

Selective catalytic reduction of nitric oxide by methane over cerium and silver ion-exchanged ZSM-5 zeolites

Zhijiang Li, Maria Flytzani-Stephanopoulos*

Department of Chemical Engineering, Tufts University, Medford MA 02155, USA

Received 1 January 1997; accepted 11 May 1997

Abstract

A new catalyst comprising cerium and silver ion-exchanged ZSM-5 zeolite is reported in this paper, for the reduction of nitric oxide by methane in the presence of excess oxygen. The bi-cation exchanged Ce–Ag–ZSM-5 catalyst was very active for this reaction, while either Ce–ZSM-5 or Ag–ZSM-5 alone showed low activity. The presence of oxygen in the feed gas mixture enhanced the activity of the catalyst and the NO conversion to N₂ increased with the CH₄/NO ratio and Ag loading of the zeolite. The presence of water vapor had a small adverse effect on the catalyst activity. The coexistence of Ce and Ag ions in the zeolite is crucial for achieving high NO conversion to N₂. A small amount of cerium is adequate to promote the selective catalytic reduction of NO. The two main functions of Ce ions are (i) to provide the Ag ion sites with NO₂ by catalyzing the oxidation of NO to NO₂ and (ii) to suppress the direct CH₄ oxidation to CO₂. The Ag sites are the active centers where the reaction of NO₂ with CH₄ takes place. © 1997 Elsevier Science B.V.

Keywords: SCR of NO; NO reduction; Methane; Methane oxidation; ZSM-5; Cerium; Silver

1. Introduction

Selective catalytic reduction (SCR) of nitric oxide by methane in the presence of excess oxygen over metal ion loaded zeolites has been studied in recent years as a promising new technology to control NO_x emissions from both stationary and mobile sources. If successful, this process can be an attractive alternative to catalytic reduction of NO_x by NH₃ for power plants, especially gas turbines. It can also be applied to NO_x emission control in lean-burn engines. Various metal ion-exchanged or impregnated zeolite catalysts have

been tested and metal ions such as Co²⁺, Mn²⁺, Ni²⁺, In³⁺, Ga³⁺ and Pd²⁺, etc. have been identified as active for SCR of NO by methane in the presence of excess oxygen when incorporated into certain types of host zeolites, such as ZSM-5, ferrierite, and mordenite [1–14].

To satisfy the stringent emission regulations and various types of exhaust gas streams, the prospective catalysts for SCR of NO must combine several properties, including high activity at high space velocity in the presence of excess oxygen as well as ability to resist SO₂ and H₂O poisoning. Since catalyst properties strongly depend on the support framework and the metal ion incorporated, the choice of active metal ion and support matrix is crucial. Often, the preparation

*Corresponding author.

E-mail: mstephanopoulos@infonet.tufts.edu.

method is also important. For instance, the protonic form Ga-H-ZSM-5 is an active catalyst for SCR of NO by CH₄, while the sodium form Ga/Na-ZSM-5 is not [1]. An attractive feature of the CH₄-SCR catalysts reported to date is that the presence of oxygen in the feed gas actually enhances their activity, while excess O₂ often has no adverse effect. Greater than 90% conversion of NO to N₂ has been reported over a Co-ZSM-5 catalyst at 400°C in the presence of excess oxygen at a space velocity of 7500 h⁻¹ [2]. However, under more demanding operating conditions, e.g. at high space velocity and with the addition of water vapor and SO₂, the conversion of NO to N₂ typically drops to 20–30% [2–5]. The coexistence of H₂O and SO₂ in the feed gas stream has been reported to lower the catalyst activity more than either gas alone [5]. The competition between H₂O and NO for the active Co sites and the poisoning of these sites by SO₂ have been invoked to explain the decline of the catalyst activity. Ga-H-ZSM-5 and In-H-ZSM-5 show very similar behavior in CH₄-SCR [1,6,7]. Both catalysts show higher NO conversion to N₂ and higher selectivity of methane for the SCR reaction than Co-ZSM-5 at high temperatures (>500°C) under dry conditions. However, they are both more sensitive to water vapor than Co-ZSM-5. Mn-ZSM-5 and Mn-ferrierite are high-temperature CH₄-SCR catalysts [8,9]. The conversion of NO to N₂ over these two catalysts does not bend over up to 550–600°C at a space velocity of 30 000 h⁻¹. The activity of Mn-ZSM-5 is comparable to that of Co-ZSM-5 at elevated temperatures. Pd-ZSM-5 was studied by Nishizaka et al. [10,11], Loughran et al. [12], Descorme et al. [13] and Kawai et al. [14]. An important finding for Pd-exchanged ZSM-5 is that the presence of acid sites is necessary for achieving high SCR activity and selectivity of methane. By following the NO₂ intermediate mechanism, Nishizaka et al. [10,11] further concluded that the presence of acidity in the Pd-ZSM-5 catalyst was necessary for the reaction of NO₂ with CH₄, while it had no effect on the NO oxidation to NO₂.

Compared to ZSM-5, ferrierite is a more attractive zeolite host for cobalt in CH₄-SCR under dry and SO₂-free conditions. Co-ferrierite was found to have twice the activity of Co-ZSM-5 at high temperatures (>450°C) and much higher selectivity [8]. The Co²⁺ sites located in the smaller 8-ring channel in the ferrierite framework were thought to possess

higher activity and selectivity than in ZSM-5 [15]. However, more detailed studies revealed that upon addition of 2.5% water vapor, the NO reduction rate was decreased by as much as three times at 450–500°C. In the presence of 53 ppm SO₂, the conversion of NO to N₂ decreased from 60% to 20% at 500°C, showing that Co-ferrierite is inferior to Co-ZSM-5 in terms of its resistance to SO₂ poisoning at dry conditions [8]. In addition to ZSM-5 and ferrierite zeolites, mordenite is also a good host material for cobalt in CH₄-SCR. However, the activity of Co-mordenite is generally lower than that of Co-ZSM-5 [9]. The ranking of the three zeolite hosts for CH₄-SCR of NO in terms of NO conversion to N₂ in a dry gas mixture was reported as: ferrierite>ZSM-5>mordenite. However, based on the results of [5], Co ion-exchanged ZSM-5 and ferrierite have similar activity when both H₂O and SO₂ are present in the feed gas mixture.

Ag-ZSM-5 has been reported as a good SCR catalyst for NO reduction by ethane [16]. More recently, Al₂O₃- and ZSM-5-supported silver catalysts, Ag/Al₂O₃ and Ag/ZSM-5, have been shown active for this reaction by Masuda et al. [17] when CH₃OH and C₃H₆ were used as the reducing agents. However, Ag-ZSM-5 has not been reported as an active catalyst for CH₄-SCR of NO. In the work of Zhang et al. [18,19] on direct NO decomposition, the addition of a second metal ion, i.e. Ce³⁺, in the Cu-ZSM-5 zeolite was found to promote the catalyst activity under both dry and wet conditions. Recently, we have systematically examined the promotion effect of cerium on several metal ion-exchanged ZSM-5 catalysts for CH₄-SCR of NO [20,21]. The largest effect was found upon addition of a small amount of cerium in silver ion-exchanged ZSM-5. This promoted significantly both the activity and the selectivity of the catalyst. In this paper, we report on the promotion effect of cerium on Ag-ZSM-5 and explore the promotion mechanism for the SCR of NO by methane.

2. Experimental

2.1. Sample preparation and characterization

Ce-Ag-ZSM-5, Ag-ZSM-5 and Ce-ZSM-5 catalyst samples were prepared by ion-exchange using

Na-ZSM-5 zeolites as the starting materials. The Na-ZSM-5 samples were obtained from the Davison Chemical Division, W.R. Grace & Co. with Si/Al=13.8 and 21.5. Ag⁺ ion exchange was carried out at room temperature for 24 h using 200 ml silver(I) nitrate solution to exchange 2 g zeolite each time. Various Ag⁺ concentrations from 0.001 to 0.01 M were used to attain different Ag loadings. After exchange the sample was filtered, rinsed with deionized water and dried at 110°C overnight in air. Calcination was performed at 500°C in air for 2 h. If necessary, the exchange was repeated 2–3 times before rinsing to reach high Ag⁺ loading. Since Ag⁺ materials may be sensitive to light, all the above procedures were carried out in the dark. The procedures for preparing Ce-ZSM-5 samples were the same as those for preparing Ag-ZSM-5 zeolites, except that 0.0003–0.01 M cerium(III) nitrate solutions were used and the ion exchange was carried out at 80°C for 2 h. To prepare the bi-cation Ce–Ag-ZSM-5 samples, Na-ZSM-5 was first exchanged with cerium(III) nitrate and then silver(I) nitrate. Rinsing, drying and calcina-

tion of Ce³⁺ exchanged samples were performed before Ag⁺ exchange to stabilize the cerium ions in the zeolite framework [18]. After the calcination step, Ce³⁺ ions can be detected in the zeolite by luminescence as reported recently [19]. The final samples were analyzed by inductively coupled plasma emission spectrometry (ICP, Perkin-Elmer Plasma 40) to determine their elemental composition. Table 1 lists the samples prepared in this work and the corresponding ICP analysis. In Table 1 the number in the parenthesis next to each element indicates the percent exchange level, assuming each Ag⁺ ion exchanges one Na⁺ ion and each Ce³⁺ ion exchanges three Na⁺ ions. The latter may hardly be possible in practice. Rather, it represents the upper bound for Ce³⁺ ion exchange. This calculation may show an artificially high charge balance in the catalyst, i.e. ((3Ce+Ag+Na)/Al) greater than 1. On the other hand, protonation of some sites may be inferred by a charge balance less than unity (see Table 1). Four sets of ion-exchanged samples were prepared in this work including two sets of single Ce³⁺ or Ag⁺ ion-exchanged

Table 1
Preparation of ion-exchanged Ce-, Ag- and Ce–Ag-ZSM-5 catalysts

Sample	Catalysts	Si/Al	Ce/Al	Ag/Al	Na/Al	Preparation conditions
000	Na-ZSM-5	13.8	—	—	1.0	As received
068	Ag(18)-ZSM-5	12.9	—	0.18	0.75	Ag: 0.002 M, once
032	Ag(54)-ZSM-5	12.8	—	0.54	0.33	Ag: 0.01 M, once
043	Ag(77)-ZSM-5	12.4	—	0.77	0.08	Ag: 0.01 M, twice
099	Ce(9)-ZSM-5	13.84	0.03	—	0.75	Ce: 0.0003 M, once
080	Ce(21)-ZSM-5	14.22	0.07	—	0.73	Ce: 0.01 M, once
040	Ce(54)-ZSM-5	13.82	0.18	—	0.54	Ce: 0.01 M, thrice
103	Ce(21)–Ag(11)-ZSM-5	12.81	0.07	0.11	0.60	Ce: 0.01 M, once; Ag: 0.001 M, once
104	Ce(21)–Ag(22)-ZSM-5	13.42	0.07	0.22	0.46	Ce: 0.01 M, once; Ag: 0.003 M, once
106	Ce(21)–Ag(42)-ZSM-5	11.74	0.07	0.42	0.33	Ce: 0.01 M, once; Ag: 0.006M, once
082	Ce(24)–Ag(61)-ZSM-5	13.75	0.08	0.61	0.20	Ce: 0.01 M, once; Ag: 0.01 M, once
071	Ce(24)–Ag(78)-ZSM-5	14.05	0.08	0.78	0.01	Ce: 0.01 M, once; Ag: 0.01 M, twice
083	Ce(21)–Ag(80)-ZSM-5	13.83	0.07	0.80	0.00	Ce: 0.01 M, once; Ag: 0.01 M, thrice
100	Ce(9)–Ag(72)-ZSM-5	13.72	0.03	0.72	0.03	Ce: 0.0003 M, once; Ag: 0.01 M, twice
071	Ce(24)–Ag(78)-ZSM-5	14.05	0.08	0.78	0.01	Ce: 0.01 M, once; Ag: 0.01 M, twice
A36	Ce(39)–Ag(75)-ZSM-5	11.66	0.13	0.75	0.00	Ce: 0.01 M, twice; Ag: 0.01 M, thrice
046	Ce(54)–Ag(67)-ZSM-5	13.20	0.18	0.67	0.02	Ce: 0.01 M, thrice; Ag: 0.01 M, thrice
074	Ce(24)–Ag(76)-ZSM-5	21.45	0.18	0.76	0.00	Ce: 0.0125 M, once; Ag: 0.01 M, thrice
112	Ag(48)-H-ZSM-5	13.3	—	0.48	0.00	Ag: 0.01 M, twice

Na-ZSM-5 was supplied by the Davison Chemical Division, W.R. Grace & Co. Lot no. SMR 5-5829-0994 for Si/Al=13.8; SMR 6-2826-1192 for Si/Al=21.5.

