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Catalysis Today 26 (1995) 129–145

CATALYSIS TODAY

Structure-function properties in Cu-ZSM-5 NO decomposition and NO SCR catalysts

Karl C.C. Kharas [a],*, Di-Jia Liu [b], Heinz J. Robota [a]

[a] *Allied Signal Environmental Catalysts, P.O. Box 580970, Tulsa, OK 74158-0970, USA*
[b] *AlliedSignal Research and Technology, 50 East Algonquin Road, Des Plaines, IL 60017-5016, USA*

Abstract

Physicochemical characteristics of Cu-ZSM-5 relevant to its abilities to catalyze the decomposition of NO to the elements and to catalyze selective catalytic reduction (SCR) of NO by hydrocarbons are reviewed. An emphasis is placed on in situ characterization of the catalyst under bona-fide catalytic conditions by X-ray absorption methods. Copper chemistry has central importance. Critical review of literature results demonstrates that Brønsted acidity of the zeolite is not a necessary factor in NO SCR. A model rationalizing 'excessive' copper ion exchange levels suggests that the exchanging species are not Cu^{2+} cations, as assumed formally, but rather $[CuOH]^+$ and its related oligomers. The working catalyst exhibits dynamic Cu(II) → Cu(I) conversions under catalytic conditions. Cu(I) can be the predominant oxidation state under SCR conditions and viable reaction mechanisms will have to take this into account. Reaction pathways for NO decomposition and NO SCR are similar but, in all likelihood, somewhat different. A brief résumé is provided concerning adsorbate chemistry which may be important in the mechanisms of both the decomposition and the SCR reactions.

Keywords: NO_x; Structure-function properties; Cu/ZSM-5; Reduction

1. Introduction

Six years have passed since the initial report [1] that Cu-ZSM-5 catalyzes decomposition of NO to the elements. Very soon after the initial report, three groups independently learned that this same material catalyzes selective catalytic reduction of NO by various hydrocarbons [2–4]. These discoveries, which may yet result in practical application, have led to a great deal of work in the catalysis community. In the ensuing years, several aspects concerning the structure and function of Cu-ZSM-5 catalysts have begun to clarify. In this review, we concentrate on structural questions related to the roles of the molecular sieve and of copper itself in catalyzing these reactions. Where possible, new observations are made regarding published information. Areas where consensus seems to be emerging are identified. We also try to note some points that remain controversial.

We begin by suggesting that the Brønsted acidity that can be present in Cu-ZSM-5 is not a necessary component of active Cu-ZSM-5 catalysts. This done, attention focuses on the role of copper. We highlight powerful in situ experiments utilizing XANES, FT-IR and EPR spectroscopies that reveal the dynamic nature of Cu-ZSM-5 catalysts under bona-fide catalytic conditions. The existence of different types of copper in Cu-ZSM-5,

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* Corresponding author.

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SSDI 0920-5861(95)00139-5

as detected by a number of methods, is then discussed. We consider issues related to chemical composition: easily attainable copper 'over-exchange' levels were initially considered anomalous but are now fairly well understood. While it is clear that different environments for Cu exist, even in a calcined, unused catalyst, the precise nature of these environments remains controversial. We suggest that part of the cause for the confusion is that relatively inactive materials that are more amenable to various types of physical characterization have been investigated rather than highly active catalysts. We conclude with a brief consideration of possible reaction mechanisms not yet ruled out by available evidence.

2. Is Brønsted acidity important for Cu-ZSM-5 NO SCR?

Solid acid catalysts can catalyze selective reduction of NO by hydrocarbons [5,6]. Given the well known Brønsted acid properties of H-ZSM-5, some early contributions assumed an important role of acidity for Cu-ZSM-5 catalyzed NO SCR. Ansell and coworkers interpreted the results of TAP experiments as consistent with the key lean NO_x reactions involving coke formed by the acid function of the zeolite while Cu chemistry was relegated principally to formation of a critical a Cu–NO_2 species [7]. Petunchi and coworkers considered, with skepticism, the possibility that acidity of Cu-ZSM-5 is important in SCR of NO by hydrocarbons, but could not rule it out [8]. Inui and coworkers suggested [9] a bifunctional mechanism involving an acid function and a redox function. Parrillo and coworkers also acknowledged the suggestion, which they attributed to their colleagues, that acidity of the zeolite may be of equal importance to the reactivity of the copper centers [10].

Two independent lines of evidence now suggest, however, that acidity is not necessary for the selective catalytic reduction of NO over Cu-ZSM-5. One line involves the catalytic properties of an analogous catalyst where boron formally substitutes for aluminum in the molecular sieve [11]. The other involves a combination of TPD and catalytic results for a series of Cu-ZSM-5 materials where Cu/Al and Si/Al were varied [10,12].

A recent, clear, set of evidence is provided by Centi and coworkers [11] who examined the SCR of NO by propane with Cu-MFI materials where the Group 13 element nominally in the molecular sieve framework is either aluminum (which they call Cu-ZSM-5) or boron (which they call Cu-BOR). With similar Cu/X and Si/X (X = Al, B) ratios, Centi and coworkers found the Cu-BOR is more active for NO SCR with propane than Cu-ZSM-5 [11]. While protons at exchange sites in ZSM-5 function as strong acids, protons in exchange sites in BOR are weak acids ([11] and references cited therein). Centi and coworkers argued [11] that the NO SCR results of their Cu,H-BOR catalyst, compared to that of Cu,H-ZSM-5, show that Brønsted acidity in not necessary in Cu-MFI.

Corroborating evidence is obtained by examining Cu-ZSM-5 at high Cu/Al or high Si/Al levels. We have shown that Cu-ZSM-5 containing Cu/Al ratios over 2 are effective for selective catalytic reduction of NO with either propene or propane [13]. At these high Cu/Al ratios, one expects the number of residual acid sites to be low. This issue has been studied in detail by a collaboration between researchers at the Ford Research Laboratory and the University of Pennsylvania. In the first study [10], sites of isopropylamine adsorption in Cu-ZSM-5 were examined by TPD- and IR-spectroscopy. Four adsorption sites were observed and assigned to adsorption at (1) Brønsted sites in ZSM-5, (2) copper at ion exchange sites in ZSM-5, (3) copper that is not at ion exchange sites in ZSM-5, and (4) non-Brønsted adsorption sites on the ZSM-5. Two Cu containing materials with no residual Brønsted acidity were prepared. One utilized a Cu/silicalite material with high Si/Al ratio while the other utilized a ZSM-5 material (Si/Al = 35) originally possessing 425 μmol/g Brønsted sites that was exchanged with cupric acetate to provide a total copper content of 743 μmol/g, 0 μmol/g

Brønsted sites, and 350 μmol/g Cu at ion exchange sites [10]. The second contribution [12] provided results of catalytic SCR of NO by propene for the Cu/silicalite and for the aforementioned Cu-ZSM-5 possessing 743 μmol Cu/g and 0 μmol H–O–Al sites/g. Both materials were revealed to have respectable catalytic activity for SCR of NO by propene. We have observed similar activity trends, both as a function of Si/Al and as a function of Cu/Al [14]. Since Cu-ZSM-5 catalysts containing no detectable Brønsted acidity nevertheless exhibit good catalytic performance, the evidence indicates that Brønsted acidity is not necessary for Cu-ZSM-5 catalyzed NO SCR by hydrocarbons.

