Decomposition of NO over [Co]-ZSM-5 Zeolite: Effect of Co-adsorbed O_2

Yun-feng Chang[*,1] and Jon G. McCarty†

[*]*ABB Lummus Global, Inc., 1515 Broad Street, Bloomfield, New Jersey 07003; and* †*Catalytica, Inc., 430 Ferguson Drive, Mountain View, California 94043*

The decomposition of NO over four Co-containing ZSM-5 zeolites and Pr-, Ga-, and Cu-exchanged ZSM-5 zeolites was investigated using the isotope labeled $^{15}N^{18}O$ and a temperature-programmed desorption (TPD) technique. We found that [Co]-ZSM-5 that contains Co in the framework had the highest activity for NO decomposition (TOF: $2.05 \times 10^{-3} s^{-1}$ at 442°C and 0.2 vol% NO and 0.8 vol% O_2), almost an order of magnitude greater than that previously reported for a zeolite catalyst, namely Cu-ZSM-5 (TOF: $2.27 \times 10^{-4} s^{-1}$ at 335°C and 0.2 vol% NO and 0.8 vol% O_2) obtained under steady-state conditions. The phenomenally high activity of [Co]-ZSM-5 is due to the unique incorporation of Co^{2+} in the siliceous MFI structure. For all the catalysts investigated, coadsorption of NO and O_2 led to a substantial increase in the amount of NO_x adsorbed. However, the adsorbed species were not necessarily NO_2 as reported by others. We believe that the interaction between adsorbed NO_x species and O_2 is responsible for enhancing the rate of NO_x decomposition. It is obvious that the framework Co^{2+} behaves very differently from Co^{2+} in the countercation position and from extra-framework CoO such as that supported on or dispersed on the surface of silicalite also having the same MFI structure. © 1998 Academic Press

Key Words: nitric oxide decomposition; NO_x reduction; cobalt zeolite, [Co]-ZSM-5; framework Co in ZSM-5; isotope $^{15}N^{18}O$; coadsorbed oxygen; Co^{2+}-, Pr^{3+}-, Ga^{3+}-, and Cu^{2+}-exchanged ZSM-5.

INTRODUCTION

Since the decomposition of NO over Cu-ZSM-5 zeolite was first reported (1), many investigators have sought more active catalysts because this catalyst is not sufficiently active for practical use. There appears to be a consensus that N_2 desorbs as a product and N_2O exists as an intermediate on zeolite catalysts, at low temperatures (300°C) in the absence of O_2. However, there is no conclusive evidence regarding which adsorbed nitrogen oxide species is the precursor for N_2, especially in the presence of oxygen.

In this study, temperature-programmed desorption (TPD) experiments using doubly labeled isotopic NO ($^{15}N^{18}O$) and nonlabeled O_2 were conducted to elucidate the mechanism of NO decomposition, the interaction between NO and the zeolite, and more importantly, the involvement of O_2 in the mechanism.

The zeolite catalysts investigated include [Co]-ZSM-5, H-ZSM-5, Co-HZSM-5, Co/silicalite, Co-HZSM5-100, Ga-HZSM-5, Cu-ZSM5-108, and Pr-HZSM5-100. [Co]-ZSM-5 was used to find out whether framework-incorporated cobalt in the 2+ oxidation state has any catalytic activity and how it is different from Co^{2+} in the countercation position of ZSM-5 zeolites. It has been demonstrated that the cobalt in the cobaltsilicate ZSM-5 and CoAPO-5 is in a 2+ state (2, 3). We found that [Co]-ZSM-5 is one order of magnitude more active than Cu-ZSM-5 for decomposing NO in the presence of oxygen. This finding may represent a milestone in the endeavor to develop zeolite-based active catalysts for NO_x reduction.

EXPERIMENTAL

Catalyst

[Co]-ZSM-5 was synthesized according to a method described by a Mobil group (4). The gel composition (molar ratio) was: 28.8 SiO_2 (Ajax's SNOWTEX-40), 3.2 Na_2O (NaOH) (Ajax, AR grade), 5.6 Na_2SO_4 (BDH, AR grade), 1.0 CoO ($CoSO_4 \bullet 7H_2O$) (Aldrich, AR grade), 1356 H_2O, 2.9 *n*-tetrapropylammonium bromide (Fluka, 99.8%), and 2.9 NaBr (BDH, 99.9%). It was treated hydrothermally at 175°C for 48 h. The product contained 0.46 wt% Co, or 78.1 $\mu mol \bullet g^{-1}$. XRD data revealed it has MFI structure and 100% crystallinity. SEM and optical microscope showed uniform chunky grains like crystals of 8–10 μm.

