



GEORGIA INSTITUTE OF TECHNOLOGY  
OFFICE OF CONTRACT ADMINISTRATION

(W)

NOTICE OF PROJECT CLOSEOUT

2-11-  
88  
2009 30

Closeout Notice Date 11/17/95

Project No. E-19-X33 \_\_\_\_\_ Center No. 10/24-6-R7881-0A0\_  
Project Director WHITE M G \_\_\_\_\_ School/Lab CHEM ENGR \_\_\_\_\_  
Sponsor ENVIRON PROTECTION AGENCY/EPA RES TRIANGLE PARK-NC \_\_\_\_\_  
Contract/Grant No. 3D1838NASA \_\_\_\_\_ Contract Entity GTRC  
Prime Contract No. \_\_\_\_\_  
Title NON-REDUCTANT CATALYTIC REDUCTION \_\_\_\_\_  
Effective Completion Date 940330 (Performance) \_\_\_\_\_ (Reports)

Closeout Actions Required:	Y/N	Date Submitted
Final Invoice or Copy of Final Invoice	Y	951025
Final Report of Inventions and/or Subcontracts	N	_____
Government Property Inventory & Related Certificate	N	_____
Classified Material Certificate	N	_____
Release and Assignment	N	_____
Other _____	N	_____

Comments \_\_\_\_\_

Subproject Under Main Project No. \_\_\_\_\_

Continues Project No. \_\_\_\_\_

Distribution Required:

Project Director	Y
Administrative Network Representative	Y
GTRI Accounting/Grants and Contracts	Y
Procurement/Supply Services	Y
Research Property Management	Y
Research Security Services	N
Reports Coordinator (OCA)	Y
GTRC	Y
Project File	Y
Other _____	N
_____	N

E-19-x33

#1

December 15, 1993

Dr. Brian Gullett  
Air and Energy Research Laboratory  
U.S.E.P.A.  
Research Triangle Park, NC 27711

Dear Brian:

Please find in the attachments a review of the literature related to the NO decomposition reaction.

Respectfully yours,

Mark G. White  
Director

Enclosure: Literature Review; Deliverable 1

# "THE DECOMPOSITION OF NITRIC OXIDE"

prepared by

Mark G. White  
Focused Research Program in Surface Science and Catalysis  
School of Chemical Engineering  
Georgia Institute of Technology  
Atlanta, GA 30332-0100

## INTRODUCTION

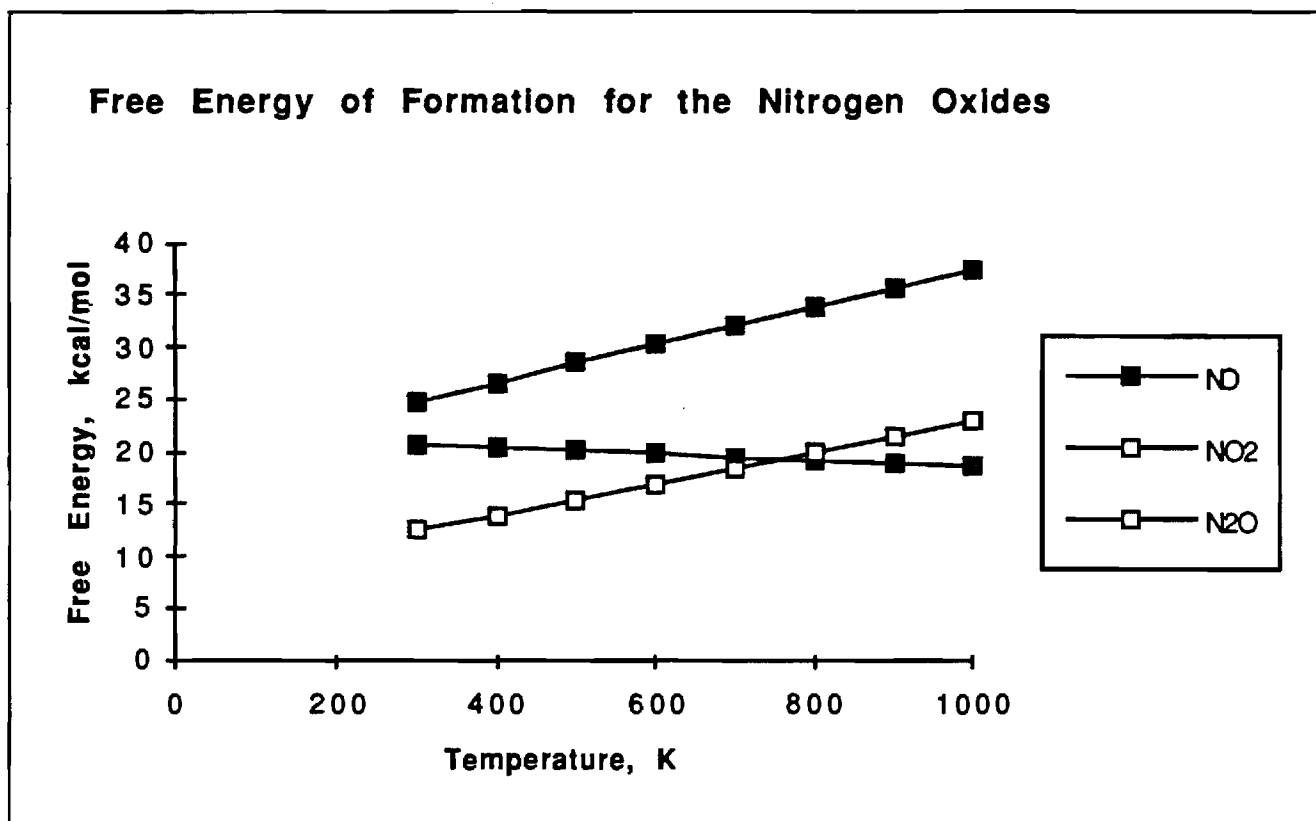
Future environmental regulations may require that the operators of coal-fired, power plants reduce the emissions of nitrogen oxides ( $\text{NO}_x$ ) into the air. This emission source shows very low concentrations of reducing agents (e.g., CO) necessary for the conventional  $\text{NO}_x$  reduction catalysts to operate efficiently. New catalysts must be devised which decompose  $\text{NO}_x$  into  $\text{N}_2$  and  $\text{O}_2$ . The following is a brief review of the literature pertaining to the decomposition of NO into the diatomic elements. The document is organized into the thermodynamics of the decomposition, a brief discussion of the homogeneous kinetics for NO decomposition, followed by a more lengthy discourse on the heterogeneous catalysis for the same reaction. This literature is discussed to formulate the necessary "elements" of a successful heterogeneous catalyst. Finally, we show the progress in our laboratory towards developing an optimum catalyst for this reaction.

## NITRIC OXIDE DECOMPOSITION -- THERMODYNAMICS

The equilibrium thermodynamics of any reaction governs the ultimate conversion which can be realized for that reaction. In the present case we consider the reactions of  $\text{N}_2$  and  $\text{O}_2$  to form the products  $\text{N}_2\text{O}$ , NO, and  $\text{NO}_2$ . Data of the free

energy of formation [1] are plotted versus absolute temperature in Figure 1.

Figure 1



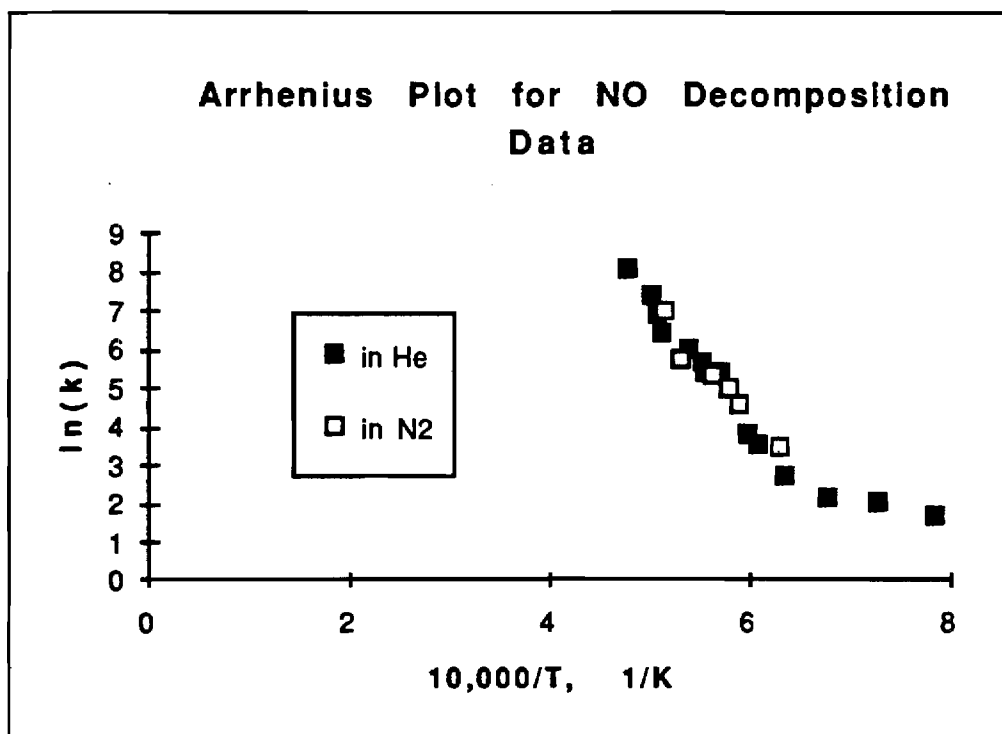
These data show that the free energy of formation for the products is positive at all temperatures between 300 - 1000 K which suggests that the *decomposition* of these molecules is favored over the temperature range. These compounds exist in flue gas streams which suggest that reaction kinetics limits the rate of decomposition thus the need for a catalyst. In the next section, we present a short review of the literature pertaining to the homogeneous kinetics for NO decomposition.

