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Infrared Spectroscopic Study of the Isocyanate Surface Complex over Cu-ZSM-5 Catalysts

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The adsorption of HNCO on H-ZSM-5 and on Cu-containing ZSM-5, SiO_2, and Al_2O_3 catalysts was investigated by means of Fourier transform infrared spectroscopy in the temperature range 200–673 K. HNCO readily adsorbs on ZSM-5 at 200–300 K to give an intense absorption band at 2260 cm^{-1}. This band is the asymmetric stretch of NCO bonded to Al^{3+}. The formation of Si^{4+}–NCO absorbing at 2300 cm^{-1} requires a higher temperature, at least 373–473 K. The migration of NCO from Al^{3+} to Si^{4+} was observed. The location of absorption bands due to NCO bonded to Cu depended on the state of the Cu; it was at 2230–2240 cm^{-1} for Cu^0–NCO, 2200–2210 cm^{-1} for Cu^+–NCO and 2180–2185 cm^{-1} for Cu^{2+}–NCO. The isocyanate on Cu metal was found to be more stable than that on Pt metals. The spillover of NCO from Cu to the support also occurred, but its extent was less than on the supported Pt metals.

1. INTRODUCTION

The isocyanate (NCO) surface compound formed in the high-temperature reaction between NO and CO on Pt metals supported by various oxides has received considerable attention in the past (1–16). One of the most interesting features of its surface chemistry is that NCO formed on the metals spills over onto the support, where it is accumulated and stabilized (8, 11–20). This led to the belief that the NCO complex detected by IR spectroscopy in the high-temperature NO + CO reaction is a spectator species, and does not play an important role in the reaction. Whether the NCO transitorily existing on the Pt metals participates in the reaction or not remains an open question, however. There are observations that even the NCO residing on the supports reacts readily with water to yield NH_3, (11), indicating that this reaction can contribute to the undesired formation of NH_3 in automobile exhaust catalysis. On the other hand, NCO can be the source of the formation of HCN and $(CN)_2$ (21), which, apart from its dangerous properties, can function as a catalyst poison (17).

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The migration of NCO from the metal onto the support was also observed in a study of the NO + CO reaction on NiY zeolite and PdY zeolite catalysts (22); this was one of the first studies in which zeolite was applied as a support in this area. The recent discovery of the Cu-ZSM-5 catalyst for NO removal in the presence of O_2 (23) initiated a great amount of work concerning the application of zeolite as a support or framework for the transition metals (24, 25) and a renewed interest in the Cu catalyst too. The role and the nature of the Cu sites in ZSM-5 have been extensively debated (24), and a great deal of attention has been paid to determination of the structure and coordination of the Cu in ZSM-5 (26). An NCO species has also been detected on this new catalyst, and its participation in NO reduction has been discussed (27, 28). Yoshida *et al.* (27, 28) found a correlation between the efficiency of NO_x reduction with hydrocarbons on Cu-containing catalysts and the formation of the NCO species. They concluded that the NCO intermediate and/or its reaction with NO are a key to efficient NO reduction in the presence of O_2.

In order to establish the possible role of the NCO complex in NO reduction with hydrocarbons, it is necessary to know whether the NCO formed on the Cu remains there or migrates to the inner or outer surface of the zeolite framework, playing no or only a minor role in NO reduction.

The primary aim of the present paper is to determine the IR characteristics of NCO on Cu-ZSM-5 and on Cu-free ZSM-5 of different compositions, and the migration of NCO from the Cu onto the zeolite. In the following papers the reactivity of NCO species towards NO, H_2O, and other gases will be examined. As an NCO species can not be produced on a metal-free support by means of the reaction of NO with CO or hydrocarbons, we used HNCO as a source of NCO complex.

2. EXPERIMENTAL

The following supports were used: Al_2O_3 (Degussa), SiO_2 (Cab-O-Sil and Aerosil), and H-ZSM-5, with Si/Al

0021-9517/95 $12.00

TABLE 1

Fundamental Vibrations for Gaseous HNCO (30)

Assignments	Absorption bands (cm^{-1})
$\nu_1(a')$	3531
$\nu_2(a')$	2274
$\nu_3(a')$	1327
$\nu_4(a')$	798
$\nu_5(a')$	572
$\nu_6(a'')$	670

ratios of 40.0 and 13.8. The Cu/support samples were prepared by incipient wetting of oxidic supports with an aqueous solution of $CuCl_2$ (Johnson-Matthey). The Cu content was in general 2 wt%. For the preparation triply distilled water was used. After impregnation, the sample was dried in air at 373 K and pressed into self-supporting wafers (30 × 10 mm, 10 mg/cm^2). The Cu-ZSM-5 sample was prepared by ion exchange of Na-ZSM-5 (Si/Al = 40.0) zeolite with aqueous solution of copper acetate. The exchanged sample was washed, dried, and calcined at 773 K for 5 h. The amount of Cu^{2+} ion exchanged was determined by X-ray fluorescence analysis and was found to be 2.3 wt%, representing a nominal exchange degree of 112% (29). The structural properties of this sample have been described elsewhere (29). The pretreatment of samples was performed in a vacuum IR cell in the following way: dried samples were oxidized with 100 Torr of O_2 for 60 min at 573 K, and evacuated at 300 K for 15 min, (denoted: T_{OX} = 573 K). Reduced samples were obtained by reduction of oxidized discs in 100 Torr of H_2 for 60 min at 673 K (denoted: T_R = 673 K). This was followed by degassing for 30 min at room temperature.

