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Mechanistic Cause of Hydrocarbon Specificity over Cu/ZSM-5 and Co/ZSM-5 Catalysts in the Selective Catalytic Reduction of NO_x

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The nature of adsorbed nitrogen oxide complexes (NO_y) has been identified by FTIR spectroscopy. *Nitrito* groups are most prominent on Co/ZSM-5. These complexes are stable at 150°C in He but are reduced upon exposure to either C_3H_8 *or* CH_4 leading to the formation of N_2. Conversely, Cu/ZSM-5 forms *nitro* and *nitrate* groups which are stable at 200°C. At this temperature these complexes are chemically reduced to N_2 upon exposure to C_3H_8 yet remain inert to CH_4. At higher temperatures, thermal decomposition yields NO/NO_2, O_2, and H_2O. The specific rate of NO reduction over Cu/ZSM-5 decreases with Cu loading indicating that isolated $Cu^{2+} \cdot NO_2$ complexes pay a significant role in the mechanism. The hydrocarbon specificity of these complexes thus matches the known catalytic specificity of NO_x reduction over Cu/ZSM-5 and Co/ZSM-5. The mechanistic cause for the catalytic specificity of the ZSM-5 hosted metals in NO_x reduction thus is traced back to the structure and reactivity of the specific NO_y adsorption complexes which these metals produce upon interacting with NO + O_2. The consumption of CH_4 when feeds containing NO, CH_4, and O_2 are exposed to Cu/ZSM-5 can be attributed to nonselective combustion with adsorbed oxygen and *not* to reactions with NO_y.

1. INTRODUCTION

Metal exchanged zeolite catalysts have been proven active in the catalytic reduction of NO by hydrocarbons (1–4). The addition of O_2 enhances the rate of NO_x reduction (5, 6). Oxidation of NO has been identified as one of the main causes of this enhancement. Several reports state that the oxidation product is not NO_{2gas} (7, 8) but rather adsorbed nitrogen oxide complexes, henceforth to be called NO_y (9–11).

A difficult, possibly rate limiting step in the reduction of NO with alkanes is the rupture of the first C–H bond. Cant and co-workers (12) observed a first order kinetic isotope effect when CH_4 and CD_4 were used as reductants. They concluded that H-abstraction was the rate limiting step for both N_2 and CO_2 formation. In general, the chemistry for the selective catalytic reduction (SCR) of NO by hydrocarbons shows some resemblance to the chemistry of cold flames (13) for which H-abstraction is the first step in hydrocarbon activation. It has therefore been suggested that the NO_y groups are instrumental in the H-abstraction reaction (9–11).

If formation of NO_y groups and H-abstraction were the only conditions for effective NO_x reduction, then one might expect that all catalysts which form NO_y would display similar hydrocarbon specificity. This, however, is known to be untrue. Not all catalysts that form NO_y are capable of catalyzing NO reduction to N_2 with any hydrocarbon. Cu/ZSM-5 requires C_{3+} paraffins or C_{2+} olefins; CH_4 does not reduce NO to N_2 over Cu/ZSM-5 in mixtures with O_2 (14). Conversely, in similar reaction mixtures, CH_4 as well as higher hydrocarbons reduce NO to N_2 over Co/ZSM-5, Ni/ZSM-5, Mn/ZSM, and Rh/ZSM-5 (2–4). This shows that formation of any NO_y complexes, though being essential for NO_x reduction catalysis, does not suffice to warrant efficient reduction of NO. In the present paper the mechanistic cause of the known hydrocarbon specificity of NO_y reduction will therefore be addressed using Cu/ZSM-5 and Co/ZSM-5.

FTIR spectroscopy has been used to identify the NO_y complexes in Cu/ZSM-5 and Co/ZSM-5 and to determine their thermal stability and chemical reactivity towards C_3H_8 and CH_4. The nature of the evolved gases has been analyzed in separate experiments by mass spectrometry. In this way, potential reaction steps which are likely to occur simultaneously in the true steady state are examined separately.

2. EXPERIMENTAL

2.1. Catalyst Preparation

Cu/ZSM-5 was prepared via ion exchange at room tempeature (r.t.) using a dilute $Cu(OAc)_2$ solution added dropwise to a Na/ZSM-5 (UOP lot #13023-60) slurry at a pH of 6.5–7.0. After 24 h, the slurry was vacuum filtered,

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washed with 1 liter doubly deionized H_2O, and air dried. This process was repeated twice. Co/ZSM-5 was prepared via ion exchange at 80°C of a dilute $Co(NO_3)_2$ solution added drop-wise to a Na/ZSM-5 slurry at a pH of 6.5–7.0. After 72 h refluxing, the sample was vacuum filtered, washed with 1 liter doubly deionized H_2O, and air dried. Elemental analysis via inductively coupled plasma spectroscopy (Thermo Jarrel Ash Corp., Atomscan 25 spectrometer) gave the following data: Cu/Al = 0.56, Si/Al = 18, Na/Al = 0.0; Co/Al = 0.34, Si/Al = 18, Na/Al = 0.21.

