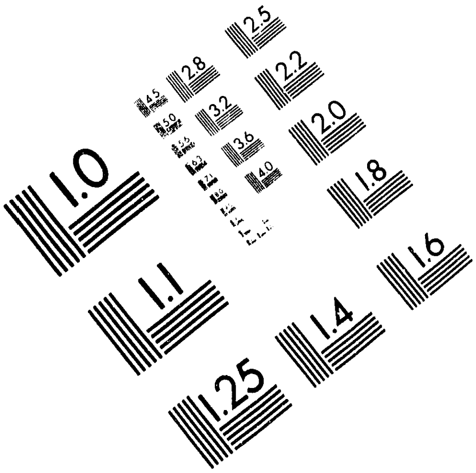

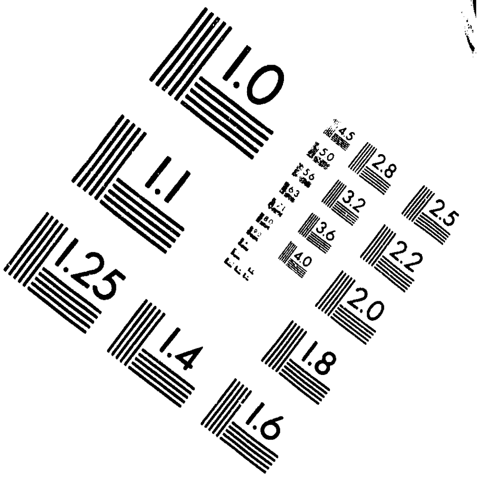

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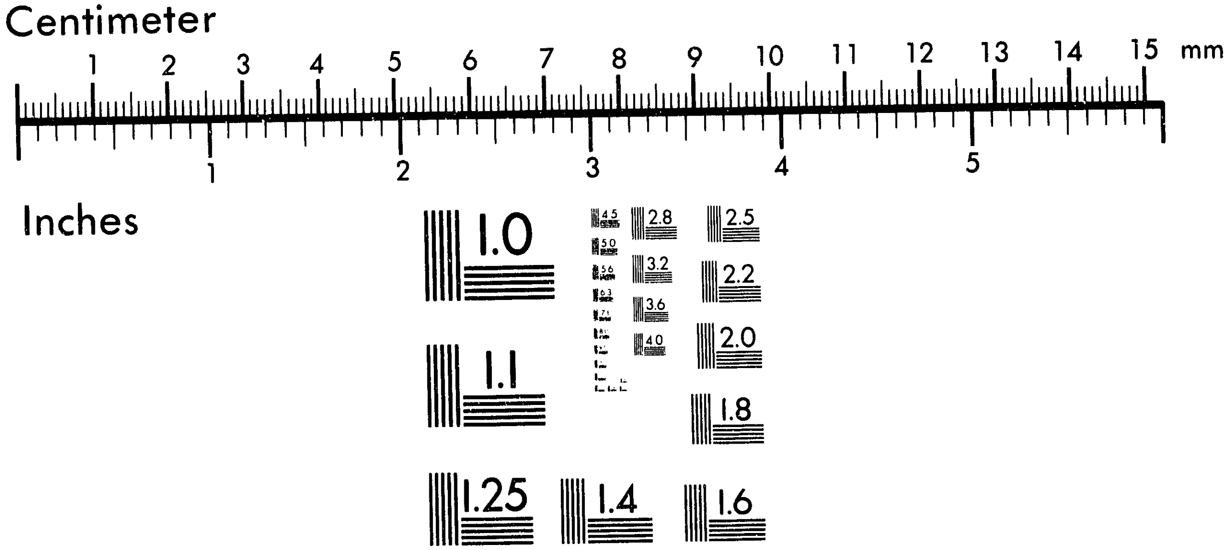

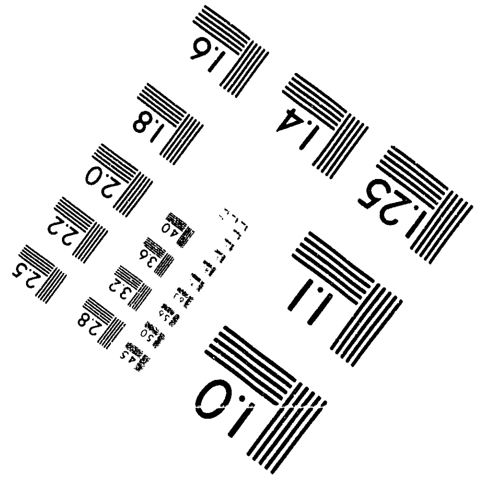

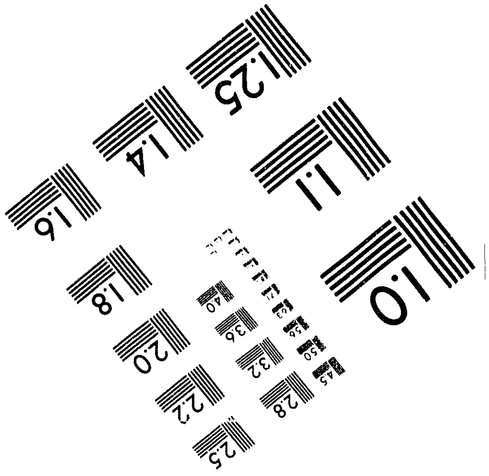

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DIRECT CATALYTIC DECOMPOSITION OF NITRIC OXIDE

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DIRECT CATALYTIC DECOMPOSITION OF NITRIC OXIDE

Abstract

This project investigates a suitable catalyst system for the direct NO decomposition in post-combustion gas streams. The process does not use a reductant, such as the ammonia used in Selective Catalytic Reduction (SCR) of NOx to nitrogen. Therefore, it is a greatly simplified process basically involving passing the flue gas through a catalytic converter.

Catalysts are prepared by incorporating metal cations into zeolite supports according to ion exchange procedures widely used in preparation of metal/zeolite catalysts. The catalysts of primary interest include copper, palladium, silver, and nickel exchanged ZSM-5 catalysts. Particular emphasis is given in this work on promoted Cu-exchanged zeolites, especially the catalyst system Mg/Cu-ZSM-5 and a few others, which are promising for NO conversion to nitrogen at typical flue gas O_2 and NO levels and over the temperature range of 723-873K. Effects of zeolite modification, copper exchange level and catalyst preparation conditions on the catalyst activity are studied in a packed-bed microreactor. Temperature-programmed desorption (TPD) and reduction (TPR) experiments will be carried out in a thermogravimetric analyzer and a single-particle electrodynamic balance (EDB). Kinetic studies of NO and O_2 interaction with catalysts over a wide temperature range as well as catalyst structural investigations are planned.

PROGRESS SUMMARY

Alkaline earth and transition metal cocation effects are reported in this quarterly report for Cu ion-exchanged ZSM-5 zeolites used for the direct decomposition of nitric oxide in oxygen-rich gases. The effect is manifested under a specific mode of ion exchange and appears to be due to stabilization of the active copper sites. The conversion of NO to N_2 is invariant to oxygen in the high temperature region (450- 600°C) for low NO concentration gases. The coexistence of rare earth ions with Cu ions in ZSM-5 produced a markedly different effect promoting the activity of copper ions for the NO decomposition at low temperatures (300- 400°C).

