Catalysis Letters 21 (1993) 291–301

In situ XANES characterization of the Cu oxidation state in Cu-ZSM-5 during NO decomposition catalysis

Di-Jia Liu and Heinz J. Robota

Research and Technology, AlliedSignal Inc., 50 E. Algonquin Road, Des Plaines, IL 60017-5016, USA

Received 26 May 1993; accepted 1 July 1993

The oxidation state of Cu in Cu-ZSM-5 has been investigated by the X-ray absorption near-edge structure (XANES) spectroscopic method during NO decomposition catalysis. We designed an in situ reactor system with which we can measure the relative NO decomposition rate while taking XANES spectra. We observed that the 1s → 4p electronic transition of Cu(I) in Cu-ZSM-5 appears as a narrow, intense peak which is an effective measure of changes in the population of copper oxidation states. This transition is quite intense after Cu-ZSM-5 is activated in inert gas flow. However, its intensity decreases but by no means disappears after the admission of a NO/N_2 gas mixture. We conducted the reaction in a temperature cycle around the optimum conversion temperature of 773 K and recorded the XANES at each temperature. We observed that the integrated intensity of the Cu(I) 1s → 4p transition, which is proportional to the cuprous ion concentration in Cu-ZSM-5, was well correlated with the NO decomposition rate. This finding supports the conjecture that Cu(I) participates in a redox mechanism during catalyzed NO decomposition in Cu-ZSM-5 at elevated temperature.

Keywords: Cu-ZSM-5; XANES; NO decomposition

1. Introduction

Although thermodynamically unstable with respect to the diatomic elements, the decomposition of NO is an extremely slow process. While many catalytically active materials will facilitate the rupture of the N–O bond, the continuous process of catalysis is typically hampered by the retention of the adsorbed oxygen. Copper, when appropriately introduced into ZSM-5 zeolite, has been shown effective at catalyzing NO decomposition to the elements [1–6]. Therefore, elucidating the mechanism of this catalysis represents an important opportunity to develop a more detailed understanding of the structural aspects of this catalyst which confers the observed activity. Among several catalytic NO decomposition mechanisms proposed [7–13], Hall and co-workers suggested a redox reaction scheme in which the formation of Cu(I) by reductive desorption of oxygen from Cu(II) is a key step [7,9]. A similar mechanism was also proposed by Iwamoto and Hamada [2]. Several analytical techniques, such as FTIR, ESR, TPR, microbalance, etc., have been applied to characterize the copper oxidation state under various conditions in order to elucidate the nature of the Cu species present [7–16]. For example, Li and Hall observed that the rate of spontaneous O_2 desorption by an oxidized Cu-ZSM-5 and the rate of NO decomposition at the same temperature, which were measured separately, are closely correlated. Based on this finding and other supporting evidence, they suggested that "the working catalysts probably consist of a relatively small number of Cu(I) centers (or adjacent Cu(I) pairs) maintained in a steady state by balance of the rate of oxidation with the rate of O_2 desorption" [7]. To investigate this conjecture experimentally, it would certainly be very desirable to study simultaneously the distribution of copper oxidation states and rate of NO decomposition during actual reaction.

Reported here is the first of a series of our recent in situ investigations of Cu in Cu-ZSM-5 by the X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectroscopic methods. Using the XANES spectroscopic technique to study the oxidation state of transition metals is a well established method [17]. The oxidation state is generally characterized by the electronic transition from the inner core (1s) to highly excited states near the ionization threshold. Because the electronic configuration of the transition metal, which is a function of the atomic oxidation state and local structure, is probed directly by the X-ray absorption process, this method provides information on Cu in Cu-ZSM-5 which complements the results derived from other indirect techniques. Another advantage of X-ray absorption spectroscopy is that X-rays can penetrate the catalyst sample without disrupting the catalytic process. It is therefore feasible to operate a catalyst at its reaction temperature and pressure while monitoring the electronic and local structure of the catalytic elements. We designed such a reactor system for NO decomposition with which we can measure the relative NO conversion level while taking EXAFS and XANES spectra.

