DIRECT CATALYTIC DECOMPOSITION OF NITRIC OXIDE

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Quarterly Technical Progress Report No.5

October-December 1992

By

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Cambridge, Massachusetts

" US/DOE Patent Clearance is not required prior to the publication of this document"

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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

Reactor System Modification

The reactor system was modified by separating the oxygen stream from the nitric oxide stream in feed gas. The reason for this is to prevent the oxygen and the nitric oxide reaction in the gas phase to form nitrogen dioxide. The oxygen stream is heated to 150°C to avoid this reaction when it is mixed with nitric oxide just at the inlet of the reactor.

A new molecular sieve 5A column of 1/8 in. O.D. and 6ft. long has been used to replace the molecular sieve 13X column in the GC. The new column can separate nitric oxide, nitrogen, and oxygen. Hence, the concentrations of NO, N_2 and O_2 can be measured simultaneously.

Catalyst Synthesis and Characterization

During this quarter, four new catalysts, namely catalysts #22, #23, #24, and #25, were prepared by exchanging metal cations, Cu^{2+}, Mg^{2+}, Ag^{1+}, into the Na^{1+}/ZSM-5 zeolite (Si/Al = 21.5) substrate. Cation exchange levels for all catalysts were determined by measuring the amount of ions in the catalysts with ICP, after the samples had been dissolved in HF. The results are listed in Table 1.

The catalysts were prepared by different procedures, which are described below. For the catalyst #22, the ZSM-5 zeolite was ion-exchanged in a solution of $Mg(NO_3)_2$ with concentration of 7mmol/dm^3 at 90°C for 2 hours, and the exchanged zeolite was separated from the solution by filtration. 45.2% of Mg^{2+} exchange level was achieved. The produced Mg^{2+} exchanged zeolite was further exchanged in a solution of $Cu(OOC_2H_3)_2$ (as

much as the amount of Cu^{2+} needed to get 150% exchange level) and $Mg(NO_3)_2$ (as much as the amount of Mg^{2+} needed to achieve 1,000% exchange level) twice at room temperature overnight. As previously reported [1], the excess Mg cations in solution are needed to keep Mg cations in the ZSM-5 zeolite from being replaced by Cu ions in the solution since the separation factor of Mg over Cu cations is very small. Finally, the Mg exchange level was 40.4%, and the Cu exchange level 91.2%.

For catalyst #23, the zeolite was exchanged in a solution of $Mg(NO_3)_2$ with the same concentration as that in the first Mg cation exchange step for catalyst #22, but at room temperature for ten hours. In the following two exchange steps in mixed solutions of the Cu and Mg cations, a lower concentration of Mg cations (as much as the amount of Mg needed to get 200% exchange level) was used and the Cu cation concentration was the same as that in the synthesis of catalyst #22. The resulting exchange levels for Cu and Mg were 86.0% and 34.0%, respectively.

For catalyst #24, the ZSM-5 zeolite was ion-exchanged in a solution of $Mg(NO_3)_2$ with concentration of 7mmol/dm^3 at 90°C for 2.5 hours, and the exchanged zeolite was separated from the solution by filtration. Mg and Na contents in the solution before and after Mg cation exchanging with the zeolite were measured by ICP to determine the Mg exchange level and Na replaced level, which were found 50.6% and 62.8%, respectively. The produced Mg exchanged zeolite was dried in air in an oven at 373K overnight, and was calcined in air in a muffle furnace at 773K for two hours. The heat treated sample was further ion-exchanged in a solution of $Cu(OOC_2H_3)_2$ only with concentration of 7mmol/dm^3 twice at room temperature for 10 hours. The sample was separated from the solution after the second Cu cation exchange step, and was washed with deionized

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water for 30 minutes. In each step of this process, the Cu, Mg, and Na concentrations were measured to monitor how cations were exchanged with each other. These are shown in Table 2.1.