Cu-BOR catalysts appear to provide greater activity than isomorphous Cu-ZSM-5 materials. Cu-ZSM-5 catalysts with very high Si/Al or Cu/Al ratios possess undetectable amounts of Brønsted acidity but are nevertheless good catalysts. These results strongly suggest that the copper species in the molecular sieve alone are sufficient to provide good catalytic activity and that Brønsted acidity is not a necessary factor for NO SCR for Cu-MFI or, probably, in other copper containing molecular sieve catalysts.

3. Structural characterization of Cu-ZSM-5 catalysts by X-ray absorption and other spectroscopic methods

Among various analytical techniques, two X-ray absorption spectroscopic methods, XANES and EXAFS, have proven to be very effective in determining both electronic and geometric structures of transition metals in zeolites. X-ray absorption spectroscopy is unique in that it samples all the copper species present during the reaction. In highly dispersed catalysts such as Cu-ZSM-5, this facilitates gaining an overall understanding of what is happening at the absorbing element under catalytic conditions. X-ray absorption near edge structure (XANES) uses information obtained in the energy region near the threshold energy of a specific core absorption. It provides information about the electronic configuration, stereochemistry and the oxidation state of the atom being investigated. For example, in the study of Cu in ZSM-5, the oxidation state of Cu is characterized by detailed examination of the K-edge, that is, the electronic transition from the inner core (1s) to valence states near the ionization threshold. The transition energy is determined by the electronic configuration of the Cu ion which is very sensitive to the local environment. Normally, the higher the oxidation number, the farther the transition energy shifts above the ionization threshold of the neutral atom. Because of the nature of a bound to bound transition, a narrow feature often occurs at the rising slope of an edge jump in the XANES spectrum which is very useful in characterizing the population of a particular oxidation state. This feature works particularly well in distinguishing the cupric and cuprous ions co existing in Cu-ZSM-5 under catalytic conditions. Cu(I) has a d^{10} closed shell electronic configuration and therefore cannot be directly probed by other powerful analytical methods such as ESR. Often information concerning Cu(I) has to be obtained indirectly through the analysis of cupric species. In the X-ray absorption spectra, the Cu(I) $1s \rightarrow 4p$ electronic transition appears as a sharp peak in the 3 to 5 eV energy range above the threshold of the edge jump. This peak is clearly separated from the corresponding Cu(II) transition which appears in the 7 to 9 eV range. The energy shift and the transition intensity depend strongly on the environment surrounding the copper ions. These features are particularly useful in characterizing the nature of the copper ions in a dynamic catalytic reaction.

Extended X-ray absorption fine structure (EXAFS) spans a broader energy region well above the threshold in the X-ray absorption spectrum. It provides atomically selective information about short range structure, i.e. the type, number and distance of the neighboring atoms localized around the absorbing atom. Since the method addresses short range structure, it compliments traditional long range structural characterization techniques, such as XRD. In the study of Cu-

ZSM-5, EXAFS has been used effectively to characterize the multiple shell structure surrounding the atomically dispersed copper ions in the zeolite.

The combination of XANES and EXAFS methods offers an excellent opportunity to study the electronic and geometric structural changes in Cu-ZSM-5 which, in retrospect, is almost uniquely suited for these X-ray absorption spectroscopic techniques because of the high degree of copper dispersion. The X-ray techniques reveal the nature of the transition metal active site in the catalyst, which compliments other characterization techniques addressing the adsorbate, such as FT-IR. The integration of the information generated from both viewpoints will provide a more comprehensive picture of the catalytic process.

Although numerous studies have been reported on the characterization of transition metal exchanged zeolites with X-ray absorption techniques, there are only a few publications on the study of Cu-ZSM-5. One of the earlier XANES and EXAFS studies on Cu-ZSM-5 was reported by Hamada and coworkers [15]. They investigated the structure and oxidation state of Cu in Cu-ZSM-5 after the sample was treated in flowing He and SO_2 at 773 K. They observed that XANES of Cu in Cu-ZSM-5 is very similar to that of $Cu(OH)_2$. They also concluded from their XANES and EXAFS results that there are no clear structural differences between fresh, pretreated and used Cu-ZSM-5 samples. Since their samples were exposed to air and packed at ambient conditions after gas treatment, it is doubtful whether they represented the true state of Cu under different reaction conditions. This concern was verified later by Liu and Robota through a series of in situ XANES and EXAFS experiments [16–21]. By examining the Cu-ZSM-5 under the various catalytic reaction conditions, such as direct NO decomposition and selective catalytic reduction with hydrocarbons, we observed a variety of dynamic changes in both electronic and geometric structures of the Cu centers. We also observed comprehensive correlation between these changes and the catalytic performance. More detailed review will be given in the following discussion. More recently, another study was published by Grünert et al. on the structure and chemistry of Cu-ZSM-5 after in situ treatments using the X-ray absorption spectroscopic method, combined with catalyst testing, XPS and ESR techniques [22].

Another significant advantage of the X-ray absorption technique is its non-intrusiveness. Since X-rays can penetrate the catalyst samples without disrupting the catalytic process, it is feasible to operate a catalyst at its reaction temperature and pressure while monitoring the electronic and local structure of the catalytic sites. It is also possible to investigate changes in these properties in real time in response to perturbations under the catalytic conditions. For example, an in situ XAS apparatus was designed and used by Liu and Robota [16–21] in their investigation of the active site in Cu-ZSM-5 during NO decomposition and NO SCR by hydrocarbons. With this approach, we observed progressive changes in ionic copper local geometry and oxidation state under various gas flows and temperatures, and established a good correlation between the proportion of cuprous ion and the catalytic activity.

Copper ions in ZSM-5 are very active species. In order to characterize their oxidation state and local geometric structure during catalytic reaction, one has to define the state of fully oxidized and reduced copper in Cu-ZSM-5. Fig. 1(a) is a XANES spectrum of Cu-ZSM-5-59 ($Si/Al=26$, $Cu/Al=0.295$, 1.02 wt.-% Cu) from Ref. [2]. This sample has been exposed to air and moisture at room temperature for a period of time after it was prepared by ion exchange and calcination procedures. The upshift of the edge energy and a very weak $1s \rightarrow 3d$ forbidden transition at near zero electron volts indicate that the copper in ZSM-5 is in the form of cupric ion, Cu(II). The radial distribution function (RDF) of copper, obtained after the Fourier transformation of the EXAFS spectrum, is shown in Fig. 2(a). The analysis shows that the cupric ion is surrounded by an average of 4.2 oxygen atoms in its first neighbor shell with shell radius of 1.96 Å. No well-defined higher shell structure was observed. The relatively high first shell coordination number and the lack

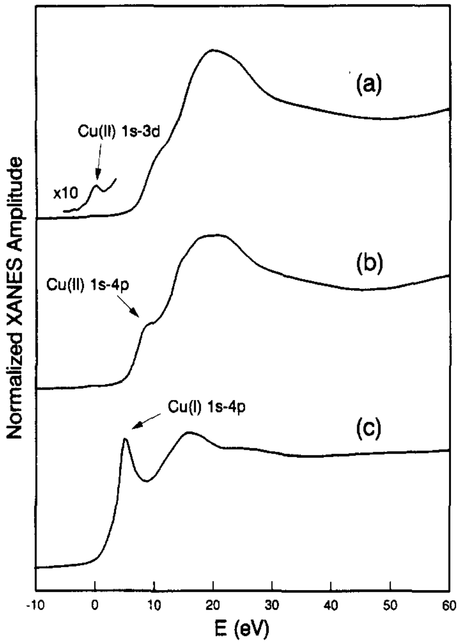

Fig. 1. XANES spectra of a dilute Cu-ZSM-5-59 at the Cu K-edge: (a) sample has been exposed to ambient air after ion exchange and calcination; (b) sample was oxidized in dry air at 773 K and was cooled in dry air to room temperature; (c) sample was auto-reduced in ultra-high purity He at 773 K and was cooled to room temperature in He.

of higher shell structure suggest that the Cu(II) ions in the zeolite are fully coordinated, possibly by O atoms from water in the zeolite, and are randomly distributed throughout the zeolite framework.