#### HOMOGENEOUS KINETICS FOR NO DECOMPOSITION

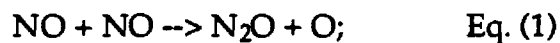
The homogeneous, uncatalyzed decomposition of NO occurs at significant

rates for gas temperatures  $> 1400^{\circ}\text{C}$ ; whereas, the heterogeneous and homogeneous reactions occur at temperatures  $< 1400^{\circ}\text{C}$  [2]. The conversion versus reaction time data were reduced according to second order kinetics to yield rate constants at several different temperatures. The raw data were re-examined to show that the conversion versus reaction time data are successfully fit by a second-order rate equation when the temperature was greater than  $1400^{\circ}\text{C}$ ; however, for temperatures less than  $1400^{\circ}\text{C}$ , the effects of a zero-order reaction were obvious. These data are plotted in Figure 2 as an Arrhenius plot for two runs for which the diluting gas was either helium or nitrogen. These data show linear relationship for temperatures greater than  $1667\text{ K}$  ( $1394^{\circ}\text{C}$ ) while the data at lower temperatures are not linear.

**Figure 2**



A fit of the data in Figure 2 for temperatures  $\geq 1300^\circ\text{C}$  revealed an activation energy of  $62.5 \pm 1.5$  kcal/mol with a pre-exponential factor of  $3.1 \times 10^{10} \text{ atm}^{-1} \text{ sec}^{-1}$ . The  $E_A$  data agree well with those published earlier although the pre-exponential factors differ by an order of magnitude [3]. The activation energy of the  $\text{N}_2\text{O}$  decomposition reaction is 60 kcal/mol and the pre-exponential factor is  $1.58 \times 10^{11} \text{ 1/sec}$  [4]. The very high activation energy observed for the gas-phase decomposition of NO shows that the rate-limiting step is kinetically controlled and that a heterogeneous catalyst is necessary to achieve a reaction pathway which experiences a lower activation energy. The similarity in the Arrhenius parameters between the NO and  $\text{N}_2\text{O}$  reactions suggest that the decomposition of  $\text{N}_2\text{O}$  may be the slow step in the sequence. Moreover the results of both studies show that the overall reaction order in second in NO partial pressure which suggests that a bimolecular reaction is involved in the rate determining step. Baulch, et al. [5a] reviewed the literature for high temperature NO decomposition to suggest that the decomposition occurs by the following sequence of elementary reactions:



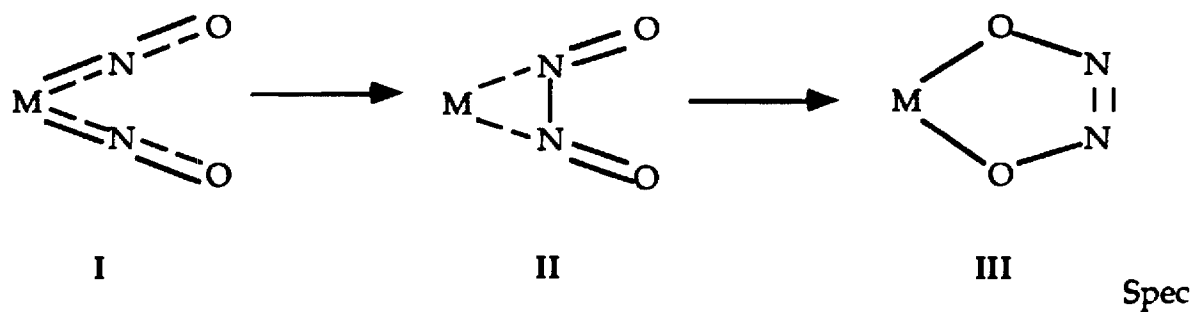
If the reaction described by Eq. (1) was reversible and very fast next to the reaction in Eq. (2), then the observed reaction rate would be described by the following:

$$\text{rate} = \{k_1 k_2 / (k_{-1} + k_2)\} [\text{NO}]^2 \quad \text{Eq. (3)}$$

where  $k_1$  and  $k_{-1}$  are the forward and reverse rate constants for reaction 1 and  $k_2$  is the forward rate constant for reaction 2. The order of reaction is two for this

sequence of elementary reactions and agrees with the kinetic data of Yuan, et al. [2] and Kaufman & Kelso [4] to suggest that  $N_2O$  and atomic oxygen are intermediates in the decomposition. Moreover, this reaction sequence would show Arrhenius parameters similar to those observed for the "unimolecular"  $N_2O$  decomposition. Thus, we expect that  $N_2O$  will be present in the gas phase at the high temperatures of the decomposition. However, reactive species such as atomic O may be sequestered quickly by solid surfaces and therefore may not be observed in the same concentrations as  $N_2O$ . Finberg estimated that the rate constant for Eq. (1) is at least a factor of 10 higher than that of Eq. (2). Thus, the combination of low rate constant for Eq. (1) and the low concentrations of O suggest that the further reaction by Eq. (2) may be the slow step.

**Homogeneously Catalyzed NO Decomposition.** One group published a theoretical study in which the energies are calculated for proposed intermediates in the homogeneously catalyzed decomposition of NO to  $N_2O$  using standard molecular orbital calculation techniques [5b]. They begin by postulating the existence of three intermediates for the catalysis by  $Fe^{2+}$ :





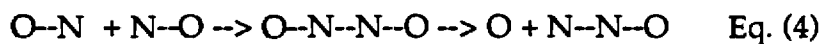
ies I is the formation of the dinitrosyls with the Fe<sup>2+</sup>; species II shows the formation of a bond between the two nitrogen atoms, and species III depicts the rearrangements of the complex to give the *cis*-hyponitrite. The energies of these three intermediates were calculated for a four-coordinate iron(II) showing species I with two NO and two Cl<sup>-</sup> as ligands and for a six-coordinate iron(II) with two NO, two Cl<sup>-</sup> and two waters as ligands. The energies for these intermediates are shown below:

	<u>Four-coordinate</u>	<u>Six-coordinate</u>
Species I	0	0
Species II	+29 kcal/mol	-24 kcal/mol
Species III	+44 kcal/mol	+4 kcal/mol

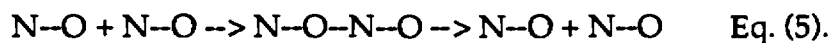
The energies developed for each species are relative to species I. These results suggest that the six-coordinate iron(II) species shows a lower energy barrier to the reaction than the four-coordinate iron(II) species. Moreover, the ligand waters are instrumental in creating this lower energy path. The authors speculate that this calculation may be valid for all group VI-VIII transition metal deNO<sub>x</sub> catalysts.

This brief review of the homogeneous literature may suggest elements of the chemistry which is to be inculcated into the design of the heterogeneous catalysts. For example, the second order kinetics suggest that a bimolecular step must be achieved on the surface by bringing together two NO molecules in a manner so that a productive event occurs readily. If N<sub>2</sub>O is one product, then a reactive ensemble is needed to bring the two NO molecules together so that the N atoms are sufficiently

close to form a bond, e. g.,



A catalyst can orchestrate this meeting with every adsorption event; whereas, bimolecular collisions do not always produce the required orientation of the NO. As a result non-productive collisions produce the following:



Moreover, the catalytic sites assist in breaking the NO bond by forming surface-adsorbate bonds; whereas, the homogeneous mechanism relies on the kinetic energy of the collision to pass over the energy barrier for NO bond breaking. These surface-adsorbate bonds may form by withdrawing electron density from the NO bonding electrons and by dative back-bonding from the metal into the NO anti-bonding orbitals. These two mechanisms, which are not available to the homogeneous mechanism, provide low energy barrier paths to activate the NO bond.

#### HETEROGENEOUS CATALYSIS OF NO DECOMPOSITION

We expect that  $\text{N}_2\text{O}$  and atomic oxygen are intermediates in the heterogeneously catalyzed reaction so that the catalyst must desorb both species in order for the reaction to continue. The function of the catalyst will be to co-adsorb the two NO molecules in such a manner so as to produce the intermediate  $\text{N}_2\text{O}$ . Moreover the catalyst must stabilize the O atom on the surface until such time that two O will recombine to form  $\text{O}_2$ ; however the catalyst must not form surface compounds which are too stable otherwise the O atoms will not recombine.

Supported transition metals are known to catalyze the selective catalytic reduction of NO; however, these same materials will not catalyze the decomposition of NO continuously when the supports are porous silica or alumina. Only a small class of microcrystalline supports will catalyze the NO decomposition reaction without the need of a reducing agent. The following review of the literature examines the adsorption of NO to metal crystals and supported metals, and the steady state catalysis of NO decomposition over novel supported Cu catalysts. We conclude the review with a preliminary report on our progress in preparing a supported Cu catalysts derived from the thermolysis of either a mononuclear or a dinuclear Cu complex supported on silica.

#### ADSORPTION OF NITRIC OXIDE TO SURFACES

Details are brief in the literature of the NO adsorption to metals such as Ni and Cu(I), Cu(II) at low temperature. Data from surface science literature suggest that associative adsorption is possible for NO on Ni (100) [6], on Ni (111) [7-9], and Pt (100) [10] when the temperature is sufficiently low. The bold face numbers in parentheses following the abbreviation of the element describe the index of the exposed crystallographic face. At least two adsorption states were observed for NO on Ni (100). One state, observed at low NO coverage, shows the NO molecules in a highly tilted state ("lying down"); whereas, the highly covered adsorbate was adsorbed in state for which the bond axis was perpendicular to the surface. The tilted adsorption state is an obvious precursor to dissociation of NO into its elements. These data from the literature of single crystals show that such an

orientation of NO is possible on model metal surfaces. Moreover, the data for single crystals may be used to infer the general properties of NO adsorption to polycrystalline metals supported on high surface area oxides, such as silica and alumina. The polycrystalline metals supported on an oxide show irregularly-shaped crystallites having a surface composed of facets which expose different crystallographic planes. These exposed facets can be visualized by cutting a crystal at various angles. Thus, the data on single crystals which have been cut to expose only certain low index shed light on the behavior of "real" catalysts which show not only these simple planes but others.