Co-HZSM-5 was prepared by refluxing a mixture containing H-ZSM-5 ([H^+]: 560 $\mu mol \bullet g^{-1}$) zeolite powder and 1.0 M $Co(NO_3)_2$ (Aldrich, AR reagent) aqueous solution at a ratio of 1 g zeolite to 20 cm^3 solution. After two consecutive exchanges, the solid was washed and dried, then calcined at 550°C for 6 h. Elemental analysis (see Table 1) showed this catalyst contained 0.38 wt% Co, which represents 23% of the total ion exchange capacity of the parent material.

Cu-ZSM5-108 was prepared following the same procedure as that for Co-HZSM-5 by refluxing Na-ZSM-5 with

TABLE 1

Composition and Properties of Catalysts Studied

Catalyst	Composition		
	SiO_2/Al_2O_3 Ratio	$[H^+]$ ($\mu mol \bullet g^{-1}$)	Metal (wt.%)[a]
H-ZSM-5	60	560	—[b]
Co/silicalite	>35,300	0	2.0
Co-HZSM-5	60	431	0.38
Co-HZSM5-100	60	0	1.65
[Co]-ZSM-5	>300,000	—[b]	0.46[c]
Ga-HZSM-5	60	—[b]	3.5
Pr-HZSM5-100	60	—[b]	2.3
Cu-NaZSM5-108	60	0	1.9

[a] Excluding framework Si and Al.
[b] Unavailable.
[c] In the framework.

1.0 M $Cu(NO_3)_2$ (Aldrich, AR reagent) aqueous solution at a ratio of 1 g zeolite to 20 cm^3 solution. Its composition is given in Table 1.

Co-HZSM5-100 and Pr-HZSM5-100. These catalysts were made by incipient wetness impregnation of H-ZSM-5 with the respective required amounts of $Co(NO)_2 \bullet 6H_2O$ (Aldrich, AR grade) or $Pr(NO_3)_3 \bullet 5H_2O$ (Alfa, 99.9%) to give 100% exchange of the protons (assuming each Co^{2+} replaced two H^+ and each Pr^{3+} replaced three H^+). The mixtures were dried at 110°C and then calcined in air at 550°C for 12 h.

Ga-HZSM-5 was prepared according to the same procedure as Co-HZSM5-100, designed to give a nominal 100% exchange of the protons (assuming Ga is in the form $(GaO)^+$, as reported by others (5)).

Materials

The isotope double-labeled $^{15}N^{18}O$ was obtained from ISOTECH (1 vol% $^{15}N^{18}O$, 1 vol% Ar, and 98 vol% He), O_2 from Liquid Carbonic (4 vol% O_2, 1 vol% Ar, and 95 vol% He), and high purity helium also from Liquid Carbonic (99.999 vol% He).

Temperature-Programmed Experiments

Before a temperature-programmed experiment, the catalyst sample (20 mg or 200 mg) was pretreated in 2 vol% O_2 flowing at 50 cm^3/min. It was heated to 600°C and then held at this temperature for 20 min before being cooled to 40°C. The adsorption of $^{15}N^{18}O$, or the co-adsorption of $^{15}N^{18}O$ and O_2, was conducted for 30 min at 40°C in a 50 cm^3/min flowing steam of 0.2 vol% $^{15}N^{18}O$ or 0.2% $^{15}N^{18}O$ and 0.8 vol% O_2, respectively. The treated catalyst was purged in a stream of He at 50 cm^3/min for 30 min before temperature-programmed desorption (TPD) was begun. The He flow used during TPD was 50 cm^3/min. The effluent was monitored by an on-line mass spectrometer

(Electronic Associates Inc.) for the following species: m^+/e: 30 for $^{15}N_2$; 31 for $^{15}N^{16}O$; 32 for $^{16}O_2$; 33 for $^{15}N^{18}O$; 34 for $^{16}O^{18}O$; 36 for $^{18}O_2$; 40 for Ar; 46 for $^{15}N_2^{16}O$; 47 for $^{15}N^{16}O_2$; 48 for $^{15}N_2^{18}O$; 49 for $^{15}N^{16}O^{18}O$; and 51 for $^{15}N^{18}O_2$. The mass spectrometer was calibrated with N_2, N_2O, NO, O_2, Ar, and NO_2.