INTRODUCTION

The direct catalytic decomposition of nitric oxide in oxygen-rich post-combustion gas streams would greatly benefit the economics of post-combustion NOx control in power plants, industrial boilers and engine systems. The initial report by Iwamoto (1) that Cu ion- exchanged ZSM-5 (Cu-Z) zeolite has stable steady- state activity for the direct decomposition of nitric oxide has been followed by many recent studies (2-9) of this catalyst system addressing pertinent issues potentially affecting its activity including copper exchange level, Si/Al ratio, oxygen effect, poisoning by SO_2, H_2O effect, etc.

The conversion of NO to N_2 over the Cu-Z materials is not a linear function of the copper ion-exchange level. Rather, almost no activity exists for up to 40-50% exchange level, above which conversion increases rapidly with the exchange level (2). Over-exchanged(>100%) Cu-Z are active either because copper ions adequately populate sites accessible to NO(e.g. in the 10-membered rings of the ZSM-5) or because catalytic activity only emerges if enough adjacent copper active sites exist (6). In recent work, Kagawa, et al (8) reported that the incorporation of cocations into Cu-Z promoted the catalytic activity of Cu ion for the direct NO decomposition at temperatures above 450-500°C. Transition metals or alkaline earths were equally effective cocations in Cu-Z at 550°C. The mode of ion exchange was important, i.e. the cocation had to be exchanged first followed by copper ion exchange, for the effect to show. The positive cocation effect was more pronounced for low Cu ion exchange level. The influence of gaseous oxygen on the conversion of NO to N_2 was not examined in that work. Iwamoto, et al(6) have reported that the activity of over-exchanged Cu-Z is not affected much by oxygen in the gas, while lower ion-exchanged Cu-Z is severely poisoned.

In this paper we examine the cocation effect on the NO decomposition reaction in oxygen-containing gases over M/Cu-Z catalysts, where M is an alkaline earth or transition metal ion. The importance of preparation method is discussed in terms of active (Cu ion) site stabilization. Rare earth metal modified Cu-Z catalysts were also prepared and tested in this work both in oxygen-free and oxygen-containing gases.

EXPERIMENTAL

Catalyst Synthesis and Characterization

Catalysts were prepared by incorporating metal cations into ZSM-5 zeolite supports according to ion exchange procedures widely used in preparation of metal/zeolite catalysts. The starting materials were the Na^+ form of ZSM-5 zeolites with Si/Al ratio of 21.5 synthesized by the Davison Chemical Division of W.R. Grace Co. In catalysts containing copper and a cocation, the ZSM-5 zeolites were first ion-exchanged with the cocation in nitrate form in dilute aqueous solution with concentration of 0.007M. The exchanges were made either at room temperature for 10 hours or at 85°C for 2 hours. After filtration, the metal ion-exchanged ZSM-5 zeolites were dried at 100°C for 10 hours, and some of them were further calcined in a muffle furnace in air at 500°C for 2 hours. The reason for calcining the catalysts was to stabilize cations in the zeolite. The catalysts were further ion-exchanged with Cu^{2+} in aqueous solution of cupric acetate with concentration of 0.007M several times, depending on desired Cu exchange levels, at room temperature. Finally, the catalysts were washed with deionized water at room temperature before drying.

The mode of exchange described here was the evolution of several different preparation attempts. A summary of observations made during this process is as follows: a) exchanging copper ions first or co-exchanging copper and magnesium ions for Na^+ in the ZSM-5 did not succeed in high-exchange levels of Mg^{2+} in the zeolite; b) even when Mg^{2+} was exchanged first followed by copper ion exchange, we would observe loss of Mg^{2+} in the solution. Both a) and b) indicate a more favorable exchange equilibrium for Cu^{2+}/Na^+ (10); c) when the Mg^{2+} ion solution was heated at 85°C for 2 hours, higher levels of exchange were obtained and better stability in subsequent room temperature copper ion exchanges; d) air calcination of Mg^{2+}-exchanged zeolite at 500°C for 2 hours was very effective in keeping the Mg^{2+} exchange high even after subsequent copper ion exchanges. This procedure was followed in preparing two Mg/Cu-Z catalysts as well as the Sr, Ni, Pd, Ce and La/Cu- catalysts shown in Table 1.

The elemental analyses were performed by Inductively Coupled Plasma Emission Spectrometer (ICP, Perkin-Elmer Plasma 40) after catalyst samples were dissolved in HF(48%). It is noted that a small amount of Si and Al was extracted from the zeolite during the ion exchange procedures. A list of catalyst syntheses and properties is shown in Table 1. In the text, the catalysts are identified in the following way: cocation type(percent exchange level)/Cu(percent exchange level)-Z, for example, Mg(16.6)/Cu(111.6)-Z.

Conversion Measurements and Kinetic Studies

Conversion and kinetic studies were performed in packed-bed reactor tubes made of quartz of I.D. equal to 11 mm(for conversion measurements) or 4 mm (for kinetic studies). The reactor was placed in a temperature-programmed furnace which was electrically heated and controlled by a temperature controller (Tetrahedron: Model Wizard). Three mass flow controllers were used to measure flow rates of NO+He, O_2+He and He. Certified standard helium and gas mixtures were from Matheson and Airco. A gas chromatograph (Hewlett Packard: Model 5890) with a thermal conductivity detector, using a 5A molecular sieve column of 1/8 in. O.D. by 6 ft. long, was used to measure concentrations of nitrogen, oxygen and nitric oxide. A NO-NOx analyzer (Thermo Electron: Model 14A) was also used to measure low NO/NOx concentrations, ranging from 0.001ppm to 2,500ppm. 0.5- 1.0 g of catalyst was placed in reactor for conversion measurements, and 30-35 mg for kinetic studies. The catalyst packing density in the reactor was about 0.5g/cc. Total flowrates of the feed gas were 30-90cc/min. The contact time, W/F, defined as a ratio of weight of catalyst in the reactor to the total flowrate of the feed gas was 0.03- 1g s/cc(STP). Total gas pressure in the reactor was 1.5 atm during conversion measurements and about 2 atm in the kinetic studies. NO concentrations varied from 0.05%- 4% in the feed gas stream, O_2 from 0%-5%, balance He. The O_2+He stream was heated to 150°C before it was mixed with NO+He at the inlet of the reactor. All measurements were made after steady state had been reached. Several catalysts were examined by X-ray diffraction(XRD) analysis to check for potential crystal structure modification. XRD patterns of ZSM-5, Cu-Z, Mg/Cu-Z, Ce/Cu-Z and La/Cu-Z catalysts were obtained with a Rigaku RU300 instrument.

RESULTS AND DISCUSSION

Nitric Oxide Decomposition in the Absence of Oxygen

The Mg/Cu-Z catalysts shown in Table 1 were evaluated and compared to Cu-Z materials in a gas containing 2% NO-He, at contact time of 1g.s/cc (STP) over the temperature range of 350 - 600°C. Figure 1 shows the NO to N_2 conversion profiles obtained for the catalysts tested under these conditions.