Work on different single-crystal surfaces of Cu show that NO is adsorbed dissociatively leading to adsorbed oxygen and nitrogen atoms adsorbed at room temperature. When the surface becomes saturated, the oxygen atoms penetrate into the subsurface; whereas, the nitrogen desorbs from the surface [11, 12, 13]. The rapid penetration of oxygen atoms into the bulk of the Cu crystal prevents the atoms from recombining to form molecular oxygen. Moreover, this vast pool of oxygen atoms residing in the subsurface of the Cu crystal will return to the surface when it should become depleted with the action of a reducing agent. The kinetics of the O diffusion in the solid may become the rate limiting process.

Subsequent studies of Cu/silica prepared by conventional techniques show that NO oxidizes the surface at temperatures near 400 K to produce Cu(I) and Cu(II) [14]. Molecularly adsorbed NO was not detected in these systems [14]. In separate experiments, exposure of the reduced catalyst to N<sub>2</sub>O produced infrared spectra

showing a peak at  $2219\text{ cm}^{-1}$  which was not removed upon evacuation at room temperature [15]. A number of IR peaks appeared in the spectrum of the same reduced catalysts when exposed to NO at 423-473 K. The surface is rapidly oxidized to Cu(I) and eventually lead to the formation of Cu(II) on the surface. These data suggest that nitrito and nitrate surface species are formed with increasing extent of surface oxidation. These species ( $\text{NO}_2$  &  $\text{NO}_3^-$ ) decompose when the sample was heated to temperatures above 473 K. NO does not decompose on completely oxidized catalysts.

Novel copper/silica catalysts were prepared by thermolysis of monolayer of  $\text{Cu}(\text{acac})_2$  supported of non-porous  $\text{SiO}_2$  having a specific surface area of  $200\text{ m}^2/\text{g}$  (Cab-O-Sil) [16]. These catalysts adsorbed NO associatively at room temperature and all of the NO was removed upon heating the sample to  $450^\circ\text{C}$  [17]; however, the same catalyst would not react with  $\text{N}_2\text{O}$  at  $100^\circ\text{C}$ . These catalysts showed high dispersions of the Cu ion on the silica which could be reduced and oxidized for many cycles without changing the state of the Cu dispersion [17]. The IR spectra of the chemisorbed NO showed evidence of linearly bound Cu-NO ( $\sim 1910\text{ cm}^{-1}$ ) and other species showing vibrations near 1826 and  $1672\text{ cm}^{-1}$ . The peak at  $1826\text{ cm}^{-1}$  has been attributed to  $\text{NO}/\text{Cu}^{1+}$  [af]; however, the peak at  $1672\text{ cm}^{-1}$  has not been assigned. These catalysts appear to have unique properties in that NO and  $\text{N}_2\text{O}$  do not react with the surface of such "isolated" Cu ions. As such, these materials would not be catalysts for the NO decomposition reaction. These results do show the sensitivity of NO and  $\text{N}_2\text{O}$  sorption and reaction towards the structure of the

surface. Our more recent results (*vide infra*) for NO and N<sub>2</sub>O sorption and reaction on Cu/silica (100% dispersion of Cu) prepared from a dinuclear Cu complex demonstrate that these molecules are sorbed with dissociation on this surface. Clearly, the Cu ensemble size has a profound effect on the mechanism by which NO and N<sub>2</sub>O sorb and react with the surface.

Others have studied the adsorption states of NO on supported copper by temperature programmed desorption (TPD) [18]. They showed NO species desorbing between 383-573 K and 648-753 K. The lower temperature peak was NO desorbing from Cu(II) sites and the higher temperature peak was the result of decomposition of a nitrate surface species which formed originally from NO and surface O. In a separate TPD study for NO adsorbed on Cu/ZSM-5, Li and Armor [19] suggest that N<sub>2</sub>O and N<sub>2</sub> are produced when NO contacts the Cu/ZSM-5 at reaction temperatures as low as 25°C. Subsequent heating of the sample showed that NO and N<sub>2</sub>O desorbed at low temperatures (90 & 140°C); whereas, NO and O<sub>2</sub> desorbed at high temperatures (ca., 360°C). These results appear to be true for both a fully oxidized and a partially reduced Cu catalyst.

These data suggest a possible mechanism to improve the rates of oxygen atom recombination. The oxygen atoms must be prevented from penetrating to the bulk of an effective catalysts. One way to prevent such penetration is to create very small ensembles of Cu which will not harbor interstitial O atoms. Secondly, the copper atoms must be sufficiently close to permit recombination of both the O and N atoms without resorting to surface diffusion across the support oxide as a means of

recombining. For metals which form strong surface bonds with O, surface diffusion will be very small; therefore an optimum will exist in the metal-oxide bond strength. Finally, the catalyst must be designed to inhibit the formation of surface metal oxides so as to decrease the possibility of forming surface nitrito and nitrate compounds. The formation of these species inhibits the reaction to form  $N_2$  and  $O_2$ .

### **CATALYST PREPARATION & CHARACTERIZATION**

Most of the successful catalysts for NO decomposition have been prepared from zeolites containing transition metals; however, much ambiguity is associated with the preparation of zeolites containing transition metal ions as a result of ion exchange from aqueous solution. The ion exchange procedure is complicated by the exchange of protons and polynuclear species in addition to the single transition metal ions [20]. Consider the example of aqueous impregnation of divalent Cu ions into zeolite Y for which the polynuclear metal species may include  $[Cu(II)OH]^+$ ,  $[Cu(II)(NH_3)_4]^{2+}$ , and others. The simple accounting for the exchange is frustrated when species enter the system which contain a formal charge other than that found on the target ion (e. g.,  $[Cu(II)OH]^+$  instead of  $Cu(II)$ ). This confusion leads to the condition known as "over-exchange" for which the number of Cu ions in the system exceeds the limit predicted from the alkali content of the unexchanged zeolite (i. e., number of  $Na^+/2$ ). Another confounding condition occurs during dehydration of the zeolite in vacuum for which some transition metal ions appear to reduce [21, 22]. The combination of "over-exchange" and vacuum reduction confuses the issue relating to gross oxidation state of the working catalysts. Consider

the reports of "auto-reduction" of Cu(II)/Y-zeolite [23] and Cu(II)/ZSM-5 [24]. The weight loss [23] was 0.2 wt% for heating the Cu(II)/Y (68% exchanged) from 673-873 K and the volatile was O<sub>2</sub>. The weight loss was used to infer that up to 0.46 O/Cu(II) were lost upon heating to 873 K. Subsequent spectroscopic studies confirmed the reduction of Cu(II) to Cu(I) [23]. The same experiment was completed for a Cu(II)/ZSM-5 which showed an auto-reduction of 0.11 O/Cu [24]. EPR measurements of the Cu(II)/ZSM-5 suggested that the weight losses attended the reduction of the Cu(II) to Cu(I) [24].

These results suggest that alternative methods must be developed to introduce transition metal ions into the zeolites so that the oxidation state and nuclearity of the metal ion is preserved. We have prepared zeolites (Y & ZSM-5) containing divalent Cu ions using *bis*-copper ethylenediamine perchlorate [(Cu(C<sub>2</sub>N<sub>2</sub>H<sub>8</sub>)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub>] as the precursor [25] in non-aqueous solvents such as acetonitrile. Copper loadings as high as 1.5 wt% Cu has been obtained in the ZSM-5 zeolite; whereas, metal loadings up to 2.4 wt% Cu were observed in the Y-faujasite. For all samples, the C/N ratio was within experimental error of the theoretical value of 4. This preparation affects ion exchange of the metal complex cation for the Na<sup>1+</sup> without the ambiguity normally associated with ion exchange using an aqueous solvent. The ethylenediamine complex is very stable to ligand-exchange reactions; therefore, only one cation species is present in the solution and we have eliminated the possibility of alervalent species in solution which could confuse the issue of ion exchange as was observed for Cu(II) in aqueous solutions.



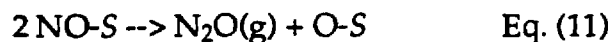
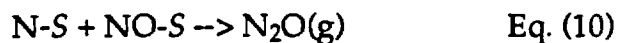
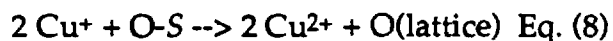
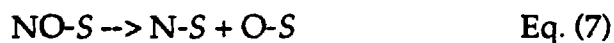
An alternative technique has been reported for the synthesis of type-A zeolite around the metal complex of *tris*-cobalt ethylenediamine perchlorate  $[(\text{Co}(\text{C}_2\text{N}_2\text{H}_8)_3(\text{ClO}_4)_3]$ . The Co-content of these solids could be increased from 0.18 to 1.26 wt% Co by decreasing the synthesis temperature from 100 to 40°C. The silica/alumina ratio in these samples varies from 1.06 to 1.17, atomic. These cobalt metal weight loadings correspond to 1 Co(III) ion for every two unit cells. Data of FT-IR showed the existence of the (en) ligands which appeared to suffer the effects of hydrogen-bonding. The EPR spectra were "silent" for these Co-containing zeolites which suggests that the Co ion is not reduced to the divalent state. One as-synthesized zeolites, which showed  $\text{Na}^+/\text{Al}^{3+} = 0.834$  and  $\text{Si}/\text{Al} = 1.11$ , could be exchanged with KCl to produce a material having a  $\text{K}^+/\text{Al}^{3+} = 0.81$ ; however, none of the  $\text{Co}(\text{en})_3^{3+}$  cations left the solid during the exchange. Thermal decomposition of the as-synthesized zeolites show the disappearance of the (en) ligands between 225-400°C; these calcined materials showed the XRD pattern expected for a zeolite-A sample. This new technology may provide a means of introducing transition metal ions into the zeolite with some degree of control.

