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Mechanistic study of the low temperature activity of transition metal exchanged zeolite SCR catalysts

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ABSTRACT

Reactor activity measurements and FTIR spectroscopy were applied to study the transient and steady state behavior of Cu and Fe exchanged zeolite catalysts for the selective catalytic reduction (SCR) of nitrogen oxides (NOx) with NH_3 at 200 °C. Different surface NOx adsorption complexes were observed on the two catalysts. IR bands assigned to surface nitrate/nitrite groups were apparent on the Cu catalyst under most testing conditions. On the Fe catalyst, IR bands assigned to surface nitro groups were also observed, in addition to nitrate/nitrite groups. Both the nitrate/nitrite and the nitro group showed high reactivity with NH_3, which explained similar initial transient SCR activity of the two catalysts. The presence of NH_3 was found to block the Fe sites from catalyzing the oxidation of NO and severely inhibited the overall SCR activity when there was no NO_2 in the gas mixture. Addition of NO_2 improved the low temperature SCR activity of both catalysts. The higher SCR activity on the Fe catalyst at the optimum NO:NO_2 = 1:1 was attributed to the high intrinsic activity of the nitro groups formed on the Fe catalyst.

1. Introduction

Selective catalytic reduction (SCR) of nitrogen oxides (NOx) with NH_3 over transition metal exchanged zeolite catalysts is one of the leading technologies for reducing NOx emission from the exhaust of diesel engines [1]. Among transition metal exchanged zeolite catalysts, Cu and Fe zeolites are currently the two catalysts intensively studied. Both have advantages depending on the desired operation conditions. Cu catalysts are capable of high NOx conversion at temperatures as low as 150 °C, which is desirable for reducing NOx emissions from the exhaust of diesel engines under normal operation conditions. A downside of the Cu catalysts is an increase in NH_3 oxidation at temperatures above 300 °C, which affects the overall NOx conversion efficiency [2]. For applications where the exhaust temperature is above 450 °C, Fe catalysts present a good alternative to Cu systems. The reduced NH_3 oxidation activity of the Fe catalysts allows for higher NOx reduction efficiency in the system.

The NH_3 SCR reaction can be expressed in general as:

$$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O \quad (1)$$

The exact reaction mechanisms are still under investigation, but a consensus has been reached in the literature as to the general role of the transition metal zeolite catalysts. To catalyze the reaction, these catalysts exhibit dual functions. The zeolite support provides acid sites for NH_3 adsorption. The transition metals play a crucial role in catalyzing the oxidation of NO and the subsequent formation of surface NOx adsorption complexes [3]. The presence of NO_2 in the feed gas has also been found to significantly promote the NH_3 SCR reaction especially at low temperatures through a so-called “fast” SCR reaction [4]:

$$2NH_3 + NO + NO_2 \rightarrow 2N_2 + 3H_2O \quad (2)$$

The higher NOx reduction efficiency of Cu zeolite catalysts compared to Fe analogues at low temperature is partially attributed to the higher NO oxidation activity of the Cu catalysts [4]. Although Fe zeolite catalysts have lower steady state NOx conversion at temperatures below 300 °C, they do exhibit comparable or even higher low temperature SCR activity under certain transient conditions [2,5–10]. Additionally at the optimum 1:1 NO:NO_2 molecular ratio where the “fast” SCR reaction is dominant, Fe catalysts are more active than Cu catalysts at low temperatures [2]. These findings suggest that besides the difference in NO oxidation activity between Cu and Fe zeolite catalysts, there are other fundamental differences in the reaction mechanisms between these catalysts.

In this study, the surface variations associated with the low temperature (200 °C) performance differences of Cu and Fe zeolite SCR catalysts are evaluated through FTIR spectroscopy. To evaluate differences in transient and steady state low temperature performance, both catalysts are exposed to simulated exhaust gas mixtures in the presence and absence of NH_3. Catalysts are,

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also, evaluated at different NO_2 fractions of total NOx to understand the impact of NO_2 on transient and steady state surface species.

2. Experimental

2.1. Catalysts

A Cu exchanged beta zeolite and an Fe exchanged beta zeolite were used in this study. To eliminate concerns of different zeolite supports, the same parent beta zeolite with a SiO_2 to Al_2O_3 ratio of 25 was used to prepare the Cu and the Fe catalysts. Both catalysts were prepared by ion-exchange methods. After ion-exchange, the powders were calcined at 500 °C for 2 h in air. The Cu or Fe loading was 5% in weight of the amount of zeolite.

