Effect of oxygen on selective catalytic reduction of NO by NH_3 over copper ion exchanged mordenite-type zeolite catalyst

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The effect of oxygen on the selective catalytic reduction of NO by NH_3 was examined over a copper exchanged mordenite type zeolite catalyst. The catalytic activity for NO reduction by NH_3 in the presence of oxygen was at least one order of magnitude higher than that in the absence of oxygen and it was fully reversible with respect to the presence of oxygen in the feed gas stream. Based upon ESR, TPD, TPO and TPSR studies, the redox behavior of copper ions was closely related to the enhancement of NO removal activity by the introduction of oxygen to the feed gases.

Keywords: selective catalytic reduction; nitric oxide; copper exchanged mordenite; electron spin resonance (ESR)

1. Introduction

The selective catalytic reduction (SCR) of nitric oxide by ammonia is the most widely commercialized process to remove NOx from stationary sources. Many investigators using different types of SCR catalysts observed that oxygen in the feed gases considerably increased the rate of reduction of NO by NH_3 [1–4]. Markvart and Pour [1] reported an enhanced reaction rate for NO reduction when oxygen was present in the feed gas stream. They concluded that oxygen accelerated the reaction by enhancing the dissociation of the ammonia on the catalyst surface, shifting its equilibrium toward more reactive species, dissociated NH_3. From IR studies, Takagi et al. [2] examined that NO reacts readily with NH_3 in the presence of oxygen via adsorbed NO and adsorbed NH_4^+ on V_2O_5 catalysts. On the other hand, Inomata et al. [5] observed that gaseous NO reacts with the adsorbed NH_3, i.e., NH_4 adsorbed adjacent to $V^{5+}{=}O$ by the Eley–Rideal mechanism.

In order to understand the role of oxygen for the zeolitic catalyst, the SCR reaction was carried out in the absence of O_2 with either only NO or NO_2 using N_2 as a carrier gas. Kiovsky et al. [3] suggested that the role of oxygen is in converting NO to NO_2, which is a more reactive species than NO in SCR, based upon the observation that the complete reduction of NO_2 is achieved, whereas no reduction of NO is observed. In recent work, Amiridis et al. [4] also reported that the NO reduction activity on iron-Y zeolite was enhanced by about two orders of magnitude by oxygen in the feed gas stream. According to their results, the rate-limiting step appears to be the reoxidation of iron in the absence of oxygen. Consistent results have been reported on the effect of oxygen on the acceleration of the NO removal reaction, although the function of oxygen is versatile with respect to catalytic and experimental systems.

The purpose of this study is to examine the influence of oxygen on NO removal activity over a copper ion exchanged mordenite catalyst, which may be a promising SCR catalyst as observed by Ham et al. [6,7]. The effect of oxygen on NO removal activity was investigated by the cyclic operation of the catalytic reaction system, alternately in the presence and the absence of oxygen. The enhancement of NO removal activity in the presence of oxygen was discussed by examining the oxidation state of copper ions on the mordenite catalyst after sequential treatments of the catalyst with NO, NH_3 and O_2. ESR studies were carried out for NH_3 and NO preadsorbed samples and for the NH_3 preadsorbed sample after temperature-programmed desorption (TPD) and temperature-programmed oxidation (TPO). To identify the oxidation state of copper ions during the SCR reaction, ESR measurements were also carried out for the NH_3 preadsorbed sample after temperature-programmed surface reaction (TPSR) by exposing it to either NO or a mixture of NO and oxygen.