After calcination in dry air at 773 K for 30 min, the catalyst is fully dehydrated and oxidized. Significant changes in both XANES and EXAFS spectra were observed, as are shown in Fig. 1(b) and Fig. 2(b). In the XANES region, the edge energy is slightly red-shifted and a weak transition appears at 8.5 eV above the zero which has been tentatively assigned to the 1s→4p transition of Cu(II). In addition, the 1s→3d forbidden transition of cupric ion maintains approximately its previous intensity. The RDF obtained from EXAFS analysis shows a well-defined second and third shell structure. The numerical fitting of the Fourier filtered first shell EXAFS of Cu-ZSM-5-59 indicates that the number of oxygen atoms in the 1st shell is 3.7 with shell radius of 1.93 Å. Analysis of EXAFS for Cu-ZSM-5-164 yields similar structural parameters. Taken collectively, the observations support the view that copper ions in ZSM-5 remain as Cu(II) upon dehydration in dry air with a likely change in coordination from anchoring Cu(II) to zeolite framework O atoms. The slight decrease in the 1st shell coordination number is likely caused by the loss of H_2O.

EPR and IR spectroscopy provide complimentary information concerning the environments of the cupric species present in the fresh, calcined catalyst. When assessing the relevance of many of these studies, it is important to keep in mind that the most active catalysts contain relatively high Cu content while many spectroscopic studies have concentrated on systems where the Cu is dilute. Our attempts to study highly active Cu-ZSM-5 catalysts by EPR were complicated by our inability to obtain a signal for the cupric ions until most of them were thermally reduced. At high Cu concentrations, dipolar interactions produce broad, poorly resolved spectra [23]. Thermal

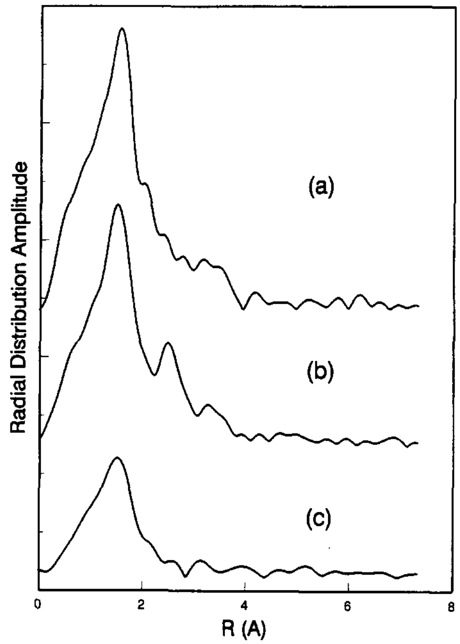

Fig. 2. The radial distribution function (RDF) obtained from the Fourier transformation of EXAFS spectra for the dilute Cu-ZSM-5-59: (a) sample has been exposed to ambient air after ion exchange and calcination; (b) sample was oxidized in dry air at 773 K and was cooled in dry air to room temperature; (c) sample was auto-reduced in ultra-high purity He at 773 K and was cooled to room temperature in He.

reduction rendered most of the copper in the catalysts that we wished to investigate, which had Cu/Al greater than 2, EPR silent. We had not been able to resolve, to our satisfaction, whether the EPR spectra, obtained from the remnant cupric species after the thermal reduction of the Cu-ZSM-5, were representative of the cupric species in relatively concentrated, fresh, oxidized samples [23]. Recent results [24] suggest that significant portions of the cupric species present in fresh, concentrated catalysts occur in environments different from those observed by EPR at high dilution. At high dilution (for example, $Si/Al = 25$, $Cu/Al = 0.33$, 1.27 wt.-% Cu), cupric cations exist in both square planar and square pyramidal environments in Cu-ZSM-5 [25]. Another recent EPR study on a material with somewhat higher copper content ($Si/Al = 23.3$, 1.9 wt.-% Cu), found a third monomeric cupric species that is more susceptible to thermal reduction than the square planar or square pyramidal species [26].

At even higher copper concentrations, closer to those that may be used in practical application, a substantial fraction of the copper species can be EPR silent [24,25]. This has been studied in detail by Lei and coworkers [24] who employed a recently developed indirect IR method [27] that is claimed to probe all the cupric [23] and cuprous species in Cu-ZSM-5. This IR method is based on the discovery that cupric and cuprous species in ZSM-5 cause an observable perturbation in the molecular sieve asymmetric internal stretching vibrations. Cupric species result in a band at 966 cm^{-1} while cuprous species result in a band at 918 cm^{-1} [27]. Lei and coworkers found the integrated EPR spectral intensity of a concentrated Cu-ZSM-5 material ($Si/Al = 20$, $Cu/Al = 0.66$, 3.1 wt.-% Cu) was only 1.4 times greater than that of a dilute material ($Si/Al = 20$, $Cu/Al = 0.06$, 0.27 wt.-% Cu) [24]. IR characterization under various treatment conditions led to the inference that a substantial portion of the cupric species occur as EPR silent dimeric $[Cu_2(\mu_2\text{–}OH)_2]^{2+}$ dications [24]. Lei and coworkers noted [24] that Chao and Lunsford [28] were able to observe cupric pairs by EPR in Y zeolite, but suggest that a superexchange pathway mediated by two bridging hydroxyls (or by one oxygen atom) results in spin coupling for the presumed bridged Cu(II) dimers in Cu-ZSM-5. Precedence for this proposal is available from the inorganic literature. The singlet–triplet splitting, $2J$, between cupric centers in hydroxyl-bridged dimers is known to be sensitive to the Cu–O–Cu bond angle [29]. Indeed, the sign of J can change, resulting either in ferromagnetically coupled Cu(II)-pairs or an antiferromagnetic interaction. A ferromagnetic interaction, yielding an observable EPR spectrum, occurs in Y. An antiferromagnetic interaction, yielding an EPR silent system, is proposed [24] for Cu-ZSM-5. Since variation of the Cu–O(H)–Cu angle by just a few degrees is known to be sufficient to change the sign of J [29], the proposed change in magnetic properties as a function of molecular sieve topology is plausible. Positive structural evidence for the proposed cupric dimers in Cu-ZSM-5 is lacking and difficult to obtain. However, it is not clear that other oligomeric forms can be ruled out. Detailed, temperature dependent magnetic susceptibility determinations may provide insight regarding the existence of any higher spin system cupric species but modeling any susceptibility data is expected to be complex due to the interference of several species already known to occur in Cu-ZSM-5.

A variety of chemical environments appears to exist for cupric species in Cu-ZSM-5. The variety of environments appears to increase, not unreasonably, as the Cu content increases. All of the known or proposed environments have a coordination number of 4 or 5 for copper, consistent with the EXAFS result.

