The Conversion of Light Amines Over Copper-Containing Zeolites.

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THE CONVERSION OF LIGHT AMINES OVER COPPER-CONTAINING ZEOLITES

A Dissertation

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College
In partial fulfillment of the Requirements for the degree of Doctor of Philosophy

in

The Department of Chemical Engineering

by
Trent Francis Guidry
B.S. (Ch.E.), Louisiana State University, 1994
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ABSTRACT

Copper-containing zeolites have been prepared by vapor, aqueous, and solid-state ion-exchange, characterized, and investigated for the conversion of light amines.

A copper-containing zeolite was synthesized by vapor ion-exchange in this study by a method that does not appear to have been previously reported. This material was prepared by reaction of the acidic zeolite with CuCl vapor, followed by oxidation of the Cu\(^{2+}\) ions to copper oxonium ions which are converted to copper hydroxyl dimers on exposure to air. The copper hydroxyl dimer exchanged zeolite is stable in air and can be converted back to a highly exchanged Cu\(^{2+}\) zeolite by either partial hydrogen reduction or thermal treatment in an inert environment.

Aqueous ion-exchanged MFI and BEA have also been prepared and investigated. These investigations indicated that, as with the vapor ion-exchanged materials, most of the copper ions in the aqueous ion-exchanged materials existed as copper hydroxyl ions but in lower loadings than we were able to achieve using the vapor ion-exchange technique.

The solid-state ion-exchange of CuO and Cu\(_2\)O with acidic MFI was also investigated. The results in this study suggested that CuO reacts with the zeolite on thermal treatment according to form zeolite coordinated Cu\(^{2+}\). During this process, some of the CuO is converted into an unreducible species such as copper metal or copper aluminates.

The results obtained suggested that under 1-propanamine reaction conditions, all of the copper ions in the zeolites were reduced to copper metal by the reactant, with regeneration of the zeolitic acid sites. Both the copper content and the dispersion of the
copper metal play a significant role in the rate of conversion of 1-propanamine and the
distribution of products produced. The acid sites in these materials catalyze the condensa-
sion of the primary amine reactant to secondary amines and ammonia. Dispersed
copper metal catalyzes the selective dehydrogenation of the secondary amine to produce
imines. The presence of copper clusters with two or more copper atoms further cata-
lyzes the dehydrogenation of the imines to nitriles.
I. INTRODUCTION

A. Background

A few years ago, zeolite catalysis research at LSU was focused on gallium loaded zeolites which are useful for light paraffin aromatization. However, several very interesting observations in this system have spun off some new and exciting research efforts in copper-containing zeolites, which is the focus of this dissertation.

One of the most important discoveries in the gallium system was that Ga\(^{3+}\) cations which were initially present in the catalyst formulation reduced to Ga\(^{+}\) cations under catalytic conditions which included the hydrocarbon reactant, and that the Ga\(^{+}\) cations migrated to ion-exchange sites in the zeolite during reduction and replaced protons [1-3]. This process could even be achieved when separate solid-state phases, Ga\(_2\)O\(_3\) and H-MFI zeolite (also known as H-ZSM-5), initially coexisted as a mechanical mixture, so the process was termed Reductive Solid-State Ion-Exchange (RSSIE).

One of the ramifications of RSSIE in the gallium system is that Ga\(^{+}\) can be loaded at three times the theoretical ion-exchange limit of the Ga\(^{3+}\) cation which is commonly stable in aqueous solutions. Researchers at LSU noted that this same principle might be applied in other metallic systems to achieve higher loadings of metals than other ion-exchange techniques can yield, and the copper zeolite system was a perfect candidate. Tremendous interest has recently been focused on this system because Cu/MFI is useful for the direct decomposition of NO to N\(_2\) and O\(_2\) [4-17] and the selective catalytic reduction of NO with hydrocarbons in the presence of excess oxygen [18-21], which has obvious environmental utility. Furthermore, the best catalytic materials are those that have high loadings of copper, and RSSIE has the potential to
provide materials with higher copper loadings than any other known technique. Copper zeolites have been prepared by RSSIE with apparent success, and the further characterization of this system is one of the focuses of this research work.

Parallel to the development of RSSIE in the Ga/MFI system was the refinement of a standard procedure for zeolite characterization, thermal desorption of light alkylamines, which is commonly applied to measure the proton content of acidic forms of zeolites. LSU researchers [22] discovered that when protons are replaced with metal cations such as gallium or copper, thermal desorption spectra of light alkylamines can be used to qualitatively indicate the presence or absence of protons. Instead of simple desorption and breakdown of amines which occurs on protons, metal cations promote dimerization of amine molecules at relatively low temperatures and polymerization reactions instead of decomposition at higher temperatures. Nitriles were discovered as an important product of the thermal desorption process. Catalytic test reactions then confirmed that the Cu/MFI materials prepared by RSSIE could promote the simultaneous dimerization/dehydrogenation of propanamine to a C₆-nitrile. Such chemistry had never been reported in the open catalytic literature before and a patent covering this invention has been issued [23].

This study is intended to further the understanding of copper-containing zeolites and their ability to catalyze the reactions of amines by investigating and characterizing copper-containing zeolites prepared by aqueous, vapor, and solid-state ion-exchange. Due to the considerable interest in the direct decomposition of NO to N₂ and O₂ [4-17] and the selective catalytic reduction of NO with hydrocarbons in the presence of excess oxygen [18-21] by copper-containing zeolites and the uncertainty of the chemistry of the
copper ions in these zeolites, particular emphasis is placed the nature of the copper ions present in copper-containing zeolites. These materials are then comparatively investigated for the conversion of light amines with the objective of determining the conditions which favor yields of dehydrogenated product and the mechanistic pathway by which they are formed.

B. Executive Summary

Zeolites are highly crystalline materials composed of silicon, aluminum, oxygen, and hydrogen. The tetrahedral aluminum atoms that are part of the framework of these materials create a negative charge on the adjacent oxygens that must be compensated with a cation. Often, various types of ion-exchange procedures are used to place catalytically active metals in these cation sites. In this study, copper-containing zeolites have been prepared by vapor, aqueous, and solid-state ion-exchange and were extensively characterized. These materials are then comparatively investigated for the conversion of 1-propanamine. The conversion of other amines is also investigated over the material with the highest activity for 1-propanamine conversion, which is a material prepared by vapor ion-exchange.

A copper-containing zeolite was prepared by vapor ion-exchange in this study by a useful method that does not appear to have been previously reported. Although previous investigations have prepared fully exchanged Cu⁺ zeolites by the reaction of CuCl vapor with acidic MFI zeolite [24-27], all of these exchanges were performed in situ due to concern about the possible reaction of Cu⁺ in the zeolite with oxygen or water in air. This problem poses significant difficulties in the commercialization of any process using these materials, but appears to have been circumvented in this study by
oxidation of the Cu⁺ ions to copper oxonium ions, [CuOCu]²⁺, which are converted to copper hydroxyl ions, [Cu(OH)]⁺ on exposure to air. These ions associate with each other forming copper hydroxyl dimers which give a strong IR absorption spectrum. The copper hydroxyl dimer exchanged zeolite is stable in air and can be converted back to a highly exchanged Cu⁺ zeolite by either partial hydrogen reduction or thermal treatment in an inert environment. These conclusions are supported on the basis of thermogravimetric reduction, H₂ TPR, IR analysis of the oxygen-hydrogen stretch region, and IR analysis of the materials after CO adsorption in the carbon-oxygen stretch region. The temperatures at which the copper ions in these materials thermally reduce to Cu⁺ is close to the temperature at which the catalytic decomposition of NO occurs over copper exchanged MFI [6]. This reaction has been proposed to be catalyzed by Cu⁺ ions in zeolites [5,7-9,14,15,17,28].

Aqueous ion-exchanged MFI and BEA (zeolite Beta) have also been prepared and investigated. These investigations indicated that as with the VIE materials, most of the copper ions in the aqueous ion-exchanged materials existed as copper hydroxyl ions, [Cu(OH)]⁺, but in lower loadings than we were able to achieve using the vapor ion-exchange technique. As with the VIE materials, the copper hydroxyl ions, [Cu(OH)]⁺, in these materials undergo thermal reduction on heating in an inert environment.

The solid-state ion-exchange of CuO and Cu₂O with acidic MFI was also investigated. The results in this study suggested that CuO reacts with the zeolite on thermal treatment according to CuO + 2 H⁺Z⁻ → Z⁻Cu²⁺Z⁻ + H₂O. During this process, some of the CuO is converted into an unreducible species such as copper metal or
copper aluminates. These conclusions are supported on the basis of thermogravimetric reduction, H₂ TPR, IR analysis of the oxygen-hydrogen stretch region, and IR analysis of the materials after pyridine adsorption. However, XANES/EXAFS spectroscopy has indicated the presence of Cu²⁺, Cu⁺, and Cu⁰ in preparations which varied from experiment to experiment [29]. These results are still being interpreted at the time of this writing. The reaction of CuO with sodium exchanged MFI was also investigated, and it was found that CuO reacts with the zeolite, presumably by CuO + 2 Na⁺Z → Z-Cu²⁺Z + Na₂O. The characterization results of the solid-state reaction of Cu₂O with H-MFI suggests that the Cu⁺ ions disproportionate (2 Cu⁺ → Cu²⁺ + Cu⁰) by desorbing water during heating, which prevents this approach from being of synthetic utility for the purposes of forming a Cu⁺ zeolite.

The reactions of amines over copper-containing zeolites were also investigated and it was found that prereduced vapor ion-exchanged zeolites were the most active materials for the conversion of amines to dehydrogenated products. The results obtained suggested that under reaction conditions, all of the copper ions in the zeolites were reduced to copper metal by the reactant, with regeneration of the zeolitic acid sites. This study indicates that both the copper content and the dispersion of the copper metal plays a significant role in the conversion of 1-propanamine and the products produced. The acid sites in these materials catalyze the condensation of the primary amine reactant to secondary amines and ammonia. Dispersed copper metal catalyzes the selective dehydrogenation of the secondary amine by the removal of the hydrogen atoms attached to the nitrogen and an adjacent carbon atom to produce imines. The presence of copper
clusters with two or more copper atoms further catalyzes the dehydrogenation and rearrangement of the imines to nitriles.

C. Literature Review

General

A review of the literature broken down according to 1) the properties of the base zeolites used in this study, 2) the three most common methods of ion-exchanging zeolites with copper, 3) the previous investigations into the nature of the materials formed by these processes, and 4) the catalytic reactions of amines over these materials, which have been categorized separately.

Acidic Zeolites

Acidic zeolites are highly crystalline materials composed of primarily of silicon, aluminum, oxygen, and hydrogen. The silicon and aluminum atoms exist in a tetrahedral geometry and are connected to each other through oxygen atoms in complex crystal structures [30,31]. The tetrahedral aluminum atoms assume a negative charge that must be compensated with a cation. The initial zeolite synthesis process often yields an alkali-metal compensating cation such as sodium, which can be ion-exchanged with other cations. Acid forms of the zeolite are common and are usually produced starting with NH₄⁺ exchange. The NH₄⁺ ions can then be thermally decomposed to yield ammonia gas and protons which serve as the compensating cation. This process imparts strong acid properties and allows for their use as catalyst for reactions similar to those catalyzed in solution with liquid acids [30,31].

The ion-exchange capacity of a zeolite can be determined by fully exchanging the zeolite with protons and then measuring the acidity by gravimetric titration with basic
molecules [32-36]. Adsorption of 1-propanamine or 2-propanamine onto an acidic zeolite followed by purging in helium and heating has been shown to produce a 1:1 amine to proton complex at temperatures between 550 K and 650 K [32-36] that decomposes to ammonia and propene at higher temperatures. The number of moles of protons, and hence the number of exchange sites, per unit mass of catalyst can be computed by determining the mass of adsorbate in the 1:1 adsorption region and using the molecular weight of the adsorbate in the titration process.

The crystal structure of MFI, also referred to as ZSM-5, consists of parallel 10 ring pores of 5.4 x 5.6 Å connected together perpendicularly by zig-zag 10 ring pores of 5.1 x 5.4 Å [37]. This structure allows for three dimensional diffusion through the crystal. While 10 ring pores are large enough to accommodate molecules of size similar to o- and m-xylene, larger molecules such as 1,3,5-trimethylbenzene are excluded [37]. Research suggests that the acid sites in well crystallized acidic MFI, which we refer to as H-MFI, are all of approximately equal strength [32].

The crystal structure of zeolite BEA (BEA is actually the International Zeolite Associations designation of the framework topology of one of the polymorphs that intergrow to form zeolite Beta. For simplicity, we will use “BEA” to refer to zeolite Beta), is more complicated than that of MFI and is considered to be a high intergrown hybrid of two distinct, but similar, structures [38]. Both structures have three dimensional 12 ring pore systems. One the two structures, referred to as polymorph A, is chiral and has parallel interconnected pores of 7.3 x 6.0 Å along the x and y axis that are connected together by spiral pores of 5.6 x 5.6 Å along the z axis [38]. The other structure, referred to as polymorph B, is achiral and has parallel interconnected pores of
7.3 x 6.8 Å along the x and y axis that are connected together by pores of 5.5 x 5.5 Å along the z axis [38].

Methods of Ion-Exchanging Zeolites With Copper Ions

The catalytic properties of a zeolite can be modified by exchanging one set of cations such as protons for other cations. In addition to metal cations which are stable in solution, ions which are not usually observed in solution such as Ga\(^{3+}\) [1-3], Pd\(^{2+}\) [39,40], Ni\(^{2+}\) [41-43], and Cu\(^{2+}\) [14,19,44-47] have also be exchanged into zeolites. Zeolites ion-exchanged with copper have been intensively investigated and characterized due to their ability to catalyze the decomposition of NO [4-17] and the selective catalytic reduction of NO [18-21]. Several methods for copper ion-exchange have been reported in the literature including aqueous ion-exchange [4-21], solid-state ion-exchange [16,48-58], and vapor ion-exchange [24-27]. Each method can give a different distribution and loading of copper cations in the zeolite, and transitions of copper cations can occur when the materials are subjected to various treatment processes. We review the important aspects of preparation and treatment that have been previously observed.

Aqueous Ion-Exchange

The most common method of ion-exchanging zeolites with copper ions is by aqueous ion-exchange. This procedure is usually performed by mixing either the sodium or acidic form of the base zeolite with an aqueous solution containing dissolved Cu\(^{2+}\) ions, usually derived from either CuCl\(_2\) or copper(II) acetate [4-21]. Aqueous ion-exchange of Cu\(^{2+}\) ions is not possible due to the instability of Cu\(^{2+}\) in aqueous solution which leads to the disproportionation reaction 2 Cu\(^{+}\) → Cu\(^{2+}\) + Cu\(^{0}\).
To determine the effect of aqueous ion-exchange on the acidity of the zeolite, infra-red adsorption analysis has been used to characterize copper exchanged zeolites [24,26,59-63]. The IR absorbance band at 3605-3615 cm⁻¹, which is generally attributed to the OH stretch of the zeolitic acid sites of MFI [24,26,59], has a significantly lower absorbance for the copper ion-exchanged materials than for the copper-free zeolite [59,64,65]. The acidity of copper exchanged MFI has also been characterized by IR analysis after pyridine adsorption [61], which is a useful method for characterizing both the Bronsted and Lewis acidity of the material [30]. Pyridine adsorbed on zeolite Bronsted acid sites have been shown to give rise to an IR absorbance band at approximately 1540 cm⁻¹, and absorbance bands at approximately 1450 cm⁻¹ have been assigned to pyridine adsorbed on Lewis sites [30]. Christner et al. have reported that cationic metals exchanged into zeolites gives rise to Lewis acidity and that the frequency of the IR absorbance band assigned to pyridine adsorbed on Lewis sites increases with increasing electron affinity of the cation, from a low value of 1443 cm⁻¹ for Na⁺ to a high value of 1455 cm⁻¹ for Zn²⁺ [63]. Connerton et al. conducted a series of experiments designed to determine the effect of copper ion-exchange on the acidity of acidic and sodium exchanged MFI by IR analysis after pyridine adsorption [61]. Their results indicated that the exchange of copper H-MFI with copper(II) acetate resulted in a decrease in the absorbance of the 1540 cm⁻¹ IR band by an order of magnitude, indicating that zeolite protons were consumed by the ion-exchange process. Copper ion-exchange also resulted in the appearance of a 1452 cm⁻¹ IR absorption band, which was attributed to pyridine adsorbed on copper ions exchanged into the zeolite by the aqueous ion-exchange process [61]. Exchange of H-MFI with Na⁺ followed by pyridine
adsorption gave rise to a 1442 cm$^{-1}$ IR, which they and others [62,63] have attributed to pyridine adsorbed on Na$^+$. Aqueous ion-exchange of Na-MFI with copper(II) acetate resulted in the appearance of both the 1452 cm$^{-1}$ and the 1540 cm$^{-1}$ IR bands, indicating that zeolite acidity was partially restored by the ion-exchange of Cu$^{2+}$ with Na-MFI [61].

Although most investigators agree that the aqueous ion-exchange process exchanges zeolitic protons or sodium ions for copper ions, there is considerable disagreement with regards to both the mechanism of the exchange process and the nature of the copper species introduced into the zeolite. Various investigators have proposed that the copper species exists as isolated Cu$^{2+}$ ions (Z'Cu$^{2+}$Z', where Z' represents an anionic zeolite exchange site), copper hydroxyl ions ([Cu(OH)]$^{[2-]}$, copper oxonium ions, Z'[CuOCu]$^{[2]}$Z' or some combination of these ions. In this work, Z' will be used to represent a zeolite ion-exchange site.

Several investigators have proposed that the ion-exchange process for Na-MFI occurs by the reaction Cu$^{2+}$ + 2 Na$^{+}$Z' $\rightarrow$ Z'Cu$^{2+}$Z' + 2 Na$^{+}$ [19,46,59,66-71]. Others have argued that while this reaction may occur for zeolites with high aluminum content, such as mordenite, it is unlikely that the anionic aluminum ion-exchange sites are sufficiently close to each other for Z'Cu$^{2+}$Z' ions to occur in zeolites with low aluminum contents (high silica zeolites) such as MFI [71]. These authors proposed that for high silica zeolites, at least some of the Cu$^{2+}$ ions in the zeolite must be coordinated to an extraframework charge compensating ion such as OH$^-$ [71]. Anderson et al. however, have argued based on electron spin resonance (ESR) and electron spin echo modulation (ESEM) spectroscopy that the Cu$^{2+}$ cations are not preferentially located adjacent to the
negatively charged zeolite ion-exchange sites [67] and, therefore, that the long distances between ion-exchange sites do not preclude the formation of \( \text{ZCu}^{2+}\text{Z}^- \) ions.

A large number of investigations have suggested that at least some of the copper ions introduced into the zeolite exist as copper hydroxyl ions, \([\text{Cu(OH)}]^+\text{Z}^-\) [12,14,19,47,60,72-78]. To account for the presence of this species, some investigators have proposed that the ion-exchange reaction of \( \text{Cu}^{2+} \) with Na-MFI occurs according to \([\text{Cu(OH)}]^+ + \text{Na}^+\text{Z}^- \rightarrow [\text{Cu(OH)}]^+\text{Z}^- + \text{Na}^+\) [12,14,72,73]. Greater copper loadings are often observed when the exchange is performed with copper(II) acetate instead of \( \text{CuCl}_2 \) [14,72,79], which has been attributed to the higher pH of the \( \text{Cu}^{2+} \) solution when the acetate counter ion is used, which is thought to favor the reaction \( \text{Cu}^{2+} + \text{OH}^- \rightarrow [\text{Cu(OH)}]^+ \) [14,72,79]. Schoonheydt \textit{et al.} however, have suggested that attempting to obtain high copper loadings by varying the pH is complicated by the precipitation of \( \text{Cu}^{2+} \) out of solution as copper hydroxide with increasing pH [79]. This proposal is supported by the common occurrence of extraframework \( \text{CuO} \) observed in copper zeolites prepared by copper(II) acetate ion-exchange [20,47,72]. Jacono \textit{et al.} however, have proposed that the \( \text{CuO} \) observed in copper(II) acetate exchanged MFI is due to the decomposition of oxonium ions according to \( \text{Z'}[\text{CuOCu}]^{2+}\text{Z}^- \Leftarrow \text{CuO} + \text{Z'}\text{Cu}^{2+}\text{Z}^- \) [72].

To account for the restoration of zeolitic protons during the exchange of Na zeolites with \( \text{Cu}^{2+} \) ions [61,73], some investigators have proposed that there are sufficient \( \text{H}^+ \) ions present in the \( \text{Cu}^{2+} \) exchange solution for the reaction \( \text{H}^+ + \text{Na}^+\text{Z}^- \rightarrow \text{H}^+\text{Z}^- + \text{Na}^+ \) to occur [61,73]. Other investigators have offered an alternative explanation for the restoration of zeolitic protons and the presence of \([\text{Cu(OH)}]^+\text{Z}^- \) after \( \text{Cu}^{2+} \)
exchange of Na-MFI by proposing that the ion-exchange process of sodium for copper occurs according to $\text{Cu}^{2+}(\text{H}_2\text{O})_x + 2 \text{Na}^+ \rightarrow Z'\text{Cu}^{2+}(\text{H}_2\text{O})_x Z' + 2 \text{Na}^+$. They further propose for the high silica zeolites that upon drying, the reaction $Z'\text{Cu}^{2+}(\text{H}_2\text{O})_x Z' \rightarrow [\text{Cu(OH)}]^{+} Z' + \text{H}^+ Z' + (\text{H}_2\text{O})_{x-1}$ occurs [47,60,72,76,77,80]. The reverse of this reaction, $[\text{Cu(OH)}]^{-} Z' + \text{H}^+ Z' \rightarrow Z'\text{Cu}^{2+} Z'$, has also been proposed [60].