For SCR activity studies, the metal ion-exchanged zeolite catalysts were washcoated onto cordierite monoliths with a cell density of 62 cells per cm^2 (or 400 CPSI) and 0.11 mm (or 4.5 mil) wall thickness. The catalyst loadings were 120 g/L of monolith substrate for both catalysts.

2.2. SCR activity studies

For transient NH_3 exposure experiments, cores of 25.4 mm diameter and 50.8 mm length were taken from the monoliths and were pretreated hydrothermally at 670 °C for 2 h in a flow reactor with a gas containing 4.5% H_2O in air at a flow rate of 3 L/min. The cores were then held at 200 °C. A gas mixture containing 350 ppm NO, 14% O_2, 4.6% H_2O, 5% CO_2 in N_2 was fed to the catalysts at a gas hourly space velocity (GHSV) of 50,000 h^{-1}. After 10 min exposure, NH_3 was added to the feed gas at 350 ppm and the outlet gas composition was measured by an FTIR gas analyzer (MKS Multigas 2030HS, scan time = 0.9 s, resolution = 0.5 cm^{-1}).

For steady state NO/NO_2 evaluations, cores of 25.4 mm diameter and 76.2 mm length were taken from the monoliths and were pretreated hydrothermally at 670 °C for 64 h in a flow reactor with a gas containing 4.5% H_2O in air at a flow rate of 3 L/min. The cores were then held at 200 °C and exposed to the full SCR gas mixture containing 350 ppm NH_3, 350 ppm NOx, 14% O_2, 4.6% H_2O and 5% CO_2 in N_2 at a GHSV = 30,000 h^{-1}. The total NOx concentration was maintained at 350 ppm, but the NO_2/NOx ($NO + NO_2$) ratio was varied from 0%, 20%, 50%, 80% and 100%. At each NO_2/NOx ratio, the catalysts were allowed to reach steady state at which point outlet gas compositions are evaluated by an FTIR gas analyzer.

2.3. FTIR spectroscopy

The ion-exchanged powder samples were pretreated hydrothermally at 670 °C for 2 h in a flow reactor with a gas containing 4.5% H_2O in air at a flow rate of 3 L/min. The pretreated powder catalyst samples were pressed into 10 mg self-supporting wafers with 10 mm diameter. The wafers were mounted between two closely packed CaF_2 rods that were inserted in an FTIR cell. The cell was purged for 1 h at 500 °C in an 8% O_2 in N_2 gas stream to clean the catalyst surface. The cell was cooled to 200 °C and a background spectrum was measured which was used to subtract all FTIR spectra in the same set of measurements.

For NO only gas mixtures, NO adsorption measurements were performed in a feed of 350 ppm NO and 12% O_2 in N_2 for 30 min. Catalysts were then purged with N_2 for 30 min to stabilize the surface species followed by exposure to a full SCR gas mixture containing 350 ppm NH_3, 350 ppm NO, and 12% O_2 in N_2 for 30 min.

For ($NO + NO_2$) containing gas mixtures, the catalysts were exposed to a full SCR gas mixture containing 350 ppm NH_3, 350 ppm NOx, and 12% O_2 in N_2 for 30 min. IR spectra were recorded at three different $NO:NO_2$ ratios—NO only, 1:1, and 1:4.

Water vapor was not included in the FTIR study to simplify the assignment of the IR bands. It should be noted that the presence of water in the actual reaction condition would reduce the intensity of some of the surface adsorption complexes because of the competitive surface adsorption. In this study, we assume that the general trends and the relative reactivity of the surface compounds observed in the absence of H_2O in the FTIR experiments are applicable to the reactions with a full gas mixture that contains water vapor.

