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In situ high temperature FTIR studies of NO_x reduction with propylene over Cu/ZSM-5 catalysts

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High temperature in situ FTIR has been used to investigate the surface species present on Cu/ZSM-5 during the reduction of NO_x with propylene in a lean environment. Parallels have been observed between adsorbed surface species and catalytic activity for this reaction. Species detected at low temperatures are not representative of those detected at high temperatures where the catalyst is active. An oxidized nitrogen-containing species has been observed at 2580 cm^{-1} on Cu during reaction conditions (400°C). In contrast, at low temperatures, where the catalyst is less active, coke and Cu^+–CO predominated. The effects of Cu weight loading, C/NO ratio, reaction temperature, and catalyst deactivation by steaming have been investigated with IR.

Keywords: in situ diffuse reflectance FTIR; selective NO_x reduction; Cu/ZSM-5

1. Introduction

Environmental regulations are driving the development of new lean NO_x catalysts capable of removing NO_x selectively from both mobile [1–3] and stationary sources in the presence of excess oxygen. For mobile sources, many countries are requiring reductions in NO_x emissions from diesel trucks and diesel passenger cars. In addition, the push for better fuel economy and lower CO_2 emissions (greenhouse gas) is leading car manufacturers around the world to develop new gasoline-fueled lean burning two- and four-stroke engines. Once developed, these vehicles will require lean NO_x catalysts. Traditional three-way catalysts, used to abate CO, HC and NO_x, will not function for NO_x abatement lean of the stoichiometric point.

Recently, extensive literature has appeared on Cu/ZSM-5 catalysts for both NO decomposition and the more promising route, selective reduction of NO_x with hydrocarbons in excess oxygen [4–10]. This catalyst, pioneered by Iwamoto [4,5],

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is considered the state of the art technology for removing NO_x under lean conditions.

Iwamoto et al. [11–13] and Li et al. [14,15] have presented data which give strong evidence that Cu cations in Cu/ZSM-5 are the active sites for NO_x decomposition in a lean environment. This reaction is inhibited by O_2 in the feed and is first order with respect to NO [15]. The reaction rate appears to be controlled by the rate of oxygen removal from the active sites. In addition, the reaction is strongly inhibited by water vapor and SO_2 [5,11].

Definitive data explaining the mechanism for the selective reduction of NO_x with hydrocarbons in excess O_2 over Cu/ZSM-5 have not been forthcoming. Unlike the decomposition reaction, this reaction is enhanced by O_2 in the feed [4,5] and is only slightly inhibited by SO_2 and water [3–5]. The active site and reaction mechanism are not yet fully understood. Several different reaction intermediates, e.g., oxygenated hydrocarbons [10,16], partially dehydrogenated hydrocarbons or carbonaceous deposits [7,17], co-adsorbed NO and NO_2, carbon–nitrogen containing species [9], etc., have been postulated. A redox mechanism has also been proposed [8], i.e. NO_x decomposition occurs on Cu^{n+} cations which are kept in their active state by HC in the feed.

Although many IR studies of the Cu/ZSM-5 system have been published, none have been carried out in situ under lean NO_x reduction reaction conditions. Several works have focussed on NO or CO adsorption and the NO decomposition reaction. Iwamoto et al. [18] used two isotopes of NO to precisely assign IR peaks on Cu/ZSM-5 in a 1% NO feed gas at room temperature. They detected Cu^+–NO, Cu^{2+}–NO, Cu^+–$(NO)_2$ and NO_2. Spoto et al. [19] found that Cu ions can form mono- and dinitrosyl complexes which transform into Cu^{2+}–(NO)X, where $X = O^-$ or NO_2^- at room temperature. Valyon and Hall [20,21] studied NO decomposition on Cu/ZSM-5 under reaction conditions at 450°C and observed adsorbed NO_2 and multiple Cu oxidation states. Sarkany et al. [22,23] have used IR to monitor Cu oxidation state in different gas feeds. They discovered that Cu^0 in Cu/ZSM-5 samples will be reoxidized by zeolitic protons in the presence of CO to form Cu^+–CO species.

Ukisu et al. [24–26] have recently published several lean NO_x IR studies on Cu/Al_2O_3 and $CuCs/Al_2O_3$ catalysts using HC's as reductants in excess oxygen. They add reagents at room temperature, ramp to high temperatures, and then collect IR data at room temperature after cooling. After reactions up to 500°C, they observe partially reduced nitrogen-containing species, i.e. Cu–NCO, N_2O, and Cu–CN.