For catalyst #25, the ZSM-5 zeolite was exchanged in a solution of $AgNO_3$ with concentration of 3.5mmol/dm^3 at room temperature for 10 hours. A 70.0% of Ag exchange level was achieved, and 62.2% of Na was replaced by Ag cations, based on measurements of Na, Ag concentration differences in the solution before and after exchange step. In the following two Cu cation exchanges with Ag exchanged ZSM-5, preparation conditions were the same as those in catalyst #24 synthesis. Following the same procedure, the Ag/Cu exchanged ZSM-5 was also washed with deionized water at room temperature for 30 minutes after the cation exchanges had been finished. Ag and Cu exchange levels and Na replaced level were determined, and results for each step exchange are listed in Table 2.2.

From the above results, it is apparent that the heat treatment after the first Mg exchange step in the catalyst #24 synthesis prevented Mg cations in the Mg exchanged ZSM-5 from being replaced by Cu cations in solution during the Cu cation exchange steps. However, for the catalyst #25, since the Ag^+-exchanged ZSM-5 was not dried and calcined before the Cu cation exchange processes, most of Ag cations in the ZSM-5 were replaced by Cu cations even though the separation factor of Ag over Cu cations is large. Catalyst preparation procedures will follow those used in catalyst #24 synthesis for making cocation exchanged ZSM-5 catalysts in the future.

It should be pointed out that it is very difficult to accurately determine the ion exchange level by measuring ion content difference in solution before and after ion exchange based on catalyst mass, since it is impossible to recover all the catalyst sample in such a long and complex catalyst

synthesis process. Hence, the ion exchange level determined by this method is not in very good agreement with that by catalyst dissolving in HF. Typical results for catalysts #24, and #25 are shown in Table 1 and 2 for the Cu, Mg, Ag, and Na exchange levels.

Experimental

During this quarter, comparative testing of six Cu^{2+}-exchanged ZSM-5 (Si/Al=21.5) was performed to study the effects of oxygen in the feed gas on the catalytic activities of unpromoted and promoted Cu^{2+}- exchanged ZSM-5 catalysts at different reaction temperatures and NO concentrations. Three of these catalysts, namely catalysts #4[Mg(16.6%)/Cu(108%)-ZSM-5], #12[Cu(133.6%)/ZSM-5], and #18[Zn(68.2%)/Cu(20.0%)-ZSM-5], were prepared last quarter[1]. The remaining three are catalysts #22, #24 and #25 (properties listed in Tables 1 and 2). The experimental conditions used this quarter are the following: reaction temperatures 350- 600°C, contact time 1g s/cc (STP), NO concentrations 0.1-2%, and O_2 concentration 0- 5%. The heat treatment of the catalysts prior to catalytic activity measurements consisted of heating the catalysts in He at 500°C for two hours.

Results and Discussion

Copper in catalyst #12 appeared to have been partially oxidized forming CuO as indicated by grey- black catalyst color. In testing this catalyst in a 2% NO - He mixture at contact time 4g s/cc, its activity was found very low, especially at low reaction temperatures. At end of the test, a gaseous mixture of 25% H_2- 75% He passed over the catalyst bed at 500°C for two hours. The bed temperature was then lowered to 450°C, and a mixture of

2% NO in He was fed into the reactor. The NO conversion to nitrogen was the same as before. But, the catalyst color had changed from grey to dark red after the reduction step, indicating the presence of CuO particles($CuO + H_2 --> Cu + H_2O$).

Catalyst #18 was not active, apparently because its Cu exchange level was low. The NO conversion to nitrogen was below 20% at NO concentration 2%, contact time 4g s/cc and temperature 350- 600°C.

Therefore, the comparison of catalyst performance in oxygen is made below for the old catalyst #4 and new catalysts #22, 24 and 25.

The effect of oxygen in the feed gas stream on the catalytic activity of catalyst #4 for NO decomposition was continuously examined at a contact time 4g s/cc, NO concentration 2%, and O_2 concentration 5%. NO conversion to nitrogen was about 50%, which was lower than that for 0% and 0.61% oxygen in the feed gas[1], over the temperature range 350-550°C. However, when temperatures higher than 500°C or lower than 400°C were used, oxygen did not affect the conversion of NO to nitrogen very much. The results are shown in Figure 1.