Additional Cu/ZSM-5 samples were prepared similarly as above. Prior to subsequent exchanges a small amount of sample was retained so that the Cu/Al ratios were 0.068, 0.185, and 0.210 after the first, second, and third exchange procedure, respectively.

Prior to IR or MS experiments the samples were calcined for 2 h at 500°C in an UHP O_2 flow.

2.2. FTIR Spectroscopy

Spectra were collected on a Nicolet 60SX FTIR spectrometer equipped with a liquid N_2 cooled detector. The samples were pressed into self-supporting wafers and mounted into a pyrex glass cell sealed with NaCl windows. Spectra were taken at r.t. accumulating 50 scans at a spectral resolution of 1 cm^{-1}. The samples could be pretreated *in situ* in a gas flow at temperatures up to 500°C in a heating zone attached to the glass cell. After *in situ* calcination in UHP O_2, as described previously, the sample was purged at r.t. for 1 h with 25 ml min^{-1} UHP He then saturated in a stream of NO (0.45%) and O_2 (75%) with a He balance. For the reduction studies the samples were heated to the reaction temperatures at 6°/min in flowing C_3H_8 or CH_4 (0.25% hydrocarbon in He) at a total flow rate of 30 ml min^{-1}. Before cooling to r.t., the sample was purged for 10 min with He. Spectra were taken at r.t.

2.3. Mass Spectrometric Analysis

For the analysis of released gases, 400 mg of sample were calcined *ex situ* to 500°C in UHP O_2 and then saturated with NO_2 (0.5%, balance He) at r.t. The reactor was transferred to a glass recirculating manifold equipped with a Dycor Quadrupole Gas Analyzer. Prior to the reduction experiments the sample was heated *in vacuo* to 225°C for Cu/ZSM-5 and 150°C for Co/ZSM-5. A sample loop was then filled with a known amount of hydrocarbon(5–10 Torr); evolved gases were allowed to recirculate over the sample. The signal intensities were normalized by an Ar standard. A secondary loop to the manifold was charged with 3 g of 5 wt% Ni/SiO_2 previously reduced at 400°C. This loop was sealed from the reactor and manifold during the experiment and was used to remove CO during the postreaction analysis of the evolved gases.

2.4. Reaction Studies

A series of Cu/ZSM-5 samples were tested in the continuous flow mode. A Pyrex reactor with a porous frit was charged with 200 mg of catalysts. After pretreatment, samples were heated in a flow of UHP He to 400°C. Gas flow rates were regulated by mass flow controllers, and the total flow rate was maintained at 200 ml/min. Inlet feed composition was 1000 ppm NO, 1000 ppm C_3H_8 and 20,000 ppm O_2 with He used as a diluent. Another series of experiments employed inlet feed compositions in which NO was excluded and the O_2 concentration was varied to compare the rates of C_3H_8 oxidation in the presence and absence of NO. The effluent gas was monitored with a Hewlett Packard 5890 GC with Alltech 13X molecular sieve and Porapak Q columns. By bypassing the catalyst bed, a background spectrum was measured to detect initial concentrations of O_2 and C_3H_8. NO_x conversion was determined from N_2 formation, and C_3H_8 conversion was determined from CO_2 formation as detected in the effluent gas.

3. RESULTS

3.1. FTIR Spectroscopy

Figure 1a shows the FTIR spectrum of Cu/ZSM-5 after the exposure to NO + O_2 at r.t., followed by purging at 200°C in He. There are three distinct bands at 1628, 1594, and 1572 cm^{-1} which are attributed to adsorbed nitrogen oxide complexes. These NO_y groups are stable in He at 200°C for over 14 h. However in a dilute C_3H_8 flow at 200°C all band intensities decrease. A plot of the band intensities, measured as peak heights and normalized by their initial intensities, is presented in Fig. 2. The rates of disappearance differ for the three NO_y groups. One of the NO_y groups (1594 cm^{-1}) reacts rapidly, whereas the other (1572 cm^{-1}) reacts sluggishly. The band at 1628 cm^{-1} initially decreases at a slower rate for 20 min then decreases at a comparable rate to the band at 1594 cm^{-1}. In CH_4, the $Cu^{2+} \cdot NO_y$ groups are not depleted at temperatures below thermal decomposition.

After calcination to 500°C in O_2, an absorption band at 966 cm^{-1} was detected. This band has previously been assigned to the T–O–T framework vibration perturbed by Cu^+ (15). Upon exposure to NO_2, the band at 966 cm^{-1} is depleted while a band a 918–923 cm^{-1}, framework perturbed by Cu^{2+}, increases. Additional NO_2 exposure to a presaturated Cu/ZSM-5 sample leads to a depletion of the band at 1628 cm^{-1} and the formation of features characteristic of $N_2O_{4\,ads}$ while the bands at 1594 and 1572 cm^{-1} are not affected by additional NO_2.