For the same copper ion-exchange level (~90%), the Mg/Cu-Z catalysts, with at least 30% Mg^{2+}-exchange level, show a positive effect, i.e. a higher NO to N_2 conversion than the Cu-Z material, especially in the high temperature region (450 -600°C). These results are in agreement with the report by Kagawa et al (8). However, a catalyst with a higher copper exchange level, such as the Cu (141)-Z shown in Figure 1, is superior. A close examination of the Kagawa's data also reveals that the cocation effect at 550°C diminishes as the copper-exchange level is increased.

Within the group of the Mg/Cu-Z catalysts, preparation condition were important. As mentioned in the previous section, heating of the solution during Mg^{2+}-exchange was necessary in order to keep Mg^{2+} exchange high upon subsequent exchange with copper ion solutions; for example, catalyst Mg (16)/Cu (111)-Z prepared after room temperature-exchanges, had very low Mg-loading and gave lower NO to N_2 conversion over the whole temperature range (Fig. 1) than the catalyst Mg (40)/Cu (91)-Z, of lower copper ion-exchange level for which heating of the Mg^{2+}-solution was used during preparation (Table 1). Even more effective was intermittent air calcination at 500°C of the Mg^{2+}-exchanged ZSM-5, as can be seen by comparing the performance of the Mg (52)/ Cu (65)-Z to Mg (40)/Cu(91)-Z catalyst in Fig. 1.

During the calcination step, Mg^{2+}-bare ions which are smaller than their hydrated complex ions, may form and migrate into the smaller 5- or 6-membered rings of the ZSM-5, where diatomics cannot enter. Effectively, this would keep the copper ions in the larger rings where reactions with gas molecules can occur. Since Mg^{2+}-Z is not a catalyst for the NO decomposition reaction, the presence of Mg ions in the large rings can not be expected to promote the Cu-Z catalytic activity. The observed cocation effect in Kagawa et al(8) and the present work, therefore, may simply be one of stabilization of the copper active sites. From Figure 1, the observation can be made that an over-exchanged Cu-Z, such as the Cu (141)-Z used in this work can achieve the same effect as a lower-level Cu ion-exchange preceded by exchange and stabilization of a different cation in the zeolite. To purse this argument further, the performance shown in Figure 1 should not be sensitive to the type of cation chosen. Figure 2 provides such data for Sr, Ni and Pd ion-modified Cu-Z catalysts (Table 1). The NO to N2 conversion profiles over these catalysts as well as the Mg (34)/Cu (86)-Z material from Fig. 1 virtually overlap.

NO Decomposition in O_2-Containing Gases

Oxygen has been reported to inhibit the NO decomposition reaction, but the inhibition decreases with temperature (7). These authors reported the oxygen effect on Cu-Z catalysts using high NO concentrations (1-4%) in the feed gas. Iwamoto, et al (6) have reported that in oxygen-containing gas the NO conversion to N_2 does not decrease as much for over-exchanged Cu-Z catalysts. However, a large decrease was shown for low Cu ion-exchanged Cu-Z. A conversion dependence on the ratio P_{O2}/P_{NO} was suggested.

In the present work we examined the effect of oxygen both with over-exchanged Cu-Z as well as with the cocation-exchanged M/Cu-Z catalysts. Figure 3 shows typical conversion- temperature plots for the Cu (141)-Z catalyst with zero and 5% O_2 containing gases with NO content fixed at 2%, W/F=1g s/cc (STP). The data display the O_2-inhibition and the lower-sensitivity to O_2 at high temperature mentioned above. However, it is very interesting that a similar plot for low NO-content (0.2%) in the gas(Fig.4), shows much less inhibition by oxygen at low temperatures and no oxygen-effect in the high-temperature region.

Similar experiments were run with the Mg/Cu-Z catalysts. The results are shown in Figures 5 and 6 for the Mg (34)/Cu (86)-Z material. While Figure 5 (for 2% NO) shows similar trends as Figure 3 for the Cu-Z catalyst, Figure 6 (for 0.2% NO) shows an amplification of the effect of oxygen depicted in Figure 4; namely, at temperatures above 450°C, conversion of NO to N2 is enhanced by the presence of oxygen. The other Mg/Cu-Z catalysts gave conversions intermediate between Cu(141)-Z (Fig.4) and the Mg(34)/Cu(86)-Z(Fig.6). Overall then, we found that in the low NO-containing gases the conversion of NO to N_2 is invariant to oxygen in the high temperature region (450-600°C). This finding is very significant for application to dilute-NO, post-combustion gas streams.

Another feature of the conversion-temperature profiles becomes evident by replotting the data of Figures 3-6 for 5% O_2-containing gas and low (0.2%)- or high (2%)-NO concentration. As shown in Figures 7 and 8 for Cu (141)-Z and Mg (34)/Cu (86)-Z, respectively, the conversion of NO to nitrogen increases as the NO-content decreases at temperatures below 450°C. Therefore, the data presented in this section indicate that the active state of copper in the ZSM-5 zeolite is preserved or even further stabilized by oxygen over the whole temperature range (350 -600°C) when low NO-content gases are used.

Kinetic Studies

The microcatalytic reactor described earlier was used with samples weighing 30 - 35mg for kinetic studies and measurements of turnover frequencies over the Cu (141)-Z and the Mg (34)/ Cu (86)-Z catalysts. Conversion-contact time plots, constructed for the NO decomposition reaction over each catalyst at 500°C with 4% NO-He gas, were straight lines for conversions up to 30% for the Mg(34)/Cu(86)-Z and 50% for Cu(141)-Z. In the kinetic studies the conversions were kept below 10% for Mg(34)/Cu(86)-Z and below 40% for Cu(141)-Z to ensure that reaction rates were not diffusion-limited.

Figure 9 shows Arrhenius type plots for the turnover frequencies over the Cu (141)-Z and the Mg (34)/Cu(86)-Z catalysts. The turnover frequency(TOF) defined as the number of NO molecules converted to N2 per second per Cu ion is higher for the Cu (141)-Z than for the Mg (34)/Cu (86)-Z catalyst over the whole range of temperatures in agreement with the conversion-temperature plot of Fig. 1. As has been reported before (7), the specific catalytic activity (turnover frequency) increases with the copper loading on the same parent ZSM-5. The difference is more pronounced at high temperatures. A maximum in the Arrhenius plots is seen, again in agreement with previous reports. In this work we have extended the measurements of activity to higher temperatures to measure the corresponding activation energy. As can be seen in Fig. 9, the apparent activation energy for NO decomposition over the Mg(34)/Cu(86)-Z catalyst is 12.3 Kcal/mole in the low temperature region, changing over to a negative value of -8.2 Kcal/mole in the high temperature region (>500°C). Over the Cu(141)-Z material, similar values of apparent activation energies, 12.6 Kcal/mole for the low temperature region and -7.6 Kcal/mole for the high temperature region, were obtained. A changing reaction mechanism or loss of copper active sites at high temperature may explain the observed reaction rate maximum. A similar study in the presence of oxygen is warranted, based on the conversion plots discussed in the previous section.

