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NO adsorption on Cu-ZSM-5: assignment of IR band at 2133 cm^{-1}

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The adsorption of nitrogen oxides on Cu-ZSM-5 was studied by infrared spectroscopy to elucidate the species associated with the band at 2133 cm^{-1}. The band was found for both NO and NO_2 adsorption. Labeling experiments with ^{15}NO revealed that the associated surface species contained nitrogen and, most likely, an N–O bond. Co-adsorption experiments of NO and oxygen produced adsorbed nitronium, NO_2^+, as the principal, associated species. Adsorption of nitrogen oxides on dispersed CuO and the HZSM-5 support demonstrated that the 2133 cm^{-1} band was not necessarily associated with copper ions. A relatively strong correlation between the bands at 2133 and 3615 cm^{-1} indicates that the primary adsorption sites of NO_2^+ are the strongly protic, bridging Si(OH)Al framework hydroxyls. Once these were filled, other, weaker acid sites began to adsorb NO_2^+.

Keywords: Cu-ZSM-5 zeolite; nitric oxide adsorption; nitrogen dioxide adsorption; acidity; infrared spectroscopy

1. Introduction

Over traditional three-way catalysts, reduction of NO_x in the presence of excess oxygen is ineffective. However, it has been shown that over Cu-ZSM-5, hydrocarbons selectively remove NO_x under net oxidizing conditions [1,2]. To characterize surface intermediate species, several researchers have probed the adsorption of NO on oxidized Cu-ZSM-5 catalysts by infrared spectroscopy. Their studies have indicated that for NO adsorption nitrosonium ions, NO^+, adsorb linearly on cupric ions (1904 cm^{-1}) and nitrosyl ions, NO^-, adsorb linearly on cuprous ions (1811 cm^{-1}); NO also adsorbs in the gem-dinitrosyl form, $(NO)_2^-$, on cuprous ions (1825 and 1730 cm^{-1}) [3–7].

Not all the infrared absorption bands for NO adsorption on Cu-ZSM-5 have been definitively assigned. In particular, for the band at 2133 cm^{-1}, the identity

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and site specificity of the surface species have not been thoroughly typified. In some studies of NO adsorption on Cu-ZSM-5, the 2133 cm^{-1} band is not observed [5], while in others it is rather conspicuous [4,6,7]. Iwamoto et al. [4] assigned the band at 2133 cm^{-1} to adsorbed NO_2^+. This assignment was based primarily on an isotopic shift which they observed when ^{15}NO was adsorbed on Cu-ZSM-5 and on the assignment by Chao and Lunsford [8] of bands in the 2200–2000 cm^{-1} region to the nitronium (or nitryl) ion, NO_2^+, adsorbed at cationic centers in NaY, CaY and decationated Y zeolites.

Valyon and Hall tentatively assigned the band at 2133 cm^{-1} to NO_2/Cu^+ [6]. The assignment was primarily based on separate adsorption of NO_2 on Cu-ZSM-5 and on the relatively high antisymmetric stretching frequency of NO_2^+ in nitrogen pentoxide, N_2O_5, at 2375 cm^{-1} [9]. However, they later withdrew this assignment when they could not reproduce the 2133 cm^{-1} band upon separate NO_2 adsorption on Cu-ZSM-5 [7]. They still left open the possibility that the 2133 cm^{-1} band may result from a reaction of NO with adsorbed oxygen atoms. It should be noted that, more recently, Centi et al. [10] assigned the band to $NO_2^{\delta+}/Cu^{2+}$ without explanation.

Our purpose is to further elucidate the identity and site specificity of the species associated with the band at 2133 cm^{-1}.

2. Experimental

2.1. CATALYST PREPARATION AND CHARACTERIZATION

The Cu-ZSM-5 catalyst (CuHZSM5) was prepared by copper ion exchange of HZSM-5. The acid form of the HZSM-5 zeolite (HZSM5), having a SiO_2/Al_2O_3 ratio of 80, was obtained from PQ. BET analysis yielded a zeolite surface area of 460 m^2/g. Copper was exchanged from copper acetate (99.9%, Johnson Matthey) in three successive exchanges with water rinses between the exchanges. The sample was then calcined at 400°C for 12 h. The copper content was analyzed by ICP and found to be 1.78 wt%. This corresponds to a nominal exchange of 147% copper as cupric ions.