Numerous investigations have indicated that some, if not all, of the $\text{Cu}^{2+}$ ions in zeolites are reduced to $\text{Cu}^+$ ions by heating the copper zeolite in the presence of carbon monoxide [6,12,17,44,75,76,81-86]. Beutel et al. proposed that $Z'\text{Cu}^{2+} Z'$ ions cannot be reduced to $\text{Cu}^+ Z'$ by carbon monoxide in the absence of zeolite dealumination, which they hypothesized could not occur under the conditions normally used for CO reductions [47]. Kucherov et al. used a similar explanation to account for the observed CO reduction of $\text{Cu}^{2+}$ ions in high silica MFI and the absence of reduction of $\text{Cu}^{2+}$ ions in aluminum rich mordenite [71]. Other investigators, however, have proposed that thermal treatment of $Z'\text{Cu}^{2+} Z'$ ions in CO reduces the copper to $\text{Cu}^+ Z'$, causes dealumination of the zeolite, and formation of $[\text{AlO}]^-$ ions [60,87].

To clarify the reduction behavior of $\text{Cu}^{2+}$ ions in zeolites during heating in CO, Petunchi et al. conducted a series of experiments in which a copper-containing Y zeolite was subjected to six cycles of reduction in CO followed oxidation in $\text{O}_2$ [76]. Using X-ray diffraction, and $^{29}$Si and $^{27}$Al NMR analysis of the materials after these cycles, the authors concluded that while some dealumination of the zeolite did occur, the amount was significantly less than would be expected from the CO reduction of $Z'\text{Cu}^{2+} Z'$ ions. Borovkov et al. have also concluded that no dealumination of MFI occurs during the CO
reduction of Cu²⁺ ions [81]. Petunchi et al. further observed that during each reduction, 0.5 oxygen atoms were lost per copper atom, and during each oxidation, 0.5 oxygen atoms were gained per copper atom [76]. They interpreted these results according to the reactions $Z'[\text{CuOCu}]^{2+}Z^- + \text{CO} \rightarrow 2 \text{Cu}^+Z^- + \text{CO}_2$ and $2 \text{Cu}^+Z^- + \frac{1}{2} \text{O}_2 \rightarrow Z'[\text{CuOCu}]^{2+}Z^- $ [76]. Other investigators have supported the proposed mechanisms of both the CO reduction [6,20,87] and the oxidation [6,75,88] reactions. Petunchi et al. also agreed with other proposals suggesting that thermal treatment in $\text{O}_2$ of copper-containing zeolites induces condensation of the initial copper hydroxyl ions to oxonium ion according to the reaction: $2 \text{[Cu(OH)]}^+Z^- \rightarrow Z'[\text{CuOCu}]^{2+}Z^- + \text{H}_2\text{O}$ [19,60,74,75]. On the basis of IR results, Vaylon et al. also proposed that the condensation reaction is reversible [75].

Carbon monoxide has also been used as a probe molecule for the determination of the oxidation state of copper ions in zeolites due to the adsorption of significant quantities of CO by monovalent zeolite coordinated copper cations [5,12,20,26,44,59,81,82,89-94], but not by divalent copper ions or by copper metal. The unusual stability of the Cu⁺Z'(CO) complex has been attributed to mutual strengthening of both the $\sigma$ and the $\pi$ bonds by back donation of electrons from the Cu⁺ to CO. The Cu⁺-CO bond is strengthened and the C-O bond is weakened by the back donation and causes the C-O stretching frequency to shift to lower wavenumbers relative to the 2143 cm⁻¹ observed for gas phase CO [91]. Adsorption of CO onto Cu⁺Z⁻ has been reported to give rise to IR absorption bands at 2178 cm⁻¹ and 2151 cm⁻¹ [81,95]. Materials with high concentrations of Cu⁺Z⁻ have also been observed to give 2137 cm⁻¹ IR absorbance bands, which has been attributed to CO adsorbed on associated Cu⁺Z⁻ sites [95].
The thermal reduction of Cu\(^{2+}\) ions to Cu\(^{+}\) ions in copper exchanged zeolites has also been observed [4-6,8,15,19,45,61,69,88,90]. Although Jacobs et al. have proposed that Z'[Cu\(^{2+}\)Z] could thermally decompose to Cu'Z' with dealumination of the zeolite and formation of [AlO]' ions [70], most investigators have attributed the thermal reduction to occur by either Z'[CuOCu]\(^{2+}\)Z' —► 2 Cu'Z' + ½ O\(_2\) [6,19,20,87] or [Cu(OH)]'Z —► Cu'Z' + ½ O\(_2\) + ½ H\(_2\)O [19,44,45]. Grunert et al. have proposed that both copper hydroxyl ions, [Cu(OH)]'Z', and copper oxonium ions, Z'[CuOCu]\(^{2+}\)Z', undergo thermal reduction to Cu'Z', and that copper hydroxyl ions reduce at lower temperatures than copper oxonium ions [19]. Other investigators, however, have proposed that copper hydroxyl ions, [Cu(OH)]'Z', reduce to Cu'Z' by a two step process; 2 [Cu(OH)]'Z —► Z'[CuOCu]\(^{2+}\)Z' + H\(_2\)O, followed by the thermal reduction of the oxonium ions [75,96,97]. Larsen et al. proposed that the thermal reduction of copper hydroxyl ions, [Cu(OH)]'Z', occurs according to: 2 [Cu(OH)]'Z —► Cu'Z' + Z'[Cu\(^{2+}\)O' + H\(_2\)O [44], and, while some investigators have supported the existence of Z'[Cu\(^{2+}\)O'] ions [13,28,45], others have disputed their existence [72]. Kucherov et al. proposed that copper hydroxyl ions do not undergo thermal reduction and that the reduction of Cu\(^{2+}\) ions observed in both his and other investigations was due to reduction by residual acetate ions [71]. Kucherov et al. also proposed in another paper that no thermal reduction of any Cu\(^{2+}\) species in copper ion-exchanged materials occurs and that previous reports of the reduction of Cu\(^{2+}\) ions were possibly due to impurities in the reactant gas [98].

The effect of heating copper exchanged zeolites in hydrogen has also been investigated. Several studies have indicated that heating copper exchanged zeolites in
hydrogen results in the stepwise reduction of Cu\(^{2+}\) (Cu\(^{2+}\) → Cu\(^{+}\) → Cu\(^{0}\)) \[9,20,46,47,83,85,87,99,100\] and that reduction of Cu\(^{2+}\) to Cu\(^{0}\) results in the regeneration of zeolitic acid site \[59,71,75,99\]. Texter et al. investigated the sintering properties of Cu\(^{0}\) produced during hydrogen reduction of ion-exchanged zeolites with optical absorption and emission spectroscopy \[99\]. The authors observed that during the hydrogen reduction of copper exchanged Y zeolite, some nucleation of copper metal clusters began to occur at 523 K - 573 K. However, even after reduction to 673 K, the copper nucleation was still relatively incomplete \[99\].

Kuroda et al. have proposed that at high degrees of copper exchange, some of the copper ions can exist as copper hydroxyl dimers in mordenite \[64,65\]. After 15 Cu\(^{2+}\) ion-exchanges of a Na-mordenite (SiO\(_2\)/Al\(_2\)O\(_3\) ratio of 10) they observed the appearance of IR absorption bands at 3440 cm\(^{-1}\) and 3350 cm\(^{-1}\) \[64,65\]. After studying this material with DRS, EPR, XANES/EXAFS, and thermogravimetric analysis, the authors proposed that the copper ions in this material existed as copper hydroxyl dimer ions \[65\]:

\[
\begin{array}{c}
\text{H}_2\text{O} & \text{H} & \text{Cu} & \text{OH}_2 \\
\text{H}_2\text{O} & \text{O} & \text{Cu} & \text{OH}_2
\end{array}
\]

\[2^+\]

Although the authors did not report the degree of exchange of zeolitic protons for copper ions, the absorbance of the 3610 cm\(^{-1}\) IR bands (which is attributed to zeolitic protons) is slightly greater than that of the absorbance of the 3440 cm\(^{-1}\) and 3350 cm\(^{-1}\) IR bands \[64,65\], indicating that full exchange of protons for copper was not achieved by
this process. There do not appear to be any reports in the literature reproducing these results.

Solid-State Ion-Exchange

Previous reports have investigated the reactions of physical mixtures of the oxides or chlorides of Cu\(^{+}\), Cu\(^{2+}\), Cr\(^{3+}\), Mo\(^{6+}\), V\(^{5+}\), Ni\(^{2+}\), Fe\(^{2+}\), and Co\(^{2+}\) with acidic or ammonium zeolites [16,48-58]. These studies suggested that upon thermal treatment, the inorganic salt migrated into the zeolite and reacted with zeolitic protons.

Kucherov et al. investigated the reactions of physical mixtures of CuO and CuCl\(_2\) with acidic MFI and mordenite by ESR after thermal treatment in air [58]. From their results, they concluded that on thermal treatment to temperatures of 823 K or higher, CuO migrated into and reacted with the zeolitic protons in both MFI and mordenite. They proposed that the copper ions in mordenite existed in a square planar geometry, while those in MFI existed in both a square planar and square pyramidal geometry [58]. They further proposed on the basis of their ESR results that the Cu\(^{2+}\) ions formed in the solid-state ion-exchanged material were the same as those present in the aqueous ion-exchanged materials [58], and that the copper ion-exchanged species in mordenite (SiO\(_2\)/Al\(_2\)O\(_3\) = 10) existed as isolated Cu\(^{2+}\) ions, ZCu\(^{2+}\)Z, while the copper species exchanged into H-MFI (SiO\(_2\)/Al\(_2\)O\(_3\) = 69) existed as copper hydroxyl ions, [Cu(OH)]\(^{+}\)Z. They attributed the differences in the structure of the copper ions to the difference in the distances between ion-exchange sites in the mordenite and MFI base zeolite [58]. The authors also implied that these copper hydroxyl ions were thermally stable and did not reduce to Cu\(^{-}\)Z ions by the thermal treatment. The study indicated that after thermal treatment to 1073 K, approximately 50% of the acidic protons in mordenite and 35% of
acidic protons in MFI were exchanged with copper ions [58]. A linear relation between the number of Cu$^{2+}$ ions formed and the number of ion-exchange sites present in the zeolite [58] was also observed. This study suggested that solid-state reaction of acidic zeolites with CuCl$_2$ gave much greater yields of copper in ion-exchange locations than the reaction with CuO, which they attributed to the lower melting point and greater thermal mobility of the chloride relative to the oxide [58].

Karge et al. have also investigated the reactions of physical mixtures of CuO, CuCl, and CuCl$_2$ with acidic MFI and Y [56]. These authors observed that thermal treatment of a physical mixture of CuO and H-MFI (0.5 Cu per zeolite ion-exchange site) to 770 K for 21 hr. resulted in a 25% decrease in zeolitic protons as measured by IR (3610 cm$^{-1}$ band) [56]. Adsorption of pyridine on this material resulted in a 1450 cm$^{-1}$ IR band (which was attributed to pyridine adsorbed on copper ions) and a decrease in the absorbance of the 1545 cm$^{-1}$ IR band (which was attributed to pyridine adsorbed on zeolitic protons) relative to the acidic zeolite [56]. The authors also reported that the conversion of zeolitic protons was initially very rapid and slowed substantially after several hours of reaction. A greater conversion of zeolitic protons was observed with a physical mixture of CuO with zeolite Y than with MFI, which they attributed to a greater mobility of protons in zeolite Y. The authors proposed that the copper ions exchanged into both zeolites existed as charged Cu$_x$O$_y$ clusters which resided within the zeolite pores [56].

Karge et al. also observed that the consumption of zeolitic protons upon thermal treatment of physical mixtures of copper chlorides with H-MFI in vacuum was greater than that observed with the physical mixtures using CuO, which they attributed to the
lower melting points of the chlorides relative to the oxides [56], in agreement with Kucherov [58]. The loss of zeolitic protons on heating physical mixtures of CuCl₂ with H-MFI in air has also been reported [16]. On heating a physical mixture of CuCl with H-MFI, the authors observed the evolution of HCl and found that conversion of zeolitic protons increased with increasing CuCl loadings [56].

Price et al. proposed that heating a physical mixture of CuO and H-MFI zeolite with a stoichiometry of one copper atom per zeolite aluminum atom to 973 K in high purity inert gas or vacuum for 16 hours [22, 101, 102] resulted in the exchange of zeolitic protons with Cu²⁺. These conclusions were based on a reduction in the ESR signal strength for bands associated with Cu²⁺ [101], the loss of nearly all the oxygen associated with the CuO [101, 102], an enhanced activity for the catalytic decomposition of NO to N₂ and O₂ [101], and the loss of zeolitic protons as measured by 1-propanamine thermal desorption [22].

The thermal treatment of physical mixtures of CuO and CuCl with sodium exchanged zeolites has also been investigated. Kucherov et al. investigated the effect of heating a physical mixture of CuO and Na-mordenite in air to 1073 K and did not observe any ESR signals attributable to Cu²⁺ ions, which they interpreted as indicating the absence of any reaction between CuO and Na-mordenite [58]. Jiang et al. studied the effect of thermal treatment on physical mixtures of CuCl and Na-MFI and Na-mordenite by IR analysis after pretreatment and pyridine adsorption [62] and observed that after pretreatment to temperatures higher than 453 K, the absorbance of the 1442 cm⁻¹ IR band (which was attributed to pyridine adsorbed on Na⁺) decreased and resulted in the appearance of a 1451 cm⁻¹ IR band (which was attributed to pyridine
adsorbed on Cu'). They interpreted these results as the following reaction: CuCl + Na\textsuperscript{+}Z\textsuperscript{−} → Cu\textsuperscript{2+}Z\textsuperscript{−} + NaCl [62]. It was also proposed that on heating to a temperature above 573 K, the reaction reversed [62].

**CuCl Vapor Ion-Exchange**

Copper-containing zeolites have also been synthesized by the reaction of CuCl vapor with acidic zeolites, presumably by CuCl + H\textsuperscript{+}Z\textsuperscript{−} → Cu\textsuperscript{2+}Z\textsuperscript{−} + HCl [24-27], and has been shown to give close to 100% exchange of copper for zeolitic protons, which is the greatest level reported [26]. All of the Cu-MFI materials investigated have been prepared *in situ* due to concern of possible reaction of the Cu\textsuperscript{2+} ions with air [24-27].

Spoto et al. exchanged H-MFI with CuCl vapor by first drying the H-MFI at 623 K for 3 hr, transferring the dried H-MFI to a heated high vacuum chamber in which pure CuCl was contained, heating the chamber to 573 K, and holding at this temperature until the 3610 cm\textsuperscript{-1} IR absorbance band disappeared. The sample was then heated to 773 K for 1 hr. to remove the excess CuCl [27]. The materials prepared this way exhibited the complete loss of absorbance of the 3610 cm\textsuperscript{-1} IR band (which is attributed to zeolitic acid sites) [26], while the 3750 cm\textsuperscript{-1} IR band (which is attributed to unreactive silanol bonds, -Si-(OH)) was unaffected by this process [26]. The observed XANES/EXAFS results were also consistent with nearly all of the copper ions existing as Cu\textsuperscript{2+}Z\textsuperscript{−} and very little existing as CuCl or Cu\textsuperscript{2+}, indicating that most of the excess CuCl was removed [26]. Adsorption of CO onto these materials gave rise to IR absorption bands previously assigned to CO adsorbed on Cu\textsuperscript{2+}Z\textsuperscript{−} [81,95] at 2178 cm\textsuperscript{-1} and 2151 cm\textsuperscript{-1}. 

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Reactions of Amines with Copper-containing Zeolites

As mentioned previously, amine adsorption/desorption is a very useful method for measuring the acidity of metal free zeolites, and a natural extension of this procedure led to the investigation of amine adsorption/desorption from copper exchanged zeolites. In a study of 2-propanamine desorption from copper exchanged MFI (prepared by aqueous ion-exchange) Gorte et al. found that one 2-propanamine molecule adsorbed per copper, which decomposed upon heating to form propene and ammonia [73,103]. The copper amine complex decomposed at a higher temperature than did the proton amine complex and these results were used to quantify the amounts of copper cations and protons present at ion-exchange sites in the zeolite. However, Kanazirev et al. reported that adsorption/desorption of 1-propanamine from a physical mixture of CuO/H-MFI pretreated to 973 K in He for 16 hrs resulted in chemistry considerably different from the same experiments using 2-propanamine, and that while ammonia desorbed at 575 K and 700 K, very little propene was produced [22,101]. Six carbon nitriles and imines were also observed among the desorbing products [22,101].

Due to the observation that nitriles and imines resulted from the thermal desorption of 1-propanamine from Cu-MFI, the catalytic conversion of amines by copper exchanged MFI prepared by the thermal treatment of a physical mixture of CuO with H-MFI has been investigated by Kanazirev et al. [22]. In this study, the conversion of 1-propanamine by a CuO/H-MFI material containing one copper per zeolite ion-exchange site after thermal pretreatment to 973 K for 16 hr. was investigated. 15.0 mbar of 1-propanamine reacted at 593 K resulted in major products consisting of a six carbon nitrile and propanitrile [73,103].
The catalytic conversion of 1-propanamine by H-MFI has been investigated by Kanazirev et al. [22], who observed that the primary product of the reaction of 15.0 mbar of reactant at 593 K was dipropanamine. Some propene was also formed. The reaction scheme proposed to interpret this reaction was [22]:

\[
\begin{align*}
C_3H_7NH_2 + H^+ Z^- & \rightarrow C_3H_7NH_3^- Z^- \\
C_3H_7NH_2 + C_3H_7NH_3^- Z^- & \rightarrow C_3H_7NH_2 \cdots C_3H_7NH_3^- Z^- \\
C_3H_7NH_2 \cdots C_3H_7NH_3^- Z^- & \rightarrow (C_3H_7)_2NH_2^- Z^- + NH_3 \\
(C_3H_7)_2NH + H^+ Z^- & \rightarrow (C_3H_7)_2NH_2^- Z^- \\
C_3H_7NH_3^- Z^- & \rightarrow C_3H_6 + NH_3 + H^+ Z^- \\
(C_3H_7)_2NH_2^- Z^- & \rightarrow C_3H_6 + C_3H_7NH_2 + H^+ Z^-.
\end{align*}
\]

On the basis of spectroscopic analysis of copper exchanged MFI during the selective catalytic reduction (SCR) of NO with propene, Hayes et al. proposed that nitriles were an intermediate in the SCR reaction [18]. They observed that while no reaction of MeCN in He occurred at 773 K over the catalyst, exposure of the catalyst with adsorbed MeCN to oxygen resulted in the immediate decomposition of the adsorbed MeCN to CO2 and N2 [18].
II. EXPERIMENTAL APPARATUS AND PROCEDURE

A. Materials

The chemical reagents used in this work are listed in Table II-1. The suppliers and lot numbers are provided where available.

All of the base zeolites were obtained from either Zeolyst or its predecessor PQ Corporation. This work used three batches of MFI zeolite, one supplied in proton form, PQ-3020E Lot ZH-35 and two batches in ammonium form, Zeolyst Lot 3020E-1525-52 and Zeolyst Lot 5534G-1597-94. The SiO₂/Al₂O₃ ratios used for the zeolite synthesis were provided by the manufacturer as 30 for the first two materials and 50 for the later batch. The surface areas of these materials, as reported by the manufacturer, were 400 m²/g of the first two materials and 424 m²/g for the second. A sample of zeolite Beta (BEA) was also obtained in proton form from PQ Corporation, Lot CP-811BL-25. The manufacturer’s synthesis SiO₂/Al₂O₃ ratio for this material was 25 and the surface area was 680 m²/g.

B. Equipment

Calcining Furnace

A controlled environment calcining furnace was used for several purposes in preparing some of the catalytic materials. It consisted of a 7 cm ID and 100 cm long quartz tube inside a three zone Lindberg/BlueM Furnace. Each of the heating zones were about 300 cm long and independently controlled with Omega proportional-integral-derivative (PID) temperature controllers. The temperature controllers were interfaced to a PC which maintained equal set points on all three controllers. The gas flow system to the tubular furnace was configured such that flow rates of up to
<table>
<thead>
<tr>
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<td>09401DZ</td>
</tr>
<tr>
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<td>Aldrich Chemical Company</td>
<td>10516CF</td>
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<td>CO</td>
<td>Matheson</td>
<td></td>
</tr>
<tr>
<td>CuCl₂</td>
<td>Aldrich Chemical Company</td>
<td>06204LX</td>
</tr>
<tr>
<td>CuCl</td>
<td>Aldrich Chemical Company</td>
<td>06526DX</td>
</tr>
<tr>
<td>CuO</td>
<td>Aldrich Chemical Company</td>
<td>01719LW</td>
</tr>
<tr>
<td>Cu₂O</td>
<td>Aldrich Chemical Company</td>
<td>05315KX</td>
</tr>
<tr>
<td>NaOH</td>
<td>EM Science</td>
<td>19118</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>LaRoche Chemicals</td>
<td></td>
</tr>
</tbody>
</table>
approximately 250 cc/min of Ar mixed with up to 100 cc/min of either oxygen or hydrogen could be achieved. The effluent gas from the furnace flowed through approximately 300 cm of 1/8 inch ID tubing to minimize back diffusion of air into the furnace.

The calcining boat was a 28.5 cm x 5.75 cm rectangular ceramic boat in which the sample was placed. For the vapor ion-exchange of the acidic zeolites, an exchange reagent, CuCl for this study, was spread on a 28.5 cm x 1.5 cm rectangular ceramic bar that was placed 1.5 cm above the zeolite in the boat. This “double-decker” ceramic boat was placed in the center of the calcining furnace to perform the exchange reaction.

**Ball-mill**

Physical mixtures of the zeolites with CuO and Cu₂O were mixed in a horizontally oriented stainless steel 12.5 cm diameter mill with 65 stainless steel balls. The mill was rotated using an external electric motor with a rotation rate of 1.4 Hz.

**Recirculating Catalytic Reactor**

The catalytic reaction experiments were performed in an recirculation batch reactor system constructed of Pyrex glass and had a total volume of 720 cc. A schematic of this system is illustrated in Figure II-1.