2. Experimental

Shown in fig. 1 is the schematic diagram of the reactor system. Reactor 1 is a flowthrough type reactor where NO decomposition was carried out. About 100 mg of 164% ion-exchanged Cu-ZSM-5 (Cu-ZSM-5-164, for details of the sample preparation, see ref. [18]) was packed as a thin, permeable disk and placed in a sample holder at the center of the reactor which is surrounded by an insulated resistive heater. The sample holder was designed in such a way that all the reactant flow has to pass through the catalyst, similar to a plug-flow reactor. A well collimated X-ray beam passed through the X-ray intensity calibrator (I_0), sample holder, and entered the transmission detector (I_t) where the absorption of X-rays was recorded. At the entrance of reactor 1 a small piece of Cu foil was placed to partially block the incident X-rays. The fluorescence excitation spectrum of the Cu foil was col-

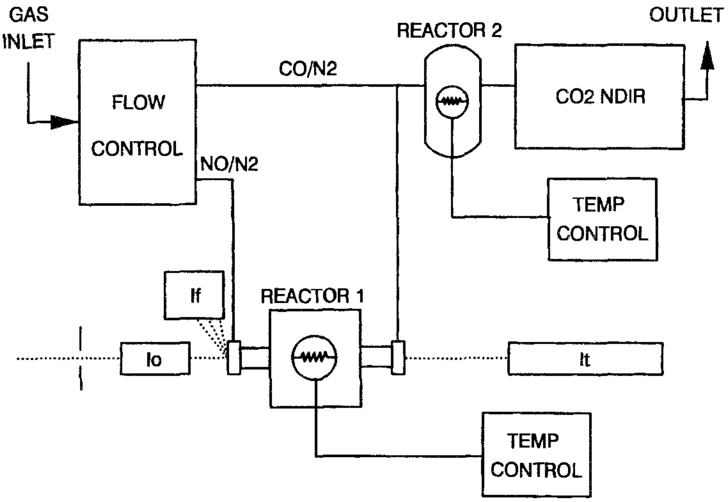

Fig. 1. Schematic diagram of the in situ reactor for X-ray absorption spectroscopic study during NO decomposition over Cu-ZSM-5.

lected simultaneously by detector (I_f) during each scan to calibrate the Cu^0 edge energy. During in situ measurement, the temperature of reactor 1 is controlled in the range of 573–873 K. The flow rate of the 1% NO/N_2 mixture, which was typically 100 ml/min, was regulated with a mass flow controller. The effluent stream, which contains N_2, O_2, NO_2, and unreacted NO, will then combine with the stream of a 1% CO/N_2 mixture before entering reactor 2 which contains a Cu,Sn/γ-Al_2O_3 catalyst. The temperature of reactor 2 was controlled at 450 K throughout the experiment. Our laboratory tests showed that under these conditions, CO will preferentially react with the decomposition product O_2 and the secondary product NO_2 [#1] to form CO_2 over the Cu,Sn/γ-Al_2O_3 catalyst while NO is virtually unaffected. The concentration of CO_2 in the effluent is detected by a non-dispersive CO_2 infrared detector downstream of reactor 2. Therefore, the relative NO conversion level can be monitored by the change of CO_2 content. The use of the secondary reactor and CO_2 NDIR instead of chemiluminescence NO_x detection or GC provided us a more robust, portable, yet inexpensive approach. Since it is an indirect measurement, we limited our determination of the NO decomposition data only as relative values for comparison. A full scale description of the design and the

---

[#1] NO_2 is formed by partial reaction of product O_2 with unreacted NO in the effluent stream at low temperature, as suggested by Li and Hall [19]. To evaluate the influence of NO_2 on the conversion level measurement, we performed a laboratory test of CO oxidation in reactor 2 by mixing known amounts of O_2 into the NO reactant stream. We observed that CO oxidation levels are stoichiometrically consistent with the added O_2 only, suggesting that NO_2 reacts with CO to form CO_2 and NO. Therefore, the amount of CO_2 measured corresponds directly with twice the amount of the O_2 formed during the decomposition.

performance of the in situ X-ray absorption spectroscopy reactor will be given in a separate publication [20].

The X-ray absorption experiments were performed at Beamline X-18B of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. The synchrotron ring current during this experiment was in the range of 110–210 mA and the ring energy was 2.53 GeV. A pair of Si(220) crystals was used in the monochromator and the slit width of the monochromator exit was 0.2 mm vertical and 15 mm horizontal to ensure optimal resolution. All the near-edge X-ray absorption spectra were taken at the Cu K-edge (8979 eV) with energy resolution of 0.5 eV.