It has been demonstrated that, at elevated temperature, Cu(II) in ZSM-5 can be auto-reduced to Cu(I) in an inert gas flow or in vacuo. For example, Li and Hall showed the formation of Cu(I) from Cu(II) ($Cu/Al = 0.83$, $Si/Al = 26$, 3.11 wt.-% Cu) in He flow by ESR spectroscopy and demonstrated that the self-reduction results from the desorption of oxygen [30]. In apparent contradiction to this finding, cupric species in dilute Cu-ZSM-5 materials ($Si/Al = 25$, Cu/

Al = 0.33, 1.27 wt.-% Cu) can be stable in flowing He at 773 K [31]. The literature suggests, however, that the material investigated in [31] may be quite inactive for NO decomposition compared to catalysts containing either more Cu or more Cu and Al [32]. The square planar and square pyramidal copper sites detected by EPR in dilute samples may not be associated with copper sites active for catalytic decomposition of NO. A less dilute Cu-ZSM-5 (Si/Al = 23, 1.9 wt.-% Cu) possesses a third cupric species detectable by EPR which is susceptible to thermal reduction at lower temperatures than the other two cupric species [26]. It may be relevant that more concentrated samples can contain EPR silent cupric species [28], that are thermally reducible [33]. By activating Cu-ZSM-5-59 in an ultra-high purity He flow at 773 K, Liu and Robota observed the growth of a narrow, intense peak at 5.3 eV above the Cu^0 K-edge in the XANES spectrum. The growth of the peak gradually stops after about one hour, indicating completion of auto-reduction from Cu(II) to Cu(I). Fig. 1(c) shows the XANES spectrum after the sample was cooled to room temperature in He flow. A similar sharp, intense feature has been previously observed in various copper compounds and is assigned to the $1s \rightarrow 4p_{xy}$ electronic transition in cuprous complexes [34]. The relationship between the peak intensity and the coordination number in cuprous complexes has been systematically studied [34] and the peak intensity in Fig. 1(c) suggests that Cu(I) is coordinated by only two ligands. The Fourier transformed EXAFS spectrum which is shown in Fig. 2(c) provides further evidence for a reduction in coordination. The numerical fitting of the 1st shell in the RDF reveals that the Cu(I) ion is surrounded by approximately two oxygen atoms with Cu–O distance of 1.94 Å. This observation is consistent with formation of Cu(I) with two ligands in Cu-ZSM-5 by desorption of oxygen [20].

It is important to point out that Cu(I) in Cu-ZSM-5 formed through auto-reduction is extremely reactive with oxidizing species at room temperature. As Liu and Robota observed in their experiments, although Cu(I) is formed at elevated temperature even in the presence of oxidizing species (NO, O_2 etc.) in the gas stream, the chemical balance shifts strongly towards Cu(II) when the reaction temperature approaches room temperature. For example, we observed a nearly 100% auto-reduction of copper ion in an Cu-ZSM-5-59 at 773 K in a high purity N_2 (99.99%, Matheson) flow, the Cu(I) ions were later completely reoxidized to Cu(II) during cooling by the trace amount of oxygen contaminant in the nitrogen [19]. Therefore, to study the structure of Cu(I) in Cu-ZSM-5 at ambient temperature, it is crucial to remove trace amount of oxidizing species in the gas flow. This high propensity toward Cu(II) at ambient temperature in the presence of oxidizing species may contribute to the current controversy among several experiments on whether cupric ion can be auto-reduced to cuprous ion in the inert atmosphere. Furthermore, this observation underscores the importance of in situ study for Cu-ZSM-5 during NO decomposition and selective reduction by hydrocarbons. Because in both cases there exists a significant amount of oxidizing species in the reactant gas stream, it is very difficult to treat the sample under reaction conditions and then study it by returning to room temperature without distorting the actual oxidation state and structure of Cu in the zeolite.

The strong Cu(I) $1s \rightarrow 4p$ absorption band provided a convenient way to monitor the content of cuprous ion during the catalysis by X-ray absorption spectroscopy. Liu and Robota monitored this transition intensity in a temperature cycle around 773 K, the optimum NO conversion temperature, in a flow of 1% NO in N_2 [16,18]. We observed that the intensity of the $1s \rightarrow 4p$ transition, which is proportional to the population of Cu(I) in Cu-ZSM-5, is highly dependent on the reaction temperature. Furthermore, we calculated the integral intensity of Cu(I) transitions by a normalized XANES difference method [34] and plotted them on a relative scale with the normalized NO decomposition rate which we obtained through simultaneous in situ monitoring. The result is shown in Fig. 3. The good correlation between the Cu(I) content and NO decomposition rate is noteworthy.

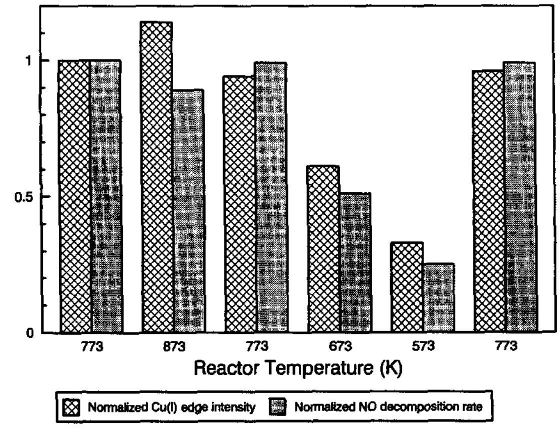

Fig. 3. The correlation between the Cu(I) pre-edge transition intensity with the relative NO decomposition rate in the temperature cycle. Both intensity and the decomposition rate are normalized to their respective values at the first $T = 773$ K.

Since the measurement was carried out under reaction conditions, it confirms the conjecture by Li and Hall that a small fraction of cuprous ion is maintained in the working catalyst [30]. Both the cuprous ion concentration and the NO conversion vary in the same way with temperature. According to the redox mechanism proposed by Li and Hall [30], the rate of NO decomposition should be proportional to the partial pressure of NO and the number of the available active sites in Cu-ZSM-5, which they attribute to Cu(I) ions. The correlation that Liu and Robota observed seems to support this notion that Cu(I) participates in a redox mechanism of NO decomposition at elevated temperature.

Recent in situ IR experiments support a change in the Cu(II)/Cu(I) ratio under NO decomposition conditions at 673 K compared with the same temperature in flowing O_2. It was observed that the framework molecular sieve vibration intensity due to cupric perturbation decreased in intensity while the framework molecular sieve vibration intensity due to cuprous perturbation increased with time when the flowing gas mixture was switched from flowing O_2 to 2% NO/He [24]. An isosbestic point was observed during the transformation, consistent with clean transformation of a portion of the cupric species to cuprous species under NO decomposition conditions at 673 K [24].

