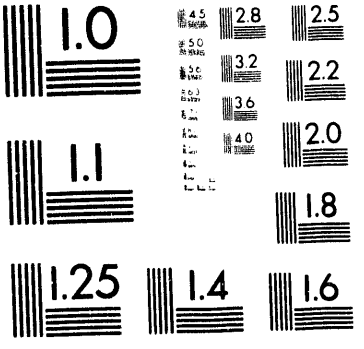
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DIRECT CATALYTIC DECOMPOSITION OF NITRIC OXIDE

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Direct Catalytic Decomposition of Nitric Oxide

This project investigates a suitable catalyst system for direct NO decomposition in post-combustion gas streams. This 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. The effect 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. 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

Fifteen catalysts were prepared according to the procedures described in our earlier reports [1,2]. Another set of Cu ion-exchanged catalysts was synthesized in a new fashion, which will be used to study Cu ionic states in the zeolites. Alkaline earth and transition metal cocation effects are further reported for Cu ion-exchanged ZSM-5 zeolites used for the catalytic decomposition of nitric oxide in oxygen-rich gases. The effect, manifested under a specific mode of ion exchange, enhances the catalytic activity at high temperatures (450-600°C) and appears to be due to the stabilization of the active copper sites. The coexistence of the rare earth ion, Ce, promotes the catalytic activity of Mg/Cu-ZSM-5, at high Cu exchange levels over whole temperatures (350-600°C). Accelerated steaming tests were performed to examine how water vapor affects the catalytic activity of the Mg/Cu-ZSM-5 and Cu-ZSM-5 catalysts.

Reactor System Modification

The reactor system was modified by installing a water-bath in the feed-gas line. The water vapor flowrate was controlled by adjusting either the water-bath temperature or the O_2+He flowrate. The modified reactor system is depicted in Figure 1.

Catalyst Synthesis and Characterization

During this quarter, 15 catalysts, namely catalysts #26-#42, were prepared by incorporating metal cations into ZSM-5 zeolite supports according to ion exchange procedures described in the earlier reports [1,2]. 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 a 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. Some were further calcined in a muffle furnace in air at 500°C for 2 hours. The reason for calcining the catalysts was to stabilize the cations in the zeolite. The catalysts were further ion-exchanged with Cu^{2+} in an aqueous solution of cupric acetate of concentration 0.007M at room temperature overnight. This was repeated several times, depending on the desired Cu exchange level. Finally, the catalysts were washed with deionized water at room temperature and dried at 100°C overnight. For simplicity, a catalyst with intermittent air calcination of cocation exchanged ZSM-5 is designated as a precalcined M/Cu-Z catalyst in the text. In catalysts containing Cu only, the ZSM-5 zeolites were ion-exchanged once with Cu in an aqueous solution of cupric acetate with the same concentration as the above, at room temperature overnight. After filtration and washing with deionized water, the catalysts were dried in air at 100°C for 10 hours. Characterization for some of these catalysts, over which the conversion of NO to N_2 will be reported, are listed in Table 1. It is worth pointing out that the sequence of ion exchange for catalyst #35 was Ce ion exchanged into ZSM-5 first, then Mg, and finally Cu.

Another set of Cu ion-exchanged ZSM-5 catalysts was prepared in a different fashion. The pH for the starting aqueous solution of cupric acetates with concentration of 0.007M, was adjusted by adding either acetic anhydride or ammonium hydroxide. After a desired pH had been attained, the ZSM-5 materials were put into the solution and ion-exchanged once with Cu ions at room temperature for 19 hours. After filtration, the catalysts were dried in air at 100°C overnight. The Cu^{2+} exchange level dependence on pH is shown in Figure 2.

The elemental analyses were performed by Inductively Coupled Plasma Emission Spectrometry (ICP) after catalyst samples were dissolved in HF(48%).