Above 300°C in a flow of O_2, NO and C_3H_8 over Cu/ZSM-5, absorption bands at 1628 and 1594 cm^{-1} are swiftly depleted. Remarkably, in a flow of NO and O_2, the

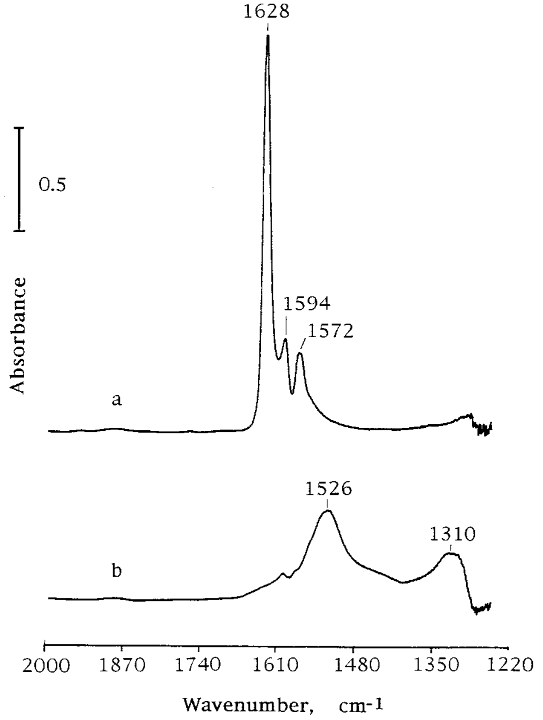

FIG. 1. (a) Spectrum of Cu/ZSM-5 after r.t. saturation with NO + O_2 and purge with He at 200°C; (b) Spectrum of Co/ZSM-5 after room temperature saturation with NO + O_2 and purge with He at 150°C for 14 h.

bands are quickly restored even at temperatures as high as 400°C. Also with this catalyst, the potential intermediate is thus formed from NO and O_2 and reduced by C_3H_8 at temperatures where NO_x reduction catalysis is known to occur. However, upon substituting CH_4 for C_3H_8, the NO_y bands of Cu/ZSM-5 are *not* affected below 400°C. This is remarkable, since CH_4 combustion with O_2 was found, in separate continuous flow experiments, to be significant below 400°C. The intensities of the IR bands for NO_y on Cu/ZSM-5 does decrease at 400°C but they remain significant. Similar experiments with Co/ZSM-5 show that no NO_y bands are detectable at 400°C even in the absence of a reductant.

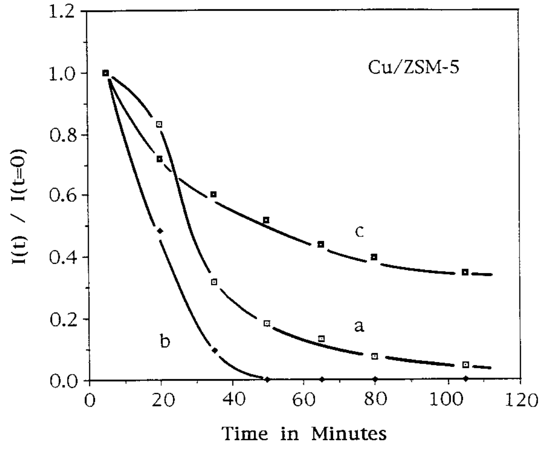

FIG. 2. Depletion of absorption bands in Cu/ZSM-5 vs time normalized by initial intensity using C_3H_8 as a reductant: (a) 1628 cm^{-1}, (b) 1594 cm^{-1}, (c) 1572 cm^{-1}.

To check the band assignments, spectra were taken of Na/ZSM-5 and SiO_2 that were impregnated with $Cu(NO_3)_2$. The samples were dried at r.t. to avoid thermal decomposition of the nitrate. Both impregnated samples display IR bands close to the doublet at 1594 and 1572 cm^{-1}. However, the band at 1628 cm^{-1} is only observed in ZSM-5 after heating to 110°C in He. This conversion is irreversible; the band at 1628 cm^{-1} remains unchanged upon cooling the sample to r.t. The band positions and their response to thermal treatment are summarized in Table 1.

In the case of Co/ZSM-5 the main feature after NO + O_2 saturation is shown in Fig. 1b. It consists of two broad bands at 1526 and 1310 cm^{-1}. The band at 1526 cm^{-1} is ascribed to an adsorbed nitrogen oxide complex. This complex is less stable than the $Cu^{2+} \cdot NO_y$; approximately 60% of the $Co^{2+} \cdot NO_y$ adsorbates are desorbed after thermal treatment at 150°C for 14 h. The reactivity of the remaining NO_y groups with C_3H_8 or CH_4 at 150°C is shown in Fig. 3 displayed as the decrease in the intensity of the absorption band at 1526 cm^{-1} normalized by the initial intensity. The band intensity decreases faster in the presence of C_3H_8 than CH_4 and remain relatively unchanged in He.

