A Comparative Study of N₂O Formation during the Selective Catalytic Reduction of NO_x with NH₃ on Zeolite Supported Cu Catalysts

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Abstract

A comparative study was carried out on a small-pore Cu-CHA and a large-pore Cu-BEA zeolite catalyst to understand the lower N₂O formation on small-pore zeolite supported Cu catalysts in the selective catalytic reduction (SCR) of NO_x with NH₃. On both catalysts, the N₂O yield increases with an increase in the NO₂/NO_x ratios of the feed gas, suggesting N₂O formation via the decomposition of NH₄NO₃. Temperature-programmed desorption experiments reveal that NH₄NO₃ is more stable on Cu-CHA than on Cu-BEA. *In situ* FTIR spectra following stepwise (NO₂ + O₂) and (¹⁵NO + NH₃ + O₂) adsorption and reaction, and product distribution analysis using isotope-labelled reactants, unambiguously prove that surface nitrate groups are essential for the formation of NH₄NO₃. Furthermore, Cu-CHA is shown to be considerably less active than Cu-BEA in catalyzing NO oxidation and the subsequent formation of surface nitrate groups. Both factors, i.e., (1) the higher thermal stability of NH₄NO₃ on Cu-CHA, and (2) the lower activity for this catalyst to catalyze NO oxidation and the subsequent formation of surface nitrates, likely contribute to the higher SCR selectivity with less N₂O formation on this catalyst as compared to Cu-BEA. The latter is determined as the primary reason since surface nitrates are the source that leads to the formation of NH₄NO₃ on the catalysts.

Keywords: Selective catalytic reduction of NO_x; Zeolite supported Cu catalysts; Surface nitrate groups; N₂O formation mechanisms; NH₄NO₃ decomposition; Pore restriction effect in zeolites.

Graphical Abstract

1. Introduction

Zeolite supported Cu catalysts have been found to be active for the selective catalytic reduction (SCR) of nitrogen oxides (NO_x) with NH₃ since the 1970s [1-4]. Most of the zeolite supports evaluated in earlier work were based on 12-membered ring (large-pore) zeolites, such as BEA, FAU, and MOR [5-11], or 10-membered ring (medium-pore) zeolites, such as MFI and FER [11-13]. It was only recently that 8-membered ring (small-pore) zeolites, such as CHA, AEI, AFX, were recognized to have significant advantages including (1) higher SCR activity; (2) improved hydrothermal stability; (3) better hydrocarbon tolerance; and (4) enhanced N₂ selectivity with less N₂O formation, as compared to large- or medium-pore zeolite catalysts [1, 2, 14-19].

The improvement of hydrocarbon tolerance on small-pore zeolite supported Cu SCR catalysts can be readily attributed to a molecular sieving effect; in particular, the openings in the small-pore zeolite supports ($\sim 4 \text{ \AA}$) are smaller than the kinetic diameters of most hydrocarbons. It restricts large hydrocarbons from entering the pores of the catalysts where the SCR reactions take place, minimizing the HC inhibition effect on SCR activity. In contrast, the openings in large- or medium-pore zeolite supports are large enough to allow most hydrocarbons to enter their pores, which can severely inhibit the SCR activity of the catalysts [1, 14, 20].

Pore size effects have also been proposed to explain the improved hydrothermal stability of small-pore zeolite supported Cu SCR catalysts. Dealumination of the zeolite supports and formation of CuAl₂O₄-like compounds have been identified as two major causes of catalyst deactivation when zeolite supported Cu SCR catalysts are exposed to high temperatures in the presence of steam [21-25]. Fickel et al. [15] suggested that the small pore openings in a CHA zeolite restrict migration of the dealumination product Al(OH)₃, thus slowing down the

dealumination process of the zeolite support. Using an *in situ* XRD technique, Blakeman et al. [20] demonstrated that the undesirable Cu-Al interactions were minimized in a small-pore Cu-CHA catalyst, concluding that this was mainly due to pore restriction.

The enhancement of SCR activity and the simultaneous reduction in N₂O formation on small-pore zeolite supported Cu catalysts are less well understood. Several groups have reported that N₂O formation on Cu-zeolite SCR catalysts follows the order of small-pore < medium-pore < large-pore zeolites [1, 18, 19]. The fundamentals on such a trend, however, have not been established. Furthermore, because of its potent greenhouse effect, N₂O emissions from transportation sources have recently been regulated by government agencies. Thus, understanding of the N₂O formation mechanisms on zeolite supported Cu SCR catalysts is of both fundamental importance and practical relevance.

In the present study, two Cu SCR catalysts with nearly identical compositions, one supported on a small-pore CHA zeolite and the other on a large-pore BEA zeolite, were compared for their N₂O formation under various SCR reaction conditions. *In situ* FTIR and temperature-programmed desorption (TPD) in combination with isotope labelling techniques were applied to study the nature of the surface complexes upon NO_x adsorption, their reactivity, and their contribution to N₂O formation.

2. Experimental

2.1 Catalyst preparation

The small-pore CHA and the large-pore BEA zeolite samples used in this study have the same SiO₂ to Al₂O₃ ratio (SAR) of 25. XRD measurements confirmed that both materials are phase pure. Cu-CHA and Cu-BEA catalysts were prepared by ion-exchange of Cu into the

corresponding zeolite supports and the Cu loading was 3 wt.% for both samples. After ion exchange, the samples were first calcined at 550 °C for 2 h in air. To ensure consistent and reproducible results during the study, the calcined powder samples were further hydrothermally treated at 650 °C for 4 h in synthetic air containing 5% H₂O. Such a pretreatment condition was sufficient to stabilize the performance of the catalysts, but remained mild enough in order not to cause appreciable deactivation to either of the catalysts.

