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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 NO_x 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 O₂ 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 O₂ interaction with catalysts over a wide temperature range as well as catalyst structural investigations are planned.

PROGRESS SUMMARY

Six Cu-ZSM-5 catalysts with different Cu exchange levels were prepared according to our earlier reports[1,2]. Experimental tests have suggested that the active sites of Cu-ZSM-5 catalysts for nitric oxide decomposition are square planar four-coordinated Cu²⁺ cations. Conversion of NO into N₂ and O₂ increases linearly with the amount of square planar four-coordinated Cu²⁺, and the turn over frequency of the NO decomposition over the catalysts is not sensitive to total Cu ion-exchanged levels in Cu-ZSM-5 catalysts at the same experimental conditions. Cocation promoter effect in metal ion modified Cu-ZSM-5 catalyst is discussed in terms of higher turn over frequency of NO decomposition than that for Cu-ZSM-5 with the same amount of Cu exchange level. Parent ZSM-5 zeolites were dealuminated after they had been treated in a gaseous mixture of 20%H₂O-4%O₂-He at 750°C for 20 hours. Cu exchange process and BET measurements showed that the dealuminated ZSM-5 materials had only 15% of Cu exchange capacity and negligible micropore volume.

Catalyst Synthesis and Characterization

During this quarter, six catalysts with 10-141% of Cu exchange levels were prepared by incorporating Cu cations into ZSM-5 zeolite supports according to ion exchange procedures described in earlier reports [1, 2]. Low Cu exchange levels were achieved by adjusting the Cu cation concentration in aqueous solution of cupric acetate, and the highest Cu exchange level, 141%, was obtained by repetition of Cu exchange processes. The catalyst properties are summarized in Table 1.

Another Cu-ZSM-5 was synthesized by incorporating Cu cations into steamed ZSM-5 zeolites. The Cu exchange level was only 15% under conditions that achieve 141% Cu exchange level on the as-received ZSM-5 zeolites.

The elemental analyses were performed by Inductively Coupled Plasma Emission Spectrometry (ICP) after samples were dissolved in 48%HF and diluted to 2% by adding deionized water into the solutions.

Experimental

Conversion and kinetic studies were performed in laboratory-scale packed-bed reactor systems, as reported earlier [1, 2]. An amount of 0.5 g of catalyst was placed in the reactor for conversion measurements, and 0.03g for kinetic studies. The catalyst packing density in the reactor was about 0.5g/cm³. Contact time defined as the ratio of catalyst weight in the reactor to the total flowrate of the feed gas was 0.03-1.0g s/cm³ (STP). The NO concentration varied from 0.2-4% in the feed gas stream. Oxygen concentrations were in the range of 1-5%. All measurements were made after steady state had been reached.

Results and Discussion

NO conversion to N₂ and O₂. The Cu-ZSM-5 catalysts shown in Table 1 were evaluated in a gas containing 2%NO-He, at contact time 1g s/cm³ (STP). The results depicted in Figure 1 are NO conversions to N₂ and O₂ over these catalysts at 500°C.

The conversions of NO to N₂ and O₂, as shown in Figure 1, show S-shaped dependence on the Cu exchange levels, and low catalytic activity at low Cu exchange level. These results are in good agreement with what has been reported by Iwamoto [3], also shown in Figure 1 as a comparison. A close examination of these results and ESR analyses of Cu-ZSM-5 materials reported by Kuchеров, et al [4] finds that the S-shape curves of Figure 1 are similar to the correlation of the amount of four-coordinated Cu²⁺ ion to the total Cu²⁺ exchange level. This implies a direct relation between the NO conversion to N₂ and the amount of square planar Cu²⁺ sites in the Cu-ZSM-5 catalysts. It is reasonable to assume that the distribution of cupric ions

