Graphical Abstract

NO oxidation on Zeolite Supported Cu Catalysts: Formation and Reactivity of Surface Nitrates

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Abstract

The comparative activities of a small-pore Cu-CHA and a large-pore Cu-BEA catalyst for the selective catalytic reduction (SCR) of NO_x with NH₃, and for the oxidation of NO to NO₂ and the subsequent formation of surface nitrates were investigated. Although both catalysts are highly active in SCR reactions, they exhibit very low NO oxidation activity. Furthermore, Cu-CHA is even less active than Cu-BEA in catalyzing NO oxidation but is clearly more active for SCR reactions. Temperature-programed desorption (TPD) experiments following the adsorption of (NO₂ + NO + O₂) with different NO₂:NO ratios reveal that the poor NO oxidation activity of the two catalysts is not due to the formation of stable surface nitrates. On the contrary, NO is found to reduce and decompose the surface nitrates on both catalysts. To monitor the reaction pathways, isotope exchange experiments were conducted by using ¹⁵NO to react with ¹⁴N-nitrate covered catalyst surfaces. The evolution of FTIR spectra during the isotope exchange process demonstrates that ¹⁴N-nitrates are simply displaced with no formation of ¹⁵N-nitrates on the Cu-CHA sample, which is clearly different from that observed on the Cu-BEA sample where formation of ¹⁵N-nitrates is apparent. The results suggest that the formal oxidation state of N

during the NO oxidation on Cu-CHA mainly proceeds from its original +2 to a +3 oxidation state, whereas reaching a higher oxidation state for N, such as +4 or +5, is possible on Cu-BEA.

Keywords: Zeolite supported Cu catalysts; Selective catalytic reduction of NO_x; NO oxidation; NO oxidation to NO₂; Surface nitrate groups; SCR reaction mechanisms

1. Introduction

Zeolite supported transition metal catalysts have been extensively studied since the early 2000s for the selective catalytic reduction (SCR) of NO_x (NO and NO₂) with NH₃. The successful commercialization of Cu- and Fe-exchanged zeolite SCR catalysts for diesel engine powered vehicles to meet the stringent US EPA 2010 and European EU5 or EU6 NO_x emission standards further motivates the investigations in the recent years [1-4]. One area attracting significant attention is the investigation of SCR reaction mechanisms on these catalysts, particularly how NO is activated and the chemical nature of the NO activation intermediates involved in the SCR reactions [2, 4-24].

It has been well established that O₂ is essential for the standard SCR reaction in which NO is the only source of NO_x in the feed gas:

The general consensus is that, catalyzed by the transition metal ions, NO is first oxidized by O₂ to form some types of surface complexes on the zeolite catalysts, which subsequently react with NH₃ to form N₂. The exact reaction pathways for NO oxidation, and the chemical nature of the surface NO_x adsorption complexes, however, are still being debated.

Since the addition of NO₂ to the feed gas can enhance the SCR activity significantly until the NO₂:NO ratio exceeds 1:1, many research groups proposed that NO oxidation to gas phase NO₂ was one of the key elementary steps during the SCR reaction, and the primary function of the transition metal ions in the zeolite catalysts is to catalyze such a reaction [2,5]. It was further suggested that, once produced, NO₂ could readily disproportionate to form surface nitrite and nitrate groups on the zeolite catalysts according to the following reaction:

The fact that a bare zeolite in the H^+ -form can achieve relatively high SCR activity in the feed with an $NO_2:NO$ ratio of 1:1 seems to support the above proposals [5].

However there has been plenty of evidence suggesting that gas phase NO_2 is not necessarily involved in the standard SCR reaction: (1) most zeolite supported transition metal catalysts show much lower NO to NO_2 oxidation reaction rates than SCR reaction rates under comparable conditions; (2) the presence of water in the feed gas inhibits the NO to NO_2 oxidation reaction, but has much less impact on the SCR activity; (3) Fe-exchanged zeolite catalysts, in general, are more active than Cu-exchanged zeolite catalysts for NO oxidation to NO_2 , but the opposite trend is observed for the SCR reaction at low temperatures (e.g., $\leq 300\text{ }^\circ\text{C}$) [9-14].

To reconcile some of these discrepancies, a few research groups argued that the reaction rates measured during NO to NO_2 oxidation cannot represent the NO oxidation activity under SCR reaction conditions [8,25]. They suggested that, under NO to NO_2 oxidation reaction conditions, the catalyst surfaces were covered by surface nitrite and nitrate complexes, and NO_2 desorption could become the rate limiting step. In contrast, under SCR reaction conditions, NH_3 would react with the surface nitrate and nitrite groups regenerating the metal sites for NO oxidation reaction to occur.

The hypothesis that the surfaces of the catalysts are covered by adsorbed nitrate or nitrite groups under NO oxidation conditions, however, contradicts the observations reported by the Harold group, and Nova, Tronconi and coworkers [9-14]. Both groups reported that, on the Fe-exchanged zeolite catalysts or the Cu-exchanged chabazite catalysts they studied, there was barely any NO_2 desorption observed after the catalysts were exposed to $NO + O_2$. In contrast, large NO_2 desorption peaks from surface adsorbed nitrate/nitrite complexes on the catalysts were

clearly detected after the same catalysts were exposed to NO_2 . Interestingly, they further noticed that the NO_2 desorption peaks disappeared on the catalysts when pre-adsorbed surface nitrate/nitrite groups (via NO_2 exposure) were subsequently exposed to $\text{NO} + \text{O}_2$. These results clearly suggest that surface nitrate/nitrite groups are unstable under NO oxidation conditions on those catalysts.

If surface nitrate/nitrite groups are not stable on metal-exchanged zeolite catalysts under NO oxidation conditions, how can these groups form on these catalysts under the standard SCR conditions, in which additional reducing agents, such as NH_3 , are also present in the feed gas? This brings up yet another question – are the SCR reaction mechanisms that involve nitrate/nitrite intermediates, proposed in literature for some metal-exchanged zeolite SCR catalysts, applicable to all types of transition metals and all type of zeolite framework structures?