3.2. MS Spectrometry

Figure 4 shows the evolution of N_2, NO, and CO_2 while propane is circulated at 225°C over a Cu/ZSM-5 sample that was presaturated with NO_2 at r.t. and evacuated at 225°C. The spectra have been normalized by a known Ar signal, and differences in sensitivity have been compensated using literature values (16). As N_2, N_2O, C_3H_8, CO, and CO_2 contribute to mass 28, the determination of N_2 is not trivial. The contribution from the fragment of C_3H_8 was calculated from the mass 29 signal and a calibration factor was determined from the spectrum of C_3H_8. Likewise, the contribution to mass 28 from the fragmentation of CO_2 was determined by calibration as a fraction of the mass 44 signal and subtracted from the mass 28 peak. With these corrections the quantity of N_2 was analyzed and found to be significant. After 2 h of propane recirculation, the reaction mixture was exposed to the previously reduced Ni/SiO_2 trap. (Separate experiments show that the prereduced Ni/SiO_2 trap is an excellent CO scavenger.) The normalized signal intensity for mass 28 did not decrease indicating that CO is not a gas phase product. A loop of the recirculation system was immersed in liquid

TABLE 1

Bands Detected on $Cu(NO_3)_2$ Impregnated Samples

Sample		1628 cm^{-1}	1600 cm^{-1}	1594 cm^{-1}	1574 cm^{-1}	1572 cm^{-1}
SiO_2	21°C		*		*	
	100°C		*		*	
Na/ZSM-5	21°C			*		*
	100°C	*		*		*

nitrogen to remove N_2O from the gas phase. The signals for mass 30 (NO) and 44 (N_2O and CO_2) decreased significantly while the mass 28 signal remained almost unchanged. This indicates that some N_2O may have formed; however, after 2 h recirculation the vast majority of the mass 28 signal can be attributed to N_2.

No reaction between NO_y groups and CH_4 was detectable for Cu/ZSM-5.

Figure 5 shows the evolution of N_2, NO, and CO_2, normalized by the measured Ar signal, while C_3H_8 was circulated at 150°C over a Co/ZSM-5 sample that was presaturated with NO_2 at r.t. and evacuated at 150°C. In a similar manner, the contributions to mass 28 of N_2O, C_3H_8, CO, and CO_2 were eliminated from the data. Again, N_2 evolution was detected and found to be significant. However, less N_2 is formed; less CO_2 relative to N_2 is formed, and NO evolution is delayed and smaller compared to Cu/ZSM-5. A similar experiment was performed using CH_4 as the reductant. In contrast to the previous observations with Cu/ZSM-5, N_2 and CO_2 evolutions are detectable in significant amounts, though their rates of formation are lower. It is thus certain that the NO_y formed in Co/ZSM-5 can be reduced with CH_4 to form N_2. A comparison of both reductants and both catalysts is presented in Fig. 6. Clearly, NO_y reduction with CH_4 is slower than with C_3H_8 and undetectable over Cu/ZSM-5.

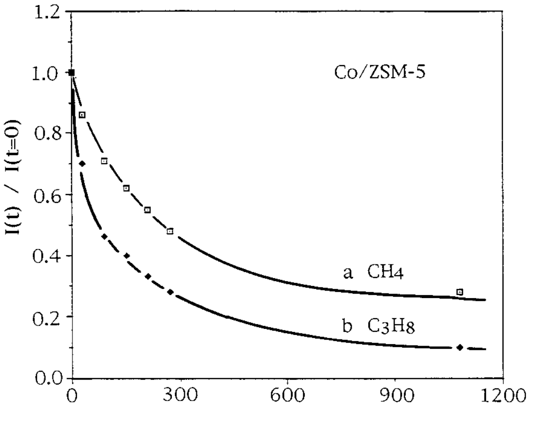

FIG. 3. Depletion of absorption band at 1526 cm^{-1} in Co/ZSM-5 vs time normalized by the initial intensity using: (a) CH_4, (b) C_3H_8 as a reductant.

3.3. *Reaction Studies*

Figure 7 shows the specific rate of NO_x reduction versus Cu exchange level. The specific rate for NO_x reduction decreases with Cu loading; this characteristically differs from the trend reported by Moretti for NO *decomposition* (17). Table 2 shows the C_3H_8 conversion to CO_2 over three Cu/ZSM-5 catalysts. A noticeable difference in the rate of C_3H_8 oxidation is detected over Cu/ZSM-5 (Cu/Al = 0.068) at O_2 concentrations as large as 20,000 ppm. This difference is seen over Cu/ZSM-5 (Cu/Al = 0.185) at 7500 ppm O_2 and is not detectable over Cu/ZSM-5 (Cu/Al = 0.56).

4. DISCUSSION

NO_x reduction over Cu/ZSM-5 and Co/ZSM-5 occurs below the light-off temperature for homogeneous combustion of hydrocarbons in NO_2 (13). The rate limiting step for NO_x reduction does not appear to occur in the gas phase. The present FTIR results show that sorbed NO_y groups (nitrito for Co and nitro/nitrate for Cu) are thermally stable at 150° and 225°C respectively, but these complexes are quite reactive towards hydrocarbons, as is manifested for both catalysts by the rapid decrease of their band intensities in the presence of C_3H_8. The present results thus indicate that these groups are potential reaction intermediates, as has been suggested previously (9–11).