3. Results and discussion

We observed that the 1s→4p electronic transition of Cu(I) in Cu-ZSM-5 appears as a narrow, intense peak; monitoring this peak provides an effective measure of changes in the copper oxidation state during NO decomposition. Shown in figs. 2a–2c are the XANES spectra of Cu-ZSM-5. The spectrum (a) represents XANES taken after the sample was activated in a pure He flow at 823 K for 1 h. Under this treatment, a fraction of the cupric ions auto-reduce to cuprous ions. The strong, sharp peak at approximately 4 eV above the Cu^0 K-edge represents a typical Cu(I) 1s→4p transition, the intensity of which increased from zero before the activation. This transition is found in Cu(I) compounds and has been systematically studied [21]. The normalized intensity of this transition in cuprous complexes is generally strong and has been used to quantitatively determine the oxidation states of the copper sites in multicopper oxidase [21]. The sharp, intense feature is assigned to the transition from 1s to $4p_{xy}$ in 2-coordinate Cu complexes. In underexchanged Cu-ZSM-5, following either reduction by CO or thermally induced auto-reduction, we find a 1s→4p pre-edge transition intensity similar to those found in 2-coordinated Cu(I) complexes [20]. Indeed our EXAFS analysis shows that Cu(I) in auto-reduced underexchanged Cu-ZSM-5 has an apparent coordination number of 2 whereas Cu(II) in oxidized Cu-ZSM-5 has a coordination number of 4 [20]. We analyzed the content of cuprous and cupric ions by simulating the observed XANES spectrum with the superposition of fractional amounts of underexchanged Cu-ZSM-5 spectra in which Cu was either fully reduced to Cu(I) or fully oxidized. Excellent agreement between the simulation and the experimental data was observed throughout the entire XANES region (from threshold up to 100 eV above the edge). As shown in ref. [21], changes in the coordination number of Cu(I) complexes alter both the intensity of the pre-edge feature and the amplitude of XANES features well above threshold. Thus, successful simulation of the observed XANES by simple superposition of oxidized and reduced Cu-ZSM-5 models supports changes in oxidation state as the reason for the spectral differences, rather than simple changes in coordination number. The details of the analy-

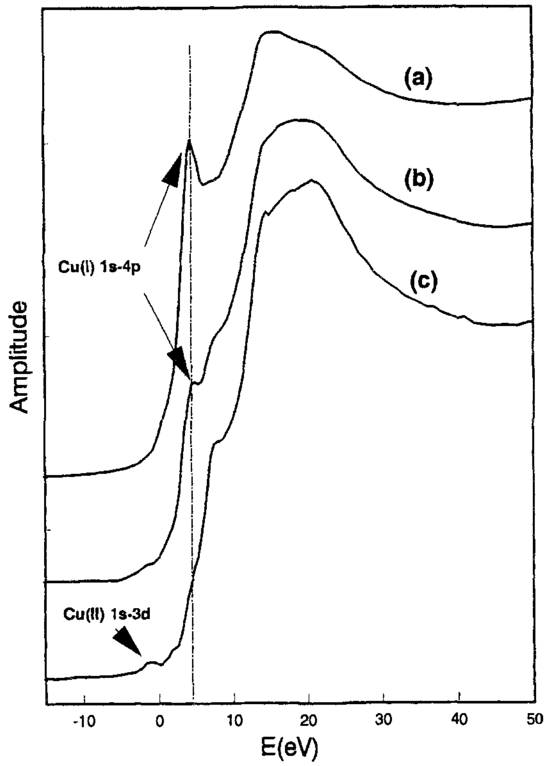

Fig. 2. (a) XANES spectra of Cu-ZSM-5-164 after the samples are pretreated in He flow at 827 K for 1 h. (b) The same sample was exposed to a 1% NO/N_2 mixture at 773 K after auto-reduction in He. (c) To compare with nearly fully oxidized Cu in Cu-ZSM-5, 59% exchanged Cu-ZSM-5 sample in dry air at 773 K is used, since even in dry air, a small fraction of Cu(I) remains in overexchanged Cu-ZSM-5.