HNCO was prepared by the reaction of saturated aqueous KNCO solution with 95% H_3PO_4 at 300 K. The product was purified several times by bulb-to-bulb distillation under vacuum conditions.

Experiments have been carried out in a greaseless vacuum IR cell, which was connected to a closed circulation system. Infrared spectra were recorded with a Bio-Rad Fourier transform IR spectrometer (FTS7) with a wavenumber accuracy of ±2 cm^{-1}. Typically 16 scans were recorded. All the spectra presented in the paper are difference spectra. Subtractions of the spectra were taken without the use of a scaling factor (f = 1.0000).

3. RESULTS

3.1. Adsorption of HNCO on H-ZSM-5 and its Constituents

Fundamental vibrations of gaseous HNCO are listed in Table 1 (30). In the present case the ν_1 and ν_2 were observed at 3535 and 2267–2277 cm^{-1}, respectively. Figure 1 shows the IR spectrum of ZSM-5 with a Si/Al ratio of 40 in the high-frequency region following HNCO adsorption at 200 and 300 K, and after subsequent degassing. Adsorption of HNCO at 200 K produced a band at 3524 cm^{-1}, which is very likely due to the ν_1 of weakly adsorbed HNCO. This band also appeared when the adsorption was performed at 300 K. Another band was detected at around 3388 cm^{-1}, which we associate with an OH group produced by the dissociative adsorption of HNCO at this temperature. The complete elimination of these bands required an extended degassing at 373–473 K.

Henceforth we deal with spectral changes observed for the asymmetric stretch (ν_2) of isocyanate, as the symmetric stretch (ν_3) can not be analyzed due to the low transmittance of silica-containing samples in the low-frequency region. After degassing the HNCO-exposed H-ZSM-5 sample at 300 K for 15 min, an intense absorption band remained at 2260 cm^{-1} in the spectrum (Fig. 2A). Further evacuation at 373–473 K led to a significant attenuation of this band. Its complete elimination required a temperature as high as 573 K. In parallel with the attenuation of

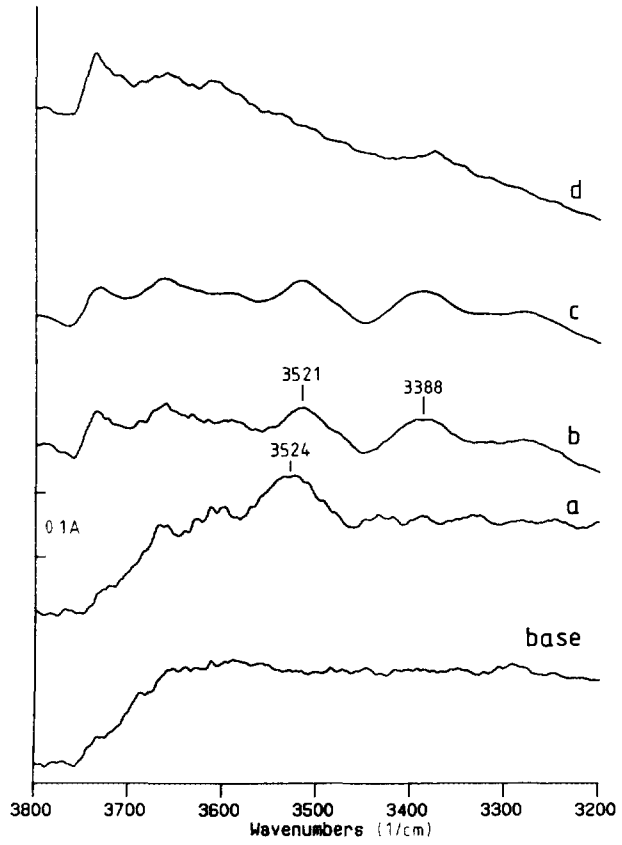

FIG. 1. Infrared spectra of ZSM-5 following HNCO adsorption at 200 K (a), and after subsequent degassing at 300 K (b), 373 K (c), and 473 K (d).