Each Ce ion exchange was performed at 80°C for 2 h with Ce(NO₃)₃·6H₂O purchased from Aldrich, Milwaukee, WI.

Each Ag ion exchange was performed at room temperature in the dark with AgNO₃ purchased from Johnson Matthey Electronics, Ward Hill, MA.

Si, Al, Ce, Ag, Na contents were measured by ICP.

ZSM-5 catalysts, one set of bi-cation exchanged ZSM-5 with a fixed Ce^{3+} exchange level of 21–24% and various Ag^+ loadings (11–80% exchange level, or equivalently 1.1–8.8 wt%), and another set of bi-cation exchanged ZSM-5 with various Ce^{3+} loadings (9–54% ion exchange level or 0.5–2.5 wt%) and approximately fixed Ag^+ ion exchange (70–80%). Sample no. 074 was prepared from the Na-ZSM-5 zeolite with $\text{Si}/\text{Al}=21.5$.

The H-form Ag-HZSM-5 was also prepared in this work to compare it with the Na-form, Ag-NaZSM-5, catalyst. To prepare Ag-HZSM-5, 20 g Na-ZSM-5 ($\text{Si}/\text{Al}=13.8$) were first exchanged with 450 ml of 0.1 M ammonium acetate solution for 5 h at 80°C. After rinsing, the sample was dried at 110°C overnight and then calcined at 500°C for 5 h. ICP analysis confirmed that all Na ions were replaced by protons. The HZSM-5 was then exchanged with Ag^+ ions following the same procedure as described above. All metal ion-exchanged catalysts were prepared from the Na-form except those denoted HZSM-5.

To compare with ion-exchanged Ce–Ag-ZSM-5, catalysts with Ce and Ag supported on Na-ZSM-5, HZSM-5, Al_2O_3 , SiO_2 , $\text{Al}_2\text{O}_3\text{--SiO}_2$ and $\text{ZrO}_2\text{--SO}_4$, as listed in Table 2, were prepared by incipient wetness impregnation. Al_2O_3 (BET surface area=95.5 m^2/g), SiO_2 (BET surface area=191.1 m^2/g) and $\text{Al}_2\text{O}_3\text{--SiO}_2$ (BET surface area=10.6 m^2/g) were purchased from

Johnson Matthey. 2–10 g of the Al_2O_3 or SiO_2 or $\text{Al}_2\text{O}_3\text{--SiO}_2$ were co-impregnated with 10–50 ml cerium(III) nitrate and silver(I) nitrate solution to reach a final Ce loading of 1.05 wt% and Ag loading of 7.7 wt%. The samples were then dried at 110°C overnight and calcined at 500°C for 2 h in air. Sulfated zirconium oxide was produced by calcination of sulfate-doped zirconium hydroxide (obtained from MEI Chemicals, Swinton, Manchester, England) at 700°C for 2 h. The resulting $\text{ZrO}_2\text{--SO}_4$ had a surface area of 63.2 m^2/g . 1.37 ml solution containing 0.6064 g AgNO_3 and 0.1164 g $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was added dropwise and under constant stirring into 4.565 g of the $\text{ZrO}_2\text{--SO}_4$ solid. The final Ce,Ag/ $\text{ZrO}_2\text{--SO}_4$ was dried at 110°C overnight and calcined at 500°C for 2 h in air.

2.2. Catalyst activity tests

Activity tests were carried out in a fixed bed micro-reactor consisting of a 1/2 inch o.d. quartz reactor tube, a temperature controller (OMEGA, CN2040), four mass flow controllers (Brooks, 5850E) and a HP 5790 gas chromatograph (GC) equipped with a thermal conductivity detector (TCD). Typically, 0.2 g sample was loaded in the reactor and was pretreated in He (Airco, 99.999%) at a flow rate of 50 ml/min and a temperature of 500°C for 2 h. After cooling to room temperature, the reactant gas mixture, consisting of

Table 2
Preparation of impregnated Ag, Ce catalysts

Sample	Catalysts	Si/Al	Ce (wt%)	Ag (wt%)
137	Ag/NaZSM-5 ^{a,e}	13.8	—	7.7
113	Ag/HZSM-5 ^{a,b,e}	13.8	—	7.7
110	Ce,Ag/HZSM-5 ^{a,b,f}	13.8	1.05	7.7
109	Ce,Ag/NaZSM-5 ^{a,f}	13.8	1.05	7.7
115	Ce,Ag/ SiO_2 ^{c,g}	—	1.05	7.7
116	Ce,Ag/ Al_2O_3 ^{d,g}	—	1.05	7.7
117	Ce,Ag/ $\text{SiO}_2\text{--Al}_2\text{O}_3$ ^{d,e}	—	1.05	7.7
W7	Ce,Ag/ $\text{ZrO}_2\text{--SO}_4$ ^h	—	1.05	7.7

^aNa-ZSM-5 was supplied by the Davison Chemical Division, W.R. Grace & Co.

^bHZSM-5 was prepared by exchanging NaZSM-5 with 0.1 M $\text{NH}_3(\text{ac})$, purchased from Aldrich, Milwaukee, WI, for 5 h at 80°C.

^c SiO_2 was obtained from The PQ, Valley Forge, PA.

^d Al_2O_3 and $\text{SiO}_2\text{--Al}_2\text{O}_3$ were purchased from Johnson Matthey Electronics, Ward Hill, MA.

^eThe impregnation was performed in the dark using 2 g of zeolite and 15 ml 0.104 M AgNO_3 solution.

^fThe impregnation was performed in the dark using 2 g of zeolite and 15 ml 0.012 M $\text{Ce}(\text{NO}_3)_3$ and 0.104 M AgNO_3 solution.

^gThe impregnation was performed in the dark using 10 g of the solids and 50 ml 0.178 M $\text{Ce}(\text{NO}_3)_3$ and 0.155 M AgNO_3 solution.

^hThe $\text{ZrO}_2\text{--SO}_4$ material was provided by MEI Chemicals, Swinton, Manchester, England. The impregnation was performed in the dark using 4.565 g of $\text{ZrO}_2\text{--SO}_4$ and 1.37 ml 0.2 M $\text{Ce}(\text{NO}_3)_3$ and 2.6 M AgNO_3 solution.

NO or NO₂, CH₄, O₂ and He, was switched in and the temperature was raised to each pre-set point at a rate of 10°C/min in a step-wise fashion. Source gases were Airco certified gas mixtures: 2.94% or 0.476% NO in He, 0.716% NO₂ in He, 4.87% CH₄ in He and 10.0% O₂ in He, used without further purification. In the studies of the effect of water vapor, water was injected into the heated inlet gas line by a calibrated syringe pump. A 10 ft, 1/8 in. o.d. 5A molecular sieve column operated at 40°C was used to separate O₂, N₂, CH₄ and NO. At each temperature steady-state data were collected. The amount of N₂ produced and CH₄ consumed during reaction were used to calculate the conversion of NO to N₂ and the conversion of CH₄ to CO₂. The selectivity of CH₄ is defined here as the ratio of N₂ produced to the amount of CH₄ consumed. No CO was formed under the conditions of these tests. The stability of catalyst performance was routinely checked by returning to a low-temperature after a series of tests in the ascending temperature mode described above.

2.3. Temperature-programmed desorption of NO

Temperature-programmed desorption (TPD) of NO was examined with the Na-ZSM-5, Ce(21)-ZSM-5, Ag(77)-ZSM-5 and Ce(54)-Ag(67)-ZSM-5 catalyst samples. A 1/4 in. o.d. quartz reactor tube and the same temperature controller as above were used. Typically, 0.1 g of sample and a total flow rate of

50 ml/min (STP) were used. The exit gas was monitored on-line by a residual gas analyzer MKS-PPT-200EM. For TPD-NO, the sample was pre-treated for 2 h at 500°C in He. After cooling down to room temperature, a gas mixture of 2.94% NO-He was switched in and adsorption usually lasted for 2 h. To desorb weakly adsorbed NO (from the catalyst and the reactor system), the sample was flushed in He at room temperature overnight (~12 h) until the corresponding signals decreased to background levels. Desorption was carried out in He at a heating rate of 10°C/min from room temperature to 650°C. Species monitored by the mass spectrometer were N(14), O(16), N₂(28), NO(30), O₂(32), N₂O(44) and NO₂(46).

3. Results

Fig. 1(a) and (b) show the NO conversion to N₂ and CH₄ conversion to CO₂, respectively, over single metal ion-exchanged and cerium-promoted Ag-ZSM-5 catalysts. In this figure, the silver ion exchange level is approximately the same for all Ag-containing samples (70–80% exchange level), while the cerium exchange level varies from 0% for Ag(77)-ZSM-5 to 54% for Ce(54)-Ag(67)-ZSM-5. All samples were pre-treated at 500°C in He for 2 h prior to the SCR tests. The feed gas stream contained (mol) 0.5% NO, 0.5% CH₄, 2.5% O₂ and balance He. The contact time

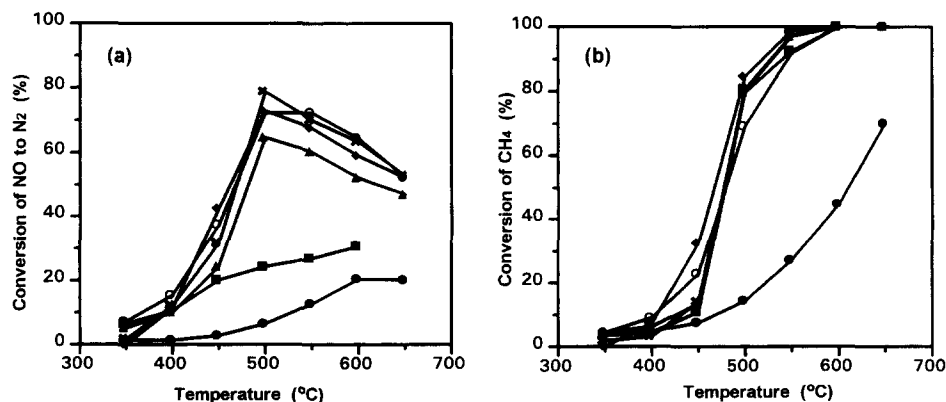


Fig. 1. Promotion effect of Ce ions on the Ag-ZSM-5 catalysts for SCR of NO by CH₄: (a) conversion of NO to N₂; (b) conversion of CH₄. Feed gas: 0.5% NO–0.5%CH₄–2.5% O₂ bal. He. SV=7500 h⁻¹. Symbols: (■) Ag(77)-ZSM-5; (●) Ce(21)-ZSM-5; (▲) Ce(9)-Ag(72)-ZSM-5; (×) Ce(24)-Ag(78)-ZSM-5; (◆) Ce(39)-Ag(75)-ZSM-5; (○) Ce(54)-Ag(67)-ZSM-5.

was 0.25 g s/cc (STP) which corresponds to a space velocity of approximately 7500 h^{-1} . In Fig. 1(a), the conversion of NO to N_2 over the single Ag^+ ion-exchanged catalyst, Ag(77)-ZSM-5, is very low (<30%) over the entire temperature range tested. Other single Ag^+ ion-exchanged Ag-ZSM-5 catalysts with Ag exchange level from 18% to 86% were also tested in this work and no significant effect of Ag loading was found. This indicates that single Ag^+ ion-exchanged Ag-ZSM-5 zeolite is not an effective catalyst for CH_4 -SCR of NO.