sis are given in ref. [20]. Our analysis showed that after activation in He, about 70% of the cupric ions in Cu-ZSM-5-164 were autoreduced to Cu(I) and the rest remained as Cu(II). This is in general agreement with the earlier experimental results by ESR, microbalance, etc. [1,7]. The Cu(I) 1s→4p transition intensity, however, decreased drastically after the admission of the 1% NO/N_2 gas mixture into reactor 1, as is shown by spectrum (b) in fig. 2. This observation indicates that a substantial amount of Cu(I) formed in the activation process was quickly oxidized back to Cu(II), possibly by O_2 formed during the decomposition reaction. Oxidation was also observed in the 1% NO/N_2 stream at room temperature by XANES [20], which is consistent with literature reports [8,13]. However, it is important to note that though the Cu(I) transition intensity is very weak at elevated temperature, it is by no means completely extinguished. This is illustrated by comparing (b) with (c) in fig. 2, where (c) is a spectrum of a nearly completely oxidized Cu-ZSM-5. Even after a prolonged period of catalytic reaction while reaching a steady state, there still exists a constant cuprous ion concentration, as is shown by the weak Cu(I) 1s→4p transition intensity. We estimated a Cu(I) content of approximately 25% of the total copper ion concentration using spectral simulation analysis mentioned above. Apparently, at elevated temperatures, a certain fraction of copper was maintained as cuprous ion even under the oxidizing environment.

To explore the relationship between the Cu(I) content and the decomposition activity proposed by Li and Hall [7], we conducted the reaction in a temperature cycle around the optimum conversion temperature of 773 K and recorded the XANES spectra in situ at each temperature. The temperature cycle used was: $T_1 = 773\ \mathrm{K} \rightarrow T_2 = 873\ \mathrm{K} \rightarrow T_3 = 773\ \mathrm{K} \rightarrow T_4 = 673\ \mathrm{K} \rightarrow T_5 = 573\ \mathrm{K} \rightarrow T_6 = 773\ \mathrm{K}$ with an approximate space velocity (GHSV) of 80000 h^{-1} at 773 K. Under this space velocity, NO decomposition was carried out in the differential region of the reactor and was not diffusion limited. The NO conversion level varied with temperature and reached a steady state after 30 min operation at a particular temperature. A maximum conversion level at 773 K was observed, as was previously reported [1]. Correspondingly, we also found that the Cu(I) 1s→4p peak intensity changed throughout the temperature cycle. Shown in fig. 3 are the normalized

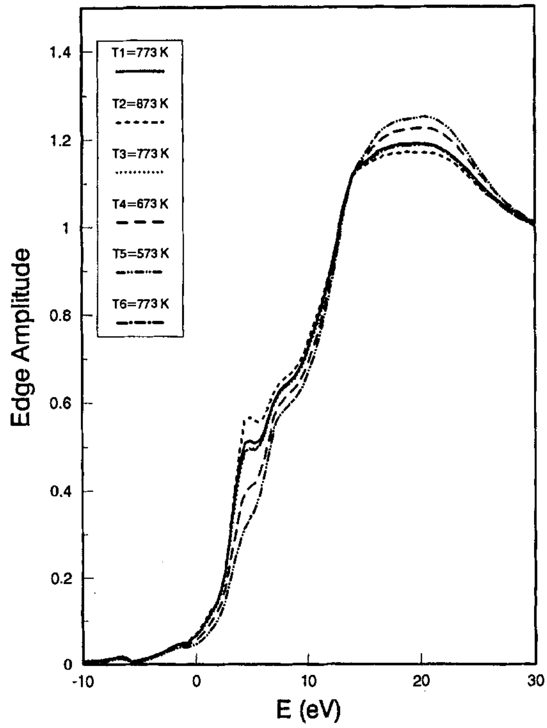

Fig. 3. The normalized XANES spectra of Cu-ZSM-5-164 during the NO decomposition temperature cycle.