is the same in our zeolite since it has the same Si/Al ratio (21.5 here, 21 in the literature). The data of Figure 1 are then plotted against the amount of four-coordinated Cu^{2+} calculated for each total Cu-exchange value from the distribution given in Kuchеров, et al [4]. A linear relationship was thus found, as shown in Figure 2. Similarly, a linear relationship is shown for the data reported by Iwamoto et al [3] in Figure 2. Further, this method was applied to data reported by Kagawa et al [5], again with a linear relationship of the conversion of NO to N_2 with the amount of square planar four-coordinated Cu^{2+} for three different temperatures. This analysis provides strong indication that only a fraction of the exchanged copper is on active sites for the NO decomposition reaction. In the earlier reported data by Kuchеров et al [4], the four-coordinated square planar Cu^{2+} cations were found to be active for the CH_4 oxidation. A difference between the four- and five-coordinated Cu^{2+} ions is that the latter are more coordinated saturated than the former, thus, less active.

How do cocations promote the catalytic activity of the Cu-ZSM-5 zeolites? It is postulated that the initial exchanged cocations into the ZSM-5 zeolites occupy the positions where five-coordinated square pyramid Cu^{2+} ions preferably form, and probably will change the environment around the later exchanged Cu^{2+} cations in the catalysts. This implies that a higher percentage of square planar Cu^{2+} sites will be available in the metal ion modified Cu ion-exchanged ZSM-5 zeolites, compared with unpromoted Cu-ZSM-5 catalysts of the same Cu^{2+} exchange level. It is deduced that this positive cococation effect is more pronounced for low Cu exchange levels, since the cocations are inert for the reaction, and there is a limit to the amount of ions that can be exchanged into ZSM-5 zeolites. This hypothesis is supported by the evidence that catalysts incorporating Cu^{2+} first, and cococation second did not show the cococation promoter effect for NO decomposition[5, 6].

Kinetic studies. The microcatalytic reactor described earlier was used with samples weighting 0.03 g for kinetic studies and measurements of turnover frequency over the Cu-ZSM-5 catalysts. The value of the contact time, 0.03 g s/cm^3 , was chosen so that the reaction was in kinetic control region.

Figure 3 shows the temperature dependence of the turnover frequency for various Cu-ZSM-5 catalysts. The turnover frequency (TOF), here, is defined as the number of NO molecules converted to N_2 per second per four-coordinated Cu^{2+} . This is constant with the total Cu exchange level at given temperature. In contrast, a TOF increasing with total Cu exchange level has been reported by Li and Hall [7], assuming all copper sites to be active.

Averaging the TOF for all the catalysts in Figure 3, an average activation energy 11.8Kcal/mole in low temperature region was calculated, changing over to a negative value of -7.3Kcal/mole for high temperature region. These results are close to that reported in our early report [6]. The loss of activity at high temperatures may be due to loss of the active sites, square planar Cu^{2+} .

RSR measurements in the literature [4] provide evidence that the four-coordinated cupric ions convert to five-coordinated ones after high calcination temperature (800°C).

Catalytic activity comparison of Mg^{2+} modified Cu-ZSM-5 with Cu-ZSM-5. We have previously reported that, for the same copper-exchange level (~70%), the Mg(52)/Cu(66)-ZSM-5 catalyst showed a positive effect, i.e., higher NO conversion to N_2 in the high temperature region (450-600°C) [2, 6]. During this quarter, the microcatalytic reactor described earlier [1, 2] was used with sample weighting about 0.03g for kinetic studies and measurements of turnover frequency for the NO decomposition over the above two catalysts. The measurements were performed in a mixture of 4%NO-He, at contact time 0.03g s/cm³ at which the reaction was in the kinetic region, and 1.4 atmospheres of total pressure. Further, the effect of oxygen on the turnover frequency of NO decomposition was also evaluated in a mixture containing 0.2% NO-He and oxygen in the range of 1-5%.

