Photocatalytic Decomposition of NO on Transition Metal Ion-exchanged Zeolite Catalysts

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Abstract: Transition metal ions (Cu⁺, Ag⁺) incorporated within the cavities of zeolites by an ion-exchange method show an efficient and unique photocatalytic performance for the decomposition of NO into N₂ and O₂ at 275 K. In situ ESR, UV-VIS, photoluminescence and XAFS (XANES and FT-EXAFS) investigations revealed that the transition metal ions exist in highly dispersed state with linear 2 coordination sphere within the pores of zeolites, the local structures of the metal ions being significantly affected by changing the kinds of zeolites. Detailed studies of the interaction of NO with the excited states of these metal ions clearly indicated that unique inner shell type excitation states of these metal ions play a significant role in the photocatalytic decomposition of NO, i.e., an electron transfer from the s orbital of the excited state of Cu⁺ or Ag⁺ ions into the π* antibonding orbital of NO initiates the decomposition reaction of NO.

Keywords: photocatalyst, Cu⁺, Ag⁺, zeolites, NO decomposition

1. Introduction

This present review concerns the role of the local structures of Cu⁺ and Ag⁺ ion photocatalysts incorporated in zeolites and their photocatalytic reactivities for the decomposition of NOx, following up on our previous work involving photocatalytic reactions on titanium oxide and vanadium oxide photocatalysts designed within zeolites [1].

In contrast to photocatalysis on semiconducting materials, it has been reported that transition metal ions such as Cu⁺ or Ag⁺ anchored onto the silica surface show unique photochemical/thermal or photocatalytic activity such as the decomposition of NO into N₂ and O₂ [2,3] or the cleavage of water to produce H₂ and O₂ [4]. In order to design photocatalysts with high activity and selectivity, it is necessary to control the dispersion or local structure of the active sites. However, the precise design of the active site on a molecular scale is difficult, especially when using amorphous materials such as SiO₂ or Al₂O₃ for the catalyst support.

On the other hand, the counter cations in zeolites are very easily exchanged onto an ion-exchangeable site with a specific local structure through different cations by conventional ion-exchange methods. Since the exchangeable sites are separated from each other within the zeolite cavities under well-controlled conditions, ion-exchange with metal ions having photocatalytic capabilities, such as Cu⁺ or Ag⁺ ions, can be used for the preparation of unique and effi-
cient photocatalysts. The large surface area of zeolites and their specific channel systems make such materials the most promising candidates for useful and highly reactive photocatalysts. In fact, we have reported that Cu$^+$ or Ag$^+$ ions can be successively exchanged onto zeolites in an isolated state, and UV-irradiation of such catalysts lead to photocatalytic reactions such as the decomposition of NO or N$_2$O into N$_2$ and O$_2$ [5-9]. The electronic excited state of Cu$^+$ or Ag$^+$ ions produces an $s^2$ electron and a $d^2$ hole on the identical one-metal ion ($d^3s^1$ electronic configuration) while the localized electron-hole pair state can induce unique photocatalytic reactions which are not possible on either semiconductor photocatalysts or on highly dispersed metal oxide photocatalysts.

\[
\begin{align*}
\text{Cu}^+ ([\text{Ar}]3d^{10}) &\rightarrow \text{Cu}^{++} ([\text{Ar}]3d^{9}s^1) \\
\text{h} &\nu \quad \text{h} &\nu \\
\text{Ag}^+ ([\text{Kr}]4d^{10}) &\rightarrow \text{Ag}^{++} ([\text{Kr}]4d^{9}s^1)
\end{align*}
\]

Besides their role as a support to control the dispersion and local structure of the active sites, zeolites have many other unique and useful properties such as a condensation effect for reactant gasses and shape selectivity which is due to the unique pore structure and its restricted size of molecular scale. These unique properties can be incorporated in the design and development highly efficient and selective photocatalysts which work to reduce toxic agents in the atmosphere or water by using the zeolite cavities as reaction fields. The combination of well-defined photocatalysts and multifunctional materials such as zeolites will make it possible to develop new and applicable photocatalytic systems, significantly to address environmental concerns.

In this review, the photocatalytic reactivities of zeolite catalysts which incorporate transition metal ions (Cu$^+$ or Ag$^+$) in their framework structures or cavities for decomposition reactions of NO at ambient temperatures will be discussed in detail. The local structures of the transition metal ion species exchanged into the nano-pores of the zeolites are also discussed based on the results obtained by means of various in situ molecular spectroscopic techniques such as photoluminescence, ESR, XAFS (XANES and EXAFS), UV-VIS, and FT-IR investigations. Special attention is focused on the relationship between the local structures of the active sites for the photocatalytic reactions and their photocatalytic reactivities.