2.2 SCR activity testing

Powder samples of the pre-treated Cu-CHA and Cu-BEA catalysts were pressed, crushed, and sieved. Samples with particle sizes ranging from 0.251 to 0.422 mm were selected for SCR activity testing. 45 mg of the coarse catalysts were loaded into a 1-cm diameter quartz tube reactor. The feed gas composition was regulated by the mass flow controllers of each individual gas line. The total flow rate was maintained at 300 sccm, which resulted in a gas hourly space velocity (GHSV) of 200,000 h⁻¹ based on the packing density of the catalysts at ~0.5 g/cm³. Concentrations of 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 activity testing was carried out in a feed of 350 ppm NO, 350 ppm NH₃, 10% O₂, 2.5% H₂O, and balance N₂. Steady-state NO_x conversions and N₂O formation levels were measured in the temperature range of 175–500 °C. In addition, N₂O formation as a function of NO₂/NO_x ratio was measured at 200 and 350 °C. In these tests, the total NO_x (= NO + NO₂) concentration was maintained at 350 ppm, and the concentrations for other feed components were maintained the same as shown above for the standard SCR testing. Prior to each testing, the catalysts were pre-treated at 500 °C for 30 min in a feed of 10% O₂, 2.5% H₂O and balance N₂ to clean their surfaces. For the experiments performed at 200 °C and high NO₂/NO_x ratios (≥ 0.5), accumulation of deposits on

the catalysts was observed. Under these circumstances, additional TPD experiments were carried out after the SCR activity testing. For these, the feed gas was switched to 10% O₂, 2.5% H₂O and balance N₂ and after a 2 min purge, the samples were heated from 200 to 500 °C at a ramping rate of 25 °C/min.

2.3 *In situ* FTIR and TPD measurements

The *in situ* transmission FTIR and TPD measurements were conducted using the same apparatus described in detail in reference [26]. About 4 mg of powder sample was 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. The cell can be isolated from the vacuum chamber by a gate valve and can be pressurized to sub-atmospheric pressures for chemisorptive FTIR experiments, or used as a static reactor. Reactions were monitored by leaking the gas mixtures in the cell into the vacuum chamber through a leak valve. After reactions, the cell was evacuated. TPD measurements were subsequently carried out with the gate valve fully open to increase the signal intensity.

The samples were first heated under vacuum ($P < 1 \times 10^{-7}$ Torr) at 500 °C for 2 h to clean the surfaces. Such a treatment also caused an auto-reduction of a portion of Cu²⁺ to Cu⁺ in the catalysts. The samples were then cooled and held at 200 °C. Oxygen was subsequently admitted into the IR cell until the pressure reached 1.5 Torr. This partially re-oxidizes the catalysts. After 30 min of oxygen exposure, the cell was again evacuated and background spectra of the pre-treated samples were recorded by averaging 256 scans at a 4 cm⁻¹ resolution. The samples were pre-treated according to these procedures prior to any of the gas exposure experiments.

For the first set of ($\text{NO} + \text{O}_2$) adsorption experiments, a mixture of (0.15 Torr $\text{NO} + 1.35$ Torr O_2) was admitted to the IR cell while the pre-treated samples were held at 200 °C. IR spectra were recorded (also 256 scans) as a function of exposure time. For the second set of stepwise ($\text{NO}_2 + \text{O}_2$) adsorption, ($^{15}\text{NO} + \text{NH}_3 + \text{O}_2$) adsorption and reaction, and TPD experiments, a mixture of (0.15 Torr $\text{NO}_2 + 1.35$ Torr O_2) was first introduced to the IR cell with the samples held at 200 °C. After 36 min of exposure, the IR cell was evacuated for 5 min until the pressure was below 1×10^{-6} Torr. A mixture of (0.15 Torr $^{15}\text{NO} + 0.60$ Torr $\text{NH}_3 + 0.75$ Torr O_2) was subsequently added to the IR cell. After 24 min, the IR cell was evacuated again for 5 min. Finally the samples were heated from 200 to 500 °C at a ramping rate of 30 °C/min. FTIR spectra were recorded during the various steps at 200 °C. Mass spectrometer signals of selected masses were continuously recorded during these gas exposure experiments although only the data collected during TPD are reported here. For the third set of experiments, the pre-treated catalysts were exposed to (0.6 Torr $\text{NH}_3 + 0.9$ Torr O_2) for 6 min for NH_3 adsorption. The IR cell was then evacuated and a mixture of (0.15 Torr $^{15}\text{NO} + 0.15$ Torr $\text{NO}_2 + 0.3$ Torr $\text{NH}_3 + 0.9$ Torr O_2) was re-introduced. After 24 min of SCR reaction, the IR cell was evacuated for 5 min. Finally TPD measurements were carried out by heating the samples from 200 to 500 °C at a ramping rate of 30 °C/min. Masses of N-containing compounds with $M/e = 17$ ($^{14}\text{NH}_3$), 28 ($^{14}\text{N}^{14}\text{N}$), 29 ($^{15}\text{N}^{14}\text{N}$), 30 (^{14}NO and the fragment of $^{14}\text{NO}_2$), 31 (^{15}NO and the fragment of $^{15}\text{NO}_2$), 44 ($^{14}\text{N}_2\text{O}$), 45 ($^{15}\text{N}^{14}\text{NO}$), and 46 ($^{15}\text{N}_2\text{O}$ and $^{14}\text{NO}_2$) are simultaneously recorded.