## HETEROGENEOUS KINETICS

While thermodynamics favors the decomposition of NO into its elements, the kinetics limit the process at the catalyst surface. Studies over CuO show that the elimination of oxygen from the surface is the rate-limiting step [24, 26]. The latest studies examine the methods of accelerating the evolution of oxygen from the surface [24, 27-29].

The catalytic decomposition of NO over copper oxide has received attention lately as researchers have reported enhanced activity for Cu supported on zeolite catalysts compared to bulk CuO which shows very low activity [24, 27-29]. Highly dispersed catalysts produced by ion exchange of copper ions show turn-over frequencies which increase with increasing copper loadings and the activities of these catalysts also depend upon the type of zeolite used as the support [24]. Some researchers speculate that the zeolite organizes the Cu ions into ensembles that are the active catalysts [24]. If this speculation is true, then an optimum size and configuration of Cu ensembles should exist.

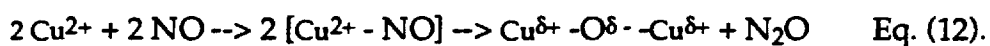
**Mechanism of NO Decomposition Reaction.** Several versions of the mechanism for NO decomposition has been reported in recent years. We begin with a review of the selective reduction mechanism reported by Knozinger [30] for the NO reaction over Cu:



This mechanism shows the NO dissociatively adsorbed onto separate sites with the chemisorbed oxygen (O-S) "reacting" with two cuprous ions to form lattice oxygen and cupric ions. In the conventional selective catalytic reduction of NO, this lattice

oxygen would be removed by a reducing agent such as ammonia or a hydrocarbon. In the catalytic decomposition, the strongly bound surface oxygen must be removed by other means if the catalyst is to operate continuously. Several other mechanisms have been reported for the selective reduction of NO by ammonia over promoted oxide catalysts [31-34]. These mechanisms will not be discussed in detail here, but some features are of interest: a. NO is oxidized to NO<sub>2</sub> on the surface, b. the reductant (e.g., S-NH<sub>2</sub>) reacts with NO<sub>2</sub> to form N<sub>2</sub> and water, and c. at least two types of sites are required to conduct the catalysis for which the actual ensemble size may be greater than two metal ions.

Other investigators have discussed the decomposition mechanism in the light of the poisoning effect by surface bound oxygen. Iwamoto shows that the NO decomposition reaction is poisoned reversibly by O<sub>2</sub>, and irreversibly by SO<sub>2</sub> and water over supported copper oxide [27]. He writes for the NO decomposition reaction



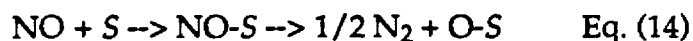
Iwamoto does not elaborate on the details of the charge ( $\delta$ ) residing on the Cu or O atoms. This equation suggests that NO is sorbed to the copper species followed by a rearrangement to give a surface dimer compound of the Cu and a gaseous product: N<sub>2</sub>O. For this scheme, he does not show the details of NO activation, but at least one NO molecule must be activated to yield the bridging O; whereas, the nitrogen is sorbed to a copper before forming the nitrous oxide. The details are not given to describe how nitrous oxide rearranges to yield nitrogen and oxygen. More

importantly, this mechanism is silent on the details by which the surface dimer rearranges to regenerate the original surface plus molecular oxygen. This picture appears to be somewhat simplified as molecular oxygen cannot be produced from the rearrangement of the dimeric copper ensemble:  $\text{Cu}^{\delta+}-\text{O}^{\delta-}-\text{Cu}^{\delta+}$ . Likewise, a single nitrous oxide cannot yield molecular oxygen upon rearrangement. We conclude that the formalism:  $\text{Cu}^{\delta+}-\text{O}^{\delta-}-\text{Cu}^{\delta+}$  describes a unit of the surface structure embodied in a larger ensemble of copper ions. One essential part of this mechanism is the specification that a *bridging* oxygen species is related to the elimination of surface bound oxygen. Other investigators comment on the kinetics of oxygen evolution from these materials.

Li and Hall [24] show that the NO decomposition kinetics over Cu/ZSM-5 catalysts are poisoned by  $\text{O}_2$  according to the following equation:

$$r = k'[\text{NO}] / (1 + K'[\text{O}_2]^{1/2}) \quad \text{Eq. (13)}$$

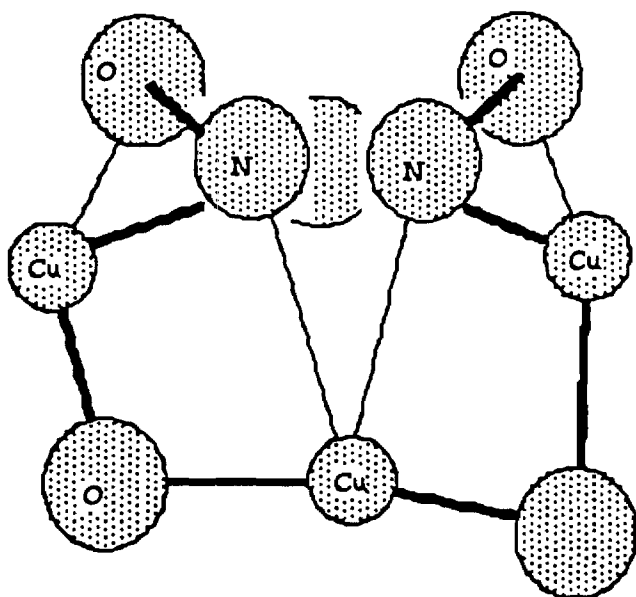
They interpret these kinetics as characteristic of a mechanism where the rate is "limited by the self-reduction of the catalytic sites by desorption of  $\text{O}_2$ ". Hall writes for the decomposition of NO the following for which the surface site is denoted as S:



Moreover, the kinetic data from Hall's study suggest that oxygen molecules are formed by combination of two adsorbed oxygen atoms. If adjacent oxygen species combine, the simple picture of the copper ensemble given previously by Iwamoto must be modified to show an ensemble size larger than two in that at least one site

must be available for binding the nitrogen and two others are required for the adjacent oxygen atoms. The curious property of the Cu/ZSM-5 catalysts to “self-reduce” is clearly demonstrated in TGA studies reported by Li and Hall [24] and subsequently by Li and Armor [19]. At 500°C, the mass of the Cu/ZSM-5 catalyst is sensitive to the partial pressure of oxygen in the gas phase. The mass of the sample decreases by an amount equal to 0.11 O/Cu atoms in the sample when the oxygen atmosphere is replaced by He. The role of nitrous oxide is apparently not discussed in the mechanism reported by Hall in the earlier publication. The mechanism given by Hall may be incomplete as recent data from both Iwamoto’s group and Hall’s researchers suggest that a dinitrosyl intermediate is formed in the reaction [27,

35]. The dinitrosyl intermediate could lead to the production of N<sub>2</sub>O. If this dinitrosyl is involved in the productive reaction path, then the minimum ensemble size for the reaction is 3 copper ions, perhaps as shown below. This trimeric complex allows for the formation of nitrous oxide with the elimination of an oxygen atom. For the model shown below, the bond lengths are 2.1 Å for



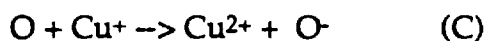
Cu-N Distance = 2.1 Å

Cu-O Distance = 2.1 Å

all the Cu-O and Cu-N bonds formed upon adsorption of the two NO molecules.

The assumption of a multinuclear Cu complex is confirmed by certain literature data which suggest that small ensembles of copper atoms are the active sites for the Cu/ZSM-5 catalysts. Results reported by Hamada [27] of extended, x-ray absorption fine structure (EXAFS) studies suggest that the presence of a phase showing a Cu - Cu distance of 3.13 Å which correlates with the NO activity. The copper-copper distance in the trimer is 3.4-3.6 Å. The exact nature of the reactive ensemble is not known.

Li and Armor [19] showed that NO<sub>2</sub> was decomposed over the Cu/ZSM-5 catalysts at temperatures near 360°C. These data suggest that the catalysts may be effective for the destruction of NO and NO<sub>2</sub>. The mechanism for destruction of NO<sub>2</sub> is not clear, but it is thought to involve NO as the intermediate. These results for both NO and NO<sub>2</sub> show that oxygen is eliminated from the catalyst at temperatures near 360°C. These results suggest the following mechanism:



All of the species in reactions A-E are assumed to be surface bound species. Pretreatment of the catalyst in oxygen results in enhanced desorption of NO<sub>2</sub> and O<sub>2</sub> at high temperatures in the thermal desorption of NO from the catalyst.

**Ensemble size effects.** This mechanism suggests that a multinuclear metal

ensemble may be appropriate to 1) adsorb two NO molecules for the disproportionation reaction (A), activate nitrous oxide into nitrogen and O which requires at least one more site (B) and to activate NO<sub>2</sub> (D). This minimum site requirement of three atoms may have to be augmented with extra sites to facilitate recombination of surface O atoms (E). If the ensemble size can accommodate the oxidation of the copper (C), the catalyst could be poisoned to further reaction. The key to the continued operation of this catalysts is the design of an ensemble to facilitate the reverse of reaction (C), i. e., the reaction to remove oxygen from the catalyst. Others have postulated the necessity of surface ensembles of a minimum size to catalyze the reaction. For example, Szakacs, et al. [36] suggest that *clusters* of surface vanadia species supported on zirconia are necessary for the de-NO<sub>x</sub> activity in SCR of NO<sub>x</sub>; whereas, isolated vanadia species are not active for the same reaction. These reports by Szakacs, et al. [36] agree in part with our own findings relating the effects of Cu ensemble size and the mechanism of NO adsorption at room temperature.