The circulation loop was equipped with a magnetically operated piston pump and check valve arrangement. The pump consisted of a 2.2 cm diameter glass tube with a Teflon coated iron piston. An alternating magnetic field generated by two solenoids outside of the glass tube moved the piston in a reciprocating motion and four check valves insured unidirectional flow.
Figure II-1: Recirculating batch reactor system.
The catalyst was placed between two plugs of quartz wool in a two shell quartz reactor constructed as shown in Figure II-2. The outer shell was 10 mm I.D. and the inner shell was 9 mm I.D. The reactant gas flow entered the reactor and flowed down the outer shell, where it was preheated to reaction temperature. It then flowed into the center shell by slits in the bottom of the reactor, contacted the catalyst, and flowed out through the top of the reactor. The temperature of the catalyst was monitored with a J-type thermocouple in a sealed quartz tube just above the catalyst sample. Heating was provided with an external concentric electric heater controlled by a proportional-integral-derivative (PID) controller.

The entire reactor system could be evacuated with a rotary mechanical vacuum pump prior to runs to approximately $10^{-3}$ torr. The system pressure was monitored with diaphragm-type pressure gauges calibrated from 0-1000 torr. Hydrogen and helium could be introduced into the system through an upper stopcock inlet, which could be connected to cylinders of the respective gas. The hydrocarbon reactants were introduced to the system through a lower stopcock inlet, which was connected to either a saturator flask or a lecture bottle of the reactant.

Samples were withdrawn for analysis by opening a stopcock connecting the system to a traced evacuated 1/16" stainless steel tubing line connected to a gas sampling valve on the gas chromatograph. Approximately 0.5% of the reaction mixture was withdrawn with each sample. A maximum of five samples were collected in any single run, suggesting that the volume loss due to sampling, approximately 2.5% after the fifth sample, did not significantly affect the results obtained.
Figure 11-2: Quartz reactor schematic.
Gas Chromatograph

The gas chromatograph attached to the reactor was an HP5890 II equipped with a 50-m PONA (crosslinked methyl silicone gum) capillary column with a 0.2 mm ID and a 0.5 um film thickness. Identification of products was done by running preliminary experiments in the reactor and performing analysis using a HP 5972 Series Mass Selective Detector. The gas chromatograph could also be configured for use with a Flame Ionization Detector (FID). The gas chromatography column was operated isobarically using a temperature program of 313 K to 423 K at 5 K/min with He as the carrier gas.

The chromatograph was interfaced to an IBM compatible personal computer through an HPIB interface and was controlled with the Chemstation software package from Hewlet-Packard. Data were stored on disk by the computer and integration of the results were performed by Chemstation. Compound identification was done by referencing the fragmentation patterns from the mass spectrophotometer with the Wiley mass spectral library. Automated search and identification algorithms are provided in the Chemstation software.

Some of the reactor experiments were performed using the mass selective detector. For these runs, the integrated area percent of the reactant and product compounds are presented. For a mass selective detector, the weight percent of a compound is approximately equal to the integrated area percent. Preliminary experiments using amines indicated that the error of this assumption was less than 10%. For some experiments, the FID detector was used to determine the conversion of reactant and the partial pressures of the products formed. The calibrations were done
using the initial reactant partial pressure and the common assumption that for an FID
detector the area percent of the detectable products is equal to the weight percent of the
detectable products. Preliminary experiments indicated that this assumption was correct
to within 1-2%.

**X-Ray Powder Diffraction**

X-ray diffraction data were collected with a Scintag PAD-V diffractometer
equipped with a Cu-Kα radiation source and a Peltier cooled solid state detector. The
diffractometer was interfaced to an IBM compatible personal computer and was
controlled using the Scintag software package DMS-NT.

**Infrared Spectrometer**

IR spectra were taken in transmission mode using an IBM IR-30 FTIR. A globar
served as the source of the IR radiation and a liquid nitrogen cooled MCT (mercury
cadmium telluride) detector was used. The interferogram was generated via a scanning
Michelson interferometer and recorded on the computer interfaced to the spectrometer.
The Fourier transform of the interferogram was done by the software package PCIR
from Nicolet. The full spectra covered 4800 to 400 wavenumbers (cm⁻¹).

An auxiliary vacuum/dosing system was attached to the IR and a schematic of
this system is given in Figure II-3. The zeolites were pressed into self supporting wafers
with a density of 6.4 mg/cm² using a ¼” diameter die. The pellets were placed in a
quartz sample holder, which was in turn was placed into a quartz cell sealed on both
ends with KBr windows. Quartz tubes connected perpendicular to the cell allowed for
the flow of reactant gas into and out of the sample cell. The gas flow configuration
allowed for the flow of helium, hydrogen, and/or carbon monoxide to the sample.
Figure II-3: IR schematic.
Diversion of the gas stream through a room temperature saturator also allowed for the introduction of pyridine into the system. The temperature was measured with a J-type thermocouple and was controlled with an external heater connected to a proportional-integral-derivative (PID) controller.

**Hydrogen Temperature Programmed Reduction Apparatus**

A Carle Analytical Gas Chromatograph 111 H Series S was reconfigured to measure hydrogen consumption and was interfaced to a PC for TPR experiments. A schematic of this device is shown in Figure II-4. In the basic TPR configuration, a reactant stream of hydrogen and argon flowed through a quartz reactor, similar to the one shown in Figure II-2, which contained the catalyst sample and then to a palladium hydrogen transfer cell, where the hydrogen in the reactant stream was transferred to a pure Ar stream flowing at 30 cc/min. The later stream is then analyzed by a thermistor detector, so that when hydrogen is removed by reaction from the stream flowing over the catalyst sample, an imbalance in the thermistor detector is recorded. The areas of the hydrogen consumption peaks were numerically integrated and quantitative measurement was made by comparison with the measured area of a 100 mg sample of a 5% CuO/H-MFI PQ mechanical mixture dried at 473 K.

**Thermogravitimetric Analysis**

Microbalance TA experiments were performed on a Perkin-Elmer TGA7 interfaced to a PC. A schematic of this device is shown in Figure II-5. Twelve to eighteen mg of sample were placed on the Pt microbalance pan. A 50 cc/min He stream continuously purged the microbalance mechanism and mixed with a 50 cc/min reagent gas stream that could be varied in composition. The weight curves obtained could also
Figure II-4: TPR apparatus flow schematic.
Figure II-5: Microbalance TGA flow schematic.
be numerically differentiated by the computer with respect to time, and the reagent gas stream could be saturated with 1-propanamine by diverting it through a room temperature saturator.

C. Procedures

Catalyst Preparation

The vapor ion-exchange catalytic materials were prepared by first spreading 5 g of the acidic zeolite on the base rectangular ceramic boat, and 1 g of CuCl was spread along the upper ceramic boat in the “double-decker” ceramic boat described previously. The sample was placed in the calcining furnace and it was dried in 200 cc/min Ar at 323 K for 2 hrs and then heated to 973 K at 5 K/min and held at that temperature for 6 hrs. All but one of the samples were then subjected to oxidation by cooling to 373 K, switching the gas flow to 50 cc/min O₂, and oxidizing for 5 hrs. The oxidized samples were cooled to room temperature in O₂ prior to exposure to air.

Three samples were made by the above procedure using different zeolite base materials. The sample referred to as Cu-MFI/VIE PQ was made with the PQ base MFI and the samples referred to as Cu-MFI/VIE and Cu-MFI-50/VIE, where the appendage numbers denote the nominal elemental SiO₂/Al₂O₃ ratio, were made with the proton form of the MFI zeolites from Zeolyst. Another material, referred to as Cu-BEA/VIE was produced using the acidic beta zeolite from Zeolyst. A summary of the vapor ion-exchanged samples is given in Table II-2.

The ammonium forms of the MFI zeolites were converted to proton form by placing 40 g of the ammonium zeolite in the 28.5 cm x 5.75 cm ceramic boat, drying in 200 cc/min Ar in the heated quartz tube at 323 K for 2 hrs, and heating from 323 K to
Table II-2. Catalytic Materials

VAPOR ION-EXCHANGED MATERIALS

<table>
<thead>
<tr>
<th>Name</th>
<th>Amount of CuCl</th>
<th>Oxidized</th>
<th>Base Zeolite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-MFI/VIE PQ</td>
<td>1.00 g</td>
<td>Yes</td>
<td>PQ MFI-30</td>
</tr>
<tr>
<td>Cu-MFI/VIE</td>
<td>1.00 g</td>
<td>Yes</td>
<td>Zeolyst MFI-30</td>
</tr>
<tr>
<td>Cu-MFI-50/VIE</td>
<td>1.00 g</td>
<td>Yes</td>
<td>Zeolyst MFI-50</td>
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</table>

AQUEOUS ION-EXCHANGED MATERIALS

<table>
<thead>
<tr>
<th>Name</th>
<th>Amount of CuCl₂</th>
<th>Base Zeolite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-MFI/AIE</td>
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<td>PQ H-MFI-30</td>
</tr>
<tr>
<td>Cu-BEA/AIE</td>
<td>3.0 g</td>
<td>H-BEA</td>
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</tbody>
</table>

PHYSICAL MIXTURES

<table>
<thead>
<tr>
<th>Name</th>
<th>Copper Source</th>
<th>Weight of Copper Source</th>
<th>Base Zeolite</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuO/H-MFI</td>
<td>CuO</td>
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<td>Zeolyst MFI-30</td>
</tr>
<tr>
<td>CuO/H-MFI-50</td>
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<td>0.883 g</td>
<td>Zeolyst MFI-50</td>
</tr>
<tr>
<td>CuO/Na-MFI</td>
<td>CuO</td>
<td>1.019 g</td>
<td>Zeolyst Na-MFI</td>
</tr>
<tr>
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<td>0.502 g</td>
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<td>Zeolyst MFI-30</td>
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<td>0.908 g</td>
<td>Zeolyst Na-MFI</td>
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<tr>
<td>CuO/Al₂O₃</td>
<td>CuO</td>
<td>1.087 g</td>
<td>LaRoche Alumina</td>
</tr>
</tbody>
</table>
823 K at 5 K/min followed by holding at 823 K for 0.5 hrs. The material was then cooled in argon to room temperature prior to exposure to air.

Separate procedures for preparation of a class of catalyst termed “aqueous ion-exchanged” (AIE) materials were used. The base zeolites used for the aqueous ion-exchanged materials were the acidic forms of MFI and Beta from PQ Corporation. The sodium form of the zeolite, Na-MFI was made by mixing 11g of the H-MFI with 0.33 g of NaOH dissolved in 250 ml of DDI water for 1 hour, followed by filtering and washing 3 times with 100 ml of distilled deionized water. Na-BEA was prepared similarly using 0.444g of NaOH. An aqueous ion-exchanged MFI, referred hereafter as Cu-MFI/AIE, was prepared by exchanging the Na-MFI material from above with 2.2 g of CuCl₂ dissolved in 100 ml of distilled deionized water at room temperature for 16 hr. This material was then filtered, rinsed 3 times with 100 ml of DDI water and dried in air at 373 K for 24 hrs. An aqueous ion-exchanged BEA, referred to hereafter as Cu-BEA/AIE, was prepared by a procedure similar to the MFI material using 3 g of CuCl₂.

A third class of catalysts termed “physical mixtures” were prepared by mixing a mass of copper oxide specified in Table II-2 with 20 g of the air equilibrated zeolite in the ball mill for 6 hrs. A physical mixture of CuO with alumina was also prepared. Immediately after the ball-milling process, the powders were converted to tablets as discussed below to ensure that the physical mixtures did not separate by the density difference of the solid phases.

A list of the sample names, the amount and type of copper oxide, and the acidic zeolite base used are shown in Table II-2. For most materials, the weight of the copper
oxide was chosen so that a 1/1 Cu/framework-Al loading would result. The two exceptions to this rule, CuO-1.9/H-MFI and CuO-0.5/H-MFI were overloaded with 1.9 Cu/framework-Al and underloaded with 0.5 Cu/framework-Al, respectively. The Na-MFI base material was made by adding 36.54 g of the Zeolyst MFI-30 with 200 ml of distilled deionized water containing 1 g of NaOH. This material was then washed with 100 ml of distilled deionized water and dried for 16 hrs at 373 K in air.

All of the catalytic materials, which were initially in powder form, were pressed into tablets, crushed, and sieved in order to achieve a consistent catalyst particle size. The powders were pressed into tablets by filling a ¾” diameter die with approximately 7 cm³ of the powdered sample, and pressing at 30000 lb in a hydraulic press for approximately 15 secs. The pressed pellets were then removed, crushed in a mortar and pestle, then sieved to particle sizes between 35 and 60 mesh.

Elemental Analysis

The copper contents of the AIE and VIE materials were determined by back-exchange and dissolution of the copper by an acidic digestion of the materials. This procedure was performed beginning by placing 0.12 g of sample in a 50 ml beaker. 10 cc of an acidic solution containing 25% HCl and 75% HNO₃ by volume was added to the beaker, then the mixture was then evaporated to dryness by heating at a temperature sufficient to produce mild simmering of the acidic mixture. This procedure was repeated two more times, and after the final digestion, 5 cc of the acid mixture and 30 cc of distilled water were added to the beaker. This solution was thoroughly mixed to produce a suspension of the zeolite powder in the solution and then filtered. The filter paper was washed four times with 10 cc of distilled water and all the filtrates were
collected and transferred to a 100 cc volumetric flask. The filter flask was rinsed twice with 10 cc of distilled water, which was also added to the volumetric flask. Sufficient distilled water was then added to the volumetric flask to bring the total volume to 100 cc, the flask was stoppered, and then shaken to ensure complete mixing. The copper content of the resulting solution was then determined with a Jarrell-Ash model 855 Inductively Coupled Argon Plasma Emission Spectrometer kindly performed by Dr. Gambrell’s lab at Louisiana State University’s Center for Wetland Resources.

**Hydrogen Temperature Programmed Reduction Experiments**

The consumption of hydrogen during reduction of the pretreated samples was determined using the hydrogen temperature programmed reduction (TPR) apparatus described previously. 100 mg of sample for all of the materials except Cu-BEA/AIE was placed in the TPR reactor between two plugs of quartz wool, purged for 5 min in 57 cc/min Ar at 323 K, and then heated at 10 K/min to either 473 K, 773 K or 973 K and held at the final temperature for 30 min. The sample was then cooled to 323 K and purged in 57 cc/min Ar. The gas flow was switched to 3 cc/min H\(_2\) in 57 cc/min Ar and the sample was heated from 323 K to 923 K at 10 K/min while hydrogen consumption was recorded. 200 mg of the Cu-BEA/AIE material had to be used in order to achieve a sufficient signal due to the low concentration of copper in this material.

Reactor studies indicated that the catalytic properties of the vapor ion-exchanged (VIE) materials could be altered by hydrogen reduction at different temperatures prior to contact with the reactant gas mixture. To investigate the chemical effects of the prereduction step, a sample of Cu-MFI/VIE PQ was placed in the TPR cell, dried at 303 K then heated to 773 K in Ar as above. The sample was then cooled to 573 K and the
gas flow was switched to 3 cc/min H₂ in 57 cc/min Ar to simulate the H₂ process which was used to pretreat materials in the catalytic reactor system. After 30 min, the gas flow was switched back to 57 cc/min Ar, the sample was cooled to 323 K, and the standard temperature programmed reduction was then performed as described in the previous paragraph.

**Microbalance Determination of Zeolitic Proton Content**

The number of acidic protons in the base zeolites was determined by gravimetric titration of the dried zeolite with 1-propanamine. A sample of the base acidic zeolite was placed in the microbalance, heated from 323 K to 773 K at 5 K/min and held at 773 K for 30 min. The sample was then cooled to 323 K and the reagent gas was diverted through a saturator containing 1-propanamine. The sample was allowed to adsorb 1-propanamine for 5 min and the reagent gas was then switched back to pure He. After purging in He for 10 min, the temperature was raised from 323 K to 823 K at 5 K/min while the sample weight was recorded. As shown previously [32-34], a stable weight exists in the 550-600 K region where the propanammonium ion formed by the 1:1 stoichiometric reaction of 1-propanamine with zeolitic protons is the only stable species. The weight of 1-propanamine adsorbed at 550-650 K can therefore be used as a measure of the proton content of the zeolite. A further assumption of 1 proton per framework-Al site is also often used as a measure of the framework-Al content of zeolites. For all of the materials investigated, the amount of 1-propanamine remaining at 573 K was used as the reference point for these calculations.
**Microbalance Reduction Studies**

Microbalance reduction experiments on the catalytic materials were performed by first pretreating the sample in the microbalance by heating in He from 323 K to either 473 K, 773 K or 973 K at 10 K/min and holding at the final temperature for 0.5 hrs. After pretreatment, the sample was cooled to 323 K and purged in He. The gas flow was then switched to 5 cc/min H₂ in 95 cc/min He and the sample was heated from 323 K to 923 K at 10 K/min while the sample weight was recorded.

Experiments on the physical mixtures were performed by pretreating the samples to 473 K, 773 K, and 973 K in an inert gas (He at 100 cc/min) prior to reduction. For the experiments with the aqueous ion-exchanged (AIE) and vapor ion-exchanged (VIE) materials, similar pretreatments to 473 K and 773 K in He prior to reduction were used. To determine weight loss due to drying, as opposed to reduction, the copper-free base zeolites of all of the samples were also similarly treated. One Cu-MFI/VIE PQ sample was pretreated to 773 K as above and then cooled to 323 K. This sample was heated in 5 cc/min CO and 95 cc/min He to 773 K at 10 K/min. When the sample reached 773 K, the gas flow was switched to 100 cc/min He and the sample was held at this temperature for 30 min. This sample was then cooled and reduced as above. This experiment was performed to determine whether the weight loss during reduction for this material was due to loss of oxygen or chlorine.

For reference purposes, bulk CuO, Cu₂O, CuCl₂, and CuCl were reduced after drying in 100 cc/min He at 323 K for 15 min by heating the samples from 323 K to 923 K at 10 K/min in 5 cc/min H₂ and 95 cc/min He. Cu₂O was also similarly reduced in 5 cc/min CO and 95 cc/min He.
Microbalance CO Adsorption Studies

As discussed previously in the literature review, Cu\textsuperscript{+} ions adsorb significant amounts of carbon monoxide at room temperature, but Cu\textsuperscript{2+} ions do not, so the amount of carbon monoxide adsorbed by the samples after various pretreatments, which was thought to give either Cu\textsuperscript{+} or Cu\textsuperscript{2+} was determined in the microbalance. The samples were placed in the microbalance, pretreated as specified later in the text, and then cooled to 323 K and purged in He. The reactant gas was then switched to 5 cc/min CO in 95 cc/min He and the sample was allowed to adsorb CO for 5 min.

Unlike the zeolite/copper oxide physical mixtures, it was observed (as will be shown later) that for the AIE and VIE materials, some of the Cu\textsuperscript{2+} ions present in the zeolite undergo a stepwise reduction to Cu\textsuperscript{+} ions followed by reduction of the Cu\textsuperscript{+} ions to Cu\textsuperscript{0} metal when heated in H\textsubscript{2}. To investigate the nature of the copper species produced by this stepwise reduction, the amount of CO adsorbed by some of these samples was measured after partial reduction of the thermally pretreated materials. Two sets of “partial reduction” experiments were performed for both the AIE and VIE materials. The first set of partial reductions was performed by pretreating a sample of the AIE or VIE materials to 473 K as above, and then cooling the sample to 323 K in helium. The gas flow was then switched to 5 cc/min H\textsubscript{2} in 95 cc/min He and the sample was then partially reduced by heating at 10 K/min to either 483 K or 533 K, for the AIE and VIE materials, respectively. The sample was held at the final temperature for 10 min, cooled to 323 K, purged in He, and the CO adsorption experiment was performed as described previously. As later results will suggest, the temperatures chosen for the partial reductions correspond approximately to temperatures at which we suspected that
most of the Cu$^{2+}$ ions have been reduced to Cu$^+$ ions for these materials. The second set of partial reductions were performed by pretreating a sample of the AIE or VIE materials to 773 K as above, and then cooling the samples to 323 K in helium. The gas flow was then switched to 5 cc/min H$_2$ in 100 cc/min He and the sample was then heated at 10 K/min to either 643 K or 633 K, for the AIE and VIE materials, respectively. The sample was held at the final temperature for 10 min, cooled to 323 K, purged in He for 15 min, and the CO adsorption experiments were then performed as described previously. The partial reduction temperatures for these experiments were chosen to coincide with the maximum in the TPR peaks of these materials pretreated to 773 K.

**Infrared Spectroscopy Experiments**

IR spectra focusing on the zeolitic OH stretch region after pretreatments, detailed later, were obtained. The zeolites were pressed into self supporting wafers, 6.4 mg/cm$^2$, which were loaded into the IR cell. The samples were pretreated by heating in an inert flow of 47.5 cc/min He from 303 K to either 473 K, 773 K, or 973 K at 10 K/min, held at the final temperature for 30 min, and then cooled to either 423 K for the zeolite/copper oxide physical mixtures, or 323 K for the AIE and VIE materials. The sample spectra were then taken at that temperature and referenced to the spectrum given by the empty IR cell at the same temperature as the sample.

To further investigate the stepwise reduction of some of the Cu$^{2+}$ ions in the AIE and VIE materials, partial reductions were performed by pretreating a sample of the AIE or VIE materials to 473 K as above, and then cooling the sample to 323 K in helium. The gas flow was then switched to 2.5 cc/min H$_2$ in 47.5 cc/min He and the sample was then heated at 10 K/min to either 483 K or 533 K, for the AIE and VIE materials,
respectively. The sample was held at the final temperature for 10 min, cooled to 323 K, purged in He for 15 min, and the IR spectrum was then recorded.

To verify that the CO adsorption occurring over some of the pretreated copper-containing samples was due to adsorption by zeolite coordinated Cu⁺ ions and not by some other species, the IR spectra in the carbon-oxygen stretch region of the samples were obtained after CO adsorption. Due to the chemistry of carbon monoxide, the number and locations of the carbon-oxygen infrared absorption bands are extremely sensitive to the coordinative environment of the adsorbed carbon monoxide. Comparison of the IR spectra of the samples after carbon monoxide adsorption with data already published in the literature for known reference compounds provides a convenient method of “fingerprinting” the species present.

The CO adsorption experiments were performed by treating the samples as in the previous section followed by cooling to 323 K. The samples were then contacted with 2.5 cc/min CO and 47.5 cc/min He for 10 min at 323 K and then purged in 47.5 cc/min He for 15 min prior to collection of the IR spectra. The spectra after CO adsorption were also obtained for the partially reduced materials in the previous section. The spectra presented are all referenced to the spectra of the sample prior to adsorption of CO at 323 K.