3. Results and discussion

3.1. Evaluation of SCR catalyst monoliths

To elucidate the differences in the transient and the steady state SCR activities between Cu and Fe zeolite catalysts, flow reactor measurements at 200 °C are performed for both catalysts at a GHSV = 50,000 h^{-1}. The catalyst is initially exposed to NO, H_2O, O_2, and CO_2 to allow the formation of surface NOx adsorption complexes on the catalyst. After 10 min of exposure, NH_3 is mixed into the feed gas and the outlet NOx conversion is monitored (Fig. 1). During the first 20 s following the addition of NH_3, both Fe and Cu catalysts display a similar rapid increase in NOx conversion. The overall NOx conversion being low during the initial 20 s is due to the need to build up sufficient NH_3 coverage on the catalysts, which is known to be one of the elemental steps for the NH_3 SCR reaction [4]. Since both catalysts are prepared on the same zeolite support, it is reasonable to assume that the initial NH_3 build-up rates are similar on the two catalysts. The fact that the NOx conversions increase at the same rate over the Cu and the Fe catalysts during the initial 20 s suggests that the two catalysts have similar SCR activity under transient conditions. After 20 s of NH_3 exposure, the NOx conversion continues to increase for the Cu catalyst until a steady state NOx conversion of ~85%. In contrast, the rate of increasing NOx conversion declines on the Fe catalyst after 20 s and reaches a maximum of 28% after 100 s. Thereafter, the NOx conversion over the Fe catalyst decreases and levels off at 15% after about 200 s. The decrease of NOx conversion over Fe zeolite catalysts at low temperature has been well recognized and attributed to the inhibition effect of high NH_3 coverage of the catalyst surface [2,5–8].

Verification of the catalysts sensitivity to feed $NO_2/(NO + NO_2)$ fraction, also, is performed in a flow reactor, but at a GHSV = 30,000 h^{-1}. Catalysts are held at 200 °C and exposed to

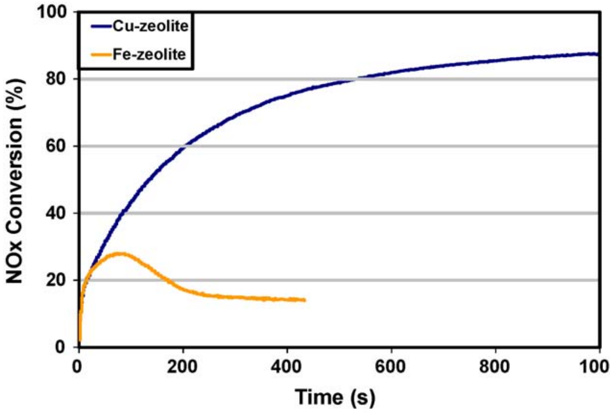

Fig. 1. Comparison of Cu and Fe SCR catalysts during transient NH_3 exposure at 200 °C. The catalysts were preconditioned with a gas mixture containing 350 ppm NO, 14% O_2, 4.6% H_2O, 5% CO_2 in N_2 at a GHSV = 50,000 h^{-1} for 10 min. 350 ppm of NH_3 was added into the gas mixture at time 0.

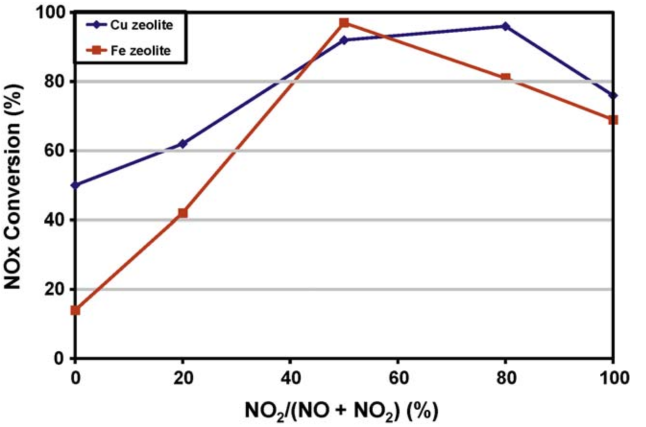

Fig. 2. Effect of $NO_2/(NO + NO_2)$ ratio on the steady state NOx conversion at 200 °C over Cu and Fe zeolite SCR catalysts. Feed gas: 350 ppm NH_3, 350 ppm $(NO + NO_2)$, 14% O_2, 4.6% H_2O, 5% CO_2 in N_2 at a GHSV = 30,000 h^{-1}.

the full SCR gas mixture and allowed to reach steady state (~45 min at each point) at five $NO_2/(NO + NO_2)$ ratios (Fig. 2). As reported in the literature for Fe zeolite catalysts [8,11], the NOx conversion reaches a maximum at a 1:1 NO:NO_2 molar feed gas ratio (50% NO_2 in feed). For the Cu zeolite catalyst, the catalyst continues to improve until the NOx in the feed consists of 80% NO_2. Above this value, the NOx conversion is reduced. At the optimum 1:1 NO:NO_2 molar ratio, the Fe catalyst reaches higher NOx conversion than the Cu catalyst.