**Copper ion oxidation state.** The oxidation state of the copper ion in the zeolite is open to some debate as a result of the preparation technique, (*vide supra*); however, the oxidation state of the copper ion during the catalysis is the most interesting question. Some effort has been forthcoming to answer this question using x-ray absorption spectroscopy near the absorption edge of the metal (XANES) [37]. This *in situ* technique monitors the oxidation state of the copper ion of a "working catalyst" without disturbing the catalysis of the NO decomposition reaction. The catalyst

contains a Cu(I) as a small fraction of the total Cu with the remainder as Cu(II). Moreover, the rate of NO decomposition was shown to correlate with the amount of Cu(I) in the sample over the temperature range of 573 - 773 K. However, the correlation did not exist for temperatures up to 873 K where the NO decomposition rate decreased but the fraction of Cu(I) continued to increase. The authors explained the discrepancy as indicative that another process was rate-limiting at temperatures above 773 K.

### PROGRESS TO DATE

We have prepared a Cu/silica catalyst (2.27 wt% Cu) derived from a dinuclear copper metal complex: copper(II) bipyridil dimer perchlorate  $[\text{Cu}(\text{N}_2\text{C}_{10}\text{H}_4)_2][\text{ClO}_4]_2$ . Elemental analyses of the sample showed the expected C/N/Cu ratios (10/2/1). Moreover, the elemental analyses showed that no perchlorate was present in the sample which suggests that the metal complex was attached to the silica by an ion exchange similar to that we have reported in the past [38-39]. This sample was activated by heating in  $\text{O}_2$  to  $450^\circ\text{C}$ ; the weight loss observed during the thermolysis corresponded to the loss of the two bipyridil ligands. Electron paramagnetic resonance of the activated samples prior to activation showed the sample was paramagnetic which confirmed that the Cu ions were divalent and this suggested that no auto-reduction had occurred during the impregnation process. The sample was pretreated in a thermal gravimetric apparatus (TGA) by reduction in  $\text{H}_2$  at  $300^\circ\text{C}$  for which the weight loss suggested that 1 O/Cu was removed. The sample was exposed to NO and  $\text{N}_2\text{O}$  in separate experiments conducted at room temperature



and at 100°C, respectively. The weight changes in the TGA suggested that both NO and N<sub>2</sub>O reacted with the sample to add 1 O/Cu in the sample plus release some volatiles. The NO experiment was repeated in a diffuse reflectance, Fourier transform infrared spectrometer (Table 1). The results showed that N<sub>2</sub>O, NO<sub>2</sub> and NO<sub>3</sub><sup>-</sup> resided on the surface with very little molecular NO on the dinuclear Cu catalysts. The nitrous oxide and nitrito species disappeared upon heating the sample to 160°C; however, the intensity of the nitrate species appear to grow slightly upon heating. We have not repeated these studies using a higher temperature to desorb the surface species. Some of the species found in this study were also observed by Valyon and Hall during their study of NO/Cu/ZSM-5 [35]. It would appear that the results of our work may lend support to the structural hypothesis concerning the existence of Cu<sup>δ+</sup>-O<sup>δ-</sup>-Cu<sup>δ+</sup> ensembles in the Cu/ZSM-5 samples prepared by Hall and others [24, 28, 29].

These results for the Cu/silica prepared by decomposing a monolayer of a dinuclear Cu complex on silica are in stark contrast to the results we reported for a Cu/silica prepared from the thermolysis of a monolayer film of Cu(acac)<sub>2</sub>/silica [16, 17]. We shall designate the sample prepared from the dinuclear Cu complex as “dinuclear” and the sample prepared from the mononuclear Cu complex as “mononuclear.” The two samples of Cu/silica showed the same dispersions of Cu (100%) for similar weight loadings (2.27 wt% Cu for the “dinuclear” sample and 2.4 wt% Cu for the “mononuclear” sample). However, NO and N<sub>2</sub>O could be dissociated on the “dinuclear” sample at temperatures < 100°C; whereas, NO was

adsorbed without dissociation on the "mononuclear" sample and the NO could be removed by heating to the sample to 450°C. Nitrous oxide did not react on the "mononuclear" sample at conditions often used to "count" surface Cu sites in supported Cu samples: 100°C and 380 Torr of N<sub>2</sub>O.

The "dinuclear" sample was observed to develop surface nitrito and nitrate species after exposure to NO at room conditions in the FTIR; however, the "mononuclear" catalyst showed chemisorbed NO on Cu<sup>2+</sup> giving rise to a peak at 1910 cm<sup>-1</sup>; chemisorbed NO on Cu<sup>1+</sup> giving rise to a peak at 1826 cm<sup>-1</sup>; and an unassigned peak at 1672 cm<sup>-1</sup>. The existence of the nitrito and nitrate species represents an unfavorable surface condition which is to be avoided in the best catalysts since the sites occupied by the surface nitrito and nitrate species are not available for the catalysis of the NO. Moreover, the formation of these surface nitrito and nitrate species are speculated to occur as a consequence of the reaction between sorbed NO, NO<sub>2</sub> and surface O species. This reaction between NO, NO<sub>2</sub> and surface O species should be avoided so that O may be desorbed as molecular O<sub>2</sub> rather than desorbing NO<sub>2</sub>. It remains to be seen if the control of surface NO<sub>x</sub> can be affected by ensemble size alone.

#### REFERENCES

1. Stull, D. R., E. F. Westrum, Jr., & G. C. Sinke, The Chemical Thermodynamics of Organic Compounds, John Wiley & Sons, Inc. (1969).
2. Yuan, E. L., J. I. Slaughter, W. E. Koerner, & F. Daniels, "Kinetics of the Decomposition of Nitric Oxide in the Range 700-1800°C," *J. Phys. Chem.*, vol. 63, 952 (1959).
3. Kaufman, F., and J. R. Kelso, *J. Chem. Phys.* 23, 1702 (1955).
4. Benson, S. W., "Kinetic Data on Gas Phase Unimolecular Reactions," U. S. National Bureau of

Standards (1969).

- 5a. Baulch, D. Drysdale, D. Horne, & A. Lloyd, "Evaluated Kinetic Data for High Temperature Reactions," Homogeneous Gas Phase Reactions in the H<sub>2</sub>-N<sub>2</sub>-O<sub>2</sub> System, Butterworths, (1973).
- 5b. Casewit, C. J. and A. K. Rappe, "Theoretical Characterization of deNO<sub>x</sub> Catalysis: The Initial Nitrogen Coupling Step," *J. Catal.* **89**, 250 (1984).
6. Sandell, A., A. Nilsson, and N. Martensson, *Surf. Sci. Letters*, 241 (1991), L1.
7. Erley, W., *Surf. Sci.* **205** (1988), L771.
8. Lehwald, S., J. T. Yates, Jr., and H. Ibach, *Proc. IVC-8, ICSS-4, ECOSS-3, Cannes 1980*, Eds. D. A. Degras and M. Costa, P. 221.
9. Netzer, F. and T. E. Madey, *Surf. Sci.* **110** (1981), 251.
10. Pirug, G., H. P. Bozel, H. Hopster, and H. Ibach, *J. Chem. Phys.* **71** (1979) 593.
11. Balkenende, A. R., O. L. J. Gijzeman, and J. W. Geus, *Appl. Surf. Sci.* **37** (1989), 189.
12. Balkenende, A. R., H. den Daas, M. Huisman, T. De Beer, O. L. J. Gijzeman, and J. W. Geus, *Appl. Surf. Sci.* **47** (1991), 341.
13. Balkenende, A. R., R. Hoogendam, T. De Beer, O. L. J. Gijzeman, and J. W. Geus, *Appl. Surf. Sci.* **55** (1992), 1.
14. Balkenende, A. R., W. E. J. van Kooten, A. R. Pieters, M. Lamers, F. J. J. G. Janssen, and J. W. Geus, *Appl. Surf. Sci.* (submitted).
15. Balkenende, A. R., C. J. G. van der Grift, E. A. Meulenkamp, & J. W. Geus, "Characterization of the Surface of Cu/SiO<sub>2</sub> Catalyst Exposed to NO and CO using IR Spectroscopy," *Appl. Surf. Sci.* **68** (1993), 161.
16. Kenvin, J. C., M. G. White and M. B. Mitchell, "Preparation and Characterization of Mononuclear Metal Complexes as Model Catalysts," *Lang.* **7**, 1198 (1991).
17. Kenvin, J. C. and M. G. White, "Selective Chemisorption and Oxidation Reduction Kinetics of Supported CuO Prepared from Copper Acetylacetonates on Cab-O-Sil," *J. Catal.*, **130**, 447 (1991).
18. Shimokawabe, M., N. Hatakeyama, K. Shimada, K. Tadokoro, & N. Takezawa, "Characterization of Unsupported Cupric Oxide and Cupric Oxide/Silica Catalysts by Temperature Programmed Desorption of Nitrogen Monoxide," *Appl. Catal. A: General*, **87** (1992), 205.
19. Li. Y. and J. N. Armor, "Temperature-programmed Desorption of Nitric Oxide Over Cu-ZSM-5," *Appl. Catal.*, **76**, L1 (1991).
20. Maksimov, N. G., K. G. Ione, V. F. Anufrienko, P. N. Kuznetsov, N. N. Bobrov & G. K. Boreskov, *Doklady Akad. Nauk S. S. S. R.*, **217**, 135 (1974).