Figure 4 shows an Arrhenius plot for the turnover frequency over the Mg(52)/Cu(66)-ZSM-5 and the Cu(72)-ZSM-5 catalysts. The turnover frequencies are higher for the Mg(52)/Cu(66)-ZSM-5 than for the Cu(72)-ZSM-5 for temperatures above 450°C. The results are in good agreement with NO conversion to N_2 measurements reported in our last quarterly report [2]. The effect of oxygen concentration varied from 1 to 5% in the gas mixture of 0.2% NO-He at 550°C on the turnover frequencies showed the specific catalytic activity to be invariant to oxygen, i.e., a reaction order of zero in oxygen was obtained, as shown in Figure 5. Here, it is again shown that the Mg(52)/Cu(66)-ZSM-5 activity is higher than that of Cu(72)-ZSM-5 over whole oxygen composition range.

Effect of water on the micropore volume and Cu cation exchange capacity of ZSM-5. The catalytic activities of Cu(97)-ZSM-5 and Mg(60)/Cu(90)-ZSM-5 catalysts drastically decreased, after 20%H₂O-4%O₂-1.6%NO-He mixture had flown through the catalyst bed at 750°C for 20 hours [2]. To check for dealumination of the ZSM-5 zeolites due to steaming, this quarter we tested the parent ZSM-5 zeolites with a gas mixture containing 20%-5%O₂-He at 750°C for 20 hours. It was found that the micropore volume decreased from 0.11cm³/g for the fresh ZSM-5 zeolites to 0.0 cm³/g for the steamed ZSM-5 materials, and the subsequent Cu ion exchange capacity was down from 142% to 15%. Similar results were obtained at 600°C. It clearly shows that the dealumination of parent ZSM-5 zeolites occurred. At the present time, we have not identified the conditions under which copper migration occurs in the absence of dealumination. Work is continuing on the issue of the hydrothermal stability of Cu-ZSM-5 catalysts.

Plans for Next Quarter

It is planned to continue to investigate the effect of water on the structure and Cu ion exchange capacity of the parent ZSM-5 zeolites and on the catalytic activity of the Cu-ZSM-5 and metal ion modified Cu-ZSM-5 catalysts for NO decomposition. Other work will focus on characterizing the copper sites in Cu/ZSM-5 catalysts by sequences of reduction-oxidation and activity tests. Characterization of the "excess copper" on samples prepared by various techniques will be performed by electron microscopy.

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Table 1. Summary of catalyst properties(a)

<u>Catalysts</u>	<u>Si/Al</u>	<u>Cu/Al</u>	<u>Na/Al</u>
Cu(10)-ZSM-5	20.5	0.05	0.89
Cu(30)-ZSM-5	19.1	0.15	0.62
Cu(50)-ZSM-5	19.4	0.25	0.44
Cu(73)-ZSM-5	21.3	0.365	0.20
Cu(97)-ZSM-5	21.9	0.485	0.13
Cu(141)-ZSM-5	20.3	0.705	0.0

(a) The ratios of Si/Al, Cu/Al and Na/Al are calculated on the basis of Si, Al, Cu, Na contents in Cu-ZSM-5 materials measured by ICP.

Figure 1. Dependence of NO conversion to N₂ on total Cu exchange level (this study: NO=2%, 500°C and W/F= 1g s/cc; Iwamoto's data [3]: NO= 1%, 500°C and W/F=4g s/cc).

Figure 2. Dependence of NO conversion to N₂ on the square planar Cu²⁺ exchange level (same conditions as in Fig. 1).

Figure 3. Temperature dependence of the turnover frequency for NO decomposition over Cu-ZSM-5 catalysts in 4%NO-He, and at 0.03g s/cm³ and 1 atm total pressure.

Figure 4. Arrhenius plots for the NO decomposition over the Mg(52)/Cu(66)-ZSM-5 and Cu(72)-ZSM-5 catalysts in 4%NO-He, and at 0.03g s/cm³ and 1.4 atm total pressure.

Figure 5. Effect of oxygen on the specific activity (TOF) of the Mg(52)/Cu(66)-ZSM-5 and Cu(72)-ZSM-5 catalysts in 0.2%NO-He, and at 0.03g s/cm³ and 1.4 atm total pressure.

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