2. Experimental

The catalyst employed in the present study was copper ion exchanged hydrogen mordenite (CuHM). It was prepared by ion-exchanging the mordenite type zeolite obtained in the sodium form (NaM) from P.Q. Corporation under the designation of 900Na. Sodium

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mordenite (NaM) was exchanged with aqueous NH_4Cl solution (1 M) at 90°C. The remaining chloride ions on the zeolite surface were washed away with deionized water until no precipitation of white AgCl was found in $AgNO_3$ solution. This was followed by drying at 100°C for 12 h. For preparation of CuHM, the NH_4^+ form of mordenite was exchanged with cupric nitrate solution. It was washed several times again with deionized water, followed by drying at 100°C for 12 h and then calcining in air stream at 500°C for 8 h. The copper content of the CuHM catalyst employed in this study was 2.3 wt% and it contained 1.2 cupric ions per unit cell of mordenite.

The measurements of the catalytic activities of CuHM in the presence and the absence of oxygen were conducted in a tubular downflow fixed bed reactor operated under isothermal conditions and slightly above atmospheric pressure. The details of the reaction apparatus employed in this study were already described in previous studies [6,7]. The typical composition of the feed gas stream was 500 ppm NO, 500 ppm NH_3, balance N_2 and 5% O_2. Inlet and outlet analyses of NO and NO_2 were obtained with a chemiluminescent NO–NOx analyzer (Thermo Environment model 10). Furthermore, the formation of NO_2 and N_2O during the course of the SCR reaction was confirmed negligible by an on-line Q-mass spectrometer (VG MMPC 300D). It revealed that NO_2 and N_2O may not be reaction intermediates for the reaction of NO with NH_3 in the presence of O_2. The conversion of NO was calculated by measuring the NO concentrations in the feed gases and downstream of the reactor. Since N_2 was employed as a balance gas, the concentration of N_2 produced from the NO reduction reaction may cannot be measured.

In order to examine the oxidation state of copper ions on the catalyst surface, ESR measurements were carried out with a Bruker ER 200D-SRC spectrometer operated in the X-band microwave frequency of 9.45 GHz. The g values were measured by comparison with that of diphenylpicrylhydrazyl (DPPH, $g = 2.0036$) as an external reference standard. ESR spectra were recorded at 100 K. The catalyst samples were pretreated in a cell, where the ESR quartz tube was connected to a U-shaped quartz cell attached to vacuum tight valves. After treatment of the catalyst with the gas stream in the U-shaped tube, the sample was transferred to the measuring cell of the ESR apparatus. Prior to each treatment, the sample was dehydrated at 500°C for 2 h under the flow of oxygen (40 cm^3/min), followed by evacuation at room temperature. After the addition of oxygen, the evacuation of the sample was mandatory to prevent dipole–dipole broadening of the Cu^{2+} signal caused by interaction of the cations with oxygen molecules. Since the evacuation of oxygen at higher temperatures would result in a partial reduction of copper on the catalyst surface, the sample was evacuated at room temperature.

The adsorption of ammonia and NO on the dehydrated catalyst sample was carried out individually with each gas of high purity without further purification at room temperature. The temperature-programmed desorption (TPD) of NH_3 preadsorbed CuHM was performed under the flow of helium up to 400°C. Following the TPD, the temperature-programmed oxidation (TPO) of the sample was carried out under the flow of oxygen up to 400°C. Temperature-programmed surface reaction (TPSR) with the NH_3 preadsorbed sample was carried out by exposing it to nitrogen oxide of 1 000 ppm in the presence and the absence of oxygen. At the end of each treatment, ESR spectra of the catalyst samples were observed to determine the oxidation state of the copper ions on the catalyst surface.

3. Results

3.1. Effect of oxygen on NO removal activity

In order to investigate the influence of oxygen on NO removal activity for the CuHM catalyst, a cyclic operation was performed alternately in the presence and the absence of oxygen, as shown in fig. 1. The activity for the NO removal reaction was fully reversible with respect to the existence of oxygen in the feed gas stream. When the oxygen feed to the reactor was terminated, NO removal activity quickly disappeared, but its original activity was rapidly recovered by again injecting oxygen. This observation clearly indicates the involvement of oxygen in the SCR reaction and that the reaction is promoted by the oxygen in the feed gas stream.

