Microwave discharge-assisted NO reduction by CH_4 over Co/HZSM-5 and Ni/HZSM-5 under O_2 excess

Junwang Tang, Tao Zhang *, Lei Ma, Lin Li, Jinfeng Zhao, Mingyuan Zheng and Liwu Lin

State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, PO Box 110, Dalian 116023, China
E-mail: taozhang@dicp.ac.cn

Received 14 December 2000; accepted 15 March 2001

Microwave discharge-assisted reduction of NO by CH_4 in the presence of excess O_2 over Co/HZSM-5 and Ni/HZSM-5 catalysts was studied. By comparing the activities of the catalysts in the microwave discharge mode with that in the conventional reaction mode, it is demonstrated that microwave discharge enhanced greatly the conversion of NO to N_2, and expanded the reaction temperature range of the catalysts. For the Co/HZSM-5 catalyst, the conversion of NO to N_2 increased by 30%, and the optimum temperature decreased by 200 °C. With the Ni/HZSM-5 catalyst, the highest activity was close to 100%, and the optimum temperature decreased by 325 °C. The conversion of CH_4 also increased in the microwave discharge mode over both of the catalysts.

KEY WORDS: microwave discharge; NO conversion; CH_4; Co/HZSM-5 and Ni/HZSM-5; reaction temperature range

1. Introduction

Presently, the microwave technique is applied in many areas of chemistry, from the organic synthesis [1,2] to the processing of ceramics [2]. For example, the preparation of a Ni/zeolite catalyst was aided by microwave radiation due to its effectiveness in splitting hydrogen molecules to hydrogen atoms, which reduced Ni^{2+} to the metallic Ni [3]. Microwave radiation has also been used to dehydrate zeolites [4], and Whittington et al. proposed a mechanism for the microwave heating of zeolites [5]. It has been demonstrated that microwave irradiation can also promote catalytic reactions, including oxidative coupling of CH_4 [6], CO oxidation and decomposition of volatile organic compounds (VOC) [7]. Recent progress in CH_4 conversion under microwave irradiation was reviewed by Parmon et al. [8]. Utilizing microwave discharge to promote chemical reaction is also considered to be a promising potential. Since microwave discharge is a non-equilibrium process produced by a high frequency electromagnetic field, it produces high temperature electrons, while the bulk temperature of the gas is very low [9,10]. It was shown that with microwave discharge under vacuum condition, highly dispersed cobalt clusters on zeolites could be prepared [9], and novel results for the conversion of CH_4 were obtained [11].

The reduction of NO has been investigated for many years. Especially in the past decade, it attracted much attention [12]. The selective catalytic reduction of NO by hydrocarbons under oxidizing atmosphere has been reported over various catalysts [13,14]. Recently, Armor has summarized the process of catalytic removal of NO carried out in the conventional reaction mode [15]. In our laboratory, high activities of In/HZSM-5 and In–Fe_2O_3/HZSM-5 catalysts for NO reduction by CH_4 have been observed [16–18]. We have also succeeded in producing stable microwave discharges at atmospheric pressure and reported on the conversion of NO to N_2 by microwave discharge without a catalyst [19]. Furthermore, the activity of the Fe/zeolite catalyst for NO reduction under microwave discharge has been investigated, and novel features of microwave discharge on chemical reactions have been illustrated [20].

In the present work, Co/HZSM-5 and Ni/HZSM-5 were chosen as the catalysts, due to the fact that they are not only highly active for the NO reduction by CH_4, but also effective microwave absorbers. By coupling the action of the microwave discharge with the catalytic properties of the catalysts, we can elucidate the effect of microwave discharge on the chemical reaction process of NO reduction over the active catalysts. Novel results from the microwave discharge-assisted reduction of NO by CH_4 in the presence of O_2 over these two ZSM-5 zeolite based catalysts have been obtained, and comparison of the results with those from the conventional reactions has been discussed.