\section{2. Preparation of the Cu/ZSM-5 Catalysts and their Photocatalytic Reactivities for the Decomposition of NO}

The protection of our environment from global air pollution caused by NOx (NO, NO$_2$, and N$_2$O) as well as SOx is currently an urgent and serious concern. As a way to address such problem, ammoxidation using the V$_2$O$_5$/TiO$_2$ catalyst has been developed as a de-NOx-ing process [10]. However, it operates only at high temperatures and requires NH$_3$. Strongly desired are catalytic systems for the direct decomposition of NOx which are able to operate at ambient temperatures and ambient pressure conditions without NH$_3$. Ion-exchanged Cu$^+$/ZSM-5 zeolite catalysts have shown much promise for efficient and effective systems in the direct decomposition of NO into N$_2$ and O$_2$ at temperature of around 723 K [11]. Moreover, the applications of photocatalytic processes in gas-solid systems also seems to be one of the most promising approaches to dissolve and reduce environmental toxins. Along these lines, the photocatalytic activity of the Cu$^+$/ZSM-5 catalyst for the decomposition of NO has been investigated and it was found that this catalyst may, in fact, act as a photocatalyst to directly decompose NO into N$_2$ and O$_2$ while the photo-excited state of the isolated Cu$^+$ ion was observed to play a significant role in the reaction [5].

In the following section, a detailed characterization of the Cu species anchored into the nanopores of the ZSM-5 zeolite by means of in situ photoluminescence, ESR, XAFS and UV-VIS measurements and their reactions with gaseous NO under UV-irradiation will be discussed on a molecular scale.

\subsection{2.1. Local Structures of the Cu$^{2+}$/ZSM-5 and Cu$/ZSM-5$ Catalysts}

The copper (II) ion-exchanged ZSM-5, i.e., Cu$^{2+}$/ZSM-5 was prepared by ion-exchange with an aqueous Cu(NH$_3$)$_4$$^{2+}$ solution, followed by a drying process in air at 373 K. Figure 1 shows the Cu K-edge XANES and Fourier transformed EXAFS (FT-EXAFS) spectra of the Cu$^{2+}$/ZSM-5 sample (a, a') and the Cu$^+$/ZSM-5 catalyst prepared by the evacuation of the original Cu$^{2+}$/ZSM-5 sample at 973 K (b, b'), respectively. The XANES and FT-EXAFS spectra both provide useful and detailed information on the coordination structure and electronic states of the elements which absorb the X-ray photons. As shown in Figure 1-(a), the Cu$^{2+}$/ZSM-5 sample dried at 373 K exhibits a well-separated weak
preedge band (A) due to the 1s-3d transition as well as an intense band due to the 1s-4p transition. Band (B) attributed to the 1s-4pz (1s-4p\,z^*) transition can be observed as a shoulder of the intense band (C) attributed to the 1s-4px, 4py (1s-4p\,\sigma^*) transition accompanied by their weak shake-down bands (B', C'). The presence of band (A) attributed to the 1s-3d transition which is forbidden by the selection rule in the case of perfect octahedral symmetry as well as the presence of the shake-down bands (B', C') arising from a 1s-4p transition coupled with a simultaneous ligand-to-metal electron transfer which is characteristic for the metal ion having d^{9} electronic configuration, indicate that the Cu^{2+}/ZSM-5 contains Cu^{2+} ions having slightly distorted symmetries as the major species [12-14]. These findings coincide with the results obtained by ESR studies (shape, g-tensors and A-factors) indicating the presence of hydrated Cu^{2+} ions with an elongated octahedral symmetry in the Cu^{2+}/ZSM-5 [5,15]. The ESR spectrum of the Cu^{2+}/ZSM-5 measured at ambient temperature gives a broad isotropic signal, suggesting that the hydrated Cu^{2+} ions are not anchored onto the zeolite surface but rotate freely in the pore structure of the ZSM-5 zeolite.

As shown in Figure 1-(b), the Cu^{2+}/ZSM-5 catalyst which is prepared by the evacuation of the original Cu^{2+}/ZSM-5 sample at 973 K exhibits a very strong and sharp band (B) due to the 1s-4p\,z transition. In the case of the Cu^{+} ion having a d^{10} electronic configuration, the shake down transition coupled with a ligand-to-metal electron transfer did not occur. The absence of the shake down peak related to the sharp band (B) indicates that Cu^{+} is the main component in the Cu^{+}/ZSM-5 catalyst. It is known that in a planar or a linear geometry, the 1s-4p\,z transition is not affected by the ligands, therefore, the copper compounds having these geometries exhibit a strong and sharp band (B) attributed to the 1s-4p\,z transition in the preedge region. Band (B) is intense enough to identify the copper species as the isolated Cu^{+} ions with a planar 3 or linear 2 coordinate geometry [12-14].

