

ON THE MECHANISM OF NO DECOMPOSITION AND SELECTIVE CATALYTIC REDUCTION BY HYDROCARBONS OVER CU-ZSM-5

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The initial reports on the catalytic activity of Cu-ZSM-5 during NO decomposition and selective catalytic reduction (SCR) by hydrocarbons[1-3] have generated a lot of excitement and the follow-up research on this catalyst in recent years. Although the lack of hydrothermal aging stability may prohibit its practical application, Cu-ZSM-5 provides an excellent system for studying the mechanism and the structure-function relationship of the zeolite based NO_x reduction catalysts. Reported here are our most recent analysis of the data obtained from the investigations of the catalytic mechanisms of NO removal over a Cu-ZSM-5 catalyst using the *in situ* X-ray absorption spectroscopy method. Two mechanism were studied and compared, they are a) direct NO catalytic decomposition and b) NO SCR by hydrocarbons in an oxygen-rich gas mixture. The difference and similarity between the two mechanisms were found through the analysis of cuprous and cupric ion transition energy shifts, the changes of local coordination structure, the influence of cuprous ion formation/catalytic activities by Cu exchange level and the type of hydrocarbon used in the catalytic reactions. The results are summarized in Table I.

In our study of direct NO decomposition[4,5], we observed that the $1s \rightarrow 4p$ 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. The number of oxygen atoms surrounding the copper ions also drops from 4 to 2 during the auto-reduction. After the admission of a NO/N₂ gas mixture, the Cu(I) $1s \rightarrow 4p$ transition intensity decreases but by no means disappears. By using a XANES linear summation method, we can calculate the Cu(I) content as a fraction of the total copper ions. Furthermore, we found that the "excessively" exchanged Cu-ZSM-5 maintains higher concentration of Cu(I) under the reaction condition than that of under exchanged catalyst. During NO decomposition, we observed that the integrated intensity of the Cu(I) transition varies with the catalytic temperature, although transition energy remains unchanged. Unshifted Cu(I) transition suggests that the coordination chemistry of the cuprous ion remains the same while the relative concentration between Cu(I) and Cu(II) changes, as is indicated by the variation of Cu(I) intensity. By using a normalized difference XANES method, we calculated the normalized cuprous ion concentration and found it correlates well with the NO decomposition rate from 300 to 500 °C. Shown in Fig. 1. This finding supports the conjecture that Cu(I) participates in a redox mechanism during catalyzed NO decomposition in Cu-ZSM-5 at elevated temperature. The active site is a two-oxygen coordinated cuprous ion.

In our study of the SCR of NO by hydrocarbons[6], we observed that, even under strongly oxidizing conditions, a significant fraction of copper ion in ZSM-5 can be reduced to Cu(I) at elevated temperature. The rate of

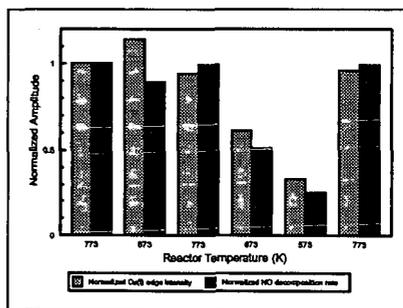


Figure 1 The correlation between the normalized Cu(I) concentration and the NO decomposition rate at different T.

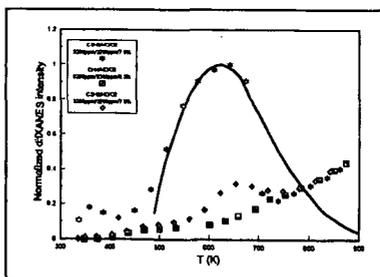


Figure 2 Comparison of the relative Cu(I) concentration in different gas mixtures with NO conversion level.

formation of Cu(I) is less sensitive to the exchange level than to the type of hydrocarbons used. The power of reducing Cu(II) to Cu(I) follows the sequence, $C_3H_6 > C_3H_8 > CH_4$, with methane practically equals to zero. The similar Cu $1s \rightarrow 4p$ transition was observed although the peak energy shifted at different reaction temperature, indicating the formation of the Cu(I)-organic ligands possibly allylic species during the catalysis. XANES spectra show that the Cu(I) $1s \rightarrow 4p$ transition intensity changes with the reaction temperature in a similar pattern as the NO conversion activity (solid line in Fig. 2, obtained from Ref. 7) in the $NO/C_3H_6/O_2$ mixture. Shown in Fig. 2. For comparison purposes, we also studied the Cu(I) concentration change in a similar gas mixture where propene is stoichiometrically replaced by methane or propane. Unlike propene, methane shows no selectivity for NO reduction over Cu-ZSM-5. We did not observe any window of Cu(I) enhancement. Propane is a selective reducing agent and we indeed observed a window of Cu(I) enhancement although the intensity is much weaker than that observed with propene. Our study indicates that, even in a strongly oxidizing environment, cupric ion can be partially reduced by propene or propane to form a Cu(I) which is a crucial step for effective NO conversion through a redox mechanism.

Table I. The difference and similarity in oxidation state, coordination structure and reaction mechanism between NO decomposition and NO SCR by hydrocarbons over Cu-ZSM-5

NO Decomposition	NO SCR by Hydrocarbons
The cuprous ion, Cu(I), is observed during the direct NO catalytic decomposition, suggesting a redox mechanism in which the catalyst's active site is Cu(I). Cu(I) is formed through the auto-reduction at elevated temperature which involves a dicopper process. Cu(I) formation is sensitive to the Cu exchange level and the "excessively" exchanged Cu-ZSM-5 maintains higher concentration of Cu(I) than that of "underexchanged" under the reaction conditions.	The cuprous ion is also observed during the NO selective catalytic reduction by hydrocarbons, suggesting a redox mechanism which involves the conversion between Cu(II) and Cu(I). Cu(I) is formed through the reduction by hydrocarbons. The rate of formation of Cu(I) is not sensitive to exchange level, rather it is very sensitive to the type of hydrocarbons used. The reducing power is $C_3H_6 > C_3H_8 > CH_4$, with methane practically equals to zero.
The $1s \rightarrow 4p$ electronic transition of Cu(I) does not shift its energy at different reaction temperature, indicating that no significant variation occurs to Cu(I) coordination environment.	The $1s \rightarrow 4p$ transition energy is shifted at different reaction temperature in the $NO/C_3H_6/O_2$ mixture, indicating that the local coordination of Cu(I) varies with the reaction conditions. No energy shift is observed in propane or methane mixture.
The cuprous ion formed through auto-reduction is coordinated by two oxygen atoms. No clear higher shell structure is observed. Under direct NO decomposition, copper ions consist of the mixture of Cu(I) and Cu(II), Cu(II) is coordinated by four oxygen atoms.	Cu(I) formed by olefine (propene) reduction is also likely to be coordinated by two oxygen atoms, with a possible Cu allylic bond which has not been identified unambiguously. No evidence of the allylic compound formation was observed for propane and methane mixtures.
Cu(I) concentration increases with the reaction temperature, and is correlated with the NO decomposition rate from 300 to 500°C. Discrepancy is observed at 600 °C.	Cu(I) concentration as the function of the reaction temperature depends on the gas compositions. For SCR by propene, normalized Cu(I) intensity at various temperature appears to overlap with the normalized reaction rate versus the temperature.
Cu(I) concentration decreases sensitively with the increase of the oxygen concentration in the gas phase.	Cu(I) concentration also decreases with the increase of the oxygen concentration, but with less degree of sensitivity.

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