Another interesting observation by Liu and Robota [20] is the distinction in Cu(I) ion concentration between so called overexchanged and underexchanged Cu-ZSM-5 during catalytic NO decomposition. It was first found by Iwamato et al. that the catalytic activities of Cu-ZSM-5 increase with copper content and levels off over the nominal 100% exchange capacity [35]. (At the nominal 100% exchange level, Cu/Al = 0.5.) From the exchange site distance analysis and UV spectroscopic study, Iwamoto et al. proposed [35] that a dimeric copper species, possibly in the form of Cu^{2+}–O^{2-}–Cu^{2+}, is the precursor for autoreduction of the complete redox cycle. Liu and Robota studied the XANES spectra of 164% and 59% exchanged Cu-ZSM-5. We observed that, in a steady flow of 1% NO in N_2 at 773 K, 35% of the copper ion in the Cu-ZSM-5-164 (Si/Al = 26, Cu/Al = 0.82, 2.78 wt.-% Cu) remains as Cu(I) while cuprous ion content in Cu-ZSM-5-59 zeolite is less than 10%. The difference in the Cu(I) $1s \rightarrow 4p$ transition is shown in the XANES spectra in Fig. 4. In addition to the change of XANES, the radial distribution function obtained from EXAFS

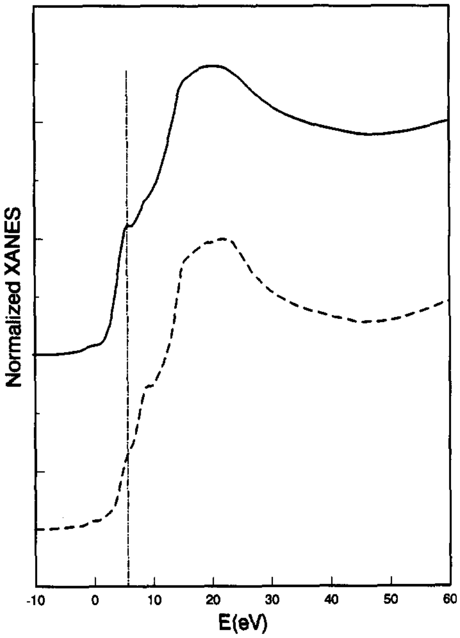

Fig. 4. XANES spectra of Cu in 164% exchanged (solid line) and 59% exchanged (dashed line) Cu-ZSM-5 during NO decomposition reaction at 773 K in 1% NO/N_2 mixture.

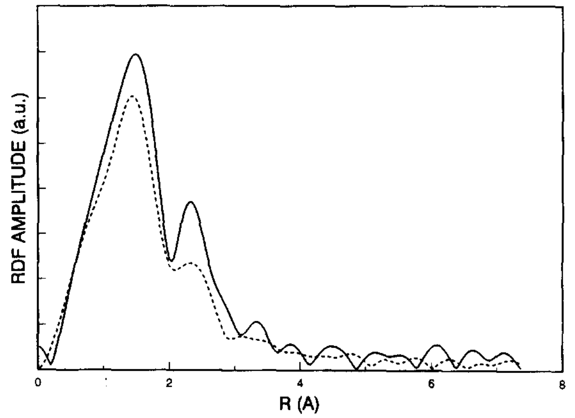

Fig. 5. The radial distribution functions of Cu in 164% exchanged (solid line) and 59% exchanged (dashed line) Cu-ZSM-5 during NO decomposition reaction at 773 K in 1% NO/N_2 mixture.

also exhibits differences, shown in Fig. 5. In comparison with the Cu-ZSM-5-59 sample, Cu-ZSM-5-164 displayed weaker first and second shell intensities, shown as the dashed line in Fig. 5. The peak intensity in the radial distribution function is attributed to the superposition of the mixture of Cu(I) and Cu(II) ion. Considering the similarity in the shell radii and phase functions between the two, the weak intensity observed in the concentrated, so called overexchanged, higher Cu content zeolite sample is simply the result of relatively high concentration of Cu(I), which has lower 1st and 2nd shell coordination than that of Cu(II). Substantial differences occur in Cu(I) contents between 164% and 59% exchanged zeolite samples during NO decomposition catalysis. These differences indicate that more concentrated Cu-ZSM-5-164 tends to sustain higher Cu(I) concentration, therefore, higher catalytic activity. It is also consistent with the hypothesis of a redox mechanism. The observations of higher O_2 desorption rate [30] and possibly ionic copper dimer [35] suggest that cuprous ion may be regenerated by a dicopper process, possibly through a surface migration of the cupric moieties [16].

Although the preceding points toward a redox catalytic mechanism for direct NO decomposition over Cu-ZSM-5, it was not at all clear whether the same mechanism can be applied to NO selective catalytic reduction by hydrocarbons. Several catalytic kinetics studies seemed to suggest otherwise. For example in NO selective catalytic reduction by hydrocarbons, an excess amount of oxygen is necessary to maintain the high catalytic activity [2]. Our NO decomposition study [16] showed that Cu(I) concentration is suppressed by the presence of oxygen. Therefore it appeared only plausible that oxygen should inhibit the reaction instead of enhancing the activity if the redox mechanism is correct. Furthermore, the SCR activity depends less on the Cu exchange level than that in direct decomposition [36], which suggests that Cu(I) generation through a dicopper process is not necessarily the key step for the SCR reaction.

To investigate the function of ionic copper in ZSM-5 during NO selective catalytic reduction Liu and Robota studied the XANES and EXAFS of Cu-ZSM-5 under SCR reaction conditions [17,20]. Using a similar experimental set-up, we studied the Cu(I) 1s → 4p transition and the average local structure of Cu in Cu-ZSM-5 in a gas mixture of NO/C_3H_6/O_2 = 3200 vppm/3200 vppm/7.5 vol.-%, balanced by N_2, from room temperature up to 873 K. Somewhat surprisingly, we observed strong variation of Cu(I) transition intensity. A significant fraction of the copper ions in ZSM-5 is reduced to Cu(I) at elevated temperature even under this strongly oxidizing condition. Shown by the solid line in Fig. 6 are a selected group of XANES spectra taken during the temperature rise. XANES spectra show a Cu(I) 1s → 4p transition similar to that observed in the NO decomposition study mentioned earlier, except for a slight red-shift in energy. Some reduction of Cu(II) to Cu(I) is observed near room temperature. The intensity of this transition starts to increase when the reaction temperature reaches about 500 K and decreases rapidly when the temperature is above 650 K. By integrating the Cu(I) 1s → 4p peak intensity using the normalized difference XANES method [34], we calculated the change in the relative Cu(I) concentration at each reaction temperature. In the reaction mixture of NO/C_3H_6/O_2/N_2 there clearly exists a window of enhanced cuprous ion concentration from 500

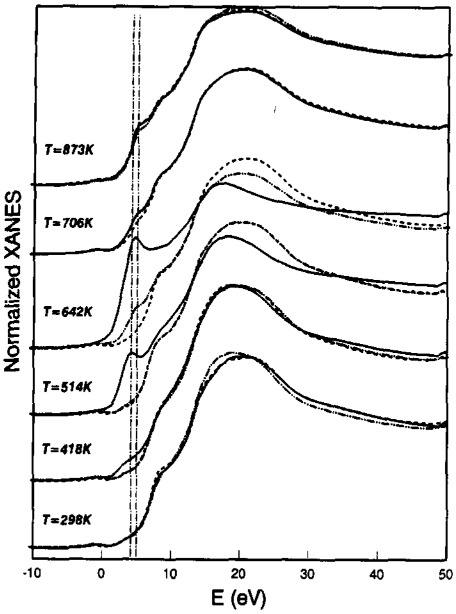

Fig. 6. XANES spectra of Cu in Cu-ZSM-5 at different temperatures in the reaction mixtures containing $NO/C_3H_6/O_2$ = 3200 vppm/3200 vppm/7.5 vol.-% (solid lines); $NO/CH_4/O_2$ = 2300 vppm/5200 vppm/5.3 vol.-% (dashed lines); and $NO/C_3H_8/O_2$ = 3200 vppm/3200 vppm/7.5 vol.-% (chain-dot lines).