To investigate the effect of pretreatment temperature on the acidity of the materials formed by the solid-state reaction of CuO with the acidic and sodium MFI zeolites, the IR spectra of the pretreated materials after pyridine adsorption was obtained. These experiments were performed by pretreating the sample from 323 K to 473 K, 773 K or 973 K as described previously for the IR analysis of the OH stretch
region. The materials were then cooled to 423 K and the 47.5 cc/min He gas flow was diverted through a saturator containing pyridine. After exposure of the samples to the pyridine gas flow at 423 K for 10 min, the samples were allowed to purge in pure He for 15 min prior to collection of the IR spectra. For these experiments, both the CuO/H-MFI and the CuO/Na-MFI materials were pretreated to 473 K, 773 K, and 973 K prior to pyridine adsorption. Pyridine adsorption experiments were also performed on the CuO-0.5/H-MFI and CuO-1.9/H-MFI materials after pretreatment to 973 K.

X-ray Diffraction Experiments

The X-ray diffraction patterns were obtained using step scans of 0.02 degrees from 3 to 60 degrees at 1 degree/min for the AIE and VIE materials and their corresponding copper-free base zeolites.

The X-ray diffraction patterns were also obtained using step scans of 0.02 degrees from 32 to 42 degrees at 0.33 degree/min for pretreated CuO/H-MFI and CuO/Na-MFI materials. The pretreatments were performed in the tubular furnace in 100 cc/min Ar using 0.7 g of sample which were heated from 323 K to either 473 K, 773 K, or 973 K at 10 K/min and holding at the final temperature for 30 min. The samples were then cooled to room temperature in Ar prior to exposure to air and collection of their X-ray diffraction patterns. The X-ray diffraction patterns of the untreated materials and the corresponding copper-free base zeolites were also obtained. The angle range used for these experiments were chosen to correspond with known strong reflections for crystalline CuO.
Catalytic Reactions

The catalytic reaction experiments were performed beginning by placing 100 mg of catalyst between two plugs of quartz wool in the reactor. The system was then evacuated using a direct drive rotary vacuum pump, and the sample was dried by heating from room temperature to 773 K at 10 K/min where it was held for 30 min. The samples which were not prereduced prior to reaction were then cooled under vacuum to the reaction temperature, the reactor section containing the catalyst was filled with 1333 mbar of He, sealed off from the rest of the system, the reactor bypass was opened, and then the remaining system was evacuated. The reactant was added to the system, the total system pressure was brought to 1333 mbar with He, and the piston pump was started. The system was allowed to mix for 10 min with the reactor section bypassed and the reactant feed gas was then analyzed by the gas chromatograph. To start the reaction, the reactor was opened to the system and the reactor bypass was closed, which forced the reactant gas through the catalyst bed.

For samples prereduced prior to reaction, the samples were cooled to the prereduction temperature after drying in vacuum to 773 K as above. The reactor section was then filled with 1333 mbar of He, sealed off from the rest of the system, the reactor bypass was opened, and the remainder of the system was then evacuated. After evacuation, the system was filled with 66.7 mbar of H\textsubscript{2} and 1267 mbar of He, the piston pump was started, the gas flow was diverted through the reactor, and the bypass was closed. The catalysts were allowed to reduce for 30 min, after which the system was evacuated and the reactor brought to the reaction temperature. The reactor section was
then back-filled with He as above, the remainder of the system evacuated, then back filled with the reactant and He as before, and the reaction initiated as given above.

One set of experiments were performed to investigate the reaction of 1-propanamine over the zeolite/copper oxide physical mixtures. For all of these experiments, 66.7 mbar of 1-propanamine in 1267 mbar of He was used as the reactant gas. The reaction temperature was 573 K and none of the samples were prereduced prior to reaction. This series of experiments were performed using the H-MFI-50, Na-MFI, CuO/MFI-30, CuO-0.5/H-MFI, CuO-1.9/H-MFI, CuO/Na-MFI, CuO/H-MFI-50, and Cu2O/H-MFI. All of these runs were performed using the FID detector.

A set of experiments similar to the previous ones were also performed for the AIE and VIE materials. These experiments used the H-MFI-30 PQ, H-BEA, Cu-MFI/VIE PQ, Cu-MFI/AIE, Cu-BEA/VIE, and Cu-BEA/AIE.

The effect of changing the silicon to alumina ratio of the base zeolite and the effect of prereduction of the catalyst on the reaction rate and product distribution for the conversion of 1-propanamine was also investigated. These experiments were all performed using 66.7 mbar of 1-propanamine in 1267 mbar of He at a reaction temperature of 573 K. Four experiments were performed with the Cu-MFI/VIE with different prereduction conditions. The catalyst used in the first experiment was not prereduced and the other three catalysts were prereduced at 573 K, 673 K, and 773 K. A reaction was also run with the unreduced Cu-MFI-50/VIE material. All of these runs were performed using the FID detector.

Three other 1-propanamine reactions were also performed over the Cu-MFI/VIE material prereduced at 673 K. The first used 66.7 mbar of 1-propanamine in 1267 mbar
of He and a reaction temperature of 593 K. The second used 13.3 mbar of 1-propanamine and a reaction temperature of 573 K. The third used 66.7 mbar of 1-propanamine and 266.7 mbar H₂ in 999.6 mbar of He. All of these runs were performed with the FID detector.

The conversion of dipropanamine was also investigated. These reactions were performed over the Cu-MFI/VIE and the Cu-BEA/VIE materials prereduced at 673 K. 26.7 mbar of dipropanamine in 1306.3 mbar of He was used as the reactant and the reaction temperature was 573 K.

Experiments were also conducted to determine the major products obtained by the conversion of other light amines. For all of these reactions, the Cu-MFI/VIE material prereduced at 573 K was used and the reactant mixture consisted of 66.7 mbar of reactant in 1267 mbar of He. The amines used for these reactions were methylamine, dimethylamine, ethylamine, and 2-propylamine. Products of all of these reactions were analyzed using the mass selective detector on the chromatograph.

An experiment using the Cu-MFI/VIE prereduced at 573 K was also conducted using 33.3 mbar of 1-propanamine and 33.3 mbar of 2-propanamine in 1267 mbar of He at a reaction temperature of 573 K. The mass selective detector was used for this experiment.
III. RESULTS

A. Physico-Chemical Characterization

Determination of Framework and Extraframework Alumina

The aluminum contents of the base zeolites were provided by the manufacturer in the form of the synthesis SiO₂/Al₂O₃. Significant differences between the framework aluminum content and this synthesis mixture aluminum content were discovered using 1-propanamine thermal desorption to determine the framework Al content. The results of these 1-propanamine adsorption/desorption experiments are shown in Figure III-1. As discussed previously in the experimental section, the weight of the plateau between 550 K and 600 K has been shown to correspond to the adsorption of one 1-propanamine per zeolite acid site. Therefore, by assuming a 1-PA/framework-Al ratio of unity in the plateau region of the desorption curve, the framework-Al content of the sample can be determined by dividing the sample weight at 573 K in the plateau region by the molecular weight of 1-propanamine. The results of these calculations are given in Table III-1 along with the synthesis SiO₂/Al₂O₃ ratios provided by the manufacturers. Also shown in this table is the fraction of the total aluminum in the zeolite that exists as framework Al.

Aqueous and Vapor Ion-Exchanged Materials

Determination of Copper Content

The results of the copper elemental analysis are given in Table III-2. The first column in this table is the measured copper concentration in parts per million of the solution obtained after the zeolite acid digestion. Using the concentration of the digestion solution and the assumption that all of the copper in catalytic samples was dissolved in the solution, the number of moles of copper per 100 g of samples is
Figure III-1: Microbalance 1-propanamine desorption weight curves a) H-BEA, b) H-MFI PQ, c) H-MFI, and d) H-MFI-50.
Table III-1. Aluminum and Proton Content of Base Zeolites.

<table>
<thead>
<tr>
<th>Material</th>
<th>SiO$_2$/Al$_2$O$_3$ Synthesis Mixture$^1$</th>
<th>Total Moles Al/100g</th>
<th>Adsorbed Mass 1-PA/100g at 573 K$^2$</th>
<th>Moles Framework/100g</th>
<th>SiO$_2$/Al$_2$O$_3$ Framework</th>
<th>% of Al in Framework</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-MFI-30 PQ</td>
<td>30</td>
<td>0.104</td>
<td>4.55</td>
<td>0.077</td>
<td>41.3</td>
<td>74.0</td>
</tr>
<tr>
<td>H-MFI-30</td>
<td>30</td>
<td>0.104</td>
<td>3.92</td>
<td>0.066</td>
<td>48.3</td>
<td>63.7</td>
</tr>
<tr>
<td>H-MFI-50</td>
<td>50</td>
<td>0.064</td>
<td>3.28</td>
<td>0.055</td>
<td>58.6</td>
<td>86.7</td>
</tr>
<tr>
<td>H-BEA</td>
<td>25</td>
<td>0.123</td>
<td>5.79</td>
<td>0.098</td>
<td>32.0</td>
<td>79.4</td>
</tr>
</tbody>
</table>

$^1$provided by manufacturer.
$^2$See Figure III-1.
Table III-2. Copper Content of Aqueous and Vapor Ion-Exchanged Materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>Aqueous Cu Conc (ppm)</th>
<th>Moles Cu/100g Zeolite</th>
<th>Moles Cu/FWAl</th>
<th>Percent of Cu deposited via VIE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-MFI-50/VIE</td>
<td>60.72</td>
<td>0.0796</td>
<td>1.435</td>
<td>39.4</td>
</tr>
<tr>
<td>Cu-MFI/VIE</td>
<td>65.56</td>
<td>0.0860</td>
<td>1.296</td>
<td>42.6</td>
</tr>
<tr>
<td>Cu-MFI/VIE PQ</td>
<td>58.45</td>
<td>0.0767</td>
<td>0.996</td>
<td>37.9</td>
</tr>
<tr>
<td>Cu-BEA/VIE</td>
<td>44.95</td>
<td>0.0590</td>
<td>0.602</td>
<td>29.2</td>
</tr>
<tr>
<td>Cu-MFI/AIE</td>
<td>24.04</td>
<td>0.0315</td>
<td>0.409</td>
<td></td>
</tr>
<tr>
<td>Cu-BEA/AIE</td>
<td>21.57</td>
<td>0.0283</td>
<td>0.289</td>
<td></td>
</tr>
</tbody>
</table>
computed in the second column. Using the results in column two and the framework Al content of the base zeolites from Table III-2, the number of copper atoms per anionic zeolite site is computed in column three of the table. Using the copper concentrations and the amount of zeolite used in the synthesis, 5 g, the percentage of the copper initially placed on the upper deck of the ceramic boat that was recovered from the zeolite is computed in column four of the table.

As shown in Table III-2, the materials produced by the vapor ion-exchange process in general have a larger amount of copper in them than do the aqueous ion-exchanged materials prepared with the same base zeolite. The ratio of copper to framework aluminum for Cu-MFI/VIE and Cu-MFI-50/VIE exceeded one, suggesting that there is extraframework CuCl which was not removed by the final heat treatment at 973 K in argon. The ratio of copper to framework aluminum increased with decreasing framework aluminum for Cu-MFI/VIE PQ, Cu-MFI/VIE, and Cu-MFI-50/VIE. The fraction of copper deposited was approximately constant for all of the MFI materials and was between 38% to 43%, suggesting that the rate of mass transfer of CuCl to and from the zeolite was a major determinant of the amount of copper present in the materials.

**X-ray Diffraction Results**

The X-ray diffraction patterns of the pure CuO, Cu2O, CuCl and CuCl2 are shown in Figure III-2 and those for Cu-MFI/AIE, Cu-MFI/VIE PQ, Cu-BEA/AIE, Cu-BEA/VIE and the copper-free base zeolites are shown in Figure III-3. The copper-free base zeolites and the AIE materials did not show any peaks attributable to crystalline species other than the zeolite including any of the copper oxides or chlorides. Both of the VIE materials show X-ray diffraction peaks at 16.0 and 32.3 degrees, which
Figure III-2: X-ray powder diffraction patterns of (a) CuO, (b) CuCl, (c) CuCl₂, and (d) CuO.
Figure III-3: X-ray powder diffraction patterns of a) H-MFI PQ, b) Cu-MFI/AIE, c) Cu-MFI/VIE, d) H-BEA, e) Cu-BEA/AIE, and f) Cu-BEA/VIE.
are consistent with the presence of some crystalline extraframework CuCl. The intensities of the peak at 23 degrees for the MFI materials is 1372, 1577, and 1276 cps for the copper-free, AIE, and VIE materials, respectively, and for the BEA material, 101, 89, and 107 cps for the copper-free, AIE, and VIE materials, respectively.

**Microbalance Hydrogen Reduction Results**

The microbalance hydrogen reduction results for the pure CuO, Cu₂O, CuCl and CuCl₂ are given in Figure III-4 and their corresponding derivatives in Figure III-5. Also shown is the reduction of Cu₂O in carbon monoxide. For these figures, the weight at the start of the reduction experiment was set equal to 100% after the samples were dried at 323 K for 15 min. The weight loss during reduction for both CuO and Cu₂O are consistent with the reduction of the oxide to the metal and occurs at 552 K and 602 K, respectively. The weight loss on reduction of Cu₂O in carbon monoxide is also consistent with reduction of the oxide to the metal and occurs at 545 K. The weight loss of the copper chlorides during reduction significantly exceeds that expected for reduction of the chloride to the metal, suggesting that some volatilization of the copper chlorides occurs prior to their reduction.

Since 1-propanamine is often used as an adsorbent for probing the proton content of our catalysts, and since copper might undergo reduction with 1-propanamine, we have also determined the susceptibility of copper oxide species to reduction by 1-propanamine. The reduction results for CuO and Cu₂O in 1-propanamine are shown in Figure III-6. The weight loss observed for both of the oxides is consistent with reduction of the copper oxide to copper metal. The reduction temperatures of 559 K and 565 K for CuO and Cu₂O, respectively, are lower than the reduction temperatures of
Figure III-4: Microbalance reduction results a) CuO reduced in H₂, b) Cu₂O reduced in H₂, c) CuCl reduced in H₂, d) CuCl₂ reduced in H₂, and e) Cu₂O reduced in CO.
Figure III-5: Microbalance reduction derivatives a) CuO reduced in H₂, b) Cu₂O reduced in H₂, c) CuCl reduced in H₂, d) CuCl₂ reduced in H₂, and e) Cu₂O reduced in CO.
Figure III-6: Microbalance 1-propanamine reduction results: a) CuO, and b) Cu$_2$O.

Derivatives: c) CuO, and d) Cu$_2$O.
the oxides in hydrogen, indicating that for at least these compounds, 1-propanamine is a stronger reducing agent than hydrogen. This result will be useful later for the interpretation of the results obtained from the catalytic conversion of 1-propanamine and other amines with the copper-containing zeolites.

The derivatives of the microbalance hydrogen reduction results for Cu-MFI/VIE PQ, Cu-MFI/AIE, and the copper-free H-MFI pretreated to 473 K and 773 K are given in Figure III-7. A Cu-MFI/VIE PQ sample that was pretreated to 773 K and then heated in carbon monoxide as discussed in the experimental section is also shown in this figure. Neither H-MFI/473K or Cu-MFI/AIE/773K show large reduction peaks. Cu-MFI/AIE/473K shows two reduction regions, one between 325 K and 560 K and the other between 560 K and 800 K. Similarly, Cu-MFI/VIE/473K also has two reduction peaks at close to the same temperatures. Only one reduction peak is observed for Cu-MFI/773K and this peak is not significantly affected by pretreating Cu-MFI/773K in CO.

Although the hydrogen reduction peak for Cu-MFI/VIE/773K occurs at approximately the same temperature as that for the reduction of Cu$_2$O, the absence of any significant effect of heating the material in carbon monoxide indicates that this peak is not due to Cu$_2$O, because it has been previously shown that carbon monoxide is capable of reducing copper ions in zeolites coordinated to non-framework oxygen [6,12,17,44,75,76,81-85]. These results suggest that the weight loss peak is due to the reduction of a chloride containing species, such as [CuCl]$^-$Z; formed by reaction of copper ions in the zeolite with the excess CuCl observed in the X-ray diffraction results. The absence of this hydrogen reduction peak in the material pretreated to 473 K indicates that it is not initially present in the zeolite, but is formed during the
pretreatment to 773 K. The weight loss peak would correspond to 0.038 moles of Cl/100 g of sample if due to chlorine.

The derivatives of the microbalance hydrogen reduction results for Cu-BEA/VIE, Cu-BEA/AIE, and the copper-free H-BEA pretreated to 473 K and 773 K are given in Figure III-8. These results are qualitatively similar to those of the MFI materials. As with those samples, pronounced reduction peaks are not observed for H-BEA/473K or Cu-BEA/AIE/773K, while two reduction regions are observed for Cu-BEA/AIE/473K and Cu-BEA/VIE/473K. One reduction peak is observed for Cu-BEA/VIE/773K and it occurs at approximately the same temperature as the one for Cu-MFI/VIE/773K.

Quantitative values from the reduction experiments are given in Table III-3. For all of these samples, the weight after reduction was set to 100%. The first column in the table is the change in the weight of the sample during the hydrogen reduction in the temperature region shown. The second column gives the corresponding weight change for the copper-free base zeolite in that temperature range. These numbers is needed to correct for the change in sample weight due to further drying of the zeolite and buoyancy effects from heating the sample (which is extremely small). The difference between these two numbers is computed in the third column and the weight loss per mole of copper, as determined from the elemental analysis, is given in the fourth column.

**TPR Reduction Results**

The TPR reduction results for Cu-MFI/VIE PQ, Cu-MFI/AIE, and the copper-free base zeolite are given in Figure III-9. These experiments are parallel and complimentary to identical experiments performed on the microbalance. Also shown is Cu-MFI/VIE/773K reduced at 573 K for 30 min. Quantitative results from these
Figure III-8: Microbalance reduction derivatives a) H-BEA/473K, b) Cu-BEA/AIE/773K, c) Cu-BEA/AIE/473K, d) Cu-BEA/VIE/473K, and e) Cu-BEA/VIE/773K.
Table III-3. Microbalance Hydrogen Reduction Results for Aqueous and Vapor Ion-Exchanged Materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>Weight Loss (g/100g)</th>
<th>Base Zeolite Weight Loss (g/100g)</th>
<th>Difference (g/100g)</th>
<th>Weight loss Per Cu (g/mole Cu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-MFI/AIE/473K</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>325-560K</td>
<td>0.4500</td>
<td>0.1400</td>
<td>0.32</td>
<td>10.06</td>
</tr>
<tr>
<td>560-800K</td>
<td>0.7700</td>
<td>0.3700</td>
<td>0.41</td>
<td>12.91</td>
</tr>
<tr>
<td>Cu-MFI/AIE/773K</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>325-800K</td>
<td>0.1400</td>
<td>0.0200</td>
<td>0.12</td>
<td>3.69</td>
</tr>
<tr>
<td>Cu-MFI/VIE/473K</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>325-595K</td>
<td>1.6700</td>
<td>0.2000</td>
<td>1.48</td>
<td>19.24</td>
</tr>
<tr>
<td>595-800K</td>
<td>1.6800</td>
<td>0.3100</td>
<td>1.37</td>
<td>17.84</td>
</tr>
<tr>
<td>Cu-MFI/AIE/773K</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>325-800K</td>
<td>1.3715</td>
<td>0.0205</td>
<td>1.351</td>
<td>17.61</td>
</tr>
<tr>
<td>Cu-BEA/AIE/473K</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>325-620K</td>
<td>0.9100</td>
<td>0.5438</td>
<td>0.3662</td>
<td>12.94</td>
</tr>
<tr>
<td>620-850K</td>
<td>1.5034</td>
<td>0.9089</td>
<td>0.5945</td>
<td>21.01</td>
</tr>
<tr>
<td>Cu-BEA/AIE/773K</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>325-850K</td>
<td>0.2860</td>
<td>0.0871</td>
<td>0.199</td>
<td>7.03</td>
</tr>
<tr>
<td>Cu-BEA/VIE/473K</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>325-630K</td>
<td>1.8018</td>
<td>0.5882</td>
<td>1.2136</td>
<td>20.57</td>
</tr>
<tr>
<td>630-850K</td>
<td>1.7713</td>
<td>0.8645</td>
<td>0.9068</td>
<td>15.37</td>
</tr>
<tr>
<td>Cu-BEA/VIE/773K</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>325-850K</td>
<td>0.9639</td>
<td>0.0871</td>
<td>0.8768</td>
<td>14.86</td>
</tr>
</tbody>
</table>
experiments are given in Table III-4. The first column gives the number of moles of hydrogen atoms consumed per 100 g of sample. The second column of the table gives the average number of electrons transferred per copper atom, which was computed by division of the results in column one by the elemental copper content given in Table III-2. The fourth column lists the mass to charge ratio of the peak, which was computed by division of the weight loss per 100 g of sample (as determined from the microbalance experiments in Table III-3), by the total hydrogen consumption given in column one. Also given in Table III-4 are results for BEA materials which will be discussed shortly.

