Catalysis Letters 57 (1999) 187–191

Microwave-assisted NO reduction by methane over Co-ZSM-5 zeolites

Yun-feng Chang *, Angel Sanjurjo, Jon G. McCarty, Gopala Krishnan, Bernard Woods and Eric Wachsman

SRI International, 333 Ravenswood Ave., Menlo Park, CA 94025, USA
E-mail: yun-feng.chang@uslum.mail.abb.com

Received 28 August 1998; accepted 14 December 1998

The microwave-assisted reduction of NO by methane in the presence of oxygen over Co-NaZSM-5, and H-ZSM-5 catalysts was studied. We demonstrated that microwave radiation at 2.45 GHz significantly enhances the catalytic conversion of NO to N_2. High conversions (>70%) of NO were achieved over both Co-NaZSM-5 and Co-HZSM-5 zeolite catalysts at temperatures 250–400 °C. Under similar conditions, thermal runs failed to show significant conversion of either NO or methane.

Keywords: microwave, NO (nitric oxide) reduction, methane as reductant, Co-NaZSM-5, Co-HZSM-5, H-ZSM-5 zeolites as catalysts

1. Introduction

Microwaves have been used in various ways for preparation and processing of zeolites. For example, preparation of Ni/zeolite samples is aided by microwave radiation due to its effectiveness in splitting hydrogen molecules to hydrogen atoms, which reduce Ni^{2+} to the metal [1]. Microwaves have also been used to dehydrate zeolites [2], and a microwave discharge has been used to prepare highly dispersed cobalt clusters in zeolites by decomposition of $Co_2(CO)_8$ [3].

We have investigated the potential effect of microwave radiation in promoting catalytic reactions including oxidative coupling of methane over MgO, CO oxidation over Pt/Al_2O_3 and decomposition of volatile organic compounds (VOC) over silicon carbide (SiC) [4]. The results of this work were system specific. Microwave radiation promoted the oxidative coupling of methane over Na/MgO supported on a commercial iron catalyst at low temperatures and in higher yields than thermal activation. For CO oxidation over Pt/Al_2O_3 (mixed with Fe_3O_4), the microwave effect was marginal compared with conventional heating. For trichloroethylene detoxification over SiC, the microwave-assisted reaction significantly suppressed the formation of noxious byproducts, carbonyl chloride (phosgene) and carbon tetrachloride. Except in the last case, the catalysts were composed of a catalytically active, microwave-transparent phase combined with an effective microwave absorber, i.e., Fe_3O_4. Hence, a large fraction of the microwave energy was used solely for heating the catalyst phase by heat transfer from the microwave absorber Fe_3O_4.

In this work, we chose Co-NaZSM-5 zeolite, because it is not only highly active for selective nitric oxide reduction by methane but also it was found that it is an effective microwave absorber. This characteristic allows us to study the direct effect of microwave radiation on the chemical reaction process occurring on the surface of the catalyst.

Zeolites have been found to be effective in selective reduction of nitric oxide by light hydrocarbons other than methane [5–14] and by methane [15–17] in the temperature range 350–550 °C, particularly in the absence of steam. Co^{2+}-, Mn^{2+}-, Ni^{2+}-, and Ga^{3+}-exchanged ZSM-5 zeolites are active catalysts for NO reduction using methane and Co-ZSM-5 is the most active.

We have examined the microwave-assisted reduction of NO by methane in the presence of oxygen over three ZSM-5 zeolite based catalysts, Co-NaZSM-5, Co-HZSM-5, and H-ZSM-5, and compared the results with those from conventional thermal runs.

2. Experimental

2.1. Catalyst preparation

Three catalysts were prepared to demonstrate the effect of cobalt and the proton on activity and selectivity for the NO–CH_4 reaction. Co-NaZSM-5 zeolite catalyst was prepared by ion exchange of a Na-ZSM-5 sample with a solution of 1.0 M $Co(NO_3)_2$ (AR grade, Aldrich) at room temperature. The parent ZSM-5 zeolite has a silica to alumina molar ratio of 56. XRD analysis of the powder sample reveals high crystallinity and SEM shows the sample consists of aggregates of hexagonal crystals. When this sample converted to proton form H-ZSM-5, it has an acidity of 560 μmol/g measured by exhaustive ion exchange by sodium nitrate aqueous solution carried out at room temperature. Co-HZSM-5 was prepared by refluxing a mixture of H-ZSM-5 and 1.0 M $Co(NO_3)_2$ aqueous solution at a ratio of 1.0 g zeolite to 20 cm^3 solution at 70–80 °C for 12 h. The

---

* To whom correspondence should be addressed.