3.2. Comparison of surface NOx adsorption complexes on Cu and Fe zeolite catalysts under transient conditions

FTIR spectroscopy is applied to understand the differences in the transient performance for Cu and Fe zeolite SCR catalysts. For the scope of this study, we will only focus on the IR spectra in the region of 1800–1500 cm^{-1}, where most of the IR bands are attributed to surface NOx adsorption complexes.

Upon exposing the Cu zeolite catalyst to NO and O_2, IR bands at 1628, 1621, 1598, and 1570 cm^{-1} emerged gradually and reached saturation in about 22 min (Fig. 3). Often IR bands in these regions are assigned to different surface nitrate or nitrite species [9,12,13]. As the relative intensity of these bands maintained about the same during the exposure, it suggests all the bands are from the similar surface adsorption complexes. These surface adsorption species are pretty stable as all the IR bands nearly maintain their intensities upon subsequent purging with N_2.

Different features are observed on the Fe zeolite catalyst. Upon exposing this catalyst to NO and O_2, new IR bands at 1650 and 1672 cm^{-1} besides IR bands at 1628, 1598, and 1570 cm^{-1} are observed (Fig. 4). The intensity of the IR bands at 1650 and 1672 cm^{-1} increases slowly during the initial 4 min of exposure but rapidly increases thereafter. These bands reach their peak after 10 min. The growth of the IR bands at 1628, 1598, and 1570 cm^{-1} is steady when the catalyst is exposed to NO and O_2, and reaches the peak intensity after 8 min. A prolonged exposure of the catalyst to the gas stream leads to a slight decrease of all the IR bands in this region although the decrease in intensity is more pronounced for the bands at 1650 cm^{-1}. Based on the IR bands in the 3700–3000 cm^{-1} range (not shown), we believe that this is due to water inhibition; low levels of water impurity in the gas steam may compete with NOx for the same adsorption sites [9]. Based on their relative intensity, it is clear that the IR bands at 1650 and 1672 cm^{-1} and the IR bands at 1628, 1598, and 1570 cm^{-1} are from two different groups of surface NOx adsorption complexes. While bands at 1628, 1598, and 1570 cm^{-1} can be assigned to surface nitrate or nitrite species [14–17], bands at 1650 and 1672 cm^{-1} are more likely from the asymmetric stretching of a bent "O=N–O" structure [18]. Since these bands (together with the set of bands at 1628 cm^{-1}) are stable upon subsequent purging, we assign them to some type of nitro group that is covalently bonded on the catalyst surface.

To simulate the transient performance differences in Fig. 1, the purged catalyst samples are exposed to a full SCR gas mixture containing NH_3 and NO at a 1:1 ratio. For the Cu catalyst (Fig. 5), exposure to the full gas mixture results in a slight decrease of the intensity of the bands at 1628 and 1621 cm^{-1} and a gradual broadening of the features in the nitrate/nitrite region. The broadening could be due to the formation of other reaction intermediates and is in line with results reported by Sjövall et al. [9] at a 1:1 NH_3 to NO ratio. Little change of the intensity of the nitrate/nitrite groups suggesting that these surface adsorption species can be easily replenished.

Exposure of the Fe catalyst to the full SCR gas mixture following the purge shows a rapid disappearance of the IR bands at 1650 and 1628 cm^{-1} (Fig. 6). A comparison of the relative intensity of the bands shows a slightly faster decrease for the band at 1650 cm^{-1} than for the band at 1628 cm^{-1}. This suggests that, while both the nitrate/nitrite and the nitro groups on the Fe/catalyst have very high reactivity towards NH_3, the nitro group seems to be more reactive. After 14 min exposure of the full SCR gas mixture, only a broad IR

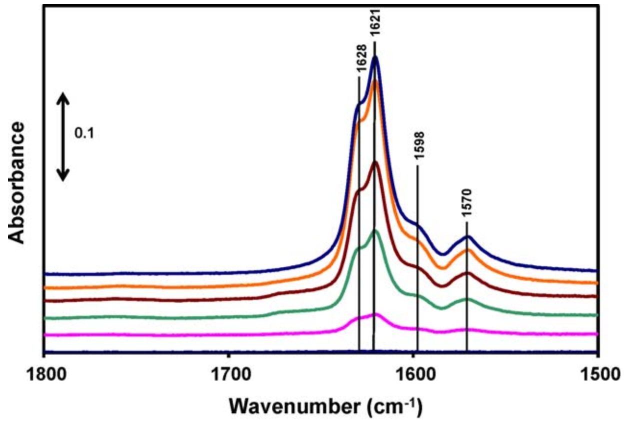

Fig. 3. FTIR spectra of the surface adsorption complexes on a Cu zeolite catalyst after exposing to a mixture of 350 ppm NO and 5% O_2 for 2, 4, 8, 12, and 22 min and subsequently purge with 5% O_2 for 30 min (increase in adsorption time from bottom to top with 30 min purged sample pattern at top).