The copper oxide catalyst (99.999% CuO, Johnson Matthey) was calcined at 400°C. The CuO/Al_2O_3 catalyst (2 wt% Cu) was prepared by impregnating defumed γ-alumina (Degussa Alumina C, 100 m^2/g) with a solution of copper nitrate (reagent grade, J.T. Baker Analytical). Sample drying at 120°C was followed by calcination at 400°C overnight.

2.2. INFRARED SPECTROSCOPY

Adsorption experiments were performed in situ using a high-vacuum IR cell (base pressure of 5×10^{-8} Torr) equipped with CaF_2 windows. Catalyst powder samples were pressed into a gold wire mesh at 2000 lb/in^2. A chromel–alumel thermocouple was spot-welded to the center of the grid. The sample was fixed onto a transposable sample holder which also allowed resistive heating of the specimen. Spectra were recorded using a Mattson Cygnus 100 FTIR spectrometer multiplexed to a computer. Unless otherwise indicated, difference spectra were presented using the spectrum of the evacuated, calcined sample as a reference. The spectral resolution was 4 cm^{-1}.

For in situ pretreatment and the adsorption experiments, the following gases were used. Oxygen (99.998%, Matheson), CO (99.99%, Matheson), and N_2O (99.0%, Matheson) were used without further purification. NO (99.0%, Matheson) was purified by multiple freezing distillation between two glass flasks, equipped with cold fingers, using liquid nitrogen as the cooling agent [11]. NO_2 was prepared using purified NO and adding excess oxygen. Equilibration at room temperature for 0.5 h was sufficient for complete conversion of NO to NO_2, as evidenced by the lack of N_2O_3 formation (dark blue color for the liquid) upon cooling below −20°C [12]. Excess oxygen was boiled off by trap-to-trap distillation using liquid nitrogen as the coolant.

In situ catalyst pretreatment was as follows. The sample was evacuated at 400°C and treated at temperature in 100 Torr oxygen for 25 min. The sample was then cooled to the adsorption temperature in 100 Torr oxygen and evacuated at temperature for 1 h.

3. Results

3.1. CO ADSORPTION ON CuHZSM5

Since the internal stretching frequency of CO adsorbed on cupric ions typically appears in the region of interest between 2140 and 2127 cm^{-1} [13], a spectrum of CO adsorption on CuHZSM5 was obtained for comparison. Fig. 1A displays strong absorption bands at 2209, 2178, and 2157 cm^{-1} upon CO adsorption. These bands were previously assigned to CO adsorbed on Lewis, Brønsted, and isolated SiOH sites, respectively [14,15]. The spectrum also indicates a red shoulder for the 2157 cm^{-1} peak. The second derivative of fig. 1A revealed an inflection point at 2131 cm^{-1}, indicating a weak band for CO adsorption.

3.2. ADSORPTION OF NITROGEN OXIDES ON CuHZSM5

Adsorption of NO on CuHZSM5 was examined at 15 Torr (fig. 2A). Various absorption bands were visible at 2133, 1904, 1823, 1811, and 1734 cm^{-1}. Table 1 gives a summary of these peaks and their respective assignments. The absorption band at 2133 cm^{-1} has not yet been assigned categorically. To determine if the species associated with the 2133 cm^{-1} band involved nitrogen, the adsorption experi-

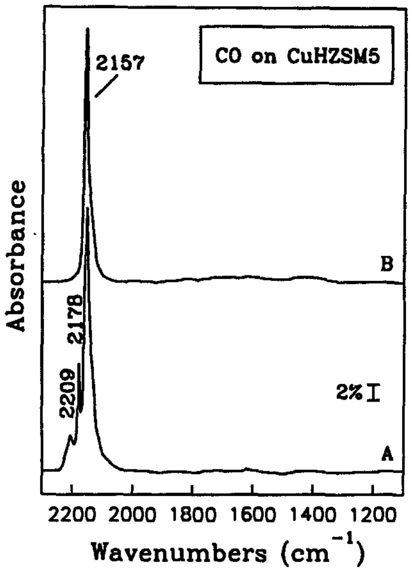

Fig. 1. IR spectra of CO on CuHZSM5 at 25°C: (A) adsorption of 15 Torr CO; (B) after 1 h evacuation of CO.