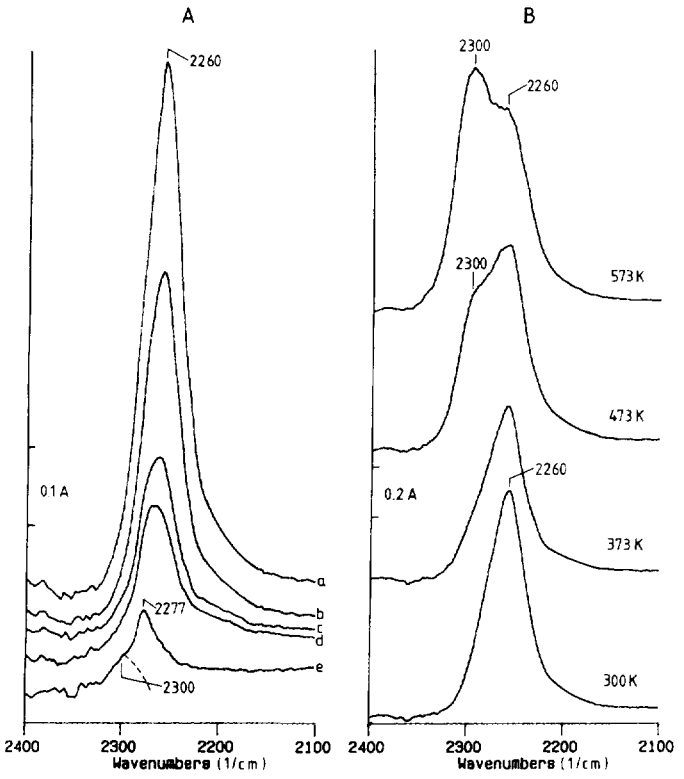

FIG. 2. (A) Infrared spectra of ZSM-5 following HNCO (5 Torr) adsorption at 300 K and after extended degassing at 300–473 K. (a) 300 K, 30 min; (b) 300 K, 180 min; (c) 373 K, 30 min; (d) 473 K, 15 min; (e) 473 K, 120 min. (B) Infrared spectra of ZSM-5 following adsorption of HNCO at different temperatures and then degassing at 300 K.

the band, it shifted slightly to a higher frequency, 2277 cm^{-1}, and at the same time, a shoulder developed at 2300 cm^{-1} (Fig. 2A).

When the sample was kept in HNCO at different temperatures for 15 min and then evacuated at room temperature, in addition to the band at 2260 cm^{-1}, a strong band developed at 2300 cm^{-1} at 473 K; its intensity increased with the increase of the adsorption temperature (Fig. 2B).

Some measurements were performed on Na-ZSM-5 and H-ZSM-5 samples with a Si/Al ratio of 13.8. We experienced similar spectral features as observed in the previous case. The difference was that the intensity ratio of the 2300 and 2260 cm^{-1} bands for the annealed samples was somewhat less.

As ZSM-5 is built up from Al–O and Si–O groups, the adsorption of HNCO was examined on Al_2O_3 and SiO_2 surfaces separately. In harmony with previous observations (14), HNCO interacts readily with Al_2O_3 at 300 K, yielding an intense absorption band at 2255 cm^{-1} (Fig. 3A). This band started to attenuate at 473 K and disappeared only after extensive evacuation above 673 K.

Figure 3B shows IR spectra of SiO_2 as a function of the temperature of HNCO adsorption. Absorption bands due to gaseous HNCO can be removed quickly by degassing the sample at 300 K, and only a very weak band remained in the spectrum at 2300 cm^{-1}. When the SiO_2 sample was kept in HNCO at higher temperatures; the intensity of the 2300 cm^{-1} band gradually increased with elevation of the adsorption temperature. This band is very stable and it weakened very slowly during continuous evacuation, even at 673 K. It could be eliminated only through high-temperature oxidation.

3.2. *Adsorption of HNCO on Cu-ZSM-5*

At low HNCO exposure, first a band at 2203 cm^{-1} appeared in the spectrum of Cu/ZSM-5 (T_R = 673 K). As the HNCO pressure was raised, its intensity increased and another band developed at 2264 cm^{-1}. The intensities of both bands decreased slightly after the prolonged evacuation, even at 300 K, but decreased markedly at 373 K. A shoulder at 2300 cm^{-1} can be seen even at 300 K, the intensity of which remained practically constant. The band at 2200 cm^{-1} could be detected even after 60 min of evacuation at 373 K. Characteristic spectra are displayed in Fig.