The effect of NO concentration in the feed gas on the catalytic activities of catalysts #4, an aged catalyst which had been run for 10 days, #22, #24 and #25 was examined in the absence of oxygen in the temperature range 350- 600°C and at contact time 1g s/cc (STP). The results are shown in the Figures 2 and 3. When NO concentration was 2% in the feed gas mixture, the NO conversion to nitrogen increased with temperature up to 500°C, and then decreased. However, the NO conversion to nitrogen for the lower NO concentration of 0.2% (0.1% for catalyst #22) in the feed gas decreased monotonically with temperature, and was lower than that for NO concentration 2%. Catalyst #25 is the most active catalyst, and catalysts

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#22 and #24 have similar activities in both high and low NO concentrations. It is worth to point out that the NO conversion to nitrogen for catalyst #4 was in good agreement with that in Figure 3 of the last quarterly report [1]. This implies that this catalyst has stable, long- term activity.

Catalyst activities in the presence of oxygen in the feed gas were examined to see how oxygen affects the process of NO decomposition. Test results showed that generally oxygen inhibits the catalytic activity. However, this effect becomes smaller as reaction temperature increases. Also it is very interesting to see that oxygen has a negligible effect on the catalyst activities at low NO concentration over the whole temperature range. Typical results are shown in the Figures 4 and 5, for catalyst #24.

The three catalysts, #22, #24 and #25 showed identical conversion of NO to N_2 over whole temperature range examined (350- 600°C) for a gas mixture containing 2% NO, 5% O_2. The profiles are flat above 500°C. Theses results are shown in Figure 6. On the other hand, the NO conversion profiles are flat throughout the temperature range of 400- 600°C, when low NO (0.1- 0.2%) containing gases are used in the presence of 5% O_2. Figure 7 shows this for catalysts #22, 24 and 25. As a consequence of this, the low- temperature (400°C) conversion of NO in the presence of oxygen is higher for gas mixtures containing low NO concentrations (compare Fig. 6 and 7). This is very significant for flue gas clean cleanup applications (low NO, high O_2). Kinetic studies are planned to further examine this phenomenon.

Plan for Next Quarter

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It is planed to synthesize new cocation Cu-exchanged ZSM-5 (Si/Al= 21.5) catalysts. The cations will be Ba^{2+}, Ce^{3+}, La^{3+}, Mg^{2+}, Mn^{2+}, Ni^{2+}, Pd^{2+}, Sr^{3+}, Y^{3+}, and Zn^{2+}. Different parent ZSM-5 zeolites (Si/Al= 110 and 320) will also be used to examine the effect of the Si/Al ratio on the catalytic activity of Cu ion-exchanged ZSM-5 for NO decomposition. Kinetic studies of NO and O_2 interaction with these catalysts will be performed. Of particular interest is kinetic information at the high temperature end (> 500°C), based on our work to-date.

Reference

1. Flytzani-Stephanopoulos, M., Sarofim, A. F. and Zhang, Y.P., Quarterly Technical Progress Report NO. 4 (1992), Grant number DE-FG22-91PC91923.

Table 1. Summary of Catalyst Properties

Catalysts	Si/Al	Na/Al	Cu/Al	Mg/Al	Zn/Al	Ag/Al
Parent zeolite[a]	21.31	0.95	-	-	-	-
#22	17.99	0	0.456 (91.2%)[b]	0.202 (40.4%)	-	-
#23	17.06	0	0.430 (86.0%)	0.170 (34.0%)	-	-
#24	18.93	0	0.328 (65.6%)	0.261 (52.2%)	-	-
#25	20.48	0	0.490 (98.0%)	-	-	0.05 (5.0%)

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

b. The values in parenthesis are ion exchange levels.