Conversion Measurements

The conversion of NO to N_2 was performed in a laboratory-scale packed-bed reactor. Concentrations of nitrogen, oxygen and nitric oxide were measured by a gas chromatograph with a thermal conductivity detector, and a 5A molecular sieve column of 1/8 in. O.D. by 6 ft. long. An amount of 0.5-1.0 g of catalyst was placed in the reactor for conversion measurements. The catalyst packing density in the reactor was approximately 0.5 g/cc. The contact

time, W/F, was 1g s/cc (STP). The NO concentration was 2% in the feed gas stream, O_2 from 0%-5%, balance He. In the accelerated steaming tests, 20%H_2O-1.6%NO-4%O_2-He passed through the catalysts at 750°C for 20 hours. All measurements were made after steady state had been reached.

Results and Discussion

Nitric Oxide Decomposition in the Absence of Oxygen. The Cu-Z and Mg/Cu-Z catalysts shown in Table 1 were evaluated in a gas containing 2% NO-He, at a contact time of 1g s/cc (STP) over the temperature range of 350 - 600°C. Control experiments with Mg-Z materials verified that the activity of Mg/Cu-Z was exclusively due to Cu ions. Figures 3-5 show the NO to N_2 conversion profiles obtained for the catalysts tested under these conditions.

For the same copper ion-exchange level (~70%), the Mg(52)/Cu(66)-Z catalyst shows a positive effect, i.e., higher NO to N_2 conversion than the Cu(72)-Z material, in the high temperature region (450 -600°C), as can be seen in Figure 3. These results are in agreement with the report by Kagawa, et al [3]. While still present, this effect is not as pronounced for Mg/Cu-Z catalysts with high Cu exchange levels, as seen in Figure 4 for catalysts Mg(60)/Cu(93)-Z and Cu(97)-Z. However, the existence of a second cocation, Ce, in catalyst Ce(42)/Mg(27)/Cu(96)-Z further promoted Mg/Cu-Z catalyst activity as depicted in Figure 4.

Within the group of the Mg/Cu-Z catalysts, preparation conditions were important. As mentioned in the previous report [2], heating of the solution during Mg^{2+}-exchange was necessary in order to preserve the Mg ions in the zeolite upon subsequent exchange with copper ion solutions. The effect of intermittent air calcination of Mg-Z material at 500°C for two hours on the catalytic activity has been evaluated. The precalcined catalyst, Mg(34)/Cu(86)-Z, gave higher NO to N_2 conversion over the whole temperature range (350-600°C) than the catalyst Mg(40)/Cu(91)-Z without intermittent air calcination, as shown in Figure 5.

At the present time, no consensus exists in the literature on the mechanism of NO decomposition over Cu-Z catalysts. This makes a mechanistic interpretation of the cocation effects reported here premature. However, the importance of the ion exchange sequence and catalyst heat treatment on the NO decomposition activity is worth discussing in terms of active site modification on the basis of available information. In ESR studies, Kucherov, et al [4, 5] have identified two types of isolated Cu^{2+} ions: one in a five-coordinated square pyramidal configuration, the other in a four-coordinated square planar. At low Cu exchange levels, the five-coordinated Cu^{2+} ions were preferably formed [5]. Shelef [6] proposed the square planar copper ions as the active sites of Cu-Z for NO decomposition. This explains the negligible activity of Cu-Z catalysts with low Cu ion-exchange level (<40%). To examine the validity of this assumption we have examined the NO conversion to N_2 over various Cu-Z catalysts as a function of the

amount of square planar Cu^{2+} ions, calculated from the data given in Kucherov, et al [5] for Cu-Z catalysts prepared from a ZSM-5 zeolite which had a similar ratio of Si/Al=21 to the ZSM-5 zeolite used in this study. A linear relationship was found and will be reported in the next quarterly report. The number of four-coordinated square planar Cu^{2+} in Cu-Z materials has been reported to decrease at high temperatures [5]. Apparently then, the inert Mg ions stabilize the relative population of square planar Cu^{2+} ions, resulting in higher NO conversion to N_2 at high temperatures, as shown in Figure 3.

The intermittent calcination effect may be explained by migration of Mg^{2+}-bare ions, formed during calcination from their respective larger hydrated complex ions, to the 5- and 6-membered rings of ZMS-5. This would effectively keep the active Cu^{2+} in the 10-membered rings, where they are accessible to the reactant gas molecules. Hence, a higher NO conversion to N_2 is expected for the pre-calcined Mg(34)/Cu(86)-Z over the non-calcined Mg(52)/Cu(91)-Z catalyst as shown in Figure 5.