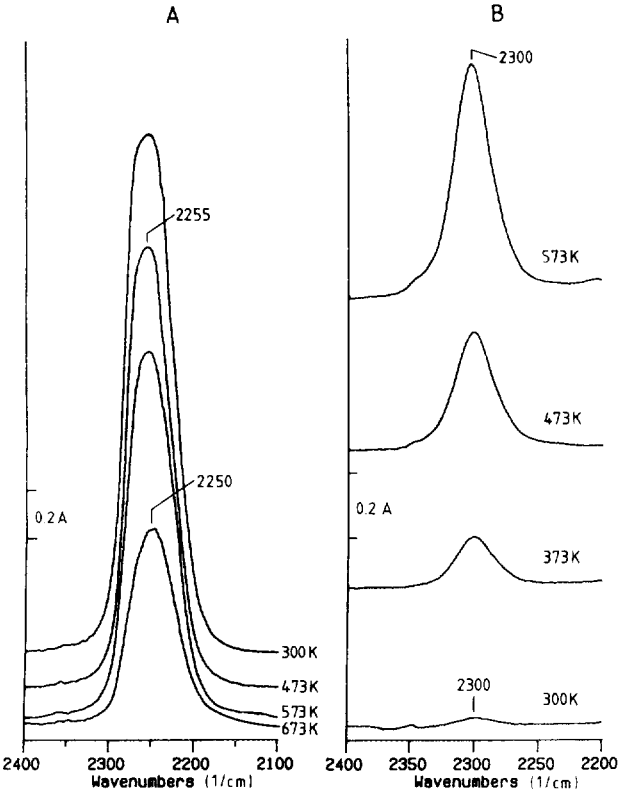

FIG. 3. Infrared spectra of Al_2O_3 (A) and SiO_2 (B) following HNCO (5 Torr) adsorption at 300 K and degassing at different temperatures for 15 min.

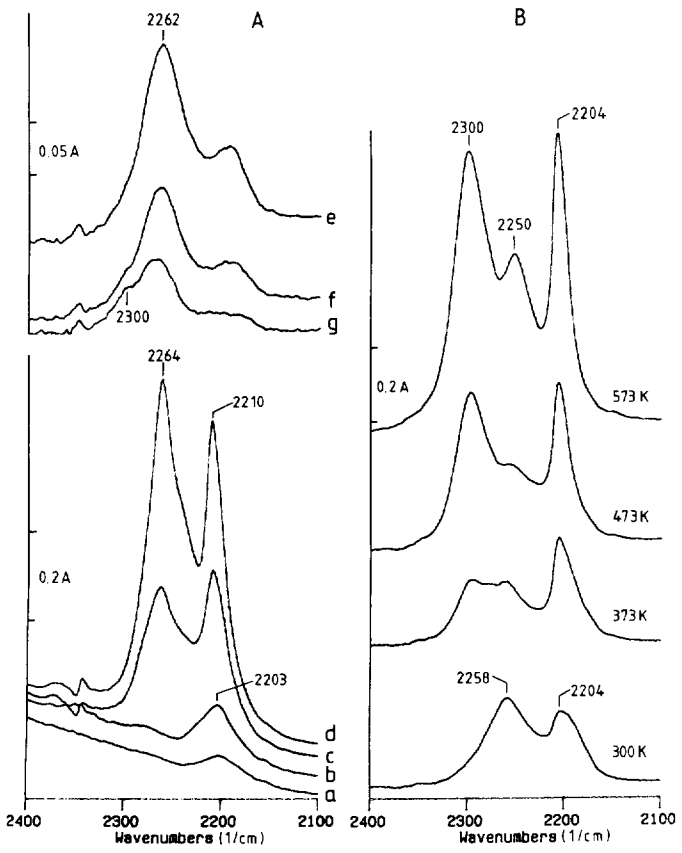

FIG. 4. (A) Infrared spectra of Cu-ZSM-5 (T_R = 673 K) following HNCO adsorption at 300 K and degassing at different temperatures, and (B) following HNCO adsorption (5 Torr) at different temperatures and then degassing at 300 K. For (A), the pressure of HNCO in Torr was (a) 3×10^{-2}, (b) 1×10^{-1}, (c) 5×10^{-1}, (d) 1.0, and evacuation was (e) at 300 K for 60 min, (f) for 180 min, and (g) 373 K for 30 min.

4A. With the increase of the adsorption temperature a new band also developed at 2300 cm^{-1} at 373 K, and the intensities of the three bands at 2200, 2250–2260, and 2300 cm^{-1} were enhanced (Fig. 4B). In this experiment, the degassing of the sample was always performed at room temperature for 15 min.

A different picture was obtained when the reduction temperature was lowered to 548 K and the adsorption of HNCO was performed at 200 K (Fig. 5). In the presence of HNCO absorption bands at 2206, 2240, and 2260 cm^{-1} were registered. Evacuation at 300 K eliminated the 2260 cm^{-1} band due to weakly held HNCO and left an intense band at 2240 cm^{-1} and a weaker band at 2203 cm^{-1}. Upon raising of the degassing temperature to 573–673 K bands can be identified at 2204, 2250, and 2305 cm^{-1}.

On an oxidized sample (T_{OX} = 573 K), a new band (undetected previously) appeared at 2180 cm^{-1} at low HNCO pressure, together with the bands at 2200 and 2240–2255 cm^{-1} (Fig. 6A). With elevation of the HNCO pressure, the intensity of the 2180 cm^{-1} band exceeded that of the other two bands. The intensity of the 2180 cm^{-1} band was only slightly reduced by room-temperature evacuation, but the band became only a shoulder on degassing at 373 K. The other two bands, at 2200 and 2240–2250 cm^{-1}, attenuated only at 373–473 K. There was no indication of the formation of a band at 2300 cm^{-1} for the sample degassed up to 573 K (Fig. 6B).