RESULTS

During the 40°C exposure of zeolite catalysts with either $^{15}N^{18}O$ or a mixture of $^{15}N^{18}O$ and O_2, a significant amount of $^{15}N^{16}O$ was observed in the reactor effluent. This indicates that the isotope exchange between $^{15}N^{18}O$ and the zeolite framework oxygen, or oxygen adsorbed on the catalyst, occurred at this low temperature. The amount of such an isotope exchange varied with the catalyst. The exchange ceased when saturation adsorption was achieved, suggesting that the process occurred by adsorption of $^{15}N^{18}O$ on the zeolites. No other products were found in the effluent, suggesting that neither disproportionation to form N_2O and NO_2 nor decomposition to N_2 and O_2 were significant at this temperature. No attempts were made to quantify the degree of exchange. A detailed analysis of the isotope exchange between $^{15}N^{18}O$ and the framework oxygen (^{16}O) of Cu-ZSM-5 and Fe-MOR zeolites at high temperatures (~500°C) was reported previously (6).

During the TPD a number of desorption products were detected, including $^{15}N^{18}O$, $^{15}N^{16}O$, $^{15}N_2^{18}O$, $^{15}N_2^{16}O$, $^{15}N_2$, $^{15}N^{16}O_2$, $^{15}N^{16}O^{18}O$, $^{15}N^{18}O_2$, $^{16}O_2$, $^{16}O^{18}O$, and $^{18}O_2$.

For simplicity, only the critical features are presented here. Figures 1 through 3 present as a function of temperature the desorption of NO_x and O_2 and the formation of N_2 for the various catalysts. The TPD profiles show two distinct desorption regions: below 300°C and above 300°C. Based on this arbitrary classification, the amounts of NO_x or O_2 adsorbed after being treated in either NO alone or a mixture of NO and O_2 measured from TPD experiments are summarized in Table 2. The maximum activities of the catalysts, as measured by TPD, are compared in Table 3.

It is worthwhile to point out that, due to the use of the argon tracer in the reactant gas stream, in both double-labeled NO and oxygen the mass balance was easily conducted. Satisfactory mass balance for both nitrogen and oxygen was obtained.