The promotion effect of the addition of cerium in Ag-ZSM-5 on the selective catalytic reduction of NO by methane is clearly shown in Fig. 1. Upon addition of cerium, the activity of the catalysts increased significantly, and a volcano-shaped profile of NO conversion to N_2 vs. temperature was obtained. For example, at 500°C with the addition of 9% exchange level of cerium (0.5 wt%), the NO conversion to N_2 increased from 25% for the Ag(77)-ZSM-5 material to 63% for the Ce(9)-Ag(76)-ZSM-5. A further increase of cerium ion exchange to 24% raised to 73% the NO conversion to N_2 , while higher Ce exchange (>24%) had no further effect. From such experiments we found that approximately 20% cerium exchange level could provide the maximum promotion to the Ag-ZSM-5 catalysts. Excess cerium ion exchange is not necessary.

The maximum NO conversion to N_2 in Fig. 1 for Ce-Ag-ZSM-5 catalysts occurs at the temperature of 500°C , i.e. it is shifted by $50\text{--}75^\circ\text{C}$ to higher temperature compared with that for Co-ZSM-5 [4,8]. However, above 500°C , the NO conversion to N_2 decreased very slowly with temperature over Ce-Ag-ZSM-5, while a much faster decrease has been observed with the Co-ZSM-5 [1], In [6] and Pd-HZSM-5 [10,11] catalysts.

To further examine the role of Ce ions, separate activity tests were conducted over single Ce^{3+} ion-exchanged Ce(54)-ZSM-5 and Ce(21)-ZSM-5 catalysts. Identical results were obtained for these two samples. Fig. 1(a) shows the performance of the Ce(21)-ZSM-5 sample. Only 20% NO conversion to N_2 was reached over the Ce(21)-ZSM-5 catalyst. Therefore, the single Ce^{3+} ion-exchanged Ce-ZSM-5 zeolite is not an effective catalyst for the CH_4 -SCR of NO. However, the coexistence of the two low-activity ions, Ce^{3+} and Ag^+ , in ZSM-5 produces a

very active catalyst for SCR of NO by CH_4 . The conversion of NO to N_2 over the bi-cation exchanged Ce-Ag-ZSM-5 catalysts, as shown in Fig. 1, is higher than the sum of the NO conversion over Ce-ZSM-5 and Ag-ZSM-5. This clearly indicates that Ce^{3+} ion addition strongly promotes the catalytic activity of Ag-ZSM-5.

To check if direct NO decomposition took place over the Ce-Ag-ZSM-5 catalysts, NO decomposition tests were carried out with the Ce(54)-Ag(67)-ZSM-5 material both in the absence and in the presence of O_2 . Decomposition of nitric oxide was not observed under either condition.

The promotion effect of Ce ions in the Ce-Ag-ZSM-5 catalysts is further evidenced by the methane conversion over these catalysts shown in Fig. 1(b). Of the two single metal ion-exchanged catalysts, Ag(77)-ZSM-5 shows high activity for CH_4 oxidation at temperatures above 450°C , although it is not very active for CH_4 -SCR of NO as shown in Fig. 1(a). This means that Ag-ZSM-5 is essentially an oxidation catalyst, but not a good catalyst for the SCR of NO by CH_4 . As a result, the selectivity of Ag-ZSM-5 is low in the presence of oxygen. Over the Ce(21)-ZSM-5 material, the CH_4 conversion is much lower than that over the Ag(77)-ZSM-5, indicating that Ce-ZSM-5 is a poor catalyst for CH_4 oxidation. Interestingly, as shown in Fig. 2(b), the bi-cation Ce-Ag-ZSM-5 catalysts have the same total methane conversion as Ag(77)-ZSM-5. Thus, the addition of cerium does not improve the catalyst activity for CH_4 oxidation. The presence of Ce ions promotes only the SCR of NO by CH_4 . Therefore, addition of cerium increases the selectivity of the Ag-ZSM-5 catalyst.

3.1. Effect of Ag loading

To study the effect of silver ion loading, samples with a fixed cerium ion exchange level of approximately 21–24% and various silver ion exchange levels from 0% for Ce(21)-ZSM-5 to 80% for Ce(21)-Ag(80)-ZSM-5 were prepared. A 21–24% cerium exchange level was chosen because it provides the maximum promotion effect on Ag-ZSM-5, as stated above, and at the same time, it is low enough to allow for higher silver ion exchange levels. The results of the activity tests over these catalysts are shown in Fig. 2(a) and (b) for the NO conversion to N_2 and

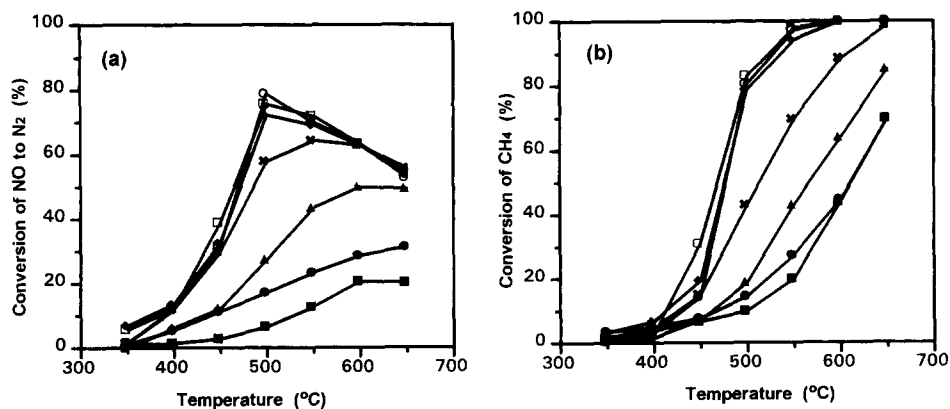


Fig. 2. Effect of Ag ion loading on the SCR of NO by CH₄: (a) conversion of NO to N₂; (b) conversion of CH₄. Feed gas: 0.5% NO–0.5% CH₄–2.5% O₂–bal. He. SV=7500 h⁻¹. Symbols: (■) Ce(21)-ZSM-5; (●) Ce(21)-Ag(11)-ZSM-5; (▲) Ce(21)-Ag(22)-ZSM-5; (×) Ce(21)-Ag(42)-ZSM-5; (◆) Ce(24)-Ag(61)-ZSM-5; (○) Ce(24)-Ag(78)-ZSM-5; (□) Ce(24)-Ag(80)-ZSM-5.

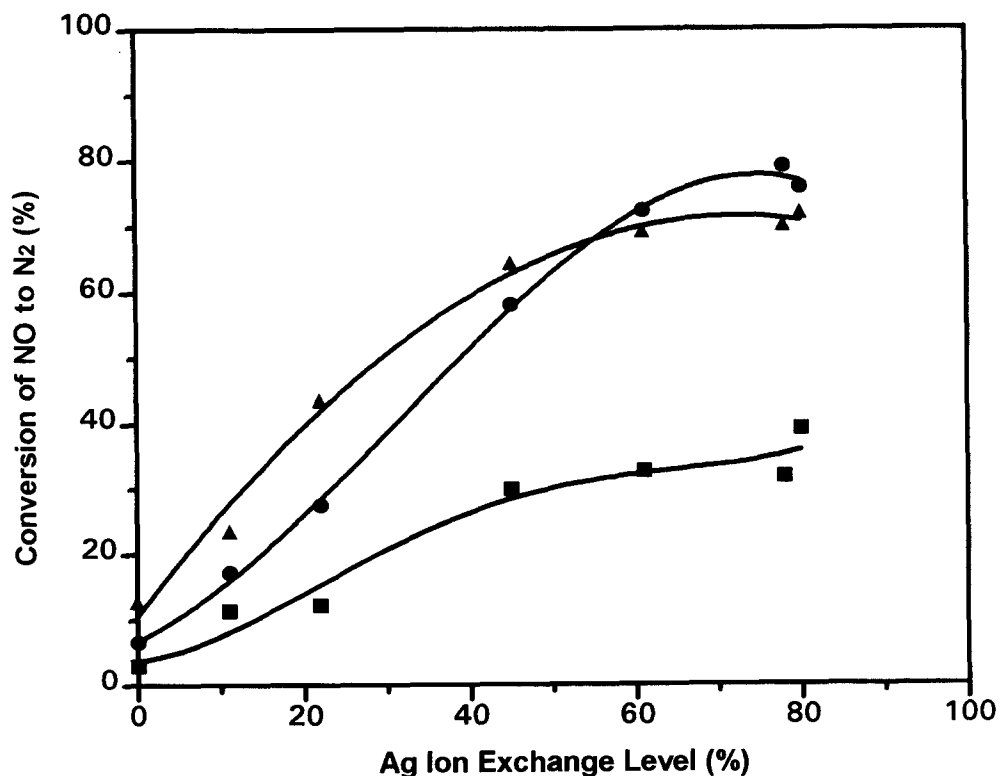


Fig. 3. Correlation between the conversion of NO to N₂ and Ag ion loading. Feed gas: 0.5% NO–0.5% CH₄–2.5% O₂–bal. He. SV=7500 h⁻¹. Ce exchange levels are 21–24%. Symbols: (■) 450°C; (●) 500°C; (▲) 550°C.

CH₄ conversion, respectively. As shown in Fig. 2(a), the NO conversion to N₂ strongly depends on the silver ion exchange level up to ~60% Ag exchange

level. A linear relationship between NO conversion to N₂ and Ag⁺ exchange level is found up to 50–60% Ag loading over the entire temperature range. Fig. 3

shows these data. This indicates that the SCR of NO takes place on Ag^+ -associated sites. Also in Fig. 2(a) the peak position shifted from high temperature (600–650°C) to lower temperature (500°C) as the Ag/Al atomic ratio was increased. Above 60% Ag ion exchange level, no further effect of Ag loading on either the NO conversion to N_2 or the peak position was observed. The silver exchange level also has a strong effect on the total CH_4 conversion as shown in Fig. 2(b). The increase of the CH_4 conversion due to the increase of Ag loading closely matches the increase of NO conversion with Ag loading, indicating that the higher CH_4 conversion at higher Ag loading is due to the consumption of CH_4 for the SCR of NO. This means that the selectivity of CH_4 remains high (does not decrease) with Ag loading in the range of 0–60%, while the SCR activity is increased. For instance, at 500°C the CH_4 selectivity

was calculated to be 0.61, 0.71 and 0.67 for samples with Ag exchanges of 11%, 22% and 42%, respectively.