ment was repeated using ^{15}NO. The resulting spectrum for ^{15}NO adsorption indicates an isotopic band shift from 2133 to 2095 cm^{-1} (fig. 2B). The band at 2095 cm^{-1} was less intense than the one at 2133 cm^{-1}. In addition, the band at 2158 cm^{-1} shows that the ^{15}NO gas was contaminated by CO. It appears that the

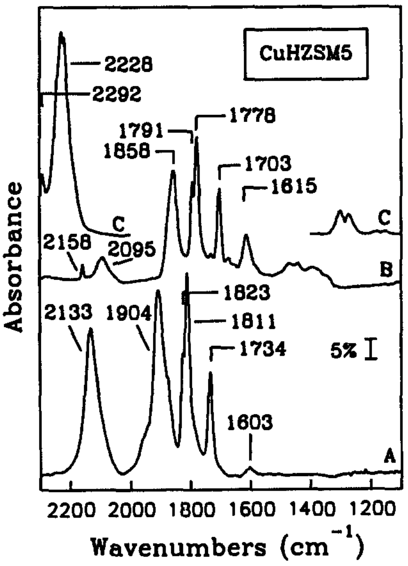

Fig. 2. Adsorption on CuHZSM5 at 25°C: (A) 15 Torr NO; (B) 15 Torr ^{15}NO; (C) 15 Torr N_2O.

Table 1
Summary of infrared absorption bands and their tentative assignments for surface species formed during adsorption of nitrogen oxides on CuHZSM5

Band (cm^{-1})	Assignment	Ref.
2224	adsorbed N_2O	[7]
2133	?	
1962	?	
1904	NO^+ on Cu^{2+}	[3]
1898, 1875, 1854	gaseous NO	[25]
1823	$(NO)_2^-$ on Cu^+, symm.	[3]
1811	NO^- on Cu^+	[3]
1744	adsorbed N_2O_4	[13]
1734	$(NO)_2^-$ on Cu^+, asymm.	[13]
1611	NO_2^-	[13]
1576	monodentate NO_3^-	[13]

lower intensity of the band at 2095 cm^{-1} may be due to adsorption of residual CO on the same sites as those of the 2133 cm^{-1} species. A simple calculation based on the reduced mass for diatomic NO yields a theoretical frequency of 2094.74 cm^{-1} for the ^{15}N-labeled species which conforms closely with the experimentally observed band at 2095 cm^{-1}. Thus, the isotopic shift indicates that the 2133 cm^{-1} species contains nitrogen while the calculation furthermore suggests that this species contains an N–O bond.

Since the isotopic experiment indicated that the species associated with the 2133 cm^{-1} band contained nitrogen, adsorption of other nitrogen oxides was performed in an attempt to identify the species. In fig. 2C, the spectrum for N_2O adsorbed on CuHZSM5 shows a large peak at approximately 2228 cm^{-1}. Gaseous N_2O has an absorption band at 2224 cm^{-1} at almost the same frequency [13]. Since there is no peak evident at 2133 cm^{-1}, N_2O may be excluded from the group of possible species associated with the latter band.

The spectrum of NO_2 adsorbed on CuHZSM5 exhibited absorption bands at 1744, 1611, and 1576 cm^{-1} (fig. 3A). These bands are thought to correspond to adsorbed forms of N_2O_4 [7,13] and NO_2 [7] and a monodentate nitrate structure [13], respectively. There was also a substantial band present at 2133 cm^{-1} at 3 Torr of NO_2. At higher pressures, this band was obscured by additional peaks in the region.