DISCUSSION

Treated in $^{15}N^{18}O$

Table 2 shows that in the absence of O_2 in the gas stream, the amount of NO_x adsorbed measured by TPD is very small (<9 $\mu mol \bullet g^{-1}$) for H-ZSM-5, Co/silicalite, Pr-HZSM5-100, and Ga-HZSM-5. In contrast, Co-HZSM-5, [Co]-ZSM-5, and Co-HZSM5-100 have much higher uptake. This illustrates the importance of active sites and also the
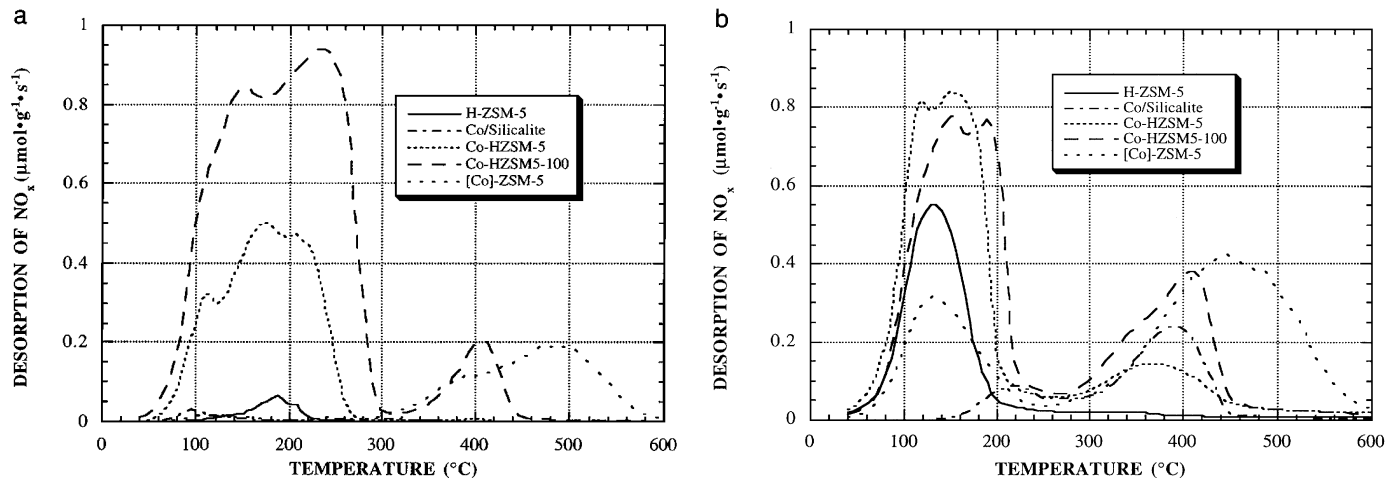
FIG. 1. (a) Desorption of NO_x from different ZSM-5 zeolite catalysts during TPD after treated in 0.2 vol% $^{15}N^{18}O$ (50 cm^3 • min^{-1}) at 40°C; catalyst mass: 0.2 g; flow of He: 50 cm^3 • min^{-1}; ramp rate: 30°C • min^{-1}. (b) Desorption of NO_x from different ZSM-5 zeolite catalysts during TPD after treated in 0.2 vol% $^{15}N^{18}O$ and 0.8 vol% O_2 (50 cm^3 • min^{-1}) at 40°C; catalyst mass: 0.2 g; flow of He: 50 cm^3 • min^{-1}; ramp rate: 30°C • min^{-1}.

importance of metal cations or the interaction between the metal cation and zeolite structure.

TPD curves for both Co-HZSM-5 and Co-HZSM5-100 are dominated by the low-temperature peaks (<300°C), whereas for [Co]-ZSM-5, high-temperature peaks predominate. This similarity in NO_x TPD characteristics between Co-HZSM-5 and Co-HZSM5-100 and its sharp contrast with [Co]-ZSM-5 strongly suggest that the local environment of Co^{2+} in the zeolite plays a very important role in determining its interaction with NO. NO is more strongly bound on framework Co^{2+} than that in the countercation positions.

The amount of oxygen desorbed during TPD experiments was negligible except for [Co]-ZSM-5 and Co-HZSM5-100. For these cases, major desorption occurred at >300°C.
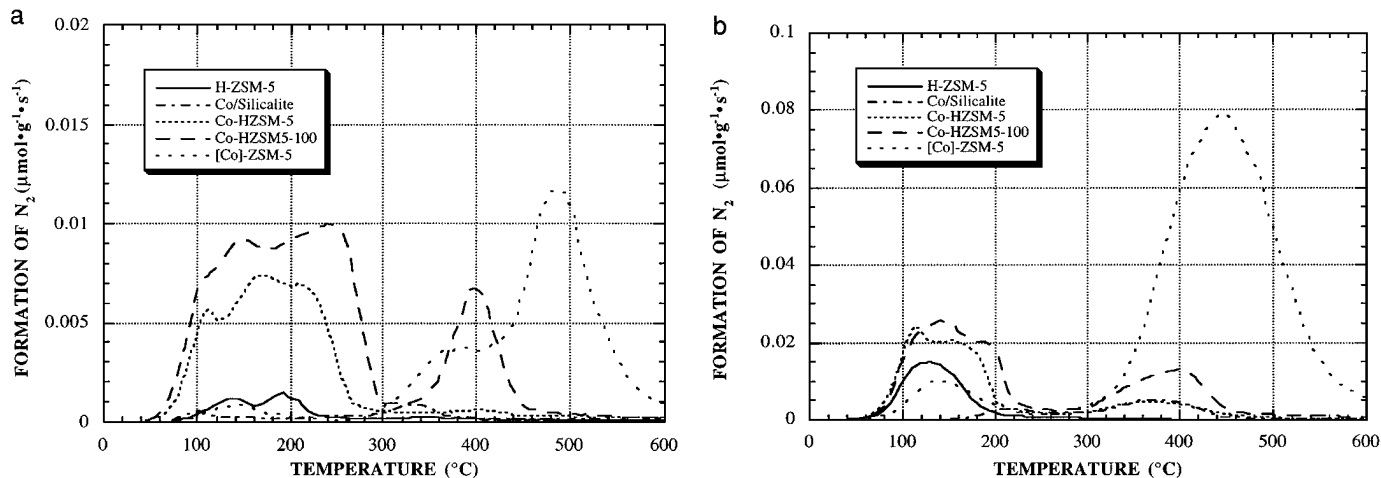
For Co-ZSM-5 and Co-HZSM5-100, major NO decomposition occurred at <300°C (see Fig. 3a). However, for [Co]-ZSM-5, NO decomposition took place exclusively at temperatures above 300°C. This difference is associated with the structural difference between Co^{2+} as countercations in both Co-HZSM-5 and Co-HZSM5-100 and the Co^{2+} as the framework cation in [Co]-ZSM-5. Regardless these differences, generally speaking, the rate of NO_x decomposition is very low.