3.2. Effect of oxygen concentration

The effect of feed gas oxygen on the performance of Ce–Ag–ZSM-5 was studied over the Ce(54)–Ag(67)–ZSM-5 catalyst. The O_2 content varied from 0 to 7 mol% in the gas mixture. The data are shown in Fig. 4. Similar to what has been observed over other metal ion-exchanged ZSM-5 catalysts, i.e. Co–ZSM-5 [2] and Pd–HZSM-5 [10], oxygen is necessary for the effective reduction of NO by methane over the Ce–Ag–ZSM-5 catalyst. Conversions of NO to N_2 and CH_4 to CO_2 increased linearly with oxygen up to ~0.5% at these test conditions and continued to increase up to 1% O_2 in the gas mixture. However,

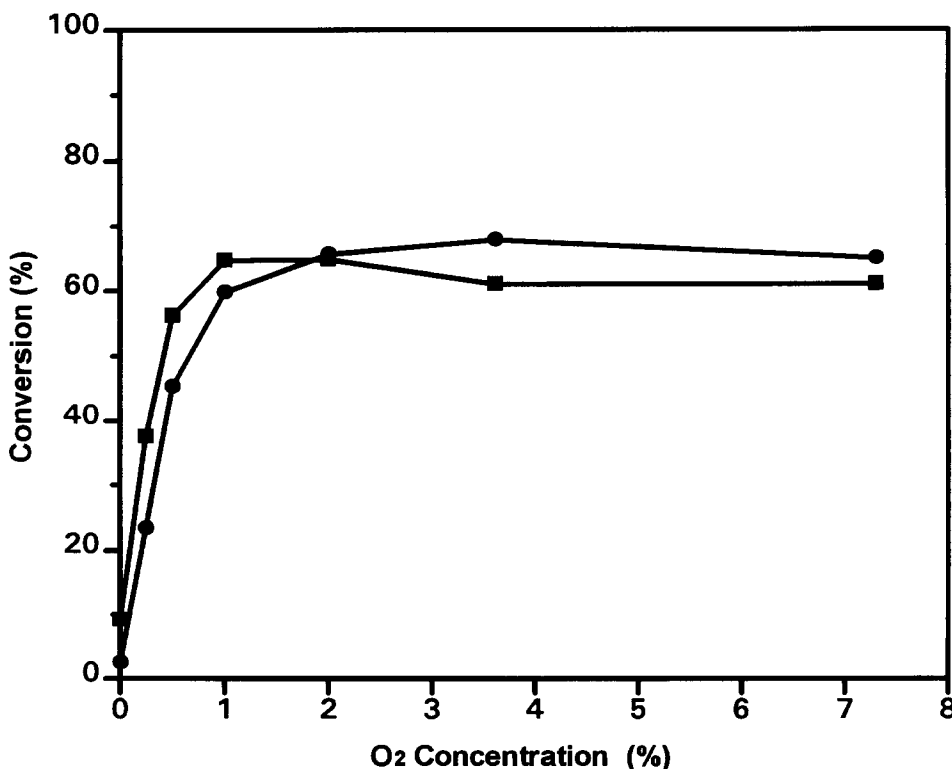


Fig. 4. Effect of O_2 concentration in the feed gas on the SCR of NO by CH_4 over the Ce(54)–Ag(67)–ZSM-5 catalyst. Feed gas: 0.5% NO–0.5% CH_4 – $x\%$ O_2 –bal. He. $T=500^\circ\text{C}$, $\text{SV}=7500\text{ h}^{-1}$. Symbols: (■) conversion of NO to N_2 ; (●) conversion of CH_4 .

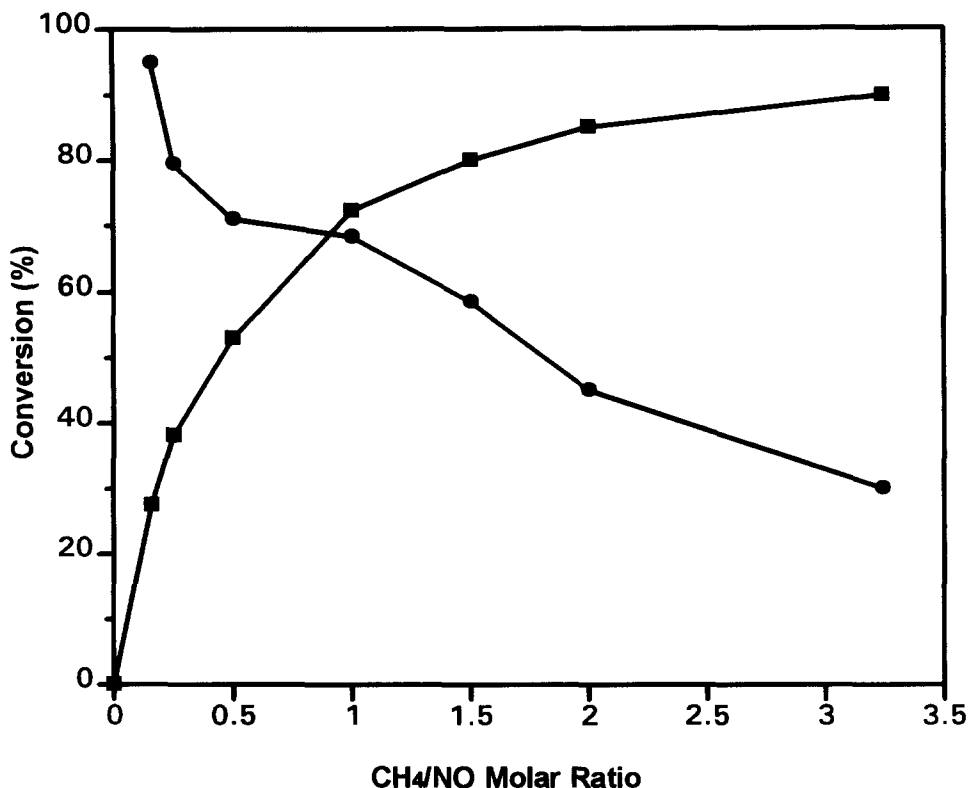


Fig. 5. Effect of CH₄/NO ratio in the feed gas on the SCR of NO by CH₄ over the Ce(54)–Ag(67)-ZSM-5 catalyst. Feed stream: 0.5% NO–*x*% CH₄–2.5% O₂–bal. He. *T*=500°C, SV=7500 h⁻¹. Symbols: (■) conversion of NO to N₂; (●) conversion of CH₄.

as shown in Fig. 4, above ~1.0% oxygen, little effect on either the NO or the CH₄ conversion was observed.

3.3. Effect of CH₄/NO molar ratio

Fig. 5 shows the effect of the CH₄/NO molar ratio on the NO and CH₄ conversions over the Ce(54)–Ag(67)-ZSM-5 catalyst at 500°C at an oxygen content of 2.5%. The conversion of NO to N₂ depends strongly on the CH₄/NO molar ratio in the feed gas stream. As can be seen from this figure, conversion of NO cannot proceed in the absence of CH₄, confirming that Ce–Ag-ZSM-5 is not an active catalyst for the direct NO decomposition. At the test condition, the NO conversion to N₂ increased rapidly with the CH₄/NO molar ratio at low CH₄/NO ratios and then the rate of increase leveled off as the CH₄/NO ratio reached a value greater than ~1.0. Similar results were reported

over Co-ZSM-5 by Li et al. [2] and over Ga-HZSM-5 by Yogo et al. [6].

3.4. Space velocity effect

The performance of the Ce–Ag-ZSM-5 catalyst at high space velocity was studied over the Ce(54)–Ag(67)-ZSM-5 material at 30 000 h⁻¹. Fig. 6 shows the conversion of both NO to N₂ and CH₄ to CO₂ under these conditions. Compared to the data of Fig. 1 for the same sample at SV=7500 h⁻¹, the conversions are lower, while the maximum NO→N₂ conversion shifted to higher temperature (600°C). However, as shown in Fig. 6, at the high space velocity of 30 000 h⁻¹, the Ce(54)–Ag(67)-ZSM-5 catalyst still has high activity (55–60% NO conversion to N₂) in the high temperature range (550–600°C). These conversions are higher than those reported for Co-ZSM-5 catalysts (32% at 500°C and 20% at 550°C) [5].

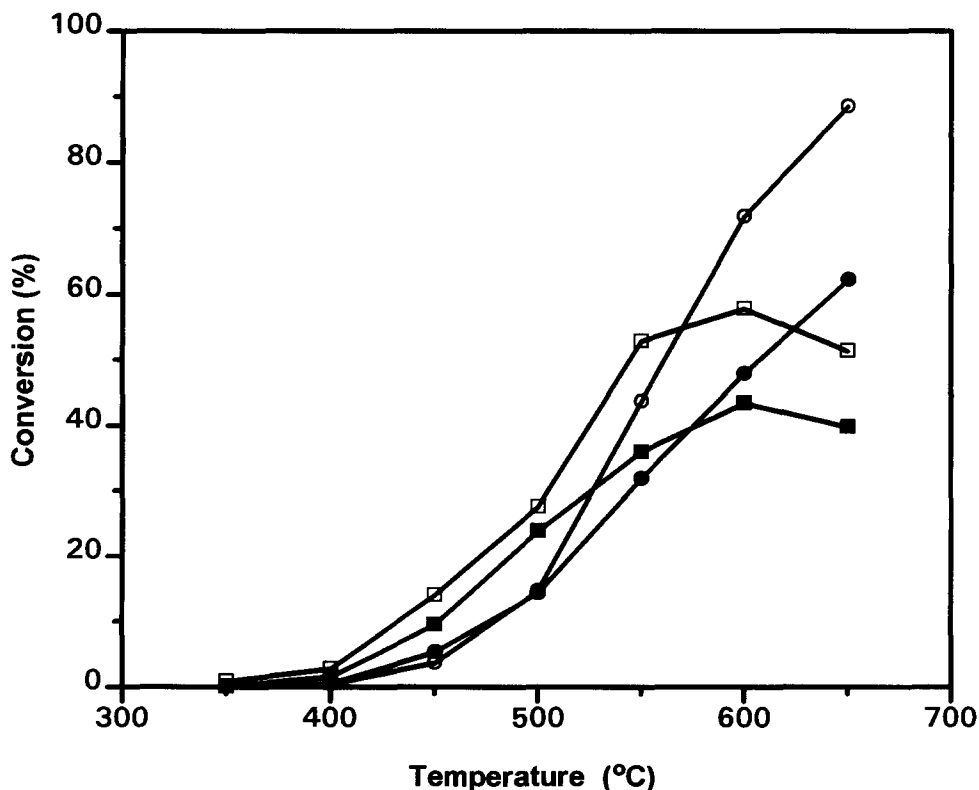


Fig. 6. CH₄-SCR of NO at dry and wet conditions and at high space velocity over the Ce(54)–Ag(67)-ZSM-5 catalyst. Feed gas: 0.5% NO–0.5% CH₄–2.5% O₂ (–8.3% H₂O)–bal. He. SV=30 000 h^{–1}. Symbols: (□) NO to N₂ in dry gas; (■) NO to N₂ in wet gas; (○) CH₄ in dry gas; (●) CH₄ in wet gas.

3.5. Effect of water vapor

The effect of water vapor was evaluated over the Ce(54)–Ag(67)-ZSM-5 catalyst in a wet gas mixture consisting of 0.5% NO, 0.5% CH₄, 2.5% O₂, 8.3% H₂O, bal. He, at the high space velocity of 30 000 h^{–1}. The data are shown in Fig. 6. Compared with the dry-gas conversion at the same space velocity, both the NO conversion to N₂ and the methane conversion decreased upon the addition of 8.3% water vapor in the feed gas mixture. A larger drop was observed at high temperatures (>550°C), while at lower temperatures (<500°C), only ~5% decrease of NO conversion to N₂ and no effect on the CH₄ conversion were observed. After the high-temperature data were collected, we checked again the dry-gas activity of the catalyst. The activity could not be restored to its initial level, indicating that H₂O, especially after the 600–650°C exposure, had caused some irreversible struc-

tural changes to the catalyst. Sintering of silver or partial dealumination of the zeolite [18,19,22] can be invoked to explain these data. Further experiments were conducted isothermally at 500°C in cyclic dry/wet conditions as shown in Fig. 7. Over a period of 70 h the conversion over the Ce(24)–Ag(78)-ZSM-5 catalyst stabilized at approximately 55% for NO to N₂ and 40% for CH₄ to CO₂, respectively. Interestingly, the selectivity increased under wet conditions as the conversion of CH₄ dropped much more than that of NO to N₂ in the wet gas stream (Fig. 7). It is noteworthy that the Ce–Ag-ZSM-5 catalyst shows much higher stability in wet gas streams than the Ce–Cu-ZSM-5 system at 500°C. The latter catalyst was reported to possess higher hydrothermal stability and activity for NO decomposition than unpromoted Cu-ZSM-5 in recent work [19]. It is possible that the presence of Ce³⁺ species in the Ce–Ag-ZSM-5 catalysts stabilizes the Ag ions in their active coordination