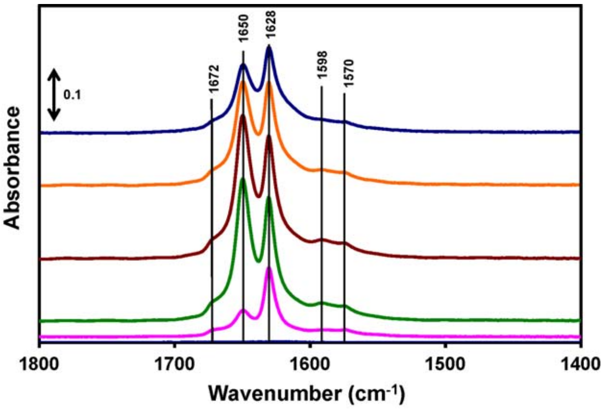

Fig. 4. FTIR spectra of the surface adsorption complexes on an Fe zeolite catalyst after exposing to a mixture of 350 ppm NOx and 5% O_2 for 2, 4, 8, 12, and 22 min, and subsequently purge with 5% O_2 for 30 min (increase in adsorption time from bottom to top with 30 min purged sample pattern at top).

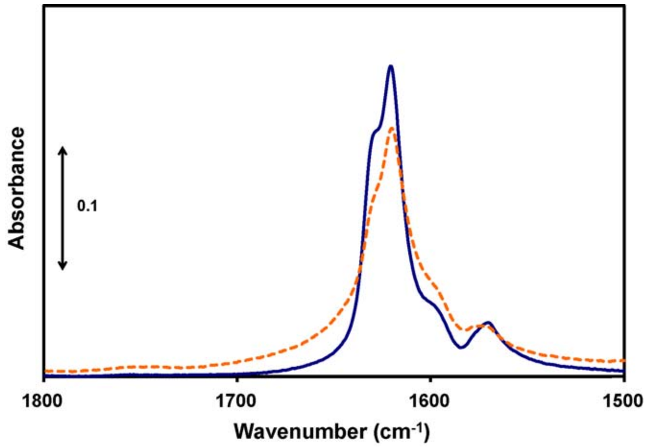

Fig. 5. FTIR spectra of the surface adsorption complexes on a Cu zeolite catalyst after exposing a NOx pre-adsorbed catalysts to a full SCR gas mixture containing 350 ppm NH_3, 350 ppm NO, and 5% O_2 in N_2 for 2 min (solid) and 24 min (dashed).

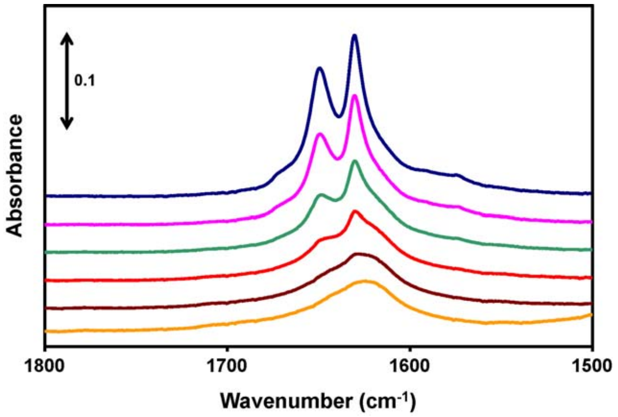

Fig. 6. FTIR spectra of the surface adsorption complexes on an Fe zeolite catalyst after exposing a NOx pre-adsorbed catalysts to a full SCR gas mixture containing 350 ppm NH_3, 350 ppm NO, 5% O_2 in N_2 for 2, 4, 6, 8, 12 and 24 min (from top to bottom).

band centered at 1626 cm^{-1} is visible. The inability of maintaining the nitrate/nitrite group or the nitro group on the Fe catalysts can be attributed to the competitive adsorption of NH_3 which blocks the sites from NOx adsorption as reported in the literature [2,5–8].