Treated in $^{15}N^{18}O$ and O_2

Adding O_2 into the gas stream resulted in sharp increase in amount of NO_x and O_2 adsorbed (see Table 2). The increment in the amount of NO_x adsorbed by the catalyst
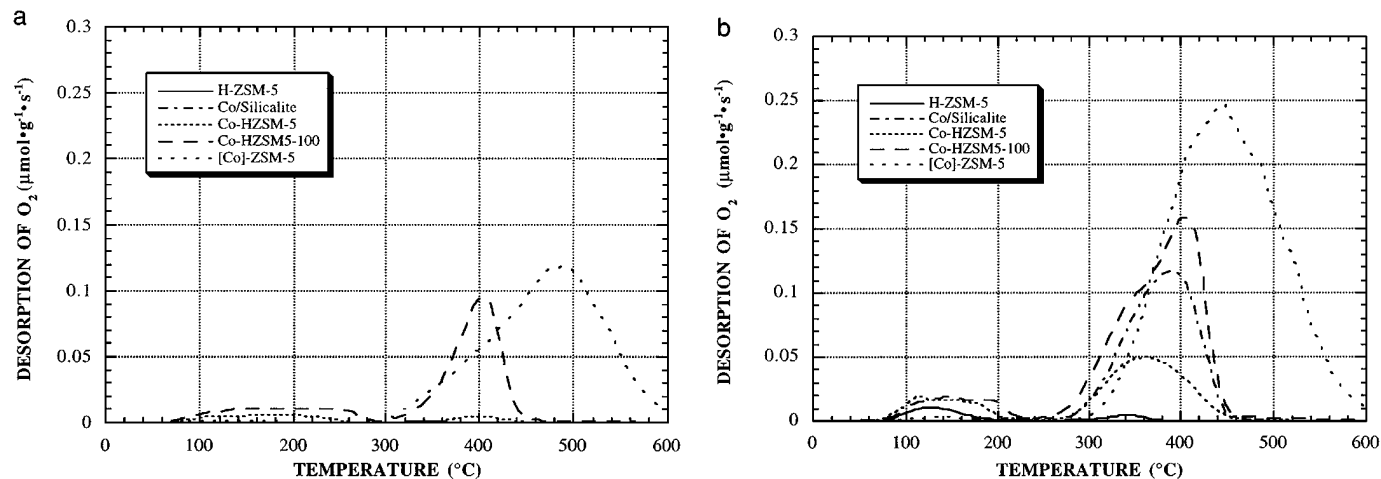
FIG. 2. (a) Desorption of O_2 from different ZSM-5 zeolite catalysts during TPD after treated in 0.2 vol% $^{15}N^{18}O$ (50 cm^3 • min^{-1}) at 40°C; catalyst mass: 0.2 g; flow of He: 50 cm^3 • min^{-1}; ramp rate: 30°C • min^{-1}. (b) Desorption of O_2 from different ZSM-5 zeolite catalysts during TPD after treated in 0.2 vol% $^{15}N^{18}O$ and 0.8 vol% O_2 (50 cm^3 • min^{-1}) at 40°C; catalyst mass: 0.2 g; flow of He: 50 cm^3 • min^{-1}; ramp rate: 30°C • min^{-1}.