21. Minachev, Kh. M., G. V. Antoshin, & E. S. Shapiro, *Izvest Akad, Nauk S. S. S. R. Ser. Khim.*, 1012 (1974).
22. Garten, R. L., W. N. Delgass, and M. Boudart, *J. Catal.* **18**, 90 (1970).
23. Jacobs, P. A., W. de Wilde, R. A. Schoonheydt, and J. B. Uytterhoeven, "Redox Behaviour of Transition Metal Ions in Zeolites; Part 3.--Auto-reduction of Cupric Inns in Y Zeolites," *Chem. Soc., Farad. Trans*, vol I. 1221 (1976).
24. Li, Y. and Hall, W. K., "Catalytic Decomposition of Nitric Oxide over Cu-Zeolites," *J. Catal.*, **129**, 202 (1991).
25. Bruce, David, private communication to the Texaco Corporation, Port Arthur, Tx; August 31, 1992).
26. Iwamoto, M., private communication, (1992).
27. Iwamoto, M., Yashiro, H., Ooe, K., Banno, Y., Okamoto, F., *Shokubai* **32**(2), 91 (1990),
28. Hamada, H., Matsubayashi, N., Shimada, H., Kintaichi, Y., Ito, T., and Nishijima, A., *Catal. Lett.* **5**, 189 (1990).
29. Li, Y. and W. K. Hall, "Catalytic Decomposition of Nitric Oxide over Cu-Zeolites," 12<sup>th</sup> Meeting of the North American Catalysis Society, paper D07 (1991).
30. Knozinger, H., *Proc. Iberoam. Symp. Catal.*, 7<sup>th</sup> (1980), 594; Hierls, R, H.-P. Urbach & H. Knozinger, "Coadsorption and Reaction of NO and Co on Cu/Al<sub>2</sub>O<sub>3</sub> Catalysts," *New Frontiers in Catalysis*, Guzzi, L. et al. (Editors), Proceedings of the 10th International Congress on Catalysis, 19-24 July, 1992, Budapest, Hungary, Elsevier..
31. Miyamoto, A., K. Kobayashi, M. Inomata and Y. Murakami, *J. Phys. Chem.*, **1982**, *86*, 2945.
32. Otto, K., M. Shelef, and J. T. Kummer, *J. Phys. Chem.*, **1970**, *74*, 2690.
33. Bleek, C. M. van den; Berg, P. J. van den, *J. Chem. Tech. Biotechnol.*, **1980**, *30*, 467.
34. Bosch, H., F. J. J. G. Janssen, J. Oldenzel, F. M. G. van den Kerkhof, J. G. van Ommen, J. R. H. Ross, *Appl. Catal.*, **1986**, *25*, 239.
35. Valyon, J, and W. K. Hall, "Studies of the Surface Species formed from NO on Copper Zeolites," *J. Phys. Chem.* **97**, 1204 (1993); "An Infrared Study of An Active NO Decomposition Catalyst," *New Frontiers in Catalysis*, Guzzi, L. et al. (Editors), Proceedings of the 10th International Congress on Catalysis, 19-24 July, 1992, Budapest, Hungary, Elsevier.
36. Szakacs, S., G. J. Altena, T. Fransen, J. G. Van Ommen, & J. R. H. Ross, "The Selective Reduction of NO<sub>x</sub> with NH<sub>3</sub> over Zirconia-Supported Vanadia Catalysts," *Catal. Today*, **16** 237 (1993).
37. Liu, D. J, and H. R. Robota, "In Situ Characterization of Cu-ZSM-5 by X-Ray Absorption Spectroscopy: XANES Study of Cu during NO Decomposition," *ACS Preprints, Division of Petroleum Chemistry*, 206<sup>th</sup> National Meeting, (1993).
38. Beckler, R. K. and M. G. White, "Polynuclear Metal Complexes as Model Mixed Oxide Catalysts:

Isomerization Activity," *J. Catal.* **110**, 364 (1988); Beckler, R. K., Ph. D. thesis, Georgia Institute of Technology, Atlanta, GA (1988).

39. Bruce, David, J. Aaron Bertrand, and Mark G. White, "Effects of Molecular Structure upon Complex-Support Interactions," *A. I. Ch. E. Journal*, vol. 39, No. 12, 1966 (1993).

**Table I Infrared Absorption Peaks and Assignments**

Frequency of absorption, cm <sup>-1</sup>			<u>Cu/Y</u>	<u>Adsorbed Species</u>	<u>Note and assignments</u>
<u>Cu/ZSM-5</u>	<u>Cu(acac)<sub>2</sub></u>	<u>Cubipy</u>			
2240		2200		N <sub>2</sub> O	on Cu <sup>1+</sup>
2160   2120				NO <sub>2</sub>	on Cu <sup>2+</sup>
1900	1910	1950	1948   1914	NO	on Cu <sup>2+</sup>
			1902-1891	NO	on isolated Cu <sup>2+</sup> moved to accessible position
1895			1912-1907		on Cu <sup>2+</sup> carrying extra-lattice O
1824   1730				(NO) <sub>2</sub>	on Cu <sup>1+</sup>
1810	1826	1820		NO	on Cu <sup>1+</sup>
		1768		?	?
	1672			?	?
1625		1620		NO <sub>2</sub>	Cu
1575		1580		O(NO <sub>2</sub> )	Cu
1320		1375		NO <sub>3</sub> <sup>-</sup>	Cu(?)

## Appendix 1

This literature review was initiated by a search of the electronic data bases at the Georgia Institute of Technology. The preliminary search using the initial set of key words produced 537 matches. An inspection of this set of matches revealed a subset of matches which were relevant to this problem. Abstracts from this subset were reviewed to generate the set of references used in this review. Other literature citations were generated from a review of the Preprints of American Chemical Society. We present in the attached a subset of the literature citations generated during the initial search.





## Report on Progress in Synthesizing a NO Decomposition Catalyst

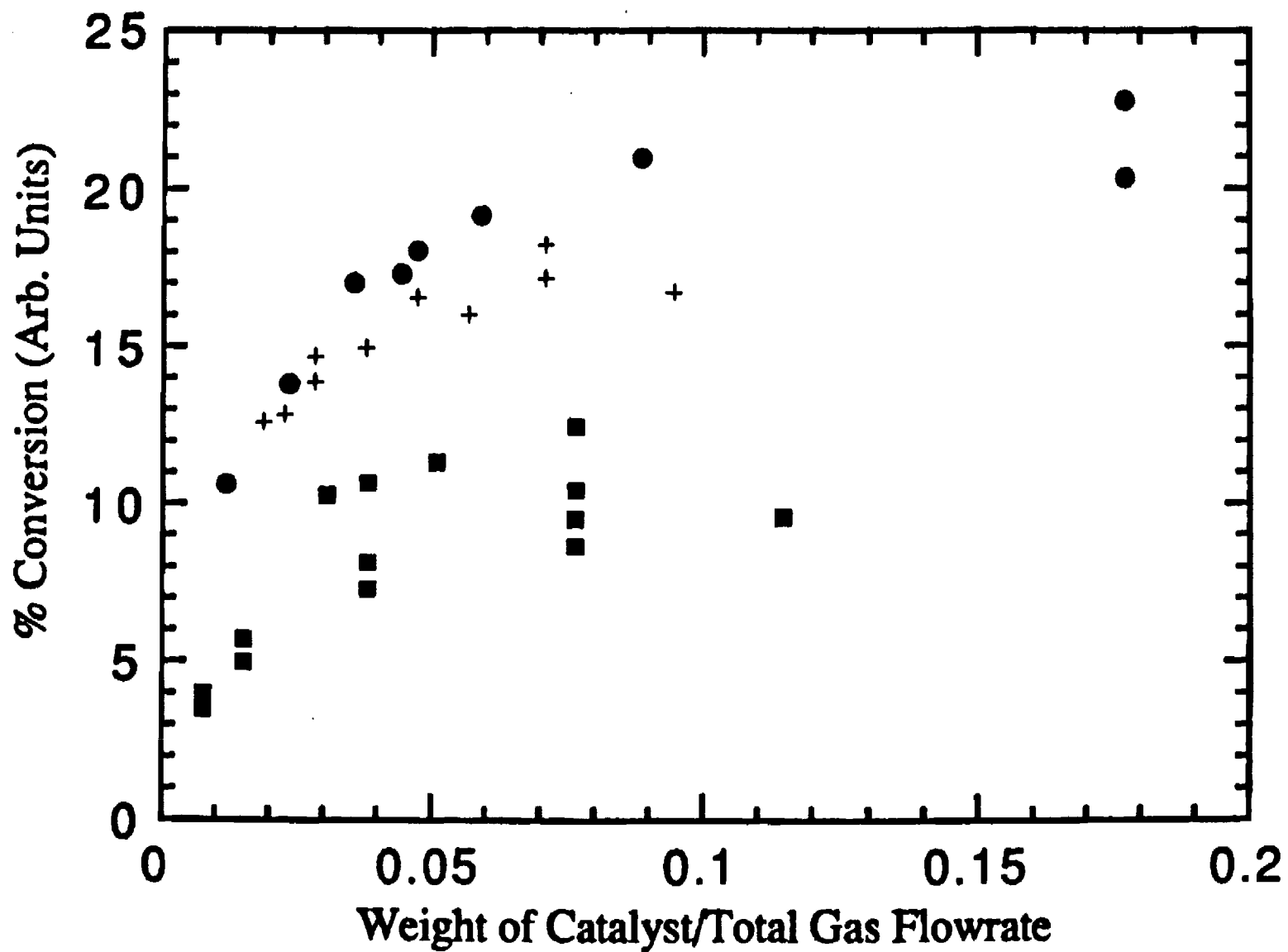
prepared by

Mark G. White, Professor and Director  
Focused Research Center in Surface Science and Catalysis  
Georgia Institute of Technology  
Atlanta, GA 30332-0101

This report shows our progress in measuring the initial activity of a Cu/ZSM-5 catalysts.