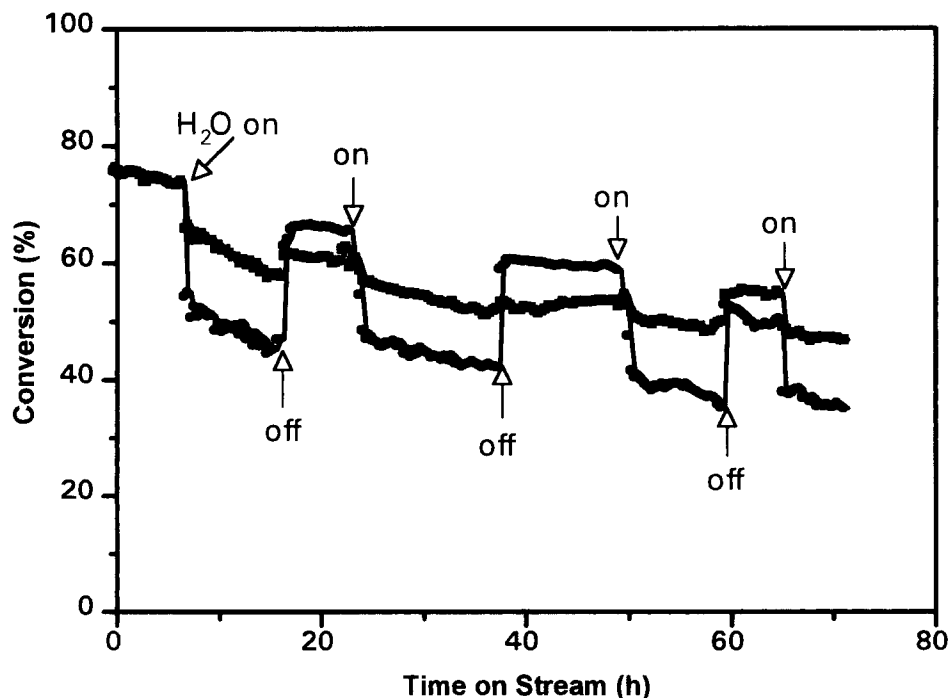


Fig. 7. Dry-wet cyclic test at 500°C over the Ce(24)-Ag(78)-ZSM-5 catalyst. Feed stream: 0.5% NO-0.5%CH₄-2.5%O₂ (-4.1% H₂O)-bal. He. SV=7500 h⁻¹. Symbols: (■) conversion of NO to N₂; (●) conversion of CH₄.

within the ZSM-5 framework and prevents the formation of large Ag clusters under wet conditions.

3.6. Studies of support effects

The effect of Si/Al ratio in the parent ZSM-5 was briefly studied on two ZSM-5 zeolites with Si/Al=13.8 and 21.5. Some results from these tests are listed in Table 3. For this range of Si/Al ratio, no significant effect on the conversion of NO to N₂ was found. However, over the catalyst with the higher Si/Al ratio of 21.5, the maximum conversion of NO to

N₂ shifted to a higher temperature (550°C), and the conversion of CH₄ decreased.

Other Ce, Ag-based materials were also prepared in this work to compare with the ion-exchanged Ce-Ag-ZSM-5 catalysts. As shown in Table 2, these materials include Ag⁺ ion-exchanged H-ZSM-5, Ag-HZSM-5, Ag-impregnated Na- and H-form, Ag/NaZSM-5 and Ag/HZSM-5, Ce and Ag co-impregnated on sodium and H-form, Ce,Ag/NaZSM-5 and Ce,Ag/HZSM-5, Ce and Ag co-impregnated on open supports: Ce,Ag/SiO₂, Ce,Ag/Al₂O₃, Ce,Ag/SiO₂-Al₂O₃ and Ce,Ag/ZrO₂-SO₄ catalysts. The Ce and Ag loadings on these

Table 3
Effect of Si/Al ratio on the activity of Ce-Ag-ZSM-5 catalysts

Sample	Catalyst	Si/Al	Conversion of NO to N ₂ (%)				Conversion of CH ₄ (%)			
			450°C	500°C	550°C	600°C	450°C	500°C	550°C	600°C
071	Ce(24)-Ag(78)-ZSM-5	13.8	31	78	70	63	14	80	97	100
074	Ce(24)-Ag(76)-ZSM-5	21.5	30	68	75	68	18	55	84	97

The feed gas mixture was 0.5% NO-0.5% CH₄-2.5% O₂-bal.He; SV=7500 h⁻¹.

Table 4
Activity of Ce, Ag-based catalysts

Sample	Catalyst	Conversion of NO to N ₂ (%)			Conversion of CH ₄ (%)		
		400°C	500°C	600°C	400°C	500°C	600°C
032	Ag(54)-NaZSM-5	9	23	24	4	81	100
112	Ag(48)-HZSM-5	11	30	37	6	17	24
137	Ag/NaZSM-5	5	34	35	4	40	65
113	Ag/HZSM-5	21	32	35	10	44	65
110	Ce,Ag/HZSM-5	28	63	53	12	70	96
109	Ce,Ag/NaZSM-5	8	46	39	8	57	82
115	Ce,Ag/SiO ₂	0	0	6	0	9	33
116	Ce,Ag/Al ₂ O ₃	5	17	17	43	93	100
117	Ce,Ag/SiO ₂ ·Al ₂ O ₃	0	0	0	0	0	0
W7	Ce,Ag/ZrO ₂ -SO ₄	6	21	37	2	27	70

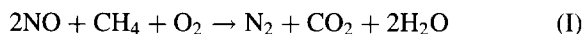
The feed gas mixture was 0.5% NO–0.5% CH₄–2.5% O₂–bal. He; SV=7500 h⁻¹.

samples were kept approximately constant, at 1.05 and 7.7 wt% for Ce and Ag, respectively. The results of the activity tests over these materials are shown in Table 4. By comparing the data obtained over the Ag(54)-NaZSM-5 and Ag(48)-HZSM-5 catalysts in this table, it can be seen that the presence of ~50% protons (relative to Al) in the zeolite had little effect on the NO conversion to N₂, while it decreased the CH₄ conversion by a factor of four at temperatures above 500°C. Thus, the presence of protons improves the catalyst selectivity. Although the single silver impregnated Ag/HZSM-5 contains more Ag than the ion-exchanged Ag(48)-HZSM-5, it has almost the same activity for converting NO to N₂ as the latter. Also, its methane conversion efficiency was higher, probably due to lower silver dispersion. In the presence of Ce, both the impregnated Ce,Ag/HZSM-5 and Ce,Ag/NaZSM-5 catalysts showed increased SCR activity compared to Ag/HZSM-5 and Ag/NaZSM-5. Thus, Ce ions promote the catalytic activity in both ion-exchanged and impregnated Ag-ZSM-5 catalysts. Among the open supports in Table 4, SiO₂ and SiO₂·Al₂O₃ were not attractive. In fact, Ce,Ag/SiO₂ and Ce,Ag/SiO₂·Al₂O₃ were completely inactive for SCR of NO by CH₄. However, Ce,Ag/Al₂O₃ and Ce,Ag/ZrO₂-SO₄ showed measurable conversion of NO to N₂. In particular, the latter has both better activity and selectivity than the former and is better than the single ion-exchanged Ag(54)-NaZSM-5 (Table 4). In other similar work in this laboratory, Kazazis [23] has recently shown that the system

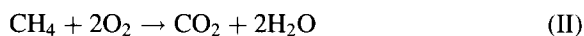
Ag,Ce/ZrO₂ is both active and stable in wet SCR of NO by CH₄.

4. Discussion

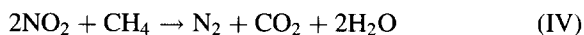
In parallel with the CH₄-SCR reaction



the direct methane oxidation also takes place



These two reactions compete with each other for CH₄, which is generally thought to lead to the volcano-shaped profile of NO conversion to N₂ vs. temperature, as more CH₄ is consumed by reaction (II) at higher temperatures. The enhancement of the catalyst activity for NO reduction by hydrocarbons when O₂ is present in the feed gas stream may be explained by the formation of an oxygen-containing intermediate, in the simplest case NO₂ [6,24,25]. In the case of reaction (I), this mechanism implies the two-step reaction



As described above, the addition of Ce ions in Ag-ZSM-5 significantly promotes the activity of the latter and the selectivity of CH₄ for SCR of NO. In this section, we explore the promotion mechanism by examining: (1) the adsorption of NO on Ag-, Ce-,

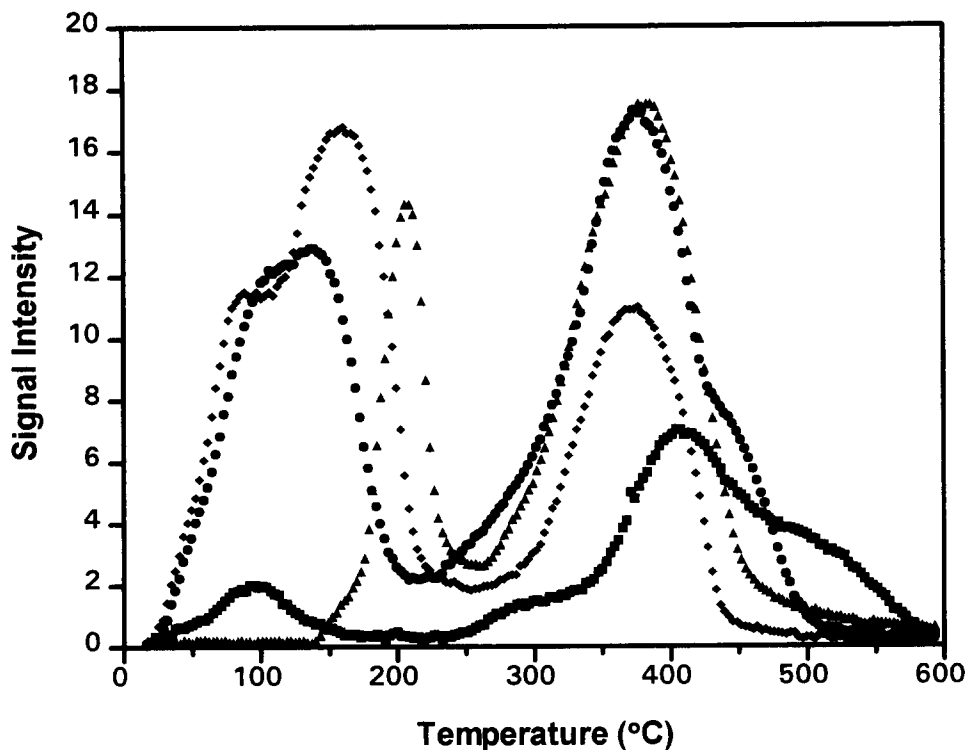


Fig. 8. TPD of NO adsorbed at room temperature over Na-, Ce-, Ag- and Ce-Ag-ZSM-5 catalysts. Symbols: (■) Na-ZSM-5; (●) Ag(77)-ZSM-5; (▲) Ce(21)-ZSM-5; (◆) Ce(24)-Ag(78)-ZSM-5.

and Ce-Ag-ZSM-5 catalysts; (2) the role of Ce and Ag ions in catalyzing the CH_4 -SCR of NO (reaction (I)), and (3) the role of Ce and Ag ions in catalyzing the CH_4 combustion (reaction (II)).

4.1. Adsorption of NO

The adsorption of NO on the Ag-, Ce-, and Ce-Ag-ZSM-5 catalysts was studied by TPD of NO adsorbed at room temperature over the Ce(21)-, Ag(77)-, and Ce(54)-Ag(67)-ZSM-5 catalysts. The TPD-NO profiles for these three samples are shown in Fig. 8 together with the baseline profile for the parent zeolite Na-ZSM-5. The Na-ZSM-5 zeolite has two major NO desorption peaks located at $\sim 100^\circ\text{C}$ and 400°C and two shoulder peaks at 300°C and 500°C . The Ag^+ ion-exchanged Ag(77)-ZSM-5 catalyst has two overlapping peaks at 120°C and 140°C and one sharp peak at $\sim 370^\circ\text{C}$. A shoulder at 460°C is also seen. The Ce^{3+} ion-exchanged Ce(21)-ZSM-5 has two clear peaks located at 210°C and 370°C . The bi-cation Ce(54)-

Ag(67)-ZSM-5 has three peaks: two at low temperatures (90°C and 140°C) and one at high temperature (370°C). These TPD-NO profiles are quite similar to those obtained over Cu-ZSM-5 catalysts [26] where two peaks, one at high temperature (380°C) and the other at low temperature ($\sim 90^\circ\text{C}$) were observed. However, they are very different from the TPD-NO profiles for Co-ZSM-5 reported by Li et al. [4]. The NO desorption peaks from Co-ZSM-5 catalysts were found mainly at low temperatures ($<300^\circ\text{C}$), were very broad and overlapped with each other. Only a very small peak appeared at temperatures above 370°C . Compared with the metal ion-exchanged ZSM-5 zeolites in Fig. 8, the parent Na-ZSM-5 zeolite only adsorbed a small amount of NO. With the incorporation of either Ag^+ or Ce^{3+} ions alone or together in the zeolite, the NO adsorption capacity increased significantly, especially in the low temperature range. The areas under the desorption curves indicate that both the single metal-loaded Ag- and Ce-ZSM-5 zeolites can adsorb a large amount of NO which is very similar

to that obtained over the bi-cation Ce(54)–Ag(67)–ZSM-5 material. However, based on the fact that neither Ag(77)–ZSM-5 nor Ce(21)–ZSM-5 is an effective SCR catalyst, it is reasonable to expect that NO adsorbed on either the Ce or Ag sites alone would not be converted to N₂ effectively without the presence of the other ion. But this does not rule out the possibility of the formation of intermediates on either of the two metal sites.