FIG. 3. (a) Formation of N_2 over different ZSM-5 zeolite catalysts during TPD after treated in 0.2 vol% $^{15}N^{18}O$ (50 cm^3 • min^{-1}) at 40°C; catalyst mass: 0.2 g; flow of He: 50 cm^3 • min^{-1}; ramp rate: 30°C • min^{-1}. (b) Formation of N_2 over different ZSM-5 zeolite catalysts during TPD after treated in 0.2 vol% $^{15}N^{18}O$ and 0.8 vol% O_2 (50 cm^3 • min^{-1}) at 40°C; catalyst mass: 0.2 g; flow of He: 50 cm^3 • min^{-1}; ramp rate: 30°C • min^{-1}.

caused by adding O_2 into the NO gas stream in more pronounced for [Co]-ZSM-5, H-ZSM-5, Pr-HZSM5-100, and Ga-HZSM-5 than for Co-HZSM5-100 and Co/silicalite. H-ZSM-5, Pr-HZSM5-100, Co-HZSM-5, and Ga-HZSM-5 have the common feature that a majority of the increment occurred at temperatures below 300°C.

In contrast, the increment in the amount of O_2 adsorbed is mostly due to that occurred at high temperatures (>300°C). [Co]-ZSM-5 has the most increase, followed by Co-HZSM5-100, then Co/silicalite, Pr-HZSM5-100, and Ga-HZSM-5 while H-ZSM-5 has the least increase.

The high efficiency of [Co]-ZSM-5 in forming NO_x species at high temperature (>300°C) suggests that framework-incorporated Co^{2+} is more effective in facilitating the formation of NO_x intermediates than Co^{2+}, H^+, or other transition metal cations and rare-earth metal cations in the countercation positions. The formation of NO_x in-

termediates may also be interpreted as oxidation of NO to NO_x (NO_2 or N_2O_3). Previously, it was concluded by Shelef *et al.* (7) that H-ZSM-5, Cu-ZSM-5, and Cu/Al$_2$O$_3$ were capable of oxidizing NO to NO_2, and more importantly, that catalyst which has the highest activity for NO oxidation to NO_2 also has the highest activity for NO decomposition.

Figures 1b and 2b show that, in addition to the increase in the amount of O_2 adsorbed, the TPD characteristics were also changed by co-adsorbing $^{15}N^{18}O$ and O_2, for instance, the dominant peak shift 40°C downwards for [Co]-ZSM-5 and Co-HZSM-5 and for Co-HZSM5-100 the appearance of a low temperature shoulder at around 350°C.

In Table 3, except H-ZSM-5, for all other catalysts only the high-temperature activity is reported and compared. This is because the moderate low-temperature (<300°C) activity is a common feature for all catalysts and is not significantly affected by metal cations.

TABLE 2

Summary of TPD Results of Different Zeolite Catalysts Treated either in NO Alone or with O_2 at 40°C

	TPD results							
	Amount of NO desorbed (μmol • g^{-1})				Amount of O_2 desorbed (μmol • g^{-1})			
	NO-treated		NO + O_2 treated		NO-treated		NO + O_2 treated	
Catalyst	^{2}300°C	>300°C	^{2}300°C	>300°C	^{2}300°C	>300°C	^{2}300°C	>300°C
H-ZSM-5	7.9	0.7	90.0	8.6	0.03	0.2	1.7	0.6
Co/silicalite	4.5	0.5	17.7	47.6	0.10	0.24	1.0	21.8
Co-HZSM-5	130.4	1.0	181.8	45.4	1.6	0.9	4.2	12.2
Co-HZSM5-100	288.0	35.4	181.6	86.8	2.5	1.0	5.5	30.1
[Co]-ZSM-5	3.5	64.4	65.5	148.3	0.4	38.0	0.8	74.6
Pr-ZSM5-100	5.5	2.4	126.9	4.0	0	2.6	4.3	17.4
Ga-HZSM-5	5.8	2.2	119.4	24.3	0	3.4	4.3	17.9

Note. Catalyst mass: 0.2 g; O_2/no: 0.2 vol% $^{15}N^{18}O$ at 50 cm^3/min; O_2/yes: 0.2 vol% $^{15}N^{18}O$ and 0.8 vol% O_2 at 50 cm^3/min; TPD: heating rate: 30°C/min in He at 50 cm^3/min.