The number of electrons transferred per copper atom for the material dried at 473 K is consistent with the copper atoms initially being in the +2 oxidation state. For Cu-MFI/AIE/473K, a very broad reduction peak between 425 K and 525 K and a sharp reduction between 525 K and 625 K is observed. The two reduction peaks are consistent with previous observations suggesting that some of the Cu$^{2+}$ ions present in aqueous ion-exchanged materials undergo stepwise reduction from Cu$^{2+}$ → Cu$^+$ → Cu$^0$ in hydrogen [9,20,46,47,83,85,87,99,100]. To determine whether thermal treatment to 773 K in argon would reduce the Cu$^{2+}$ ions, TPR experiments were performed after pretreating the material to 773 K. Thermal pretreatment of the aqueous ion-exchanged material to 773 K results in the elimination of the low temperature reduction peak and a decrease in the number of hydrogen atoms consumed during hydrogen reduction. These results are consistent with previous observations which suggested that some of the Cu$^{2+}$ ions in aqueous ion-exchanged zeolites can thermally reduce to the +1 oxidation state [4-6,8,15,19,45,61,70,88,90]. These results also suggest that the TPR peak at
Table III-4. TPR Reduction Results for Aqueous and Vapor Ion-Exchanged Materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>Moles H Consumed /100g sample</th>
<th>e⁻/Cu</th>
<th>Mass/e⁻ ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-MFI/AIE/473K</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>325-560K</td>
<td>0.0197</td>
<td>0.63</td>
<td>16.0</td>
</tr>
<tr>
<td>560-800K</td>
<td>0.0437</td>
<td>1.39</td>
<td>9.3</td>
</tr>
<tr>
<td>325-800K</td>
<td>0.0634</td>
<td>2.01</td>
<td>11.4</td>
</tr>
<tr>
<td>Cu-MFI/AIE/773K</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>325-800K</td>
<td>0.0343</td>
<td>1.09</td>
<td>3.4</td>
</tr>
<tr>
<td>Cu-MFI/VIE/473K</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>325-595K</td>
<td>0.0796</td>
<td>1.04</td>
<td>18.5</td>
</tr>
<tr>
<td>595-800K</td>
<td>0.0850</td>
<td>1.11</td>
<td>16.1</td>
</tr>
<tr>
<td>325-800K</td>
<td>0.1646</td>
<td>2.15</td>
<td>17.2</td>
</tr>
<tr>
<td>Cu-MFI/VIE/773K</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>325-800K</td>
<td>0.1059</td>
<td>1.38</td>
<td>12.8</td>
</tr>
<tr>
<td>Cu-BEA/AIE/473K</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>325-620K</td>
<td>0.0209</td>
<td>0.74</td>
<td>17.6</td>
</tr>
<tr>
<td>620-850K</td>
<td>0.0303</td>
<td>1.07</td>
<td>19.7</td>
</tr>
<tr>
<td>325-800K</td>
<td>0.0512</td>
<td>1.81</td>
<td>18.8</td>
</tr>
<tr>
<td>Cu-BEA/AIE/773K</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>325-850K</td>
<td>0.0272</td>
<td>0.96</td>
<td>7.3</td>
</tr>
<tr>
<td>Cu-BEA/VIE/473K</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>325-630K</td>
<td>0.0622</td>
<td>1.05</td>
<td>19.6</td>
</tr>
<tr>
<td>630-850K</td>
<td>0.0630</td>
<td>1.07</td>
<td>14.4</td>
</tr>
<tr>
<td>325-800K</td>
<td>0.1252</td>
<td>2.12</td>
<td>17.0</td>
</tr>
<tr>
<td>Cu-BEA/VIE/773K</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>325-850K</td>
<td>0.0560</td>
<td>0.95</td>
<td>15.6</td>
</tr>
</tbody>
</table>

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approximately 645 K is due to the reduction of Cu'Z' ions to copper metal and zeolite acid sites by the hydrogen.

The results for Cu-MFI/VIE/473K are also consistent with the copper ions being in the +2 oxidation state. The two reduction peaks each transfer approximately one electron per copper atom and are consistent with the stepwise reduction of the Cu²⁺ to Cu⁺ and finally to copper metal. Thermal treatment of this material to 773 K results in the disappearance of the first reduction peak and a decrease in the total hydrogen consumption of this material, which is consistent with the thermal reduction of some of the Cu²⁺ ions to Cu⁺ ions by this pretreatment. The reduction peak has a pronounced shoulder on the lower temperature side, possibly due to the reduction of the[CuCl]'Z' ions discussed previously. It is unlikely that this peak is due to the reduction of the extraframework CuCl observed by the X-ray diffraction experiments since the previous microbalance hydrogen reduction results indicated that CuCl volatilizes prior to reduction and because this reduction peak is not observed in the material pretreated to 473 K. The rest of the reduction peak occurs at the same temperature as the peak assigned to Cu⁺ ions bound to the zeolite for the aqueous ion-exchanged material.

Reduction of Cu-MFI/VIE/773K for 30 min at 573 K in H₂ results in the elimination of all of the TPR peaks. This result is consistent with reduction of all of the copper ions to the metal by this procedure.

The BEA materials behave similarly to the MFI material as seen in Figure III-10 and Table III-4. The aqueous ion-exchanged material pretreated to 473 K gives two reduction peaks and the low temperature peak disappears on heating to 773 K. The vapor ion-exchanged BEA materials also behave similar to the similarly prepared MFI
Figure III-10: TPR results a) H-BEA/473K, b) Cu-BEA/AIE/473K, c) Cu-BEA/AIE/473K, d) Cu-BEA/VIE/473K, and e) Cu-BEA/VIE/473K.

Hydrogen Consumption (A.U.)
samples. Two reduction peaks are observed for the material pretreated to 473 K, with one electron transferred per copper for each peak. Thermal treatment to 773 K eliminates the low temperature peak and decreases the number of electrons transferred per copper atom.

**Microbalance CO Adsorption Results**

As discussed previously in the literature review, Cu\(^+\) adsorbs significant amounts of CO while Cu\(^{2+}\) and Cu\(^0\) do not [5,12,20,26,44,59,81,82,89-93]. Transient CO adsorption at 323 K after pretreatment of the AIE and VIE catalysts to 473 K or 773 K are shown in Figures III-11. Cu-MFI/VIE/773K experiences the greatest weight gain on exposure to CO, while significant amounts of CO are also adsorbed on the similarly treated Cu-MFI/AIE material. These results are consistent with the presence of Cu\(^+\) ions in these materials pretreated to 773 K. Substantially less CO adsorption occurs on Cu-MFI/VIE/473K, Cu-MFI/AIE/473K, and H-MFI/473K, indicating the absence of Cu\(^+\) ions in these materials pretreated to 473 K.

To assist in the assignment of the hydrogen reduction peaks observed by the microbalance and TPR, CO adsorption experiments were performed after partial reduction of pretreated AIE and VIE materials. These results are shown in Figure III-12. Partial hydrogen reduction of Cu-MFI/VIE/773K and Cu-MFI/AIE/773K at 633 K and 643 K, respectively, results in a considerable decrease in the amount of CO adsorbed relative to the unreduced material. (The partial reduction temperatures correspond to the peak maxima in the TPR curves for these two materials). These results are consistent with the assignment of the reduction peak between 633 K to 643 K to the reduction of zeolite bound Cu\(^+\) ions to copper metal and zeolite acid sites. Partial
reduction of Cu-MFI/VIE/473K and Cu-MFI/AIE/473K at 533 K and 483 K, respectively, results in a considerable increase in the amount of CO adsorbed compared to the unreduced materials. (These partial reduction temperatures approximately correspond to the first peak maximum in the TPR curves for these materials). These results are consistent with the assignment of the low temperature reduction peak for the AIE and VIE materials to the reduction of zeolite bound Cu$^{2+}$ ions to zeolite bound Cu$^{+}$ ions. The Cu$_2$O/H-MFI physical mixture does not significantly adsorb CO, suggesting that the CO adsorption of the copper containing zeolites was not due to the formation of Cu$_2$O and the adsorption of CO by the oxide.

**IR Spectroscopy Results**

The IR spectra of the OH stretching region of the materials are shown in Figure III-13. Four important peaks which we focus on are initially observable for H-MFI/473K. The 3738 cm$^{-1}$ band, which is present in all of the samples shown, has been attributed to hydroxyl groups which are known to be relatively inert attached to terminal silicon atoms [8,59,65,75,77]. The 3610 cm$^{-1}$ has been attributed to stretching of the acidic hydroxyl group in MFI zeolites [59]. Two other minor bands at 3690 cm$^{-1}$ and 3661 cm$^{-1}$ are also observed. Previous investigations have assigned bands at 3690 cm$^{-1}$ [77] and 3656 cm$^{-1}$ [8] to vibrations associated with AlOH groups, suggesting that the minor bands we have observed at slightly different wavenumbers are also due to these species. The Na-MFI material dried to 473 K does not possess the 3610 cm$^{-1}$ band, which is consistent with the replacement of all of the zeolitic protons with Na$^{+}$ ions. An increase in the IR bands at 3690 cm$^{-1}$ and 3661 cm$^{-1}$ which is noted for Na-MFI is possibly due to hydroxylation of extraframework alumina by NaOH during sodium
exchange. The bands between 3590 cm\(^{-1}\) and 3575 cm\(^{-1}\) may be due to water bound to the sodium ions.

Recalling that Cu-MFI/AIE materials are made starting with Na-MFI, we only intended to replace sodium cations with copper cations in the exchange process. However, our IR results indicate that some protons are also restored when the aqueous ion-exchange is performed, as evidenced by the partial restoration of the 3610 cm\(^{-1}\) band for Cu-MFI/AIE/473K relative to Na-MFI. The bands at 3737 cm\(^{-1}\), 3690 cm\(^{-1}\) and 3661 cm\(^{-1}\) show little change, indicating that the SiOH and AlOH species were not significantly affected by the aqueous ion-exchange. The 3590 cm\(^{-1}\) and 3575 cm\(^{-1}\) bands observed for Na-MFI material are not present after the copper exchange, which is consistent with their assignment to water coordinated to sodium ions and replacement of sodium by copper in the exchange process. The broad band between 3600 cm\(^{-1}\) and 3300 cm\(^{-1}\) has been previously observed for copper ion-exchanged MFI and was attributed to water and hydroxide ions associated with Cu\(^{2+}\) ions [8]. Cu-MFI/AIE/773K shows significantly weaker bands at 3600 cm\(^{-1}\) to 3300 cm\(^{-1}\) compared to Cu-MFI/AIE/473K, in agreement with previous studies [8]. Other bands in Cu-MFI/AIE/773K are similar to those present in Cu-MFI/AIE/473K. Partial reduction of Cu-MFI/AIE/473K at 483 K results in the formation of a broad band between 3600 cm\(^{-1}\) and 3300 cm\(^{-1}\), possibly due to water produced by the reduction of copper hydroxides. The zeolitic proton peak at 3610 cm\(^{-1}\) does not appear to be significantly affected by the partial reduction process.

Like other materials, the vapor ion-exchange material, Cu-MFI/VIE/473K possesses a silanol band at 3739 cm\(^{-1}\), but a very small band is observed at 3610 cm\(^{-1}\) which
is due to zeolitic protons indicates that the reaction of CuCl with H+ is not quite complete. Two other pronounced absorption regions are observed, one at 3448 cm⁻¹ and another at 3360 cm⁻¹ - 3319 cm⁻¹, which are comparable to bands at 3440 cm⁻¹ and 3350 cm⁻¹ that have been observed for "excessively" ion-exchanged copper mordenites [64,65] and are thought to be due to bridged OH groups coordinated between two Cu²⁺ ions and water coordinated to the copper ions in a copper hydroxyl dimer [64,65]. The occurrence of several peaks in the 3360 cm⁻¹ to 3319 cm⁻¹ region in our materials may be due to the varying distances between the copper hydroxyl ions in the MFI zeolite. The copper-oxygen-copper bond angle increases with increasing distances between the copper hydroxyl ions. The increase in bond angle changes the relative contributions of the bonding orbitals for both this bond and oxygen-hydrogen bond and would be expected to change the OH absorption frequency. Partial reduction to 533 K of Cu-MFI/VIE/473K results in the elimination of the bands which appear to be associated with a copper hydroxyl dimer, but the 3610 cm⁻¹ acidic proton band is not restored by the partial reduction. Cu-MFI/VIE/773K shows no bands that could be associated with the copper hydroxyl dimer peaks or significant protons.

The spectra of materials after CO adsorption is shown in Figure III-14. In agreement with the microbalance results, neither H-MFI nor Cu₂O/H-MFI materials show any significant CO absorption bands, while Cu-MFI/AIE/473K shows some absorbance attributable to adsorbed CO [95] at approximately 2175 cm⁻¹ and 2150 cm⁻¹. The absorption attributable to adsorbed CO increases for Cu-MFI/AIE/773K relative to Cu-MFI/AIE/473K, and partial hydrogen reduction of Cu-MFI/AIE/473K also results in an increase in these absorption bands. Cu-MFI/VIE/473K also shows some adsorbed
CO absorption bands, which is consistent with the microbalance results indicating that some CO is adsorbed on this material. Cu-MFI/VIE/773 K gives a significant increase in the absorption bands associated with the $[\text{Cu(CO)}_2]^+$ ions relative to Cu-MFI/VIE/473K. An absorption band at 2137 cm$^{-1}$ is also present, which is not normally observed for MFI samples with low copper concentrations, and has been attributed to CO adsorbed on associated Cu$^+$ ions [95]. Partial reduction of Cu-MFI/VIE/473K to 533 K also produces similar bands with absorption intensities that are somewhat greater than that of Cu-MFI/VIE/773K.

Zeolite/Copper Oxide Physical Mixture Materials

Microbalance Hydrogen Reduction Results

The derivatives of the weight curves of the microbalance hydrogen reduction results of CuO/H-MFI and H-MFI-30 are shown in Figure III-15. Quantitative results from these experiments are given in Table III-5. The columns of this table were computed by the same method as in Table III-3. Increasing the pretreatment temperature results in an overall decrease in the weight loss during reduction. Two weight loss peaks are observed in the hydrogen reduction derivative curves for the material pretreated to 473 K, with the strongest at 545 K. Pretreatment to 773 K results in the disappearance of the weak hydrogen reduction band and pretreatment to 973 K results in a shift of the major hydrogen reduction band to lower temperatures. The weight loss on reduction of CuO/H-MFI/473 K corresponds to 16.5 g per mole of copper, suggesting that little or no reaction of the CuO with the zeolite occurs with this pretreatment. The weight loss during reduction decreases with increasing pretreatment temperature, suggesting that the
Table III-5. Microbalance Hydrogen Reduction Results for Zeolite/Copper Oxide Physical Mixtures. Weight loss during hydrogen reduction from 323 K to 773 K.

<table>
<thead>
<tr>
<th>Material</th>
<th>Weight Loss (g/100g)</th>
<th>Base Zeolite Weight Loss (g/100g)</th>
<th>Difference (g/100g)</th>
<th>Weight loss Per Mole of Cu (g/mole Cu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuO/H-MFI/473K</td>
<td>1.448</td>
<td>0.353</td>
<td>1.094</td>
<td>16.5</td>
</tr>
<tr>
<td>CuO/H-MFI/773K</td>
<td>0.823</td>
<td>0.007</td>
<td>0.816</td>
<td>12.3</td>
</tr>
<tr>
<td>CuO/H-MFI/973K</td>
<td>0.356</td>
<td>-0.07</td>
<td>0.428</td>
<td>6.5</td>
</tr>
<tr>
<td>CuO-0.5/H-MFI/473K</td>
<td>0.992</td>
<td>0.353</td>
<td>0.639</td>
<td>19.2</td>
</tr>
<tr>
<td>CuO-0.5/H-MFI/773K</td>
<td>0.456</td>
<td>0.007</td>
<td>0.449</td>
<td>13.5</td>
</tr>
<tr>
<td>CuO-0.5/H-MFI/973K</td>
<td>0.109</td>
<td>-0.07</td>
<td>0.178</td>
<td>5.4</td>
</tr>
<tr>
<td>CuO-1.9/H-MFI/473K</td>
<td>2.39</td>
<td>0.353</td>
<td>2.037</td>
<td>16.0</td>
</tr>
<tr>
<td>CuO-1.9/H-MFI/773K</td>
<td>1.64</td>
<td>0.007</td>
<td>1.633</td>
<td>12.8</td>
</tr>
<tr>
<td>CuO-1.9/H-MFI/973K</td>
<td>0.766</td>
<td>-0.07</td>
<td>0.835</td>
<td>6.5</td>
</tr>
<tr>
<td>CuO/H-MFI-50/473K</td>
<td>1.376</td>
<td>0.315</td>
<td>1.061</td>
<td>17.8</td>
</tr>
<tr>
<td>CuO/H-MFI-50/773K</td>
<td>0.212</td>
<td>0.021</td>
<td>0.191</td>
<td>3.2</td>
</tr>
<tr>
<td>CuO/H-MFI-50/973K</td>
<td>0.044</td>
<td>-0.008</td>
<td>0.052</td>
<td>0.9</td>
</tr>
<tr>
<td>CuO/Na-MFI/473K</td>
<td>1.601</td>
<td>0.467</td>
<td>1.134</td>
<td>16.1</td>
</tr>
<tr>
<td>CuO/Na-MFI/773K</td>
<td>0.974</td>
<td>-0.005</td>
<td>0.978</td>
<td>13.9</td>
</tr>
<tr>
<td>CuO/Na-MFI/973K</td>
<td>0.434</td>
<td>-0.048</td>
<td>0.482</td>
<td>6.8</td>
</tr>
<tr>
<td>Cu₂O/H-MFI/473K</td>
<td>1.042</td>
<td>0.353</td>
<td>0.689</td>
<td>10.4</td>
</tr>
<tr>
<td>Cu₂O/H-MFI/773K</td>
<td>0.454</td>
<td>0.007</td>
<td>0.447</td>
<td>6.7</td>
</tr>
<tr>
<td>Cu₂O/H-MFI/973K</td>
<td>0.268</td>
<td>-0.07</td>
<td>0.337</td>
<td>5.1</td>
</tr>
</tbody>
</table>
CuO reacts with H-MFI for the materials pretreated at temperatures of 773 K and 973 K.

The derivatives of the microbalance hydrogen reduction curves for the other CuO and H-MFI physical mixtures are qualitatively similar to that of CuO/H-MFI material and quantitative results from these experiments are also given in Table III-5. The experiments with the CuO/H-MFI materials with different copper loadings were performed to determine whether the extent of reaction between the zeolite and CuO was stoichiometrically limited by the number of protons per copper atoms. As with CuO/H-MFI, the weight loss resulting from hydrogen reduction decreases for all of the materials with increasing pretreatment temperature.

For CuO-1.9/H-MFI (which contains 1.9 mol of copper per mol of framework aluminum), the weight loss per copper during hydrogen reduction for the material pretreated to 473 K is consistent with the loss of one oxygen atom per copper atom, suggesting that little reaction of the copper oxide with the zeolite occurs at this pretreatment temperature. The difference between the weight loss during hydrogen reduction of the material pretreated to 473 K and the material pretreated to 973 K, 1.20 g/100 g of sample, corresponds to the loss of 1.13 oxygen atoms per framework aluminum.

For CuO-0.5/H-MFI (which contains $\frac{1}{2}$ the copper loading of CuO/H-MFI), the weight loss of 19.2 g per mole of copper is greater than 16, which is the maximum expected. This anomaly may be due to extremely small overall weight loss of 0.639 g/100 g zeolite especially when compared to the weight loss of drying which is 0.353 g/100 g zeolite.
The microbalance hydrogen reduction results for CuO/H-MFI-50 are similar to those of the other CuO/H-MFI materials, except that the decrease in the weight loss per mole of copper upon hydrogen reduction drops very quickly as the thermal treatment temperature rises.

The microbalance hydrogen reduction results for CuO/Na-MFI and Na-MFI are shown in Figure III-16. The Na-MFI base zeolite does not show any significant weight loss peaks on reduction. CuO/Na-MFI/473K shows one major peak at 525 K with a weight loss of 16.1 g per mole of copper. This result suggests that little or no reaction of the CuO with Na-MFI occurs with this pretreatment. Pretreatment to higher temperatures results in a decrease in the temperature of the reduction peak and a decrease in the weight loss per mole of copper, suggesting that the CuO reacts with Na-MFI with these pretreatments.

The derivatives of the weight curves during the reduction of pretreated Cu₂O/H-MFI is given in Figure III-17. The sample pretreated to 473 K shows two strong reduction peaks at 665 K and 710 K. A weak peak can also be observed at 490 K. Pretreatment to 773 K results in a decrease in the intensity of the peak at 490 K. Pretreatment to 973 K results in the elimination of the high temperature bands and an increase in the 490 K band. The weight loss per copper for the material pretreated to 473 K, 10.4 g per mole of copper, is slightly greater than the value of 8 g per mole of copper expected for the reduction of Cu₂O. This discrepancy may be due to the low weight change during reduction relative to the weight loss due to drying, as discussed previously for the half loaded CuO/H-MFI material. As with the other copper
Figure III-17: Microbalance hydrogen reduction derivatives a) Cu$_2$O/H-MFI/473K, b) Cu$_2$O/H-MFI/773K, and c) Cu$_2$O/H-MFI/973K.
oxide/H-MFI materials, the weight loss on reduction decreases with increasing pretreatment temperature.

**TPR Results**

The TPR results for CuO/H-MFI and H-MFI-30 are given in Figure III-18. The H-MFI-30 shows no reduction peaks. CuO/H-MFI/473K possesses two reduction peaks at similar temperatures to those observed with the microbalance. As with the microbalance hydrogen reduction results, the high temperature reduction peak is eliminated by pretreatment to 773 K or 973 K. Pretreatment to 973 K also results in a shift of the TPR peak to lower temperatures.

Quantitative results from the TPR experiments are given in Table III-6. The values in this table were computed in a similar manner to those in Table III-4. The mass to charge ratio of the reduction peak, 8.24, is very close to the value of 8 expected for the reduction of CuO. These results suggest that little or no reaction of the CuO with the H-MFI occurs with this pretreatment. Thermal treatment of the material to 773 K results in a decrease in the number of electrons transferred per copper atom, indicating that the copper ions undergo either thermal reduction to a lower oxidation state or conversion to an unreduceable species by this pretreatment. This pretreatment also results in a decrease in the mass to charge ratio of the reduction peak. Pretreatment to 973 K results in a further decrease in the number of electrons transferred per copper atom and the mass to charge ratio of the reduction peak. No reduction peaks are observed in the temperature region expected for Cu$_2$O, indicating that the CuO is not reducing to Cu$_2$O. Further, in the absence of other reactions, reduction of CuO to copper metal would not
Figure III-18: TPR results a) H-MFI/473K, b) CuO/H-MFI/473K, c) CuO/H-MFI/773K, and d) CuO/H-MFI/973K.
Table III-6. TPR Reduction Results for Zeolite/Copper Oxide Physical Mixtures.