The observed cocation effect in Kagawa, et al [3] and the present work, therefore, may simply be one of stabilization of the copper active sites.

Nitrogen Oxide Decomposition in O_2-Containing Gases. Oxygen in the feed gas inhibits the NO decomposition reaction, but the inhibition decreases with temperature. In this quarter, we examined the effect of oxygen both with Cu-Z as well as with the cocation-exchanged M/Cu-Z catalysts. Experiments were performed in a mixture of 2%NO-5%O_2, W/F= 1g s/cc (STP). The profiles of NO conversion to N_2 for catalysts Mg(34)/Cu(86)-Z and Cu(97)-Z are shown in Figure 6.

We have shown that the cocation promoted effect on the catalytic activity of Cu ion-exchanged zeolites decreases with increasing Cu exchange level, as seen in Figures 3, 4 and 6. For Mg(34)/Cu(86)-Z, the promoter effect is not pronounced (as shown in Figure 3), but, in the presence of oxygen, the positive effect becomes pronounced. Figure 6 shows these comparisons.

The Cu(97)-Z and Mg(60)/Cu(90)-Z catalysts were evaluated and compared in a gas containing 2%NO-5%O_2-He at a contact time of 1 g s/cc (STP) over the temperature range 400-600°C, before and after 20%H_2O-1.6%NO-4%O_2-He mixture flowed through the catalyst bed at 750°C for 20 hours. We found that the catalytic activity for both catalysts was virtually lost at high temperatures. The results are shown in Figures 7 and 8.

Elemental composition analysis of zeolites and the condensate collected from the cold trap at dry ice temperature were performed by ICP. We found some Cu ions in the cold trap after the H_2O vapor passed through the catalyst bed. However, most of the Cu and Al ions were still in the zeolites. Since the steaming conditions were very harsh, such that de-alumination of the zeolite could have occurred, we do not know where the Al and the copper ions were after the steam tests. External-lattice Al ions and migration of Cu ions out of the cages could both have occurred. More detailed analysis of our sample is

presently underway to examine the predominant cause of deactivation. Also, mild steaming tests (with lower % H_2O and lower temperature) are planned.

Plans For Next Quarter

It is planned to test the catalyst activity for direct NO decomposition over the catalysts synthesized at different pH levels for starting aqueous solutions of cupric acetate, to examine the effect of catalyst preparation on the catalyst activity. The above catalysts will be washed with either dilute ammonium hydroxide or acetic anhydride solutions, to examine the bonding strength of the Cu ions on the ZSM-5 zeolites. Temperature-programmed reduction experiments will be carried out in a thermogravimetric analyzer to examine the Cu ion states in the zeolites. Parent ZSM-5 materials will be treated by a gas mixture containing 5%O_2-He at 750°C for 20 hours, then exchanged with Cu^{2+} ions. The catalytic activity for this steam pretreated parent zeolite Cu ion-exchanged catalyst will be tested. The relationship between the catalytic activity and the amount of four-coordinated square planar Cu^{2+} will be finalized.

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Table 1. Summary of Catalyst Syntheses and Properties

Catalysts	Si/Al[a]	Cu/Al[a]	Mg/Al[a]	Ce/Al[a]	Na/Al[a]	Cu exchange
#22, Mg/Cu-Z[b]	18.0	0.456 (91%)	0.202 (40%)		~0	twice, RT
#23, Mg/Cu-Z[c,d]	17.1	0.430 (86%)	0.170 (34%)		~0	twice, RT
#24, Mg/Cu-Z[b,d]	19.5	0.33 (66%)	0.26 (52%)		~0	twice, RT
#32, Cu-Z	20.6	0.466 (93%)	0.30 (60%)		~0	once, RT
#35, Ce/Mg/Cu-Z[c,d]	21.3	0.483 (96%)	0.134 (27%)	0.14 (42%)	~0	twice, RT
#38, Cu-Z	21.9	0.485 (97%)			0.08 (8%)	
#39, Cu-Z	19.9	0.36 (72%)			0.25 (25%)	once, RT

a. The values in parentheses are ion exchange levels, on the basis of Al content as measured by ICP.
b. Cocations exchanged once with Na/ZSM-5 at 85°C for 2 hours.
c. Cocation exchanged once with Na/ZSM-5 overnight at RT.
d. The cocation-exchanged ZSM-5 catalysts were dried in air at 100°C overnight, and calcined at 500°C for 2 hours.