2. Experimental

2.1. Microwave discharge unit

The microwave discharge unit is shown in figure 1. It consisted of a 200 W, 2.45 GHz magnetron microwave source, connected through a rectangular waveguide to a single-mode resonant cavity which was terminated with a tuning plunger. With this unit, the resonance of the microwave irradiation on the catalysts could be easily tuned. The cavity was equipped with taps to measure the incident and reflected power. A tubular quartz reactor of 14 mm i.d. was aligned vertically at the center of the cavity, so that it seated in the

* To whom correspondence should be addressed.

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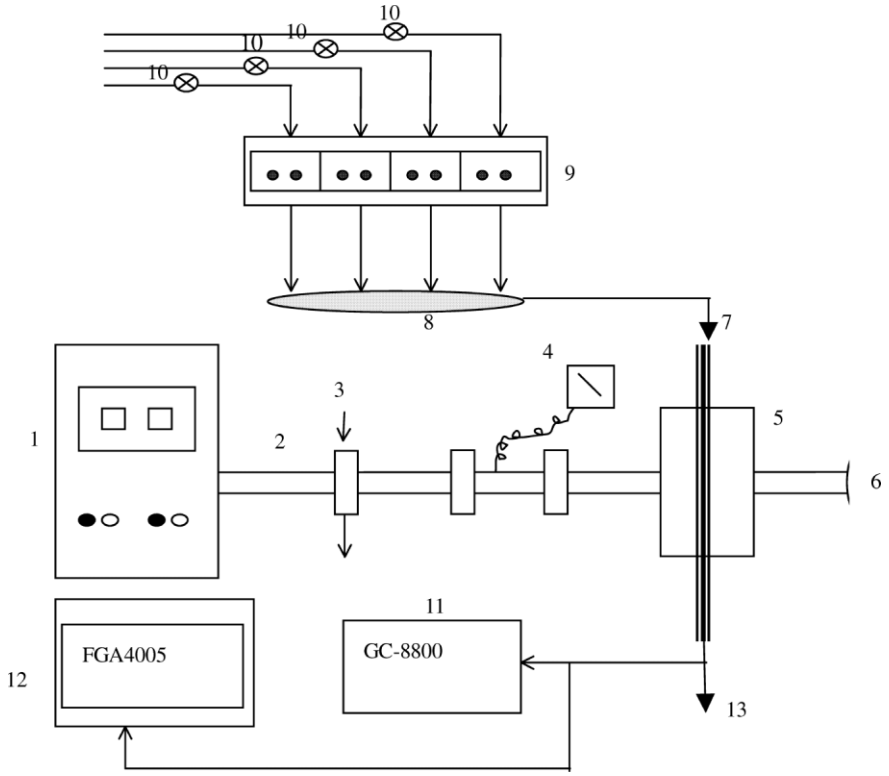

Figure 1. The microwave discharge system diagram: 1 – microwave generator, 2 – waveguide, 3 – cooling water, 4 – reflectometer, 5 – resonant cavity, 6 – tuning plunger, 7 – quartz reactor, 8 – manifold, 9 – mass flowmeter, 10 – stopcock, 11 – gas chromatograph, 12 – NO_x analyzer, 13 – vent.

region of maximum microwave field intensity. The catalyst bed was supported on a fused quartz frit of medium porosity. The reactor was filled with 1 ml granular catalyst for each run. An infrared pyrometer (Shanghai Institute of Technical Physics, PR China) with temperature range of 150–1000 °C was used to measure the temperature of the catalyst bed. The measurements of the catalyst were checked by a thermocouple, which was inserted immediately to measure the temperature of the catalyst bed as soon as the microwave generator was turned off. The temperatures measured by these two different methods were basically consistent with each other [21,22]. During the microwave discharge, the pyrometer was focused on a 2 mm diameter spot on the catalyst bed and the indicated temperature was taken as the temperature of the catalyst bed. Microwave discharge was ignited in the reactant mixing gas by the catalyst. By controlling the location of the catalyst, the discharge could be made to disperse around the catalyst. The discharge region was approximately 4 ml.