3.3. NO ADSORPTION ON CuO

With increased catalyst oxidation, it was observed that the intensity of the 2133 cm^{-1} band increased. Therefore, the possibility was considered that the unknown species may be associated with cupric ions, since as the number of cupric ions increases upon prolonged oxidation, the population of the species would

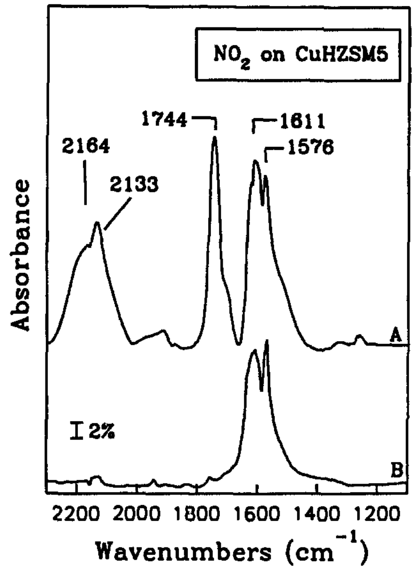

Fig. 3. Spectra of CuHZSM5 at 25°C: (A) after adsorption of 3 Torr NO_2; (B) after 1 h evacuation of NO_2.

increase. To verify this, NO adsorption experiments were conducted on CuO catalysts. The peaks at 1898, 1875, and 1854 cm^{-1} in fig. 4A were due to gaseous NO. No bands could be detected for NO adsorbed on unsupported CuO due to the low BET surface area of the material (<2 m^2/g). However, fig. 4B reveals no absorp-

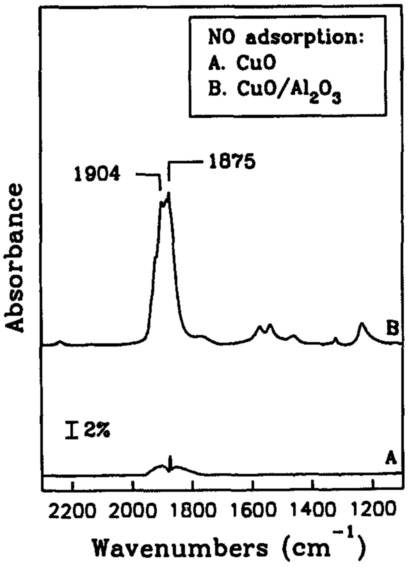

Fig. 4. Adsorption of 15 Torr NO at 25°C on: (A) CuO; (B) CuO/Al_2O_3.

tion band at 2133 cm^{-1} in the spectrum for NO adsorption on dispersed CuO/ Al_2O_3 (2 wt% Cu). In this spectrum, the bands below 1600 cm^{-1} are characteristic of nitrite and nitrate complexes on the alumina support [16]. Since there is no 2133 cm^{-1} peak evident in the spectrum, it appears that the species is not associated with *nonexchanged* cupric ions.

3.4. ADSORPTION OF NITROGEN OXIDES ON HZSM5

Since the 2133 cm^{-1} species could not be associated with cupric ions, NO and NO_2 adsorption studies were conducted to determine if the unknown species may be associated with the base, nonexchanged HZSM5 zeolite. Spectra for NO and NO_2 adsorbed on HZSM5 are shown in fig. 5. The spectrum for NO on HZSM5 (fig. 5A) shows a weak band at 2133 cm^{-1}, along with the triplet due to gaseous NO (1898, 1875, 1854 cm^{-1}). At 3 Torr of NO_2, the infrared spectrum (fig. 5B) also shows the unassigned band at 2133 cm^{-1}, as well as bands associated with adsorbed NO_2. It should be noted that at higher pressures of NO_2 (>3 Torr), the 2133 cm^{-1} band was obscured by additional peaks in the region.

3.5. CO-ADSORPTION OF NO AND OXYGEN

A co-adsorption experiment of NO and oxygen was conducted on CuHZSM5 to differentiate between adsorbed NO and NO_2 as the 2133 cm^{-1} species. First, NO was adsorbed on CuHZSM5 at 3 Torr (fig. 6A). Previous experiments indicated

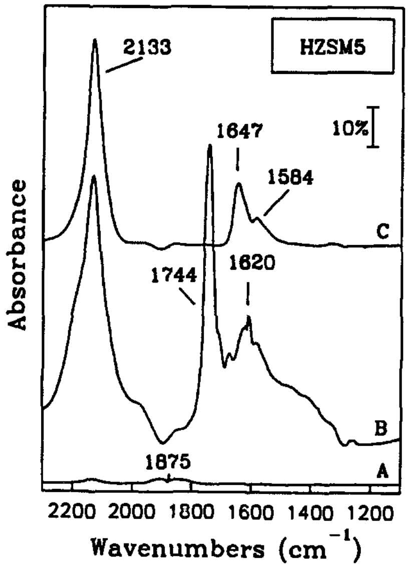

Fig. 5. Spectra for HZSM5 at 25°C: (A) after adsorption of 15 Torr NO; (B) after adsorption of 3 Torr NO_2; (C) after 1 h evacuation of NO_2.