Table 1
Composition and some properties of the ZSM-5 catalysts.

Catalyst	Co loading (wt%)	Extent of Co^{2+} exchange[a] (%)	Number of H^+ per g of zeolite $[H^+]$ (μmol/g)
Co-NaZSM-5[b]	1.24	75	0
Co-HZSM-5	0.38	23	434
H-ZSM-5	0	0	560

[a] Extent of ion exchange by Co^{2+} based on each Co^{2+} replacing two univalent cations.

[b] The parent NaZSM-5 zeolite has a SiO_2/Al_2O_3 molar ratio of 56 and is in the Na-form: $[Na^+] = 560\ \mu mol\, g^{-1}$ and $[H^+] = 0\ \mu mol\, g^{-1}$.

mixture was then filtered and washed thoroughly with distilled water before being dried at 110 °C. The cobalt loading of the catalysts was determined by the atomic absorption method. The results are summarized in table 1.

2.2. Microwave reactor system

The microwave reactor system is given in figure 1. It consisted of a 1.2 kW, 2.45 GHz magnetron microwave source connected through a rectangular waveguide to a single-mode resonant cavity terminated with a tunable short. The cavity was equipped with taps to measure incident and reflected power. The quartz tubular reactor (i.d. 12 mm) was aligned vertically at the center of the cavity, so that it seated in the region of maximum microwave field intensity. The catalyst bed was supported on a fused quartz frit of medium porosity. The feed gas and gaseous products of reaction were analyzed by an on-line Extrel C50 quadrupole mass spectrometer. The reactor was charged with 0.5 g of catalyst powder for each run. A quartz thermocouple well was seated in the catalyst bed, but thermocouple was inserted and temperature measurements were made only immediately after microwave power was turned off. Such measurements serve to confirm the bed temperature, which was also measured optically with an IRCON Modline Plus 6000 pyrometer (temperature range 240–760 °C) that views the bed temperature through a side tubulation in the waveguide. The pyrometer sensor measures thermal radiation in the wavelength range from 2 to 2.6 μm. It was calibrated against a thermocouple in a resistively heated tubular furnace. During the microwave runs, the pyrometer was focused on a 2 mm diameter spot on the catalyst bed and the indicated temperature was taken as that of the catalyst bed.

In a typical run, the reaction gas mixture, containing 0.1–0.5 vol% NO, 0.5–2.0 vol% O_2, 0.25–3.0 vol% CH_4, and the balance helium, was prepared by metering 1.0 vol% NO (Liquid Carbonic), 5.0 vol% CH_4 (Liquid Carbonic), 2.0 vol% O_2 (Liquid Carbonic), and pure helium (Matheson Gas) into a common manifold. The total flow was varied over the range 50–150 cm^3/min. The amount of microwave radiation applied to the catalyst bed depended on the location of the catalyst bed in the microwave cavity, the nature of the catalyst powder, and how the microwave was tuned. In our experiments, the system was so adjusted to give maximum microwave–catalyst interaction and to bring the catalyst bed temperature to a required level. In some microwave runs, the temperature range investigated was limited because of formation of microwave-induced plasma within the reactor. Plasma formation leads to nonselective NO reduction. All results presented in this paper were obtained in the absence of plasma. The reactor effluent was analyzed by the on-line quadrupole mass spectrometer, using AMU 2 for hydrogen, 15 for methane, 30 for nitric oxide, 32 for oxygen, 46 for nitrogen dioxide, 28 for nitrogen and carbon monoxide, and 44 for carbon dioxide. Signals at AMU 12 and 14 were used to distinguish nitrogen from carbon monoxide.