Figure 1 also shows the corresponding FT-EXAFS spectra of the copper cation sample and catalyst. All data are given without any corrections for phase shifts. Table 1 shows the results obtained by the curve-fitting analyses of the Cu K-edge EXAFS spectra employing the iterative nonlinear least-squares method of Levenberg [16] and the empirical backscattering parameter sets extracted from the shell features of the copper compounds.

As can be seen in Figure 1-(b'), the Cu^{+}/ZSM-5 catalyst exhibits only the Cu-O peak at around 1.5 Å due to the presence of the neighboring O atom adjacent to the Cu atom and neither the Cu-O-Cu peak which is observed for the aggregated Cu oxide species nor the Cu-Cu peak which is observed for the Cu metal species can be observed. These results clearly indicate the presence of isolated Cu^{+} ions on the Cu^{+}/ZSM-5 catalyst. The curve-fitting analysis of the Cu-O peak indicates that the isolated Cu^{+} ions are present in the Cu^{+}/ZSM-5 catalyst having a 2 or 3-coordinate geometry [14]. The presence of the isolated 2 or 3-coordinate Cu^{+} ions directly suggests the formation of Cu^{+} ions with a planar 3 or linear 2 coordinate geometry, as suggested by the XANES studies.

Figure 2 shows the effect of the evacuation temperature of the original Cu^{2+}/ZSM-5 sample on the intensity of the ESR signals attributed to the Cu^{2+} ions (a), the intensity of the UV-VIS spectra of the Cu^{2+} (b) and Cu^{+} ions (c), and the intensity of the XANES band due to the 1s-4p\,z transition of the

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Table 1. The Results of the Curve-fitting of Cu K-edge EXAFS Data for Cu^{2+}/ZSM-5 Sample and Cu^{+}/ZSM-5 Catalysts Evacuated at Various Temperatures

<table>
<thead>
<tr>
<th>Samples</th>
<th>Tm. (K)</th>
<th>Shell</th>
<th>R(Å)</th>
<th>CN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu^{2+}/ZSM-5</td>
<td>373</td>
<td>Cu-O</td>
<td>2.00</td>
<td>4.2</td>
</tr>
<tr>
<td>Cu^{+}/ZSM-5</td>
<td>573</td>
<td>Cu-O</td>
<td>1.94</td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td>773</td>
<td>Cu-O</td>
<td>1.94</td>
<td>2.4</td>
</tr>
<tr>
<td></td>
<td>973</td>
<td>Cu-O</td>
<td>1.94</td>
<td>2.3</td>
</tr>
</tbody>
</table>

Tm.: Evacuation temperature. R: Bond distances. CN: Coordination number.
Cu$^+$ ions (d). As can be seen in Figure 2, the temperature dependence of the ESR, UV-VIS and XANES spectra of Cu$^{2+}$/ZSM-5 and Cu$^+$/ZSM-5 also clearly indicate that the isolated Cu$^{2+}$ species are reduced to isolated Cu$^+$ ions by the evacuation of the Cu$^{2+}$/ZSM-5 samples at temperatures higher than 473 K. Temperature-programmed desorption profiles with the Cu$^{2+}$/ZSM-5 sample show the desorption of large amounts of H$_2$O, NH$_3$, N$_2$, and O$_2$ in the temperature range above 473 K [5]. From these results, the reduction mechanism of Cu$^{2+}$ ions can be proposed in the following equations, where H$_2$O and NH$_3$ coordinated to the Cu$^{2+}$ ions act as reductants [17]:

\[ 2\text{Cu}^{2+} + \text{H}_2\text{O} \rightarrow 2\text{Cu}^+ + 2\text{H}^+ \text{ (Brønsted acid)} + 1/2\text{O}_2 \]
\[ 3\text{Cu}^{2+} + \text{NH}_3 \rightarrow 3\text{Cu}^+ + 3\text{H}^+ + 1/2\text{N}_2 \]

