 5.88%; molar fractions of NO, 1×10^{-3} and GHSV, 1920 h^{-1} and ambient temperature, 32˚C)

Based on the experimental results, we consider the activated carbons were selectively heated in the microwave field, because there are both better and poorer absorbers of microwave in the activated carbon[27]. When the temperature of activated carbon bed reached reaction temperature, the temperature of the better absorbers of microwave would be much higher than that of activated carbon bed, whereas the temperature of the poorer absorbers of microwave would be much lower than that of activated carbon bed. It suggests that microwave heating for the activated carbon on a microscopic level is uneven. The better absorbers of microwave with higher temperature in the activated carbon were just the active sites of the NO reduction reaction. NO and O_2 reacting with activated carbon were adsorbed on such active sites by chemical adsorption with a higher temperature, as a result, the reaction products may have a close temperature comparing with such active sites. However, non-reaction occurred to N_2, which could only be adsorbed on the poorer absorbers of microwave with a lower temperature in the activated carbon by physical adsorption. The exhaust gases consist of excess N_2 with lower temperature and little reaction products gas with higher temperature. Therefore, the temperature of the exhaust gases was determined by the temperature of N_2. Under the conventional heating conditions, the activated carbons were heated as a whole and the complete activated carbon

reaction bed was heated to a designed temperature. When the reactant gas entered into the reaction bed, either the reaction product of NO and O_2 or the N_2 were heated to the same temperature. Consequently, under the same reaction temperature, the exhaust gas temperature heated with the microwave irradiation is lower than that heated with the conventional heating.

THE EFFECTS OF REACTION PARAMETERS ON NO CONVERSION UNDER MICROWAVE IRRADIATION

(1) Effects of reaction temperature

With the same molar fractions of NO (1×10^{-3}) and O_2 (5.88%) in the feed, GHSV (1920 h^{-1}) and microwave power (500 W), the influences of reaction temperature on NO conversion were investigated. The temperature of reaction bed was controlled by adjusting the velocity of flow of cooling water. As presented in Fig. 3, the results show that NO conversion increases with the increasing of reaction temperature. As the reaction temperature was changed from 250 ℃ to 600 ℃, the conversion of NO increased from 62.9% to 99.8%, suggesting almost a full conversion under these conditions.

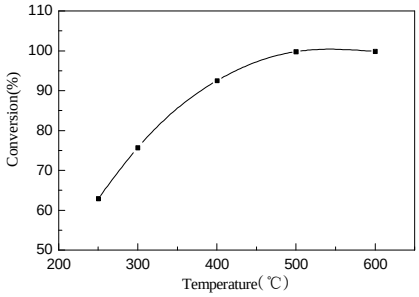

Fig. 3 Effects of reaction temperature on NO conversion

(2) Effects of microwave power

The temperature of activated carbon bed was controlled by adjusting microwave power and the flow rate of cooling water, and it maintained invariable at a constant cooling water flow rate and a constant microwave power. Table 2 shows the effect of microwave power on NO conversion with molar fractions of NO and O_2 in the feed of 1×10^{-3} and 5.88%, respectively, and GHSV of 1920 h^{-1}. It shows that NO conversion increases with the increasing of microwave power. As the microwave power was changed from 300 W to 800 W, the conversions of NO increased from 38.6% to 98.8%.

By comparison of Fig. 3 and Table 3, it can be seen that NO conversion increases with the increasing of microwave power at the same reaction temperature. When the reaction temperature is 424 ℃, the conversion of NO increases from 92.5% to 98.8% as the microwave power changes from 500 W to 800 W, which indicates that microwave irradiation has non-thermal effect besides thermal effect.

Table 3 Effect of microwave input power on NO conversion

Microwave power (W)	Reaction temperature (℃)	NO conversion (%)
300	167	38.6
400	213	55.6
500	352	87.4
800	424	98.8

(3) Effects of NO feed concentration

With molar fraction of O_2 (5.88%), GHSV of 1920 h^{-1}, and microwave power of 500 W at 400 ℃, the influence of NO feed concentration on NO conversion is illustrated in Fig. 4. It shows that NO has similar conversion yields with molar fraction from 0.5 $\times10^{-3}$ to 2.5 $\times10^{-3}$ in the feed, which are all higher than 90%. Moreover, the conversion is independent of the initial concentration of NO.