In this paper, in situ high temperature FTIR is used to study the adsorbed surface species present during selective NO_x reduction with propylene in excess oxygen over Cu/ZSM-5. Adsorbed species are characterized as a function of Cu loading, HC/NO ratio, temperature, and steam aging.

2. Experimental

2.1. CATALYST PREPARATION

Cu/ZSM-5 catalyst powders were prepared following the methods described by Iwamoto et al. [4]; ion exchange of HZSM-5 obtained from Mobil ($SiO_2/Al_2O_3 = 50$) with $Cu(NO_3)_2$ followed by precipitation with dilute NH_4OH solution at pH = 7. The samples were washed with deionized water, then dried at 110°C for 2 h. Calcinations in air were carried out on all samples with the following temperature profile: 25–550°C (4 h), hold 550°C (2 h). Sample nomenclature is as follows: x%Cu/ZSM-5; where x% refers to the copper weight loading determined by atomic adsorption.

For activity testing, standard washcoating techniques were used to load Cu/ZSM-5 powders onto 400 cpsi cordierite honeycombs with washcoat loadings of 2 g/in^3. Steamed samples, designated S-x%Cu/ZSM-5, were steamed in 10% steam/90% air for 5 h at 700°C.

2.2. CATALYST TESTING

NO_x reduction activity was measured in a laboratory reactor using the following model gas stream composition:

333–1330 ppm C_3H_6 (1000–4000 ppm C_1),
1000 ppm NO,
10% O_2
10% H_2O
50 ppm SO_2.

Samples were catalyzed honeycombs 1.5″ diameter×3.0″ length (5.3 in^3 volume). Flow rate was 72 ℓ/min to obtain a GHSV of 50 000/h. Data were collected as the temperature of the feed gas was ramped from 150 to 550°C at 8°C/min. Total hydrocarbons were measured with a Rosemount model 400A analyzer equipped with an FID detector. Nitrogen oxides were measured with a chemiluminescence detector (Beckman model 955).

2.3. IN SITU FTIR MEASUREMENTS

2.3.1. General procedures/equipment

In situ FTIR experiments were carried out on a BioRad FTS7 spectrometer with a MCT detector. Powdered samples were held in a SpectraTech high temperature/pressure chamber within a SpectraTech Collector diffuse reflectance accessory.

IR figures are in units of absorbance, i.e., the ratio of a reacting sample's spectra to its background spectra obtained in He at the same temperature. Heating affects band frequencies as much as 15 cm^{-1}, therefore some of the frequencies listed in table 1, for 400°C, are shifted relative to literature values. Bands between 4000 and 2000 cm^{-1} had typical adsorbance intensities of 0.002 at 400°C.

Below 2000 cm^{-1} NO gas bands and low signal to noise ratios made reproducibility more difficult. Four very weak bands were observed between 1950 and 1800 cm^{-1} where $Cu-(NO)_x$ species are expected [18–21] but they could not be reliably monitored. Although clearly they do not occupy most of the Cu sites under reaction conditions, these species may still be involved in the reaction mechanism.

2.3.2. Sample treatment

Calcination was carried out in situ in 10% O_2/He at 550°C for 1 h on each 50 mg sample before IR measurement. After calcination, samples were cooled in the O_2/He feed to the test temperature where the appropriate gases were introduced. Total gas flow was 50 ml/min. Although water was not added to the feed, low levels of sorbed product water were detected by IR. Standard reaction conditions for in situ IR measurements were as follows:

10% O_2
1000 ppm NO,
1333 ppm C_3H_6 (4000 ppm C_1),
balance N_2
370 to 400°C.

These conditions were varied to study the effect of temperature and C/NO ratio on detected surface species.

Table 1
IR band frequencies at 400°C

Frequency (cm^{-1})	Width	Assignment
3200–2800	3 sharp bands	propylene
3300–2700	broad	coke
2580	sharp	$Cu-(N_xO_y)_z$ [a]
2363, 2330	sharp	sorbed CO_2
2290	sharp	$Cu-N_2$ [b]
2260	sharp	organic NCO
2250–2240	broad	sorbed N_2O [c]
2230–2200	v. weak	Cu–NCO [d]
2186	v. weak	CO gas lobe
2158	sharp	Cu^+-CO [e]
2120	broad	sorbed NO_2^+ [c]

[a] Ref. [28].
[b] Refs. [29,30].
[c] Ref. [18].
[d] Refs. [24–26].
[e] Refs. [22,23].