K to 700 K, which peaks at about 650 K, as is shown by the solid circles in Fig. 7. Plotted in Fig. 7 as the solid line is the NO conversion level to N_2 in the selective reduction by propene measured under similar conditions by Iwamoto and coworkers [35]. Both NO conversion level and the relative Cu(I) concentration are normalized to their respective peak values in this figure. They match quite well in the temperature range between 500 K to 700 K. Above 700 K, however, a considerable discrepancy was observed between the two.

A recent in situ EPR study of dilute Cu-ZSM-5 appears to reveal similar phenomena [37]. Unfortunately, most of the conditions examined are not directly relevant to NO SCR since, generally, only binary subsets of the ternary NO/propene/O_2 mixture truly of interest were employed. Thus, reduction of Cu(II) is reported at 573 K in a propene/O_2/He mixture but results from a NO/propene/O_2/He mixture were not provided at this temperature. Results of the only ternary condition reported, viz. at 773 K, show little reduction of Cu(II), which is consistent with our XANES results. At present, too little information is available concerning EPR characterization of dilute Cu-ZSM-5 materials to determine whether their behavior is comparable in all aspects with phenomena we observe for Cu-ZSM-5 by XANES under in situ NO SCR conditions.

The first in situ FT-IR study of NO SCR by propene over Cu-ZSM-5 yielded disappointingly little new information [38]. Various adsorbates could be observed. At temperatures below the onset of SCR activity, carbonaceous deposits, Cu(I)–CO, and organic isocyanate were observed, consistent with the low temperature EPR and XANES results. At higher temperatures,

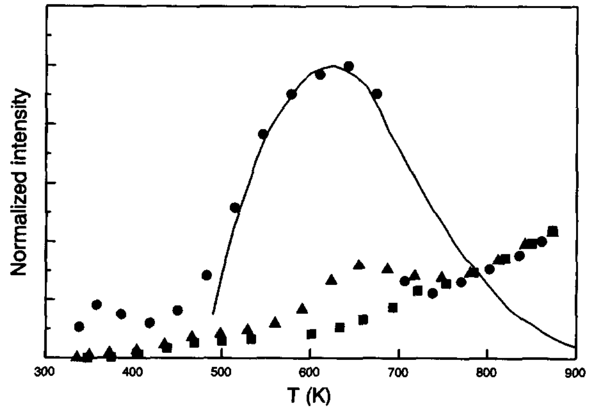

Fig. 7. The normalized concentration of Cu(I) at different temperatures in the reactant streams of $NO/C_3H_6/O_2$ = 3200 vppm/3200 vppm/7.5 vol.-% (solid circles); in $NO/CH_4/O_2$ = 2300 vppm/5200 vppm/5.3 vol.-% (solid squares); and in $NO/C_3H_8/O_2$ = 3200 vppm/3200 vppm/7.5 vol.% (solid triangles). To compare with the catalytic result, the NO conversion level to N_2 measured by Iwamoto and coworkers [35] (normalized at the peak value) is also plotted (solid line).

Cu–N_2 was observed, but shown to be irrelevant to the catalytic pathway. In addition, at higher temperatures a complex defined only as $Cu(N_xO_y)_z$ was observed, and it was suggested that this species might be a reaction intermediate. The stoichiometry of the complex and the oxidation state of copper are unknown, rendering comparison of this proposal with others problematic. At relatively high temperature only CO_2 and Cu(I)–N_2 was detected by FT-IR, although substantial NO SCR activity is retained.

The XANES results clearly demonstrated the presence of cuprous ions in ZSM-5 during the selective reduction of NO by propene in excess oxygen. The variation of Cu(I) concentration with temperature seems to correlate well with the NO conversion rate. Liu and Robota estimated that more than 50% of the copper is in the form of Cu(I) at the optimum selective NO reduction temperature. The temperature correlation between the NO conversion rate with Cu(I) content is very similar to the observation in the direct NO decomposition study, except that the maximum of both Cu(I) content and the NO conversion window is shifted to a lower reaction temperature in SCR. The existence of this correlation suggests a redox mechanism in which transient species formed through interaction of cuprous ions and the nitrogen oxides, parallel the reaction route suggested for NO decomposition. Given the crucial dependence of Cu(I) formation on the presence of propene however, it is unlikely that Cu(I) ions are formed through auto-reduction by desorption of oxygen from a dicopper process, as suggested for direct NO catalytic decomposition. Instead, the majority of cuprous ion is formed directly through reduction by hydrocarbon, C_3H_6 in this case. The center of the Cu(I) 1s → 4p transition under SCR conditions with propene is 4.2 eV above zero, which is defined as the first inflection point of the copper metal foil fluorescence excitation spectrum [17]. Under NO decomposition conditions or in gas mixtures where methane is substituted for propene when the Cu(I) 1s → 4p transition is generated by thermal reduction of Cu(II), the center of the Cu(I) 1s → 4p is 5.3 eV above zero [17]. This difference in the Cu(I) 1s → 4p transition energy was suggested to be due to formation of a cuprous allyl under NO SCR conditions with propene. Our confidence in this assignment would be greater if we could find XANES analysis of well defined organocuprous compounds in the literature to compare with our observations. Since the catalytic site is generated by reaction of the ionic copper with adsorbed propene, the rate of Cu(I) formation depends more critically on the C_3H_6 partial pressure than the copper content. Therefore the difference of Cu(I) fractional concentration between lower and higher copper content Cu-ZSM-5 becomes less significant.

Not all hydrocarbons have the same impact on the activity of Cu-ZSM-5 during NO selective catalytic reduction. For example, it has been shown that methane has no significant catalytic selectivity for NO over Cu-ZSM-5 [39] although Li and Armor have shown recently that it is an effective reducing agent over Co-ZSM-5 [40]. Propane does exhibit some selectivity for NO reduction over Cu-ZSM-5 but with a lesser activity and higher conversion temperatures [13]. How are these observations related to the nature of the active site, ionic copper, and the redox mechanism?

To compare the effect of different kinds of hydrocarbons on Cu oxidation state and local geometry, Liu and Robota also studied X-ray absorption spectra of Cu-ZSM-5 in the gas mixtures where C_3H_6 is nearly stoichiometrically replaced by CH_4 or C_3H_8 [17,19]. For example, we studied the Cu(I) concentration change at different reaction temperatures in a NO/CH_4/O_2 = 2300 vppm/5200 vppm/5.3 vol.-% mixture. XANES spectra at the same selected temperatures as that in the propene study are plotted as the dashed lines in Fig. 6. Indeed, at the temperature for the optimum NO conversion by propene, XANES spectra show no strong increase of Cu(I) transition intensity in the methane mixture. Rather, a weak Cu(I) peak gradually increases with increasing temperature. At $T = 873$ K, XANES spectra are basically identical in both gas mixtures. Using the same peak area integration method discussed earlier, we calculated the Cu(I) transition intensity at various reaction temperatures and plotted them in Fig. 7 as the solid squares. No window of Cu(I) enhancement is found over the same temperature range studied. Rather, a monotonic, slowly increasing Cu(I) intensity with increasing of the reaction temperature is observed.

In a similar approach, Liu and Robota studied the Cu(I) transition intensity as a function of reaction temperature in a gas mixture where C_3H_6 is simply replaced by C_3H_8. Selected XANES spectra at corresponding temperatures are also plotted as chain-dot lines in Fig. 6. At both low and high temperatures, the XANES spectra are practically overlapping with those observed in the other two gas mixtures. The XANES spectra with propane represent somewhat intermediate cases between that of methane and propene at the medium temperature range. For example, at $T=642$ K, the 1s→4p transition of Cu(I) is clearly observed, although the intensity is significantly weaker than that observed in the propene mixture. The relative Cu(I) transition intensities are plotted as solid triangles in Fig. 7. A window of Cu(I) ion concentration enhancement is also observed for this SCR reaction, except that the intensities are significantly lower and temperature span is narrower than those in the case of propene. The variation of Cu(I) seems consistent qualitatively with the Cu-ZSM-5 catalytic performance of the propane mixture. In addition to the narrow temperature window, a continually rising Cu(I) background with increasing temperature is also observed which overlaps those observed for propene and methane mixtures.