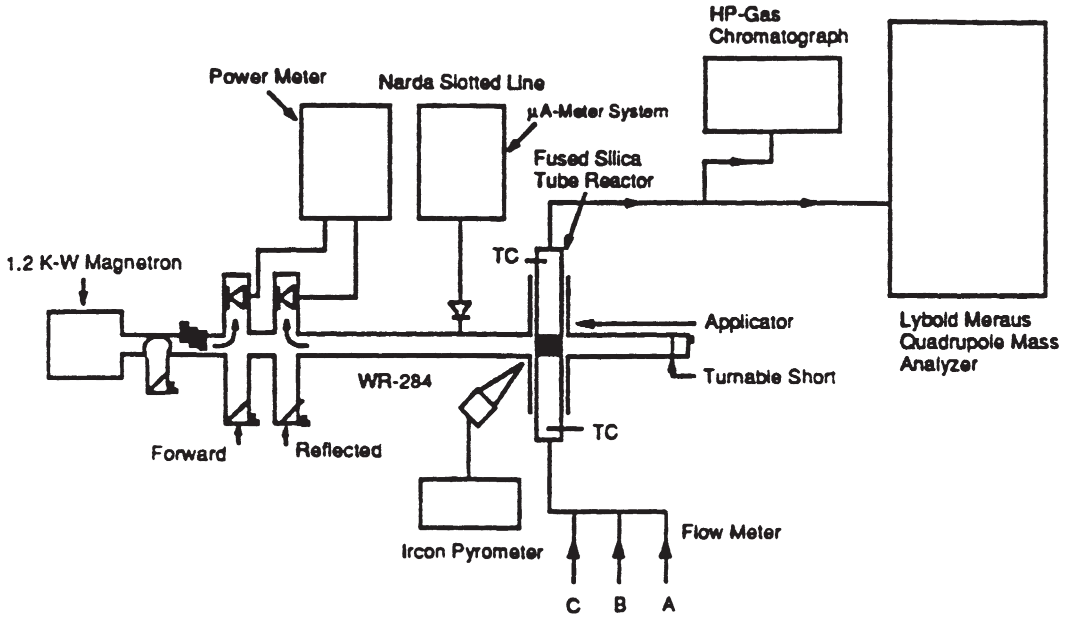

Figure 1. Microwave reactor system.

2.3. Thermal reactor test

For comparison, thermal runs were conducted in a tubular quartz reactor (i.d. 8 mm) under identical gas composition and gas space velocity conditions. The reactor was charged with 0.25 g catalyst for each run. A quartz sheathed thermocouple touched the catalyst bed. The catalyst was exposed to the feed gas stream at 40 °C for 20 min, followed by ramp up at 30 °C min^{-1} to 700 °C. The effluent was analyzed by on-line quadrupole mass spectrometry.

3. Results and discussion

3.1. Microwave runs

3.1.1. Co-NaZSM-5

Results obtained for Co-NaZSM-5 are presented in table 2. The conversion of methane in the temperature range 269–402 °C was nearly complete and the conversion of NO appeared constant at 72%. The power level of the microwave was varied in between 200 and 300 W. No plasma discharge was observed in the reactor during these runs.

3.1.2. Co-HZSM-5

For the Co-HZSM-5 catalyst, the results (table 3) show very high conversion of NO in the temperature range 249–395 °C in the presence of excess methane. Lower temperature resulted in lower NO conversion.

Table 2
Reactivity of Co-NaZSM-5 zeolite catalyst in the reaction of NO, O_2, and CH_4.[a]

Microwave power (W)	Temperature (°C)	Conversion (mol%)		
		CH_4	O_2	NO
210–220	338	100	70	72
	337	100	70	72
	274	95	70	72
	269	95	68	72
230–240	367	100	72	72
	365	100	72	72
250–260	402	100	76	75
	392	100	70	72
	388	100	70	72

[a] Co-NaZSM-5 0.5 g; total flow 100 $\text{cm}^3\,\text{min}^{-1}$; CH_4 0.25 vol%, O_2 0.40 vol%, NO 0.30 vol%.

Table 3
Reactivity of Co-HZSM-5 zeolite catalyst in the reaction of NO, O_2, and CH_4.[a]

Microwave power (W)	Temperature (°C)	Conversion (mol%)		
		CH_4	O_2	NO
100–120	395	33	94	85
	293	37	91	77
	249	37	91	68

[a] Co-HZSM-5 0.5 g; total flow 100 $\text{cm}^3\,\text{min}^{-1}$; CH_4 2.0 vol%, O_2 0.4 vol%, NO 0.4 vol%.

3.1.3. H-ZSM-5

Under similar conditions to Co-HZSM-5 (table 3), H-ZSM-5 (table 4) shows significantly lower fractional conversion of NO compared with O_2.

These results suggest that the presence of Co^{2+} promotes essential selectivity for NO reduction by methane. The additional cation (e.g., Na^+ of H^+) seems to be less important in determining the selectivity for NO reduction by methane, because Co-NaZSM-5 (table 2) and Co-HZSM-5 (table 3) behave similarly under similar conditions.