In an *in situ* FTIR study, Fedeyko et al. reported that the surface adsorption complexes were indeed somewhat different between Fe- and Cu-exchanged beta zeolite SCR catalysts synthesized using the same parent beta zeolite support [26]. They found that, in addition to some of the nitrate/nitrite groups observed on the Cu catalyst, a unique nitro group was present only on the Fe catalyst. They further noticed that the nitro group on the Fe catalyst was more reactive to NH_3 than the nitrate/nitrite groups. These results, together with the fact that the Fe catalyst showed much less N_2O formation than the Cu catalyst, seem to indicate that other SCR reaction pathways may exist, besides the nitrate/nitrite mechanism commonly cited in literature.

In this study, two Cu-exchanged zeolite catalysts, Cu-BEA and Cu-CHA, were selected to investigate if different zeolite framework structures affect NO oxidation rates, and/or the formation of surface NO_x adsorption complexes and their reactivity. The two catalysts have nearly identical compositions but different zeolite framework structures, with extra-framework

Cu-ions exchanged into a 12-membered ring BEA zeolite and an 8-membered ring CHA zeolite, respectively. Activities under standard SCR and NO oxidation conditions were compared on the two catalysts. Temperature-programmed desorption (TPD) experiments on samples after exposure of a series of ($\text{NO} + \text{NO}_2 + \text{O}_2$) mixtures with different NO_2/NO_x ratios were carried out to quantify the amounts of surface nitrates/nitrites formed and their stability on the two catalysts. *In situ* FTIR and isotope-exchange techniques were further used to characterize the surface adsorption complexes and their reactivity to NO on the two catalysts.

2. Experimental

2.1. Catalyst preparation

The two Cu catalysts, Cu-BEA and Cu-CHA, had also been used in our earlier studies [27,28], were prepared by solution ion-exchange. Both zeolites have the same SiO_2 to Al_2O_3 ratio (SAR) of 25. The Cu loading was kept at 3 wt.% for both catalysts. After ion exchange, the samples were calcined at 550 °C for 2 h in air. To ensure consistent and reproducible results, they were further hydrothermally treated with 5% H_2O in air at 650 °C for 4 h. Such a pretreatment condition was sufficient to stabilize the performance of the catalysts, yet remained sufficiently mild as not to cause appreciable deactivation of either of the catalysts.

2.2. SCR activity, NO oxidation, and TPD measurements under flowing conditions

The same flow reactor setup as described in Ref. [28] was used in this study. Powder samples of the pre-treated Cu-BEA and Cu-CHA catalysts were pressed, crushed, and sieved. Samples with particle sizes in the range of 0.251 to 0.422 mm were selected. The packing density of the samples was measured as $\sim 0.5 \text{ g/cm}^3$. For each test, 45 mg of sample was loaded in the quartz tube reactor (1-cm diameter). Individual gases were dosed, through mass flow

controllers, into the gas manifold to achieve good mixing prior to introduction into the reactor. N₂ was used as a balance gas to maintain the total flow rate at 300 sccm. This resulted in a gas hourly space velocity (GHSV) of 200,000 h⁻¹. Concentrations of NO, NO₂, and NH₃ in the feed gas and products were measured by an online Nicolet Magna 560 spectrometer equipped with a 2-m gas cell that was maintained at 150 °C.

Standard SCR activities of the catalysts were measured with a feed of 350 ppm NO, 350 ppm NH₃, 10% O₂, 2.5% H₂O, and balance N₂. Steady-state NO_x conversions were recorded in the temperature range of 175–500 °C. NO to NO₂ oxidation activities of the catalysts were measured under similar conditions except that no NH₃ was added to the feed. Steady state conversions were recorded in the same temperature range of 175–500 °C after the catalysts were exposed to the feed for 30 min at each temperature. Thereafter the catalysts were purged at the set temperature for 5 min in 10% O₂, 2.5% H₂O and balance N₂. TPD experiments were subsequently carried out by ramping up the temperature to 500 °C at a rate of 25 °C/min to determine if there is deposition of surface NO_x adsorption complexes on the catalysts.

To further compare the stability and to quantify the amount of the adsorbed nitrates/nitrites on the two catalysts, another set of TPD experiments were carried out. The catalysts were first exposed to a feed of 350 ppm NO_x, 10% O₂, 2.5% H₂O, and balance N₂ at 200 °C. Separate experiments were carried out with the NO₂/NO_x ratios in the feed gas varying from 1, 0.82, 0.5, to 0.15. After 30 min of exposure, NO_x was turned off and the samples were purged for 10 min in a flow of 10% O₂, 2.5% H₂O, and balance N₂. Subsequent TPD experiments were performed under the same conditions as described above.

In addition, a third set of TPD experiments were performed by first exposing the catalysts to a feed of 350 ppm NO₂, 10% O₂, 2.5% H₂O, and balance N₂ at 200 °C for 30 min, followed by

a 10-min of purge in a flow of 10% O₂, 2.5% H₂O, and balance N₂. Subsequently, 350 ppm NO was re-introduced to the feed. Concentrations of NO and NO₂ in the outlet of the reactor were recorded during this step. After 30 min exposures, the samples were purged again at 200 °C for 10 min before the TPD experiments were carried out.

2.3. *In situ* FTIR and isotope-exchange experiments

The *in situ* transmission FTIR and isotope-exchange experiments were conducted using the same apparatus described in detail in Ref. [28,29]. For each experiment, about 4 mg of the powder samples were pressed onto a tungsten mesh and mounted in a static IR cell placed in the sample compartment of a Bruker Vertex 80 spectrometer. The cell is connected to a gas manifold and an ultrahigh vacuum chamber with a mass spectrometer. Prior to any experiments, the sample was pre-treated with the following procedures to ensure clean surfaces: it was first heated under vacuum ($P < 1 \times 10^{-7}$ Torr) at 500 °C for 2 h, then cooled and held at 200 °C; oxygen was subsequently admitted into the IR cell until the pressure reached 1.5 Torr; after 30 min of oxygen exposure, the cell was evacuated. Background spectra of the pre-treated samples were then recorded by averaging 256 scans at a 4-cm⁻¹ resolution.