3. Results

3.1. Comparison of N_2O formation on the Cu-BEA and Cu-CHA catalysts

Steady state NO_x conversions and the corresponding N₂O formation levels as a function of temperature for Cu-BEA and Cu-CHA are presented in Fig. 1. Both catalysts show comparable and high NO_x conversions in the temperature region from 175 to 500 °C. On both catalysts, NO_x conversions increase with temperature from 175 to 250 °C, and reach nearly 100% NO_x reduction efficiencies at temperatures between 250 and 350 °C before decreasing above 350 °C. The decline in NO_x conversions at temperatures above 350 °C is caused, at least in part, by the parallel unselective NH₃ oxidation reactions on the catalysts, which compete with the SCR reactions for NH₃ and reduce overall NO_x reduction efficiency.

The profiles of the N₂O level versus temperature for the two catalysts are also similar. In both cases, N₂O levels first increase with increasing temperature, then decrease and reach their minima at 350 °C. At temperatures above 350 °C, the N₂O levels gradually increase again with temperature. However, the amount of N₂O formed on the two catalysts is drastically different. Notably, at any given temperature, the N₂O yields on Cu-BEA are ~3-6 times higher than on Cu-CHA, in line with prior reports in the literature [1, 18, 19].

At temperatures above 350 °C, although unselective NH₃ oxidation may directly contribute to some of the observed N₂O production the contribution is likely small. Rather it is more likely that this reaction effectively reduces the NH₃/NO_x ratios to values below the stoichiometric point (1:1) needed for standard SCR, which significantly affects the selectivity of SCR reactions and lead to N₂O formation. A detailed reaction mechanism for N₂O formation at temperatures above 350 °C is, however, beyond the scope of the present study. Instead, we focus here on the origins of N₂O formation at temperatures $\leq$ 350 °C, where unselective NH₃ oxidation rates are negligible.

3.2. Effect of NO₂/NO_x ratios on the formation of N₂O

It is generally accepted that, under low temperature SCR reaction conditions, N_2O is formed via the decomposition of NH_4NO_3 , an intermediate formed on the catalyst when ammonia reacts with the surface nitrate groups [6-10, 27-30]. It is also well established that formation of surface nitrates is facilitated with the increase of the NO_2/NO_x ratios in the feed and, correspondingly, N_2O formation on Cu SCR catalysts also increases. Indeed, as can be seen in Fig. 2 where the N_2O formation rates are plotted as a function of the NO_2/NO_x ratio in the feed gas, such a trend is clearly evident for the large-pore Cu-BEA catalyst at both 200 and 350 °C when the NO_2/NO_x ratio gradually increases from 0 to 0.82. This trend also holds for the small-pore Cu-CHA catalyst at 350 °C, although the absolute N_2O formation rate at a given NO_2/NO_x ratio is always lower than that observed for Cu-BEA. At 200 °C, however, N_2O formation on Cu-CHA increases only slightly when the NO_2/NO_x ratio increases from 0 to 0.5. A further increase of the NO_2/NO_x ratio to 0.82 even leads to a decline in N_2O formation for the catalyst (see Fig. 2).

Of significant interest is an inhibition phenomenon observed for Cu-CHA at 200 °C with an SCR feed containing a NO_2/NO_x ratio of 0.82. Fig. 3A plots outlet concentrations of NO, NO_2 , N_2O and NH_3 during the experiment on Cu-CHA. Starting from a freshly pre-treated sample, both NO and NO_2 concentrations decrease first with reaction time, achieving nearly 65% instantaneous total NO_x conversion at a reaction time of ~10 min. Thereafter, the NO outlet concentration increase monotonically until a reaction time of ~40 min and levels off thereafter. During this period, the NO_2 outlet concentration keeps decreasing. After ~40 min of reaction, the NO_2 outlet concentration increases sharply and approaches a plateau of around 230 ppm. NH_3 also starts to break through rapidly after a reaction time of ~50 min. Upon reaching a quasi-steady state after a reaction time of ~100 min, only ~23% of NO_x conversion is achieved for the

Cu-CHA catalyst. Note that under SCR reaction conditions at NO₂/NO_x ratios below 0.5, steady-state NO_x conversions are always $\geq 98\%$ at 200 °C for this catalyst. This clearly indicates that, with an NO₂/NO_x ratio of 0.82 in the feed, a significant quantity of deposits are generated on the small-pore Cu-CHA catalyst and inhibit the SCR reaction at 200 °C. In contrast, no noticeable inhibition is observed for the large-pore Cu-BEA catalyst at the same reaction conditions. Indeed, as demonstrated in Fig. 3B, the NO_x conversion reach steady state at ~92% for Cu-BEA with an NO₂/NO_x ratio of 0.82 in the feed, which is only a few percent lower than the NO_x conversions observed on the catalyst at lower NO₂/NO_x ratios.

TPD experiments were subsequently conducted on the samples to probe the nature of the deposits, formed on the catalysts after SCR reactions at 200 °C at high NO₂/NO_x ratios (0.5 and 0.82). During the experiments, NO₂ (with a negligible amount of NO), N₂O and NH₃ desorption is observed. Clearly these molecules are products from decomposition of NH₄NO₃ deposited on the catalysts through a number of possible pathways [31, 32], such as:

Since the plug-flow reaction system is only equipped with an FTIR analyzer for gas analysis, we were unable to measure N₂ formation in the TPD experiments. Hence we cannot quantify NH₄NO₃ deposits on the catalysts or the percentage of the NH₄NO₃ deposits that decompose to N₂O during TPD. However, as a first approximation, it is reasonable that the amount of N₂O released during TPD is proportional to the amount of NH₄NO₃ deposited on the catalysts.