Detailed kinetic studies are presently underway in our laboratory with over-exchanged Cu-Z, and Mg/Cu-Z catalysts. One interesting series of tests is reported here as it provides support to the data of Figure 6. A gas containing 0.2% NO in He and oxygen in the range of 0-5% was reacted over the Mg (34)/Cu (86)-Z catalyst at contact time of 0.03g s/cc(STP) and reaction temperature of 600°C. Conversion below 30% was used to measure TOF. The results, plotted in Fig. 10, show the specific catalytic activity to be invariant to oxygen, i.e. a reaction order of zero in O_2 was obtained.

Rare Earth Metal Cation Modified Cu-ZSM-5

Two rare earth metal modified Cu-Z catalysts, namely Ce/Cu-Z and La/Cu-Z shown in Table 1, were evaluated and compared to Cu-Z, a mixture of 50% Cu-Z - 50% Ce/Cu-Z by weight, and Mg(36)/Cu(86)-Z catalysts in a gas containing 2% NO-He at contact time of 1g s/cc (STP) over the temperature range of 300-600°C. Figures 11 and 12 show the NO conversion to N_2 profiles obtained for these catalysts under the above conditions.

The coexistence of rare earth ions with copper in the ZSM-5 produced a markedly different effect promoting the activity of copper ions for the NO decomposition at low temperatures (300-400°C). The Ce ion-exchanged ZSM-5 has very low (but measurable) activity, below 10% conversion of NO to N_2, over the temperature region of 300-500°C. However, the Ce/Cu-Z catalyst showed higher conversion of NO to N_2 than the Cu-Z catalyst at temperatures in the range of 300- 400°C, and higher than the Mg/Cu-Z catalyst at temperatures below 450°C(Figures 11 and 12). When a 50 - 50 mixture (by weight) of Ce/Cu-Z and Cu-Z was tested, its catalytic activity was between those of Cu-Z and Ce/Cu-Z(Figure 12).

Contact time tests showed that the activity of Cu-Z and Mg(34)/Cu(86)-Z catalysts did not decrease much at low NO concentration and oxygen-rich gas as the contact time decreases. This is very important for the practical application of the catalysts. Fig.13 shows profiles of NO conversion to N_2 over the Mg(34)/Cu(86)-Z and Cu-Z catalysts at 2,000ppm NO and 2.5% O_2 in the feed gas and 0.05g s/cc of contact time(36,000 hr^{-1} S.V.). Conversions are similar to those in Figures 4 and 6 obtained under higher contact time. Figure 13 also shows that the Ce/Cu-Z catalyst remained more active than Cu-Z and Mg/Cu-Z at 400°C.

X-ray Diffraction Patterns

XRD analysis of the catalysts showed that there was no change of the diffraction pattern between the parent ZSM-5 and the Cu-Z, or the Mg/Cu-Z catalysts. However, the diffraction patterns of La/Cu-Z and Ce/Cu-Z showed differences from that of parent ZSM-5. As shown in Figure 14, all peaks for the La/Cu-ZSM-5 shifted to lower 2θ, and for the Ce/Cu-Z a more pronounced shift was obtained. Moreover, the diffraction pattern of the Ce/Cu-ZSM-5 shows that two peaks at 2θ= 7.5-9 degrees totally disappeared. Detailed studies of the rare earth metal- modified Cu-ZSM-5 are currently underway in our laboratory. Differences in the La amount were measured by ICP when the La/Cu-Z was digested in HCL or HF according to a recently published method for differentiating between extra- and intra-framework Ga^{3+} in ZSM-5(11). These results suggest that La and Ce ions did not only exchange Na^+ ions in the zeolite, but also were incorporated in the zeolite framework.

SUMMARY/CONCLUSION

Alkaline earth and transition metal ion-exchanged ZSM-5 zeolites further exchanged with copper ions are active catalysts for the NO decomposition reaction in the presence or absence of oxygen and over a wide range of temperature (350 - 600°C). Proper mode of ion exchange is crucial for a positive cocation effect. Conversion and activity similar to over-exchanged

Cu-ZSM-5 catalysts can be obtained with M/Cu-Z catalysts with ~40% M ion exchange and less than 100% Cu ion exchange.

An extensive study of Mg/Cu-Z catalysts was performed in this work. The conversion and kinetic data indicate that the role of Mg ions is one of stabilizing the activity of copper ions, potentially by occupying the "hidden" sites of the zeolite. Both the over-exchanged Cu-Z and the Mg/Cu-Z catalysts have low sensitivity to oxygen in dilute NO gases. At 600°C, a reaction order of zero in O_2 was found with the Mg(34)/Cu(86)-Z catalyst. Detailed kinetic studies with oxygen-containing gases are underway to further evaluate the effects observed here.

The performance of (Ce, La)/Cu-Z catalysts is markedly different, the cocation effect being promotion of the Cu ion activity. This is displayed by the NO conversion to N2 maximum shifting to lower temperatures ($\leq$400°C).

The Ce/Cu-Z catalyst activity remained higher than that of the over-exchanged Cu-Z in 2.5% oxygen, low NO content and high space velocity (36,000h-1). Additional studies with rare earth modified Cu exchanged ZSM-5 are warranted.

PLAN FOR NEXT QUARTER

It is planed to synthesize new Mg/Cu-ZSM-5 catalysts with high Cu exchange levels (>100%) and Ce/Cu-ZSM-5 catalysts with different Ce exchange levels. A new procedure will be used for the determination of major and minor elements in catalysts, especially for rare earth cation promoted Cu exchanged zeolite catalysts since Ce, La etc. are fluoride insoluble. Continued kinetic studies of NO and O_2 interaction with M/Cu-ZSM-5 catalysts will be conducted.

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Table 1. Summary of Catalyst Syntheses and Properties

Catalysts [M/Cu-ZSM-5]	Si/Al	Cu/Al	Cocation/Al	Na/Al
Parent zeolite [a]	21.3			1.0
Mg/Cu-Z	20.3	0.558 (111.6%) [b]	0.083 (16.6%)	~0
Cu-Z	20.3	0.705 (141%)	-	~0
Mg/Cu-Z[c]	18.0	0.456 (91.2%)	0.202 (40.4%)	
Mg/Cu-Z [d]	17.1	0.430 (86.0%)	0.170 (34.0%)	~0
Mg/Cu-Z [c,d]	18.9	0.328 (65.6%)	0.216 (52.2%)	~0
Ce/Cu-Z[c,d,e]	19.5	0.583 (116.6%)	-	~0
La/Cu-Z[c,d,e]	19.4	0.627 (123.4%)	0.06 (18.0%)	~0
Sr/Cu-Z[c,d,e]	20.8	0.524 (104.8%)	0.194 (38.8%)	~0
Ni/Cu-Z[c,d,e]	20.8	0.478 (95.6%)	0.877 (175.4%)	~0
Pd/Cu-Z[c,d,e]	20.7	0.45 (90%)	0.44 (88%)	~0

a. as received low ratio(Si/Al) ZSM-5 from W.R. Grace. Co.

b. The values in parentheses are ion exchange levels.

c. Cocations exchanged with Na/ZSM-5 at 85°C for 2 hours.

d. The cocation-exchanged ZSM-5 catalysts were dried in air at 100°C for 10 hours, and calcined at 500°C for 2 hours.

e. The first Cu cation exchange of cocation-exchanged ZSM-5 was made by adding NH_4OH(NH^+/Cu^{2+}=0.7 by mole) in the copper acetate solution at room temperature for 2 hours; second Cu exchange in the copper acetate solution at room temperature for 10 hours.