2.2. Gas system

The gas mixture, containing 2000 ppm NO, 1600 ppm CH_4, 2% O_2, and the balance helium, was prepared by metering 1.0% NO, 1.0% CH_4, 20.0% O_2 and pure helium (all gases were provided by Guangming Gas Company of Dalian, PR China) with a mass flowmeter into a manifold. The total gas flow rate was kept at 60 ml/min in all runs. The feed gas and the gaseous products of the reaction were analyzed by an on-line NO_x analyzer and gas chromatograph (GC8800, with 13X and PQ columns).

2.3. Preparation of catalysts

Co/HZSM-5 and Ni/HZSM-5 were both prepared by the impregnating technique. HZSM-5 (supplied by Nankai University, PR China) has a silicon to aluminum mole ratio of 25. It was impregnated with an aqueous solution of $Co(NO_3)_2{\cdot}6H_2O$ (AR grade, Shenyang Agent Company, PR China) of 0.11 g/ml. The sample was stirred vigorously for 0.5 h at 60 °C, dried at 120 °C for 10 h and calcined at 700 °C for 4 h. Then the sample was crushed and meshed, and granules of 1.25–1.60 mm were used for the reaction. The cobalt loading of the catalyst was 7 wt% (weight percent). Ni/HZSM-5 was prepared by a similar procedure, with a slightly different concentration of $Ni(NO_3)_2{\cdot}6H_2O$ (AR grade, Shenyang Agent Company, China), and the nickel loading of the catalyst was 10 wt%.

2.4. Reaction tests

For the sake of convenience in comparison, the microwave discharge reaction and the conventional reaction were conducted in the same quartz reactor with the same amount of catalyst under identical gas composition and space velocity conditions. In the conventional reaction runs, the temperature of the catalyst bed was measured by a thermocouple inserted in the catalyst bed.

3. Results and discussion

We have investigated the activity of an Fe/zeolite for NO reduction in the microwave discharge mode [20]. The Fe/zeolite catalyst has a special high ability for absorbing microwave radiation [23]. After it had run for a short period of time, the temperature of the catalyst became out of control, and the activity of the catalyst decreased. Based on the observations, catalysts demonstrating higher activities in the conventional reaction mode, but with stable abilities for absorbing microwave radiation, were used in the present work for the study of microwave discharge-assisted catalysis.

3.1. Results of Co/HZSM-5

The catalyst was designed to possess both functions of NO reduction and microwave absorption for discharge generation. Co_3O_4 is a good microwave absorbent [23,24], and Co/HZSM-5 has showed high activity for NO reduction in the conventional reaction mode [25,26].

The quality of microwave discharge is strongly influenced by the loading amount of microwave absorbent. At lower loading, microwaves cannot be absorbed enough to ignite discharge, while at too high loading most of the absorbed microwave energy is dissipated as radiation heat instead of discharge generation due to the enhanced heating (>600 °C) [24]. Thus, to utilize microwave radiation effectively for NO reduction, the loading should be controlled strictly in a range favorable for discharge formation. In the present work, the loading of cobalt was 7%, which not only could ensure the stable discharge formation, but also exhibited high activity for NO reduction in the conventional reaction mode. The discharge was tuned to fill the full cross section of the reactor by the plunger. The results obtained in the microwave discharge mode over Co/HZSM-5 are presented in figure 2.

From the results, it can be seen that the conversion of NO over Co/HZSM-5 follows a volcano curve in the lower temperature range under the action of the microwave discharge. At about 200 °C, the conversion of NO was 80%. However, when the temperature of the catalyst bed was increased further, the conversion of NO leveled to 60%. The conversion of CH_4 had a similar tendency within the experimental temperature range.

In order to elucidate the effect of microwave discharge on the NO reduction reaction, the conventional reaction of NO reduction over Co/HZSM-5 was also conducted for comparison, and the results are shown in figure 3. The highest conversion of NO was 50% in this case, which was consistent with the reports reported by other workers [25]. However, the NO highest conversion was 30% higher in the case of the microwave discharge mode. When NO conversion was up to the highest, the reaction temperature decreased by 200 °C in the microwave discharge mode, as compared with the result of the conventional reaction.