When the NO_2/NO_x ratios in the feed are below 0.5 during the SCR activity testing, no N_2O is detected in the subsequent TPD experiments either for Cu-BEA or Cu-CHA (data not shown). At NO_2/NO_x ratios of 0.5 and 0.82, the N_2O desorption profiles are shown in Fig. 4. At an NO_2/NO_x ratio of 0.5, no N_2O desorption is observed for the Cu-BEA sample, but small amount of N_2O desorbs from Cu-CHA (maximum concentration ~ 25 ppm, peak temperature ~ 375 °C). At an NO_2/NO_x ratio of 0.82 during SCR activity testing, dramatic increase in N_2O desorption is found in the subsequent TPD. For the Cu-BEA catalyst, N_2O starts to desorb from the catalyst at ~ 290 °C and reaches its peak concentration of ~ 65 ppm at ~ 328 °C; on the other hand for the Cu-CHA catalyst, the N_2O peak is substantially stronger and reaches a peak concentration of ~ 445 ppm, about 6 times higher than that measured for the Cu-BEA catalyst. In combination with the NO_x and NH_3 outlet traces shown in Fig. 3A, it can be concluded that the small-pore CHA structure can stabilize NH_4NO_3 at 200 °C to such an extent that nearly all the CHA pores are blocked, resulting in the severe inhibition effect as shown in Fig. 3A.

The N_2O desorption temperatures in the TPD experiments can be an indication of the stability of NH_4NO_3 on the catalysts. However, for desorption from zeolite materials, the desorption temperatures are affected by the coverage of the adsorbents because they may undergo multiple desorption/re-adsorption steps prior to the final release. Therefore, it is unfair to compare the N_2O release temperatures for the Cu-CHA and Cu-BEA catalysts based on the just-described SCR/TPD experiments where the NO_2/NO_x ratios are at 0.82 because of the very different amounts of NH_4NO_3 deposits. Instead, a more reasonable comparison can be made on the N_2O TPD profiles for the Cu-BEA sample after SCR reaction in a feed with $\text{NO}_2/\text{NO}_x = 0.82$ and that for the Cu-CHA sample in a feed with $\text{NO}_2/\text{NO}_x = 0.5$. In these two cases, the amounts of N_2O released from the catalysts are comparable. As shown in Fig. 4, the N_2O releases

temperature for the Cu-CHA sample is ~ 50 °C higher than that for the Cu-BEA sample, which further corroborate the fact that NH_4NO_3 is more stable on the small-pore Cu-CHA than on the large-pore Cu-BEA.

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

Formation of NH_4NO_3 requires surface nitrates on the catalysts [9]. *In situ* FTIR is used in this study to elucidate the surface complexes formed during NO_x adsorption, and to compare their reactivity towards NH_3 on the Cu-BEA and Cu-CHA catalysts.

Fig. 5 compares the IR spectra of the surface complexes formed on the two catalysts when these are exposed to a mixture of ($\text{NO} + \text{O}_2$) at 200 °C. On the Cu-BEA sample, bands at 1902 and 1812 cm^{-1} are observed immediately after introduction of $\text{NO} + \text{O}_2$. These two bands can be assigned to N-O stretching vibrations from NO adsorbed on Cu^{2+} and Cu^+ sites, respectively [26, 33, 34]. The presence of Cu^+ on the catalyst is due to auto-reduction of Cu^{2+} during the high temperature vacuum pretreatment [26]. Note that the subsequent re-oxidation step at 200 °C is not able to fully re-oxidize the sample. During the ($\text{NO} + \text{O}_2$) adsorption experiment, however, the remaining Cu^+ is gradually oxidized as evidenced by the disappearance of the band at 1812 cm^{-1} after 36 min of $\text{NO} + \text{O}_2$ exposure. A group of bands are also observed on the sample in the region of 1550-1650 cm^{-1} , with peaks at 1629, 1623, 1598 and 1570 cm^{-1} . Bands in this region are typically attributed to surface nitrate and nitrite groups [7, 26, 35], but based on most recent publications [36-39] these bands are more likely due to surface nitrates with different types of coordination, such as bridging nitrates and bidentate nitrates. It is worth noting that the intensities of the surface nitrates increase monotonically with time and become the dominant bands after 36 min of exposure.

The IR spectra of the surface NO_x adsorption complexes on the Cu-CHA sample are noticeably different. The band at 1812 cm⁻¹ attributed to NO adsorbed on Cu⁺ is not visible on the Cu-CHA sample, suggesting Cu⁺ is readily re-oxidized upon O₂ pretreatment at 200 °C [40-42]. The bands in the region of 1550-1650 cm⁻¹ also show some differences; the peaks appear at 1624, 1593, and 1570 cm⁻¹. At any given exposure time, the intensity of this group of bands is always substantially lower than that observed on the Cu-BEA sample. Another significant difference between the two catalysts is that a relatively intense and broad band, centered at 2155 cm⁻¹, and assigned to NO⁺ [26], is observed on the Cu-CHA sample and its intensity barely changes with exposure time. Notably, this 2155 cm⁻¹ band is almost non-existent in the spectrum from the Cu-BEA sample.

The intensity of the IR bands in the 1550-1650 cm⁻¹ region becomes much higher and rapidly reaches saturation on both Cu-BEA and Cu-CHA when these are exposed to a mixture of (NO₂ + O₂) (see Fig. 6). Compared with the much weaker IR bands in other regions, this clearly indicates that nitrate ad-species dominate on both catalysts with the exposure of (NO₂ + O₂).