Formation of surface adsorption complexes as a function of exposure time was monitored by IR spectra when the samples were exposed to (¹⁵NO + O₂), (NO + O₂), or (NO₂ + O₂) mixtures while the temperature was maintained at 200 °C. In each experiment, the NO_x (¹⁵NO, NO, or NO₂) partial pressure was kept at 0.15 Torr and O₂ at 1.35 Torr.

The isotope-exchange experiments were also carried out in the IR cell with the sample being held at 200 °C. The pre-treated samples were first exposed to a mixture of (0.15 Torr NO₂ + O₂) for 30 min, followed by evacuation of the IR cell for 5 min. A mixture of (0.15 Torr ¹⁵NO

+ O₂) was subsequently re-introduced. During this final experimental step, IR spectra of the surface adsorption complexes as well as the gas compositions in the IR cell were monitored.

3. Results

3.1. SCR activity and NO to NO₂ oxidation activity

Fig. 1 shows steady state NO_x conversions as a function of temperature under standard SCR reaction conditions for Cu-BEA and Cu-CHA. Both catalysts are very active and selective, achieving nearly 100% NO_x conversions between 250 to 350 °C. At temperatures below 250 °C, NO_x conversions on Cu-CHA are noticeably higher, suggesting Cu-CHA is more active than Cu-BEA for SCR reactions.

Steady state NO to NO₂ conversions under comparable reaction conditions (same as the standard SCR conditions, but without NH₃ in the feed) for Cu-BEA and Cu-CHA are also plotted in Fig. 1. Similar to what has been reported in the literature [13-18], NO oxidation activity for either catalyst is very poor. Neither Cu-BEA nor Cu-CHA shows appreciable amounts of NO₂ formation at temperatures below 250 °C. Even at 500 °C, the NO to NO₂ conversion is still below 20% on either catalyst. At temperatures between 250 to 500 °C, NO₂ formation for Cu-BEA appears to be slightly higher than that for Cu-CHA, indicating Cu-BEA may be slightly more active than Cu-CHA in catalyzing NO oxidation to NO₂.

It has been suggested in the literature that the poor NO to NO₂ oxidation activity on zeolite supported transition metal catalysts could be due to the formation of stable surface nitrates on the catalysts, which block accessibility of the active sites [8,25]. To verify this, TPD experiments were performed on the catalysts immediately after the NO oxidation tests at temperatures from 175 to 500 °C. Barely any N-containing compounds were detected from the

Cu-CHA sample during any of the TPD experiments. Although a very weak NO₂ desorption peak at around 400 °C was observed from the Cu-BEA samples for the experiments with NO oxidation tests being carried out at low temperatures (<350 °C), the amount of NO₂ desorbed from the catalysts was very low. These results suggest that the amount of N-containing deposits formed on either of the catalysts in the flow of (NO + O₂ + H₂O) is insignificant and cannot account for the low NO to NO₂ oxidation activity of the catalysts.

3.2. TPD after exposure of (NO_x + O₂ + H₂O) at 200 °C

However, it is well documented that a considerable amount of stable N-containing complexes can be formed on zeolite supported transition metal catalysts during NO₂ exposure. Indeed, after Cu-BEA or Cu-CHA catalysts were exposed to a feed of (NO₂ + O₂ + H₂O) at 200 °C, an intense NO₂ desorption peak was clearly registered in the subsequent TPD experiments (shown in Fig. 2). The NO₂ desorption peaks, centered at about 400 °C for Cu-BEA and at about 450 °C for Cu-CHA, can be attributed to the decomposition of surface nitrates formed on the catalysts during the exposure step. The higher desorption temperature observed for Cu-CHA also indicates that the surface nitrates on Cu-CHA are more stable than those on Cu-BEA.

Therefore, it appears that the formation of surface nitrates on the catalysts is influenced by the feed gas compositions. To gain more details on such a correlation, a series of adsorption/desorption experiments were carried out by varying the NO₂/NO_x ratio (while maintaining the total NO_x concentration the same at 350 ppm) in the feed gas during the adsorption step. The TPD profiles from the subsequent desorption experiments for both catalysts are compiled in Fig. 2, and the quantitative analysis results of these experiments are summarized in Table 1. It is interesting to note that, on both catalysts, the intensity of the NO₂ desorption

peak decreases rapidly with the decrease of the NO_2/NO ratio in the feed gas, even though the peak temperatures remain similar. This suggests that the NO_2 desorption is due to thermal decomposition of surface nitrates and that different NO_2/NO_x ratios in the feed gas do not affect the nature of the surface nitrates but simply affect their quantity. However, once the NO_2/NO_x ratios in the feed dropped below 0.5 (not shown in Fig. 2), no N-containing compounds were detected from the Cu-CHA sample. Under similar conditions, the NO_2 desorption peak from the Cu-BEA sample was also much smaller with a trace amount of NO_2 being detected in the TPD experiments (see Table 1).

The results above clearly indicate that the presence of NO in the feed gas actually reduces the formation of surface nitrates on the catalysts. To better understand the process, a set of experiments were performed by sequentially exposing the catalysts to a feed of ($\text{NO}_2 + \text{O}_2 + \text{H}_2\text{O}$), followed by a feed of ($\text{NO} + \text{O}_2 + \text{H}_2\text{O}$), prior to the TPD measurements. As shown in Fig. 2, when the nitrates covered Cu-CHA sample was subsequently exposed to the feed of ($\text{NO} + \text{O}_2 + \text{H}_2\text{O}$), barely any surface nitrates remained on the catalysts as indicated by a nearly flat baseline in the final TPD experiment (see the “ NO_2 followed by NO” curves in Fig. 2). Similar results were also observed on the Cu-BEA sample although the quantitative analysis indicates that there is a very low level of surface nitrates remaining on the Cu-BEA catalyst (see Table 2).