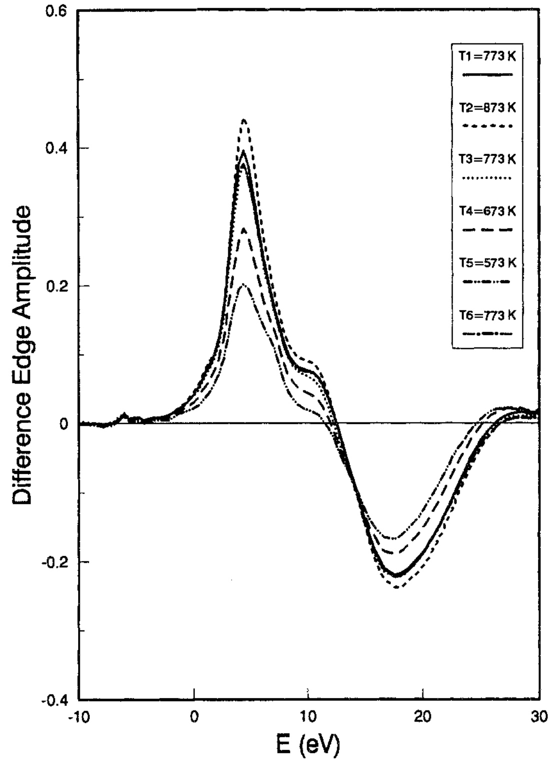

Fig. 4. The normalized difference edge XANES spectra of Cu-ZSM-5-164 during a temperature cycle in 1% NO/N_2. Notice that the integrated intensity depends on the temperature and returns nearly to its original level at the end of the cycle.

XANES spectra taken at each temperature. To better examine the change of Cu(I) transition intensity and calculate the relative Cu(I) concentration we employed the normalized difference edge absorption spectra obtained by subtracting the normalized edge of the oxidized Cu-ZSM-5 spectrum from that of Cu-ZSM-5-164 at each point of the temperature cycle [#2]. This produces the characteristic derivative-shaped signals which are shown in fig. 4. We observed that the intensity of the 1s → 4p transition, which is proportional to the population of Cu(I) in Cu-ZSM-5, indeed depends rather strongly on the reaction temperature. We calculated the integral intensity of these peaks and plotted them in fig. 5 on a relative

---

[#2] In order to study the correlation between the Cu(I) concentration and the relative NO decomposition rate, we used only the relative Cu(I) concentration here. To obtain the absolute cuprous ion content one can simply scale the relative value with that obtained at 773 K, which has 25% Cu(I) under NO decomposition condition. For the method to calculate the normalized difference edge absorption spectrum, see ref. [21].

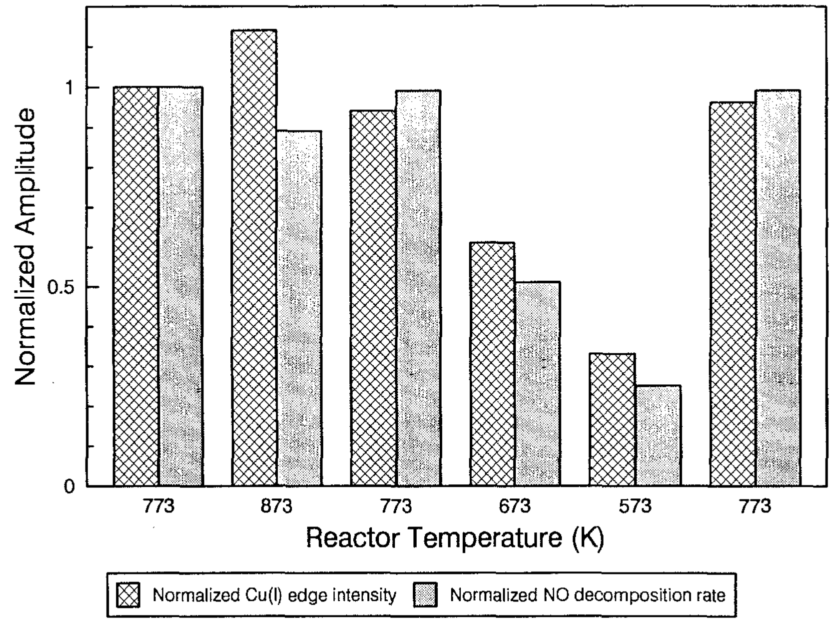

Fig. 5. The correlation between the Cu(I) pre-edge transition intensity with the relative NO decomposition rate in the temperature cycle. Both intensity and the decomposition rate are normalized to their respective values at T_1.

scale with the normalized NO decomposition rate which we calculated from the relative conversion level at each point of the reaction cycle.

The good correlation between the Cu(I) content and NO decomposition rate is noteworthy. Since the measurement was carried out under reaction conditions, it confirms the conjecture by Hall et al. that a small fraction of cuprous ion is maintained in the working catalyst [7,9]. Both the cuprous ion concentration and the catalyst efficiency vary in the same way with temperature. According to the redox mechanism proposed by Li and Hall [7], 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 we observed supports their notion that Cu(I) participates in the mechanism of NO decomposition at elevated temperature.