The infrared data clearly show that the NO_y complexes can be removed from the surface of the sample below the temperatures of their thermal decomposition. The mass spectrometric analysis of the desorbed products shows that NO_y can be reduced to N_2 by hydrocarbons at temperatures where no thermal decomposition occurs. Moreover, ther-

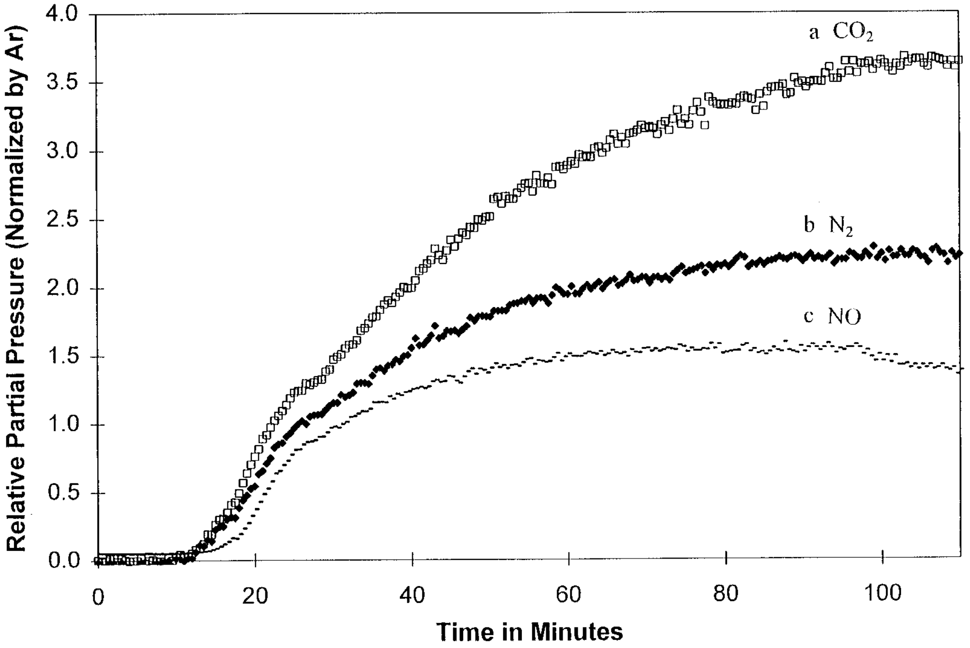

FIG. 4. Evolution at 225°C of (a) CO_2, (b) N_2, and (c) NO from Cu/ZSM-5 upon exposure to C_3H_8 as detected by mass spectrometry. The Cu/ZSM-5 sample was presaturated with NO_2 at r.t. and evacuated to 225°C.

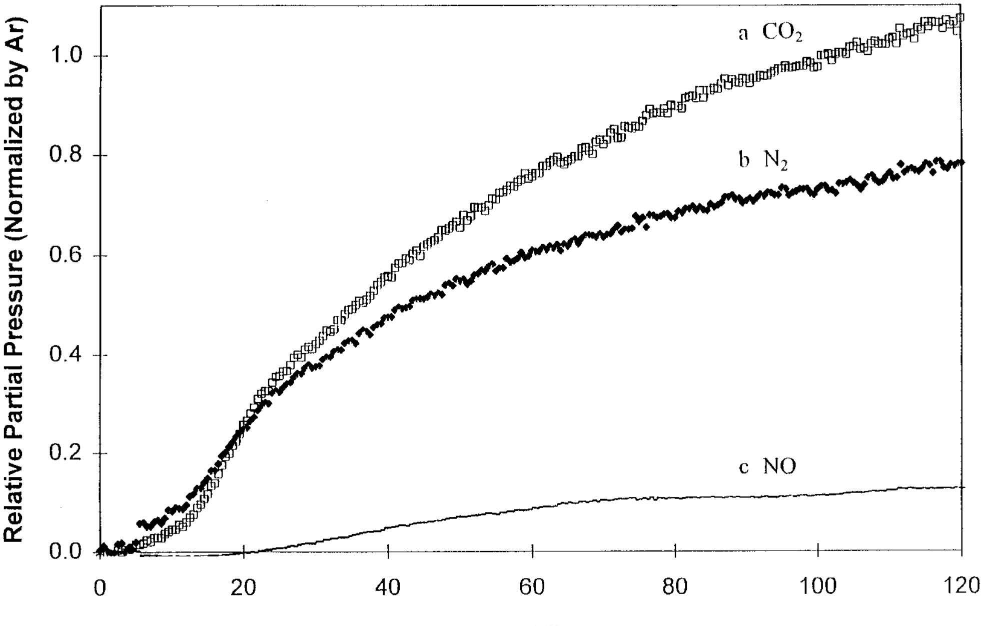

FIG. 5. Evolution at 150°C of (a) CO_2, (b) N_2 and (c) NO from Co/ZSM-5 upon exposure to C_3H_8 as detected by mass spectrometry. The Co/ZSM-5 sample was presaturated with NO_2 at r.t. and evacuated to 150°C.