A closer examination of the NO and NO_2 outlet concentrations during the ($\text{NO} + \text{O}_2 + \text{H}_2\text{O}$) exposure step provides additional insights. As shown in Fig. 3, a sharp NO_2 desorption peak is registered immediately after the nitrates covered catalyst was exposed to the ($\text{NO} + \text{O}_2 + \text{H}_2\text{O}$) feed. The peak is so intense that it exceeds the inlet NO_x level of 350 ppm in the feed gas. This is a clear indication that NO, even in the presence of O_2 , destabilizes the nitrates already formed on the catalyst surface from the previous ($\text{NO}_2 + \text{O}_2 + \text{H}_2\text{O}$) adsorption step, and results

in nearly complete desorption of the surface nitrates. Overall, the results on Cu-BEA and Cu-CHA are consistent with what has been reported in prior literature for other zeolite supported transition metal SCR catalysts [9-14].

3.3. *In situ* FTIR spectra following ($\text{NO}_2 + \text{O}_2$), ($\text{NO} + \text{O}_2$), and ($^{15}\text{NO} + \text{O}_2$) adsorption

A detailed FTIR study of the surface adsorption complexes on Cu-CHA and Cu-BEA when the catalysts are exposed to ($\text{NO}_2 + \text{O}_2$) and ($\text{NO} + \text{O}_2$) has been reported in our earlier paper [28]. In summary, when the catalysts are exposed to the ($\text{NO}_2 + \text{O}_2$) mixture, surface nitrates are the dominant adsorption complexes; they form and reach the saturation levels rapidly. Although the same type of surface nitrates also form on the catalysts when the catalysts are exposed to the ($\text{NO} + \text{O}_2$) mixture, the intensities of the nitrate bands are much weaker and increase very slowly with exposure time. In addition, other bands attributed to NO adsorption on Cu^{2+} and Cu^+ are also visible. On Cu-CHA, a relatively intense band at 2155 cm^{-1} , assigned to NO^+ located close to the Cu sites, is also observed. For comparison purpose (see below), the IR spectra for the samples after 24 min of exposure time to ($\text{NO}_2 + \text{O}_2$) or ($\text{NO} + \text{O}_2$) are plotted in Fig. 4. The related IR bands and their assignments are summarized in Table 2.

Prior to the isotope exchange experiments that will be discussed next, it is important to determine the locations and the assignments of the IR bands when ^{15}N -labeled ^{15}NO is used to replace natural abundance, primarily ^{14}NO during the ($\text{NO} + \text{O}_2$) adsorption step. Fig. 5 shows the evolution of the IR spectra when Cu-CHA and Cu-BEA are exposed to a mixture of ($^{15}\text{NO} + \text{O}_2$) at $200\text{ }^\circ\text{C}$. The change of the intensities for a few selected bands as a function of exposure time is plotted in Fig. 6. As expected, the results are nearly identical to what we have recently

reported in Ref. [28] for the ($\text{NO} + \text{O}_2$) adsorption experiments, except for the shift of the wavenumbers of the IR bands due to isotope effects.

On Cu-BEA, the IR bands at 1868 and 1783 cm^{-1} , which appear immediately after introduction of ($^{15}\text{NO} + \text{O}_2$), can be attributed to ^{15}NO adsorbed on Cu^{2+} and Cu^+ , respectively. The band at 1783 cm^{-1} slowly declines and disappears after 36 min exposure, indicating that the Cu^+ in Cu-BEA is gradually oxidized during the experiment [28]. The intensity of the band at 1868 cm^{-1} remains essentially constant during the adsorption period. The group of bands with peaks at 1595 , 1587 , 1560 , and 1531 cm^{-1} are related to the surface ^{15}N -nitrates. The intensities of these bands increase slowly during the adsorption experiment. Another weak but broad band at 2091 cm^{-1} is also apparent. This can be assigned to $^{15}\text{NO}^+$ at exchange sites. The sharp band at 2159 cm^{-1} , however, is not from N-compounds but due to a very low level of impurity of CO in the ^{15}NO feed gas.

For the Cu-CHA catalyst, the IR band at 1866 cm^{-1} with a shoulder at 1877 cm^{-1} formed after exposure to ($^{15}\text{NO} + \text{O}_2$) is assigned to ^{15}NO adsorbed on Cu^{2+} . The intensity of the band remains at the same level during the adsorption. The group of bands with peaks at 1590 , 1554 , and 1531 cm^{-1} are from surface ^{15}N -nitrates. Their intensities increase slowly with time, but overall are much lower than the bands assigned to the same species observed on Cu-BEA. In contrast, the band at 2119 cm^{-1} is relatively intense. This band can be assigned to $^{15}\text{NO}^+$ at the exchange sites. As discussed above, the shoulder at 2159 cm^{-1} within the 2119 cm^{-1} band is likely due to CO impurity from the ^{15}NO feed gas.

For a better comparison of the isotope shifts and of the differences in the IR band intensities when the catalysts are exposed to ($\text{NO}_2 + \text{O}_2$), ($\text{NO} + \text{O}_2$) and ($^{15}\text{NO} + \text{O}_2$), IR spectra of the samples after 24 min exposure to each of the mixtures are plotted in Fig. 4. The

corresponding IR bands and their assignments are summarized in Table 2. In the third column of Table 2, ratios of the wavenumbers for the corresponding IR bands from the ($^{15}\text{NO} + \text{O}_2$) experiments and those from the ($\text{NO} + \text{O}_2$) experiments are calculated. The values range from 0.9752 to 0.9840, very close to the value of 0.9821 predicted based on the simple harmonic oscillator model for the isotopic shift from a $^{15}\text{N-O}$ vibration relative to a $^{14}\text{N-O}$ vibration [29]. This confirms that the shifts of the IR bands are due to a normal isotope effect and that, more importantly, the isotopic shifts between $^{14}\text{N-O}$ and $^{15}\text{N-O}$ are significant enough to differentiate the origin of the N-containing features in the IR studies to be described below.