It is interesting to compare the peak position of these TPD–NO curves. As can be seen from Fig. 8, all three types of catalysts (i.e. Ag(77)–, Ce(21)–, and Ce(54)–Ag(67)–ZSM-5) have a peak appearing at the same high temperature (370°C). However, the location of the low temperature peaks is different. Ag(77)–ZSM-5 started to desorb NO as soon as the temperature was increased from room temperature, indicating that it adsorbed this portion of NO weakly. The first NO peak for the Ce(21)–ZSM-5 appeared at 210°C which is 120°C higher than the first peak obtained over the Ag(77)–ZSM-5, implying that NO was more strongly adsorbed on the Ce–ZSM-5 zeolite. The low temperature peak for the bi-cation Ce(54)–Ag(67)–ZSM-5 catalyst is interesting. This is found at ~160°C, i.e. midway between the low temperature peaks for Ce(21)–ZSM-5 (210°C) and for Ag(77)–ZSM-5 (120°C). This peak probably resulted from NO adsorbed on sites associated with both Ag and Ce ions. It may be indicative of the interaction of Ce³⁺ and Ag⁺ ions in ZSM-5.

4.2. The role of Ag and Ce in CH₄–SCR of NO

As shown in Figs. 2 and 3, the conversion of NO to N₂ over the Ce–Ag–ZSM-5 catalyst increases linearly with the Ag loading from 0% to ~60% exchange level, i.e. from 0% to ~6.7 wt%. This means that with the increase of the number of Ag⁺ ions, the activity of the catalyst increased accordingly, implying that reaction (I) takes place on Ag-associated sites. However, as indicated in Fig. 1, the formation of N₂ would not proceed extensively without the presence of Ce³⁺ ions. In fact, the conversion of NO to N₂ increased dramatically upon the addition of Ce³⁺ ions. Therefore, Ce³⁺ ions must also contribute to the reaction of NO with CH₄.

In a study of NO reduction by propane over Ce–ZSM-5 catalysts by Yokoyama et al. [27], Ce–ZSM-5

was found to have certain unique properties. In addition to its ability to adsorb a large amount of NO, as shown above, Ce–ZSM-5 is also capable of oxidizing NO to NO₂ in the presence of oxygen. This suggests that a potential role of the Ce³⁺ ions in the Ce–Ag–ZSM-5 catalyst is to adsorb NO and convert it to NO₂, while the reaction of NO₂ with CH₄ takes place on Ag sites. More importantly, the oxidation property of the Ce–ZSM-5 is not so strong as that of several oxide materials studied by Yokoyama et al. [27], including CeO₂, Mn₂O₃, CuO, etc. In general, if a catalyst is strongly oxidizing, e.g. CuO or Cr₂O₃, the reaction of CH₄ with O₂ would preferably take place. Ce–ZSM-5, however, is a moderate or weak oxidation catalyst. In separate CH₄ oxidation tests, we found Ce–ZSM-5 to be a poor catalyst for the direct CH₄ oxidation, although it can catalyze the reaction of NO→NO₂ well [21,27]. The reaction of CH₄ with O₂ does not light off on Ce–ZSM-5 catalyst until the temperature is above 550°C (see below). Thus, an important property of Ce–ZSM-5 is that it selectively catalyzes the NO oxidation to NO₂ rather than the CH₄ combustion. As a promoter of Ag–ZSM-5, cerium ions selectively enhance the SCR reaction, by providing NO₂ as the (preferred) oxidant of methane.

To further examine this hypothesis, NO₂ was substituted for NO in tests over the Ag(77)–, Ce(54)– and Ce(54)–Ag(67)–ZSM-5 catalysts using a feed gas of 0.2% NO₂, 0.5% CH₄, 2.5% O₂, and balance He. The results are shown in Fig. 9(a) and (b) in terms of NO₂ conversion to N₂ and CH₄ conversion to CO₂, respectively. For comparison, the corresponding conversions for NO and CH₄ are shown in Fig. 10(a) and (b) under the same operation conditions. Clearly, the switch to NO₂ increased the production of N₂ over the Ag(77)–ZSM-5 catalyst significantly (Fig. 9(a) and Fig. 10(a)), especially in the low temperature range (<450°C), where it became identical to that of Ce(54)–Ag(67)–ZSM-5 (Fig. 9(a)). This indicates that once NO₂ is available (either gas-phase or adsorbed), the Ag–ZSM-5 is capable of converting NO₂ to N₂. The corresponding CH₄ conversion was also increased, Fig. 9(b). The high-temperature deviation of the performance of Ag(77)–ZSM-5 from that of the bi-cation Ce(54)–Ag(67)–ZSM-5 in Fig. 9(a) can be explained in part by a decrease in the concentration of gas-phase NO₂, as determined by the equilibrium of the decomposition reaction of NO₂→NO. In other experiments

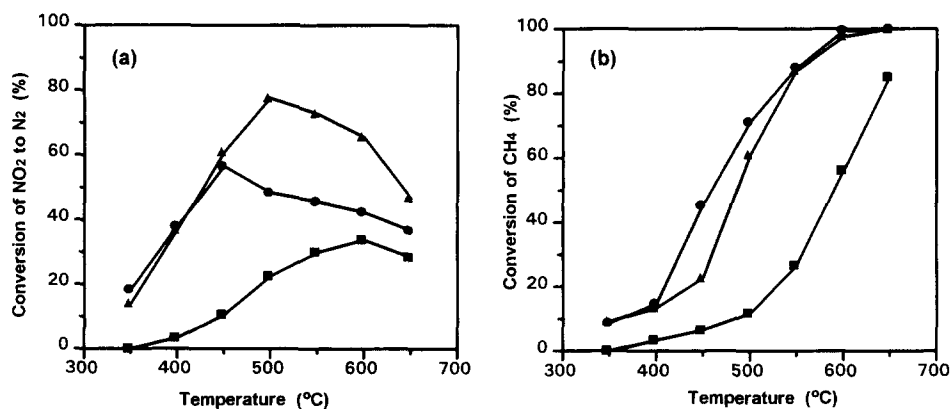


Fig. 9. SCR of NO₂ by CH₄ over Ce-, Ag- and Ce-Ag-ZSM catalysts: (a) conversion of NO₂ to N₂; (b) conversion of CH₄. Feed gas: 0.2% NO₂-0.5% CH₄-2.5% O₂-bal. He. SV=7500 h⁻¹. Symbols: (■) Ce(54)-ZSM-5; (●) Ag(77)-ZSM-5; (▲) Ce(54)-Ag(67)-ZSM-5.

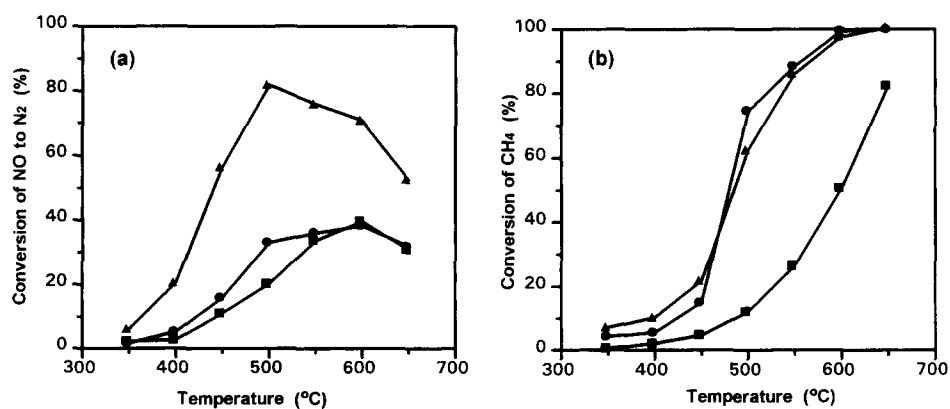


Fig. 10. SCR of NO by CH₄ over Ce-, Ag- and Ce-Ag-ZSM catalysts: (a) conversion of NO to N₂; (b) conversion of CH₄. Feed gas: 0.2% NO-0.5% CH₄-2.5% O₂-bal. He. SV=7500 h⁻¹. Symbols: (■) Ce(54)-ZSM-5; (●) Ag(77)-ZSM-5; (▲) Ce(54)-Ag(67)-ZSM-5.

Table 5

Conversion of NO₂ and NO to N₂ over Ag(77)- and Ce(54)-Ag(67)-ZSM-5 catalysts (%)

Catalysts	0.2% NO ₂ +0.5% CH ₄			0.2% NO+0.5% CH ₄ +2.5% O ₂		
	400°C	450°C	500°C	400°C	450°C	500°C
Ag(77)-ZSM-5	44	45	35	5	16	33
Ce(54)-Ag(67)-ZSM-5	34	44	39	20	56	81

The space velocity for these experiments was 7500 h⁻¹.

(Table 5) we found that the NO₂ conversion to N₂ over the Ag(77)-ZSM-5 material in the absence of oxygen was higher than the NO conversion to N₂ when the feed gas contained NO, CH₄ and O₂ at temperatures below 500°C. As reported by Lukyanov et al. [28] a substantial fraction of the inlet NO₂ (>95%) would

reach the catalyst bed before it decomposed into NO and O₂ in gas phase at conditions similar to those used here even without O₂ in the feed gas. At high-temperatures, however, the presence of 'prompt' NO₂ from the cerium ion centers may be more important than gas-phase NO₂ for the NO-CH₄-O₂ reaction.

Such adsorbed NO_2 is unavailable to the Ag(77)-ZSM-5 material.

The importance of the proximity of Ce ions to silver in regards to the adsorbed NO_2 pathway is evident. Confirming results were obtained by testing of well-mixed powders of Ag(77)- and Ce(54)-ZSM-5. After pretreatment with He for 2 h at 500°C , the NO conversion to N_2 over the physically mixed catalysts was intermediate between the values for the Ag(77)- and Ce(54)-Ag(67)-ZSM-5 materials. However, no enhancement of the SCR activity of Ag-ZSM-5 was observed in a 'zoning' control experiment, whereby a first zone of Ce(54)-ZSM-5 catalyst was placed over a second zone of Ag(77)-ZSM-5.

The above function of Ce ions cannot be provided by protons. For example, the Ag(48)-HZSM-5 catalyst has much lower SCR activity than the Ce(21)-Ag(42)-ZSM-5 material, while it is comparable to the sodium form of the catalyst, Ag(54)-NaZSM-5 (see Table 4). Thus, the presence of the protons does not promote the

SCR activity of a well dispersed silver ion-exchanged zeolite. In other words, acidity is not an important factor in CH_4 -SCR of NO over silver ion-exchanged ZSM-5. One possible reason for this is that NO may not be oxidized to NO_2 on the proton sites, which is in agreement with the report over Pd-HZSM-5 by Nishizaka et al. [11] which stated that the presence of protons was important for the reaction of NO_2 with CH_4 , while it had little effect on the NO oxidation to NO_2 . However, the impregnated sample Ce,Ag/HZSM-5 was superior to the sodium form Ce,Ag/NaZSM-5 (Table 4). It is not clear at this point whether this may be due to different states of silver on the impregnated catalyst which can alter the CH_4 selectivity.