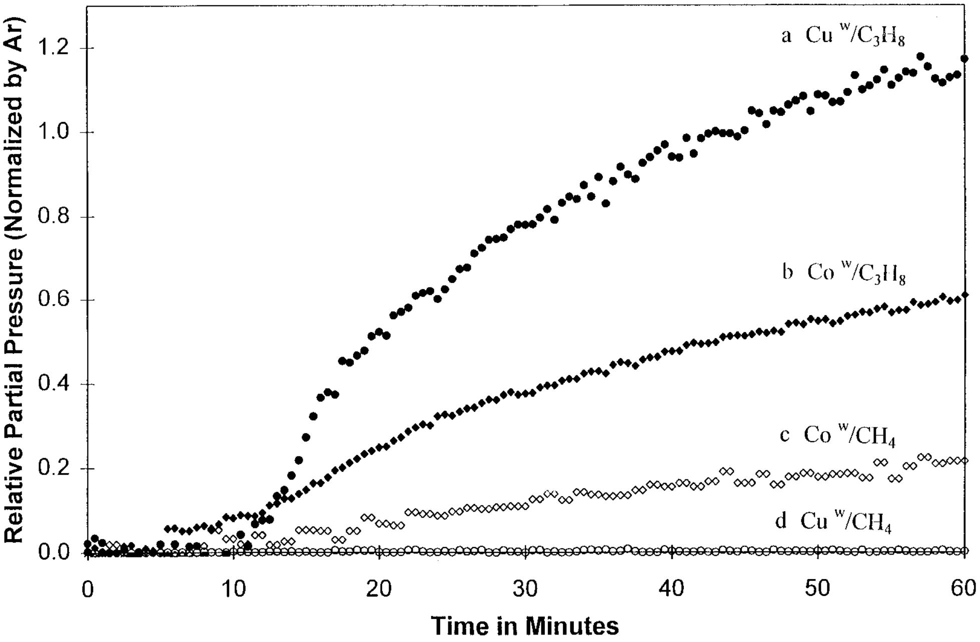

FIG. 6. Evolution of N_2 from (a) Cu/ZSM-5 exposed to C_3H_8 at 225°C; (b) Co/ZSM-5 exposed to C_3H_8 at 150°C; (c) Co/ZSM-5 exposed to CH_4 at 150°C; (d) Cu/ZSM-5 exposed to CH_4 at 225°C.

mal decomposition of NO_y on Cu/ZSM-5 leads to the evolution of NO, NO_2, O_2, and H_2O; only chemical reduction leads to N_2. It follows that formation and reduction of NO_y groups are important steps in the reaction mechanism of SCR over both Co/ZSM-5 and Cu/ZSM-5.

None of the band intensities for Cu/ZSM-5 decrease in the presence of CH_4 at 200°C. Additionally, nonselective interaction between CH_4 and NO_y at 225°C has been ruled out since evolution of NO and CO_2 is not detected by mass spectrometry. However, when feeds containing NO, O_2, and CH_4 are exposed to Cu/ZSM-5 at elevated temperatures, CH_4 combustion is rapid (2, 4, 14). At 350°C in a flow of NO and O_2, the IR NO_y band intensities are not affected by the addition of CH_4. Yet, at this temperature, CO_2 evolution and CH_4 consumption are detected in the continuous flow system. It is conceivable that this CH_4 combustion depletes the coverage of the surface with adsorbed oxygen. The observed decrease in intensity of the NO_y band at 400°C might be due to a reversible equilibrium of NO_y and adsorbed oxygen rather than any direct chemical interaction between NO_y and CH_4. Whereas thus no interaction between NO_y and CH_4 is observed for Cu/ZSM-5, the situation is different for Co/ZSM-5; in this case all data indicate direct chemical interaction between

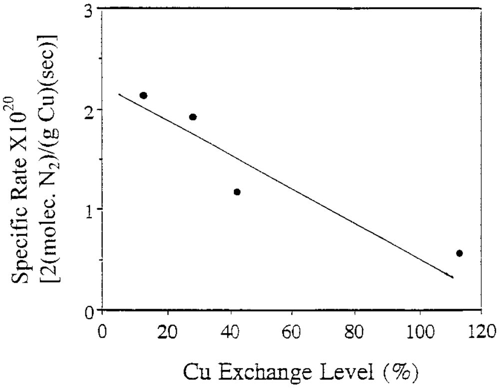

FIG. 7. Specific rate versus Cu exchange level. 0.20 g Cu/ZSM-5; 1000 ppm NO, 1000 ppm C_3H_8, 20,000 ppm O_2 and He balance. T_{rxn} = 400°C. Total flow rate 200 ml/min^{-1}.

TABLE 2

Cu/Al	O_2 inlet concentration	% NO_x conversion	% C_3H_8 conversion
0.068	20000 ppm	37.8	20.2
	20000 ppm	without NO	56.2
0.185	7500 ppm	92.4	81.7
	7500 ppm	without NO	91.2
0.560	20000 ppm	64.1	97.1

Note. Inlet feed composition: 1000 ppm NO, 1000 ppm C_3H_8. Total flow rate: 200 ml min^{-1}. T_{rxn} = 400°C. 0.20 g catalyst.