The surface nitrate groups on both catalysts are relatively stable in vacuum, showing no decrease in intensity after evacuation at 200 °C (plotted in Fig. 7 as Cu-BEA (0 min) and Cu-CHA (0 min), respectively). However, they are very reactive to NH₃. As shown in Fig. 7, the 1629 cm⁻¹ band on Cu-BEA and the 1624 cm⁻¹ band on Cu-CHA vanish within 1 min when a mixture of (¹⁵NO + NH₃ + O₂) is admitted into the IR cell. In the meantime, very broad bands in the region of 1300-1900 cm⁻¹ appear. Because of their broadness, the nature of the surface species corresponding to these bands cannot be readily elucidated. In general, they can be attributed to ammonium nitrates on the catalyst surface [7, 28, 35]. An additional broad IR feature in the region between 1350 and 1550 cm⁻¹ also becomes apparent for the Cu-CHA

sample. This band has been assigned to NH_3 adsorbed on the Brønsted acid sites of the CHA support [43].

These new IR bands are very broad and they overlap with the original nitrate bands on the samples. In order to gain additional insights into the relative reactivity of the original surface nitrate groups, the IR spectra of the Cu-BEA or the Cu-CHA sample after exposure to the ($^{15}\text{NO} + \text{NH}_3 + \text{O}_2$) mixture for 1 or 3 min, are further subtracted by the IR spectrum of the corresponding sample after exposure to this mixture for 24 min. The plot is inserted in Fig. 7. For the Cu-BEA catalyst, it is clear that the IR bands at 1623, 1598 and 1570 cm^{-1} decline slower than the 1629 cm^{-1} band. It also appears that the intensity decrease of the three lower-frequency bands follows the same trend, indicating that they might be from the same surface complex, but different from the species responsible for the IR band at 1629 cm^{-1} . For the Cu-CHA catalyst, the situation is less obvious, but the 1624 cm^{-1} band also drops faster than the bands at 1593 and 1570 cm^{-1} , suggesting these are from two different groups of surface complexes. These results seem to support the IR band assignments made by recent publications [36-39] that the two types of surface complexes are from surface nitrates with two different types of coordination.

The newly formed ammonium nitrate species and the adsorbed NH_3 on the Cu-CHA sample are stable and remain on the catalyst surface with no change in IR signal intensity upon evacuation at 200 °C. The ammonium nitrate on the Cu-BEA sample appears to be less stable, showing a moderate decrease in intensity of their IR features after evacuation. (see Fig. 7).

It should be pointed out that isotope-labeled ^{15}NO has been intentionally used in the second step of the FTIR experiments for several reasons. First, if new surface nitrate groups form on the catalyst surface after ($^{15}\text{NO} + \text{NH}_3 + \text{O}_2$) introduction to the IR cell, they should contain ^{15}N and, therefore, their IR bands should appear at lower frequencies and will not overlap with

the original surface nitrate groups formed during the first ($\text{NO}_2 + \text{O}_2$) adsorption step. This enables us to determine that the intensity changes for the original nitrate groups are truly due to their consumption through reactions with NH_3 in the second step.

Second, by monitoring the gas phase product of $^{14}\text{N}^{14}\text{N}$ during the ($^{15}\text{NO} + \text{NH}_3 + \text{O}_2$) exposure period, it is possible to elucidate the possible reaction pathways between the original ^{14}N -containing surface complexes and NH_3 . For both catalysts, the $M/e = 28$ ($^{14}\text{N}^{14}\text{N}$) signals remain at the baseline level while the $M/e = 29$ ($^{15}\text{N}^{14}\text{N}$) signal intensities increase. These results indicate that the reactions between the ^{14}N -containing surface nitrates and NH_3 mainly lead to the formation of ammonium nitrate deposits on the catalysts regardless of the type of coordination of the surface nitrate groups. In addition, these results also suggest that there is no appreciable amount of surface nitrites formed on the catalysts during the first ($\text{NO}_2 + \text{O}_2$) adsorption step. Surface nitrites are known to be highly reactive with NH_3 and decompose to N_2 according to the following reaction [30],

The lack of $^{14}\text{N}^{14}\text{N}$ in the ($^{15}\text{NO} + \text{NH}_3 + \text{O}_2$) reaction step rules out this reaction pathway, indicating negligible amount of surface nitrites on the catalysts.

Finally, and perhaps most importantly, by monitoring the isotope-labeled N products in the following TPD experiments, it allows us to determine the origins of the nitrate species in the ammonium nitrate deposits formed on the catalysts.

3.4. TPD under vacuum

After the in situ FTIR experiments described above, i.e., after the sequence of (1) ($\text{NO}_2 + \text{O}_2$) adsorption, (2) evacuation, and (3) ($^{15}\text{NO} + \text{NH}_3 + \text{O}_2$) exposure and reaction, the IR cell is evacuated again until the pressure drops to below 1×10^{-6} Torr. TPD experiments were then

carried out at a ramping rate of 30 °C/min. Release of NH₃ is observed on the catalysts during the TPD experiments. Because NH₃ desorption from the acid sites of the zeolite support and ammonium nitrate decomposition both contribute to the M/e = 17 signal, its relative intensity is much higher than any other masses. The NH₃ TPD profiles are not presented here for simplicity. On the other hand, the signals at M/e = 44, 45, and 46 remain at their baseline levels, indicating negligible amounts of N₂O desorption during TPD. This implies that ammonium nitrate decomposition according to reaction (1) is not a major pathway during the TPD experiments under vacuum.