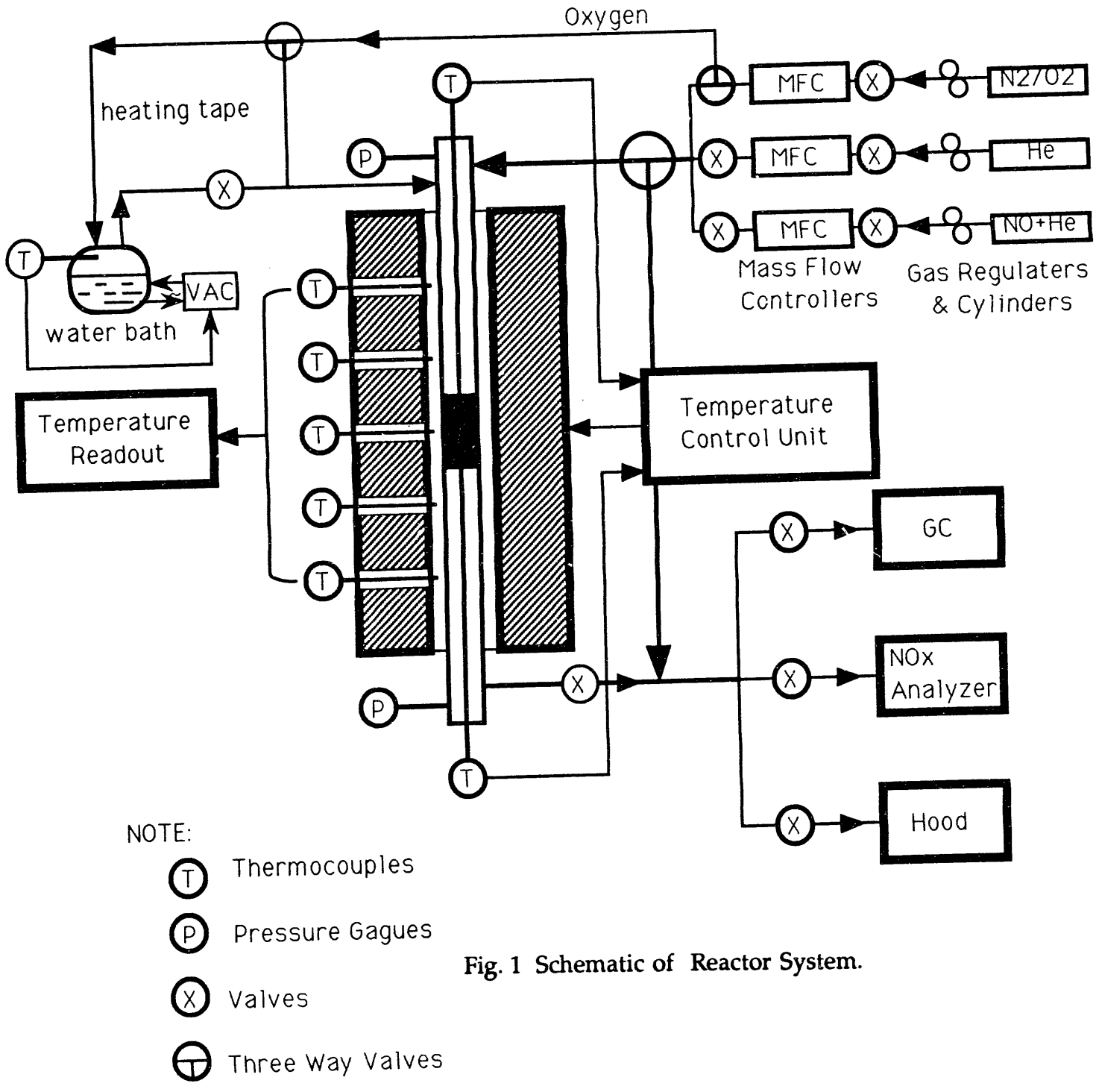

Fig. 1 Schematic of Reactor System.