2.2. Excited State of the Cu$^+$/ZSM-5 Catalyst

As shown in Figure 2, after the evacuation of the Cu$^{2+}$/ZSM-5 sample at 973 K, the ESR signal assigned to the Cu$^{2+}$ species became very weak in its intensity. It is clear that at this temperature most of the Cu$^{2+}$ ions were reduced to Cu$^+$ ions. Figure 3 shows that the Cu$^+$/ZSM-5 catalyst prepared in this way exhibits a photoluminescence spectrum with its maxima at around 440 nm upon excitation at around 280 - 300 nm. It has been reported that the emission spectrum of the free Cu$^+$ ion in the gas phase is observed at around 450 nm and is attributed to the radiative deactivation (3d$^9$4s$^1$→3d$^{10}$ + hv) of the free Cu$^+$ ion, while the presence of a crystal field due to the zeolite makes the emission peak shift to higher energy by raising the energy of the 4s orbital with respect to that of the 3d orbitals [18]. On the other hand, as the distance between the Cu$^+$ ions decreases, the overlap of the 4s atomic orbitals which leads to the formation of the $\sigma$ (4s) molecular orbital increases, pushing the $\sigma$ (4s) bond energy down closer to that of the $\sigma^*$ (3d) antibonding molecular orbital derived from the 3d atomic orbitals. Thus, Cu$^+$-Cu$^+$ pairs are expected to exhibit photoluminescence ($\sigma$ (4s)$\rightarrow$ $\sigma^*$ (3d)) in wavelength regions longer than the position of the photoluminescence band due to the free Cu$^+$ ion in the gas phase (450 nm) [19]. With these results in mind, the excitation (absorption) and photoluminescence spectra shown in Figure 3 can be attributed to the presence of isolated Cu$^+$ ions coordinated by the lattice oxygen in the zeolite framework, i.e., the electronic excitation of the isolated Cu$^+$ ion (3d$^{10}$ +hv$\rightarrow$3d$^9$4s$^1$) and its reverse radiative deactivation(3d$^9$4s$^1$→3d$^{10}$ + hv$'$), respectively [19-24]. This assignment of the photoluminescence is well supported by the results obtained by FT-EXAFS which indicate that in the ZSM-5 zeolite most of the copper cations are included as isolated Cu$^+$ monomer species.

On the other hand, in the case that the Y-zeolite is used as a support instead of the ZSM-5 zeolite, the Cu$^+/Y$-zeolite exhibits two different intense bands at around 420 nm due to the Cu$^+$ monomer and at around 515 nm due to the radiative deactivation ($\sigma$ (4s)$\rightarrow$ $\sigma^*$ (3d)) of Cu$^+$ dimer species, re-
Figure 4. Effects of the evacuation temperature of the Cu$^{2+}$/ZSM-5 sample on the relative intensity of the ESR signal due to Cu$^{2+}$ (a), the relative yields of the photoluminescence due to Cu$^+$ (b) and the relative conversions (yields) of the photocatalytic decomposition of NO (NO pressure: 2 Torr) at 298 K (c).

respectively [14-19]. Considering the differences in the void space volumes of the supercages and types of channel connections in these two types of zeolites, it can be expected that the copper (I) cations in the Y-zeolite diffuse more easily to form the Cu$^+$-Cu$^+$ dimer species, while in the narrow channels of ZSM-5, the mobility of the copper (I) cations is low and remain intact as isolated Cu$^+$ monomer species. In addition to these differences, the density or number of the ion-exchangeable sites in the zeolites is remarkably different. In the case of the Y-zeolite, the SiO$_2$/Al$_2$O$_3$ ratio (5.5) is lower than ZSM-5 (23.3), having a large density of ion-exchangeable sites which allow the copper cations to exist close to each other. Such a situation easily causes the aggregation of copper cations during thermal treatments at high temperatures [14]. In accordance with these results, the FT-EXAFS spectrum of the Cu$^+$/Y-zeolite exhibits an intense peak at 2.6 Å due to the neighboring copper atoms (Cu-O-Cu) in addition to a peak at 1.5 Å due to the Cu-O bond, indicating that the aggregation of the Cu$^+$ ions easily occurred on the Cu$^+$/Y-zeolite [14].

Figure 4 shows that the intensity of the photoluminescence spectrum of the Cu$^+$/ZSM-5 catalyst increases when the degassing temperature of the original Cu$^{2+}$/ZSM-5 sample is increased, passing through a maximum at 1173 K, and then decreasing in the region of much higher evacuation temperatures. In the highest temperature region where the intensity of the photoluminescence becomes weaker, the color of the catalysts changed from white to light red and also the peak due to the Cu-Cu bond was observed in the FT-EXAFS spectrum of the catalyst, suggesting that the evacuation of the sample at temperatures higher than 1173 K leads to the further reduction of copper (I), from Cu$^+$ to Cu$^+$. It can be seen in Figure 4 that there is a gap between the temperature where the intensity of the ESR signal starts and where the increase in the intensity of the photoluminescence begins. This can be explained by the quenching of the photoluminescence of the Cu$^+$ ions due to the existence of surface OH groups and/or adsorbed O$_2$ near the Cu$^+$ ions in the temperature regions of 473-673K and these quenchers can be desorbed only by evacuation treatment at temperatures higher than 673K.