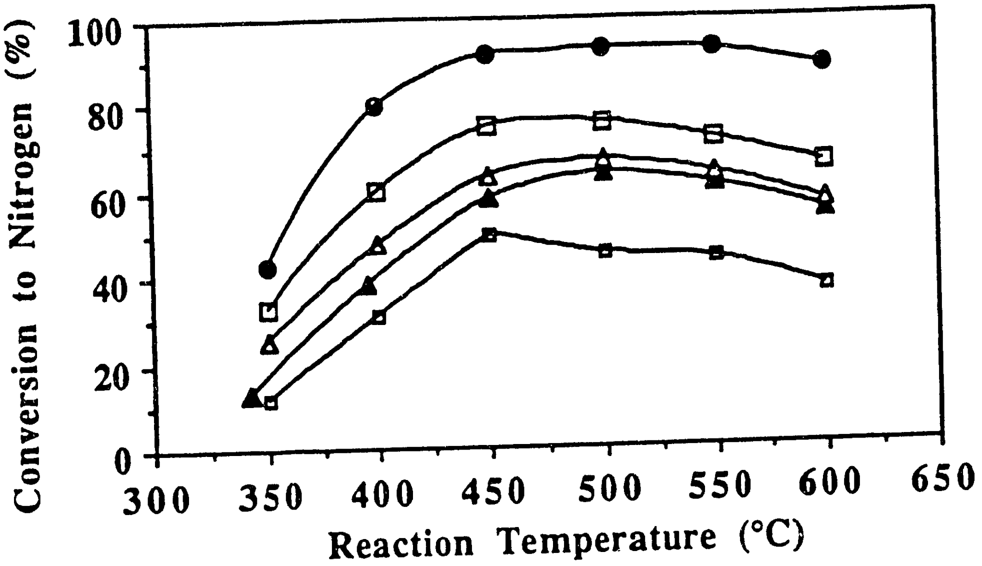

Fig.1 NO decomposition over Cu-Z and Mg/Cu-Z catalysts at 2% NO and 1g s/cc contact time (● :Cu(141)-Z, □ :Mg(34)/Cu(86)-Z, △ :Mg(65.6)/Cu(52.2)-Z, ▲ :Mg(40.2%)/Cu(91.2)-Z, ▫ :Mg(16.6)/Cu(111.6)-Z)

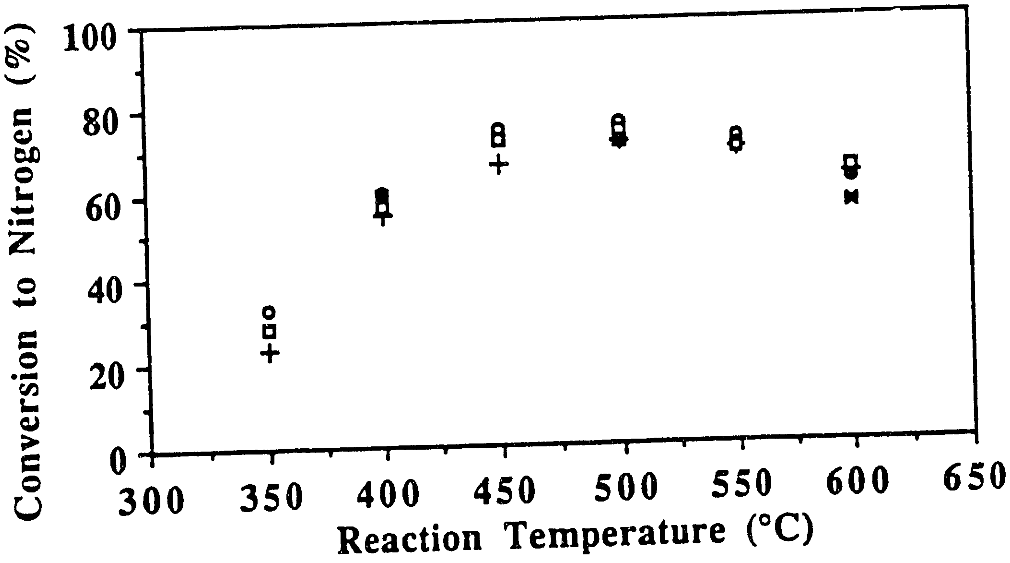

Fig.2 NO decomposition over M/Cu-Z catalysts at 2% NO and 1 g s/cc contact time (○ : Mg(34)/Cu(86)-Z, ✖ :Sr/Cu-Z, ▫ :Pd/Cu-Z, + :Ni/Cu-Z)

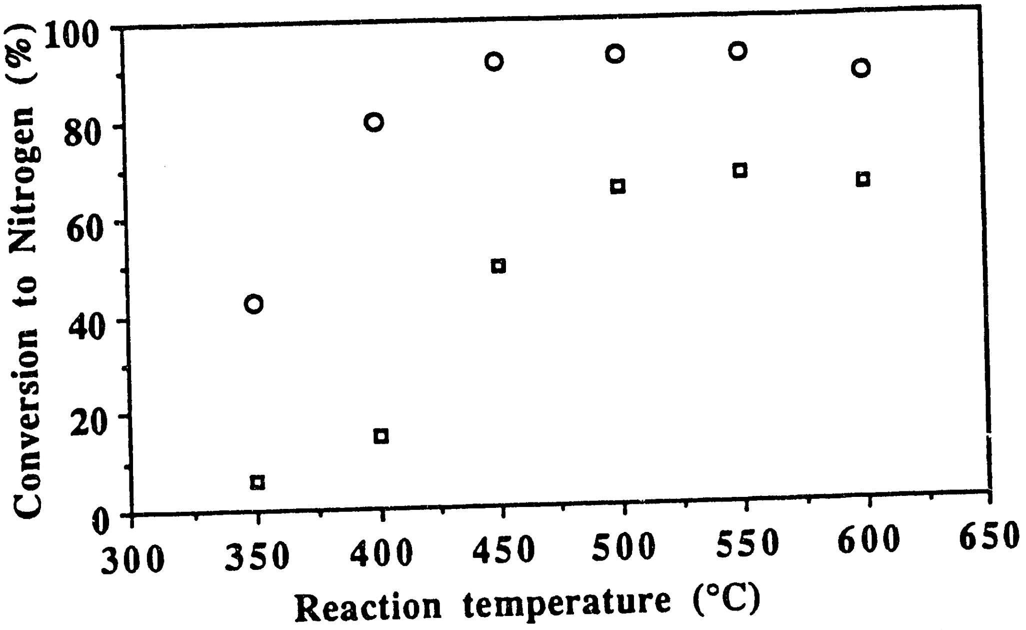

Fig.3 Effect of oxygen on Cu(141%)-ZSM-5(20.3%) activity at 1g s/cc and 2% NO(○ : without oxygen, ▫ : with 5% oxygen)