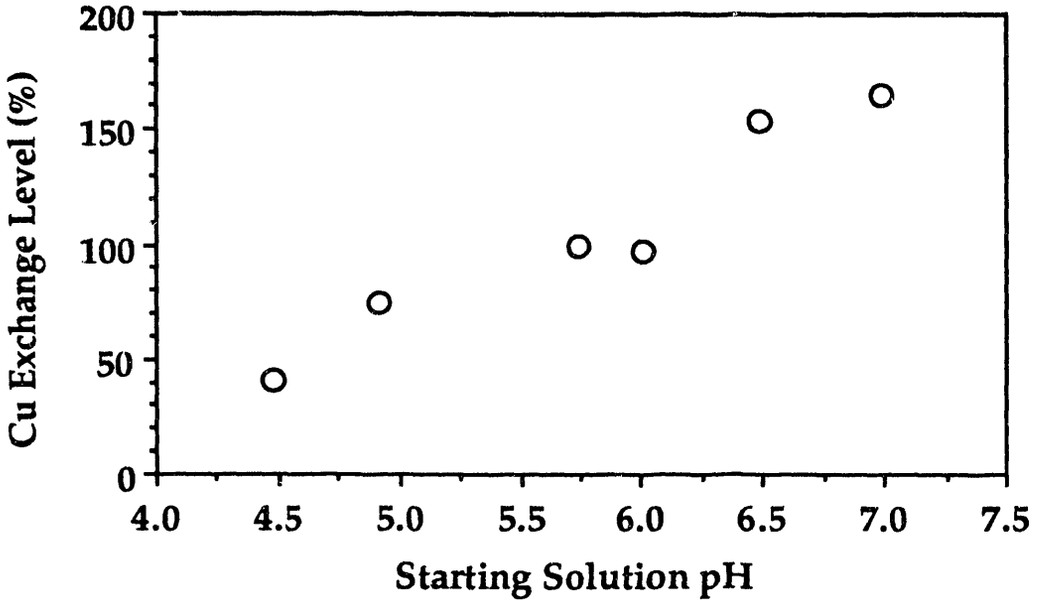

Fig. 2 Dependence of Cu exchange level on pH of starting cupric acetate solution.

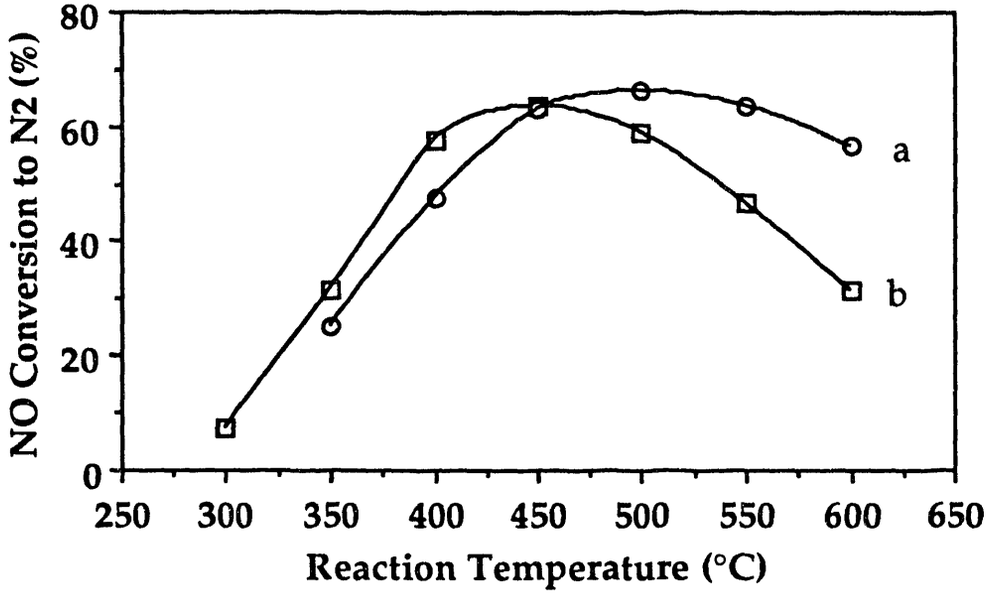

Fig. 3 Comparison of NO conversion to N_2 over (a) Mg(52)/Cu(66)-Z; (b) Cu(72)-Z at 2%NO and W/F=1g s/cc (STP).