2.3. The Interaction of NO with the Cu$^+$/ZSM-5 Catalyst

Figure 5 shows the ESR signal due to the NO species adsorbed on the Cu$^+$/ZSM-5 catalyst. Four equally spaced $g_1$ components and the spin Hamiltonian parameter of the spectrum indicate that NO molecules are adsorbed on the Cu$^+$ ion ($I = 3/2$) to form nitrosylic adducts on Cu$^+$ having a slight electron transfer from Cu$^+$ to NO (i.e., Cu$^+$-NO$^-$) [15,25-27]. However, the fact that the ESR signal due to Cu$^{2+}$ cannot be observed clearly indicates that the complete one-electron transfer from Cu$^+$ to NO did not occur. The Cu$^+$-NO$^-$ adduct species are stable in the presence of low pressure of NO (< 1 Torr) while after the evacuation of the system at an ambient temperature the ESR signal disappears. On the other hand, in the presence of a high pressure of NO (> 1 Torr) the ESR signal of Cu$^{2+}$ can be

the photocatalytic decomposition reaction of NO greatly depend on the pretreatment degassing temperature of the Cu'//ZSM-5 samples, showing a good parallel relationship with the dependency of the photoluminescence intensity attributed to the Cu' ion. These results indicate that the photoexcited states of the Cu' ion play a significant role in the photocatalytic decomposition reaction of NO.

As shown in Figure 6, the Cu'//ZSM-5 catalyst exhibits a higher photocatalytic activity as compared to the Cu'/Y-zeolite catalyst. In the Cu'//ZSM-5 catalyst, isolated Cu' ions are the predominant species, whereas with the Cu'/Y-zeolite, a considerable amount of Cu' dimer species exist together with the Cu' monomer species. Therefore, it can be concluded that the photocatalytic reactivity of the Cu' monomer species is higher than that of the Cu' dimer species. In fact, the photoluminescence spectrum of the Cu'//ZSM-5 catalyst at around 440 nm is quenched more efficiently than the Cu'/Y-zeolite, indicating that the photoexcited state of the Cu' monomer species interact with NO more efficiently than the Cu' dimer species [5,14]. It should also be noted that the CuO powder, which is a model oxide compound of the aggregated Cu', did not show any photocatalytic activity for the reaction, suggesting that the presence of a highly dispersed Cu' species is essential for the photocatalytic reaction.

UV-irradiation of the Cu'//ZSM-5 catalyst having an Cu'-NO^3- adduct species leads to a decrease in the intensity of the ESR signal assigned to the Cu'-NO^+ species with the UV-irradiation time and without the appearance of any new signal. After UV-irradiation was ceased, the intensity of the signal returned to its original level. These reversible changes in the ESR signal assigned to the Cu'-NO^+ adduct species suggest not only that this species act as reaction precursors but also that the photoinduced decomposition of NO proceeds catalytically. The addition of NO onto the Cu'//ZSM-5 catalyst led to the efficient quenching of the photoluminescence due to Cu'. The lifetime of the photoluminescence is shortened by the addition of NO, its value becoming shorter with the increase in the pressure of NO, i.e., an increase from about 85 μsec in vacuum to 70 μsec in the presence of 1.0 Torr pressure of NO [5]. These results clearly suggest that the added NO can easily interact with the Cu' species both in its ground and excited states.

From these investigations together with the results obtained by in situ photoluminescence, ESR, and FT-IR measurements, the mechanisms of the photocatalytic decomposition of NO into N_2 and O_2 on

2.4. Photocatalytic Decomposition of NO on the Cu'/ ZSM-5 Catalyst

UV-irradiation of the Cu' ion catalyst even at 275 K in the presence of NO was found to lead to the formation of N_2 and O_2, with a good linear relationship between the UV-irradiation time and the NO conversion. Figure 6 shows the reaction time profiles of the photocatalytic decomposition of NO at 275 K on the Cu'//ZSM-5 and Cu'/Y-zeolite. The formation of by-products such as N_2O and NO_2 was negligible. As also shown in Figure 4, the yields of

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the Cu'/ZSM-5 catalyst at 275 K under UV-irradiation can be proposed as follows (scheme 1): an electron transfer from the excited state of Cu' (3d¹⁴s¹ state) to the π-anti-bonding orbital of NO and a simultaneous electron transfer from the π-bonding orbital of another NO to the vacant electronic state of the Cu' ion (3d¹⁴s⁰ state) occur causing local charge separation and a weakening of the N-O bond of the two NO molecules that initiate the decomposition of NO into N₂ and O₂ [5]. Two different NO adsorbates, i.e., NO which constitutes the Cu'-NO⁺ adduct and NO which is supplied from the gas phase, are simultaneously activated on the photo-excited Cu' site in the local electron transfer, resulting in the selective formation of N₂ and O₂ without any formation of N₂O and/or NO₂ on the Cu'/ZSM-5 catalyst at 275 K.