The adsorption of HNCO (5 Torr) at increasing temperature (and evacuation at 300 K) produced four rather strong bands, at 2182, 2200, 2240–2250, and 2300 cm^{-1}. The latter markedly intensified after high-temperature adsorption.

HNCO was also adsorbed on the Cu-ZSM-5 sample which was evacuated at 1123 K for 90 min. According to the measurements of Anpo *et al.* (31), this treatment leads to the reduction of Cu^{2+} to Cu^{1+}. In this case the adsorption temperature was 200 K. IR spectra of the adsorbed HNCO

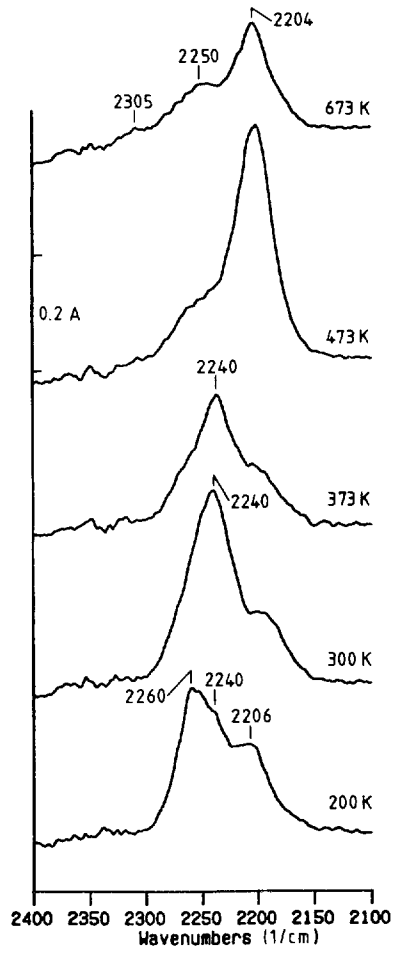

FIG. 5. Infrared spectra of Cu-ZSM-5 (T_R = 548 K) following HNCO (2×10^{-1} Torr) adsorption at 200 K and subsequent degassing at different temperatures.

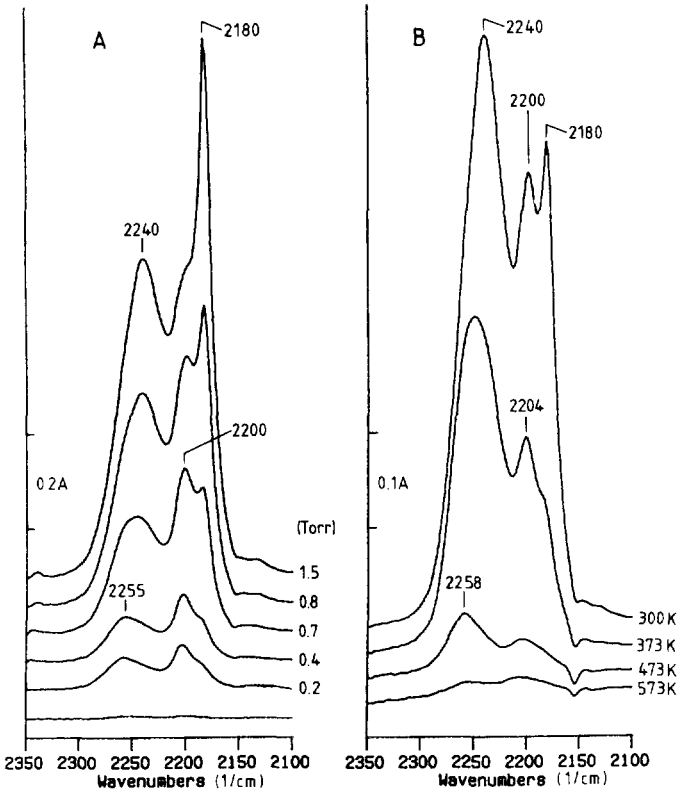

FIG. 6. (A) Infrared spectra of Cu-ZSM-5 (T_{OX} = 573 K) following HNCO adsorption for different pressures at 300 K and (B) degassing at different temperatures.

are displayed in Fig. 7A. Absorption bands developed at 2206, 2227, and 2263 cm^{-1}, even at low HNCO pressure. The bands at 2206 and 2263 cm^{-1} became very strong at 5×10^{-1} Torr of HNCO, when the 2227 cm^{-1} band is no longer discernible. Above this pressure, the spectral features of gaseous HNCO dominated the spectrum. Extended degassing (60 min) at 300 K eliminated these features, and two strong absorption bands remained, at 2207 and 2253 cm^{-1}. These bands markedly attenuated at 373 K, when the 2253 cm^{-1} band shifted to 2267 cm^{-1}. Both bands disappeared at 473 K (30 min) or decayed to a very low level. A weak, stable band at 2300 cm^{-1} is distinguished at and above 373 K (Fig. 7B)

3.3. Adsorption of HNCO on Cu/SiO_2 and Cu/Al_2O_3

In order to promote an understanding of the spectra obtained for Cu-ZSM-5, some measurements were performed on SiO_2- and Al_2O_3-supported Cu.