It is interesting at this point to compare our experimental results with those of Li and Hall [7]. They proposed that the following two reactions form the redox cycle of the NO decomposition over Cu-ZSM-5:

$$\mathrm{NO} + (\mathrm{S}) \rightarrow \mathrm{NO{-}(S)} \rightarrow \tfrac{1}{2}\mathrm{N_2} + \mathrm{O{-}(S)} \tag{1}$$

and

$$2\mathrm{O{-}(S)} \rightleftharpoons \mathrm{O_2} + 2(\mathrm{S})\,, \tag{2}$$

where (S) represents surface vacancies in reduced from, i.e. Cu(I); NO–(S) and

O–(S) represent adsorbed NO and oxygenation atom sites, respectively. As part of their experimental approach to the redox mechanism, they measured the weight loss of oxidized Cu-ZSM-5-166 in He flow from 623 to 823 K and attributed the loss to the desorption of dioxygen. In a separate experiment, they also measured the turnover frequency of NO decomposition at the same temperatures. They observed that the rates of these two distinct processes were correlated (table 4 of ref. [7]). Since the desorption of O_2 will lead to the reduction of Cu(II) to Cu(I) which is believed to be the active site (S), they suggest that the rate of cuprous ion formation is associated with the rate of NO decomposition and the oxygen desorption process in eq. (2) is the rate limiting step in the redox cycle.

The oxygen desorption rate provides the information on the forward reaction of eq. (2); i.e., how fast the cuprous ion in Cu-ZSM-5 regenerates by auto-reduction. On the other hand, the Cu(I) in the catalyst during reaction will be continuously depleted by the oxidizing agents, as is shown in eq. (1) and the backward reaction of eq. (2). Therefore the cuprous ion content is actually controlled by a dynamic balance of the desorption of oxygen, adsorption of NO as well as the re-oxidation by product oxygen. The rate constants in eqs. (1) and (2), and therefore the steady state concentration of Cu(I), should depend on the reaction temperature. The presence of a significant amount of Cu(I) during NO decomposition, e.g. 25% of all copper species at 773 K, indicates that although the forward reaction in eq. (2) may be the rate-limiting step in the redox cycle, it is not much slower than the re-oxidation and decomposition reactions. Otherwise we would see much less steady state Cu(I) due to fast depletion by reaction in eq. (1) and backward reaction in eq. (2). In fact, our experimental results show that the oxygen desorption rate increases with temperature until it surpasses the NO adsorption and reaction rate. In fig. 5 we observe that the correlation between cuprous ion concentration and NO decomposition rate breaks down at 873 K; the Cu(I) intensity reaches a maximum yet the decomposition rate decreases slightly from that at 773 K. Similar behavior was also observed in Li and Hall's study where they reported a higher oxygen desorption rate at 827 than at 773 K, although the decomposition rate decreased. These observations suggest that the rate of Cu(I) regeneration ceases to be the rate determining step at higher temperature. Otherwise the decomposition rate would continue to increase with temperature. The NO adsorption, which leads to the formation of a reactive intermediate with Cu(I), may decline in rate at very high temperature, possibly due to fast desorption. It has been observed in FTIR experiments that the intensities of several infrared bands assigned to NO adsorbed on Cu(I) sites decrease rapidly with the increase of temperature [22]. The mononitrosyl $Cu^{(1+\delta)+}(NO)^{\delta-}$ and dinitrosyl $Cu^{(1+\delta)+}(NO)_2^{\delta-}$ species are suggested as the reaction intermediates for NO decomposition. Similar to oxygen adsorption, the formation of nitrosyl intermediates will oxidize Cu(I) to cupric ion through electron transfer. The fact that we detected more Cu(I) at 873 K suggests that the rate at which reactive intermediates are formed is outpaced by the NO desorption and auto-reduction rates. The negative temperature dependence of the NO decomposition rate at $T > 773$ K may simply indicate that eq. (1) becomes a rate-limiting step and its rate constant declines rapidly with temperature.