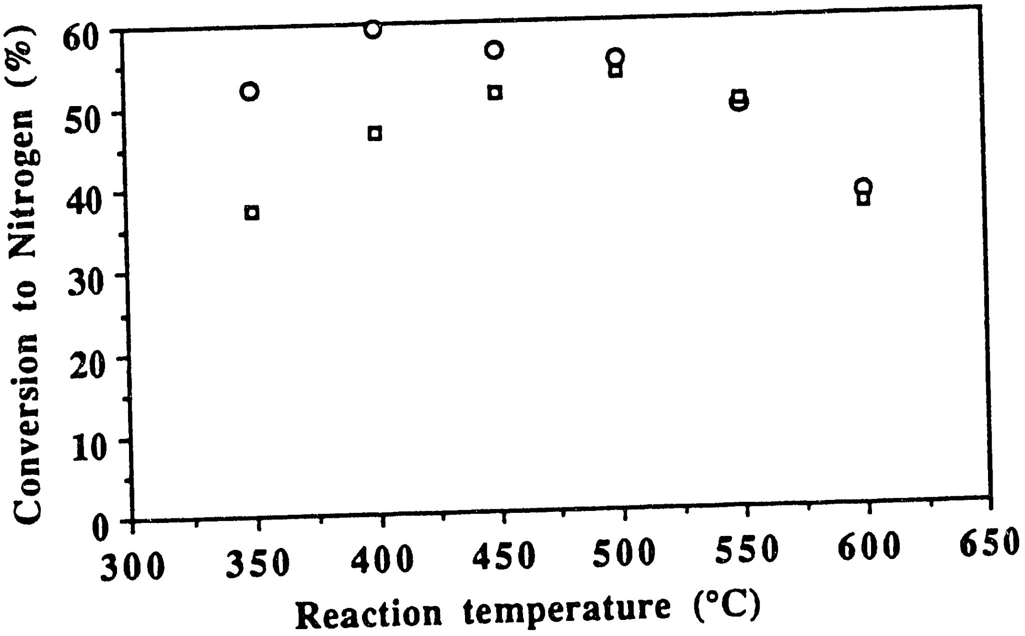

Fig.4 Effect of oxygen on Cu(141%)-ZSM-5(20.3) activity at 1g s/cc and 0.2% NO(○ : without oxygen, ▫ : with 5% oxygen)

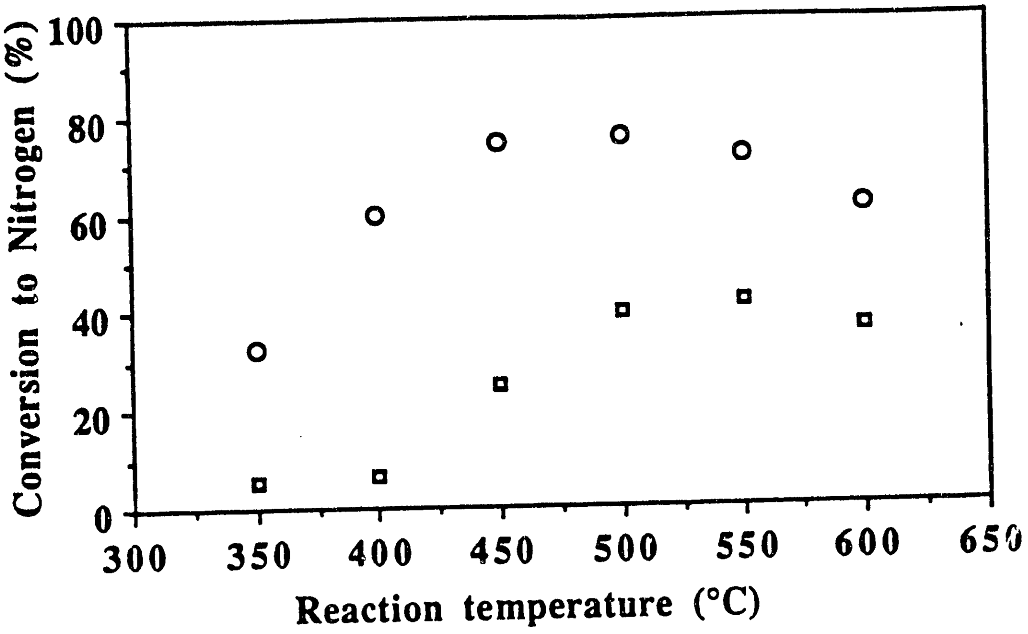

Fig.5 Effect of oxygen on Mg(34%)/Cu(86%)-ZSM-5(17.06) activity at 1g s/cc and 2% NO(○ :without oxygen, □ : with 5% oxygen)

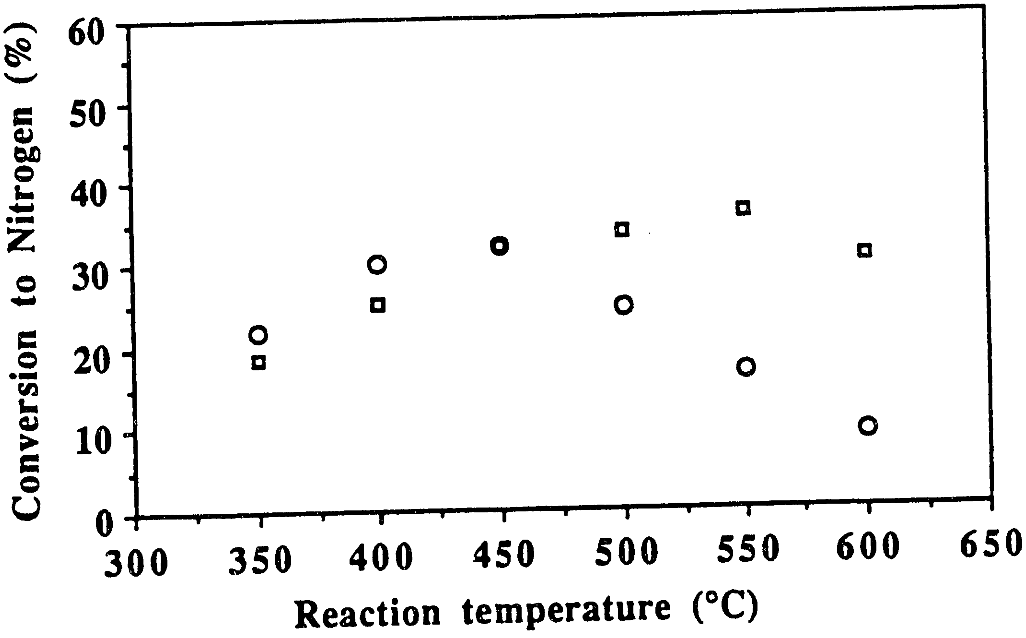

Fig.6 Effect of oxygen on Mg(34%)/Cu(86%)-ZSM-5(17.06) activity at 1g s/cc and 2,000ppm NO(○ : without oxygen, □ :with 5% oxygen)