3. Design of the Ag⁺/ZSM-5 Catalysts and their Photocatalytic Reactivity for the Decomposition of NO

As has been shown, the Cu'/ZSM-5 catalyst can decompose NO into N₂ and O₂, however, the preparation of these Cu' ion catalysts require a pretreatment of the original Cu⁺/ZSM-5 samples at temperatures higher than 973 K to reduce Cu⁺² to Cu⁺ ions. On the other hand, the Ag⁺ ion has the same electronic configuration as a Cu⁺ ion (d¹⁰). Therefore, it can be expected that the Ag⁺ ion may exhibit similar catalytic and photocatalytic reactivity as the Cu' ion, while the Ag⁺ ion has the advantage of being chemically stable even in an oxidative atmosphere. In fact, ion-exchanged silver/zeolite catalysts have been reported to show very high activity for the disproportionation of ethylbenzene,

![Scheme 1. Reaction scheme of the photocatalytic decomposition of NO into N₂ and O₂ on the Cu⁺/ZSM-5 catalyst at 275 K.](image)

![Figure 7. XANES (left) and FT-EXAFS (right) spectra of the Ag⁺/ZSM-5 catalyst (a, a'). AgO powder (b, b') and Ag foil (c, c').](image)

[28,29] the photochemical/thermal cleavage of water to produce H₂ and O₂ [4] photo-oxygen production from water, [30] photo-dimerization of alkanes, [31] and the selective reduction of NO by ethylene at around 823 K [32] or by ethanol at around 723 K. [33] The following section shows that the Ag⁺/ZSM-5 catalyst shows remarkably high photocatalytic reactivity for the decomposition of NO compared with the Cu⁺/ZSM-5 catalyst even in the coexistence of H₂O or O₂.

3.1. Local Structure of the Ag⁺/ZSM-5 Catalyst

Silver(I) ion-exchanged ZSM-5, Ag/zeolite samples were prepared by ion-exchange with an aqueous Ag(NH₃)₂Cl solution, followed by evacuation at 298 K, calcination at 673 K in the presence of O₂, degassing at 473 K. The Ag⁺/ZSM-5 catalyst was prepared by heating Ag⁺/ZSM-5 at 673 K in the presence of an H₂/H₂O mixture at a total pressure of 20 Torr (H₂/H₂O=1).

Figure 7 shows the FT-EXAFS spectra of the Ag⁺/ZSM-5 catalyst (a') together with bulk AgO (b') and Ag foil (c') as references, respectively. The FT-EXAFS spectrum of AgO (b') exhibits a peak at around 3.5 Å (phase shift is not corrected) which can be attributed to the Ag-O-Ag bonding, while FT-EXAFS studies of the Ag foil (c') shows a peak.
at around 2.5 Å due to the Ag-Ag bonding. However, the \( \text{Ag}^+ / \text{ZSM-5} \) catalyst exhibits only a well-defined peak due to the neighboring oxygen atoms (Ag-O) at around 1.8 Å. These results suggest that silver is anchored within the micro pores of the ZSM-5 zeolite in an isolated state forming neither clusters nor Ag metal or oxide crystals.

Figure 8 shows the UV-VIS spectra of the \( \text{Ag}^+ / \text{ZSM-5} \) (a), \( \text{H}^+ / \text{ZSM-5} \) (b), and \( \text{Ag}^- / \text{ZSM-5} \) catalyst (c), respectively. \( \text{H}^+ / \text{ZSM-5} \) exhibits no intense absorption band in the 200-250 nm wavelength ranges. On the other hand, as shown in Figure 8-(a), the \( \text{Ag}^+ / \text{ZSM-5} \) catalyst exhibits an intense absorption band at around 220 nm which is attributed to the \( 4d^{10} \rightarrow 4d^95s^1 \) electronic transition of the \( \text{Ag}^+ \) ions. [34-36] Although the \( \text{Ag}^+ \) atoms, as well as \( \text{Ag}_{m^+} \) and \( \text{Ag}_{m^+} \) clusters are known to exhibit absorption bands at wavelengths above 250 nm, [37,38] no absorption band of the \( \text{Ag}^+ / \text{ZSM-5} \) appears in this region. Furthermore, no ESR signals assigned to the \( \text{Ag}^+ \) atoms or \( \text{Ag}^+ \) species were observed with the \( \text{Ag}^+ / \text{ZSM-5} \) catalyst. These results firmly support the conclusion that silver ions are included within the pore structure of the ZSM-5 zeolite as highly dispersed \( \text{Ag}^+ \) ions [8,9].