Following the adsorption of HNCO on Cu/SiO_2 (T_R = 673 K) at 200 K, degassing of the sample at the same temperature produced intense absorption bands at 2243 and 2260 cm^{-1} (Fig. 8). The intensity of the latter gradually decreased with elevation of the evacuation temperature between 200–300 K, suggesting that it is due to weakly adsorbed HNCO. The 2243 cm^{-1} band remained unaltered up to 300 K, when two weak bands could be distinguished, at 2200 and 2300 cm^{-1}. These two remained practically constant after high-temperature degassing, whereas the 2240 cm^{-1} band shifted slightly to lower frequencies, and significantly decayed (Fig. 8). It disappeared completely only at 673 K. When the Cu/SiO_2 sample was kept in HNCO at 373 K, a strong band developed at once at 2300 cm^{-1}; it became more intense at higher adsorption temperature.

Adsorption of HNCO on oxidized 2% Cu/SiO_2 (T_{OX} = 573 K) at both 200 and 300 K produced two intense bands, at 2185 and 2206 cm^{-1}, at low pressure. At higher HNCO pressure, the feature characteristic of gaseous HNCO appeared, and a weaker band at around 2300 cm^{-1} could also be separated. After degassing at 300 K, three bands remained in the spectrum, at 2185, 2215, and 2300 cm^{-1} (Fig. 9).

In the subsequent experiments, the interaction of HNCO with the Cu_2O/SiO_2 catalyst was examined. This sample was prepared by the oxidation of reduced Cu/SiO_2 (T_R = 623 K) with 100 Torr of N_2O at 623 K for 17 h (31). Adsorption of HNCO on this sample at 200 K produced a very strong band at 2206 cm^{-1} and a weak one at 2233 cm^{-1}. No other spectral features were detected when the adsorbed layer was heated to 300 K under constant evacuation.

The adsorption of HNCO produced different features for Cu/Al_2O_3. Independent of the adsorption temperature, we obtained only a strong absorption band at 2255–2260 cm^{-1}, as in the case of Cu-free Al_2O_3.

In order to obtain further information on the location of the NCO band on Cu^{2+} a 2 wt% $CuCl_2/SiO_2$ sample was prepared. SiO_2 impregnated in $CuCl_2$ solution was dried at 300 K. The $CuCl_2/SiO_2$ disc was evacuated at 300 K for 30 min in the IR cell without any further treatment. Adsorption of HNCO on this sample at 200 K produced a band at 2190 cm^{-1}. With increase of the HNCO pressure, the band intensified, and features of gaseous HNCO appeared. After the degassing of the sample the position of the band shifted to 2186 cm^{-1}, and it gradually attenuated at increasing degassing temperatures. No other bands (except for the usual weak band at 2300 cm^{-1}) were seen in the spectra at 200–300 K. The 2185 cm^{-1} band was present up to 373 K (Fig. 10).

Table 2 lists the IR bands observed for NCO species on the Cu-containing samples studied in this work.

4. DISCUSSION

4.1. NCO on Oxide Surfaces

Before our interpretation of the results, we should summarize the main features of NCO species on oxide surfaces