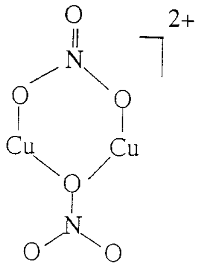

FIG. 8. Proposed structure of mono- and bidentate nitrate formed by the reaction of NO_2 with $[Cu–O–Cu]^{2+}$ oxocations.

NO_y and CH_4 even at 150°C as seen by the evolution of N_2 and CO_2 in the MS experiments.

It is important to note that the MS data show a behavior similar to the steady state data. The mass spectrometric data reveal that C_3H_8 reacts rapidly over pre-saturated Cu/ZSM-5. Additionally, the N_2/CO_2(0.61) and N_2/NO(1.5) ratios are low indicating that C_3H_8 is a less selective reductant. Over Co/ZSM-5, C_3H_8 reacts somewhat more slowly than over Cu/ZSM-5 while the N_2/CO_2(0.72) and N_2/NO(4.9) ratios are higher. This parallels the behavior under steady state conditions, Co/ZSM-5 is known to be more selective than Cu/ZSM-5, and CH_4 is known to react more slowly than C_3H_8. Co/ZSM-5 requires a higher temperature with CH_4 than with C_3H_8 to obtain similar conversions. This indicates that the results of the recirculation experiments are relevant for the steady state reactions as reported previously (10).

The pronounced difference in the chemical behavior towards CH_4 of the NO_y groups in Cu/ZSM-5 and Co/ZSM-5, with N_2 formation occurring only over the latter, shows that the cause of the known specificity of these two catalysts can be traced back to the different reactivity of their NO_y groups. It is therefore of relevance that the NO_y groups in these two catalysts show indeed significant differences in their IR spectroscopic signature and their thermal stability in addition to their different chemical reactivity towards hydrocarbons.

It is known that Cu/ZSM-5 contains Cu^{2+} ions, $[Cu–O–Cu]^{2+}$ oxocations and CuO oxide clusters (18). Upon interaction with NO_2, the oxocations and oxides react to form *nitrate ions*, whereas Cu^{2+} ions form *nitro complexes*. This statement is based on the following data:

(1) The samples that were impregnated with Cu nitrate show IR bands which are close to the doublet at 1594 and 1572 cm^{-1}. These bands are therefore assigned to nitrate ions. These are most likely bridging two Cu sites in a bidentate and monodentate form as shown in Fig. 8. The distinction between the latter two forms suggests assignment of the 1594 cm^{-1} band to a bridging monodentate nitrate while the band at 1572 cm^{-1} is more likely a bidentate nitrate. A band at 1575 cm^{-1} has been ascribed by London and Bell to a $Cu(NO_3)_2$ on silica (19).

(2) When NO is adsorbed on Cu/ZSM-5, $Cu^+ \cdot NO$ complexes are formed as evident by the T–O–T framework vibration at 966 cm^{-1}. Adsorption of NO + O_2 erodes the band intensity at 966 cm^{-1} and causes an increase in the band intensity at 918–923 cm^{-1}. These changes are indicative of Cu^+ oxidation to Cu^{2+} as nitrate groups are formed. Therefore all NO_y groups are coordinated to Cu^{2+}.

(3) After additional exposure to NO_2, only the band at 1628 cm^{-1} transforms to a feature that is characteristic of $N_2O_{4\,ads}$, suggesting that the band at 1628 cm^{-1} is a nitro group (N bound NO_2 complex) associated with a Cu^{2+} ion. This process was found to be reversible as the band at 1628 cm^{-1} reappears upon elimination of NO_2 from the gas phase.

The different rate of response to C_3H_8 of three NO_y bands proves that they correspond to different species with different chemical reactivities.

Moretti (17) and Campa *et al.* (20) have shown that for the decomposition of NO over Cu/ZSM-5 the specific rate increases with Cu loading and Al/Si ratio; these authors, therefore, propose a multiatomic Cu_n site (17, 20). Applying the same logic to the present findings that the specific rate *decreases* with Cu loading would suggest that for reduction of NO with C_3H_8 a high dispersion of the Cu is desirable. Therefore of the several complexes formed on Cu/ZSM-5, the mononuclear $Cu^{2+} \cdot NO_2$ complex seems to play a more active role in the mechanism.

The decrease in the rate of C_3H_8 oxidation upon addition of NO, as seen in Table 2, indicates an inhibition by NO_y groups of the nonselective combustion of the hydrocarbon. The rate of reaction of NO_y groups with hydrocarbons is lower than the rate of direct combustion with O_2.