Table 2.1 Summary of Catalyst #24 Synthesis

Cation	Precursor salt concentration (mmol/dm^3)	Mg exchange level(%)	Cu exchange level(%)	Na replace level(%)	note
Mg	11	50.6		62.82	90C,2.5hr.
(Mg exchanged ZSM-5 was dried at 100C overnight, and then calcined at 500C for 2 hours)					
Cu	7.9	-4.8	70.6	33.92	RT, over-night
Cu	7.9	-1.4	18.54	5.3	RT,over-night
Washing catalyst		0	-10.6	0	RT,30min.
Total exchange		44.4	78.54	102.04	

Table 2.2 Summary of Catalyst #25 Synthesis

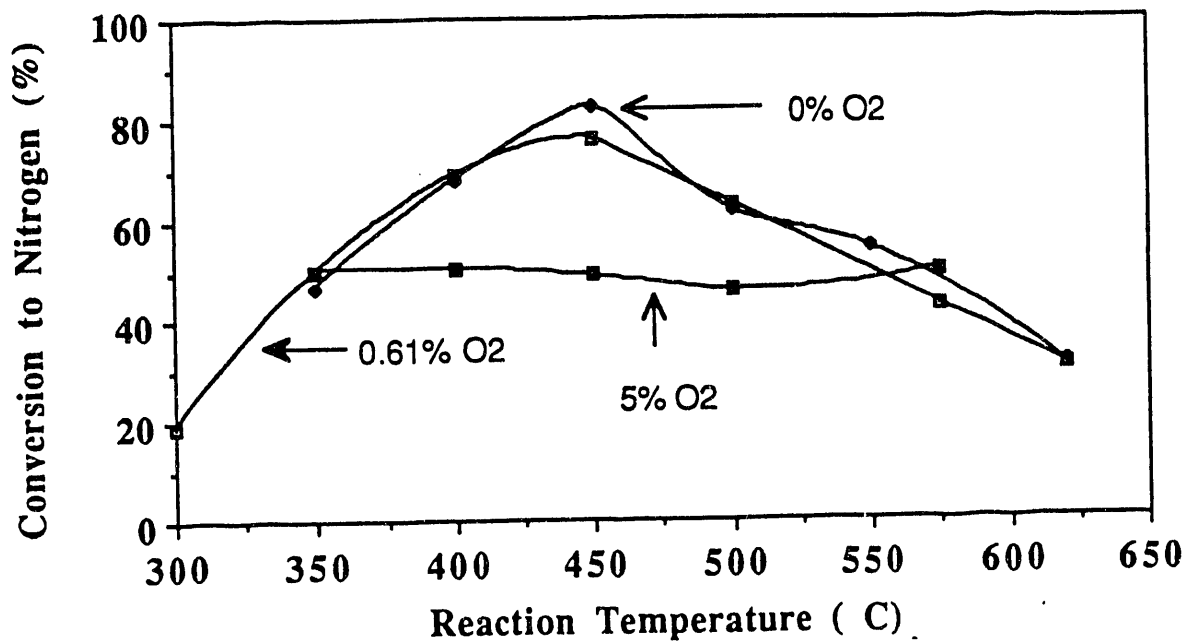| Cation	Precursor salt concentration (mmol/dm^3)	Ag exchange level(%)	Cu exchange level(%)	Na replace level(%)	note
Ag	7.2	69.96		62.21	RT,over-night
Cu	5.6	-47.2	75.8	31.5	RT, over-night
Cu	6.3	-8.26	42.02	2.84	RT,over-night
Washing catalyst		-7.6	-10.6	0	RT,30min.
Total Exchange		6.9	107.8	96.6	