*Reactivity of Cu-ZSM-5.* We prepared a sample according to the technique of Li and Hall. [Li, Y. & W. K. Hall, *J. Catal*, **129**, 202 (1991)]. Three samples (1.38, 1.70, and 2.13 g) of this powdered catalyst were mounted in a tubular flow reactor for testing in three separate runs at a common temperature (773 K) and for a common inlet concentration of NO in He (4.21% NO). The data (Figure 1) were reported as conversion of NO to N<sub>2</sub> as a function of spacetime (weight of catalyst/total gas flowrate). The data for the smallest amount of catalyst (1.38 g -- solid squares) appeared to show smaller conversions at each spacetime that the data for the larger weights of catalysts (1.7 g - crosses and 2.13 g--filled circles). At low spacetimes, the data at the two larger weights appeared to coincide. These results suggest that mass transfer effects appeared to influence the data collected from the run involving the smallest amount of catalyst in the reactor. Therefore this diagnostic confirms that no less than 2.5 g of catalyst should be used in the reactor for this temperature so that we may measure the effects of kinetics in the absence of the confounding effects of mass transfer.

Figure 1 Conversion of NO versus Spacetime Data





E-19-x33  
# 3

Third Deliverable to EPA-RTP  
NO Decomposition over Supported CuO Catalysts  
Synthesized from Copper Metal Complexes

by

Mark G. White, Professor and Director  
Focused Research Program in Surface Science and Catalysis  
School of Chemical Engineering  
Georgia Institute of Technology  
Atlanta, GA 30332-0100

## INTRODUCTION

Several catalysts for NO decomposition have been reported in the literature to include the following: Cu/ZSM-5; [1-3] Cu/Y [3]; Cu/mordenite [3]; Cu/ $\beta$  zeolite [3]; and Cu/silica [4] which have been studied less than Cu/ZSM-5. The catalytic properties for NO conversion is different on these samples [3] with the ZSM-5 supported catalysts showing the highest activity in a dry environment free from sulfur oxides. The purpose of this study is to have a better fundamental understanding on the roles of Cu and the support in the catalysis.

The source of Cu ion in the previous studies is the aqueous salt which is known to show dynamic and facile equilibrium between aqueous species having different charges and copper ion nuclearity. For example, copper acetate in aqueous solutions shows the neutral, hydrated dimer along with hydroxy Cu cations and hydrated divalent Cu cations [5]. Therefore, the catalyst synthesized from this solution will show these Cu complexes in contact with the surface.

We use stable, cationic metal complexes in non-aqueous solvents as sources of the Cu ions for these and other catalysts [6]. For example, Kenvin showed that Cu(acac)<sub>2</sub> decorated silica as a single layer which produced a stable, high dispersion of Cu/silica when the ligands were removed [7]. Choksi, *et al.*, produced a similar robust catalyst beginning with the dimer of Cu(bipy) cation on silica [8]. Bruce, *et al.*, showed, how Cu(en)<sub>2</sub><sup>2+</sup> could be affixed to silica using acetonitrile as the solvent [9]. Very stable complexes, such as the Cu(en)<sub>2</sub><sup>2+</sup>, appear to resist dissociation even when contacted with strong acids. Thus, we use a set of stable metal complexes as

the sources of Cu in producing model catalysts for which the fate of the source molecule is known and is controlled during the ion exchange/impregnation. We compare the performance of the model catalysts to one prepared by aqueous impregnation of ZSM-5 zeolite. The performance of the dinuclear metal complex on silica is compared to the same complex in Y-zeolite.

## EXPERIMENTAL

### *Chemicals*

Cu[ClO<sub>4</sub>]<sub>2</sub> and ethylene diamine were obtained from Alfa Inorganics and used without further purification. 2, 2'-bipyridine was purchased from Aldrich Chemicals. The NO/He gas mixture (4 vol % NO) was purchased from Matheson. High purity He was obtained from. The gases were passed through a Matheson Gas Purifier to remove water prior to use.

### *Metal complexes*

The complexes Cu(en)<sub>2</sub>[ClO<sub>4</sub>]<sub>2</sub>, where (en) is the ethylenediamine ligand, and the dimer of Cu(bipy)[ClO<sub>4</sub>]<sub>2</sub>, where (bipy) is the bipyridil ligand, were synthesized by the standard preparations [8, 9, 10].

### *Supports*

The zeolites ZSM-5 and Y were obtained in the sodium forms from Dr. P. S. Dai of Texaco Research and Development Co. (Port Arthur, TX). Elemental analyses of the zeolites are shown in Table 1 to include the bulk Si/Al ratio. Cab-O-Sil (M-5 grade) silica was obtained from Cabot Corporation. The framework Si/Al ratio was determined using the reactive probe, *iso*-propyl amine described by Kofke, *et al.* [11].

**Table 1 Elemental Analyses**

<u>Element</u>	<u>HZSM-5</u>	<u>Y</u>
Silicon, wt%	41.5	26.54
Aluminum, wt%	1.14	7.67
Sodium, wt%	0.76	0.08
Si/Al, molar (bulk)	36.40	3.32
Si/Al, molar (framework)	55	
Na/Al, molar	0.78	0.0

*Preparation methods*

We prepared state-of-the-art catalysts according to the method of Li and Hall as described in reference [3] using the acetate salt of Cu(II). These catalysts are designated as CuLH4. The model catalyst derived from copper ethylenediamine were prepared by dissolving the required mol of Cu(en)<sub>2</sub><sup>2+</sup> in acetonitrile at room temperature under constant stirring. The zeolite, 2 g, was added and the system allowed to stir for 24 hours. The supernatant solution was removed by filtering and the catalyst was washed with fresh acetonitrile so as to remove metal complexes not ion exchanged with the zeolite which were identified as CUZ5EN21. Additional catalysts were prepared to show the effect of copper ensemble size using stable Cu complexes of a known nuclearity on different supports: Cu(bipy) dimer on silica (CUSIBPD), and on Y-zeolite (CUZYBPD). We report in Table 2 the metal loadings of these catalysts.

We prepared another set of catalysts by re-impregnation with Cu(en)<sub>2</sub><sup>2+</sup> of a

Cu/ZSM-5 which was prepared from the same metal complex cation and was calcined prior to the second impregnation (CUZ5EN22). The purpose of this preparation was to increase the copper loading and hopefully increase the average Cu ensemble size.

#### *Elemental analyses*

Samples were sent to Galbraith Laboratories, Inc. (Knoxville, TN) for analysis of metals (Na, Cu, Si, and Al) plus non-metals (C, N, and H.)

#### *Reaction studies*

A tubular flow reactor was constructed of stainless steel tubing (12 mm OD) serviced by two mass flowmeter/controllers (Matheson model 8274 control electronics, Matheson 8172 flowmeter and Matheson 8242 control valve) in a gas-metering manifold fabricated from stainless steel tubing (6 mm OD). The gases were mixed after metering and sent to the reactor. The desired mass of catalyst (2-4 g) was confined in the reactor by filamentous alumina (Safil). Thermocouples were installed up- and down-stream of the catalyst bed and the heater (Lindberg Furnace) was controlled by an Omega Engineering controller, model #CN 8600. The product gases were sent to a HP 5780 Series II+ gas chromatograph equipped with a HP 5972A mass selective detector with ChemStation and an air-operated gas sampling valve. The partitioning agent was a zeolite column by Alltech Associates (Deerfield, IL 60015; GS-MOL, P/N 115-3632; 0.53 mm x 30 m long) operated at 100°C for a He carrier gas flowrate of 2 STP cm<sup>3</sup>/min.



## RESULTS

### *Elemental analysis*

The catalysts were analyzed for C, N, H, and Cu analyses before the samples were calcined to determine the apparent C/N/Cu stoichiometry of the supported metal complexes (Table 2). Shown in the same table is the predicted C, N, and H

**Table 2 Elemental Analyses of Cu/Zeolite Catalysts**

*Analyses: Weight Percent*

<u>Sample ID</u>	<u>Carbon</u>	<u>Nitrogen</u>	<u>Hydrogen</u>	<u>Copper</u>	<u>% Cu</u> <u>Exchg</u>
CUZ5EN21	4.19	2.3	1.47	1.44	57
Theoretical	1.09	1.27	0.18	1.44	
CUZ5EN22	2.65	1.81	1.17	1.88	75
Theoretical	1.42	1.66	0.24	1.88	
CuZ5LH4	2.10	--	1.38	1.81	72
Theoretical	1.37	--	0.26	1.81	
CUZYBP	6.16	2.96	1.81	1.7	
Theoretical	3.21	0.75	0.13	1.7	
CUSIBPD	3.99	0.87	<0.5	2.02	
Theoretical	3.81	0.89	0.16	2.02	

Note: It is assumed that Cu analysis is correct in predicting the theoretical analyses for C, N, and H.

analyses assuming that the Cu analyses was correct and using the stoichiometry of the parent Cu complex in predicting the analyses. We assumed the following stoichiometries for these predictions: CUZ5EN21 and EN22 --  $\text{Cu}(\text{N}_2\text{C}_2\text{H}_6)_2$ ; CUZ5BPM --  $\text{Cu}(\text{N}_2\text{C}_{10}\text{H}_8)$ ; CUZ5BPD and CUSIBPD --  $[\text{Cu}(\text{N}_2\text{C}_{10}\text{H}_8)]_2$ ; CuLH4 --  $\text{Cu}_2(\text{O}_2\text{CCH}_3)_4$ . One sample showed predicted carbon and nitrogen analyses near the observed values (CUSIBPD); whereas, all of the over catalysts show C, N, and H analyses which are higher than the theoretical. We have observed this same result in earlier studies where the solvent (acetonitrile) was strongly adsorbed by the support [12]. In the same table we show the percentage of Cu ion exchange level based on the Si/Al ratio calculated from the bulk analyses.

#### *Reaction studies*

The micro reactor results are shown in Fig. 1 for the catalyst prepared from aqueous impregnation of the acetate salt into ZSM-5 (CuLH4) and the two catalysts prepared by non-aqueous impregnation of ZSM-5 with  $\text{Cu}(\text{en})_2^{2+}$  (CUZ5EN21 and CUZ5EN22). These catalysts demonstrate steady-state activities after 24 h which are only 5-10% less than the initial values. Oxygen is evolved in a proportion which is less than the stoichiometric amount expected from the nitrogen production. We estimate the rate constant for this reaction by measuring the slope of the conversion versus spacetime curve at zero space-time. The space-time is calculated by multiplying the fractional loading of copper in the catalyst (g Cu/g catalyst) by mass of catalyst in the reactor and dividing by the volumetric flowrate over the catalyst ( $\text{cm}^3/\text{sec}$ ). This limiting slope has the units of % conversion- $\text{cm}^3/\text{g Cu-second}$ ).