TABLE 3
Summary of NO Decomposition Results Obtained from TPD Measurements[a]

Catalyst	TPD results			
	Max. N_2 formation (μmol $\bullet$ g^{-1} $\bullet$ s^{-1})	TOF $\times 10^3$ (molec $\bullet$ M^{-1} $\bullet$ s^{-1})[b]	Max. conversion (%)	Temperature (°C)
[Co]-ZSM-5	0.081	2.051	26.8	442
Cu-NaZSM5-108[f]	0.034	0.227	10.6	335
Co-HZSM5-100	0.013	0.093	6.7	418
Ga-HZSM-5	0.008	0.032	10.2	412
Pr-HZSM5-100	0.008	0.098	8.6	410
Co/silicalite	0.005	0.029	4.4	370[c]
Co-HZSM-5	0.005	0.155	7.7	370
H-ZSM-5	0.015	0.054[d]	5.1	134[e]

[a] Catalyst: 0.2 g, 0.2 vol% $^{15}N^{18}O$, 0.8 vol% O_2; flow rate: 50 cm^3 $\bullet$ min^{-1}.
[b] TOF: NO turnover frequency per metal site.
[c] Other than a low temperature maximum at around 200°C.
[d] Per proton.
[e] Characteristic of H-ZSM-5 zeolite.
[f] Data from Chang and McCarty [16].

Noting from Fig. 1b, co-adsorbing $^{15}N^{18}O$ and O_2 reduced the high-temperature portion of the low-temperature NO peak while it increased sharply the high-temperature peak. This is also true for O_2 (see Fig. 2b).

From Fig. 3b it is clear that co-adsorbing $^{15}N^{18}O$ and O_2 led to significant enhancement in the rate of NO decomposition. However, the increase for H-ZSM-5, Co-HZSM-5, and Co-HZSM5-10 is moderate, compared to that of [Co]-ZSM-5. The TOFs (turn over frequency: number of NO molecules converted to N_2 and O_2 per metal site per second at 0.2 vol% $^{15}N^{18}O$ and 0.8 vol% O_2) calculated for all catalysts studied are contained in Table 3. The highest activity achieved on [Co]-ZSM-5 at 442°C, 2.051×10^{-3} mol $\bullet$ Co^{-1} $\bullet$ s^{-1} is almost one order of magnitude higher than that of the most active known catalyst, Cu-ZSM-5, 0.227×10^{-3} mol $\bullet$ Cu^{-1} $\bullet$ s^{-1} at 335°C obtained under steady-state conditions. The TOF for Cu-ZSM-5 obtained in this work is very close to those reported by others for Cu-ZSM-5. A comprehensive review of rate data on NO decomposition over a large variety of Cu-ZSM-5 catalysts prepared by different methods with different Cu-loading and different ZSM-5, conducted by Campa *et al.* revealed that NO decomposition rate is approximately first order to the concentration of NO (8). Based on a universal activity versus the NO partial pressure curve constructed for previously reported NO decomposition data the TOF corresponding to the experimental conditions employed in this work are estimated to be $0.12 (\pm 0.02) \times 10^{-3}$ mol $\bullet$ Cu^{-1} $\bullet$ s^{-1}.

The extremely high activity displayed by the framework incorporated Co^{2+} in the highly siliceous MFI structure is unique because Cu^{2+} incorporated into a similar MFI structure was shown to be not active at all for decomposing NO (9).

Results in Figs. 2a and 3a show that for all four Co-containing zeolite catalysts in the low-temperature region, desorption of N_2 is accompanied by desorption of O_2 and the ratio of N_2 to O_2 is close to 2, suggesting stoichiometric decomposition of NO to N_2O and O_2. This is different from Li and Armor results on Co-FERR (10). Using TPD, these authors found that in addition to the desorption of NO, a major desorption peak of N_2 at 40–100°C and a major desorption peak of N_2O at 200–300°C. However, no desorption of O_2 was observed. A TPD carried out in the flow of 10% O_2 in He showed a similar peak for N_2 but disappearance of the N_2O peak. They believed that formation of N_2O, indicating disproportionation of NO to N_2O and NO_2, although they did not observe NO_2 as a major desorption product. The lack of N_2O as a desorption product when O_2 was present in the carrier gas indicates that the presence of O_2 suppresses the disproportionation reaction.