In these two reaction modes over Co/HZSM-5, the plots of NO conversion both contained a volcano shape, but their difference was clear. With increasing further the temperature, NO conversion in the microwave discharge mode leveled at a stable value (about 60%), even a little up. However, in the conventional reaction, the conversion decreased to zero on end. This indicated microwave discharge not only increased the conversion of NO, but also expanded the reaction temperature range of the catalyst.

3.2. Results of Ni/HZSM-5

Ni/HZSM-5 has approximately similar ability of absorbing microwave radiation and NO catalytic reduction. The activities of the catalyst in both the microwave discharge mode and the conventional reaction mode were investigated, and the results are presented in figures 4 and 5, respectively.

The conversions of NO and CH_4 over Ni/HZSM-5 had similar tendencies with that over Co/HZSM-5 in both these reaction modes. Over the Ni/HZSM-5 catalyst under the action of microwave discharge, the maximum conversion of NO increased from 60% of the conventional reaction condition mode to 96%, while the temperature at the maximum

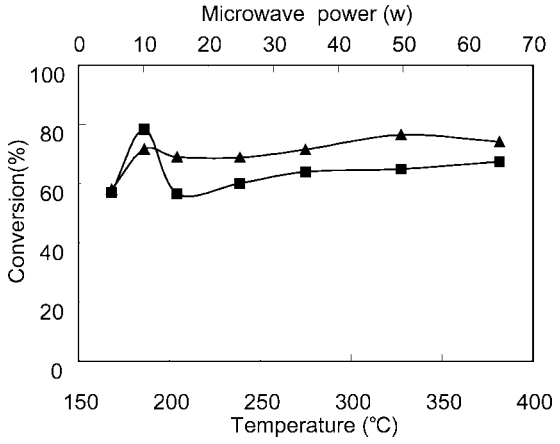

Figure 2. The conversions of NO and CH_4 over Co/HZSM-5 catalyst in the microwave discharge mode. NO conversion (■) and CH_4 conversion (▲). 2000 ppm NO, 1600 ppm CH_4, 2% O_2, He balance gas, GHSV = 3600 h^{-1}.

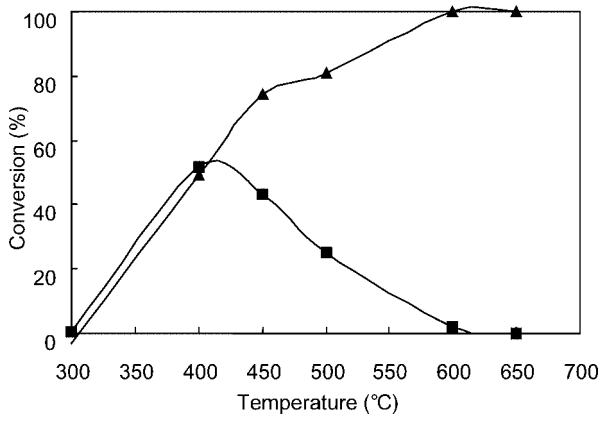

Figure 3. The conversions of NO and CH_4 over Co/HZSM-5 catalyst in the conventional reaction mode. NO conversion (■) and CH_4 conversion (▲). 2000 ppm NO, 1600 ppm CH_4, 2% O_2, He balance gas, GHSV = 3600 h^{-1}.

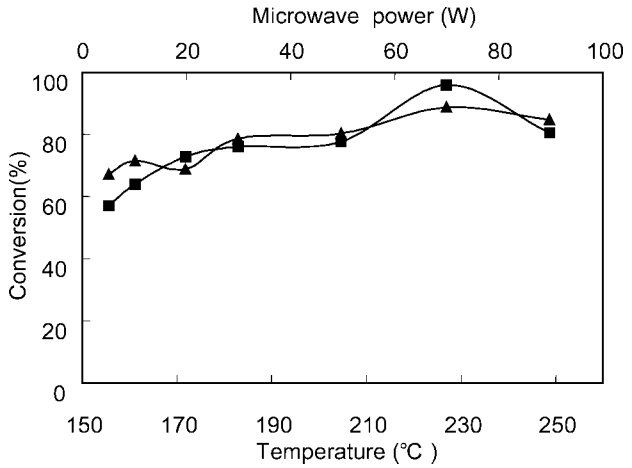

Figure 4. The conversions of NO and CH_4 over Ni/HZSM-5 catalyst in the microwave discharge mode. NO conversion (■) and CH_4 conversion (▲). 2000 ppm NO, 1600 ppm CH_4, 2% O_2, He balance gas, GHSV = 3600 h^{-1}.