3. Results and discussion

3.1. IR BAND ASSIGNMENTS

Table 1 is a summary of the IR bands observed in this work. Some species, such as CO_2, carbonaceous deposits, and propylene are commonly known. The nitrogen containing species are less common. Literature references and/or behaviors with selected feed gases have been used to assign IR bands.

The exact structure of the copper–nitrogen–oxygen species, $Cu(N_xO_y)_z$, which appears at 2580 cm^{-1} under reaction conditions, is not known. On Cu/ZSM-5, it appears in an $NO/O_2/N_2$ feed, but not in NO/N_2, indicating that it is an oxidized nitrogen species. This band is also detected for a physical mixture of $Cu(NO_3)_2$ and silica heated in air to 150°C [27]. Ferraro et al. [28] have reported a band at this same frequency for anhydrous copper nitrate, however the other bands they observe are not detected on Cu/ZSM-5 samples.

A second major nitrogen-containing species is observed on Cu/ZSM-5 at 2290 cm^{-1} under reaction conditions. It is most intense in pure N_2 and is absent in He or reaction feeds containing He as the carrier gas. It does not form on CuO/silica or on H-ZSM-5 in N_2. It is due to N_2 interacting with exchanged copper ions which are not otherwise bound to CO, $(N_xO_y)_z$ or OH. Kuroda et al. [29] have reported similar IR bands on Cu cations exchanged in mordenite. Theoretical and experimental work by Yamazaki et al. [30] reports $M^{n+}-N_2$ IR bands for M^{n+} exchanged ZSM-5 samples, where M = Li, Na, K, Rb and Cs.

Other nitrogen-containing species have been reported in studies carried out at room temperature, which are not observed in significant quantities in this work at high temperatures, i.e. $Cu^{n+}-NO$ [18], Cu^+-NO_2 [18], $Cu^+(NO)_2$ [19], and Cu–NCO [24–26]. The Cu^+-NO_2 and $Cu^+(NO)_2$ species have been seen at high temperature by Valyon and Hall [20] in their studies on NO decomposition, i.e. without hydrocarbons and excess oxygen. It is likely that these species are much more reactive in the NO reduction reaction than in NO decomposition and thus may not be seen in the IR. Definitive frequencies for copper isocyanate on ZSM-5 have not been reported, but bands have been seen on similar systems between 2240 and 2200 cm^{-1} [24]. It is possible that an isocyanate species may overlap with sorbed N_2O at 2250 cm^{-1}.

3.2. EFFECT OF Cu WEIGHT LOADING

Iwamoto et al. [11] have reported higher NO_x reduction activities for excessively (>100%) ion exchanged Cu/ZSM-5 samples. Their work is consistent with the current data presented in fig. 1 on fresh and steamed 1.5%Cu/ZSM-5 (75% exchange) and 3%Cu/ZSM-5 (150% exchange) samples. Even in the fresh state, the activity of the 3%Cu/ZSM-5 sample is much higher than that of the 1.5%Cu/

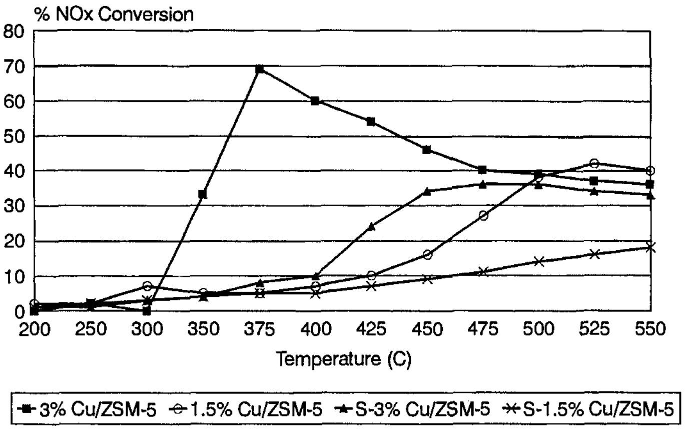

Fig. 1. % NO_x conversion versus temperature for 1.5%Cu/ZSM-5 and 3%Cu/ZSM-5 as a function of steaming.