The chemistry of zeolite hosted Co differs significantly from that of Cu. Separate temperature programmed reduction experiments performed in this laboratory show that Co is present in ZSM-5 only as Co^{2+} ions not as Co_3O_4 as evidenced by a single H_2 consumption peak at 625°C. Since Co is not known to form oxocations such as $[Co–O–Co]^{2+}$ and no Co_3O_4 is present, only *nitro* or *nitrito* (O bound ONO complexes) groups can form. Li *et al.* (20) have reported similar data for Co/FER. They ascribe a band at 1540 cm^{-1} to a cobalt nitrate complex. However, in the present Co/ZSM-5 catalyst with constant valence of Co^{2+}, nitrate ions should be a minority species if present at all, as their formation would appear to violate the principle of charge conservation. Based on the greater line width of the absorption band at 1526 cm^{-1} as compared to the nitro complex formed on Cu^{2+} ions (band at 1628 cm^{-1}, see Fig. 1a), we prefer to ascribe the band at 1526 cm^{-1} to a $Co^{2+} \cdot ONO$ complex rather than to a $Co^{2+} \cdot NO_2$ complex. Windhorst and Lunsford (22) observed a band at 1520

TABLE 3

Band Assignments of NO_y Groups

	Support	Assignment	Ref.
1628 cm^{-1}	Cu/ZSM-5	NO_2 (nitro)	This work
1594 cm^{-1}	Cu/ZSM-5	NO_3^- (monodentate)	This work
1572 cm^{-1}	Cu/ZSM-5	NO_3^- (bidentate)	This work
		NO_3^- (monodentate)	19
1526 cm^{-1}	Co/Y	ONO (nitrito)	22
1310 cm^{-1}	Co/ZSM-5	ONO (nitrito)	This work
		NO_2 (nitro)	23
		O_2N (chelating nitro)	23

cm^{-1} upon adsorption of NO_2 on Co/Y which they assign to a $Co^{2+} \cdot ONO$ complex. Additionally, chelating, $Co^{2+} \cdot O_2N$, complexes have antisymmetric stretching frequencies in the range of 1300 cm^{-1} and nitro, $Co^{2+} \cdot NO_2$, complexes have symmetric and antisymmetric stretching frequencies at 1330 and 1430 cm^{-1}, respectively (23). It is possible that the broad absorption at 1310 cm^{-1} contains several components, $Co^{2+} \cdot O_2N$, $Co^{2+} \cdot NO_2$ and $Co^{2+} \cdot ONO$ with $Co^{2+} \cdot ONO$ being the dominant moiety. Unlike $Cu^{2+} \cdot NO_2$, the $Co^{2+} \cdot NO_y$ complexes formed are most likely nitrito complexes.

A list of band assignments is presented in Table 3.

In summarizing, the chemistry of the NO_y groups in zeolite hosted Cu and Co systems is distinctly different. Both can form nitro or nitrito complexes; however, N bound nitro complexes ($Cu^{2+} \cdot NO_2$) are predominant on Cu/ZSM-5 while O bound nitrito complexes ($Co^{2+} \cdot ONO$) are predominant on Co/ZSM-5. Only in Cu/ZSM5 are nitrate ions formed. They exist in two structures as bridging mono- and bidentate nitrates. In the recirculation experiments, only NO_y on Co/ZSM-5 reacts with CH_4, and N_2 evolution is detected. With higher hydrocarbons, NO_y on both Co/ZSM-5 and Cu/ZSM-5 reacts with C_3H_8, and N_2 evolution is detected. These differences are responsible for the known hydrocarbon specificity observed during steady state flow reactions even though hydrocarbon activation occurs in all cases via H-abstraction mediated by the NO_y groups. Since the NO_y formed on Co/ZSM-5 differs greatly from those on Cu/ZSM-5, it is therefore possible to rationalize the observation that not all catalysts which form NO_y groups are capable of catalyzing NO reduction to N_2 with any hydrocarbon even though their formation is pivotal in the reaction mechanism.

The reaction steps of the hydrocarbon radical formed after loss of a hydrogen atom are not yet clear. It has been proposed that a reactive intermediate containing at least one carbon, nitrogen and oxygen atom is formed on the catalyst surface (24–26). This problem is still under investigation and so is the question whether the two nitrogen atoms which form N_2 have equal or different histories.

5. CONCLUSIONS

The different chemistry of zeolite ZSM-5 hosted Cu and Co results in different types of chemisorbed NO_y complexes when these materials are exposed to NO + O_2. These have been identified by FTIR spectroscopy, their reactivity towards hydrocarbons and their thermal decomposition have been measured and compared with the literature. With Co/ZSM-5 nitrito groups are most prominent, they are able to react with CH_4 and higher hydrocarbons; this interaction leads to formation of N_2. The different NO_y complexes formed, nitrate and nitro groups, upon interaction of NO + O_2 with Cu/ZSM-5 reflect the variety of Cu species in this zeolite: Cu^{2+} ions, oxo-complexes and oxide clusters. None of these NO_y groups interact with methane under the conditions studied; but these complexes react with propane, and N_2 is formed. The decrease in specific rate as Cu loading increases indicates that mononuclear Cu^{2+} and, therefore the nitro groups, play a more active role in the reduction mechanism. In contrast to chemical reduction, thermal decomposition of these complexes results in formation of NO and NO_2 but not N_2. On both catalysts, when a chemical interaction between a hydrocarbon molecule and adsorbed NO_y occurs, this reaction leads to H-abstraction and possibly formation of free radicals. The known differences in steady state hydrocarbon specificity arise from the different chemistry of the NO_y groups in both catalysts. CH_4 combustion over Cu/ZSM-5 does not proceed via the NO_y groups.

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