3.4. Isotope exchange experiments

As shown in Fig. 3, the introduction of ($\text{NO} + \text{O}_2 + \text{H}_2\text{O}$) to the nitrate covered catalysts results in removal of the surface nitrates. To better understand this process, a similar set of experiments were performed in the IR cell. Isotope labelled ^{15}NO was used in the last step so that the origin of the surface complexes and the gas phase products can be readily derived. Since H_2O exhibits strong IR absorption bands, which overlap with the nitrate vibration region, H_2O was omitted from the feed in the IR experiments to eliminate its interference. In addition, these IR experiments were performed in a static chamber. This leads to some subtle differences observed in the two sets of experiments (static vs. flow reactions), and these will be discussed further in the next section.

The “0 min” spectrum in Fig. 7A or Fig. 7B is the IR spectrum from the corresponding Cu-BEA or Cu-CHA sample at 200 °C after being exposed to a feed of ($\text{NO}_2 + \text{O}_2$) for 36 min followed by evacuation ($<1 \times 10^{-6}$ Torr) for 5 min. The presence of intense IR bands at 1629, 1623, 1598, and 1570 cm^{-1} for Cu-BEA, or at 1624, 1593, and 1570 cm^{-1} for Cu-CHA, confirms

that a considerable amount of surface nitrates are formed and that these surface nitrates are thermally stable at 200 °C on the catalysts. When the nitrate covered catalysts were subsequently exposed to a feed of ($^{15}\text{NO} + \text{O}_2$), isotope exchange between the gas phase ^{15}NO and the surface nitrates was observed on both catalysts as indicated by the gradual decrease of the signal intensity of $M/e = 31$ (^{15}NO) and the simultaneous increase of the signal intensity of $M/e = 30$ in the gas mixture of the IR cell (shown in Fig. 8). As indicated by the results in Fig. 3, NO_2 is expected in the gas mixture during the isotope exchange experiments. Since NO_2 easily fragments to NO in a mass spectrometer, it is reasonable to attribute the $M/e = 30$ signal to be mainly from NO_2 .

The evolution of the IR spectra during the isotope exchange experiments for the two samples, however, is different as demonstrated in Fig. 7. To further illustrate the differences between the two catalysts, the intensities of the nitrate-related IR bands at 1629, 1623, 1598, and 1570 cm^{-1} for the Cu-BEA sample, and those at 1624, 1593, and 1570 cm^{-1} for the Cu-CHA sample, measured from each of the IR spectra in Fig. 7, are normalized to the intensity of the corresponding IR bands recorded just prior to the introduction of ($^{15}\text{NO} + \text{O}_2$) gas mixture (*i.e.* those at “0 min”). The normalized intensities for each of IR bands are subsequently plotted in Fig. 9 as a function of exposure time.

On Cu-CHA, The IR bands at 1624, 1593, and 1570 cm^{-1} all decrease monotonically as a function of exposure time. The decline of the relative intensities for the three bands follows a similar trend, indicating that the surface nitrates formed on the catalyst from the previous ($\text{NO}_2 + \text{O}_2$) adsorption step are gradually reduced and displaced when the sample is subsequently exposed to the gas mixture of ($^{15}\text{NO} + \text{O}_2$). The situation for Cu-BEA, however, is different. Although the IR bands at 1629 and 1623 cm^{-1} decline with the same trend, the band at 1570 cm^{-1}

declines more slowly (see Fig. 9). More significantly, the IR band centered at 1598 cm^{-1} only decreases slightly in the initial 6 min, but starts to grow in intensity thereafter. It becomes evident that new surface compounds are formed on the Cu-BEA sample. Based on the isotopic shifts reported in Fig. 5 and Table 2, the increase in intensity in this region can be attributed to the formation of ^{15}N -containing surface nitrates, which contribute to IR bands at 1595 and 1587 cm^{-1} . The formation of ^{15}N -containing surface nitrates on the Cu-BEA sample is further confirmed by the increase of intensity of a weak IR band in the region near 1531 cm^{-1} , which corresponds to bidentate nitrates on the catalyst.

As discussed above and shown in Table 2, the isotopic shifts for the ^{14}N -O and ^{15}N -O vibration bands on both catalysts match well with the simple harmonic oscillator model. Therefore, it is possible to estimate the relative amounts of ^{14}N -nitrates and ^{15}N -nitrates by deconvolution of the IR bands in the region of $1650\text{-}1500\text{ cm}^{-1}$, assuming that they are linear combination from both groups. Data analysis for the IR spectra after 36 min exposure to ($^{15}\text{NO} + \text{O}_2$) is illustrated in Fig. 10. In the analysis, “Sim. (1)” simply attenuates the intensities of the “0 min” IR spectra that have been recorded after ($\text{NO}_2 + \text{O}_2$) exposure followed by evacuation. “Sim. (2)” shifts the wavenumbers of the “0 min” IR spectra as well as attenuates the intensities. For simplicity, however, the $^{15}\text{N}/^{14}\text{N}$ isotopic shift factor determined for the bridging nitrate band (i.e. 0.9791) is applied to the entire region of $1650\text{-}1500\text{ cm}^{-1}$. In this way, “Sim. (1)+(2)” is a linear combination of “Sim. (1)” and “Sim. (2)”. As shown in Fig. 10, the simulated IR spectra based on two portions of independent contributions from ^{14}N -nitrates and ^{15}N -nitrates fits the actual IR spectra very well. Accordingly, the results in Fig. 10 indicate that, on the Cu-BEA sample, about 38% ^{14}N -nitrates were displaced, with the formation of 16% ^{15}N -nitrates during

the isotope exchange experiment. In contrast, nearly no ^{15}N -nitrates are formed (<3%) on the Cu-CHA sample although about 25% ^{14}N -nitrates are displaced.