ZSM-5 sample at temperatures below 500°C. At 400°C for example, NO_x reduction activities are 60% and <10% respectively for the 3% and 1.5% Cu/ZSM-5 samples. In fig. 2 the IR spectra of the two fresh Cu/ZSM-5 samples are compared to that of H-ZSM-5 under standard reaction conditions at 400°C. On H-ZSM-5 the major features are CO_2 and organic isocyanates. Carbonaceous deposits form rapidly. On 1.5%Cu/ZSM-5, CO_2 is detected along with Cu^+–CO. Carbonaceous deposits form at about 1/3 of the rate observed on H-ZSM-5. For 3%Cu/ZSM-5 there is CO_2 but no Cu^+–CO and little carbonaceous deposits. Instead, $Cu(N_xO_y)_z$

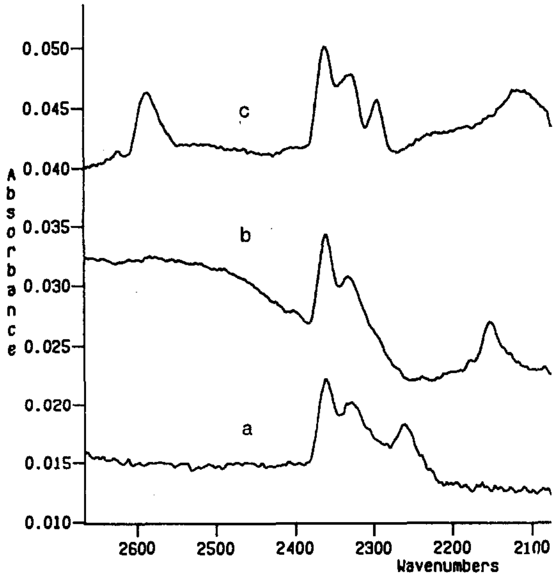

Fig. 2. FTIR spectra in 1000 ppm NO/1333 ppm C_3H_6/10% O_2/balance N_2 at 400°C of (a) H-ZSM-5; (b) 1.5%Cu/ZSM-5; (c) 3%Cu/ZSM-5.

is detected indicating that the surface species on the sample with the higher Cu loading are more oxidized. One reason why samples with higher Cu loadings are more active may be that they contain less carbonaceous deposits and Cu^+-CO. Another band, due to $Cu-N_2$, is barely visible in the 1.5%Cu/ZSM-5 sample, but is strong on the 3%Cu/ZSM-5 sample at 2290 cm^{-1}.

3.3. EFFECT OF C/NO RATIO

Increasing C/NO ratio increases NO_x reduction activity over 3%Cu/ZSM-5, as can be seen in fig. 3. IR studies show that this activity increase correlates with the relative abundances of adsorbed species. Fig. 4 shows the effect of increasing C/NO ratio on adsorbed surface species at 380°C. The intensity of the $Cu(N_xO_y)_z$ species decreases dramatically with increasing C/NO ratio. Simultaneously, $Cu-N_2$ and Cu^+-CO increase indicating a competition of these species with $Cu(N_xO_y)_z$ for Cu sites. The Cu^+-CO intensity increase is due to more partially oxidized HC at higher C/NO ratios. At $C/NO = 4$, the $Cu(N_xO_y)_z$ band is about half its intensity at $C/NO = 1$. This corresponds to a decrease in NO_x conversion from ca. 70% to ca. 25% as C/NO ratio is decreased in this range (fig. 2). It is possible that $(N_xO_y)_z$ is a tightly bound intermediate on Cu sites. In separate studies we have noticed that He purging removes Cu^+-CO and $Cu-N_2$ bands about four times faster than $Cu(N_xO_y)_z$ bands at 380°C.

3.4. EFFECT OF TEMPERATURE

The activity of Cu/ZSM-5 depends strongly on the reaction temperature and therefore one would expect different species to occupy surface sites as a function of temperature. Fig. 5 shows the effect of temperature on the IR spectra of 3%Cu/ZSM-5 with the standard feed gases, i.e. $NO/O_2/C_3H_6$.