For the catalyst examined in this study the rate of recovering the activity is more rapid than that of the disappearance of activity. After oxygen was turned off, it takes about 70 to 80 min to attain steady-state activity,

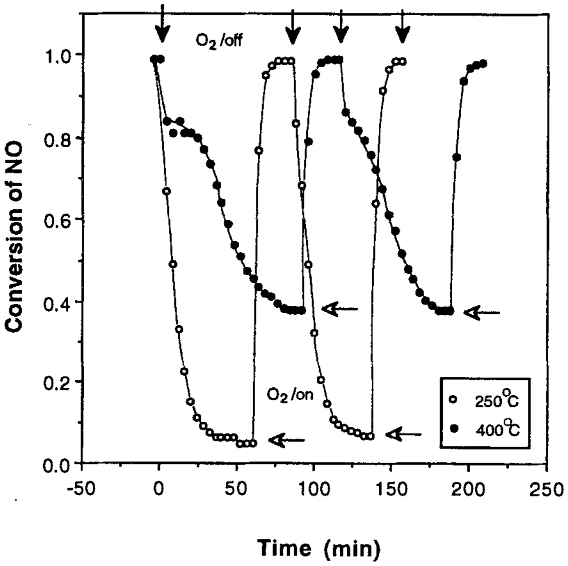

Fig. 1. Transient behavior of NO removal activity in the presence and the absence of oxygen (reactor space velocity = 100 000/h).

while it takes about 20 min to recover the original activity when oxygen was re-injected. NO removal activity decreased more slowly at the higher reaction temperature of 400°C than at 250°C, probably due to the effect of temperature on the reaction rate. In addition, the participation of oxygen of the zeolite structure in the reaction may not be excluded.

Fig. 2 shows the NO conversion over the CuHM catalyst with respect to reaction temperature in the presence and the absence of oxygen. Within the range of reaction temperatures covered in this study, the NO removal activity in the presence of oxygen is higher than that in the absence of oxygen. NO removal activity with oxygen significantly increases from the reaction temperature of about 200°C and reaches maximum activity at about 250°C, while the activity without oxygen is very low, revealing at most 40% conversion of NO even at the reaction temperature of 500°C. It clearly presents that oxygen enhances NO removal activity by at least one order of magnitude within the reaction temperature range covered in this study. The activities with and without O_2 were compared by calculation of the first-order rate constants at given reaction temperatures. It should be noted that the NO removal by NH_3 over the CuHM catalyst occurs as a first-order reaction with respect to NO concentration. This was extensively discussed in previous studies [6,8].

3.2. ESR study

3.2.1. NO and NH_3 adsorption on CuHM catalyst

Fig. 3A shows the ESR spectrum of the dehydrated CuHM catalyst recorded at 100 K. Prior to ESR measurements the catalyst was dehydrated at 500°C for 2 h under oxygen atmosphere (40 cm^3/min), followed by evacuation at room temperature. The low-field portion of the spectrum shows four well-resolved hyperfine components, which are typical characteristics of Cu^{2+} ions existing in isolated locations in the structure of zeolite. Its $g_{\|}$ and $g_{\perp}$ values were 2.312 and 2.054, respectively.

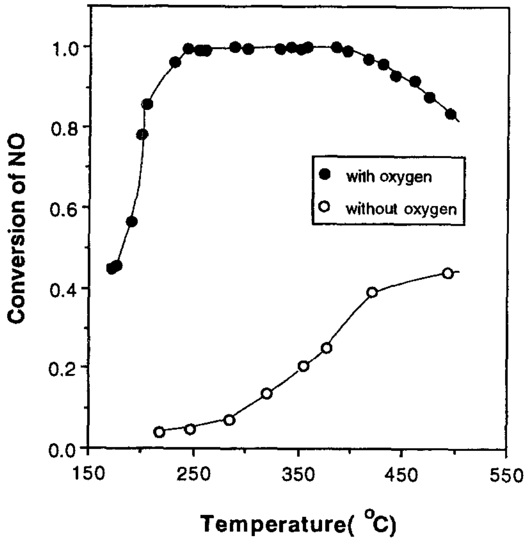

Fig. 2. NO removal activity with respect to reaction temperature in the presence and the absence of oxygen (reactor space velocity = 100000/h).