Based on the microwave power applied and the resulting temperature rise observed in the catalyst bed, it is evident that ZSM-5 zeolite effectively adsorbs microwave radiation. From the relationship between power and bed temperature shown in tables 2–4, it appears that the proton in the zeolite enhances absorption of microwave energy. However, other factors such as bed geometry and position, cavity tuning can also affect microwave coupling.

3.2. Thermal runs

Results obtained from Co-NaZSM-5, Co-HZSM-5, and H-ZSM-5 in thermal runs are presented in tables 5–7. Co-HZSM-5 and H-ZSM-5 are really inactive for the reac-

Table 4
Reactivity of H-ZSM-5 zeolite catalyst in the reaction of NO, O_2, and CH_4.[a]

Microwave power (W)	Temperature (°C)	Conversion (mol%)		
		CH_4	O_2	NO
80–90	402	26	100	35
	395	28	100	42
	389	27	100	42
	370	25	100	35

[a] H-ZSM-5 0.5 g; total flow 100 $\text{cm}^3\,\text{min}^{-1}$; CH_4 2.0 vol%, O_2 0.4 vol%, NO 0.4 vol%.

Table 5
Reactivity of Co-NaZSM-5 zeolite catalyst in the reaction of NO, O_2, and CH_4.[a]

Temperature (°C)	Conversion (mol%)		
	CH_4	O_2	NO
300	2	3	–[b]
340	10	25	–[b]
380	36	46	<1
420	56	70	3
460	76	94	5
500	88	96	9
540	90	99	14
580	93	100	17
620	96	100	19

[a] Co-NaZSM-5 0.25 g; total flow 50 $\text{cm}^3\,\text{min}^{-1}$; CH_4 0.3 vol%, O_2 0.48 vol%, NO 0.3 vol%.

[b] Conversion data not reported due to interference from large amount of NO desorbed during the TPR from 40 to 700 °C at 30 °C min^{-1}.

Table 6
Reactivity of Co-HZSM-5 zeolite catalyst in the reaction of NO, O_2, and CH_4.[a]

Temperature (°C)	Conversion (mol%)		
	CH_4	O_2	NO
300	0	0	–[b]
340	0	0	–[b]
380	3	10	<1
420	10	17	10
460	26	25	20
500	45	47	28
540	65	70	37
580	80	86	42
620	90	85	48

[a] Co-HZSM-5 0.25 g; total flow 50 $cm^3\,min^{-1}$; CH_4 0.3 vol%, O_2 0.48 vol%, NO 0.3 vol%.

[b] Conversion data not reported due to interference from large amount of NO desorbed during the TPR from 40 to 700 °C at 30 °C min^{-1}.

Table 7
Reactivity of H-ZSM-5 zeolite catalyst in the reaction of NO, O_2, and CH_4.[a]

Temperature (°C)	Conversion (mol%)		
	CH_4	O_2	NO
300	0	0	–[b]
340	0	0	–[b]
380	<1	1	0
420	1	3	0
460	2	6	2
500	4	9	5
540	11	12	6
560	14	16	7
600	31	26	12

[a] H-ZSM-5 0.25 g; total flow 50 $cm^3\,min^{-1}$; CH_4 0.3 vol%, O_2 0.48 vol%, NO 0.3 vol%.

[b] Conversion data not reported due to interference from large amount of NO desorbed during the TPR from 40 to 700 °C at 30 °C min^{-1}.

tion of NO and O_2 with methane at temperatures below 400 °C.

Co-NaZSM-5 catalyzes the combustion of methane at temperatures <420 °C. At higher temperatures, some reduction of NO also occurred, but at a much lower level than the reaction of methane with oxygen.

The Co-HZSM-5 catalyst showed the highest activity of all these catalysts for NO reduction at higher temperatures.

The three catalysts studied behave quite differently in the microwave runs and thermal runs at temperature below 400 °C. In the thermal runs, the activity for NO reduction is nearly absent for all these catalysts, and reduction of oxygen is very low. In contrast, under the same thermal conditions in the microwave runs, high conversion of oxygen was achieved on all three catalysts and conversion of NO in excess of 68% was obtained on the Co-exchanged catalysts. H-ZSM-5 is less selective than the others for NO reduction by methane. These results suggest that absorption of microwave energy at the catalyst surface may alter reaction pathways, favoring the reduction of NO by CH_4 rather than O_2 by CH_4. The mechanism may involve microwave activation of NO, leading to direct reaction with CH_4. An alternative pathway could involve formation of NO_2 from the activated NO and O_2. NO_2 is known to react rapidly with organic compounds [11,18]. On the other hand, activation of methane by microwave radiation to form methyl radicals cannot be discounted. Due to the electron structure of the NO molecule, radical in nature, reaction with a methyl radical will lead to the weakening of the N–O bond by donating an electron from the methyl radical to the antiorbital of the NO molecule, thus leading to higher NO conversion rate. Recent findings of Zhang et al. [19] that good catalysts for oxidative coupling of methane, for example, Li/MgO, are also active catalysts for selective reduction of NO by methane support the idea that selective reduction of NO by methane involves methyl radicals. Such microwave-assisted reduction of NO_x by methane over Co-containing zeolite catalysts holds promise for NO_x emission control technologies in a variety of industrial and commercial applications.