On Co-HZSM-5, Co-HZSM5-100, [Co]-ZSM-5, and the other catalysts studied, the formation of N_2O and NO_2 was negligible when treated in $^{15}N^{18}O$ alone. However, treatment in the gas stream containing both $^{15}N^{18}O$ and O_2 resulted in the formation of NO_2s ($^{15}N^{18}O_2$, $^{15}N^{16}O_2$, $^{15}N^{16}O^{18}O$). This is in agreement with others finding that oxidation of NO by O_2 to form NO_2 is effectively catalyzed by H-ZSM-5 (11), H-MOR, Fe-MOR, and Cu-MOR (12), Cu-ZSM-5 (13) at relatively low temperature, e.g., room temperature. Except for [Co]-ZSM-5, all other catalysts showed two major NO_2 desorption peaks at <300°C and >300°C. For [Co]-ZSM-5 no NO_2 desorption occurred at >300°C, presumably due to the high rate of NO_2 decomposition on framework Co^{2+} at high temperatures.

The fact that co-adsorbing NO and O_2 resulted in the formation of NO_2 and a higher rate of NO_x decomposition

seems to suggest that NO_2 is the reactive intermediate responsible for NO_x decomposition to form N_2 and O_2. However, NO_2 is not the only reactive intermediate because in the absence of any formation of NO_2, decomposition of NO also occurs. In this case, it is via an N_2O intermediate. This is in agreement with others (10).

The enhancement of NO_x adsorption by zeolites in the presence of O_2 was also observed by others. For instance, it was reported that the uptake of NO_x by Na-ZSM-5, Na-Y, and Cu-ZSM-5 zeolite catalysts was enhanced by co-adsorbing NO and NO_2 or NO and O_2 (14). The same authors also concluded that the formation of NO_x is facilitated by the zeolite structure, not by the presence of Cu^{2+} although the adsorbed quantities are enhanced by Cu. Further, they postulated the NO_x intermediates are N_2O_3.

Our TPD results (see Table 3) suggest the composition of NO_x species formed on our catalysts are in between NO and NO_2, probably close to N_2O_3 proposed above (14).

Quantum mechanic calculations by Kishner et al. (15) show that the N-N bond in N_2O_3 is of σ type with high p-type character. The N-N bond order is reduced by the oxygen lone pair antibonding delocalization onto the nitrogen.

Therefore, the formation of N_2O_3-like NO_x intermediates on the catalyst surface has weakened the N-O bonding, leading to higher rate of NO_x decomposition.

We have not conducted structural characterization of our [Co]-ZSM-5 catalyst. Using solid state NMR and XRD, Szostak et al. (2) concluded that cobaltsilicate ZSM-5 have Co^{2+} incorporated into the zeolite framework. Using XAFS, Zhang and Harris (3) demonstrated that cobalt in CoAPO-5 are Co^{2+} incorporated in the tetrahedral molecular sieve framework. Each Co^{2+} is coordinated with four oxygen atoms at 1.93 Å. They also found that calcination of CoAPO-5 at $\sim 600°C$ did not cause any significant loss of cobalt from the framework nor did reduction in hydrogen. Inferred from the above results, we believe that in our [Co]-ZSM-5 zeolite, it is Co^{2+} incorporated in the MFI framework which are responsible for the extremely high activity for NO decomposition.

CONCLUSIONS

Using TPD technique, we have found [Co]-ZSM-5 which contains Co^{2+} incorporated in the siliceous MFI framework has almost an order of magnitude higher activity for the decomposition of NO in the presence of O_2 than the most active catalyst, Cu-ZSM-5, previously reported. Co-adsorption of NO and O_2 led to substantial enhancement in the amount of NO_x adsorbed on the catalysts irrespective of cation type or degree of metal loading. The framework-incorporated Co^{2+} is responsible for the high rate of NO_x decomposition. Contrary to previous findings by others, the presence of O_2 is essential for higher NO decomposition activity. We believe that the formation of a NO_x intermediate with structure close to N_2O_3 may be responsible for the enhancement in the rate of NO decomposition when NO and O_2 are co-adsorbed. In the absence of oxygen, formation of NO_x is limited by the amount of oxygen retained by the catalyst, resulting in lower activity in the NO decomposition.

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