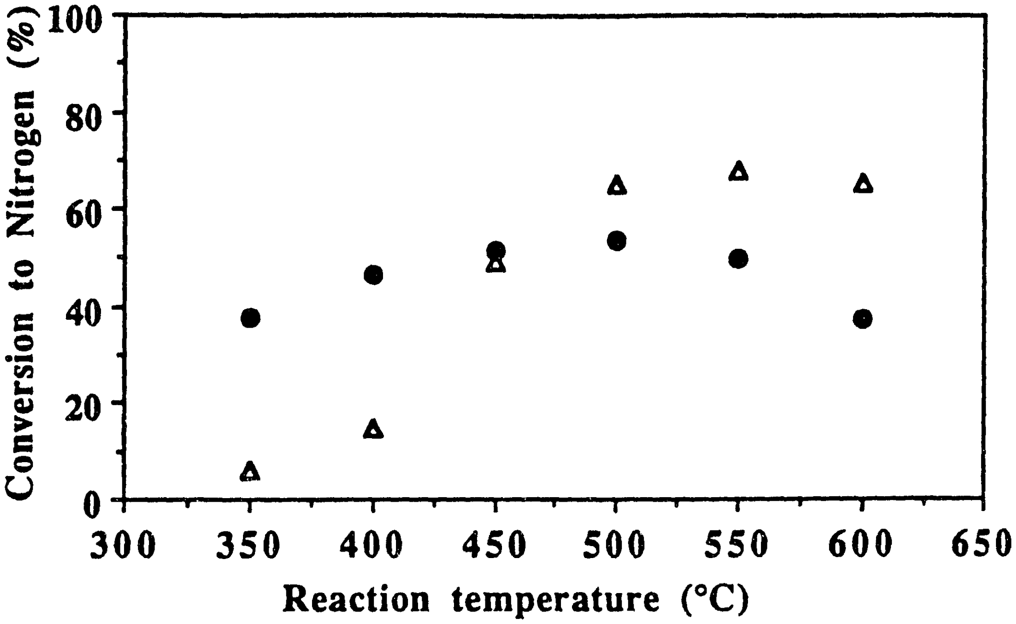

Fig.7 Effect of NO concentration on Cu(141%)-ZSM-5(20.3) activity at 1g s/cc and 5% O2(● : 0.2% NO, △ : 2% NO)

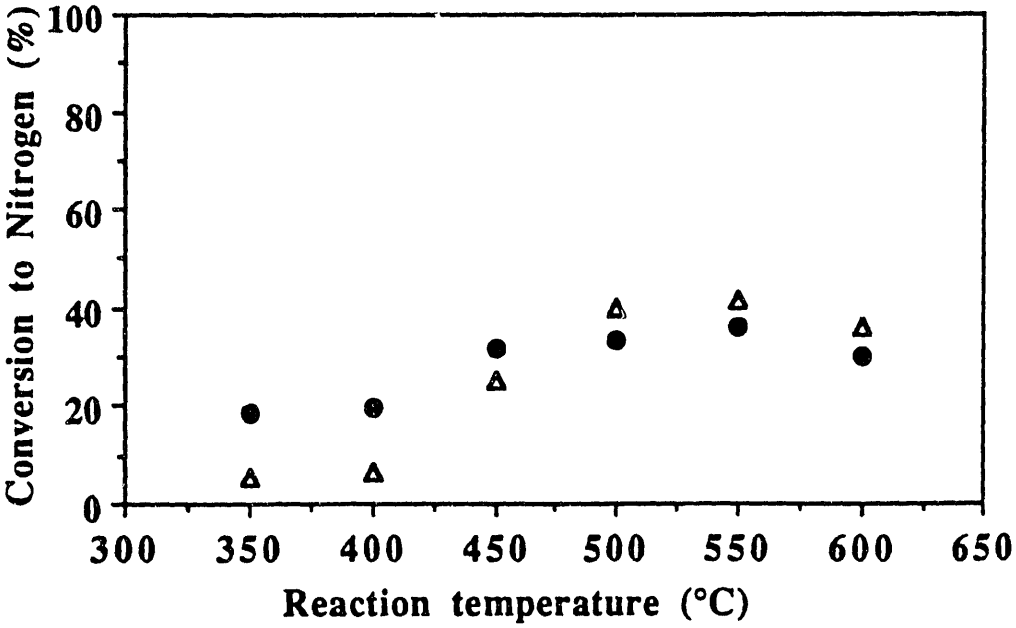

Fig.8 Effect of NO concentration on Mg(34%)/Cu(86%)-ZSM-5(17.06) activity at 1g s/cc and 5% oxygen(△ : 2%NO, ● : 0.2% NO)

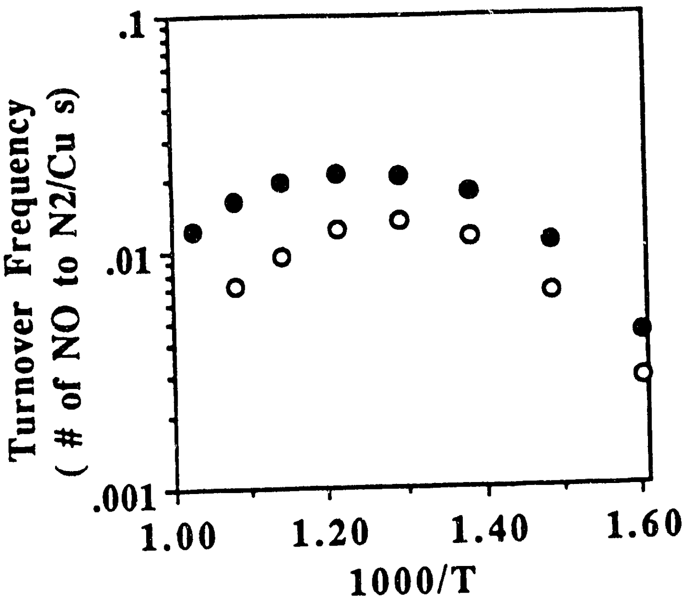

Fig.9 Arrhenius plots for NO decomposition over Cu-Z and Mg/Cu-Z at 4% NO in feed gas and 1.7 atm total pressure.

● - Cu(141%)-ZSM-5(20.3),

○ - Mg(34%)/Cu(86%)-ZSM-5(17.1)

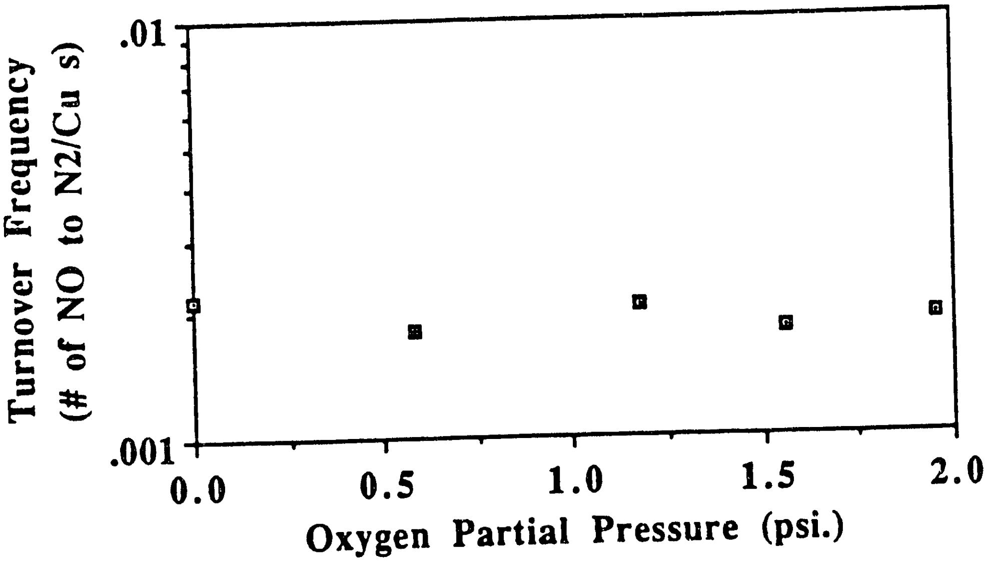

Fig.10 The effect of oxygen on NO decomposition over Mg(34)/Mg(86)-Z at 2000ppm NO, 0.03g s/cc of contact time and 600°C