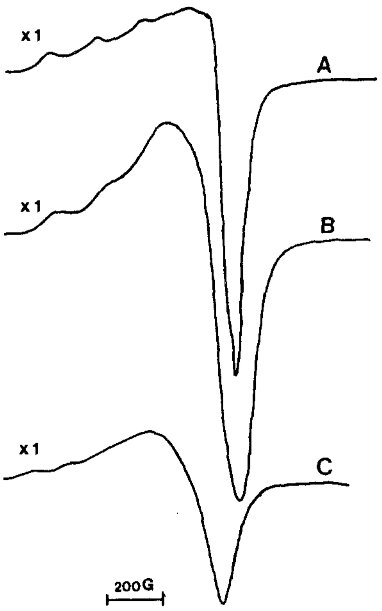

Fig. 3. ESR spectra of CuHM catalyst recorded at 100 K: (A) dehydrated in oxygen (500°C, 2 h); (B) addition of NH_3 for 1 h, followed by evacuation for 1 h at room temperature; (C) addition of NO for 1 h, followed by brief evacuation at room temperature.

Fig. 3B shows the ESR spectrum of the dehydrated CuHM catalyst after the adsorption of NH_3 at room temperature. Upon the addition of the NH_3 to the zeolite, the low-field portion of four hyperfine components was poorly resolved and only a symmetric line of high intensity with $g_{iso} = 2.058$ was developed. However, the $g_{\|}$ value was not identified due to the poor resolution of the low-field hyperfine components. During the adsorption of NH_3 on the zeolite, the pale green color of the dehydrated sample changed to a deep blue color. The development of the deep blue color upon the addition of NH_3 indicates the formation of a copper–amine complex on the catalyst surface [9,10].

The disappearance of the low-field hyperfine in the spectrum of the catalyst adsorbing NH_3 can probably be attributed to the following two reasons: (1) blurring of the hyperfine structure owing to the free rotation of the molecules in the mordenite channel, (2) dipole–dipole broadening owing to an interaction with paramagnetic Cu^{2+} cations. However, considering that the CuHM catalyst contains about 1.2 ions of copper per unit cell of the zeolite, it may not be due to the dipole–dipole interaction of copper ions on the catalyst surface. It has been reported that highly copper-loaded zeolite revealing a large symmetric line due to the dipole–dipole interactions of cupric ions rather exhibited an anisotropic spectrum due to the isolated copper–amine complex upon the addition of NH_3 [10]. Therefore, by the comparison of the size of the complex and the pore of CuHM catalyst, the reason for the poor resolution of the low-field hyperfine upon the addition of NH_3 seems to be the free rotation of the copper–amine complex formed on the catalyst surface. Then, copper ions are still existing on the catalyst surface in the form of Cu^{2+} ions, although they form copper–amine complexes with adsorbed NH_3 molecules.

As shown in fig. 3C, upon the adsorption of NO to the CuHM catalyst, the intensity of the ESR signal for Cu^{2+} significantly decreased and its g_{iso} value was 2.089. This may be due to the fact that the electron transfer of the unpaired electron from the antibonding orbital of NO to empty or partially filled 3d orbitals of transition metal ions easily occurs, followed by lone pair donation from NO and by backbonding to the NO orbitals producing a nitrosyl complex. Although the molecular orbital structure of the nitrosyl is rather complex, the mechanism can be well described by

$$Me^{x+} + NO \rightleftharpoons Me^{(x-1)+}NO^{+} \qquad (1)$$

This has been widely discussed [11,12] and seems to be the reaction responsible for the marked decrease of the Cu^{2+} signal intensity in the ESR spectrum of the CuHM catalyst:

$$Cu^{2+} + NO \rightleftharpoons [Cu^{+}NO^{+}] \qquad (2)$$

The nitrosyl is diamagnetic due to spin pairing between the NO molecule and the Cu^{2+} ion on the catalyst surface and its formation would result in the decrease of the intensity of the Cu^{2+} paramagnetic signal, as shown in fig. 3C.