It should be pointed out that not all Ag^+ ions incorporated into the ZSM-5 support are equivalent in terms of their contribution to CH_4 -SCR. As shown in Fig. 2, in the range of 0–60% Ag exchange, the conversion of NO to N_2 increases with the level of

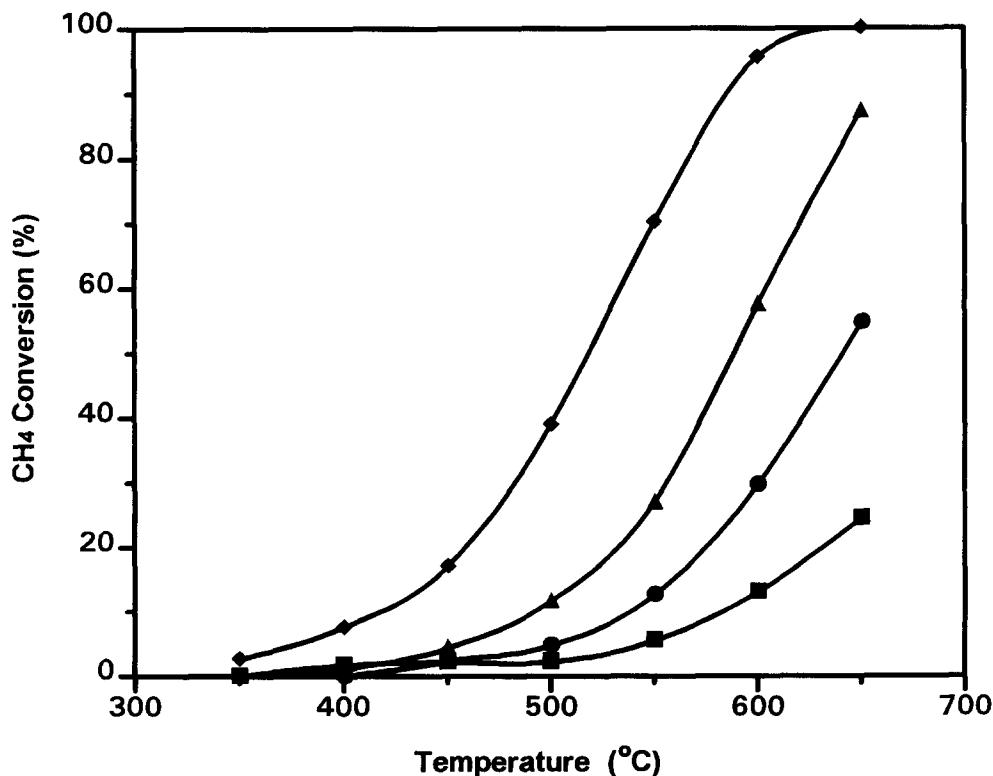


Fig. 11. CH_4 oxidation over Ce-Ag-ZSM-5 catalysts. Feed gas: 0.5% CH_4 -2.5% O_2 -bal. He. SV=7500 h^{-1} . Symbols: (■) Ce(21)-ZSM-5; (●) Ce(21)-Ag(22)-ZSM-5; (▲) Ce(21)-Ag(42)-ZSM-5; (◆) Ce(24)-Ag(78)-ZSM-5.

Ag⁺ ion exchange. These Ag⁺ ions are equivalent to each other as the activity of the catalyst is a linear function of the Ag loading in this range (Fig. 3). However, further increase of silver loading (to 80% exchange) did not enhance the SCR reaction. As Fig. 2(b) shows this may be due to methane depletion above 500°C, at which temperature almost complete conversion of CH₄ takes place on all catalysts with Ag ion exchange level of 60% or higher. Alternatively, this may be explained by a different state of silver, e.g. clusters, in the highly exchanged catalyst, which favors methane combustion as discussed below.

4.3. The role of Ag and Ce in CH₄-oxidation by O₂

Reduction of NO by hydrocarbons in the presence of oxygen can also be viewed as a competition between the two main reactions, i.e. SCR of NO

(reaction (I)) and oxidation of hydrocarbons by O₂ (reaction (II)) [29]. Therefore, gaining insight into the role of Ag⁺ and Ce³⁺ ions for the direct CH₄-oxidation by oxygen is important for understanding the promotion of the SCR reaction by Ce addition into Ag-ZSM-5. To achieve this, separate methane oxidation tests were conducted in this work over various catalyst compositions. A feed gas of 0.5% CH₄-2.5% O₂ bal. He was used in these tests at a space velocity=7500 h⁻¹. The results for several Ce-Ag-ZSM-5 catalysts with approximately fixed Ce loading and various Ag loadings are shown in Fig. 11. As can be seen from this figure, the conversion of CH₄ increases with the Ag loading over the entire temperature range. This dependence is more clearly shown in Fig. 12 in terms of CH₄ conversion vs. Ag loading at three temperatures of 450°C, 500°C and 550°C. In this figure, a non-linear relationship

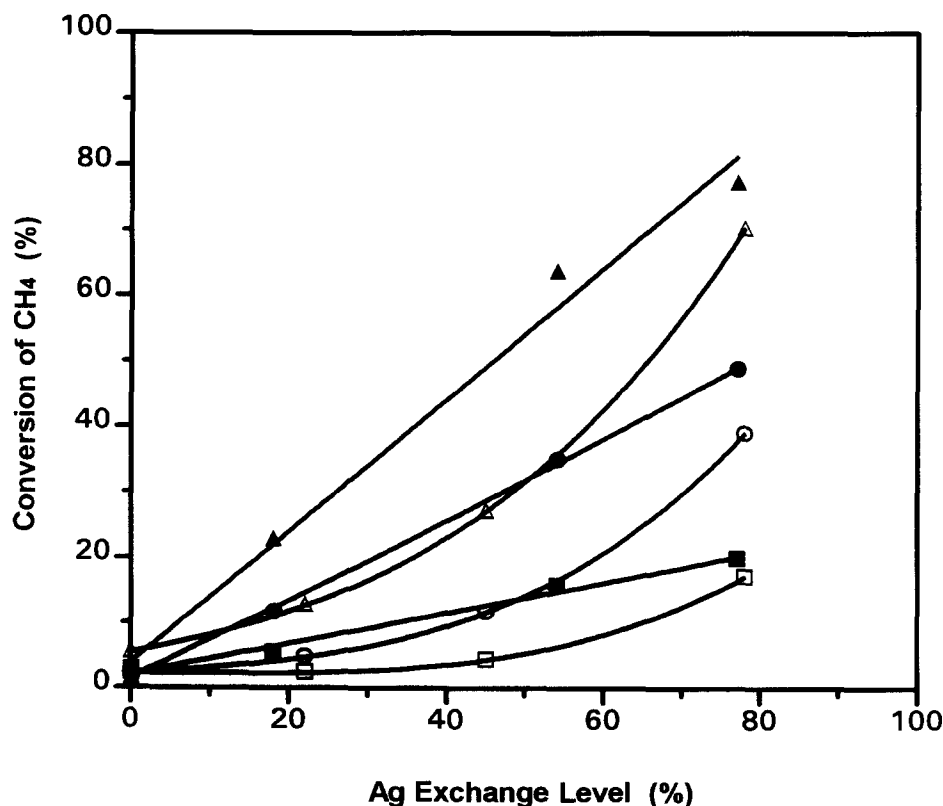


Fig. 12. Correlation between CH₄ conversion and Ag ion loading for CH₄ oxidation over Ag-ZSM-5 and Ce-Ag-ZSM-5 catalysts. Feed gas: 0.5% CH₄-2.5% O₂-bal. He. SV=7500 h⁻¹. Ce exchange levels are 21–24%. Symbols: solid: Ag-ZSM-5; open: Ce-Ag-ZSM-5. (■) and (□) 450°C; (●) and (○) 500°C; (▲) and (△) 550°C.

between CH_4 conversion and Ag loading for the Ce–Ag–ZSM-5 catalyst was observed. The increase of the CH_4 conversion with Ag loading is faster at higher Ag exchange levels ($\text{Ag} > 50\%$) than at lower exchange levels at each of the three temperatures. This means that at higher Ag loadings, the direct CH_4 oxidation is faster. This observation is contrasted to the correlation of NO conversion to N_2 with Ag loading shown in Fig. 3. As stated earlier, the NO conversion to N_2 reached a plateau above $\sim 60\%$ Ag exchange level. However, no such saturation is observed in Fig. 12.

This difference in NO conversion to N_2 and CH_4 conversion with Ag loading can be explained by the presence of different silver states. At low Ag ion exchange levels (0–60%), Ag ions are dispersed, presumably at the AlO_2^- sites of the zeolite. These Ag ions preferably catalyze the SCR reaction (reaction (I)), and are equivalent to each other as indicated by the linear dependence of NO conversion to N_2 on Ag

ion exchange level. At high Ag exchange levels ($> \sim 60\%$), silver clusters might form, favoring the direct CH_4 oxidation over the SCR of NO . Structural differences of silver as a result of loading in ZSM-5 are under investigation [21]. The formation of Ag clusters was examined by scanning transmission electron microscopy/energy dispersive X-ray analysis (STEM/EDS) of fresh, air-calcined Ce–Ag–ZSM-5 catalyst samples. 5–10 nm silver clusters were observed in the Ce(24)–Ag(77)–ZSM-5 sample. However, no evidence of clustering was found in the Ce(21)–Ag(42)–ZSM-5 sample.

To compare with the Ce–Ag–ZSM-5 material, CH_4 oxidation experiments were also carried out over the single metal ion-exchanged Ce–ZSM-5 and Ag–ZSM-5 (Figs. 13 and 14, respectively) at the same conditions as in Fig. 11. For the Ce–ZSM-5 material (Fig. 13), the conversion of CH_4 was very low for all three catalysts tested ($< 10\%$ at $T < 550^\circ\text{C}$ and 15–20% at $T = 550\text{--}650^\circ\text{C}$). The Ce exchange level has no

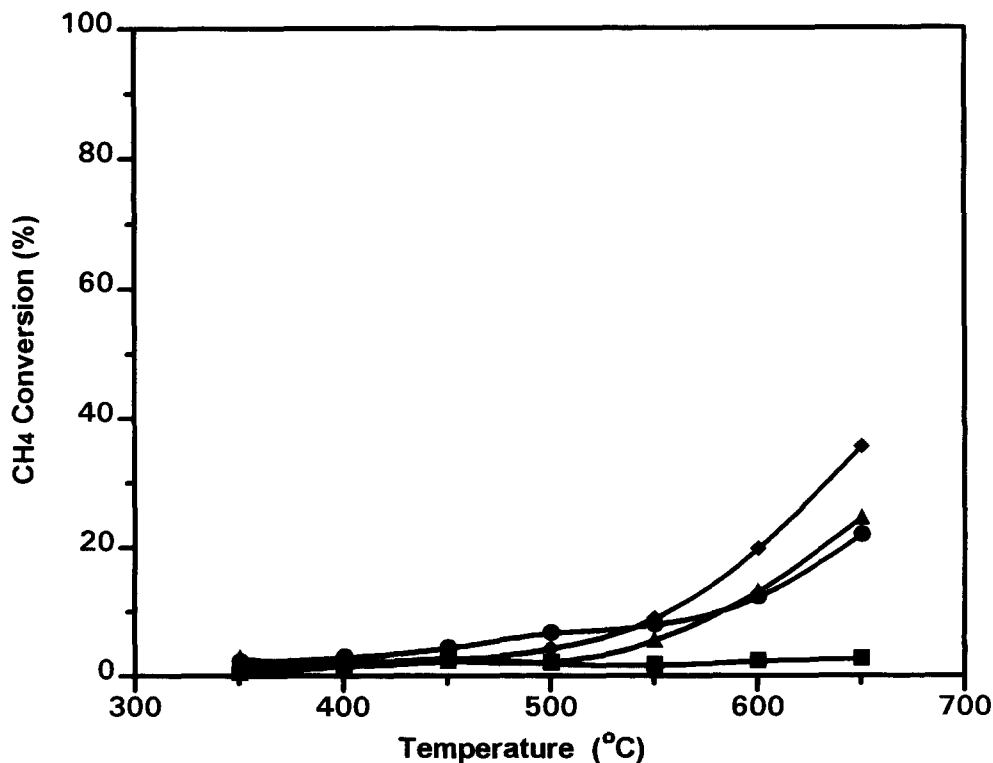


Fig. 13. CH_4 oxidation over Na-ZSM-5 and Ce-ZSM-5 catalysts. Feed gas: 0.5% CH_4 –2.5% O_2 –bal. He. $\text{SV} = 7500 \text{ h}^{-1}$. Symbols: (■) Na-ZSM-5 (as received); (●) Ce(9)-ZSM-5; (▲) Ce(21)-ZSM-5; (◆) Ce(54)-ZSM-5.