Analysis of the cuprous ion concentration in methane, propane, propene mixtures with NO and O_2, leads us to a sequence of reducing power, $CH_4 < C_3H_8 < C_3H_6$, from Cu(II) to Cu(I) in Cu-ZSM-5, with that of methane practically equal to zero. This sequence represents the same sequence of catalytic activity in NO SCR. Energy measurements indicate that the peak observed in the methane mixture at elevated temperature is the same transition observed in the direct NO decomposition case where the transition is assigned as the 1s→4p transition of Cu(I) coordinated by two oxygen atoms [17]. Cu-ZSM-5 does not adsorb methane; therefore the Cu(I) transition observed in 'non selective reduction' by CH_4 at high temperature is generated by the same O desorption process. The rate of oxygen desorption increases with temperature which explains the continually rising intensity of the peak in Fig. 6 and 7. In the mixture of propane and propene, the overall Cu(I) intensity variation with temperature can be deconvoluted into two parts. One increases with temperature monotonically due to the Cu(I) formation through O desorption, following the same path as in the $CH_4/NO/O_2$ mixture. On this increasing background, another part rises and falls in a narrow temperature range. This second part of Cu(I) ion formation, or the 'window' which is directly related with the NO selective reduction, is observed in both the propane and propene mixture. The existence of this 'window' distinguishes between hydrocarbons capable of NO SCR and hydrocarbons incapable of NO SCR. The chemical difference between propane and propene is reflected by the height and the width of the 'window'. This difference, nonetheless, should only be interpreted qualitatively rather than quantitatively when addressing catalytic activity. More Cu(I) content and wider temperature span in propene do correlate with the higher NO conversion activity than that in the propane mixture. The C=C bond in the olefin tends to interact with a p orbital of the ionic copper. Indeed, propene is observed to chemisorb onto Cu-ZSM-5 while only physisorption occurs with propane [13,41]. Chemisorption of propene onto ionic copper may generate a precursor state to hydrogen atom abstraction that results in the putative cuprous allyl. Therefore the cupric ions are reduced to cuprous ions at a faster rate. The Cu(I) ions observed in the experiment only represent the potential active site, instead of the actual transient reaction intermediate. Although we identify Cu(I) species, perhaps Cu(I) alkyls, as the active site, our X-ray absorption research has not yet yielded more precise information needed to more completely characterize reaction intermediates and the reaction pathway. A quantitative relationship between NO SCR activity and Cu(I) concentration may not exist under all conditions. It is not clear that a Cu(I) species is involved in the rate limiting step under all conditions, but such species likely occur before the rate limiting step under most conditions.

Having reviewed insights provided by the X-ray absorption spectroscopy, we briefly consider two additional topics. The first, which we believe is moving toward resolution, concerns the stoichiometry of the copper incorporation reaction during Cu-ZSM-5 preparation. The second, which remains far from resolution, provides a brief résumé reflecting the state of our knowledge concerning reaction pathways.

4. The stoichiometry of copper incorporation into Cu-ZSM-5

In an early Letter [1] on NO decomposition catalyzed by Cu-ZSM-5, Iwamoto and coworkers noted, with interest, that levels of Cu incorporation well above the theoretical 100% ion exchange limit are readily feasible by simple aqueous procedures. Their synthetic procedure involved the use of cupric acetate under pH neutral or slightly basic conditions. It was suggested [35] that $[\mathrm{Cu{-}O{-}Cu}]^{2+}$ species may occur. Catalytic preparation experiments coupled with chemical analysis led to suggestions [23,42–44] that the exchanging species may be $[\mathrm{Cu{-}OH}]^{+}$ or other more highly charged clusters derived from dehydration/deprotonation reactions of the aquated cupric dications that occur in aqueous solutions at low pH.

The isopropylamine TPD characterization of Cu-ZSM-5 by Parrillo and coworkers provides insight into this puzzle [10]. Two types of TPD features related to copper are observed. One is assigned to cupric species that have substituted for protons at exchange sites. They increase in concentration while the concentration of Brønsted sites decreases in concentration. The stoichiometry of this exchange reaction is roughly 1:1. Parrillo and coworkers suggested $[\mathrm{CuOH}]^{+}$ is the copper species participating in this reaction. However, $[\mathrm{Cu_2(OH)_2}]^{2+}$ is believed to be the dominant cupric species near neutral pH [24]. We suggest the reaction resulting in Cu(II) substitution at acid sites in H-ZSM-5 can be represented as

$$\mathrm{Z{=}OH} + [\mathrm{Cu_2(OH)_2}]^{2+}_{\mathrm{aq}} \rightarrow \mathrm{Z{=}OCuOH} + [\mathrm{Cu(OH_2)}]^{2+}_{\mathrm{aq}} \qquad (1)$$

where Z= represents the Si and Al atoms of the molecular sieve associated with the acidic bridging hydroxyl. Reaction (1) is sufficient to account for synthesis of Cu-ZSM-5 with Cu/Al = 1, that is, a material with a nominal ion exchange of 200%.

Even at the lowest exchange level, a second copper associated TPD feature is observed. The structure of this second copper species, which lacks a stoichiometric relationship with Al associated exchange sites, is unclear. Parrillo and coworkers suggested this second type of copper may involve a cupric species associated with a deprotonated silanol site at defects in the sieve or, alternately, could be due to 'polymeric or other stable forms of Cu oxide' that form in the zeolite [10]. Parrillo and coworkers did not suggest that the two types of copper detectable by isopropylamine TPD correlate with structurally unique sites. Rather, they seem to suggest one type of copper is associated with cupric ions at molecular sieve ion exchange sites while the other is associated with cupric species at other sites.

It is plausible that one or two oxygen atoms associated with the ion exchange site may bond to Cu(II) in the Z=OCuOH complex. Given the propensity of Cu(II) to adopt pseudo-square planar or 4 + 2 pseudo-octahedral coordination in oxygen donor environments [45], the Z=OCuOH complex would appear to possess at least one or two water ligands. Compared to free water, the water coordinated to Cu(II) should be weakly acidic. At high copper content, a second reaction appears to occur which is represented schematically in reaction 2

$$Z{=}OCuOH(OH_2) + [Cu_2(OH)_2]^{2+}_{aq} \rightarrow Z{=}OCu(OH)_2CuOH + [Cu(OH_2)]^{2+}_{aq} \quad (2)$$

Formally, reaction 2 is another $[H^+]/[CuOH^+]$ exchange reaction, just as reaction 1. The zeolite-bound product of this reaction is proposed to contain dicopper unit bridged by two hydroxide ligands. This product bears a strong resemblance to the dimeric $[Cu_2(\mu_2\text{–}OH)_2]^{2+}$ dications proposed to occur by Lei and coworkers in Cu-ZSM-5 [24] but the third hydroxide satisfies charge neutrality considerations relevant to ZSM-5, where exchange sites are believed to be dilute. Analogies based on coordination chemistry of Cu(II) suggests that higher oligomers could form [46]. Reaction 2 could account for the ready formation of Cu-ZSM-5 with nominal Cu(II) ion exchange levels greater than 200% and may result in the type of Cu not associated with exchange sites observed by Parrillo and coworkers in their isopropylamine TPD study [10].