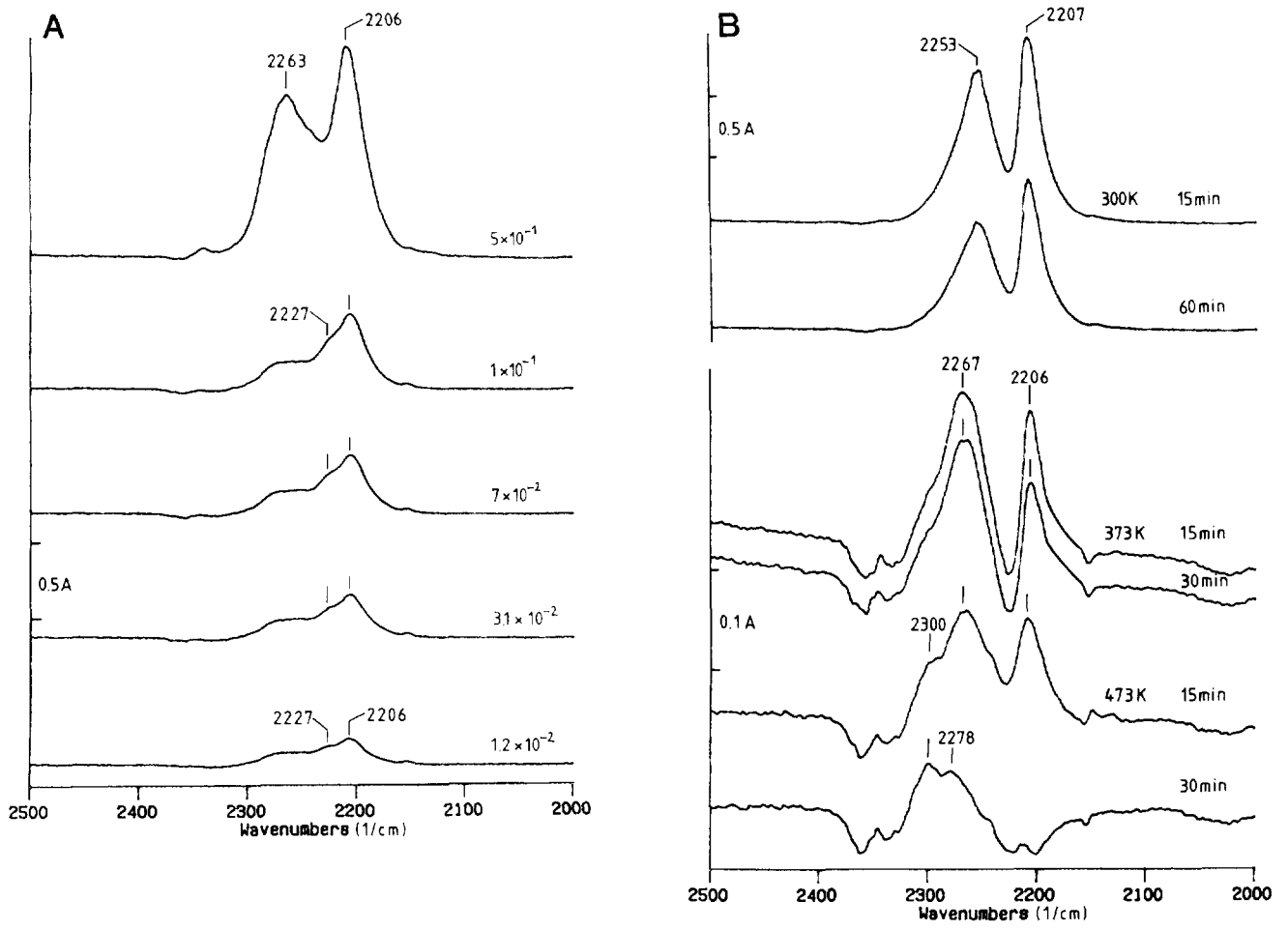

FIG. 7. (A) Infrared spectra of Cu-ZSM-5 (evacuated at 1123 K for 90 min) following HNCO adsorption at 300 K and (B) degassing at different temperatures.

(13). Characteristic vibrations of NCO adsorbed on various oxides are collected in Table 3. The data clearly show that the position of the asymmetric stretch of NCO depends on the nature of the support, it decreases in the sequence $SiO_2 > Al_2O_3 > MgO > Cr_2O_3 > TiO_2$. The stability of the NCO band follows the same sequence; it is very stable on SiO_2, from which its complete removal can be achieved only by oxidation above 673 K. In contrast, on TiO_2 and Cr_2O_3 the NCO species decomposes quickly, even at 473 K.

4.2. NCO on H-ZSM-5

The results obtained in this work revealed that the positions of the NCO bands produced by HNCO adsorption depend on the adsorption temperature and on the composition of the zeolite. For adsorption up to room temperature, the development of a band of 2260–2267 cm^{-1} is favored for both H-ZSM-5 samples studied in this work. The position of this band suggests that it is due to NCO bonded to Al^{3+}. Annealing of the adsorbed layer causes not only the attenuation of this band, but also the appearance of a weak band at 2300 cm^{-1}. On the basis of the data obtained for SiO_2, this latter band is associated with NCO bonded to Si^{4+}. The development of this band suggests that a fraction of the NCO migrates from Al^{3+} to Si^{4+}. The driving force of this migration is the higher stability of the Si–NCO bond compared to that of the Al–NCO bond.

At higher adsorption temperatures, the formation of Si–NCO is clearly favored. In this case, the initial intensity of the 2300 cm^{-1} band (Si–NCO) was much higher than that of the 2260 cm^{-1} band (Al–NCO). This was particularly so when gaseous HNCO was evacuated at the adsorption temperature.