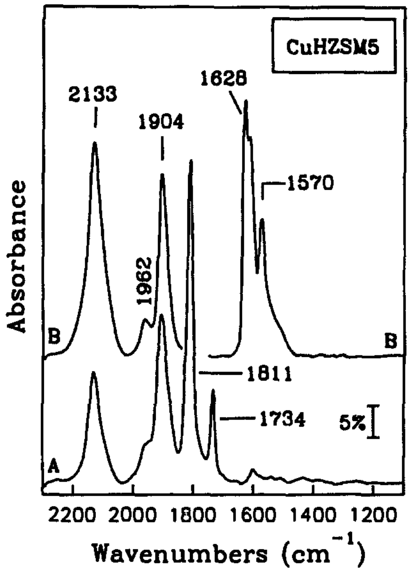

Fig. 6. Co-adsorption experiment for CuHZSM5 at 25°C: (A) after initial adsorption of 3 Torr NO; (B) after subsequent addition of a small dose of O_2.

that at this NO pressure, the sites involving the 2133 cm^{-1} species were not yet saturated. Next, a small amount of oxygen was leaked into the system (fig. 6B). The amount added was less than what would be required for total conversion of NO to NO_2. Fig. 6 shows that upon oxygen addition, the band at 1904 cm^{-1} due to NO^+ on cupric ions did not change significantly. The bands due to NO^- and $(NO)_2^-$ on cuprous ions were completely extinguished. Instead, bands assigned to adsorbed NO_2^- and monodentate NO_3^- appeared; however, the band due to adsorbed N_2O_4 was not manifest. Fig. 6 also reveals a sharp increase of the band at 2133 cm^{-1} after addition of a small amount of oxygen.

For the experiments of fig. 6, there were changes in the hydroxyl stretching region, as well. The spectrum of the evacuated sample before adsorption (fig. 7A) revealed bands at 3744 and 3615 cm^{-1} due to O–H stretching of isolated SiOH and bridging Si(OH)Al framework hydroxyls, respectively [15,17]. Upon adsorption of NO (fig. 7B), both these bands decreased but the band due to the more acidic Brønsted sites (3615 cm^{-1}) attenuated more sharply. No frequency shifts due to hydrogen bonding were observed. Upon subsequent addition of oxygen, the band at 3615 cm^{-1} attenuated even more, while the band at 3744 cm^{-1} hardly changed (fig. 7C).

4. Discussion

Currently, the most effective catalyst for the reduction of NO in net-oxidizing automotive exhaust is Cu-ZSM-5 [2]. Infrared spectroscopic studies of NO adsorp-

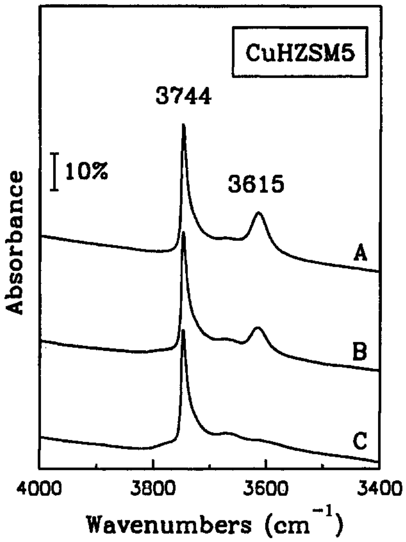

Fig. 7. Hydroxyl stretching region during co-adsorption experiment for CuHZSM5 at 25°C: (A) after 1 h evacuation of oxygen; (B) after initial adsorption of 3 Torr NO; (C) after subsequent addition of a small dose of O_2. Note: these difference spectra are with respect to the spectrum of the empty, evacuated IR cell.

tion on Cu-ZSM-5 have permitted the characterization of various surface species and several absorption bands have been definitively assigned. However, for the band at 2133 cm^{-1}, several questions remain regarding the identity and the adsorption site of the species involved.