4. Discussion

The results in Fig. 1 demonstrate that, although both Cu-BEA and Cu-CHA are highly active in catalyzing the SCR reactions, they are relatively poor in converting NO to gas phase NO_2 under conditions comparable to SCR reactions. Such poor NO oxidation activity is not due to the formation of stable surface nitrates that block the active sites for the forward reaction. In fact, only a very low level of N-containing compounds on the Cu-BEA sample, and barely anything on the Cu-CHA sample, have been registered in the subsequent TPD experiments. On the other hand, the lack of surface nitrates on the catalysts is not due to the low thermal stability of the nitrate groups either. As shown in Fig. 2 and Table 1, a considerable amount of surface nitrates can be formed on both catalysts when they are exposed to a flow of $(\text{NO}_2 + \text{O}_2 + \text{H}_2\text{O})$. Once formed, the surface nitrates are thermally stable and remain on the catalyst surface until the temperature reaches above $\sim 325^\circ\text{C}$ for Cu-BEA, or above $\sim 375^\circ\text{C}$ for Cu-CHA.

The strong correlation between the NO_2/NO_x ratios in the feed gas for the $(\text{NO}_x + \text{O}_2 + \text{H}_2\text{O})$ adsorption step and the amounts of surface nitrates formed on the catalysts (indicated by the amounts of NO_2 desorbed in the subsequent TPD experiments, as shown in Fig. 2 and Table 1, indicates that the surface nitrates are reduced by NO. The results in Fig. 3 clearly support this notion: NO_2 desorption is observed immediately when the nitrate covered catalysts are exposed to a feed of $(\text{NO} + \text{O}_2 + \text{H}_2\text{O})$. After 30-min of exposure, nearly all of the surface nitrates formed from the previous $(\text{NO}_2 + \text{O}_2 + \text{H}_2\text{O})$ adsorption step are consumed resulting in little or barely

any NO₂ desorption in the final TPD experiments (see the “NO₂ followed by NO” curves in Fig. 2).

Similar results to those shown in Fig. 3 were also obtained by Nova, Tronconi and coworkers, and the Harold group for a variety of zeolite supported transition metal SCR catalysts, as well as for V-based SCR catalysts [9-14]. Nova, Tronconi and coworkers proposed that the reduction of nitrates by NO proceeds via two consecutive reactions with the first step as follows:

They hypothesized that the newly formed surface nitrite groups were not stable, and could react with the remaining nitrate groups on the catalyst surfaces to generate more NO₂ according to the following reaction:

A combination of the two steps results in a global reaction of:

This implies that every mole of NO is able to reduce two moles of surface nitrate ions and produce three moles of NO₂ into the gas phase. Or in other words, there is a net gain of gas phase NO_x during the reduction process. Indeed, the results shown in Fig. 3 confirm a net increase of the NO_x concentration in the outlet of the catalysts when NO is introduced to the nitrate covered samples.

On the other hand, Reaction (5) also implies that, while the surface nitrates are reduced to gas phase NO₂, part of the NO in the original feed gas is also oxidized to NO₂ and subsequently becomes a portion of the NO₂ released from the catalysts. Since NO₂ is known to readily go through a disproportionation reaction (Reaction (2)) to form surface nitrates, it is reasonable to

expect that nitrogen from the original feed gas may land on the catalyst surface through re-adsorption of NO₂ (or the reverse reaction of Reaction (5)). Unfortunately, in the experiments with regular ¹⁴N-reagents, the origin of nitrogen sources cannot be distinguished.

This expectation, however, may be confirmed by using different N-isotopes during the two steps. For example, with ¹⁵NO replacing NO in the feed gas, the processes of Reactions (3)-(5) can be more accurately expressed as follows:

Accordingly, the reaction schemes predict some of the gas phase ¹⁵NO will be oxidized to ¹⁵NO₂. If ¹⁵NO₂ indeed forms during the process, some of it will be re-adsorbed and form ¹⁵N-nitrates on the catalyst surfaces via Reaction (2).

The results shown in Fig. 5 and Table 2 indicate that the IR bands for the ¹⁴N-nitrate groups are located at wavenumbers distinct from the IR bands for the ¹⁵N-nitrate groups. Furthermore, all of the vibrational modes and their isotopic shifts fit well with the simple harmonic oscillator model. These make it possible to differentiate the origin of the surface nitrates by monitoring the IR spectra of the surface complexes when ¹⁵NO is used to react with the surface ¹⁴N-nitrate groups. This forms the basis of the isotope exchange experiments carried out in this study.

Slightly different from the experiments conducted in the flow reactor, the isotope exchange experiments were carried out in a static IR cell. As such, the products release from the catalyst surfaces remain in the cell. This actually increases the probabilities for the gas phase products to react with the catalyst surfaces. Although H₂O is not included in the isotope

exchange experiments because it would show strong IR signals that mask the nitrate bands, this difference should not alter the reaction pathway. In fact, Ruggeri et al., as well as other groups, reported that H₂O only moderately inhibits the NO oxidation activity [13-19].

The gas phase product distributions during the isotope exchange experiments shown in Fig. 8 clearly demonstrate that, as soon as the ¹⁴N-nitrate covered samples are exposed to the gas mixture of (¹⁵NO + O₂), ¹⁴N-containing compounds are released while ¹⁵N-containing complexes are adsorbed on the catalysts. Although the gas phase compositions are similar, the evolution of the IR spectra during the isotope exchange process is considerably different between Cu-BEA and Cu-CHA (see Fig. 7).

For Cu-CHA, a monotonic reduction of the IR bands corresponding to ¹⁴N-nitrates is observed, with barely any ¹⁵N-nitrates being detected on the sample during the entire experiment (see Fig. 7B, Fig. 9, and Fig. 10B). The lack of ¹⁵N-nitrates on the Cu-CHA sample challenges the assumptions made for the reaction schemes discussed above. As ¹⁴N-compounds are detected in the gas phase and the intensities of the IR bands corresponding to ¹⁴N-nitrates decrease with the exposure time, it is reasonable to believe that Reaction (3') still correctly describes the first step of the NO-induced nitrate reduction process. Therefore, Reaction (4') becomes questionable at least for the case of Cu-CHA. If Reaction (4') does not proceed at all on the Cu-CHA sample, but with only Reaction (3') going forward, accumulation of ¹⁵N-nitrites on the surfaces is expected. Unfortunately IR bands corresponding to surface nitrites appear at quite low wavenumbers, in a region that overlaps with the zeolite framework vibrations and, as such, are extremely difficult to observe.