3.2.2. *Redox behavior of CuHM catalyst*

The redox property of copper ions on zeolite was well understood [13,14]. When treated with reducing gases such as NH_3, CO and H_2 at higher temperature, cupric ions on zeolite are readily reduced to cuprous ions or even metallic copper. The reduction of cupric ions occurs via a two-step mechanism in which Cu^{+} is formed and then further reduced to metallic copper [13,14]. The first reduction step may occur under rather mild conditions, i.e., at low temperatures and in a short period of time. If it is further reduced under relatively severe conditions, metallic copper can be formed on the catalyst surface. However, if oxygen is introduced to the reduced sample, copper on zeolite is immediately reoxidized to cupric ions.

Temperature-programmed desorption (TPD) and temperature-programmed oxidation (TPO) techniques are used along with ESR measurements to examine the redox behavior of the CuHM catalyst. Fig. 4A shows the ESR spectrum of the NH_3 preadsorbed CuHM catalyst after TPD up to 400°C under helium atmosphere. The ESR spectrum of the CuHM catalyst after TPD shows that the intensity of the Cu^{2+} ESR signal significantly decreased; it was at least one order of magnitude smaller than that of the initial dehydrated sample. The color of the CuHM catalyst after TPD changed from pale-green to white. This indicates that most of copper ions on the sample were nearly reduced to cuprous ions (Cu^{+}).

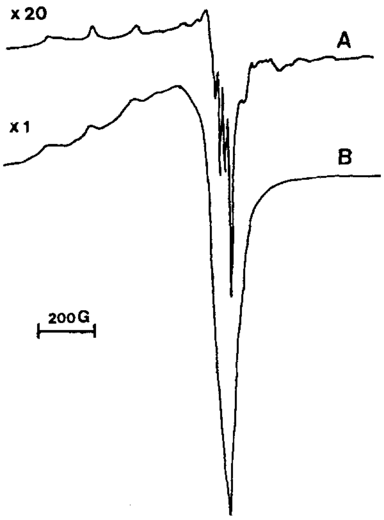

Fig. 4. ESR spectra of CuHM catalyst recorded at 100 K: (A) addition of NH_3 for 1 h, followed by evacuation and then treated in flowing helium up to 400°C (heating rate 10°C/min); (B) sample (A) after treatment in flowing O_2 up to 400°C (heating rate 10°C/min).

Fig. 4B shows the ESR spectrum obtained after TPO experiment with the reduced sample (fig. 4A). The spectrum of fig. 4B is quite similar to that of the dehydrated CuHM catalyst in fig. 3A. It should be noted that the oxidation of the reduced sample in the oxygen atmosphere at the temperature up to 400°C results in the reappearance of the ESR spectrum of Cu^{2+} ions, which reveals identical shape and intensity of the ESR spectrum of the original dehydrated sample shown in fig. 3A. The color of the sample after TPO also recovers its original, pale-green color. It means that almost all copper ions in the reduced state (Cu^{+}) were oxidized to cupric ions by TPO.

3.2.3. *Copper state during the course of SCR reaction*

Temperature-programmed surface reaction (TPSR) technique was employed to identify the oxidation state of the copper ions during the course of the SCR reaction. TPSR was conducted by exposing NH_3 preadsorbed CuHM to either diluted NO (1 000 ppm) or a mixture of NO and oxygen. Fig. 5A shows the ESR spectrum of the CuHM sample obtained after TPSR in the presence of oxygen. The signal was very broad and symmetric, which was already observed in fig. 3C. The shape and intensity of the spectrum were identical to those of the NO adsorbed dehydrated sample and it also exhibited $g_{iso} = 2.086$, which is also similar to that of the NO adsorbed dehydrated sample (fig. 3C). During the TPSR, NH_3 preadsorbed on the catalyst is depleted by the reaction with NO and the continuously introduced NO may be adsorbed on the copper of the catalyst surface.