4.1. NATURE OF THE 2133 WAVENUMBER SPECIES

In section 3, carbon-based impurities and N_2O were excluded as sources of the 2133 cm^{-1} band observed during NO adsorption. NO_2 adsorption on CuHZSM5 revealed a relatively strong band at 2133 cm^{-1} (fig. 3A). However, the band observed for 3 Torr of NO_2 was less intense than the one observed for 3 Torr of NO (15 vs. 20% absorption). By itself, this observation would oppose an assignment of the 2133 cm^{-1} band to an adsorbed NO_2 species such as NO_2^+ [4]. This is because under 3 Torr of NO, the small amount of NO_2 present is not expected to yield an intensity greater than that observed under 3 Torr of NO_2. In fact, fig. 6A confirms that at 3 Torr of NO only a small amount of adsorbed NO_2 is apparent at 1603 cm^{-1}.

For NO_2 adsorption on CuHZSM5, however, increasing pressures resulted in additional bands in the region between 2300 and 1900 cm^{-1} (fig. 3). If these additional bands were also the result of NO_2^+, possibly due to adsorption on slightly different sites [8,18], this would increase the likelihood that the 2133 cm^{-1} band is due to NO_2^+ since now, at least, the total amount of NO_2^+ would be greater under NO_2 than under NO. In addition, if adsorbed NO_2 occupies the same adsorption sites as NO_2^+, this would also make the assignment of the 2133 cm^{-1} band to NO_2^+ more plausible. This is because during NO_2 adsorption, adsorbed NO_2 would effectively poison these sites, whereas this poisoning effect would be largely absent during NO adsorption.

Oxygen addition creates a competition between adsorbed NO and NO_2 species for the adsorption sites associated with the band at 2133 cm^{-1}. Fig. 6B shows that upon addition of the oxygen aliquot to NO adsorbed on CuHZSM5, the 2133 cm^{-1} band nearly doubled. This would suggest that the 2133 cm^{-1} band is due to the formation and adsorption of NO_2. Considering the band assignment by Teranishi and Decius [9] for NO_2^+ in nitrogen pentoxide, the 2133 cm^{-1} species is most likely adsorbed NO_2^+. Upon NO adsorption, NO_2 may form due to reaction of NO with residual surface oxygen atoms [7]; it has been shown that copper ions in Cu-HZSM-5 effectively catalyze the reaction [19].

4.2. SITE SPECIFICITY OF THE 2133 WAVENUMBER SPECIES

Previously, the 2133 cm^{-1} band has been assigned to adsorbed NO_2^+ ions on cupric [10] or cuprous [6] ions. Regarding the first site assignment, the absence of the 2133 cm^{-1} band in the spectrum of NO adsorbed alumina-dispersed CuO (fig. 4B) meant that the corresponding species was not adsorbed on nonexchanged copper ions. The NO_2^+/Cu^+ site assignment was later withdrawn [7] but here, for CuHZSM5, it seems particularly reasonable when one considers ESR studies [18] which indicated the formation of $Cr^+NO_2^+$ and $Ni^+NO_2^+$ complexes upon adsorption of NO_2 on Cr- and Ni-exchanged zeolite Y. However, subsequent experiments on the HZSM5 support revealed absorption bands at 2133 cm^{-1} for both NO and NO_2 adsorption (fig. 5). This indicates that the adsorbed species was not necessarily associated with the metal. In fact, since the highest intensities for the band at 2133 cm^{-1} were observed during NO_2 adsorption on HZSM5, it appears that the primary adsorption sites for the 2133 cm^{-1} species were on the zeolitic support.

Observations in the O–H stretching region may further elucidate the site specificity of the 2133 cm^{-1} species in the zeolite. Figs. 7B and 6A indicate that, upon NO adsorption and the attendant formation of the 2133 cm^{-1} species, the number of framework hydroxyls (3615 cm^{-1}) decreased sharply. Addition of oxygen to induce the formation of a small amount of NO_2 doubled the population of the 2133 cm^{-1} species (fig. 6B) and sharply decreased the number of framework hydroxyls further (fig. 7C).