Fig.1 Effect of O_2 on catalytic activity of catalyst #4 for NO decomposition at contact time 4g s/cc and NO concentration 2%
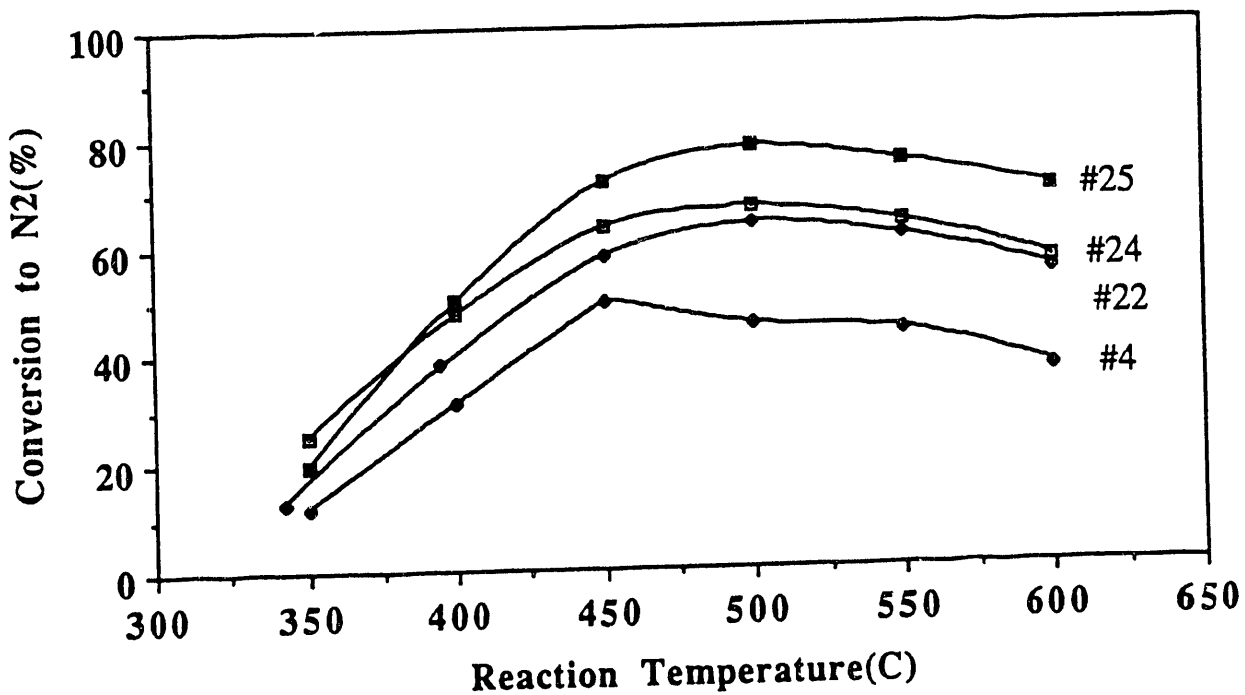

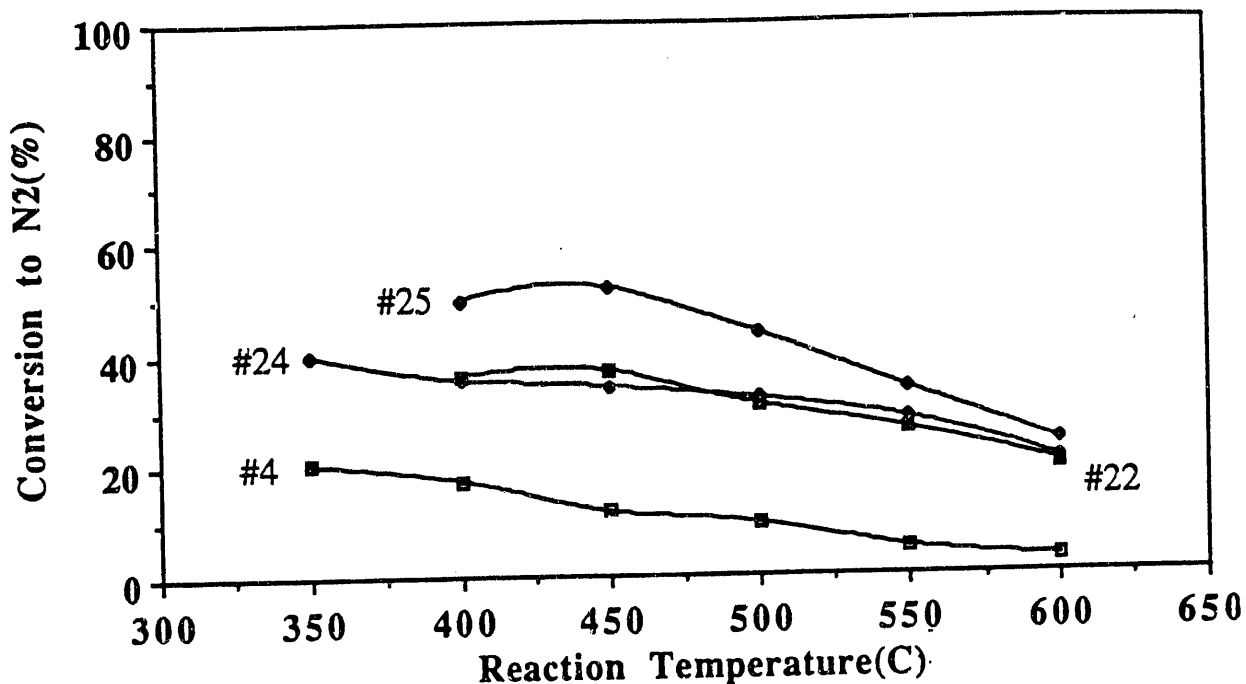Fig.2 NO decomposition over catalysts #4, #22, #24 and #25 at contact time 1g s/cc and NO concentration 2%