Since barely any NO or NO₂ was detected in the TPD experiments carried out in the flow reactor for samples after the NO-induced reduction process (see the cases of “NO₂ followed by

NO⁺ in Fig. 3 and in Table 1), this indicates that surface nitrites, even if they are formed on the catalysts, are not thermally stable and must have decomposed either during the exchange process or in the subsequent purging period. Such a process can be described as:

Interestingly, an IR band centered at 2119 cm⁻¹, that is assigned to NO⁺ at exchange sites, is indeed observed on the Cu-CHA sample once the nitrate covered sample was exposed to (¹⁵NO + O₂). This band does exhibit low thermal stability and its intensity declines upon purging.

Although the nature of the adsorbed NO⁺ complex is not fully understood and additional characterization work is needed, this complex has been identified and proposed as a potential intermediate in SCR reactions on Cu-CHA catalysts [24]. Based on the results from this study, it is difficult to assert if the NO oxidation products on the catalyst are NO⁺ or NO₂⁻, or both. The key message is clear that, on Cu-CHA, NO from the gas phase can only be oxidized to some types of compounds with a formal oxidation state for the N of +3. This is likely the fundamental reason why Cu-CHA exhibits very low catalytic activity for NO oxidation to NO₂, as the formation of gas phase NO₂ requires a change in the oxidation state of the N to +4.

The situation is different for Cu-BEA as formation of ¹⁵N-based surface nitrates is observed, with the intensities of the corresponding IR bands increasing with exposure time (see Fig. 7A, Fig. 9, and Fig. 10A). Although these results fit well in general with the reaction schemes proposed in Reactions (3')-(5'), they are insufficient to determine if gas phase ¹⁵NO₂ has to be formed first, which then goes through the disproportionation reaction to form surface ¹⁵N-nitrates on the catalyst. It is also plausible that the ¹⁵N-nitrite formed from Reaction (3') can be directly oxidized to ¹⁵N-nitrates on Cu-BEA and, thus, not requiring the formation of gas phase ¹⁵NO₂. Nevertheless, it is evident that Cu-BEA is able to catalyze a change in the N

oxidation state during NO oxidation to a value higher than +3. Such a property of Cu-BEA is, thus, fundamentally different from that of Cu-CHA.

Even though the results from the just-described isotope exchange experiments clearly suggest that Cu-BEA is much more active than Cu-CHA in catalyzing NO oxidation, the two catalysts exhibit equally poor steady-state NO to NO₂ oxidation activity when tested in a flow reactor; that is, the NO to NO₂ conversions for Cu-BEA are only marginally higher than that for Cu-CHA. These puzzling observations can be reconciled by invoking multiple types of active sites, each with different populations on these catalysts. For simplicity, we will consider only two types of active sites in the following discussion: (1) Type I sites that can only change the N oxidation state from +2 to +3 (e.g., NO to NO⁺ or NO₂⁻) during NO oxidation; (2) Type II sites that can change the N oxidation state during NO oxidation from +2 to a higher values, such as +4 (e.g., NO₂) or +5 (e.g., NO₃⁻).

Considering this model, it is clear that Type I sites dominate on the Cu-CHA catalyst. As a result, it shows low intrinsic NO to NO₂ oxidation activity. For Cu-BEA, although both types of active sites co-exist on the catalysts, the relative population of Type II sites is still very low compared to that of Type I sites. When evaluated in the flow reactor, where the NO to NO₂ oxidation reaction is kinetic limited, the catalyst exhibits poor activity because of the low population of Type II sites. In contrast, when evaluated under static conditions in the isotope exchange experiment where NO oxidation to a higher oxidation state is less constrained by kinetics, the features of the Type II sites become apparent.

The hypothesis of the presence of two types of active sites can further explain the different trends in the relative activity observed between Cu-BEA and Cu-CHA for SCR reactions and for NO oxidation (see Fig. 1). As Type I sites are highly active in converting NO to

NO^+ or NO_2^- , both having been proposed by many research groups as key intermediates during SCR reactions [13,14,21-22,24] it is reasonable to consider Type I sites in the catalysts as the preferred active centers for SCR reactions. Type I sites being dominant in Cu-CHA, this catalyst exhibits high SCR activity and selectivity. On the other hand, the presence of Type II sites in Cu-BEA perhaps not only reduces the population of Type I sites, but may also cause the undesirable NO oxidation to higher N oxidation states leading to the formation of surface nitrates. According to equation (2) shown in the introduction, NO_2 disproportionation to surface nitrite and nitrate necessarily requires participation of an active O^{2-} species. One likely form of such species is the so-called extra-lattice oxygen (ELO) that only associates with multinuclear Cu sites [31]. Therefore, we tentatively suggest here that Type I sites are isolated Cu-ions, which are known to dominate in Cu-CHA [3,4,15-19], while Type II sites are Cu sites with higher nuclearity [32]. It is known, under SCR conditions, that NH_3 can readily react with surface nitrates, and part of which can subsequently decompose to N_2O [28]. The fact the Cu-BEA is less active in SCR reactions but with a higher selectivity for N_2O formation compared to Cu-CHA supports this theory. Therefore, it also follows that the nitrates identified on most of the zeolite supported transition metal SCR catalysts are the less reactive intermediates responsible for the desirable SCR reactions, and they also contribute to the formation of the undesirable reaction product, N_2O .