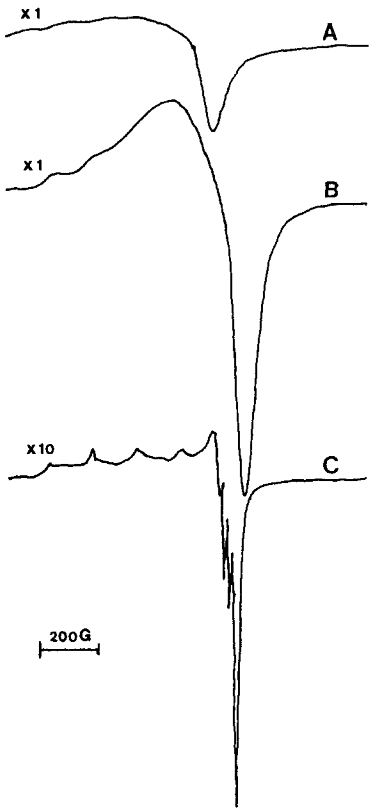

Fig. 5. ESR spectra of CuHM catalyst recorded at 100 K: (A) after TPSR in the presence of O_2 up to 400°C (heating rate 10°C/min); (B) after SCR reaction in the presence of O_2 at 250°C; (C) after TPSR in the absence of O_2 up to 400°C (heating rate 10°C/min).

Fig. 5B shows the ESR spectrum of the CuHM catalyst after SCR reaction conducted with simultaneous and continuous flow of NH_3, NO and O_2 in a fixed bed reactor. After SCR reaction, the catalyst was removed from the reactor, charged to the ESR cell and subjected to evacuation at room temperature. Although the catalyst after SCR reaction was exposed to the atmosphere during the transfer of the catalyst from the fixed bed reactor to the ESR cell, the state of the copper ions may not be altered due to the fact that the SCR reaction had also been done in oxygen atmosphere. The shape and intensity of the ESR spectrum after SCR reaction in the presence of oxygen were similar to those of the NH_3 preadsorbed sample shown in fig. 3B. The poor resolution of low-field hyperfine seems to be due to the formation of copper–amine complex on the catalyst surface. Note that there may be still NH_3 molecules adsorbed on the catalyst surface even after SCR reaction [7]. After SCR reaction, the copper ions are still in the form of cupric ions on the catalyst surface, although they form copper–amine complexes with NH_3 based upon the ESR spectrum obtained after SCR reaction in the presence of oxygen.

In contrast, the intensity of the ESR spectrum of fig. 5C observed after TPSR in the absence of oxygen decreased at least by one order of magnitude as compared with that of the initial dehydrated sample, indicating that the copper ions were reduced to cuprous ions. Therefore, it can be concluded that the predominant copper species are cupric ions during the course of the SCR reaction with oxygen, while the cuprous ions are primary copper species on the catalyst surface without oxygen.

4. Discussion

As previously observed, oxygen in the feed gas stream significantly accelerates the rate of NO reduction by NH_3 and its effect on NO removal activity is fully reversible. For metal exchanged zeolites, the increase of NO removal activity by oxygen is known to be closely related to the redox couple of the exchanged metals on the catalyst surface [4,15]. Ito et al. [15] reported that NO reduction over CeNa-mordenite was controlled by a reaction with the crucial involvement of a Ce^{3+}/Ce^{4+} redox couple. In their catalytic system, the role of oxygen was to oxidize Ce^{3+} to Ce^{4+} species, which are more reactive ions for NO reduction. The activity of iron-exchanged Y zeolite in the SCR reaction was also enhanced by two orders of magnitude in the presence of oxygen [4].