Fig.3 NO decomposition over catalysts #4, #22, #24 and #25 at contact time 1g s/cc and NO concentration 0.2%(0.1% for catalyst #22)
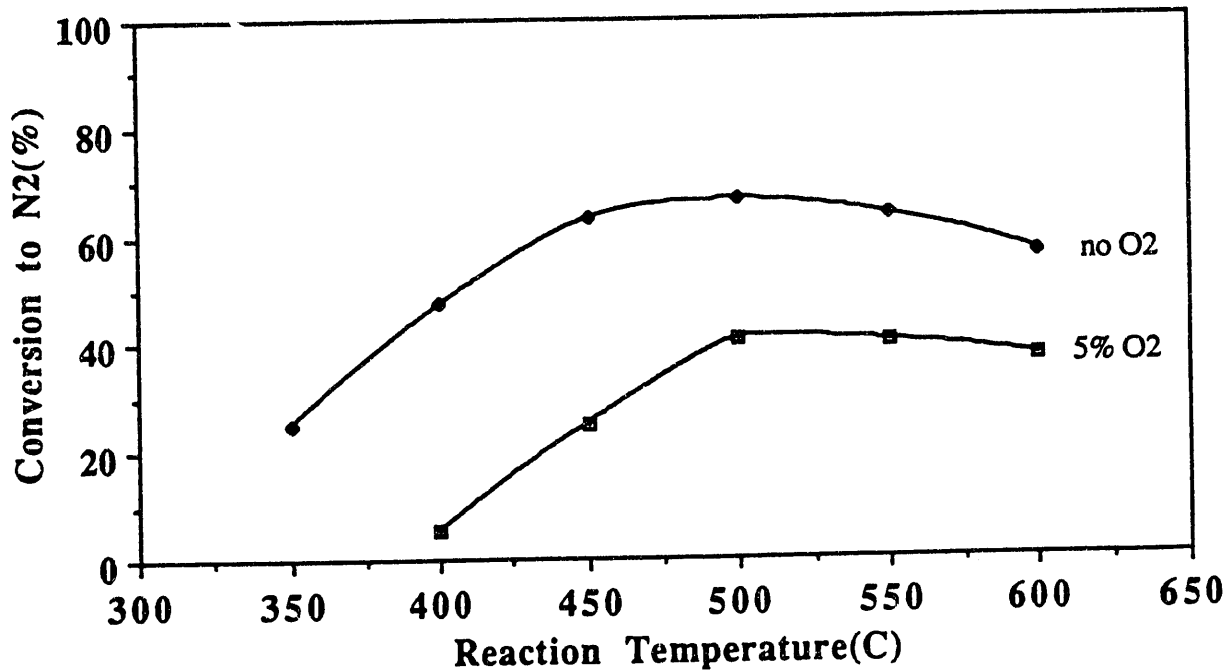