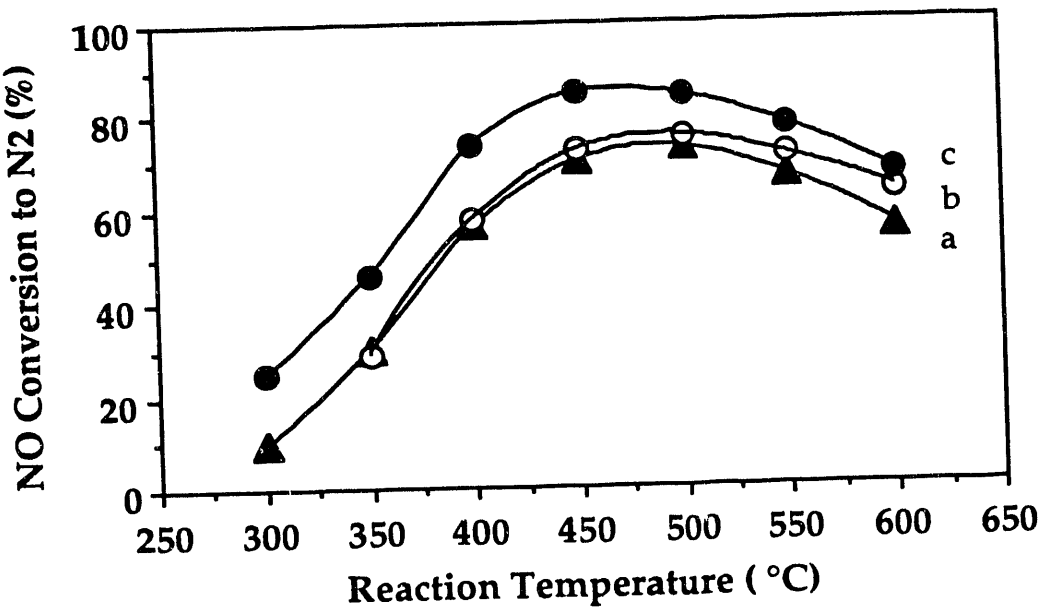

Fig. 4 Comparison of NO conversion to N_2 over (a) Cu(97)-Z; (b) Mg(60)/Cu(93)-Z; (c) Ce(42)/Mg(27)/Cu(96)-Z at 2%NO and W/F=1g s/cc (STP).