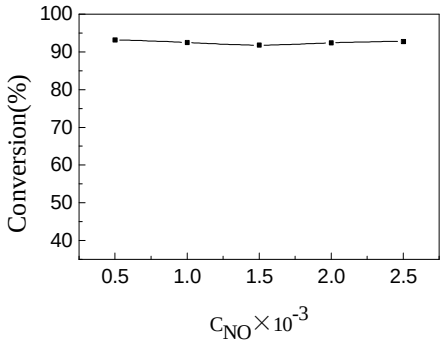

Fig. 4 Effects of NO feed concentration on NO conversion

(4)Effects of O_2 content in the feed

With molar fraction of NO (1×10^{-3}), GHSV of 1920 h^{-1}, and microwave power of 500 W at 400 ℃, the influence of O_2 content in the feed on NO conversion was also investigated. As shown in Fig. 5, NO conversion increases rapidly with O_2 content in the feed increasing from 4% to 10% and then levels off with further increasing the O_2 content (> 10%). This observation is due to the fact that the activated carbon reacts with oxygen in the gas mixture to produce partly carbon monoxide (CO). The latter readily reacts with nitrogen oxides, thereby promoting the conversion of NO.

According to Rideal-Eley's mechanism [26], the oxygen in the reaction partially comes from the oxygen adsorbed on the activated carbon. The content of adsorbed oxygen on the activated carbon increases with the increase of O_2 content in the reaction mixture, which in turn promotes the conversion of NO. When oxygen adsorption on the activated carbon reaches saturation, NO conversion tends to be stable.

Fig. 5 Effects of O_2 content in the feed on NO conversion

(5)Effects of GHSV

With molar fractions of NO (1×10^{-3}) and O_2 (5.88%) in the feed and microwave power of 500W, the influence of GHSV on NO conversion was investigated at 400 ℃. As presented in Fig. 6, NO conversion decreases with increasing the GHSV. NO conversion is higher than 90% when the GHSV is under 4000 h–1, and it decreases to 62.9% with a GHSV of 7200 h^{-1}.

In general, the efficiency of a gas-solid reaction is not only related to the reaction but also the transfer process, and the reactant must pass the external and internal diffusions before reaching the active site for reaction. When the GHSV is relatively lower, the contacting time of the reactant with the activated carbon is longer. This is helpful in diffusion, adsorption and reaction of reactants, as well as desorption and diffusion of products inside the activated carbon pores. As a result, low GHSV favors the improvement of NO conversion. Therefore, a value of 1920 h^{-1} was selected for GHSV in preset study.

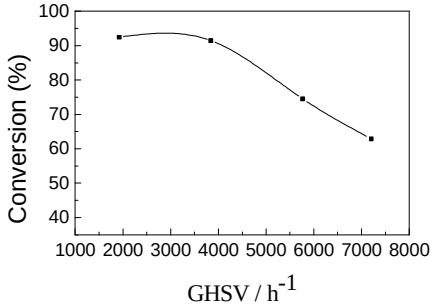

Fig. 6 Effects of GHSV on NO conversion

CONCLUSION

In this study we investigated the catalytic reduction of NO on activated carbon bed using both microwave irradiation and conventional heating modes. The results show that the microwave irradiation is effective for environmentally friendly catalytic conversion of NO, and NO is mainly converted to N_2 with maximum conversion up to 99.8% under optimized conditions. With the same reaction temperature, the conversion of NO to N_2 under microwave heating remarkably increases compared to conventional heating. The exhaust gas temperature near the activated carbon bed outlet under microwave irradiation is much lower compared to conventional heating; There are different adsorption mechanisms of activated carbon under different heating modes. The NO conversion also increases with the increasing of the microwave power, which indicates that microwave irradiation has non-thermal effect besides thermal effect. Furthermore, under the microwave irradiation, the conversion of NO increases with the increasing of reaction temperature, content of O_2 and microwave power, respectively. It is independent of the NO inlet concentration and decreases significantly with increasing the GHSV.

Acknowledgments
This work was supported by Foundation of Hu’nan Educational Committee (11C1086); Foundation of Department of science and technology of Hunan Province (2013SK3122) and doctoral Science Foundation of University of South China (2012XQD33)

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