The signals of M/e = 28, 29, 30, and 31 are plotted in Fig. 8. A simultaneous increase of the signal intensities of M/e = 28 and 30 upon temperature increase is observed for both catalysts. The M/e = 28 signal can be attributed to the release of ¹⁴N₂ from the catalysts. Since no NO was observed in the TPD experiments under flowing conditions (as mentioned in section 3.2.), and it is known that NO₂ easily fragment to NO in a mass spectrometer, it is reasonable to attribute the M/e = 30 signal to be originated mainly from NO₂. Therefore, the simultaneous occurrences of M/e = 28 and 30 signals can be attributed to the release of ¹⁴N₂ and ¹⁴NO₂ from the catalysts due to the decomposition of NH₄NO₃ according to reaction (2). For the Cu-BEA sample, the signals at M/e = 28 and 30 maximize at ~300-325 °C, suggesting ammonium nitrate decomposition is essentially complete around these temperatures. At higher temperatures, the signals level off due to NH₄NO₃ depletion. For the Cu-CHA sample on the other hand, the increase in intensities for M/e = 28 and 30 is slightly slower than that for the Cu-BEA sample at temperatures below 300 °C, but significantly greater at temperatures above 300 °C. In fact, both of these M/e signals grow continuously during the TPD experiment, demonstrating substantially more NH₄NO₃ deposition on the Cu-CHA sample.

It is very interesting to notice that the signals at $M/e = 29$ ($^{14}\text{N}^{15}\text{N}$) and 31 (fragment of $^{15}\text{NO}_2$) in Fig. 8 remain at their baseline levels during TPD. This indicates that there are essentially no $\text{NH}_4^{15}\text{NO}_3$ deposits formed on either of the catalysts during the exposure of ($^{15}\text{NO} + \text{NH}_3 + \text{O}_2$). Therefore, it seems that all of the ammonium nitrate deposits formed on the catalysts are from the ^{14}N -containing surface nitrate groups deposited on the catalysts during the first ($\text{NO}_2 + \text{O}_2$) adsorption step.

To further probe the reaction pathways for ammonium nitrate formation on the Cu-BEA and Cu-CHA catalysts under SCR reaction conditions, another set of experiments were carried out by admitting a mixture of ($^{15}\text{NO} + \text{NO}_2 + \text{NH}_3 + \text{O}_2$) to the catalysts that were pre-dosed with NH_3 . The mole ratio of $^{15}\text{NO}/\text{NO}_2$ is adjusted to 1:1 for these experiments, and the mixture was introduced into the IR cell immediately after mixing ^{15}NO and NO_2 to minimize isotope scrambling from homogeneous gas phase reactions. After 24 min of exposure and a subsequent evacuation step at 200 °C, TPD experiments were conducted on both catalysts. The TPD profiles for the $M/e = 28, 29, 30$, and 31 signals for both catalysts are plotted in Fig. 9.

For the Cu-BEA sample, all signals remain close to their baseline levels except weak $M/e = 28$ signals from ~250 to 300 °C. This suggests that there is only trace amount of nitrate deposition on this catalyst, likely from NO_2 in the feed. In contrast, relatively large quantities of N_2 ($M/e=28$) and NO_2 ($M/e = 30$) are released from the Cu-CHA sample, yet again, no $^{15}\text{N}^{14}\text{N}$ ($M/e=29$) or $^{15}\text{NO}_2$ ($M/e=31$) desorption is observed. This unambiguously demonstrates that ammonium nitrate is more stable on the Cu-CHA catalyst, and that only NO_2 , but not ^{15}NO , contributes to its formation.

4. Discussion

Reaction data in Fig. 1 demonstrate that, under the SCR reaction conditions where the two catalysts exhibit comparable overall NO_x reduction efficiencies, N₂O formation on the small-pore Cu-CHA catalyst is noticeably lower than that on the large-pore Cu-BEA catalyst. The results are consistent with what has been reported in the literature [1, 18, 19], hence allowing us to use these two catalysts to address the fundamental question of why small-pore zeolite supported Cu SCR catalysts are, in general, more selective to N₂ with less N₂O formation. As has been proposed in the literature that low-temperature N₂O formation is via the decomposition of SCR intermediate NH₄NO₃ [6-10, 28-30], we first discuss the possible correlation between N₂O yield and the tendency of NH₄NO₃ formation on the Cu-BEA and Cu-CHA catalysts.

NH₄NO₃ formation involves surface nitrate groups [9]. One way to promote the formation of surface nitrate groups is to increase the NO₂/NO_x ratio of the reactant feed. Surface nitrate groups are readily generated via NO₂ disproportionation [30]:

Therefore, higher NO₂/NO_x ratios in the feed favor surface nitrate formation. At 350 °C, a temperature high enough that NH₄NO₃ decomposes immediately upon formation, the N₂O yields on both catalysts increase monotonically with an increase in the NO₂/NO_x ratios (Fig. 2). The results are fully consistent with the generally accepted conclusion that N₂O formation is through NH₄NO₃ decomposition.

N₂O formation on the Cu-BEA catalyst at 200 °C follows a similar trend with respect to NO₂/NO_x ratios. This correlation is, however, no longer evident for the Cu-CHA catalyst at this low temperature. Subsequent TPD experiments (Fig. 4) reveal that this is because NH₄NO₃ is more stable for the Cu-CHA catalyst and it does not readily decompose at 200 °C. In fact, a self-

inhibition phenomenon caused by the NH_4NO_3 deposits for the Cu-CHA catalyst is observed at this temperature when the NO_2/NO_x ratio in the feed gas is at 0.82 (Fig. 3).

NH_4NO_3 has long been proposed to be involved in SCR according to the following reactions [30]:

As our results substantiate, NH_4NO_3 is more stable on the small-pore Cu-CHA catalyst, it is reasonable to assume that it has higher probabilities to react with NO (especially under SCR reaction conditions with a feed of NO_2/NO_x ratio less than 0.5) and subsequently decomposes to N_2 via a nitrite intermediate. Note that reactions (7) and (8) compete with the decomposition pathway (1); this provides a reasonable explanation on the lower N_2O formation over Cu-CHA.