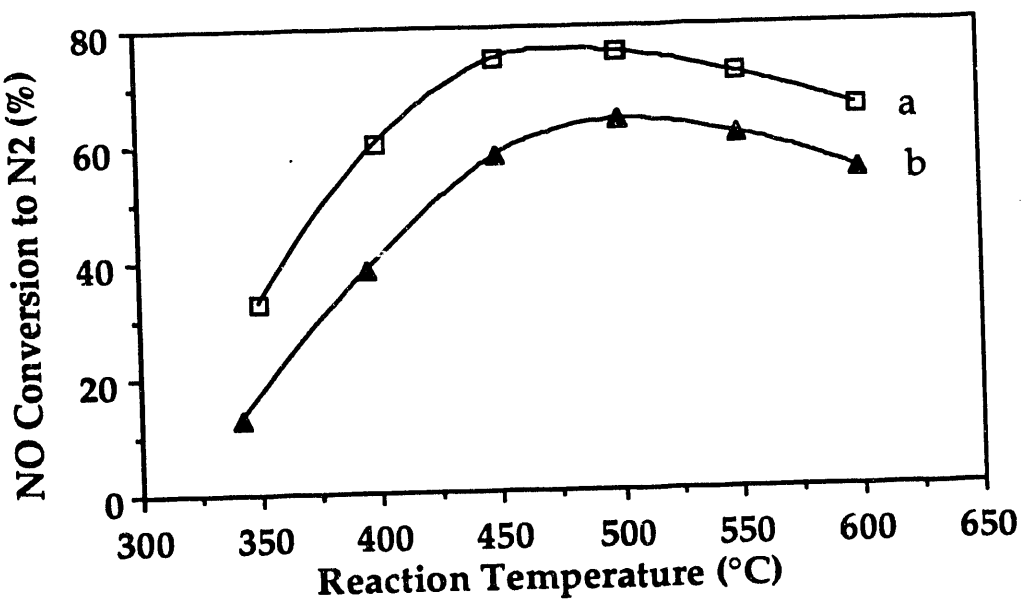

Fig. 5 Effect of intermittent Mg-Z calcination on Mg/Cu-Z catalyst activity for NO conversion to N_2 at 2%NO and W/F=1g s/cc (STP); (a) calcined Mg(34)/Cu(86)-Z; (b) non-calcined Mg(40.4)/Cu(91.2)-Z.

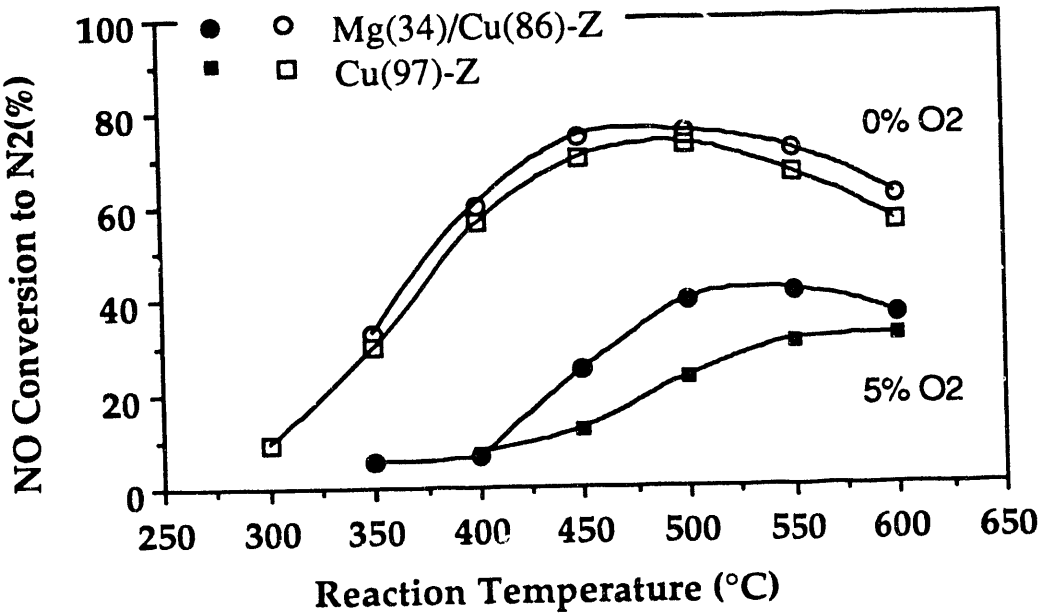

Fig. 6 Comparison of Mg/Cu-Z activity with Cu-Z activity at 2%NO, W/F=1g s/cc (STP), and 0% and 5% O_2, respectively.