3.3. Comparison of surface NOx adsorption complexes on Cu and Fe zeolite catalysts under SCR reaction conditions with different NO:NO_2 ratios

FTIR spectroscopy also is applied to study the effects of different NO:NO_2 ratios in the full SCR gas mixture on the surface NOx adsorption complexes on the Cu and the Fe catalysts. For the Cu catalyst, surface nitrate/nitrite groups are apparent following 4 min of exposure to the SCR gas mixtures independent of the NO:NO_2 ratio (Fig. 7). With the NO only gas mixture, the surface nitrate/nitrite species reaches an equilibrium point after 10 min exposure. With the NO:NO_2 = 1:1 gas mixture, the surface nitrate/nitrite species also reaches an equilibrium point after 10 min exposure. However, the overall intensity of the nitrate and nitrite bands with the NO:NO_2 = 1:1 gas mixture is about 30% lower as compared to the NO only case. With the NO:NO_2 = 1:4 gas mixture, the surface nitrate/nitrite bands keep growing during the measurement (32 min), suggesting continuous accumulation of surface compounds on the catalyst.

For the Fe zeolite catalyst, initial exposure (4 min) to the full gas mixture shows the formation of both surface nitro and nitrate/nitrite species, with their intensity depending on the NO:NO_2 ratio. For the NO only gas mixture the bands are barely visible. They become apparent in the case with NO:NO_2 = 1:1 in the gas mixture. In both cases, the nitro and nitrate/nitrite groups disappear after 8 min exposure because of the NH_3 inhibition effect. For the NO:NO_2 = 1:4 gas mixture intensive nitro and nitrate/nitrite groups appear on the catalyst after 4 min, and keep increasing during the measurement likely due to the continuous accumulation of surface compounds on the catalyst.

4. Discussion

Combining the results from the flow reactor tests and from the FTIR spectroscopy study, it is clear that the oxidation of NO and the subsequent formation of surface NOx adsorption complexes are

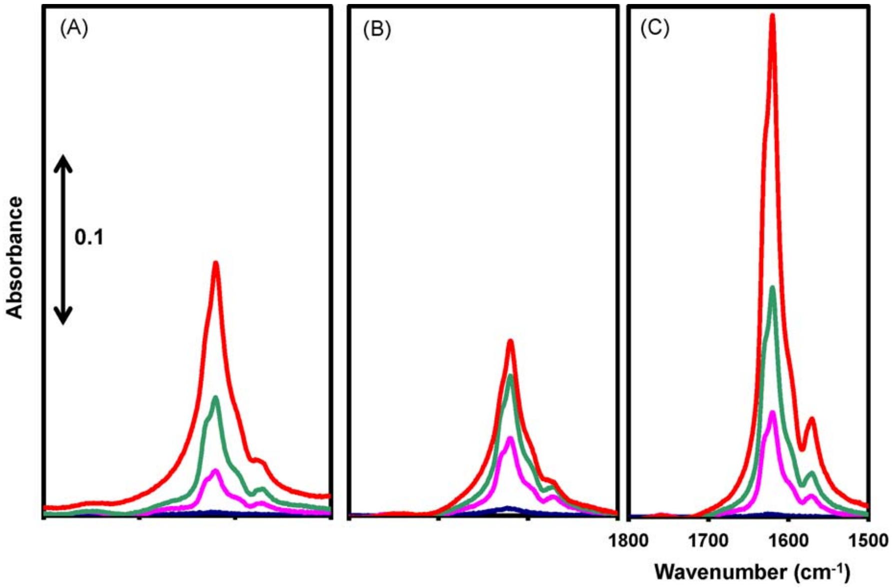

Fig. 7. FTIR spectra of adsorbed NOx species on a Cu zeolite SCR catalyst during exposure to a full SCR gas mixture at different NO:NO_2 ratios. Spectra are taken at increasing exposure times (from bottom to top: 2, 4, 6, and 32 min) under NO only (A), 1:1 NO:NO_2 (B), and a 1:4 NO:NO_2 (C), SCR mixtures at 200 °C.

key elemental steps in NH_3 SCR reaction. This is in line with what has been reported in literature [2,5–11,17–19].