<table>
<thead>
<tr>
<th>Material</th>
<th>Moles H Consumed /100g sample</th>
<th>e'/Cu</th>
<th>Mass/e' ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuO/H-MFI/473K</td>
<td>0.1327</td>
<td>2.00</td>
<td>8.24</td>
</tr>
<tr>
<td>CuO/H-MFI/773K</td>
<td>0.1183</td>
<td>1.78</td>
<td>6.89</td>
</tr>
<tr>
<td>CuO/H-MFI/973K</td>
<td>0.0722</td>
<td>1.09</td>
<td>5.97</td>
</tr>
<tr>
<td>CuO-0.5/H-MFI/473K</td>
<td>0.0693</td>
<td>2.08</td>
<td>9.23</td>
</tr>
<tr>
<td>CuO-0.5/H-MFI/773K</td>
<td>0.0524</td>
<td>1.58</td>
<td>8.55</td>
</tr>
<tr>
<td>CuO-0.5/H-MFI/973K</td>
<td>0.0243</td>
<td>0.73</td>
<td>7.38</td>
</tr>
<tr>
<td>CuO-1.9/H-MFI/473K</td>
<td>0.2595</td>
<td>2.03</td>
<td>7.87</td>
</tr>
<tr>
<td>CuO-1.9/H-MFI/773K</td>
<td>0.2302</td>
<td>1.80</td>
<td>7.11</td>
</tr>
<tr>
<td>CuO-1.9/H-MFI/973K</td>
<td>0.1464</td>
<td>1.15</td>
<td>5.67</td>
</tr>
<tr>
<td>CuO/H-MFI-50/473K</td>
<td>0.1154</td>
<td>1.93</td>
<td>9.22</td>
</tr>
<tr>
<td>CuO/H-MFI-50/773K</td>
<td>0.0727</td>
<td>1.22</td>
<td>2.62</td>
</tr>
<tr>
<td>CuO/H-MFI-50/973K</td>
<td>0.0541</td>
<td>0.91</td>
<td>0.99</td>
</tr>
<tr>
<td>CuO/Na-MFI/473K</td>
<td>0.1414</td>
<td>2.01</td>
<td>8.02</td>
</tr>
<tr>
<td>CuO/Na-MFI/773K</td>
<td>0.1242</td>
<td>1.76</td>
<td>7.87</td>
</tr>
<tr>
<td>CuO/Na-MFI/973K</td>
<td>0.0864</td>
<td>1.23</td>
<td>5.57</td>
</tr>
<tr>
<td>Cu₂O/H-MFI/473K</td>
<td>0.0581</td>
<td>0.87</td>
<td>11.85</td>
</tr>
<tr>
<td>Cu₂O/H-MFI/773K</td>
<td>0.0499</td>
<td>0.75</td>
<td>8.95</td>
</tr>
<tr>
<td>Cu₂O/H-MFI/973K</td>
<td>0.0403</td>
<td>0.61</td>
<td>8.36</td>
</tr>
<tr>
<td>CuO/Al₂O₃/473K</td>
<td>0.1374</td>
<td>2.11</td>
<td></td>
</tr>
<tr>
<td>CuO/Al₂O₃/773K</td>
<td>0.1248</td>
<td>1.92</td>
<td></td>
</tr>
<tr>
<td>CuO/Al₂O₃/973K</td>
<td>0.0909</td>
<td>1.40</td>
<td></td>
</tr>
</tbody>
</table>
change the mass to charge ratio of the reduction. These results suggest that the CuO reacts with the H-MFI at pretreatment temperatures of 773 K and higher.

The TPR results for CuO-1.9/H-MFI and CuO/Al₂O₃ materials are given in Figure III-19. As with the microbalance results, the high temperature reduction peak for CuO-1.9/H-MFI/473K is eliminated by pretreatment to 773 K and 973 K. Pretreatment to 973 K results in a shift of the TPR peak to lower temperatures. The pronounced shoulder on this peak suggests that there are two different copper species.

The TPR results for CuO/Al₂O₃/473K show peaks at similar temperatures to the high temperature reduction peak observed for CuO-1.9/H-MFI/473K. Pretreatment to 773 K results in the elimination of the high temperature peak and the formation of a lower temperature peak. This peak occurs at a similar temperature to the one observed for CuO-1.9/H-MFI/973K. As with CuO-1.9/H-MFI, pretreatment to 773 K and 973 K results in a decrease in the number of electrons transferred per copper atom.

CuO-0.5/H-MFI behaves qualitatively similar to the other CuO/H-MFI materials. The number of electrons transferred per copper atom for CuO-0.5/H-MFI/973K, 0.73, is significantly less than 1, indicating that the copper ions are either reducing to the metal or forming an irreducible species.

The TPR results for CuO/H-MFI-50 are also qualitatively similar to those of the other CuO/H-MFI materials, with both the number of electrons transferred per copper atom and the mass to charge ratio of the reduction peak decreasing with increasing pretreatment temperature.

The TPR results for CuO/Na-MFI and Na-MFI are given in Figure III-20. CuO/Na-MFI pretreated to 473 K consumes 2.01 electrons per copper atom and has a
Figure III-19: TPR results a) CuO-1.9/H-MFI/473K, b) CuO-1.9/H-MFI/773K, c) CuO-1.9/H-MFI/973K,
d) CuO/Al₂O₃/473K, e) CuO/Al₂O₃/773K, and f) CuO/Al₂O₃/973K.
Figure III-20: TPR results a) Na-MFI/473K, b) CuO/Na-MFI/473K, c) CuO/Na-MFI/773K, and d) CuO/Na-MFI/973K.
mass to charge ratio of 8.02 for the reduction peak. These results are consistent with little or no reaction between the CuO and Na-MFI with this pretreatment temperature. At higher pretreatment temperatures, both the number of electrons transferred per copper atom and the mass to charge ratio of the reduction peak decreases.

The TPR results for Cu₂O/H-MFI are shown in Figure III-21. The TPR peaks for Cu₂O/H-MFI occur at similar temperatures to the ones observed with the microbalance. As with those results, two high temperature peaks are observed for Cu₂O/H-MFI/473K. Cu₂O/H-MFI/773K gives an extremely broad hydrogen consumption region between 500 K and 750 K and only a low temperature reduction peak is observed for Cu₂O/H-MFI/973K.

**X-ray Diffraction Results**

The X-ray diffraction results for the pretreated CuO/H-MFI, CuO/Na-MFI, and H-MFI are given in Figure III-22. Although the signal to noise ratio is too low for quantitative comparisons, all of the CuO/H-MFI and CuO/Na-MFI materials pretreated at 473 K, 733 K, and 973 K show peaks at 35.8° and 38.6° 2θ, indicative of extra-framework CuO. These results suggest that some of the reduction peaks observed using the microbalance and TPR, even after pretreatment to 973 K, are due to the reduction of unreacted CuO. The much lower reduction temperature observed for CuO and zeolite mixtures treated to 973 K may be due to increased dispersion, and hence increased surface area, of the CuO.

**IR Spectroscopy Results**

The IR spectra of the OH stretching region for the pretreated CuO/H-MFI and H-MFI samples are given in Figure III-23. As discussed previously, the IR band at 3610
Figure III-21: TPR results a) Cu₂O/H-MFI/473K, b) Cu₂O/H-MFI/773K, and c) Cu₂O/H-MFI/973K.
Figure III-23: IR results a) H-MFI/473K, b) CuO/H-MFI/473K, c) CuO/H-MFI/773K, d) CuO/H-MFI/973K, and e) CuO-0.5/H-MFI/973K.
cm⁻¹ is usually assigned to the oxygen hydrogen stretch of the acid sites in MFI zeolite [24,26,59]. Both H-MFI and CuO/H-MFI/473K show strong absorption in this region. This band decreases in intensity with increasing prereduction temperature, suggesting that the CuO reacts with the zeolitic protons, which results in their disappearance. The 3610 cm⁻¹ band for CuO-0.5/H-MFI/973K shows a greater absorbance than the similarly treated fully loaded material. This is also consistent with the loss of protons due to reaction with CuO.

The IR results for CuO-1.9/H-MFI/973K, CuO/Na-MFI, and Na-MFI are given in Figure III-24. CuO-1.9/H-MFI/973K shows only a slight band due to zeolitic acid sites. The sodium materials do not shown any significant bands in this region.

To further investigate the influence of pretreatment temperature on the acidity of the CuO zeolite physical mixtures, pyridine adsorption experiments were performed. The IR results after pyridine adsorption are shown in Figure III-25. Previous research has assigned the IR band at 1552 cm⁻¹ to pyridine adsorbed on Bronsted acid sites, the band at 1450 cm⁻¹ to pyridine adsorbed on Lewis acid sites, and the band at 1520 cm⁻¹ to pyridine adsorbed on either type of site [61-63]. The spectrum of both H-MFI and CuO/H-MFI/473K are quite similar, which is consistent with the previous results suggesting little or no reaction between the CuO and zeolite with this pretreatment temperature. Increasing the pretreatment temperature results in a decrease in the band associated with Bronsted acid sites and an increase in the band associated with Lewis sites, which indicates that the product of the reaction of CuO with the zeolitic protons possesses Lewis acidity. Increases in Lewis acidity has been previously reported from the ion-exchange of metal cations into zeolites [61]. The CuO-1.9/H-MFI/973K
Figure III-24: IR results a) CuO-1.9/H-MFI/973K, b) Na-MFI/473K, c) CuO/Na-MFI/473K, d) CuO/Na-MFI/773K, and e) CuO/Na-MFI/973K.
spectrum is similar to that of CuO/H-MFI/973K. For the CuO-0.5/H-MFI/973K spectrum, the band associated with Bronsted sites shows a stronger absorbance and the band associated with Lewis sites show a weaker absorbance than CuO/H-MFI/973K.

The IR results in the Lewis acid site region after pyridine adsorption for Na-MFI and CuO/Na-MFI materials are given in Figure III-26. The Na-MFI possesses an absorbance peak at 1442 cm\(^{-1}\). CuO/Na-MFI/473K possesses this same peak along with a very weak shoulder at 1450 cm\(^{-1}\). The absorbance of this band increases with increasing pretreatment temperature. These results are consistent with reaction of the CuO with Na-MFI and replacement of the zeolite coordinated sodium ions with copper.

**B. Reaction Results**

**Aqueous and Vapor Ion-Exchanged Materials**

The conversions of 1-propanamine as a function of time over the acidic, aqueous ion-exchanged, and vapor ion-exchanged materials are given in Figure III-27. The conversion level of 1-propanamine at comparable times is greater over H-BEA than over H-MFI, which is probably due to both the greater framework aluminum content and larger pore volume of H-BEA. For both the MFI and BEA materials, the AIE materials are more active than the copper-free base zeolites and the VIE materials are more active than the AIE materials. These results are consistent with increasing conversion of 1-propanamine with increasing catalyst copper content. The greater conversion resulting from Cu-MFI/VIE catalysis relative to Cu-BEA/VIE is possibly due to the greater copper content of the former material.

Dipropanamine is one of the major products of the 1-propanamine reaction and its partial pressures as a function of time over various catalysts are compared in Figure...
Figure III-26: IR results after pyridine adsorption a) Na-MFI/473K, b) CuO/Na-MFI/473K, c) CuO/Na-MFI/773K, and d) CuO/Na-MFI/973K.
Figure III-27: L-Propanamine conversion results. $T=573$ K, $P_{\text{propylene}}=66.7$ mbar, using 0.100 mg catalyst.
Dipropanamine is one of the expected products of the acid catalyzed condensation of 1-propanamine [22], so it is not surprising that H-BEA, which has a higher proton content than H-MFI, gives a higher yield of dipropanamine than H-MFI. The yield of dipropanamine decreases with increasing copper content, and for the VIE materials experiences a maximum at 2.1 ksec. This maximum suggests that the dipropanamine is an intermediate undergoing further conversion over the copper-containing zeolites.

The partial pressures as a function of time for the other major product, an imine formally known as 1-propanamine, N-(1-propylidene), are shown in Figure III-29. Very little of this imine is formed over the copper-free materials. The introduction of copper into the zeolite by aqueous ion-exchange increases the yield of imine and the yield is further increased by introduction of copper using vapor ion-exchange. Although Cu-BEA/VIE has a lower loading of copper than Cu-MFI/VIE, the yield of imine is greater for the former material. This could be due to the greater activity of H-BEA to form dipropanamine than H-MFI, especially if dipropanamine is an intermediate in the formation of the imine.

The conversion of 1-propanamine over Na-MFI is shown in Figure III-30. Very little conversion is obtained with this material and the only product observed is a trace of the imine. The absence of dipropanamine production with this material supports the previous hypothesis that dipropanamine is formed by acid catalysis with the zeolitic protons for the copper-free zeolites.

The conversion of 1-propanamine over H-MFI-50 is shown in Figure III-31. As with H-MFI-30, dipropanamine is the major product, but the final partial pressure of dipropanamine for this material is 3.37 mbar, is less than the 4.70 mbar of dipropanamine.
Figure III-28: Partial pressure of dipropanamine from 1-propanamine conversion. T=573 K, P_{1-propanamine}=66.7 mbar, using 0.100 mg catalyst.
Figure III-29: Partial pressure of 1-propanamine, N-(1-propylidene) from 1-propanamine conversion. T=573 K, P_{1-propanamine}=66.7 mbar, using 0.100 mg catalyst.
Figure III-30: Conversion of 1-propanamine over Na-MFI. T=573 K, P_{1-propanamine}=66.7 mbar, using 0.100 mg catalyst.
Figure III-31: Conversion of 1-propanamine over H-MFI-50. T=573 K, P_{1-propanamine}=66.7 mbar, using 0.100 mg catalyst.
observed for H-MFI-30. The ratio of the amount of dipropanamine formed over H-MFI-30 to that formed over H-MFI-50 at 7.2 ksec, 1.39, is very close to the ratio of the number of zeolitic protons for these materials, 1.40. This result suggests that the rate of formation of dipropanamine is first order in the number of zeolitic acid sites for the MFI materials, and is consistent with previous reports indicating the one to one adsorption of 1-propanamine molecule to zeolitic protons in this temperature range [32-34] and suggests that the rate limiting step for this reaction is the reaction of a surface propanammonium cation with another 1-propanamine molecule.

The ratio of the amount of dipropanamine formed over H-BEA relative to H-MFI-30 at 7.2 ksec, 2.22, is greater than the ratio of the zeolitic protons, 1.27, Which suggests that the acid sites in H-BEA are more active catalytically than those in H-MFI. This may stem from the large pores of H-BEA and therefore lower steric inhibition of the condensation reaction, or alternatively, the easier access of the 1-propanamine reactant to the active sites in the zeolite.

The conversions of 1-propanamine over Cu-MFI-50/VIE and Cu-MFI/VIE after different prereduction temperatures are given in Figure III-32. Cu-MFI/VIE and Cu-MFI-50/VIE give similar conversions of 1-propanamine. Prereduction of Cu-MFI/VIE increases the conversion of 1-propanamine. The material prerduced at 673 K shows the highest conversion rates followed by the material prerduced at 573 K. Note that the previous TPR results suggests that we are dealing with copper metal in the prerduced materials.

The partial pressures of dipropanamine as a function of time during the reactions over the pre-reduced materials are given in Figure III-33. Both Cu-MFI/VIE and
Figure III-32: 1-Propanamine conversion results. T=573 K, P_{1-propanamine}=66.7 mbar, using 0.100 mg catalyst.
Figure III-33: Partial pressure of dimpropanamine from 1-propanamine conversion. T=573 K, P_{\text{dimpropanamine}}=66.7 mbar, using 0.100 mg catalyst.
Cu-MFI-50/VIE behave similarly, with greater amounts of dipropanamine formed over the material with the greater aluminum content. The greatest amount of dipropanamine is formed over the material prerduced at 573 K, with decreasing amounts of dipropanamine formed with increasing prereduction temperature. All of the materials give a maximum in the dipropanamine partial pressure at approximately 2.1 ksec.

The partial pressures of the imine (1-propanamine, N-(1-propylidene)) as a function of time during these reactions are given in Figure III-34. The yields of imine formed over Cu-MFI-50/VIE and Cu-MFI/VIE are similar, with slightly greater yields over the former material. All of the prerduced materials experience a maxima in the imine partial pressures at about 2.1 ksec. At this time, the maximum amount of imine is formed over the material prerduced at 673 K with the second greatest amounts formed over the material prerduced at 573 K. At longer times, the rate of imine disappearance is fastest over the material prerduced at 673 K.

The maxima in the imine partial pressures at 2.1 ksec is consistent with the further conversion of the imine to other products as the reaction progresses. The material with the greatest initial yield of imine also has the lowest final yield of this product.

The partial pressures of propanitrile as a function of time during these reactions are shown in Figure III-35. Both Cu-MFI-50/VIE and Cu-MFI/VIE give similar yields of propanitrile, with slightly greater amounts formed over the later material. Prereduction increases the yield of propanitrile over these materials. The greatest yields are obtained over the material prerduced at 673 K with the second highest yields over the material prerduced at 773 K. All of the partial pressure curves intersect the y-axis

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Figure III-34: Partial pressure of 1-propanamine, N-(1-propylidene) from 1-propanamine conversion. T=573 K, $P_{\text{1-propanamine}}=66.7$ mbar, using 0.100 mg catalyst.
Figure III-35: Partial pressure of propananitrile from 1-propanamine conversion. T=573 K, P_{\text{propanamine}}=66.7 mbar, using 0.100 mg catalyst.
with what appears to be a zero slope, suggesting that the propanitrile observed is not a primary product from the direct dehydrogenation of 1-propanamine.

The partial pressures of the last major product, 4-methylpentanitrile, as a function of time during these reactions are given in Figure III-36. With increasing prereduction temperature, the yield of 4-methylpentanitrile increases for all sampling times except the last. As with propanitrile, the intersection of the partial pressure curves with the y-axis at zero slope indicates that 4-methylpentanitrile is also not a primary product of the 1-propanamine conversion.

The effect of added hydrogen on the reaction of 1-propanamine over Cu-MFI/VIE prerduced at 673 K is shown in Figure III-37. Comparison of these results with the results for the conversion of 1-propanamine in the absence of hydrogen indicates that the yield of propanitrile increases from 9.43 mbar to 19.22 mbar by the addition of hydrogen. The yield of 4-methylpentanitrile also increases from 0.67 mbar to 1.41 mbar by hydrogen addition. The number of moles of 1-propanamine consumed during this reaction exceeds the total yield of products formed, suggesting that some of the 1-propanamine is being converted into coke, and the addition of hydrogen reverses this trend, suggesting that hydrogen assists in the removal of adsorbed species that otherwise would be converted to coke. The ratio of propanitrile to 4-methylpentanitrile changes almost imperceptibly from 14.0 to 13.6 by the addition of hydrogen, which indicates that while hydrogen does have a significant effect on the conversion of 1-propanamine, it does not significantly affect the selectivity among the nitriles. The ratio of nitriles to imines increases from 0.5 to 3.4 at 2.1 ksec with hydrogen addition.
Figure III-36: Partial pressure of 4-methylpentanitrile from 1-propanamine conversion. T=573 K, P_{1-propanamine}=66.7 mbar, using 0.100 mg catalyst.
Figure III-37: Conversion of 66.6 mbar of 1-propanamine over Cu-MFI/VIE/RED 673K with 266.6 mbar hydrogen. 

T=573 K, P_{1-propanamine}=66.7 mbar, using 0.100 mg catalyst.
The results of the conversion of 1-propanamine at 593 K, which is 20 K higher than the previous reaction temperature, are given in Figure III-38. The higher temperature increases the amount of propanitrile formed at 7.2 ksec from 9.43 mbar to 10.68 mbar and increases the amount of 4-methylpentanitrile from 0.67 mbar to 0.97 mbar. The higher temperature also decreases the ratio of propanitrile to 4-methylpentanitrile from 14.0 to 11.0, indicating that the selectivity to 4-methylpentanitrile increases with temperature.

The effect of lowering the reactant partial pressure on the course of the reaction is shown in Figure III-39. At 5.1 ksec, partial pressures of 3.59 mbar and 1.38 mbar are obtained for propanitrile and 4-methylpentanitrile, respectively. The ratio of propanitrile to 4-methylpentanitrile, 2.60, is significantly lower than the other materials, indicating that lower reactant partial pressures increase the selectivity to 4-methylpentanitrile.

The results of the conversion of dipropanamine over Cu-MFI/VIE prerduced at 673 K is given in Figure III-40. The products from the conversion of dipropanamine are similar to those from the conversion of 1-propanamine. The primary product of this reaction is the imine, 1-propanamine, N-(1-propylidene), previously mentioned, which suggests that selective dehydrogenation of dipropanamine by removal of the hydrogen atoms attached to the nitrogen and adjacent carbon is responsible for the appearance of the imine in both this reaction and the reaction of 1-propanamine.

The conversion of dipropanamine over Cu-BEA/VIE prerduced at 673 K are shown in Figure III-41. As with H-MFI, the major product of this reaction is 1-propanamine, N-(1-propylidene). Propanitrile, 4-methylpentanitrile, and 1-propanamine are also observed.
Figure III-38: Conversion of 66.6 mbar of 1-propanamine over Cu-MFI/VIE/RED 673K at 593 K using 0.100 mg catalyst.
Figure III-39: Conversion of 13.3 mbar of 1-propanamine over Cu-MFI/VIE/RED 673K. T=573 K, using 0.100 mg catalyst.
Figure III-40: Conversion of 26.7 mbar of dipropanamine over Cu-MFI/VIE/RED 673K. T=573 K, using 0.100 mg catalyst.
Figure III-41: Conversion of 26.7 mbar of dipropanamine over Cu-BEA/VIE/RED 673K. T=573 K, using 0.100 mg catalyst.
The results of the conversion of 2-propanamine are given in Figure III-42. The mass selective detector was used for these experiments and the area percent of each product is given. We should note here that area percent from the FID detector (which was used in the 1-propanamine and dipropanamine studies) is known to be a very accurate method for determination of weight percent. A similar assumption for area percent from the mass selective detector is less accurate, but acceptable for our comparative purposes. The expected acid catalyzed condensation products, diisopropanamine and ammonia, are two products of this reaction, while the major product of this reaction 2-propanamine, N-(1-methylethylidene), is the expected product of the selective dehydrogenation of diisopropanamine by removal of the hydrogen atoms attached to the nitrogen atom and an adjacent carbon.