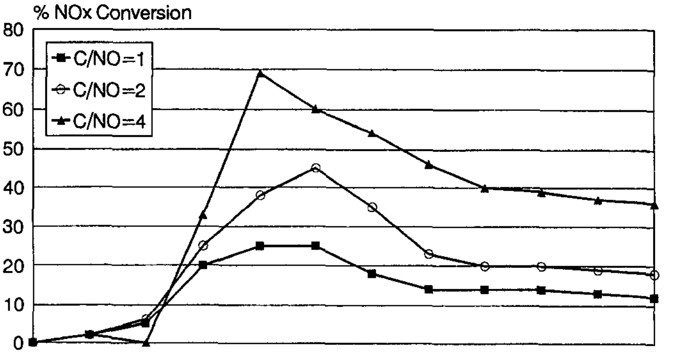

Fig. 3. NO_x conversion versus temperature for 3%Cu/ZSM-5 as a function of C/NO.

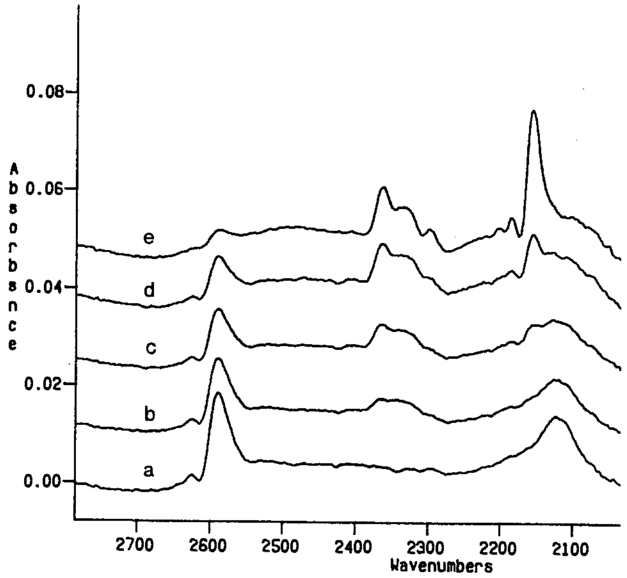

Fig. 4. FTIR spectra of 3%Cu/ZSM-5 in 1000 ppm NO/0–2667 ppm C_3H_6/10% O_2/balance N_2 as a function of C/NO ratio at 380°C. (a) C/NO = 0; (b) C/NO = 1; (c) C/NO = 2; (d) C/NO = 4; (e) C/NO = 8.

At low temperature, where HC and NO_x conversions are negligible, IR detects mainly carbonaceous deposits, Cu^+–CO, and organic isocyanate. At 200°C, an isocyanate band is present at ca. 2270 cm^{-1}. Bands due to CO_2 are weak, indicat-

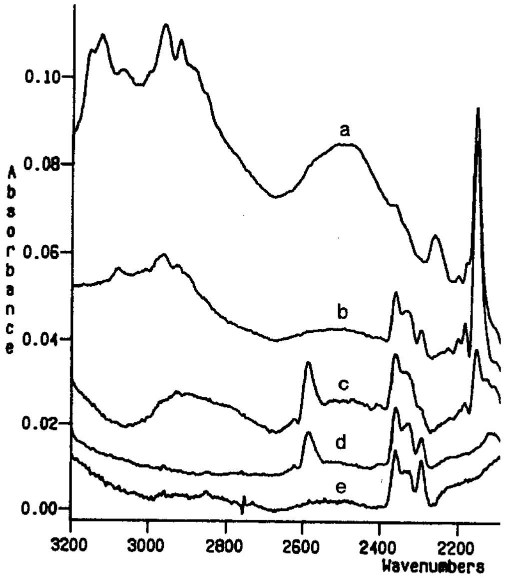

Fig. 5. FTIR spectra of 3%Cu/ZSM-5 in 1000 ppm NO/1333 ppm C_3H_6/10% O_2/balance N_2 as a function of temperature. (a) 200°C; (b) 300°C; (c) 380°C; (d) 450°C; (e) 540°C.

ing the absence of hydrocarbon oxidation. Carbonaceous deposits cover the catalyst's surface rapidly, similar to the behavior of H-ZSM-5 at 400°C. At 300°C, CO_2, Cu–N_2 and Cu^+–CO are present along with slowly forming carbonaceous deposits.