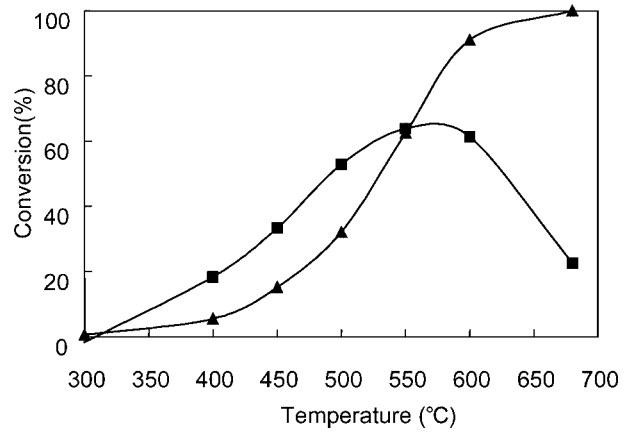

Figure 5. The conversions of NO and CH_4 over Ni/HZSM-5 catalyst in the conventional reaction mode. NO conversion (■) and CH_4 conversion (▲). 2000 ppm NO, 1600 ppm CH_4, 2% O_2, He balance gas, GHSV = 3600 h^{-1}.

conversion of NO decreased from 550 to 225 °C. From these figures, it can be concluded that microwave discharge not only enhances remarkably the conversion of NO and decreases the reaction temperature, but also can give rise to a wide reaction temperature range for the NO reduction.

In the present work, the activity of Co/HZSM-5 was lower than that of Ni/HZSM-5 in the conventional reaction mode, which was different from the results of the catalysts prepared by the ion-exchanging method [26]. By the action of microwave discharge, the activities of both catalysts for NO reduction increased clearly, but their active orders were not changed. Namely in the microwave discharge mode, the conversion of NO over Co/HZSM-5 was still lower than that over Ni/HZSM-5. So it could be concluded that microwave discharge was able to increase the activities of the catalysts, but did not change their activity order. It could also be seen that the conversion of CH_4 increased clearly in the microwave discharge mode over these two catalysts in the low temperature range.

Although the mechanism for NO reduction was vague under the action of microwave discharge, the following reactions were suggested. In the microwave discharge mode, reaction gas is constantly ionized to neutral atoms, positive and negative ions, and free electrons. Neutral molecules and gaseous ions have temperature ranges between ambient and a few hundred degrees. The electrons, on the other hand, have energies corresponding to high temperature values [9,10,27]. NO could be activated to N, O radicals and high-energy NO_x^* by the high-energy electrons [19,21,28,29], CH_4 is also decomposed to CH_x. These active species are then adsorbed on the catalysts, subsequently they can react selectively [20,21,28].

In this paper, microwave discharge also showed the high activation of CH_4 at the low temperature. It is clear that the activation of CH_4 is due to microwave discharge. This indicated the method could be used to investigate the oxidative coupling of CH_4 and partial oxidation of CH_4 to make syngas or oxygenates.

4. Conclusions

The microwave discharge-assisted catalytic conversion of NO was investigated. By comparing the activities of Co/HZSM-5 and Ni/HZSM-5 catalysts in the microwave discharge mode with those in the conventional reaction mode, the reduction of NO by CH_4 in the presence of excess O_2 increased greatly by the action of microwave discharge. Especially over the Ni/HZSM-5 catalyst, the conversion of NO could be as high as nearly 100% at 225 °C in the microwave discharge mode. Moreover, the reaction temperature range for both catalysts could be widened remarkably. The probable mechanism may be that NO_x^* excited by the microwave discharge reacted selectively with activated CH_x in the microwave discharge over the catalysts.

Acknowledgement

Professor Can Li, director of State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, is greatly appreciated for his helpful discussions.

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