It is well known that NO_2^+, the species assigned to the band at 2133 cm^{-1}, is formed in sulfuric acid solutions of HNO_3, N_2O_4, N_2O_5, and $H_5C_2NO_3$, where concentrated H_2SO_4 acts as a strong proton donor [20]. ZSM-5 zeolites also contain very strong acid sites [21,22]. To determine if there is a correlation between the 2133 cm^{-1} species and the strongly acidic Si(OH)Al sites of the zeolite, we prepared a correlation plot for the intensity changes at 3615 and 2133 cm^{-1} (fig. 8). Particularly for NO adsorption on HZSM5 and CuHZSM5 there appears to be a strong

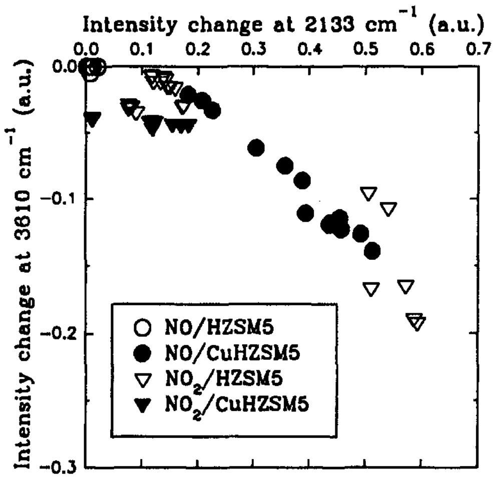

Fig. 8. Correlation plot for the intensities of the bands at 2133 and 3610 cm^{-1} for NO or NO_2 adsorption on HZSM5 or CuHZSM5 at 25°C and at varying times and pressures.

correlation between the intensity changes of these bands (fig. 8, open and solid circles). For NO_2 adsorption, most of the data follow the general trend observed for NO adsorption. There are some data, particularly for NO_2 adsorption on CuHZSM5, that do not appear to follow the general trend. It is possible that these deviations were due to excessive interaction between NO_2^- or NO_3^- ions and framework hydroxyls upon adsorption of NO_2 at relatively high pressures.

It should also be noted that for the co-adsorption experiment of NO and oxygen on CuHZSM5 (fig. 6), upon addition of even more oxygen, the population of isolated SiOH (3744 cm^{-1}) further decreased and the bands at 2165 and 1962 cm^{-1} intensified. These apparent shifts from 2133 cm^{-1} to 2165 and 1962 cm^{-1} are similar to shifts observed when CO [15,17] or nitrogen [23] was adsorbed on weak Lewis and weakly protic SiOH sites, respectively, rather than on strongly acidic Si(OH)Al sites in H-ZSM-5. For NO adsorption on CaY zeolite, Chao and Lunsford [24] also observed several bands which they attributed to NO_2^+ adsorbed on different relatively positive sites.

5. Conclusions

We addressed the nature and site specificity of the species associated with the band at 2133 cm^{-1} observed during NO adsorption on a Cu-ZSM-5 catalyst. Experiments with ^{15}N-labeled NO and separate adsorption experiments with NO_2 on CuHZSM5 indicated that the band at 2133 cm^{-1} was due to adsorbed NO or NO_2. Co-adsorption of NO and oxygen on CuHZSM5 favored adsorbed NO_2 as the corresponding species. Because of the relatively high N–O stretching frequency, the band at 2133 cm^{-1} was assigned to adsorbed NO_2^+ [8,9].

NO and NO_2 adsorption on HZSM5 revealed that NO_2^+ was not necessarily associated with copper ions. The results suggest that the primary adsorption sites were on the zeolitic support. There appears to be a strong correlation between the band intensities at 2133 and 3610 cm^{-1}. This suggests that NO_2^+ vibrating at 2133 cm^{-1} was primarily associated with the framework hydroxyls of the zeolite. These strong acid sites were the first ones to be occupied by NO_2^+. Subsequently, weaker acid sites also adsorbed NO_2^+.

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