Cu/ZSM-5 exhibits its maximum NO_x conversion between 380 and 450°C. In general, IR shows a shift from carbonaceous deposits, Cu^+–CO and isocyanate species at low temperatures (<380°C) to CO_2, N_2 and $Cu(N_xO_y)_z$ species at 380–450°C indicating that the surface of the catalyst is more oxidized at higher temperatures. Only subtle differences are observed between the spectra obtained at 380 and 450°C. At 380°C, a small amount of Cu^+–CO is observed, whereas at 450°C this band is gone. At both temperatures, the formation of carbonaceous deposits is very slow and no isocyanate band is detected. Strong $Cu(N_xO_y)_z$ and Cu–N_2 bands are present along with minor NO_2^+ bands at 2120 cm^{-1}.

At 540°C, HC oxidation is still complete, but NO_x reduction activity has dropped somewhat from its maximum level at ca. 380°C. Few species are present with significant concentration on the surface of Cu/ZSM-5 at these temperatures. IR detects only CO_2 and Cu–N_2.

3.5. EFFECT OF STEAMING ON CATALYST DEACTIVATION

Steaming has a strong negative effect on NO_x reduction activity for both Cu/ZSM-5 samples, particularly for S-1.5%Cu/ZSM-5, which is significantly more deactivated than S-3%Cu/ZSM-5 , fig. 1. In addition, the temperature where maximum NO_x conversion is reached increases significantly from 380–400°C to 500–540°C after steaming.

Fig. 6 compares the in situ IR spectra for fresh and steamed 3%Cu/ZSM-5 samples at 400 and 540°C under standard reaction conditions, i.e. $NO/O_2/C_3H_6$. At 400°C, the S-3%Cu/ZSM-5 sample shows a broad band centered at 2250 cm^{-1}, probably due to N_2O, and a very strong Cu^+–CO band, which is absent in the spectra of the fresh sample. In addition, the $Cu(N_xO_y)_z$, and Cu–N_2 species observed in the fresh sample are not detected in the steamed sample. At this temperature, the steamed sample has little NO_x reduction activity (fig. 1) and IR shows poor hydrocarbon and NO oxidation. IR results at 400°C are essentially the same for S-1.5%Cu/ZSM-5 (not shown) and S-3%Cu/ZSM-5.

At 540°C, S-3%Cu/ZSM-5 shows significantly more NO_x reduction and HC oxidation activity than at 400°C. Under these conditions, only CO_2 is clearly detected with IR. Again, the IR data show that maximum NO_x conversion occurs under oxidizing conditions, this time occurring at higher temperature. The spectrum of the fresh sample at 540°C is similar to that of the steamed sample with one notable exception; the fresh catalyst still has a significant Cu–N_2 peak. The NO_x reduction activity of the S-1.5%Cu/ZSM-5 sample was so low (<20%) that its IR spectrum was not obtained at 540°C.

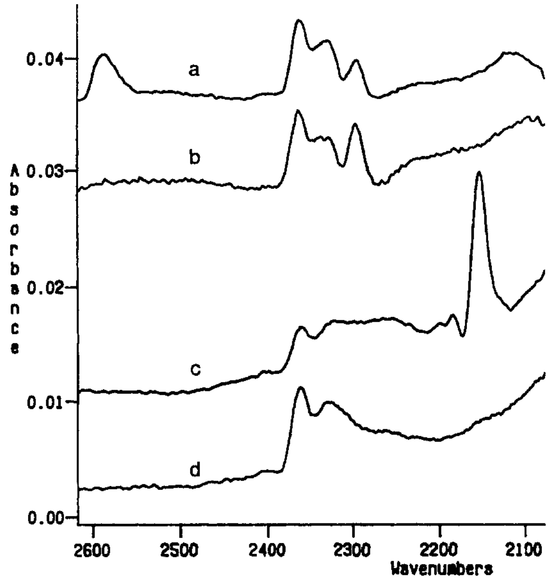

Fig. 6. FTIR spectra of 3%Cu/ZSM-5 in 1000 ppm NO/1333 ppm C_3H_6/10% O_2/balance N_2 of (a) 3%Cu/ZSM-5 at 400°C; (b) 3%Cu/ZSM-5 at 540°C; (c) S-3%Cu/ZSM-5 at 400°C; (d) S-3%Cu/ZSM-5 at 540°C.