The catalyst derived from the acetate salt is more active (1850 % converted-cm<sup>3</sup>/g Cu-sec) than the two catalysts derived from the (en) salts (650 and 480 % converted-cm<sup>3</sup>/g Cu-sec). The difference in activities cannot be attributed to Cu metal loading as the activities have been corrected for metal content by the space-time expression. The catalysts developed from the (en) precursor show the beneficial effect of re-impregnating the catalyst with the precursor after calcining the catalyst prepared from the first impregnation (650 for two impregnations vs 480 % converted-cm<sup>3</sup>/g Cu-sec for one impregnation).

The silica-supported catalyst (CUSIBPD) derived from the Cu(bipy) dimer complex (1.5 g) shows low initial activity (6% conversion to N<sub>2</sub>) at a flow rate of 25 STP cm<sup>3</sup>/min at 773 K which decreases to 1% conversion after 1.5 h (Fig 2). Finally, the faujasite supported catalysts (CUZYBP, 1.88 g) developed from the Cu(bipy) dimer rapidly deactivates from 100% conversion to 3% conversion in 0.5 h at the same reaction conditions (Fig 2). No oxygen is evolved from this last catalyst at 100% conversion to N<sub>2</sub>.

## DISCUSSION

The elemental analyses together with the vibrational analyses lead us to conclude that (en) metal complexes mount the support without wholesale destruction of the precursors. If such destruction did occur, then the observed carbon and nitrogen analyses would be lower than the predicted values. The analyses do show that the samples are contaminated with the solvent before the calcination. The catalysts were prepared with Cu exchange levels lower than 100%

based upon the chemical analyses of the zeolite [11].

The reaction studies suggest that catalytic activity may be developed from model catalysts derived from thermolysis of cationic, mononuclear Cu complexes on ZSM-5. The level of activity in the model catalyst is a factor of 3-5 times smaller than the state-of-the-art catalysts developed from the aqueous acetate salt [1-3]. We suggest that the difference in activity between these catalysts may be the result of Cu ensemble size since the mass of Cu is similar (1.4-1.9 wt% Cu) in the CULH4, CUZ5EN21 and CUZ5EN22 catalysts.

To explore the effect of ensemble size further, we synthesized a family of catalysts using Cu(bipy) dimer on the following supports: silica, and Y-faujasite showing Cu loadings of 1.7-2.5 wt% . The dimer on silica showed very low activity (6% conversion) which decreased to no conversion rapidly on stream. Choksi, et al. [9] showed this catalyst will dissociate NO at room temperature to leave O atoms on the surface which cannot be removed by heating to 550°C. The dimer in the Y-zeolite showed almost total conversion, initially; however, it too deactivated rapidly to very low conversion. The Y-supported catalyst did not evolve gaseous oxygen during the test which suggest that it was sequestered by the catalyst; perhaps by the Cu species thus rendering the sites inactive. During thermolysis we suggest that Cu ensembles may be formed having many Cu atoms. The activity of this catalyst was very low compared to that observed for CUZ5EN22 and CULH4 catalysts which showed steady state conversions to N<sub>2</sub> of 30 and 80% at these same conditions.

We suggest that a minimum ensemble size for the catalysis is two Cu ions

residing on a support such as ZSM-5. The ZSM-5 support plays an important role in the catalysis as very little conversion is observed for a dinuclear Cu ensemble residing on a neutral support such as Cab-O-Sil. The maximum ensemble size for the catalysis may be as small as 4-6 Cu atoms as rapid deactivation by strong oxygen adsorption apparently occurs on the Y-supported catalysts.

#### ACKNOWLEDGEMENTS

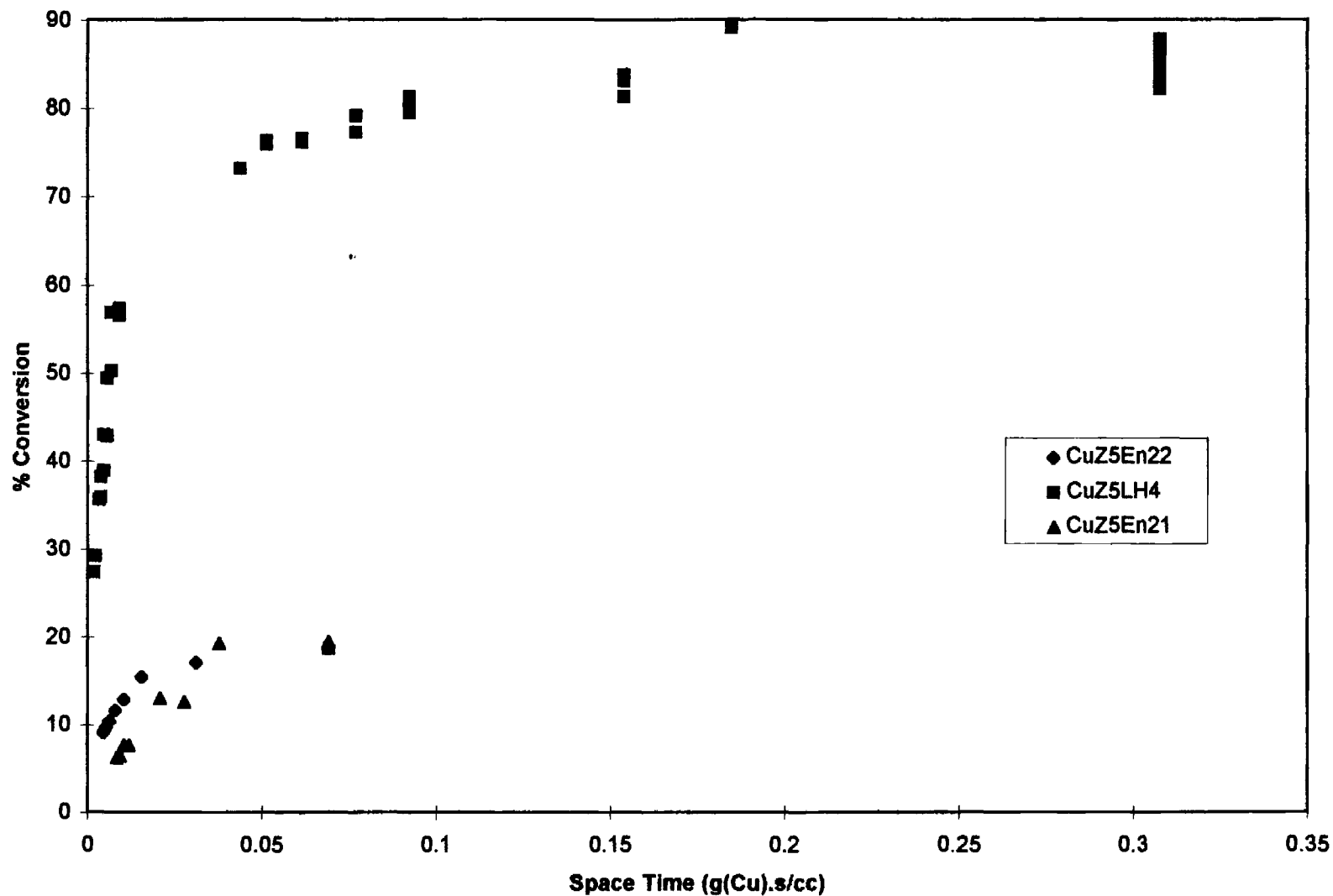
We acknowledge the support from contracts with the U. S. Department of Energy (DE-FG22-90PC90292) and the U. S. EPA (FK3137).

#### REFERENCES

1. Iwamoto, M., S. Yokoo, K. Sakai, S. Kagawa, *J. Chem. Soc., Faraday Trans. 1* (1981), 77, 1629.
2. Li, Y. and W. K. Hall, *J. Phys. Chem.* vol. 94, No. 16, pp. 6145-48. (1990).
3. Li, Y. and W. K. Hall, *J. Catal.* **129**, 202-215 (1991).
4. Balkende, A. R., C. J. C van der Gritt, E. A. Meulenkamp, J. W. Geus, *Appl. Surf. Sci.* **68** (1993), 161.
5. Brown, George, M., and R. Chidambaram, *Acta Cryst.* (1973), **B29**, 2393.
6. White, M. G., *Catal. Today*, **18**, (1993), 73.
7. Kenvin, J. C., and M. G. White, *J. Catal.* **135** (1992), 81.
8. Choksi, H. N., A. Zippert, P. Berdahl, J. A. Bertrand, D. L. Perry, M. B. Mitchell, and M. G. White, *J. Mol. Catal. A: Chemical*, **97** (1995) 85-99.
9. Bruce, D. A., J. A. Bertrand, and M. G. White, *A. I. Ch. E. Journal*, vol. **39**, No. 12, (1993), 1966-75.

10. Venable, M. H., M. S. thesis, Georgia Institute of Technology (1990).
11. Kofke, T. J. Gricus, R. J. Gorte, and W. E. Farneth, *J. Catal.*, **114**, 34-45 (1988).
12. Rao, S. N. R., M. S. thesis, Georgia Institute of Technology (1993); Rao, S. N. R., E. Waddell, M. B. Mitchell, and Mark G. White, "Selective Sulfur Dioxide Adsorbents Prepared from Designed Dispersion of Group IA and IIA Metal Oxides on Alumina," submitted to the *J. Catalysis*.

Figure 1 Conversion of NO to N<sub>2</sub> on Cu/ZSM-5 Catalysts



**Figure 2 Transient Conversion of NO to N<sub>2</sub> on Cu/ZSM-5 Catalysts**