5. Conclusions

Both Cu-BEA and Cu-CHA exhibit very poor NO to NO_2 oxidation activity, even though both are highly active in catalyzing the SCR reaction. Such poor NO oxidation activity is not due to the formation of stable surface nitrates on the catalyst. On the contrary, NO is found to reduce

and decompose surface nitrates. It is proposed here that two types of active sites for NO oxidation may exist on the catalysts, with Type I sites only catalyzing N oxidation state changes during NO oxidation from +2 to +3, and Type II sites that catalyze N oxidation state changes from +2 to higher values, such as +4 or +5. Furthermore, our results suggest that Type I sites are the preferred active centers for SCR reactions. It appears that Type I sites are dominant in Cu-CHA and, thus, contribute to the high SCR activities and selectivity for this catalyst. Low levels of Type II sites are also present in Cu-BEA in addition to Type I sites, and lead to the formation of surface nitrates and, thus, higher N₂O formation compared to Cu-CHA.

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Table 1: Quantitative analysis of the amount of NO₂ desorbed in the TPD experiments relative to the gas feed composition during the adsorption step.

NO ₂ /NO _x ratio in the feed of (350 ppm NO _x + 10% O ₂ + 2.5% H ₂ O)	Amount of NO ₂ desorbed in the subsequent TPD experiment (* in the unit of “x10 ⁻⁶ mole of NO ₂ /g catalyst”; ** in the unit of “mole of NO ₂ / mole of Cu”)	
	Cu-BEA	Cu-CHA
NO ₂ /NO _x = 1	80* (0.17**)	81* (0.17**)
NO ₂ /NO _x = 0.82	44* (0.093**)	57* (0.12**)
NO ₂ /NO _x = 0.5	18* (0.039**)	21* (0.44**)
NO ₂ /NO _x = 0.15	6* (0.012**)	0* (0**)
NO ₂ , followed by NO	7* (0.015**)	1* (0.003**)

Table 2: IR bands detected during ($\text{NO}_2 + \text{O}_2$), ($\text{NO} + \text{O}_2$), and ($^{15}\text{NO} + \text{O}_2$) adsorption experiments and their assignment

IR band for ^{14}N -compounds (cm^{-1})	IR band for ^{15}N -compounds (cm^{-1})	$^{15}\text{N-O} / ^{14}\text{N-O}$ isotopic shift factor	Assignment [14,20- 22,28,30]
Cu-BEA			
	2091		NO^+ at exchange sites
1902	1868	0.9821	NO-Cu^{2+}
1812	1783	0.9840	NO-Cu^+
1629	1595	0.9791	Bridging nitrates
1623	1587	0.9778	Bridging nitrates
1598	1560	0.9762	Bidentate nitrates
1570	1531	0.9752	Bidentate nitrates
Cu-CHA			
2155	2119	0.9833	NO^+ at exchange sites
1902	1866	0.9811	NO- Cu^{2+}
1624	1590	0.9791	Bridging nitrates
1593	1554	0.9755	Bidentate nitrates
1570	1531	0.9752	Bidentate nitrates

Figure captions

Fig. 1. Steady state activities of the standard SCR reactions and the NO to NO₂ oxidation reactions for Cu-BEA and Cu-CHA.

(SCR reaction conditions: 350 ppm NO, 350 ppm NH₃, 10% O₂, 2.5% H₂O, and balance N₂, GHSV = 200,000 h⁻¹; NO oxidation reaction conditions are similar to the SCR reaction conditions except NH₃ addition)

Fig. 2. TPD profiles for Cu-BEA and Cu-CHA after exposure to (NO_x + O₂ + H₂O) feeds with different NO₂/NO_x ratios

Fig. 3. Outlet concentrations of NO, NO₂, and NO_x (=NO + NO₂) when nitrates covered Cu-BEA and Cu-CHA are subsequently exposed to (350 ppm NO + 10% O₂ + 2.5% H₂O, and balance N₂)

Fig. 4. *In situ* FTIR spectra at 200 °C of samples after 24 min exposure to (0.15 Torr NO₂ + 1.35 Torr O₂), (0.15 Torr NO + 1.35 Torr O₂), or (0.15 Torr ¹⁵NO + 1.35 Torr O₂)

Fig. 5. *In situ* FTIR spectra at 200 °C of samples upon exposure to (0.15 Torr ¹⁵NO + 1.35 Torr O₂)

Fig. 6. Change of the intensities for a few selected IR bands as a function of exposure time during the *in situ* FTIR experiments shown in Fig. 5

Fig. 7. *In situ* FTIR spectra at 200 °C of samples after ¹⁴N-nitrate pre-adsorption (labeled as “0 min”); and upon subsequent exposure to (0.15 Torr ¹⁵NO + 1.35 Torr O₂)

Fig. 8. Mass spectrometer signals from the IR cell during the *in situ* FTIR experiments shown in Fig. 7

Fig. 9. Change of the relative intensities for the IR bands at a few selected wavenumbers as a function of exposure time during the *in situ* FTIR experiments shown in Fig. 7

Fig. 10. Deconvolution of the “36 min” IR spectra shown in Fig. 7 assuming that they are linear combination from ¹⁴N-nitrates (labelled as “Sim. (1)”) and ¹⁵N-nitrates (labelled as “Sim. (2)”)

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Fig. 4. *In situ* FTIR spectra at 200 °C of samples after 24 min exposure to (0.15 Torr NO₂ + 1.35 Torr O₂), (0.15 Torr NO + 1.35 Torr O₂), or (0.15 Torr ¹⁵NO + 1.35 Torr O₂)

Fig. 5. *In situ* FTIR spectra at 200 °C of samples upon exposure to (0.15 Torr ^{15}NO + 1.35 Torr O_2)

Fig. 6. Change of the intensities for a few selected IR bands as a function of exposure time during the *in situ* FTIR experiments shown in Fig. 5

Fig. 7. *In situ* FTIR spectra at 200 °C of samples after ¹⁴N-nitrate pre-adsorption (labeled as “0 min”); and upon subsequent exposure to (0.15 Torr ¹⁵NO + 1.35 Torr O₂)

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Fig. 10. Deconvolution of the “36 min” IR spectra shown in Fig. 7 assuming that they are linear combination from ^{14}N -nitrates (labelled as “Sim. (1)”) and ^{15}N -nitrates (labelled as “Sim. (2)”)