3.6. IMPLICATIONS TO THE MECHANISM OF LEAN NO$_x$ REDUCTION

In this work several parallels between adsorbed surface species and catalytic activity for lean NO$_x$ reduction have been seen on Cu/ZSM-5 . In general, under conditions where carbon-containing species predominate the IR spectra, the catalyst has poor NO$_x$ reduction activity. In addition, several nitrogen-containing species have been observed on Cu sites. These may or may not be directly involved in the reaction mechanism. Surprisingly, these species are not partially reduced NO$_x$ or carbon–nitrogen-containing species, but rather are oxidized nitrogen species ($Cu(N_xO_y)_z$) and in certain cases completely reduced N_2.

It is possible that $Cu(N_xO_y)_z$ is a reaction intermediate for the lean NO$_x$ reaction with HC over Cu/ZSM-5 . The fact that this species is observed in the IR at high temperatures under conditions where the catalyst is active gives indirect evidence that it might be involved in the reaction mechanism. Several researchers have postulated that the conversion of NO to more oxidized species such as N_xO_y may play a critical role in the reaction pathway.

The $Cu{-}N_2$ species, however, is not critical to the reaction mechanism because nitrogen sorption is too weak to occur unless its concentration is high in the gas feed, i.e. product N_2 sorption is not detected when using a He carrier gas. The presence of the $Cu{-}N_2$ band in this work, under reaction conditions in a N_2 carrier gas, could, however, be interpreted as follows. Under conditions where Cu sites do not tightly bond other species such as CO, $(N_xO_y)_z$, or OH, perhaps because they react too quickly, free Cu sites can adsorb N_2 in the feed. The $Cu{-}N_2$ band is present in the IR under conditions where NO_x conversions are high, possibly suggesting that the real catalysis of interest occurs more rapidly when copper sites are not occupied by excess CO or $(N_xO_y)_z$. It is possible that IR cannot detect the reactive species because they are not IR active or have short life times on the catalyst surface. This interpretation of the current data would imply that $Cu-(N_xO_y)_z$ is an unreactive species not directly involved in the lean NO_x reaction.

IR alone cannot distinguish between these two possible roles of the $Cu-(N_xO_y)_z$ species observed under reaction conditions in this work. Clearly, additional studies are needed to determine the precise mechanism for lean NO_x reduction over Cu/ZSM-5.

4. Conclusions

This work is the first high temperature in situ FTIR investigation of the NO_x reduction reaction between HC and NO_x in a lean environment over Cu/ZSM-5. IR studies at low temperatures cannot fully explain the surface species present during the lean NO_x reduction process. Several important features in this catalytic system have been identified.

First, a parallel has been observed between adsorbed species and catalytic activity. Conditions leading to low hydrocarbon oxidation and NO_x reduction activities result in high concentrations of carbon-containing species on the surface. These species appear to be occupying sites for which NO_x reduction intermediates cannot effectively compete. This is especially clear when comparing fresh and steam deactivated catalysts where significant activity is not observed until the temperature is high enough to prevent formation of carbonaceous deposits, Cu^+-CO and N_2O. Also in the fresh state at 400°C, the less active 1.5%Cu/ZSM-5 had much higher levels of carbon-containing species present on its surface than the more active Cu/ZSM-5.

Second, as the reaction temperature is increased, the detected NO_x species are increasingly oxidized. This suggests that NO_x reduction does not occur stepwise via an N_2O or N–C species, but rather via an oxidized intermediate. At low temperatures where NO_x reduction activity is low, IR detects mainly carbonaceous deposits, Cu^+-CO and organic isocyanates. At the temperature of maximum NO_x reduction, IR detects $Cu(N_xO_y)_z$ and $Cu-N_2$. It is clear that, as the catalyst becomes more active for hydrocarbon oxidation, nitrogen-containing species can compete more favorably for copper sites. Overall, the effects of increasing temperature on the surface species detected by IR are similar to those observed upon increasing copper concentration.

Finally, steaming at 700°C results in significant deactivation of Cu/ZSM-5 as evidenced by decreases in hydrocarbon oxidation and NO_x reduction activities. IR data at 400°C show a corresponding increase in Cu^+-CO, carbonaceous deposits and N_2O. The steamed samples IR spectra at 400°C resemble the data obtained on fresh samples at much lower temperatures, i.e., 200 and 300°C. Raising the temperature to the point where carbon-containing species are no longer detected on the surface increases NO_x reduction activity.

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