Copper possesses a redox property (Cu(II)/Cu(I)) similar to many other transition metals [13,14]. The reduction of Cu(II) ions on zeolite to Cu(I) ions or even metallic copper can occur by treatment of the catalyst with reducing gases, such as H_2, CO and NH_3. However, it can be readily reoxidized to Cu(II) species by oxygen. The redox characteristics of copper ions on a mordenite type zeolite catalyst was examined by the present ESR study, as shown in fig. 4. Copper ions on mordenite were reduced to cuprous ions by TPD of NH_3 preadsorbed catalyst and almost all of the reduced copper species were reoxidized to Cu(II) species by oxygen.

The oxidation state of copper during SCR reaction in the presence of oxygen was mainly cupric ions, which are more reactive species than the cuprous ions which dominantly exist on the catalyst surface in the absence of oxygen. The predominant coverage of NH_3 on the surface of mordenite catalyst can be inferred from the first-order reaction kinetics with respect to NO indicating the independence of the reaction rate of NH_3 concentration, as confirmed in the previous studies [6,8]. Note that a cupric ion can accommodate four NH_3 molecules by the formation of an amine complex [8,16]. Moreover, the active center for NO reduction by NH_3 over copper exchanged zeolites was known to be a copper–amine complex on the catalyst surface [8,17]. Therefore, SCR reaction over copper exchanged mordenite proceeds between coordinated NH_3 on the copper ion and weakly adsorbed NO producing N_2 and H_2O. It has been extensively discussed in previous studies [9,18]. During this step, the cupric ions are reduced to cuprous species.

However, oxygen plays an important role for the reoxidation of cuprous ions to cupric ions, which are active reaction sites for NO reduction by NH_3.

Based upon the examination of the redox property of copper ions on zeolite, the following reaction scheme can be postulated with the presence of oxygen, as proposed by Mizumoto et al. [19]:

$$\begin{array}{l}
\mathrm{Cu(II)(NH_3)}_n + \mathrm{NO} \rightarrow [\mathrm{Cu(II)(NH_3)}_n\mathrm{NO}] \rightarrow \\
\quad \mathrm{Cu(I)(NH_3)}_m + \mathrm{N_2} + \mathrm{H_2O} + (n-m-1)\mathrm{NH_3} + \mathrm{H^+(ads)} \\
\mathrm{Cu(I)(NH_3)}_m + \tfrac{1}{4}\mathrm{O_2} + \mathrm{H^+(ads)} \rightarrow \mathrm{Cu(II)(NH_3)}_m + \tfrac{1}{2}\mathrm{H_2O} \\
\mathrm{Cu(II)(NH_3)}_m + (n-m)\mathrm{NH_3} \rightarrow \mathrm{Cu(II)(NH_3)}_n \\
\hline
\mathrm{NO} + \mathrm{NH_3} + \tfrac{1}{4}\mathrm{O_2} \rightarrow \mathrm{N_2} + \tfrac{3}{2}\mathrm{H_2O}
\end{array}$$

The complete reversibility of NO reduction activity with respect to the existence of oxygen in the feed gas stream over the CuHM catalyst seems to be attributable to the redox characteristics of copper ions. The oxidation of cuprous ions by oxygen appears to be very fast. This may be a reason why the rate of recovering NO removal activity by the introduction of oxygen to the reactor was much faster than the decaying rate of NO conversion without oxygen.

5. Conclusions

NO removal activity of copper exchanged hydrogen mordenite catalyst for selective catalytic reduction of NO by NH_3 in the presence of oxygen was at least one order of magnitude higher than that in the absence of oxygen and it was fully reversible with respect to the existence of oxygen in the feed gas stream. The effect of oxygen seems to be closely related to the oxidation state of copper on the catalyst surface as cupric ions, which are known as more active reaction sites for NO reduction as observed by electron spin resonance measurements.

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