The results of the conversion of an equimolar mixture of 1-propanamine and 2-propanamine are shown in Figure III-43. The conversion of the primary amine, 1-propanamine, is greater than that of the secondary amine, 2-propanamine, at all reaction times. The presence of both ammonia and all of the expected propylamine condensation products is consistent with the catalysis of amine condensation reactions by the zeolitic protons.

The other products observed during the conversion of the propylamine mixture are given in Figure III-44. As with the previous reactions, propanitrile is a major product. All of the imine products observed could be obtained by the dehydrogenation of the condensation products observed in Figure III-43. The 1-propanamine, N-(1-propylidene) and 2-propanamine. N-(1-methylethylidene) products could be obtained from the dehydrogenation of dipropanamine and diisopropanamine, respectively. The
Figure III-42: 2-Propanamine conversion results. T=573 K, $P_{2$-propanamine}$=66.7$ mbar, using 0.100 mg catalyst.
Figure 1: Propanamine and 2-propanamine conversion results. Using 0.100 mg catalyst.
Figure III-44: 1-Propanamine and 2-propanamine conversion results

T=573 K, P_{1\text{-propanamine}}=33.3 \text{ mbar}, P_{2\text{-propanamine}}=33.3 \text{ mbar},
using 0.100 \text{ mg catalyst}. 
2-propanamine, N-(1-propylidene) and 1-propanamine, N-(1-methylethylidene) products could be obtained from the dehydrogenation of 1-propanamine, N-1-methylethyl. All of these products are consistent with the selective dehydrogenation of the acid catalyzed condensation product by removal of the hydrogen atoms attached to the nitrogen atom and one of the adjacent carbon atoms.

The results of the conversion of methanamine over Cu-MFI/VIE PQ prerduced at 573 K are given in Figure III-45. The principal products of this reaction are consistent with the acid catalyzed condensation of the reactant. No dehydrogenated products are observed for this reaction.

The products of the reaction of dimethanamine is shown in Figure III-46. The products of this reaction are similar to those of the previous reaction, except some ethylenimine is also observed among the reaction products.

The results of the conversion of ethanamine is given in Figure III-47. The primary product at all times during the reaction is 2-ethylaziridene. The expected acid catalyzed condensation products, diethanamine and ammonia, are also observed. Acetonitrile is also produced during this reaction.

Physical Mixtures

The conversions as a function of time for the reaction of 1-propanamine over the physical mixtures are given in Figure III-48. The lowest conversions are obtained with CuO/Na-MFI. For the CuO/H-MFI materials, the conversion increases with increasing copper content. Cu2O/H-MFI gives conversion rates between that of the half and fully loaded CuO/H-MFI materials.
Figure III-45: Methanamine conversion results. $T=573 \text{ K}$, $p_{\text{Methanamine}}=66.7 \text{ mbar}$, using 0.100 mg catalyst.
Figure III-46: Dimethanamine conversion results. $T=573\, \text{K}$, $P_{\text{Dimethanamine}}=66.7\, \text{mbar}$, using 0.100 mg catalyst.
Figure III-47: Ethanamine conversion results. $T=573$ K, $P_{\text{ethanamine}}=66.7$ mbar, using 0.100 mg catalyst.
Figure III-48: 1-Propanamine conversion results. $T=573$ K, $P_{\text{prop}}=66.7$ mbar, using 0.100 mg catalyst.
The partial pressures of dipropanamine as a function of time during these reactions are given in Figure III-49. The greatest yields of dipropanamine are obtained over CuO/Na-MFI. For the CuO/H-MFI materials, the partial pressure of dipropanamine increases with decreasing copper content. With regard to dipropanamine formation, the Cu$_2$O/H-MFI behaves similar to the CuO-0.5/H-MFI (half loaded) material.

The partial pressures of 1-propanamine, N-(1-propylidene) as a function of time over several catalysts are given in Figure III-50. CuO/Na-MFI gives the lowest yield of imine. The partial pressure of the imine, 1-propanamine, N-(1-propylidene), increases with increasing copper content for CuO/H-MFI physical mixtures. With regard to imine formation, the Cu$_2$O/H-MFI behaves similar to the fully loaded CuO/H-MFI.

The partial pressures of propanitrile as a function of time during these reactions are given in Figure III-51. The partial pressure of propanitrile increases with increasing copper content for CuO/H-MFI physical mixtures, while Cu$_2$O/H-MFI gives propanitrile partial pressures between that of the half and fully loaded CuO/H-MFI materials. CuO/Na-MFI material gives an initially rapid rise in the propanitrile partial pressure followed by a very slow rise at longer times.

The partial pressures of 4-methylpentanitrile as a function of time are shown in Figure III-52. The only physical mixture to show any yield of this product was CuO-1.9/H-MFI.
Figure III-49: Partial pressure of dipropanamine from 1-propanamine conversion. \( T = 573 \) K, \( P_{\text{propanamine}} = 66.7 \) mbar, using 0.100 mg catalyst.

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Figure III-50: Partial pressure of 1-propanamine, N-(1-propylidene) from 1-propanamine conversion. T=573 K, $P_{1\text{-propanamine}}=66.7$ mbar, using 0.100 mg catalyst.
Figure III-51: Partial pressure of propanonitrile from 1-propanamine conversion. T=573 K, P_{propanamine}=66.7 mbar, using 0.100 mg catalyst.
Figure III-52: Partial pressure of 4-methylpentanitrile from 1-propanamine conversion. $T = 573$ K, $P_{\text{total}} = 66.7$ mbar, using 0.100 mg catalyst.
IV. DISCUSSION

A. Physico-Chemical Characterization.

One of the most important aspects of the research work was to gain the knowledge necessary to be able to predict the state of copper (especially the oxidation state) which exists after the copper-containing catalysts are treated by reagent gases under well-defined thermal conditions. We have used TPR, microbalance hydrogen reduction, IR of adsorbed CO and zeolitic OH bands, and X-ray diffraction to help us construct this picture. Similarities and differences exists for the basic classes of materials we have studied which include vapor ion-exchange (VIE), aqueous ion-exchange (AIE), and solid-state ion-exchange materials. We consider each of these classes in detail.

Vapor Ion-Exchanged Materials

Recall that VIE materials are prepared beginning with the high temperature deposition of CuCl on the H-zeolite followed by oxidation in dry O$_2$, which was performed in order to eliminate disproportionation of the Cu$^+$ ions caused by exposure to humid air upon exposure to the atmosphere. We therefore predict that copper exists in the 2+ oxidation state when the material is removed from the furnace. When we run TPR on Cu-MFI/VIE/473K and Cu-BEA/VIE/473K (recall that these are treated at 473 K = 200 °C where we expect only drying), we note two reduction bands at about 490 K and 610 K (see Figures III-9 and III-10) which we believe are due to the stepwise reduction process $\text{Cu}^{2+} \rightarrow \text{Cu}^+ \rightarrow \text{Cu}^0$. These individual bands in each material have similar areas and transfer approximately one electron per copper atom, which is consistent with the reduction of Cu$^{2+}$ ions to Cu$^+$ ions in the first peak and Cu$^-$ ions to
copper metal for the second. The stepwise reduction of Cu$^{2+}$ ions in hydrogen has also been previously reported [8,14,46,47,76,99,100].

CO adsorption experiments were also performed because CO selectively adsorbs on Cu$^+$ [8,44,59,70,81,82,95] and allows for verification of the assignments made for the H$_2$ TPR and microbalance hydrogen reduction peaks observed. The relatively small amounts of CO adsorbed on Cu-MFI/VIE/473K and Cu-BEA/VIE/473K as observed via microbalance and IR are consistent with the absence of significant quantities of Cu$^+$, suggesting that most of the copper ions are in the +2 oxidation state under these conditions, since Cu$^{2+}$ ions do not strongly adsorb CO [8,59,95]. In order to further elucidate the reaction occurring during the first H$_2$ TPR reduction peak, CO adsorption experiments were performed after partial hydrogen reduction at the temperature of the peak maximum observed by the H$_2$ TPR experiments. Partial hydrogen reduction of Cu-MFI/VIE/473K to 533 K (which corresponds approximately to the maximum of the first TPR peak of Cu-MFI/VIE/473K) results in a considerable increase in the CO adsorption capacity which is also consistent with a large number of copper ions existing as Cu$^+$. The presence of significant amounts of Cu$^+$ after the partial reduction is consistent with the assignment of the first H$_2$ TPR reduction peak to the hydrogen reduction of Cu$^{2+}$ to Cu$^+$. In order to verify that the CO adsorption observed after partial hydrogen reduction of Cu-MFI/VIE was due to adsorption of CO on Cu$^+$ and not due to adsorption on other sites, the IR spectrum of the materials after partial reduction and CO adsorption was obtained. The IR bands at 2175 cm$^{-1}$, 2146 cm$^{-1}$ and 2137 cm$^{-1}$ which are observed when CO is adsorbed on partially reduced Cu-MFI/VIE/473K are consistent with the presence of significant quantities of zeolite-bound Cu$^+$ ions [95]. No other
absorbance bands are observed, indicating that all of the CO adsorption is due to adsorption on Cu⁺.

A comparison of the H₂ TPR and microbalance hydrogen reduction process assist in determining the stoichiometry of the copper species undergoing reduction. Even though the reaction which takes place is identical for both experiments, hydrogen consumption is measured by TPR while weight loss from the catalysts is recorded by the microbalance reductions, so that reactions which produce a volatile product such as Z'[CuOH]⁺ + ½ H₂ → Z'Cu⁺ + H₂O are recorded by both TPR and microbalance experiments. Experiments which do not result in a volatile product such as Z'Cu²⁺Z⁻ + H₂ → 2 Z'H⁺ + Cu⁰ have almost no effect on the microbalance reduction experiments due to the low molecular weight of H₂, but are easily observed by the TPR apparatus. By ratioing the microbalance weight loss to the hydrogen consumption, an average molecular weight of the volatile product can be obtained. The mass to charge ratios (where ½ H₂ consumption = 1 e⁻) of 18.5 and 16.1 for the first and second reduction peaks for the Cu-MFI/VIE/473K and the mass to charge ratios of 19.6 and 14.4 Cu-BEA/VIE/473K are consistent with the loss of a coordinated water or a hydroxide group for each reduction step. Further, the IR data for Cu-MFI/VIE/473K shows OH bands previously attributed to bridging copper hydroxyl dimers and water coordinated to them [64,65]. Oxygen bridges between copper atoms have also been observed in copper exchanged mordenite by single crystal X-ray diffraction experiments [104]. These results suggest that most of the copper atoms in Cu-MFI/VIE/473K and Cu-BEA/VIE/473K (recalling again that these materials are treated in O₂ after the CuCl exchange) exist as dimers like those shown in Fig. IV-1a, which are similar to dimers...
Figure IV-1: Chemical Structure of a) copper hydroxyl dimer b) isolated copper hydroxyl ion.
proposed by Kuroda et al. in mordenite [64,65]. Since it is unlikely that all of the copper hydroxyl species are sufficiently close to form dimers, isolated copper hydroxyl ions like in Fig. IV-1b are likely present as well. The reduction of these isolated copper hydroxyl species may be the origin of the shoulder at 463 K observed in the hydrogen TPR spectrum for the CuCl vapor ion-exchange materials. The number of hydrogen atoms consumed by Cu-MFI/VIE/473K in both the first and second peak is fairly close to the number of protons present in the zeolite, suggesting that nearly all of the zeolite ion exchange sites are occupied by one copper ion, and is also consistent with the weakness of the 3610 cm\(^{-1}\) IR band associated with zeolitic protons. The amount of hydrogen consumed by the reduction of copper in Cu-BEA/VIE/473K is less than the initial number of protons in the H-BEA base, which may be the result of dealumination of the zeolite caused by the high temperatures and/or the presence of HCl which is a product of the vapor ion-exchange process. The loss of crystallinity of this material relative to the base H-BEA as indicated by X-ray diffraction also supports this suggestion.

The results presented for the vapor ion-exchanged materials pretreated in vacuum or an inert atmosphere to 473 K suggest that the first H\(_2\) TPR peak is due to the hydrogen reduction of copper hydroxyl ions and copper hydroxyl dimers to (Cu-H\(_2\)O)\(^{+}\). The second H\(_2\) TPR reduction peak corresponds to reduction of these species to Cu\(^{0}\) and H\(^{+}\). The weight loss observed during microbalance hydrogen reduction is likely due to loss of the coordinated water molecule.

When Cu-MFI/VIE and Cu-BEA/VIE are treated in vacuum or an inert atmosphere at 773 K instead of 473 K, we believe that the restoration of most of the Cu\(^{+}\) occurs. The relative decrease in the amount of hydrogen consumed during hydrogen
reduction after pretreatment of Cu-MFI/VIE and Cu-BEA/VIE to 773 K rather than 473 K is consistent with the thermal reduction of the Cu^{2+} ions to Cu^{+} ions by this pretreatment. Further, the reduction temperature of the major H\textsubscript{2} TPR peak after pretreatment of the vapor ion-exchanged MFI to 773 K is very close to previously reported temperatures for the hydrogen reduction of zeolite coordinated Cu^{+} ions [59,100]. The 2175 cm\textsuperscript{-1}, 2146 cm\textsuperscript{-1} and 2137 cm\textsuperscript{-1} IR bands present after exposure of the Cu-MFI/VIE/773K to CO is also consistent with this hypothesis. Both Cu-MFI/VIE/773K and Cu-BEA/VIE/773K possess weight loss peaks on reduction at approximately 602 K. Heating Cu-MFI/VIE/773K in CO to 773 K does not significantly affect this weight loss peak. The general assumption that oxygen containing copper species are reduced by heating in CO [100] suggests that the weight loss peak is not due to loss of oxygen, and is probably due to reduction of small amounts of [CuCl]\textsuperscript{2-} ions produced by reaction of the zeolite with the residual CuCl which was observed by XRD.

The reaction pathway leading to the formation of the copper hydroxyl ions and dimers in the CuCl VIE materials likely proceeds through several steps. Previous investigations have shown that CuCl vapor reacts with zeolitic protons to form HCl and Cu\textsuperscript{+} ions coordinated to zeolite ion-exchange sites [24-27], which we also expect in the first step of the formation process for the VIE materials. In the second step, which is oxidation at 373 K, we expect that [Cu-O-Cu]\textsuperscript{2+} oxonium ions are formed, because previous reports [6,75,76,88] have shown that this reaction occurs. Other investigations have demonstrated that [Cu-O-Cu]\textsuperscript{2+} ions can react with water to form [Cu(OH)]\textsuperscript{+} ions [75] which we expect happens when the catalyst is removed from the furnace and exposed to humid air in the final step of the formation process. The unique feature of
these materials is that they can be taken off the shelf and converted back to materials with very high a Cu* ion content by simple thermal treatment in vacuum or an inert atmosphere at 773 K or by partial hydrogen reduction.

The active sites for the catalytic decomposition of NO to O2 and N2 over Cu zeolites have been proposed to be adjacent Cu*Z* that can be oxidized by NO to form oxonium ions, Z*[CuOCu]*Z*, which thermally decompose back to Cu* with the release of O2 [5]. The large concentration of copper hydroxyl dimers in the vapor ion-exchanged materials indicates that in these materials, most of the Cu*Z* ions are sufficiently close to form the necessary oxygen bridges for this reaction. There does not appear to be any previous reports in the literature of the observation of copper hydroxyl dimer IR absorption bands in copper MFI prepared by aqueous ion-exchange, suggesting that the concentration of active sites in previous studies is significantly less than in materials prepared by vapor ion-exchange. Although the vapor ion-exchanged materials have not been tested for the catalytic decomposition of NO, it would be expected that these materials would be much more active for this reaction than any previously reported material and that the potential of copper-containing MFI for the NO decomposition reaction is greater than has been previously thought.

Aqueous Ion-Exchanged Materials

Aqueous ion-exchanged materials have also been investigated in this study both to investigate the mechanism of the aqueous ion-exchange procedure and the nature of copper introduced into the zeolite by this process. This study indicates that the copper exchange occurs according to the previously proposed mechanism Cu**(H2O)x + 2 Na*Z* → Z*Cu**(H2O)xZ* + 2 Na*, which is followed by Z*Cu**(H2O)xZ* → [Cu(OH)]*Z* + H*Z*. 

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+ (H₂O)ₓ₋₁ on drying [47,60,72,76,77,80]. According to this mechanism, ion-exchange by this process cannot introduce more than 0.5 Cu²⁺ per framework aluminum, which is consistent with the copper content of 0.41 and 0.29 Cu²⁺ per framework aluminum for the aqueous ion-exchanged MFI and BEA, respectively. The restoration of zeolitic protons, observed via IR (Figure III-13), into the Na-MFI by the copper ion-exchange possess is also consistent with this mechanism. The 3448 cm⁻¹ and 3360 cm⁻¹ - 3319 cm⁻¹ IR absorbance bands attributed to copper hydroxyl dimers are not observed with the aqueous ion-exchanged materials, which is expected since the formation of the copper hydroxyl dimer requires the presence of adjacent copper hydroxyl ions. The aqueous ion-exchange mechanism, Z'Cu²⁺(H₂O)ₓZ' → [Cu(OH)]⁺Z' + H⁺Z' + (H₂O)ₓ₋₁, indicates that the closest ion-exchange site to each copper hydroxyl ion is occupied by a hydrogen ion, and not another copper hydroxyl ion with which it can form a dimer.

The H₂ TPR and microbalance hydrogen reduction results also suggest that the copper ions exist as copper hydroxyl ions. As expected, Cu-BEA/AIE/473K behaves similar to Cu-BEA/VIE/473K, only with a lower overall copper concentration. The similar hydrogen consumption of the first and second TPR peaks and the mass to charge ratios suggest that this material is also composed predominantly of copper hydroxyl ions and dimers. As with the CuCl VIE materials, these ions thermally reduce to Cu⁻ ions on heating to 773 K.

The Cu-MFI/AIE/473K is more complicated than the other materials. The hydrogen consumption corresponding to the low temperature TPR peak is significantly less than that of the second, which is not consistent with Cu²⁺ → Cu⁺ → Cu⁰. Furthermore, two weight loss peaks are observed via microbalance in the high temperature region and
the mass to charge ratio in this reduction region, 9.31, is much less than the ratios of 14.4-19.6 which we have attributed to the loss of coordinated water and hydroxyl groups for the other materials. These differences can be resolved with the following arguments. Previous investigations have indicated that thermal reduction of Cu$^{2+}$ ions in aqueous ion-exchanged MFI begins at temperatures slightly greater than 373 K [8,44]. Also, the reduction temperature of the first high temperature peak observed on the microbalance, 589 K, is fairly close to the reduction temperature of bulk Cu$_2$O, 602 K. Furthermore, the mass to charge ratio for Cu$_2$O + H$_2$ → 2 Cu$^0$ + H$_2$O is 8. Therefore, we believe that the first high temperature reduction band is due to reduction of dispersed Cu$_2$O and that the low temperature band and the second high temperature band are due to the reduction of copper hydroxyl ions. Previous investigations have indicated that during the thermal reduction of Cu$^{2+}$ ions to Cu$^+$ ions in Cu$^{2+}$ ion-exchanged MFI, the EPR signal associated with zeolite coordinated Cu$^{2+}$ ions disappears prior to the formation of photoluminescence bands associated with zeolite coordinated Cu$^+$ ions [105]. These results and the results published in this work are consistent with the thermal reduction of at least some [Cu(OH)]$^+$ ions to Cu$_2$O (which serves as the precursor to zeolite coordinated Cu$^+$), oxygen, water and zeolitic protons in Cu-MFI/AIE/473K. Oxygen desorption from ion-exchanged Cu-MFI materials during heating has been previously reported [8,70]. Cu$_2$O (which is not found in Cu-MFI/AIE/773K) may then react with zeolitic protons to form zeolite coordinated Cu$^+$ ions and water. The lower stability of the [Cu(OH)]$^+$ ions in MFI relative to BEA may be due to the lower pore volume of MFI, and the absence of significant reduction of
[Cu(OH)]$^+$ to Cu$_2$O in the Cu-MFI/VIE material may be due to the greater stability of the dimer (Fig. IV-1a) with respect to the isolated copper hydroxyl ions (Fig. IV-1a).

Another reason that we prepared and characterized the aqueous ion-exchanged materials was to allow for comparison of these materials, which are the common materials reported in the open literature, to the vapor ion-exchanged and solid-state ion-exchanged materials, which was really the focus of much of our work. The results of this study indicate that the VIE materials are quite similar to the AIE materials, except that the VIE materials possess much greater copper loadings. The similar reduction/oxidation properties of these materials and the ability of copper aqueous ion-exchanged materials to catalyze the decomposition of NO and the selective catalytic reduction of NO further suggests that the vapor ion-exchanged materials would also be active for this reaction.

**Physical Mixtures**

The solid-state ion-exchange of copper oxides with MFI was investigated both to determine the usefulness of this procedure for the synthesis of copper-containing zeolites and because most copper aqueous ion-exchanged zeolites active for the catalytic decomposition of NO and the selective catalytic reduction of NO contain extraframework CuO [20,47,72]. Also, previous studies at LSU had not conclusively demonstrated the state of copper in these materials [22,101,102]. The results of this study are consistent with two different reactions occurring when a physical mixture of CuO and H-MFI is heated in an inert atmosphere. One of these reactions is that of CuO with the zeolite according to CuO + 2 H$^+$ $\rightarrow$ Z$^+$Cu$^{2+}$Z$^-$ + H$_2$O [19,47,58] and the other is the reduction of CuO to the metal according to CuO $\rightleftharpoons$ Cu + $\frac{1}{2}$O$_2$. 
In agreement with previous investigations [56,58], the results of this study are consistent with the exchange of copper ions with protons during the high temperature thermal treatment of a physical mixture of CuO with acidic zeolite. The decrease in the absorbance of the IR band at 3610 cm\(^{-1}\) associated with zeolitic protons upon heating is consistent with the loss of protons due to reaction of them with the CuO. The decrease in the intensity of this band for the CuO/H-MFI materials increases with the copper content, which is consistent with the above mechanism. As expected, the IR absorbance band attributed to pyridine adsorbed on zeolite Bronsted acid sites after pretreatment of the samples and adsorption of pyridine behaves similar to the IR absorbance band attributed to zeolitic protons. The IR absorbance band attributed to pyridine adsorbed on Lewis acid sites increases as the band associated with Bronsted sites decreases. This is also consistent with the exchange of zeolitic protons with copper ions since the exchange of protons with metal cations in zeolites is generally observed to increase the Lewis acidity of the zeolite [61-63].