Fig.4 Catalytic activity of catalyst #24 for NO decomposition at contact time 1g s/cc, NO concentration 2% and different oxygen concentrations
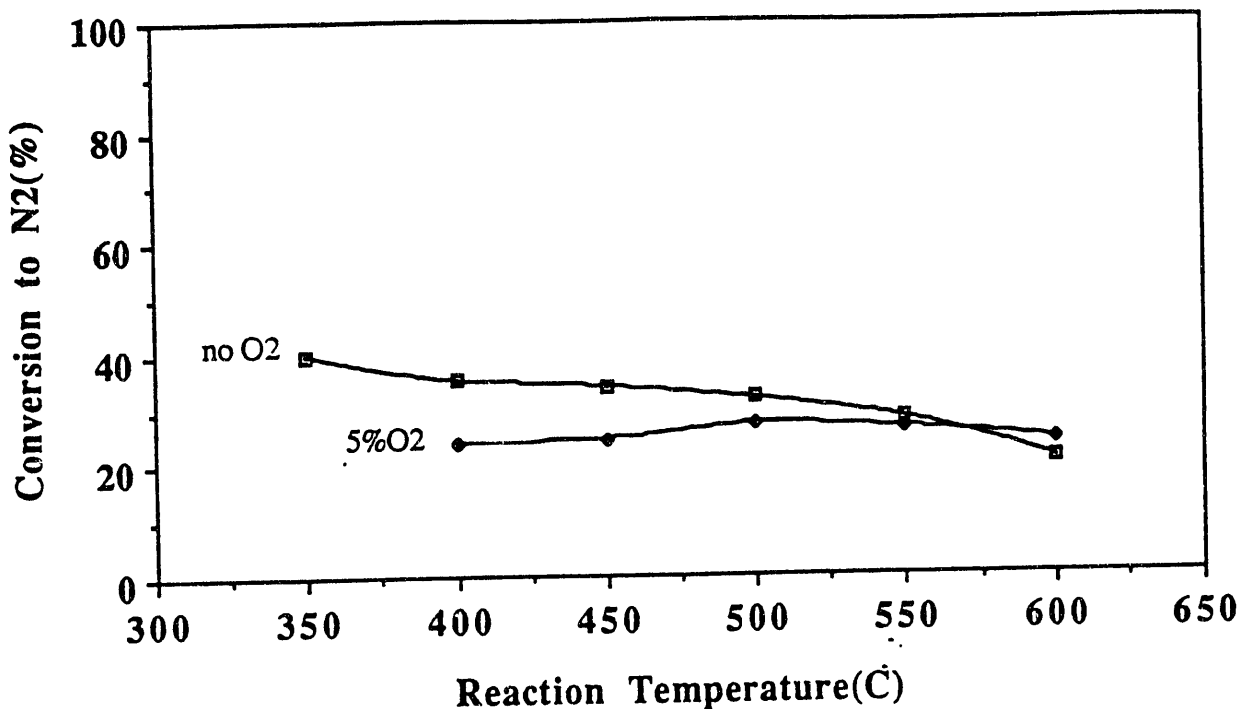
Fig.5 Catalytic activity of catalyst #24 for NO decomposition at contact time 1g s/cc, NO concentration 0.2% and different oxygen concentrations
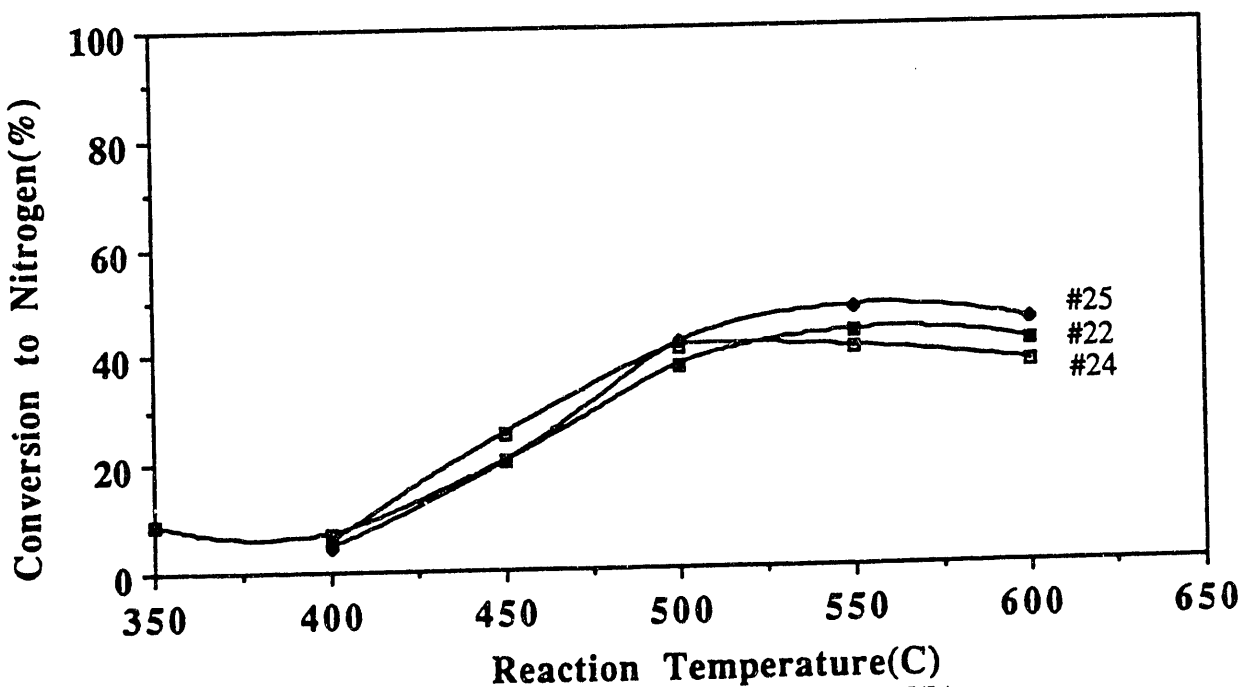