As shown in Figure 8-(c), after \( \text{H}_2 \) treatment of the \( \text{Ag}^+ / \text{ZSM-5} \) catalyst at 673 K, the intensity of the absorption band of the \( \text{Ag}^+ \) ions at around 220 nm drastically decreases and broad absorption bands due to the \( \text{Ag}_{m^+} \) or \( \text{Ag}_{m^+} \) clusters appear at wavelengths longer than 250 nm, indicating that reduction and aggregation of the \( \text{Ag}^+ \) ions have occurred. Since \( \text{Ag}^- / \text{ZSM-5} \) did not show any photocatalytic reactivity for the decomposition of NO, it could be concluded that the \( \text{Ag}_{m^+} \) or \( \text{Ag}_{m^+} \) clusters are not associated with the reaction. On the other hand, in the case of the \( \text{Ag}^+ / \text{Y}-\text{zeolite}, \) UV absorption bands above 250 nm appear and with the same catalyst a peak due to the neighboring Ag atom was observed in the FT-EXAFS spectrum at around 2.5 Å, suggesting the presence of \( \text{Ag}_{m^+} \) or \( \text{Ag}_{m^+} \) clusters on the \( \text{Ag}^+ / \text{Y}-\text{zeolite}. \)

3.2. Excited State of the \( \text{Ag}^+ / \text{ZSM-5} \) Catalyst and Interactions with NO

The addition of NO onto the \( \text{Ag}^+ / \text{ZSM-5} \) catalyst at 77K leads to the appearance of a specific ESR signal due to the adsorbed NO species \( g_e=1.875, \quad g_{\perp}=1.996, \quad A_{\perp}=78.3 \, G \). The hyperfine splitting of the signal into the equally spaced lines due to the interaction of the electron spin of NO with the nucleus of \( \text{Ag}^+ \) \((I=1/2)\) clearly indicates that the NO molecules are adsorbed on the \( \text{Ag}^+ \) ions to form a nitrilosyl adduct species, i.e., \( \text{Ag}^+\text{-NO} \) [39]. The evacuation of the system after the adsorption of NO onto the \( \text{Ag}^+ / \text{ZSM-5} \) led to the disappearance of the signal, suggesting that the interaction of NO with the \( \text{Ag}^+ \) ion is weak. Upon evacuation no new ESR signals appeared, indicating that the oxidation of \( \text{Ag}^+ \) to \( \text{Ag}^2+ \) by the addition of NO at high pressure (> 1 Torr) did not occur, unlike the case of \( \text{Cu}^+ / \text{ZSM-5} \).

UV-irradiation of the \( \text{Ag}^+ / \text{ZSM-5} \) catalyst having a \( \text{Ag}^+\text{-NO} \) adduct species led to a decrease in the intensity of the ESR signal with UV-irradiation time and without the appearance of any new signal. After UV-irradiation was ceased, the signal was found to recover to its original intensity. These
reversible changes suggest that the Ag⁺-NO adduct species act as reaction precursors for the photocatalytic decomposition of NO.

Figure 9 shows the photoluminescence spectrum (a) and its corresponding excitation spectrum (b) of the Ag⁺/ZSM-5 catalyst. A good coincidence of the excitation band position (220 nm) with that of the absorption band due to the isolated Ag⁺ ion (220 nm), indicates that these excitations and photoluminescence are attributed to the absorption due to the 4d⁰⁰ → 4d⁵⁵s³ transition and its reverse radiative deactivation process 4d⁵⁵s³ → 4d⁰⁰, respectively [8,9].

Figure 9 also shows the effect of the addition of NO on the photoluminescence of the Ag⁺/ZSM-5 catalyst. The addition of NO led to an efficient quenching of the photoluminescence and the evacuation of the system after a complete quenching of the photoluminescence led to the recovery of the photoluminescence to its original intensity. These results also suggest that the interaction of NO molecules with the Ag⁺ ions is weak, thus being in agreement with the results obtained by ESR analysis, while the added NO easily interacts with the Ag⁺ species in its ground and excited states. The photoluminescence of the Ag⁺/ZSM-5 catalyst was found to be more efficiently quenched by NO than the Cu⁺/ZSM-5 catalyst, suggesting that the photo-excited states of the Ag⁺ ions interact with NO more efficiently than Cu⁺ ions.

3.3. Photocatalytic Decomposition of NO on the Ag⁺/ZSM-5 Catalyst

UV-irradiation of the Ag⁺/ZSM-5 catalyst in the presence of 10 Torr of NO at 298 K was found to lead to the formation of N₂, N₂O and NO₂. The reaction time profiles of the formation of N₂ and N₂O are shown in Figure 10. The formation of N₂ and N₂O is found only under UV-irradiation and their yields increase with a good linearity against the irradiation time, clearly indicating that the reaction proceeds photocatalytically. In fact, after prolonged irradiation, the turnover frequency (number of N₂ per number of Ag⁺ in the catalyst) exceeded 1.0, showing that the reaction proceeds catalytically.