The microbalance hydrogen reduction and H\(_2\) TPR results are also consistent with the reaction of CuO with H-MFI when pretreated to 773 K or higher. The results for CuO/H-MFI-50/973K indicates that during the hydrogen reduction, 0.91 electrons are transferred per copper atom and is accompanied by a weight loss of 0.9 g per mole of copper. The very low weight loss on reduction indicates that contrary to previous proposals [56,58], very little extraframework oxygen is associated with the zeolite coordinated copper prepared by the solid-state ion-exchange process. Since CuO/H-MFI-50 initially contained one copper atom per zeolite ion-exchange site, the reduction results are consistent with either all of the copper existing as Z\('Cu\(^{+}\) or half of
the copper existing as $Z^+Cu^{2+}Z'$ and the other half existing as a species that does not reduce at 923 K in $H_2$, such as copper metal. Both of these possibilities would give hydrogen reduction results indicating the consumption of one electron per copper and negligible change in the sample weight. The temperature at which the reduction occurs during $H_2$ TPR of CuO/H-MFI-50/973K, approximately 450 K, is significantly lower than the 640 K reduction temperature previously attributed to the reduction of $Z^+Cu^-$ in both this work and previous investigations [47,100]. This result supports the hypothesis that half the copper ions exist as $Z^+Cu^{2+}Z'$. Unlike the $Cu^{2+}$ ions we find in the AIE and VIE materials (which contained extraframework oxygen), the hydrogen reduction results of the physical mixtures suggest that the $Z^+Cu^{2+}Z'$ ions reduce directly to the metal and do not undergo stepwise reduction through $Cu^-$ ions.

With increasing pretreatment temperature, the number of electrons transferred per copper atom decreases for all of the CuO and H-MFI physical mixtures and for CuO/Al$_2$O$_3$. These results indicate that the $Cu^{2+}$ ions, initially present as CuO, either undergo reduction to $Cu^-$ ions or are converted into an unreducible species such as copper metal. The 0.73 electrons transferred per copper atom for CuO-0.5/H-MFI/973K is significantly less than the value of 1.0 expected for conversion of the $Cu^{2+}$ ions to $Cu^-$ ions, which again suggests that the $Cu^{2+}$ ions are converted to an unreducible species such as copper metal. The decrease in the number of electrons transferred per copper atom with increasing pretreatment temperature for CuO/Al$_2$O$_3$ indicates that zeolitic protons are not necessary for the formation of the unreducible species. The number of electrons transferred per copper atom decreases with decreasing initial CuO content, which is consistent with the reversible reaction CuO $\rightleftharpoons Cu + \frac{1}{2} O_2$. 

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Traces of oxygen desorbed by the thermal reduction of CuO and not efficiently swept away with carrier gas would inhibit the further reduction of the CuO and the materials with the lower initial CuO content could be expected to yield greater fractional conversions of CuO if lower oxygen partial pressures remain in the reactor. A decrease in the number of electrons transferred per copper atom has also been observed after prolonged exposure of copper exchanged MFI to reactant during the selective catalytic reduction of NO [20]. To explain this, Yan et al. proposed that the copper atoms in the zeolite could react with extraframework alumina to form copper aluminates [20]. Their H$_2$ TPR investigations suggested that copper aluminates are extremely difficult to reduce and do not give well defined H$_2$ TPR peaks. Therefore, some of the decrease in the number of electrons transferred per copper atom observed during thermal treatment of the CuO/H-MFI physical mixtures may also be due to formation of copper aluminates. However, we should point out that we have had many difficulties learning to obtain reproducible results using mechanical mixtures of CuO and H-MFI. The results we mention here are those that are obtained under the cleanest conditions resulting from meticulous exclusion of water and O$_2$ from our experiments. Previous studies [22,101,102] may well have produced a different distribution of Cu$^{2+}$, Cu$^+$, and Cu$^0$.

The results of this study also indicate that CuO reacts with Na-MFI when thermally treated. After the thermal treatment process, as with the CuO and H-MFI physical mixtures, the microbalance weight loss, number of electrons transferred per copper atom, and the mass to charge ratio occurring upon hydrogen reduction decreases with increasing treatment temperature. The adsorbed pyridine IR results performed after thermal treatment of CuO/Na-MFI suggest the exchange of Na$^+$ with Cu$^{2+}$, possibly by
CuO + 2 Na⁺ → Z′Cu²⁺Z⁺ + Na₂O. A pyridine IR absorbance band at 1442 cm⁻¹ observed on Na-MFI and all of the thermally treated CuO/Na-MFI materials is probably due to pyridine adsorbed on zeolite bound Na⁺ [61-63]. A pyridine IR absorbance at 1449 cm⁻¹ is only present for the thermally treated CuO/Na-MFI materials and its intensity increases with increasing treatment temperature. Frequency shifts in IR bands associated with Lewis acid sites have previously been reported to occur upon substitution of a zeolitic cation [63], so we postulate that the band we observe is due to the exchange of copper ions for Na⁺. As with the CuO/H-MFI and CuO/Al₂O₃ materials, the number of electrons transferred per copper atom decreases with increasing treatment temperature, which is probably due to thermal reduction of the CuO to copper metal, but could be due to the formation of copper aluminates which are not reducible at high temperatures in hydrogen. However, we have found no evidence of a crystal phase with X-ray diffraction.

Cu₂O/H-MFI/473K and Cu₂O/H-MFI/773K gives microbalance reduction and H₂ TPR results with very broad ill defined peaks, which suggests that multiple species of copper are present in these materials. This is could be due to disproportionation of the Cu⁺ ions (2 Cu⁺ → Cu²⁺ + Cu⁰) by water desorbing from the zeolite on drying. Zeolitic protons may assist in the disproportionation process by assisting in the dissolution of the Cu₂O. As discussed in the literature review, aqueous ion-exchange using Cu⁺ salts is not possible because the disproportionation of Cu⁺ occurs. Solid-state ion-exchange using Cu₂O is of similarly limited utility.

Future studies could be conducted to investigate solid-state ion-exchange in a chemically reactive environment. In a few exploratory experiments, we have found some
evidence indicating that Cu$^+$Z$^-$ forms during high temperature thermal treatment of physical mixtures of CuO and H-MFI in the presence of water vapor which might explain why previous studies [22,101,102] found evidence for Cu$^+$Z$^-$ formation. Copper chemistry we have observed in this study suggests the following sequence may be occurring:

$$\text{CuO} + 2 \text{H}^+\text{Z}^- \rightarrow \text{Z}:\text{Cu}^{\text{II}}\text{Z}^- + \text{H}_2\text{O}$$

$$\text{Z}:\text{Cu}^{\text{II}}\text{Z}^- + \text{H}_2\text{O} \rightarrow [\text{Cu(OH)}]^\text{+}\text{Z}^- + \text{H}^+\text{Z}^-$$

$$[\text{Cu(OH)}]^\text{+}\text{Z}^- \rightarrow \text{Cu}^+\text{Z}^- + \frac{1}{4} \text{O}_2 + \frac{1}{2} \text{H}_2\text{O}$$

Regeneration of protons during the second step of the proposed reaction sequence above allows for complete exchange of zeolitic protons for Cu$^+$ in theory. A reaction similar to the one above may occur with copper(II) acetate exchanged MFI (which has been shown to possess extraframework CuO) during the selective catalytic reduction of NO. H$_2$ TPR results published by Yan et al. for copper exchanged MFI after 19.5 hr of reaction [20] are quite similar to TPR spectra observed for materials we have found to contain copper hydroxyl dimers. In their study [20], dimers may result from reaction of the zeolite with the extraframework CuO according to a mechanism similar to the one shown above.

**B. Catalytic Reaction Studies**

In agreement with previous studies, the results in this study suggest that the zeolite acid sites are active for the catalytic condensation of primary amines to secondary amines and ammonia [22]. As mentioned in the results section of this work, the reaction is first order with respect to zeolitic proton content, suggesting that the rate limiting step for this reaction is the reaction of a surface propanammonium cation with a
1-propanamine molecule. The hypothesis that protons are the active sites for the condensation reactions is further supported by the suppression of dipropanamine formation during the conversion of 1-propanamine over Na-MFI, which contains few protons.

The results in Figure III-6 indicate that 1-propanamine is a stronger reducing agent than hydrogen for the reduction of CuO and Cu2O, which suggests that 1-propanamine is capable of reducing all copper ions in the zeolite as well. Therefore we believe that the active catalytic material under 1-propanamine reaction conditions probably consists of zeolitic protons and dispersed copper metal. For the CuO/H-MFI physical mixtures, the partial pressure of dehydrogenated products (primarily the imine, 1-propanamine, N-(1-propylidene)) increases while the partial pressure of dipropanamine decreases with increasing copper loading. This suggests that copper is the active site for the formation of the imine and that the imine is formed from dipropanamine, which in turn is produced by the condensation of 1-propanamine over protons. The chemical structure of the imine also suggests that it is formed by the selective dehydrogenation of dipropanamine by the removal of the hydrogen atoms attached to the nitrogen and an adjacent carbon.

The increase in the conversion rates of 1-propanamine with increasing copper content, which we observed for the CuO/H-MFI physical mixtures, could be due to the lower dipropanamine partial pressures which are observed over the materials with higher copper loadings. Dipropanamine, which is a stronger base than 1-propanamine, may more strongly adsorb on the protons and inhibit further condensation reactions.

The CuO/H-MFI materials with the highest copper loadings also give yields of propanitrile and 4-methylpentanitrile. The appearance of 4-methylpentanitrile and
Propanitrile is possibly due to further dehydrogenation of the imine. This hypothesis is supported by the observed maxima in the imine partial pressures around 3.5 ksec for the reactions which produce nitriles as products. CuO-1.9/H-MFI/773K, which gives the greatest yield of nitriles, also shows the greatest decrease in imine partial pressure after 3.5 ksec (Figure III-50).

Conversion of 1-propanamine over Cu₂O/H-MFI/773K gives results between that of the CuO-0.5/H-MFI/773K and CuO/H-MFI/773K, which is consistent with reduction of the copper ions in this material by the 1-propanamine reactant and the formation of dispersed copper metal and zeolitic protons. The lower conversions obtained over Cu₂O/H-MFI/773K relative to CuO/H-MFI/773K, which has a similar copper loading, could be due to differences in the surface areas of the dispersed copper metal.

Conversion of 1-propanamine over CuO/Na-MFI/773K is not unexpected due to the results which indicated that copper ions are exchanged for Na⁺ zeolitic cations. Reduction of the zeolite coordinated copper ions by the reactant could then generate copper metal and zeolitic protons. Since the results in Figure III-26 indicate that not all of the sodium ions were exchanged for copper ions, the material (after reduction under reaction conditions) would possess fewer zeolitic protons than the other materials prepared as physical mixtures and would be expected to give lower conversions of 1-propanamine, which has been observed.

A similar trend is also observed with the AIE and VIE materials. The vapor ion-exchanged materials are more active for the conversion of 1-propanamine and the formation of imine than the aqueous ion-exchanged materials, which is likely due to the greater copper loadings of the vapor ion-exchanged materials relative the aqueous...
ion-exchanged materials. The greatest partial pressure of imine obtained during the reaction catalyzed by Cu-MFI/VIE/773K is 3.9 mbar compared to 2.8 mbar observed for CuO/H-MFI/773K, which has a very similar copper content. This difference is probably due to the greater dispersion of copper on the material prepared by vapor ion-exchange relative to the material prepared by solid-state ion-exchange. In the absence of surface diffusion and sintering of the copper metal produced during reduction of the copper ions by the 1-propanamine reactant, the copper would be mono-atomically dispersed in the VIE and AIE materials.

The most catalytically active materials for the formation of dehydrogenated products (imines and nitriles) are the prereduced zeolites prepared by vapor ion-exchange (VIE). The TPR results in Figure III-9 for Cu-MFI/VIE/773K suggest that prereduction of this material at 573 K results in complete reduction of copper to the metal by this pretreatment. The reduction is also expected to restore zeolitic protons. The greatest yields of nitriles from the VIE materials are obtained over the material prereduced at 673 K. Since characterization studies predict that all of the copper ions in these materials have been reduced to the metal by the reduction step, the differences in yields between the materials reduced at 573 K, 673 K, and 773 K likely arises from differences in the dispersion of the copper metal. Because the surface mobility of metal particles on a support generally increases with temperature, it is likely the size of the copper metal crystallites in the VIE materials increases with increased prereduction temperature due to sintering [99]. The catalytic testing results suggest that two or more copper atoms are required for extensive dehydrogenation which results in the formation of nitriles. Accordingly, a material with 100% dispersion of copper atoms that are
geometrically isolated would be inactive for the formation of nitriles. Although the material prereduced at 573 K probably has a greater copper surface area than the material prereduced at 673 K, the activity of the former for the formation of nitriles is lower, possibly due to the lower concentration of adjacent copper atoms in that material. The decrease in the activity for nitrile formation when the prereduction is performed at 773 K is likely due to a loss of copper surface area via formation of larger clusters.

Hydrogen addition decreases the amount of 1-propanamine converted to coke and increases the yields of nitriles, suggesting that adsorbed nitriles may serve as coke precursors on these catalysts. The hydrogen may react with the coke formed from the nitriles and reverse the coking reaction.

The conversion of dipropanamine over prereduced VIE materials (MFI and BEA based) gives products similar to those observed from the conversion of 1-propanamine. The primary product of this reaction is the imine (1-propanamine, N-(1-propylidene)) which is consistent with the previously proposed mechanism of 1-propanamine condensation to dipropanamine over the zeolitic protons followed by the selective dehydrogenation of dipropanamine through the removal of the hydrogen atoms attached to the nitrogen and an adjacent carbon.

The results of the conversion of 2-propanamine are also consistent with this mechanism. The expected acid catalyzed condensation product of 2-propanamine, diisopropanamine, is observed during this reaction, and the major product of the reaction is, 2-propanamine, N-(1-methylethylidene), the expected imine. As with the imine formed from 1-propanamine, this imine has a structure suggesting it is formed from the selective
dehydrogenation of the diisopropanamine by removal of the hydrogen atoms attached to the nitrogen and an adjacent carbon.

Similarly, the observed reaction products for a mixture of 1-propanamine and 2-propanamine are also in agreement with this mechanism. A greater conversion rate of the primary amine, 1-propanamine, is observed relative to the secondary amine, 2-propanamine, which is consistent with the reaction of a propanammonium cation with another propanamine molecule by a S_N2 (bimolecular nucleophilic substitution) reaction. S_N2 reactions generally proceed faster when the electrophilic reactant is primary rather than secondary due to the decreased steric hindrance of the attack on the antibonding orbital of the leaving group on the electrophilic reactant by the nucleophilic reactant. The expected products of the self condensation reaction, dipropanamine and diisopropylamine are observed as is the expected cross condensation product, 1-propanamine, N-1-methylethyl. The formation of the imines 1-propanamine, N-(1-propylidene) and 2-propanamine, N-(1-methylene) from dipropanamine and diisopropanamine, respectively, were discussed previously. The asymmetric structure of the cross condensation product, 1-propanamine, N-1-methylethyl, is expected to give two possible imines, 1-propanamine, N-(1-methylene) and 2-propanamine, N-(1-propylidene), which are indeed observed.

The reactions of the lighter amines, dimethylamine and ethylamine, are more complex than those of the propylamines. While ethylenimine and 2-ethylaziridine are isomers of the expected products of these reactions, they are structurally different from the expected products. This may be due to lower stability of the low molecular weight imines which results in a rearrangement to the nitrogen bridged compounds observed.
V. CONCLUSIONS AND RECOMMENDATIONS

A. Conclusions

The conclusions from the study of the various methods of exchanging zeolites with copper and the reactions of light amines over these materials are categorized separately and a few recommendations are suggested for further studies.

**Aqueous Ion-Exchanged Materials**

1. The results suggest that the copper ions in the aqueous ion-exchanged materials exist primarily as copper hydroxyl ions, \([\text{Cu(OH)}]^+Z^-'\).

2. The copper hydroxyl ions arise from the relatively large distances between zeolite ion-exchange sites, which favors the reaction \(Z^-'\text{Cu}^{2+}(\text{H}_2\text{O})_xZ' \rightarrow [\text{Cu(OH)}]^+Z^- + \text{H}^+Z^- + (\text{H}_2\text{O})_{x-1}\).

3. The copper hydroxyl ions undergo reduction during heating in hydrogen according to the stepwise process \(\text{Cu}^{2+} \rightarrow \text{Cu}^+ \rightarrow \text{Cu}^0\).

4. The copper hydroxyl ions thermally reduce on heating to 773 K in an inert atmosphere to \(\text{Cu}^+Z^-\), oxygen, and water.

**Vapor Ion-Exchanged Materials**

1. In agreement with previous studies [24-27], exposure of an acidic zeolite to CuCl vapor results in the reaction \(\text{CuCl} + \text{H}^+Z^- \rightarrow \text{Cu}^+Z^- + \text{HCl}\).

2. The \(\text{Cu}^+Z^-\) ions can be oxidized with oxygen at 373 K to form oxonium ions according to the reaction \(2\text{Cu}^+Z^- + \frac{1}{2}\text{O}_2 \rightarrow Z'[\text{CuOCu}]^{2+}Z^-\).
3. The oxonium ions are unstable in the presence of air due to their reaction with water to form copper hydroxyl ions according to the reaction $Z'[CuOCu]^2^+Z^- + H_2O \rightarrow 2 [Cu(OH)]^Z^-$.

4. The close proximity of the copper hydroxyl ions to each other induces the formation of hydroxyl bridged dimers, which give strong IR absorbance bands at 3448 cm$^{-1}$ and 3360 cm$^{-1}$ - 3319 cm$^{-1}$. These bands have only been observed previously in a copper exchanged mordenite [64,65] with a much high concentration of ion-exchange sites. For those materials, the absorbance of the copper hydroxyl dimer bands was less than the absorbance of the zeolitic proton bands, indicating that much higher copper exchange levels were achieved in this study.

5. The reduction behavior of the copper hydroxyl dimers in the VIE materials is similar to that of the copper hydroxide ions in the aqueous ion-exchanged materials. The copper hydroxyl dimers thermally reduce on heating to 773 K in an inert atmosphere to $Cu^Z^-$, oxygen, and water and undergo stepwise reduction during heating in hydrogen.

**Solid-State Ion-Exchanged Materials**

1. CuO reacts with acidic MFI according to $CuO + 2 H^Z^- \rightarrow Z'Cu^2^+Z^- + H_2O$ on heating to high temperatures in an inert atmosphere.

2. Unlike zeolite bound $Cu^{2^+}$ with extralattice ligands, isolated $Cu^{2^+}$ ions ($Z'Cu^{2^+}Z^-$), do not undergo thermal reduction to $Cu^Z^-$ ions and are reduced directly to the metal when heated in hydrogen.

3. Some of the $Cu^{2^+}$ ions initially present in the CuO undergo conversion to an irreducible species such as copper metal or copper aluminates.
4. CuO reacts with sodium exchanged MFI according to CuO + 2 Na"Z' —► ZCu2"Z' + Na2O on heating to high temperatures in an inert atmosphere.

5. Heating a physical mixture of Cu2O and an acidic zeolite causes the disproportionation of some of the Cu" to Cu2" and Cu°, which limits this usefulness of this method for copper-containing zeolite synthesis.

Reactions of Amines over Copper-containing Zeolites

1. Under the reaction conditions used in this study, the copper ions in the copper-containing zeolites are reduced to the metal with restoration of the zeolitic acid sites.

2. The active catalyst operates by a bifunctional mechanism. The zeolite acid sites catalyze the condensation of the primary amine feed to secondary amines and ammonia. Imines are formed from the secondary amines by the selective removal of hydrogen atoms attached to the nitrogen and an adjacent carbon by the dispersed copper metal. The imines are further dehydrogenated to nitriles when sufficiently large copper clusters are present.

3. VIE materials have the greatest activity per mole of copper due the very high dispersion of copper metal, which in the absence of sintering, would be dispersed as isolated copper atoms after reduction of these materials. Mild thermal sintering of the catalyst during reduction increases the yields of nitriles due to the formation of larger copper clusters, but extensive sintering reduces the catalyst activity due to loss of copper surface area.
B. Recommendations for Future Investigations

The following recommendations for future investigations are provided which may lead to a further understanding of the chemistry of copper ions in zeolites and the usefulness of these materials for catalytic reactions.

1. Due to the high degree of exchange of copper for zeolitic protons, it is expected that the VIE materials would be more active for the catalytic decomposition of NO than previously reported copper exchange zeolites, and these materials could be investigated for use as catalysts for that reaction.

2. Previous investigators have suggested that zeolitic protons are necessary for the activation of the hydrocarbon in the selective catalytic reduction of NO [19]. The very low proton content of the VIE materials would allow for the testing of this hypothesis.

3. Further investigations could be conducted to determine whether or not the vapor ion-exchange procedure can be simplified. A physical mixture of the zeolite with CuCl was not used due to the disproportionation of Cu\(^+\) during heating of the Cu\(_2\)O and H-MFI physical mixture. It is, however, possible that CuCl is more stable with respect to disproportionation than Cu\(_2\)O. Further, if oxidation of the Cu\(^+\) in CuCl exchanged zeolites by oxygen in air at room temperature is significantly faster than disproportionation of Cu\(^+\) by water adsorbed from air, then the oxidation step used in this work may not be necessary.

4. The solid-state ion-exchange of CuO with acidic zeolites in chemically reactive atmospheres, such as oxygen and water, could be investigated. As mentioned in the discussion section, the source of previously reported Cu\(^+Z^+\) ions in thermally
treated CuO and H-MFI materials [22,101,102] may have been due to the presence of water vapor during the exchange.
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Candidate: Trent Francis Guidry

Major Field: Chemical Engineering

Title of Dissertation: The Conversion of Light Amines over Copper-containing Zeolites

Approved:

[Signatures]

Major Professor and Chairman
Dean of the Graduate School

EXAMINING COMMITTEE:

[Signatures]

Date of Examination:

October 22, 1998