Fig.6 NO decomposition over catalysts #22, #24 and #25 at contact time 1g s/cc, NO concentration 2% and oxygen 5%
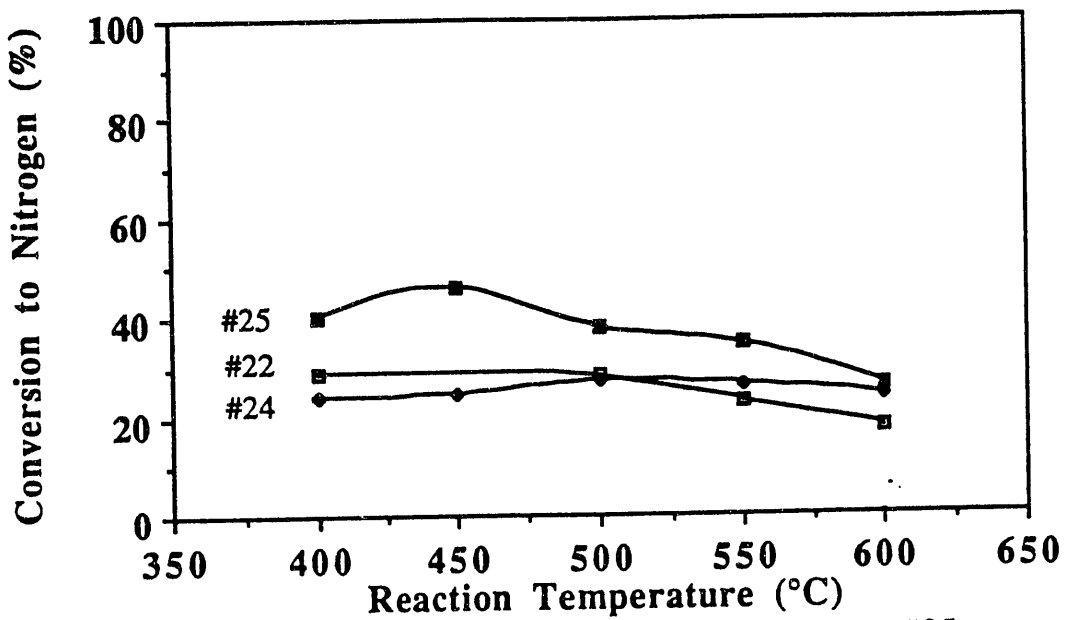
Fig.7 NO decomposition over catalysts #22, #24 and #25 at contact time 1g s/cc, NO concentration 0.1- 0.2% and oxygen concentration 5%

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