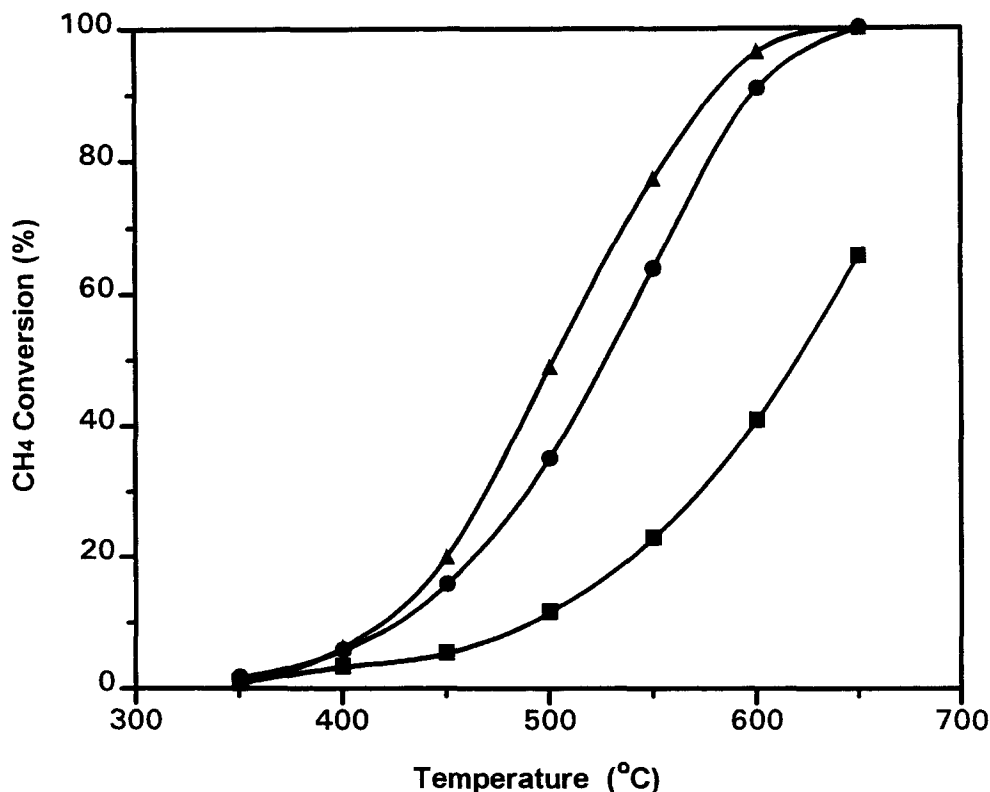


Fig. 14. CH_4 oxidation over Ag-ZSM-5 catalysts. Feed gas: 0.5% CH_4 -2.5% O_2 -bal. He. $\text{SV}=7500 \text{ h}^{-1}$. Symbols: (■) Ag(18)-ZSM-5; (●) Ag(54)-ZSM-5; (▲) Ag(77)-ZSM-5.

significant effect on the catalyst activity for methane combustion. Thus, the Ce^{3+} ion-exchanged zeolite, Ce-ZSM-5, is not an effective catalyst for methane oxidation (reaction (II)). However, as shown in Fig. 14 for the Ag-ZSM-5 catalyst, the conversion of CH_4 increases with the Ag loading, similar to what was observed for the Ce-Ag-ZSM-5 catalysts. In the case of Ag-ZSM-5, however, a linear relationship between the conversion of CH_4 and Ag loading was found for the whole range of Ag^+ ion exchange (Fig. 12). Apparently, CH_4 oxidation (reaction (II)) takes place on Ag^+ associated sites.

The effect of the addition of Ce ions on the CH_4 oxidation (reaction (II)) over Ag-ZSM-5 becomes clear when the conversion of CH_4 is compared between the Ce-Ag-ZSM-5 and the Ag-ZSM-5 catalysts as a function of Ag loading, as shown in Fig. 12. Over the entire range of Ag loading tested (0–80%), the CH_4 conversion over the single Ag ion-exchanged

Ag-ZSM-5 is higher than that over the bi-cation Ce-Ag-ZSM-5 catalyst at a fixed Ag loading. Apparently, Ce^{3+} ions do not promote the CH_4 combustion. On the contrary, they suppress or inhibit this reaction. This indicates that Ag-ZSM-5 is a better CH_4 oxidation catalyst, not only better than Ce-ZSM-5, but also better than Ce-Ag-ZSM-5 at all temperatures in the range of 450–650°C. Therefore, the second major function of Ce ions in promoting the activity of Ag-ZSM-5 for the CH_4 -SCR of NO is that they inhibit the CH_4 combustion. Potentially, this inhibition is structural, i.e. cerium ions keep silver ions highly dispersed, thus curbing their efficiency for CH_4 combustion. The observed inhibition manifests itself primarily at high temperatures where CH_4 oxidation is fast. If Ce^{3+} ions suppress the CH_4 combustion at these elevated temperatures, then the CH_4 -SCR of NO would proceed to a higher conversion, as observed here over the Ce-Ag-ZSM-5 catalysts.

5. Conclusions

In this work, we have investigated Ce–Ag–ZSM-5 as a new catalyst for the NO reduction by methane in the presence of excess oxygen. The bi-cation Ce–Ag–ZSM-5 catalyst is very active for this reaction, while either Ce-ZSM-5 or Ag-ZSM-5 alone shows low activity. The presence of oxygen in the feed gas mixture enhanced the activity of the catalyst and NO conversion to N₂ increased with the CH₄/NO ratio and Ag loading of the zeolite. The coexistence of Ce and Ag ions in the zeolite is crucial for achieving high NO conversion to N₂.

With addition of Ce ions in Ag-ZSM-5, the nature of the catalyst changes from an oxidation catalyst, e.g. Ag-ZSM-5, to a bifunctional catalyst, Ce–Ag-ZSM-5. On Ag-ZSM-5 catalysts, such as the Ag(77)-ZSM-5, the CH₄ combustion (reaction (II)) is strongly favored on the Ag sites; hence, the highly exchanged Ag-ZSM-5 is a good CH₄ oxidation catalyst. However, over Ce–Ag-ZSM-5, such as the Ce(21)–Ag(78)-ZSM-5 catalyst, the NO-SCR (reaction (I)) is the preferred reaction in a feed stream of NO, O₂ and CH₄. In the absence of NO from the feed gas, the Ce–Ag-ZSM-5 catalyzes the direct oxidation of CH₄, but not as well as Ag-ZSM-5.

Ce ions have a dual function in promoting the Ag-ZSM-5 catalyst: (i) they supply Ag ion sites with NO₂ by oxidizing NO to NO₂ and (ii) they suppress the direct oxidation of CH₄ (reaction (II)). However, cerium sites have low activity for the NO₂–CH₄ reaction. The Ag ions are the active centers where the reaction of NO₂ with CH₄ takes place. In addition to ZSM-5, Al₂O₃, ZrO₂ and ZrO₂–SO₄ are good supports of Ce and Ag for this application and merit further investigation. The new catalysts also show stable performance in wet gas streams at 500°C.

Acknowledgements

We gratefully acknowledge the financial support of this work by the Gas Research Institute under contract No. 5093-260-2580.

References

- [1] Y. Li, J.N. Armor, *J. Catal.* 145 (1994) 1–9.
- [2] Y. Li, J.N. Armor, *Appl. Catal. B* 1 (1992) L31–L40.
- [3] Y. Li, J.N. Armor, US Patent 5 149 512, 1992.
- [4] Y. Li, P.J. Battavio, J.N. Armor, *J. Catal.* 142 (1993) 561–571.
- [5] Y. Li, J.N. Armor, *Appl. Catal. B* 5 (1995) L257–L270.
- [6] K. Yogo, E. Kikuchi, *Stud. Surf. Sci. Catal.* 84 (1994) 1547–1554.
- [7] E. Kikuchi, M. Ogura, N. Aratani, Y. Sugiura, S. Hiromoto, K. Yogo, in: G. Centi et al. (Eds.), *Environmental Catalysis, First World Congress on Environmental Catalysis, Pisa, Italy, 1995*, pp. 29–32.
- [8] Y. Li, J.N. Armor, *Appl. Catal. B* 3 (1993) L1–L11.
- [9] Y. Li, J.N. Armor, *Appl. Catal. B* 2 (1993) 239–265.
- [10] Y. Nishizaka, M. Misono, *Chem. Lett.*, (1993) 1295–1298.
- [11] Y. Nishizaka, M. Misono, *Chem. Lett.* (1994) 2237–2240.
- [12] C.J. Loughran, D.E. Resasco, *Appl. Catal. B* 7 (1996) 127–136.
- [13] C. Descorme, A. Farkche, E. Garbowski, M. Primet, 1995 International Gas Research Conference, pp. 505–511.
- [14] Y. Kawai, European Patent Application 499 286, 1992.
- [15] Y. Li, J.N. Armor, *J. Catal.* 150 (1994) 376–387.
- [16] S. Sato, Y. Yu-u, H. Yahiro, N. Mizuno, M. Iwamoto, *Appl. Catal.* 70 (1991) L1–L5.
- [17] K. Masuda, K. Tsujimura, K. Shinoda, T. Kato, *Appl. Catal. B* 8 (1996) 33–40.
- [18] Y. Zhang, Ph.D. Dissertation, MIT, 1995.
- [19] Y. Zhang, M. Flytzani-Stephanopoulos, *J. Catal.* 164 (1996) 131–145.
- [20] M. Flytzani-Stephanopoulos, Z. Li, US Patent Application, 1996.
- [21] Z. Li, Ph.D. Thesis, Tufts University, in progress.
- [22] R.A. Grinstead, H.-W. Jen, C.N. Montreuil, M.J. Rokosz, M. Shelef, *Zeolites* 13 (1993) 602–605.
- [23] C. Kazazis, M.S. Thesis, Tufts University, 1996.
- [24] M. Sasaki, H. Hamada, Y. Kintaichi, T. Ito, *Catal. Lett.* 15 (1992) 297–304.
- [25] J.O. Petunchi, G. Sill, W.K. Hall, *J. Catal.* 141 (1993) 323–336.
- [26] V.A. Sadykov, G.M. Alikina, R.V. Bunina, S.L. Baron, S.A. Veniaminov, V.N. Romannikov, V.P. Doronin, A.Ya. Rozovskii, V.F. Tretyakov, V.V. Lunin, E.V. Lunina, A.N. Kharlanov, A.V. Matyshak, in: G. Centi (Ed.), *Environmental Catalysis, First World Congress on Environmental Catalysis, Pisa, Italy, 1995*, pp. 315–318.
- [27] C. Yokoyama, M. Misono, *Catal. Lett.* 29 (1994) 1–6.
- [28] D.B. Lukyanov, G. Sill, J.L. d'Itri, W.K. Hall, *J. Catal.* 153 (1995) 265–274.
- [29] D.B. Lukyanov, E.A. Lombardo, G. Sill, J.L. d'Itri, W.K. Hall, *J. Catal.* 163 (1996) 447–456.