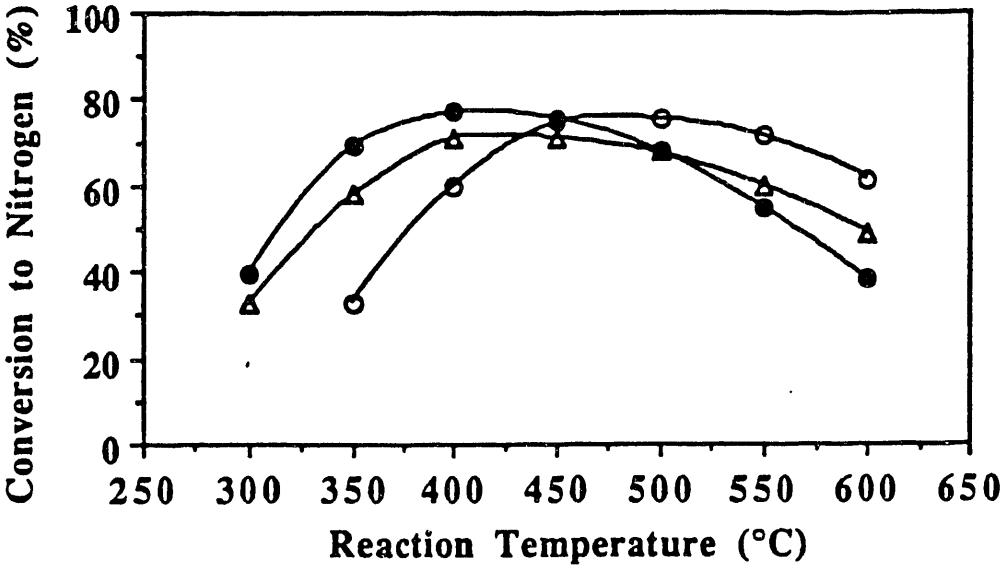

Fig.11 NO decomposition over Ce/Cu-Z(●), La/Cu-Z(▲) and Mg(34)/Cu(86)-Z(○) at 2% NO and 1g s/cc(STP) contact time

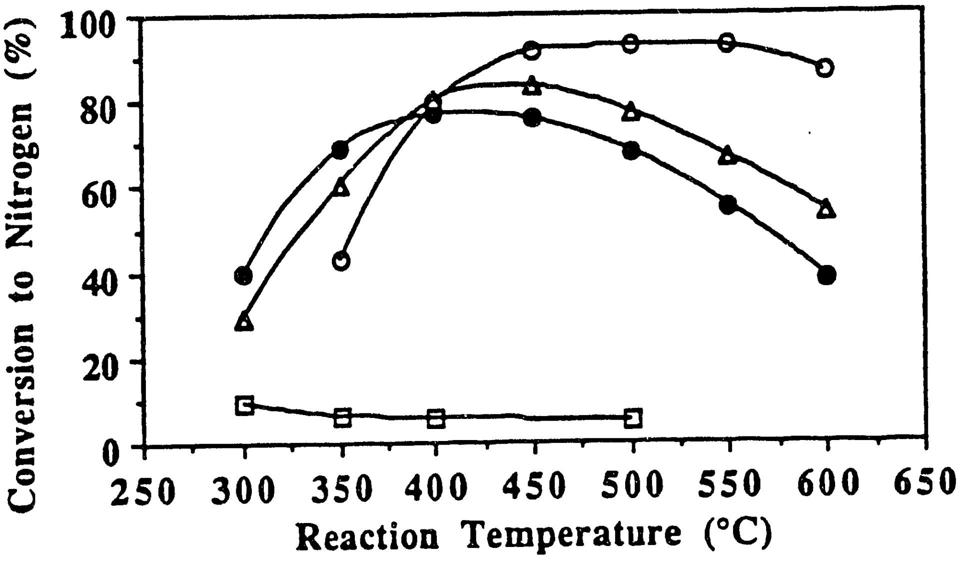

Fig.12 NO decomposition Over Ce-Z(◻), Ce/Cu-Z(●), Cu(141)-Z(○), Ce/Cu-Z+ Cu(141)-Z(50-50)(▲) at 2% NO and 1g s/cc(STP) contact time

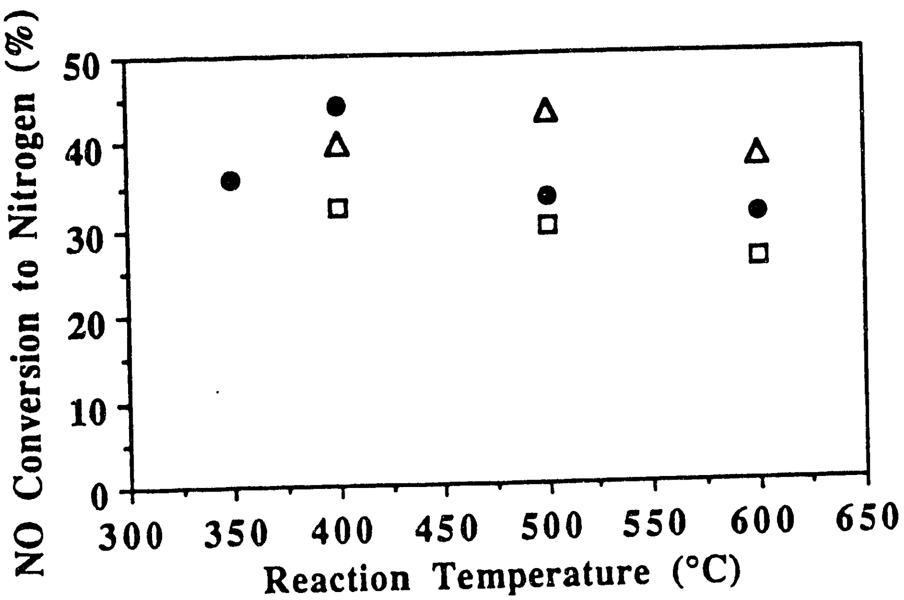

Fig.13 NO decomposition over catalysts at 2000ppm NO, 2.5% O2 and 0.05 g s/cc of contact time(● : Ce/Cu-Z, □ : Mg(34)/Cu(86)-Z, △ : Cu-Z)

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