4. Conclusion

By using the XANES spectroscopic technique, we verified the presence of cuprous ion in overexchanged Cu-ZSM-5 during NO decomposition catalysis. The overall Cu(I) concentration in Cu-ZSM-5-164 is about 25% of the total Cu in a 1% NO/N_2 reactant mixture at 773 K. We observed also that the Cu(I) content depends on the reaction temperature and found that it correlates well with the rate of NO decomposition at temperatures below 773 K. These observations provide experimental support to the conjecture of the redox mechanism in which the regeneration of Cu(I) is a critical step. The cuprous ions form active sites in ZSM-5 which participate in first order NO decomposition catalysis. At temperatures above 773 K, the correlation between cuprous ion content and NO decomposition rate breaks down. Our experiment shows that the negative temperature dependence of NO decomposition rate above 773 K is not due to lack of Cu(I). Rather, the rate of formation of reactive intermediates decreases significantly, possibly due to the fast desorption of NO from Cu-ZSM-5.

Although our XANES results support the redox mechanism in the NO decomposition reaction, additional important questions in this research area remain unanswered: (1) why is there higher activity in ZSM-5 compared with other zeolites [1,7]; (2) what Cu species are produced in overexchanged Cu-ZSM-5 which lead to the higher observed activity [1,7]; and (3) what structurally stable or transiently created Cu species actually give rise to NO decomposition catalysis [8,9]? It is our hope that in situ X-ray absorption spectroscopy will prove useful in further addressing such structure–property relationships.

Acknowledgement

We thank Dr. Karl C.C. Kharas for providing the samples and interesting discussions during this investigation. Financial support of AlliedSignal Research and Technology is gratefully acknowledged.

References

[1] M. Iwamoto, N. Mizuno and H. Yahiro, Sekiyu Gakkaishi 34 (1991) 375, and references therein.

[2] M. Iwamoto and H. Hamada, Catal. Today 10 (1991) 57.

[3] T. Inui, S. Kojo, M. Shibata, T. Yoshida and S. Iwamoto, Stud. Surf. Sci. Catal. 69 (1991) 355.

[4] Y. Teraoka, H. Ogawa, H. Furukawa and S. Kagawa, Catal. Lett. 12 (1992) 361.

[5] M. Iwamoto, H. Yahiro, K. Tanda, N. Mozino, Y. Mine and S. Kagawa, J. Phys. Chem. 95 (1991) 3727.
[6] W. Held, A. König, T. Richter and L. Puppe, Society of Automotive Engineers, paper 900496.
[7] Y. Li and W.K. Hall, J. Catal. 129 (1991) 202.
[8] M. Iwamoto, H. Yahiro, N. Mizuno, W.-X. Zhang, Y. Mine, H. Furukawa and S. Kagawa, J. Phys. Chem. 96 (1992) 9360.
[9] W.K. Hall and J. Valyon, Catal. Lett. 15 (1992) 311.
[10] M. Shelef, Catal. Lett. 15 (1992) 305.
[11] E. Giamello, D. Murphy, G. Magnacca, C. Morterra, Y. Shioya, T. Nomura and M. Anpo, J. Catal. 136 (1992) 510.
[12] G. Spoto, S. Bordiga, D. Scarano and A. Zecchina, Catal. Lett. 13 (1992) 39.
[13] J. Valyon and W.K. Hall, J. Phys. Chem. 97 (1993) 1204.
[14] Y. Li and J.N. Armor, Appl. Catal. 76 (1991) L1.
[15] J. Sárkány, J.L. d'Itri and W.M.H. Sachtler, Catal. Lett. 16 (1992) 241.
[16] A.V. Kucherov, A.A. Slinkin, D.A. Kondrat'ev, T.N. Bondarenko, A.M. Rubinstein and Kh.M. Minachev, Zeolite 5 (1985) 320.
[17] A. Bianconi, in: *X-ray Absorption, Principles, Applications, Techniques of EXAFS, SEXAFS and XANES*, eds. D.C. Koningsberger and R. Prins (Wiley, New York, 1988).
[18] K.C.C. Kharas, Appl. Catal. B (1993), accepted.
[19] Y. Li and W.K. Hall, J. Phys. Chem. 94 (1990) 6145.
[20] D.-J. Liu and H.J. Robota, to be published.
[21] L.-S. Kau, D.J. Spira-Solomon, J.E. Penner-Hahn, K.O. Hodgson and E.I. Solomon, J. Am. Chem. Soc. 109 (1987) 6433.
[22] J. Valyon and W.K. Hall, in: *Proc. 10th Int. Congr. on Catalysis*, Budapest 1992, eds. L. Guczi, F. Solymosi and P. Tétényi, in press.