In the absence of NH_3, both the Cu and the Fe catalysts are active in catalyzing the oxidation of NO, which leads to the formation of surface NOx adsorption species. The nature of the surface adsorption complexes on the two catalysts is somewhat different. On the Cu catalysts, the adsorption species are attributed to nitrate/nitrite groups based on their IR bands. On the Fe catalysts, however, surface adsorption nitro groups also are observed besides nitrate/nitrite groups. Upon exposing to NH_3, all the surface nitrate/nitrite and nitro groups show high reactivity, although the nitro group on the Fe catalyst appears to be more active than the nitrate/nitrite group. This explains why, under transition conditions, both the Cu and the Fe catalysts exhibit similar initial SCR activity.

A major difference is observed between the Cu and the Fe catalysts after exposing them to the full SCR gas mixture for a time sufficient for NH_3 to accumulate on the catalyst surface. Apparently, the presence of NH_3 on the Cu catalyst has little impact on its NO oxidation activity, nor does it significantly affect the formation of the surface nitrate/nitrite groups. In contrast, the presence of NH_3 readily suppresses the formation of the surface nitrate/nitrite and nitro groups on the Fe catalyst, leading to a decline of the overall SCR activity. This leads to the question: why is the inhibition effect on Fe zeolite catalysts more severe than on Cu catalysts? Since the same parent zeolite support is used in this study to make the Cu and the Fe catalysts, it is reasonable to speculate that the difference is related to the nature of the transition metal sites in the zeolite.

One of the main roles of transition metals in these catalysts is to serve as the redox sites where NO oxidation occurs. The redox cycles have been identified to be $Cu^{2+} \leftrightarrow Cu^{+}$ for the Cu zeolite catalysts [12] and $Fe^{3+} \leftrightarrow Fe^{2+}$ for the Fe catalysts [16] although the exact nature of the active sites is still a matter of debate. Regardless of the state of the metal sites proposed, whether they are isolated metal ions or oxygen-bridged metal dimers, the metal ions are generally believed to reside at zeolite exchange sites. For Cu catalysts, each Cu^{+} ion is fully charge balanced by the zeolite framework, whereas each Cu^{2+} is charge balanced by a zeolite exchange site and the oxo-group attached to it. Therefore, no additional ligand is required to associate with Cu ions. For the Fe system, each Fe ion has an extra (1+) charge under either oxidation or reducing state, which cannot be readily compensated by the zeolite framework. It is possible that the Fe^{2+} ion in the zeolite channels could be charge balanced by two exchange sites; but in the high SiO_2:Al_2O_3 ratio materials common to these applications, the probability of two neighboring exchange sites is very low [20]. Likely, an Fe^{2+} ion is located only at one exchange site and partially (1−) charge balanced by the zeolite framework. To compensate the extra (1+) charge of the Fe ion, an additional ligand is needed. Indeed, an IR band assigned to the –OH group presumably from Fe–OH species has been identified and reported in the literature [21–23] on Fe zeolite catalysts, whereas no corresponding IR bands are observed on Cu zeolite catalysts. It is plausible that the additional ligands, such as the –OH group, that is associated with the Fe ions on the Fe zeolite catalyst provide sites for NH_3 adsorption, which may interfere with the redox cycle. As a result, the low temperature SCR activity of Fe zeolite catalysts is severely inhibited by NH_3.

With the addition of NO_2 into the SCR gas mixture, oxidation of NO becomes a less limiting step. Improvement of NOx conversion is seen on both Cu and Fe zeolite catalyst, and it is more obvious on the Fe catalysts. At the optimum NO:NO_2 = 1:1 ratio, surface nitrate/nitrite and nitro groups are observed on the Fe catalyst immediately after exposing it to the SCR gas mixture. These surface species vanish in a few minutes although the catalyst exhibits very high steady state SCR activity. This implies that the lack of IR bands from the nitrate/nitrite and the nitro groups on the Fe catalysts under steady state conditions is not because of the inability of forming these surface adsorption species, rather it is due to the high reactivity of these surface species with NH_3; they readily react with NH_3 once they are formed and exhibit very short life on the catalyst surface.