The most effective wavelengths of UV light for the photocatalytic decomposition of NO was determined by using various UV-cut filters. Under UV-irradiation of the catalyst through a UV-25 filter (λ > 250 nm), the photocatalytic decomposition of NO proceeded at 15% the rate obtained under irradiation without any filters, i.e., under full arc irradiation of the high pressure mercury lamp. This shows that the most effective UV light for the reaction lies in the wavelength regions of 200 nm to 250 nm, where the absorption (excitation) of the Ag⁺ ions (220 nm) can be observed. These results clearly show that the photo-excited state of the Ag⁺ ions plays a significant role in the photocatalytic decomposition of NO.

Under UV-irradiation of the Ag⁺/ZSM-5 and H⁺/ZSM-5 catalysts and Ag₂O powder, the decomposition of NO scarcely proceeded and the formation of N₂ and N₂O were negligible, while on the Ag⁺/Y-zeolite catalyst, the photocatalytic reaction proceeded at about 15% the rate obtained on the Ag⁺/ZSM-5 catalyst. These results suggest that an isolated Ag⁺ ion is responsible for the photocatalytic reaction while Agn⁺ or Agm⁺ clusters are not. As also shown in Figure 10, the rate of N₂ formation in the photocatalytic decomposition of NO on the Ag⁺/ZSM-5 catalyst is 10 times faster than on the Cu⁺/ZSM-5 catalyst [5,9]. Such high efficiency of the Ag⁺/ZSM-5 catalyst can be explained by the efficient interaction of the photo-excited Ag⁺ ion with NO as compared to the Cu⁺ ion.

The effect of the addition of O₂ on the photocatalytic decomposition of NO on the Ag⁺/ZSM-5 catalyst was also investigated. As suggested by ESR measurements, the addition of O₂ or NO at high pressures (> 1 Torr) did not lead to the oxidation of Ag⁺ to Ag²⁺ in the Ag⁺/ZSM-5 catalyst, in clear contrast to the easy oxidation of Cu⁺ to Cu²⁺ in the Cu⁺/ZSM-5 catalyst [15]. Such chemical stability of Ag⁺ even in an oxidative atmosphere is one of the main advantages in the use of the Ag⁺/ZSM-5 catalyst as an effective photocatalyst for the elimina-


4. Conclusions

In this paper, the local structures of the transition metal ion (Cu\textsuperscript{2+}, Ag\textsuperscript{+}) exchanged into the zeolite cavities were discussed from the results of various in situ spectroscopic techniques such as ESR, UV-VIS, photoluminescence and XAFS (XANES and EXAFS). The interactions of these active species with gaseous NO were investigated and the photocatalytic reactivity of these catalysts for the decomposition of NO have been summarized.

The highly dispersed Cu\textsuperscript{2+} and Ag\textsuperscript{+} ions act as efficient and unique photocatalysts for the decomposition of NO into N\textsubscript{2} and O\textsubscript{2}. In the case of the Cu\textsuperscript{2+} and Ag\textsuperscript{+} ion-exchanged ZSM-5 zeolite catalysts, the interaction of Cu\textsuperscript{2+} or Ag\textsuperscript{+} ions with the reactant NO molecules was observed by ESR, IR and photoluminescence spectroscopic measurements [40]. Based on these results, the reaction mechanisms involving a local electron transfer from the excited Cu\textsuperscript{2+} or Ag\textsuperscript{+} ions to the π-anti-bonding orbital of NO and simultaneous electron transfer from the π-bonding orbital of another NO to the vacant orbital of the Cu\textsuperscript{2+} or Ag\textsuperscript{+} ions have been proposed for the decomposition of NO into N\textsubscript{2} and O\textsubscript{2} at 275 K.

The inner shell type excitation of Cu\textsuperscript{2+} or Ag\textsuperscript{+} ions lead to unique photocatalytic properties quite different from semiconductor type photocatalysts (ex. TiO\textsubscript{2}, ZnO, etc.) [41-45] in which the photo-formed holes and electrons rapidly separate from each other in relatively large distances. It was also found that by using zeolites as a support, the local environment of the introduced cations can be significantly modified, and it becomes possible to achieve a mono-atomic dispersion of metal ions resulting in a remarkable enhancement of photocatalytic performance as compared to corresponding bulk metal oxides such as CuO or Ag\textsubscript{2}O.

Thus, it can be seen that the use of zeolites is one of the most promising approaches to the efficient design of the local structures of photocatalysts at the molecular level in order to establish efficient photocatalytic systems for reducing global air and water pollution.
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References