

Microwave discharge-assisted catalytic conversion of NO to N₂

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By coupling microwave discharge with an Fe/HZSM-5 catalyst, novel effects have been observed for the conversion of NO to N₂ in the presence of excess oxygen with high efficiency.

The reduction of NO has been investigated for many years. Especially in the past decade, it has attracted much attention.¹ Recently, with the progress of advanced techniques, many papers have described the application of new methods in different branches of chemistry.² Among these techniques, microwave dielectric heating is a convenient and effective way of bringing about chemical reactions in the field of catalysis.³ The use of microwave heating to stimulate catalytic reactions has provided some remarkable results,^{4–6} Bond *et al.* and Wan and co-workers have investigated the effect of microwave heating on many catalytic reactions.⁷ The reduction of NO by CH₄ by a microwave heating technique has also been reported by this laboratory.⁸ Here, we report on a new process for the removal of NO by coupling the microwave discharge (not microwave heating) with the selective catalytic reduction (SCR) reaction by CH₄. We designate this kind of process as catalysis assisted by microwave discharge (CAMD).

A Fe/HZSM-5 catalyst was employed to demonstrate the effect of the CAMD of NO–CH₄. The Fe/HZSM-5 was prepared by impregnating HZSM-5 (SiO₂/Al₂O₃ = 25) in an aqueous Fe(NO₃)₃ solution (Fe in the catalyst was 10 wt%); all catalysts prepared were of 1.25–1.60 mm granule size. The flow rate of the feed, which consisted of 2000 ppm NO, 1600 ppm CH₄ and 2.0% O₂ (helium as a balance gas), was 60 ml min⁻¹ (GHSV = 3600 h⁻¹).

A special quartz tubular reactor (i.d. 10 mm) was aligned vertically at the center of the microwave cavity. The catalyst bed was supported on a fused quartz frit of medium porosity. The gas composition was determined by an on-line NO_x-analyser and gas chromatograph (GC-8800 type, with 13X and PQ columns).

In this work, Fe/HZSM-5 was used not only as a catalyst, but also as a discharge igniter, by which discharge was achieved without any electrode at atmospheric pressure: after the microwaves were induced in the reactor, red discharge with weak sounds was observed among the catalyst granules.

Results obtained over the Fe/HZSM-5 in a conventional reaction mode (CRM) are presented in Table 1. From these data, it is apparent that the Fe/HZSM-5 was almost inactive for the

reduction of NO with CH₄ in excess O₂ in the CRM. When CH₄ was wholly consumed, the conversion of NO to N₂ did not exceed 5%, which is almost in accordance with the results of Chen *et al.*⁹ The results indicate that the activity of the Fe/HZSM-5 catalyst for CH₄–NO reaction is very low in the presence of excess O₂ in the CRM.

Results obtained over Fe/HZSM-5 in the CAMD process are presented in Table 2. It can be seen from these results that the conversion of NO to N₂ is increased to 44.5% in the presence of excess O₂, while at the same time the CH₄ consumption is 50.5%.

In order to confirm the enhancement of the catalytic activity by the microwave discharge, another microwave discharge experiment without any catalyst was conducted and the results are also given in Table 2. In this experiment, the average conversion of NO to N₂ was 18.2%. It can be noted that even the sum of the conversion of NO to N₂ in the microwave discharge mode without any catalyst and that in the CRM were still lower than that of NO to N₂ via CAMD.

From the above results it can be seen that, regardless of temperature, the Fe/HZSM-5 catalyst is inactive in the CRM for the CH₄–NO reaction (Table 1). However, when in the microwave discharge mode the conversion of NO to N₂ on Fe/HZSM-5 increases from *ca.* 5 to 44%. Apparently the catalytic activity of the Fe/HZSM-5 is enhanced remarkably by the microwave discharge. This increase in catalytic activity cannot be readily explained by an increase in reaction temperature, suggesting that microwave discharge can cause non-Arrhenius effects.

As we know, in the CRM all reactants gain energy by thermal conduction. In fact, the reaction of CH₄ with O₂ proceeds more rapidly than the reaction of CH₄ with NO at high temperatures so that a large portion of CH₄ is consumed by O₂, resulting in the restraint of the reaction rate for CH₄ with NO. Therefore, the conversion of NO to N₂ in the presence of excess O₂ is both very low and independent of temperature in the CRM. On the other hand, in the microwave discharge mode a high frequency electromagnetic field is formed easily in the reactor, and since the molecules in the gas phase are transparent to the electromagnetic field no interaction will take place between the electromagnetic field and the gaseous molecules. Our temperature-programmed desorption (TPD) experiments on Fe/HZSM-5 indicated that supported Fe₂O₃ is a good material for the adsorption of NO_x, which agrees well with the report of Otto and Sheref.¹⁰ Moreover, it is known that the high frequency

Table 1 Activity of Fe/HZSM-5 catalyst in the conventional reaction mode^a

T/°C	NO conversion (%)	CH ₄ conversion (%)
300	0.7	2.0
400	4.5	4.5
500	5.0	7.3
600	4.4	9.0
650	3.0	27.3
700	3.3	81.3
740	2.1	100.0

^a Reaction conditions: 2000 ppm NO, 1600 ppm CH₄, 2% O₂, balance He; total flow rate 60 ml min⁻¹ (GHSV = 3600 h⁻¹).

Table 2 Performance of the system with Fe/HZSM-5 catalyst and without a catalyst in the microwave discharge mode^a

Catalyst	Microwave power/W	NO conversion (%)	CH ₄ conversion (%)
Fe/HZSM-5	43–54	40.0	37.1
	54–65	42.0	47.3
	65–76	44.5	50.5
No catalyst	54–65	18.0	70.2
	65–76	18.4	74.1

^a Reaction conditions: 2000 ppm NO, 1600 ppm CH₄, 2% O₂, balance He; total flow rate 60 ml min⁻¹ (GHSV = 3600 h⁻¹).

electromagnetic field is beneficial for the activation of polar molecules. So, it is speculated that the NO_x adsorbed on the Fe/HZSM-5 but not the O_2 in the gas phase, can be activated effectively by the high frequency electromagnetic field. This speculation agrees with the results of our previous paper.⁸ Then again, microwave discharge can produce many active electrons with higher energy and higher temperature, and by the action of these electrons plenty of radicals, especially CH_x , can be produced. However, the average temperature of the gas feed is still very low in the microwave discharge mode, which is beneficial for lowering the energy consumption greatly and hence retarding the reaction of CH_4 with O_2 . Under the same circumstances, the reaction between the activated NO_x adsorbed on the catalyst and the CH_x radicals is easily accelerated by the Fe/HZSM-5 catalyst so that the conversion of NO to N_2 can be enhanced greatly *via* CAMD on the Fe/HZSM-5. Although the mechanism of CAMD is not yet clear, it is likely that the reaction pathways in the CMR are different from those in the CAMD, and this may be the reason why the activity of the Fe/HZSM-5 catalyst varies significantly under the two modes.

In conclusion, the Fe/HZSM-5 catalyst exhibits a rather remarkable catalytic performance in the SCR of NO by CH_4 in the CAMD process, indicating that CAMD has a beneficial effect on the activation of reacting molecules.

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