On the Cu catalyst, IR bands corresponding to surface nitrate/nitrite groups maintains at a certain level even at the optimum NO:NO_2 = 1:1 ratio. It has been reported that at low temperatures ammonia may react with the nitrate groups forming ammonium nitrates on the transition metal zeolite catalysts [6]. Once formed, ammonium nitrates need to react with NO to form intermediates such as ammonium nitrite to decompose to N_2. At high NO_2/(NO + NO_2) ratio, when there is not sufficient NO available to reduce the surface ammonium nitrate, it can lead to the accumulation of this

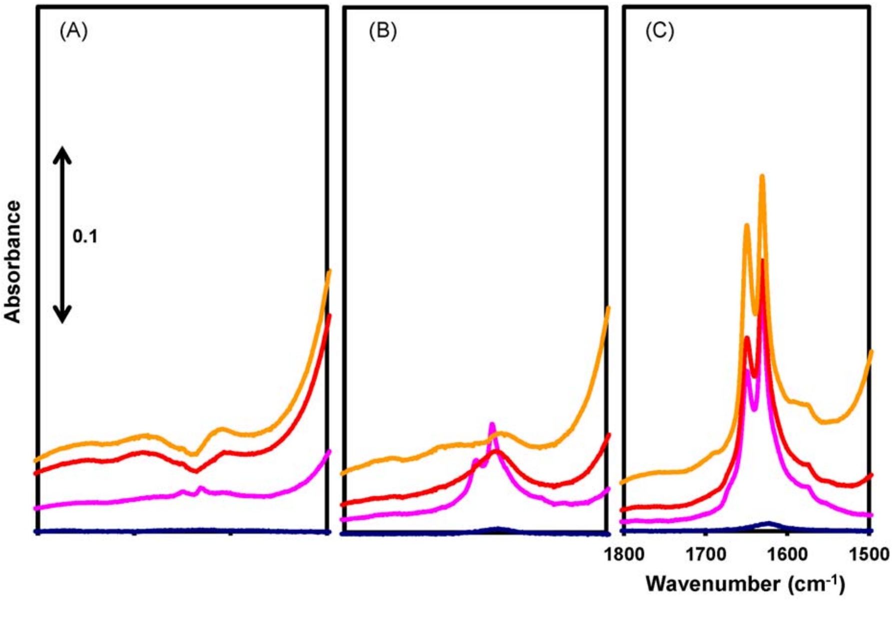

Fig. 8. FTIR spectra of adsorbed NOx species on a Fe zeolite SCR catalyst during exposure to a full SCR gas mixture at different NO:NO_2 ratios. Spectra are taken at increasing exposure times (from bottom to top: 2, 4, 8, and 32 min) under NO only (A), 1:1 NO:NO_2 (B), and a 1:4 NO:NO_2 (C), SCR mixtures at 200 °C.

compounds on the catalysts as observed in Fig. 7. The presence of nitrate/nitrite groups on the Cu catalyst at lower $NO_2/(NO + NO_2)$ ratio could be a combined contribution from surface NOx adsorption species and their reaction intermediates.

At high $NO_2/(NO + NO_2)$ ratio, compounds such as ammonium nitrate may also form on the Fe catalyst as indicated by the result in Fig. 8. At low $NO_2/(NO + NO_2)$, the formation of ammonium nitrate on the Fe catalyst appears negligible. Part of the reason could be attributed to the high reactivity of the nitro groups on the Fe catalysts; they readily react with NH_3 and decompose to N_2. As a result, this may drive the conversion of the surface nitrate/nitrite groups to nitro groups, hence little surface ammonium nitrate is formed on the Fe catalyst. The high reactivity of surface nitro groups and their presence on the Fe catalyst may explain that at the optimum $NO:NO_2 = 1:1$ ratio, the Fe catalyst is more active than the Cu catalyst.

5. Conclusions

The oxidation of NO and the subsequent formation of surface NOx adsorption complexes are key elemental steps in NH_3 SCR reaction over transition metal exchanged zeolite catalysts. In the absence of NH_3, both Cu and Fe zeolite catalysts have adequate activity to catalyze NO oxidation, although different surface NOx adsorption species are observed. Surface nitrate/nitrite groups are apparent on the Cu catalyst. Surface nitro groups, in addition to surface nitrate/nitrite groups, are observed on the Fe catalyst. Both the nitrate/nitrite and the nitro groups exhibit high reactivity with NH_3 (with the nitro groups showing slightly higher reactivity), which explains why the Cu and the Fe catalysts show similar initial SCR activity under transient conditions. The presence of NH_3 does not significantly affect the NO oxidation and the formation of surface NOx adsorption complexes on the Cu catalyst, but severely inhibits the NO oxidation step on the Fe catalyst probably due to site blocking effect. The addition of NO_2 into the gas mixture may circumvent the limiting step of NO oxidation over the Fe catalyst, allowing the formation of surface nitro groups on the Fe catalyst. As a result, the Fe catalyst is found to be more active than the Cu catalyst at the optimum $NO:NO_2 = 1:1$ ratio.

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