Although the results of this study cannot explain the fundamentals of the higher thermal stabilities for NH_4NO_3 in the small-pore Cu-CHA catalyst, it is speculated that the pore restriction plays a major role in the stabilization of NH_4NO_3 . It is plausible that the small dimension of the openings in the CHA framework confines NH_4NO_3 in the CHA cages and makes it more stable. The general trend that N_2O yields on zeolite supported Cu SCR catalysts decrease following the order of small-pore < medium-pore < large-pore zeolite structures seems to support this hypothesis: the smaller the pores of the zeolite support, the higher the stability of NH_4NO_3 in the zeolite cages, hence the lower N_2O yields on the catalysts under SCR reaction conditions.

Since surface nitrate groups are crucial for the formation of NH_4NO_3 , we also have to consider and compare the activity of the two catalysts in the formation of these surface complexes. The FTIR results presented in Fig. 5 indicate that the intensity of the IR bands

corresponding to the nitrate groups on the Cu-CHA catalyst is noticeably weaker than that on the Cu-BEA catalyst after exposure to the same ($\text{NO} + \text{O}_2$) mixture. However, this does not necessarily indicate that Cu-CHA is less active in catalyzing NO oxidation and the subsequent formation of surface nitrate groups. This is because the exact nature of the surface nitrate groups deposited on the two catalysts is still not fully understood. For example, some of the IR bands do not appear at the same frequencies on the two samples. However, since the saturation signal intensities for the nitrate groups on both catalysts are readily achieved upon exposure to a ($\text{NO}_2 + \text{O}_2$) mixture (Fig. 6), these saturation intensities can be used to normalize the intensities of the corresponding sample in the ($\text{NO} + \text{O}_2$) experiments. Accordingly, Fig. 10 plots the normalized intensities for the IR band at 1629 cm^{-1} (for Cu-BEA) and 1624 cm^{-1} (for Cu-CHA) as a function of exposure time in the ($\text{NO} + \text{O}_2$) experiments. By comparing the normalized signal intensities in Fig. 10, we can conclude that the Cu-CHA catalyst is indeed less active than the Cu-BEA catalyst in catalyzing NO oxidation and the subsequent formation of surface nitrate groups.

The nitrate groups on both catalysts are thermally stable at $200\text{ }^\circ\text{C}$, but are reactive toward NH_3 (under the atmosphere of ($^{15}\text{NO} + \text{NH}_3 + \text{O}_2$)) as demonstrated by the FTIR spectra in Fig. 7. Based on the rate of their disappearance, the surface nitrate complexes can be further divided into two sub-groups: on the Cu-BEA sample, the group giving rise to the 1629 cm^{-1} band is more reactive than the group with IR bands at 1623 , 1598 , and 1570 cm^{-1} ; on the Cu-CHA sample, the situation is less obvious because of more severe band overlapping, but the same trend is also envisioned. Based on assignments by Ruggeri et al. [36], the IR band at 1629 cm^{-1} for the Cu-BEA sample and of that at 1624 cm^{-1} for the Cu-CHA sample can be assigned to surface bridging nitrate species while the rest of the IR bands in the $1500\text{--}1700\text{ cm}^{-1}$ region (at 1623 , 1598 , and 1570 cm^{-1} on the Cu-BEA sample, and at 1593 and 1570 cm^{-1} on the Cu-CHA

sample) are attributed to surface bidentate nitrate moieties. On both catalysts, although the bridging nitrate species appear to be more reactive, both the bridging nitrates and the bidentate nitrates react with NH_3 forming NH_4NO_3 deposits. Consistent with the strong NH_4NO_3 inhibition effect only observed on Cu-CHA at 200 °C (Fig. 3), much stronger signal in the NH_4NO_3 vibrational region ($1300\text{-}1500\text{ cm}^{-1}$) is observed on Cu-CHA following NH_3 and surface nitrate interactions (Fig. 7).

In the subsequent TPD experiment, it is evident based on the product distribution shown in Fig. 8 that the ammonium nitrate deposits left on either of the catalysts are all in the form of NH_4NO_3 with a negligible contribution from $\text{NH}_4^{15}\text{NO}_3$. Since isotope-labelled ^{15}NO is used in the second ($^{15}\text{NO} + \text{NH}_3 + \text{O}_2$) adsorption/reaction step, the only reaction pathway leading to the NH_4NO_3 deposit formation is the reaction of NH_3 with the ^{14}N -containing surface nitrate groups already formed on the catalyst during the first ($\text{NO}_2 + \text{O}_2$) adsorption step. From the signal intensities, it is also evident that the amount of NH_4NO_3 deposits on the Cu-BEA sample is much less than that on the Cu-CHA sample. This indicates that a portion of the NH_4NO_3 , formed on the Cu-BEA catalyst from the original surface nitrates, decompose or undergo SCR reactions during the ($^{15}\text{NO} + \text{NH}_3 + \text{O}_2$) adsorption/reaction step. The already facile ammonium nitrate decomposition reaction on the Cu-BEA catalyst at 200 °C makes it difficult to argue whether the absence of $\text{NH}_4^{15}\text{NO}_3$ deposits on the Cu-BEA catalyst is due to the lack of its formation, or because its decomposition/reaction is rapid enough, therefore, it cannot accumulate on the catalyst. The situation, however, is much more straight-forward for the Cu-CHA catalyst. The results from Fig. 8 and Fig. 4 clearly demonstrate that ammonium nitrate is stable on this catalyst at 200 °C. Were there an appreciable amount of $\text{NH}_4^{15}\text{NO}_3$ formed on the catalyst during the ($^{15}\text{NO} + \text{NH}_3 + \text{O}_2$) adsorption/reaction step, the majority of the $\text{NH}_4^{15}\text{NO}_3$ would have remained

on the catalyst and ^{15}N -based compounds would have been detected in the subsequent TPD experiment. Clearly this is not the case as displayed in Fig. 8 – no ^{15}N -containing species are observed in the post-reaction TPD experiment. This implies that, under SCR reaction conditions with $\text{NO} + \text{O}_2$ in the feed, the Cu-CHA catalyst is unable to oxidize and convert NO to surface nitrates, at least at 200 °C.