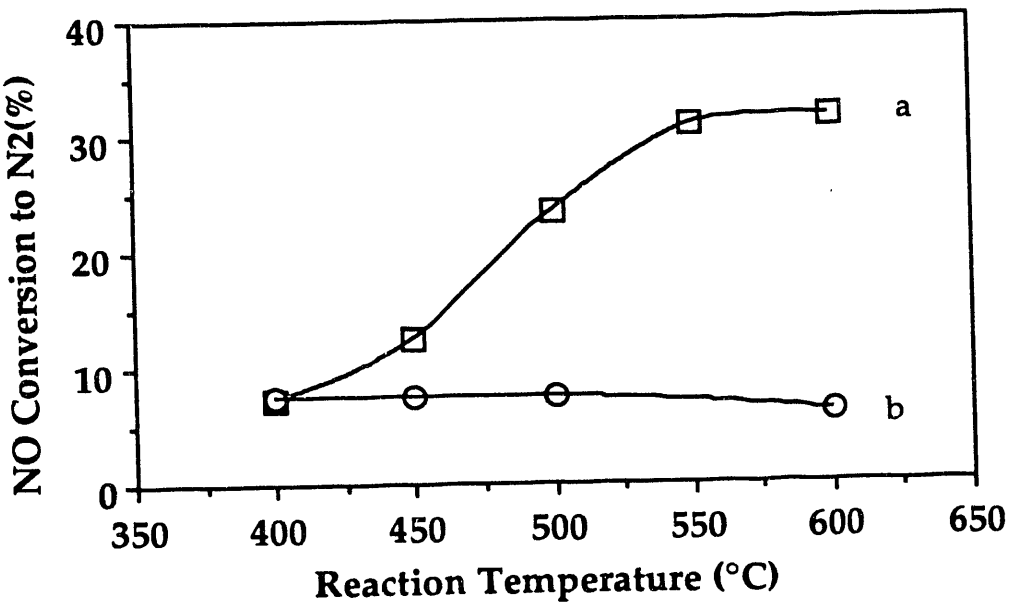

Fig. 7 Effect of water, (a) before and (b) after 20%H_2O-1.6%NO-4%O_2-He passed through catalyst bed at 750°C for 20 hours, on Cu(97)-Z activity for NO decomposition at 2%NO, 5%O_2 and W/F=1g s/cc (STP).

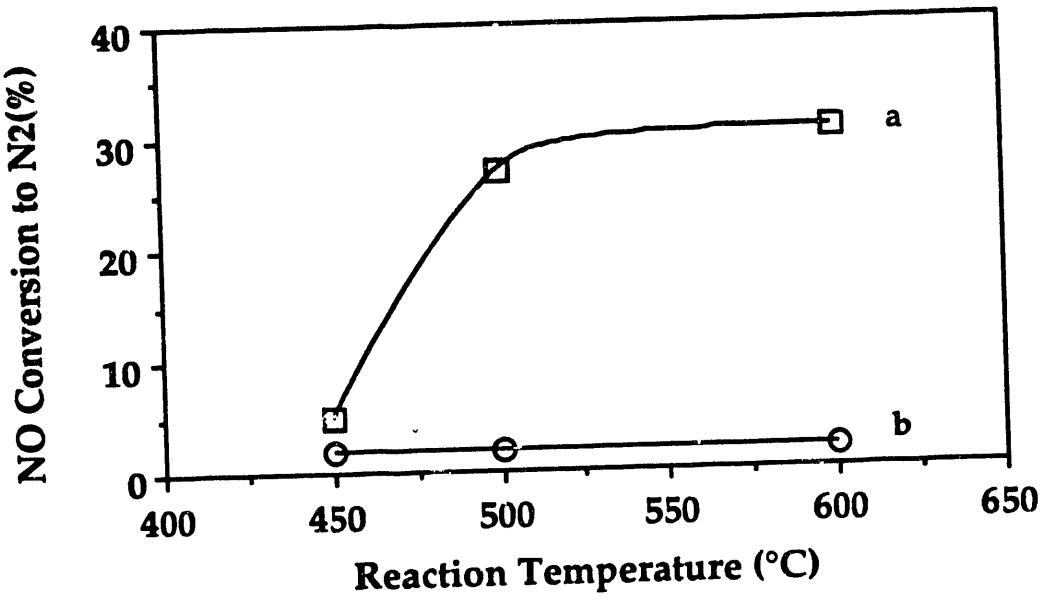

Fig. 8 Effect of water, (a) before and (b) after 20%H_2O-1.6%NO-4%O_2-He passed through catalyst bed at 750°C for 20 hours, on Mg(60)/Cu(93)-Z activity for NO decomposition at 2%NO, 5%O_2 and W/F=1g s/cc (STP).

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