Results in table 2 show that very high conversions of methane were achieved at temperatures as low as 270 °C. This temperature is substantially lower than those observed by others under thermal heating conditions using the same type of catalysts. It is clear that the activation of methane is due to combination of Co-containing ZSM-5 zeolites and microwave radiation. This aspect itself deserves further investigation in light of the importance of methane activation in oxidative coupling of methane and partial oxidation of methane to make syngas or oxygenates.

4. Conclusions

We have demonstrated that microwave radiation significantly enhances the catalytic reduction of NO by methane in the presence of oxygen over Co-exchanged ZSM-5 zeolite catalysts. High conversions (>70%) of NO were achieved over both Co-NaZSM-5 and Co-HZSM-5 at temperature 250–400 °C. Under similar conditions, thermal runs essentially show no conversion of NO and substantially lower conversion of methane. The high activity and selectivity for NO reduction by methane achieved on Co-containing ZSM-5 zeolites with microwave radiation is probably due to activation of methane to form methyl radicals at relatively low reaction temperatures.

Acknowledgement

Technical assistance in data acquisition system set-up by Victor Wong is greatly appreciated.

References

[1] D. Olivier, M. Richard, L. Bonneviot and M. Che, in: *Growth and Properties of Metal Clusters*, ed. J. Bourdon (Elsevier, Amsterdam, 1980) p. 193.

[2] M. Roussy and P. Chenot, J. Phys. Chem. 85 (1981) 2199.

[3] R.P. Zerger, K.C. McMahon, M.D. Seltzer, R.G. Michel and S.L. Suib, J. Catal. 99 (1986) 498.

[4] R. Varma, D. Sheu, B.J. Wood and G.N. Krishnan, Microwave-assisted surface-enhanced reactions, Unpublished report, Electric Power Research Institute, contract No. RP8000-45 (1990).

[5] H. Hamada, Y. Kintaichi, M. Sasaki, T. Ito and M. Tabata, Appl. Catal. 64 (1990) L1.

[6] Y. Kintaichi, H. Hamada, M. Tabata, M. Sasaki and T. Ito, Catal. Lett. 6 (1990) 39.

[7] H. Hamada, Y. Kintaichi, M. Sasaki, T. Ito and M. Tabata, Appl. Catal. 70 (1991) L15.

[8] M. Misono and K. Kondo, Chem. Lett. (1991) 1001.

[9] S. Sato, Y. Yu-u, H. Yohiro, N. Mizuno and M. Iwatomo, Appl. Catal. 70 (1991) L1.

[10] S. Sato, H. Hirabay, H. Yohiro, N. Mizuno and M. Iwatomo, Catal. Lett. 12 (1992) 193.

[11] J.O. Petunchi, G. Sill and W.K. Hall, Appl. Catal. B 2 (1993) 303.

[12] M. Iwatomo, in: *Future Opportunities in Catalytic and Separation Technologies*, eds. M. Misono, Y. Moro-oka and S. Kimura (Elsevier, Amsterdam, 1990) p. 121.

[13] Y. Li and W.K. Hall, J. Catal. 129 (1991) 202.

[14] Y. Li and J.N. Armor, Appl. Catal. 76 (1991) L1.

[15] Y. Li and J.N. Armor, Appl. Catal. B 1 (1992) L31.

[16] Y. Li, P.J. Battavio and J.N. Armor, J. Catal. 142 (1993) 561.

[17] Y. Li and J.N. Armor, J. Catal. 145 (1994) 1.

[18] H. Hamada, Y. Kintaichi, M. Sasaki and T. Ito, Appl. Catal. 88 (1992) L1.

[19] X. Zhang, A.B. Walters and M.A. Vannice, J. Catal. 146 (1994) 568.