The results in Fig. 9 further support the conclusions described above. In the TPD experiments after exposing the catalysts to a mixture of ($^{15}\text{NO} + \text{NO}_2 + \text{NH}_3 + \text{O}_2$) with the $^{15}\text{NO}/\text{NO}_2$ molar ratio of 1/1, only ^{14}N -containing products are detected to desorb from the Cu-CHA sample. This proves that the Cu-CHA catalyst does not convert ^{15}NO to surface nitrates. Surface nitrates (which react rapidly with NH_3 to form ammonium nitrate deposits) are formed on the Cu-CHA catalyst only when sufficient NO_2 is present in the gas phase. The reaction pathway that leads to nitrate formation is likely NO_2 disproportionation, as illustrated in reaction (6). The lack of any deposits on the Cu-BEA catalyst following the same adsorption and TPD steps (Fig. 9) confirms that ammonium nitrate is not stable on this catalyst under the SCR reaction conditions; it decomposes immediately upon formation.

The results in this study reveal two major differences between the small-pore Cu-CHA and the large-pore Cu-BEA catalysts: (1) NH_4NO_3 is thermally more stable on Cu-CHA than on Cu-BEA; (2) The Cu-CHA catalyst is less active in catalyzing NO oxidation and the subsequent formation of surface nitrate groups. Although both factors may account for the lower N_2O formation for the Cu-CHA catalyst during SCR, the second factor appears to be more important as it reduces the formation of NH_4NO_3 , the primary source for N_2O formation at relatively low SCR reaction temperatures.

5. Conclusions

This comparison study has demonstrated much less N_2O formation on a small-pore Cu-CHA catalyst than a large-pore Cu-BEA catalyst under SCR reaction conditions where the two catalysts exhibit comparable overall NO_x reduction efficiencies. N_2O is formed via the decomposition of NH_4NO_3 , an intermediate that is formed on the catalysts when NH_3 reacts with surface nitrate groups. NH_4NO_3 is more stable on the small-pore Cu-CHA catalyst. It is likely that the smaller pore openings of the CHA structure (or other small-pore zeolite structures in general) add additional confinement to NH_4NO_3 in the zeolite cages, thus enhancing its thermal stability. Although the higher stability of NH_4NO_3 can contribute to the decrease in N_2O formation on the Cu-CHA catalyst, the primary reason is that Cu-CHA is less active than Cu-BEA in catalyzing NO oxidation and the subsequent formation of surface nitrate groups. This results in less NH_4NO_3 formation on Cu-CHA during standard SCR reaction, thus eliminating its decomposition to N_2O .

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Figure captions

Fig. 1. Steady state NO_x conversions and the corresponding N₂O formation levels as a function of temperature 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)

Fig. 2. Effect of NO₂/NO_x ratios in the feed gas on the N₂O formation rates for Cu-BEA and Cu-CHA.

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Fig. 3. Outlet concentrations of NO, NO₂, N₂O, and NH₃ downstream of (A) Cu-CHA and (B) Cu-BEA.

(Reaction conditions: 350 ppm NO_x (at an NO₂/NO_x = 0.82), 350 ppm NH₃, 10% O₂, 2.5% H₂O, and balance N₂, GHSV = 200,000 h⁻¹, temperature = 200 °C)

Fig. 4. N₂O TPD of samples after SCR reaction at 200 °C

(TPD was carried out in 10% O₂, 2.5% H₂O, and balance N₂, at a GHSV = 200,000 h⁻¹, with a ramping rate of 25 °C/min; SCR reaction was performed in a feed of 350 ppm NO_x (at an NO₂/NO_x = 0.5 or 0.82), 350 ppm NH₃, 10% O₂, 2.5% H₂O, and balance N₂, at a GHSV = 200,000 h⁻¹)

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

Fig. 6. *In situ* FTIR spectra at 200 °C of samples upon exposure to (0.15 Torr NO₂ + 1.35 Torr O₂)

Fig. 7. *In situ* FTIR spectra at 200 °C of samples after nitrate pre-adsorption (labeled as (0 min)); and upon subsequent exposure to (0.15 Torr ¹⁵NO + 0.6 Torr NH₃ + 0.75 Torr O₂) for 1, 3, and 24 min; and finally after evacuation (labeled as (Vacuum)). The (1 min) and the (3 min) spectra in the inset plot were further subtracted by the corresponding spectrum after 24 min exposure.

Fig. 8. Mass spectrometer signals in the TPD experiments after the samples were exposed to (0.15 Torr NO₂ + 1.35 Torr O₂) followed by (0.15 Torr ¹⁵NO + 0.6 Torr NH₃ + 0.75 Torr O₂), both at 200 °C

Fig. 9. Mass spectrometer signals in the TPD experiments after the samples were exposed to (0.15 Torr NO₂ + 0.15 Torr ¹⁵NO + 0.3 Torr NH₃ + 0.9 Torr O₂) at 200 °C

Fig. 10. Normalized intensities of IR bands at 1629 cm⁻¹ (for Cu-BEA) and 1624 cm⁻¹ (for Cu-CHA) as a function of exposure time in the (0.15 Torr NO + 1.35 Torr O₂) experiments of Fig. 5.

Figures

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