5. What is known of possible reaction intermediates?

Under NO decomposition conditions, it appears that NO chemisorption to Cu(I) is necessary. Interaction between NO and Cu(I)-ZSM-5 at low pressure and room temperature results in formation of a cuprous nitrosyl whose characterization by EPR and IR spectroscopies [47] presaged characterization of the first cuprous nitrosyl coordination compound [48]. The low g and high A^{NO} values observed in both systems led both research groups to deduce a Cu(I)–NO structure for the adduct rather than a Cu(II)–NO^- structure. Subsequent full characterization of a cuprous nitrosyl coordination compound by single crystal X-ray diffraction, IR, UV visible, and magnetic circular dichroism spectroscopies, coupled with ab initio Hartree-Fock and post-Hartree-Fock calculations support this essentially neutral, covalent model for the adduct [48]. Two [49] or three [26] cuprous species are thought to be present in the Cu(I)-ZSM-5. NO adsorption onto Cu(I)-ZSM-5 results in formation of only one Cu(I)–NO-ZSM-5 adsorbate complex was distinguishable by EPR spectroscopy [47]. It is not clear whether only one of the cuprous sites binds NO, or the various cuprous sites react with NO to give an identical cuprous nitrosyl, or the spectroscopic method, together with the conditions employed, was insufficient to resolve multiple cuprous nitrosyls. As NO pressure is increased, an EPR silent, IR active Cu(I)–$(NO)_2$ appears [47,49]. This appears to be the last observable precursor to NO disproportionation and oxidation of Cu(I). It is unclear whether N_2O is the only primary product of NO decomposition or whether N_2 is also a primary product of NO decomposition [50].

The situation appears to be different for the NO SCR, with propene at least, over Cu-ZSM-5. Our in situ XANES work under selective reduction conditions led us to suggest the formation of an organocuprous intermediate. NCO species have also been observed on Cu-ZSM-5 catalysts, but not at temperatures where NO SCR occurs [38]. Thus, if NCO ligands are important in the NO SCR pathway, they occur after the rate limiting step, and the observation of such species at room temperature is of dubious significance. Nevertheless, investing the reactivity of known [51] Cu(II)–NCO compounds with NO may help assess whether such species in Cu-ZSM-5 possess activities necessary for NO reduction. Cuprous alkyls, nitro-alkyls, and NCO species have been proposed as immediate precursors to NO reduction. It has recently been determined that C–H bond scission is the rate determining step in NO SCR by methane over Co-ZSM-5 [52]. It has been suggested that NO_2 adsorbed on cobalt is the hydrogen atom abstracting species [53]. It is possible that a role of NO_2 in NO SCR with Cu-ZSM-5 is also hydrogen atom abstraction to form either a metal alkyl, or a nitroso- or nitro-alkyl, or perhaps even a free radical. As discussed earlier [13], a substantial literature of potential model compounds led to the suggestion that an alkyl migration in a putative cuprous alkyl nitrosyl could yield a N-nitroso-N-alkylhydroxylamate with reduction of 2 NO molecules per molecule of hydrocarbon. Examination of the thermal decomposition chemistry of transition metal, and particularly copper, N-nitroso-N-alkylhydroxylamates may shed light on whether these complexes have suitable reactivities consistent with their nomination as reaction intermediates. Fig. 5 from reference [8] is readily understood if N-nitroso-N-alkylhydroxylamates, which would presumably decompose thermally to produce N_2 among other products, or if nitroalkanes, analogously suggested to react with another molecule of NO to form products including N_2, occur along the NO SCR reaction pathway. A plot of NO conversion against that NO/hydrocarbon mole ratio appears to show NO conversion maximizes when this ratio is ≤ 2 but decreases at high ratios. But Fig. 5 of reference [8] cannot be clearly understood if NCO is the immediate precursor to oxidized nitrogen reduction. Unlike Co-ZSM-5, the rate determining step has not yet been precisely determined for Cu-ZSM-5. So far, no unambiguous evidence is available permitting determination whether the cuprous alkyls or cupric NCO species observed in Cu-ZSM-5 are the reaction intermediates or spectators. Examining the thermal chemistry of known cupric N-nitroso-N-alkylhydroxylmates or the reactivity of cupric isocyanates, such as the known tetrameric LCu(II)NCO compounds [38], with NO, may determine whether these proposed intermediates possess the required reactivities to participate in the catalytic pathway. The known hydrocarbon selectivity trend of isobutane > propene > propane [8,13] would be due to a combination of electronic effects (ease of hydrogen atom abstraction [13]) and steric effects (protection of a putative cuprous alkyl active site) controlling NO SCR over Cu-ZSM-5. Determination of the isotope effects of these hydrocarbon substrates may provide additional insight into the chemical mechanism of NO SCR over Cu-ZSM-5.

6. Summary

Although several early contributions suggested Brønsted acidity may be an important physicochemical property of active Cu-ZSM-5 catalysts for NO SCR, more recent results permit the conclusion that Brønsted acidity is unimportant. Cu-BOR catalysts, which are more basic than Cu-ZSM-5, may in fact be a better SCR catalysts. Catalysts known to contain no residual Brønsted acidity are also known to be active. Therefore, attention focuses on the role of copper. During catalyst synthesis at neutral pH, Cu(II) appears to react with exchange sites in ZSM-5 with a 1:1 stoichiometry rather than the 1:2 stoichiometry expected if $[Cu^{2+}]_{aq}$ were the Cu(II) reactant. Several research groups have suggested $[CuOH]^+$ may be Cu(II) reactant. The zeolite-bound product of exchange with $[CuOH]^+$ would almost certainly also contain at least one Cu(II) coordinated water molecule whose protons should have greater acidity than free water. Additional $[H]^+/[CuOH]^+$ exchange reactions may result in EPR silent Cu(II) species known to occur in active Cu-ZSM-5 that possess relatively high Cu content. X-ray absorption spectroscopy reveals the existence of dispersed Cu species in Cu-ZSM-5 that engage in a dynamic Cu(II)/Cu(I) redox chemistry under catalytic conditions. Qualitative trends in relative amounts of Cu(I) detected by XANES closely track relative activities of Cu-ZSM-5 under NO decomposition conditions and under SCR conditions with propene, propane, and methane. Higher proportions of copper appear to occur as Cu(I) in relatively concentrated catalysts, consistent with their higher activities. So far, FT-IR and EPR spectroscopic experiments performed under in situ conditions have yielded a modest amount of supplemental insight. Additional research ongoing in several laboratories will hopefully alter this situation. Many important questions remain unresolved concerning structure, function, and mechanism in Cu-ZSM-5. Little is known concerning the nature of copper adsorbates in NO SCR under reaction conditions. XANES evidence suggests Cu(I) alkyls exist along the reaction pathway prior to the rate limiting step. The rate limiting step for SCR in Cu-ZSM-5 remains unidentified. Whether NO reduction proceeds via associative or dissociative pathways, together with the molecular nature of the participation of hydrocarbon molecules or fragments in NO reduction, remain an open questions.

Acknowledgements

We thank Dr. Danan Dou for painstaking review of this contribution. Resources provided AlliedSignal Research and Technology, AlliedSignal Environmental Catalysts, and Brookhaven National Laboratory enabled and supported this work.

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