From a comparison of the spectra obtained for H-ZSM-5 samples with different compositions the adsorption of HNCO on a sample with a lower Si/Al ratio, 13.8, produced

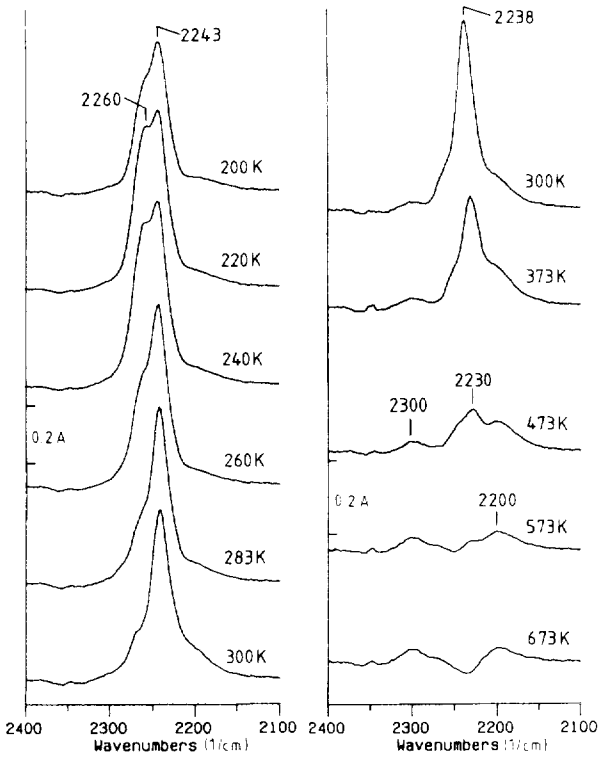

FIG. 8. Infrared spectra of 2% Cu/SiO_2 (T_R = 673 K) following HNCO adsorption at 200 K and degassing at different temperatures.

a less intense band at 2300 cm^{-1} due to Si–NCO; and the development of the band due to Al–NCO occurred more easily.

4.3. *NCO on Cu/SiO_2 and Cu/Al_2O_3*

Determination of the locations of NCO bands on various supports greatly facilitates an evaluation of the positions of the NCO bands on Cu. From the data presented in Table 2, it appears that the asymmetric stretch of the NCO species on metallic Cu is at 2230–2240 cm^{-1}. The formation of this band was observed at as low as 200 K. This species is stable up to room temperature, whereas it is attenuated above 373 K. This attenuation is mainly due to the decomposition of NCO, for its migration from Cu to SiO_2 is rather limited under these conditions, as indicated by the relatively weak band at 2300 cm^{-1}. The spillover of NCO to SiO_2 proceeded to a greater extent when Cu/SiO_2 was kept in HNCO vapor at higher temperatures (at and above 373 K) for an extended period of time.

Different spectral features were observed for fully oxidized Cu/SiO_2. At 200 K, when formation of the Si–NCO species can be excluded, we distinguished two bands, at 2185 and 2200–2100 cm^{-1}. For an evaluation of the adsorption sites of these bands, the results obtained for other Cu-containing SiO_2 samples should be taken into account. Adsorption of HNCO on $CuCl_2/SiO_2$ produced only one intense band, at 2185–2190 cm^{-1} (Fig. 10). As this sample underwent no treatment under vacuum above room temperature it appears safe to conclude that it contains only the Cu^{2+} ion. The absorption band at 2185–2190 cm^{-1} is associated with the Cu^{2+}–NCO species.

The NCO band appeared at 2200–2210 cm^{-1} when HNCO was adsorbed on SiO_2 containing Cu^+. Accordingly, we attribute this band to the vibration of NCO bonded to Cu^+.

In the light of these results and considerations, the 2180–2185 and 2200–2210 cm^{-1} bands observed for oxidized Cu/SiO_2 catalysts are ascribed to the asymmetric stretches of NCO bonded to Cu^{2+} (Cu^{2+}–NCO) and Cu^{1+} (Cu^{1+}–NCO), respectively. The fact that the NCO band associated with Cu^+ appeared for the oxidized sample is in harmony with the experience that the partial reduction of CuO occurs on SiO_2 under high vacuum, even at room temperature. If this explanation is accepted, the sequence of stability of NCO on different Cu samples is as follows: Cu^{1+} – NCO > Cu° – NCO > Cu^{2+} – NCO. Note that this stability order is different from what expected on the basis of the structure of *d* orbitals and electronic properties of

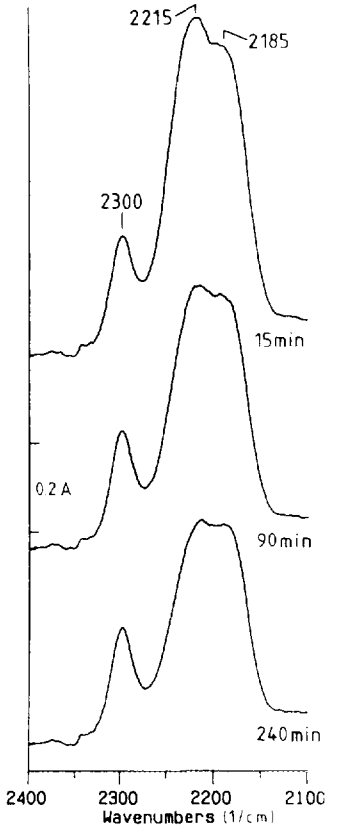

FIG. 9. Infrared spectra of 2% Cu/SiO_2 (T_{OX} = 573 K) following HNCO adsorption at 300 K and degassing for different times at 300 K.

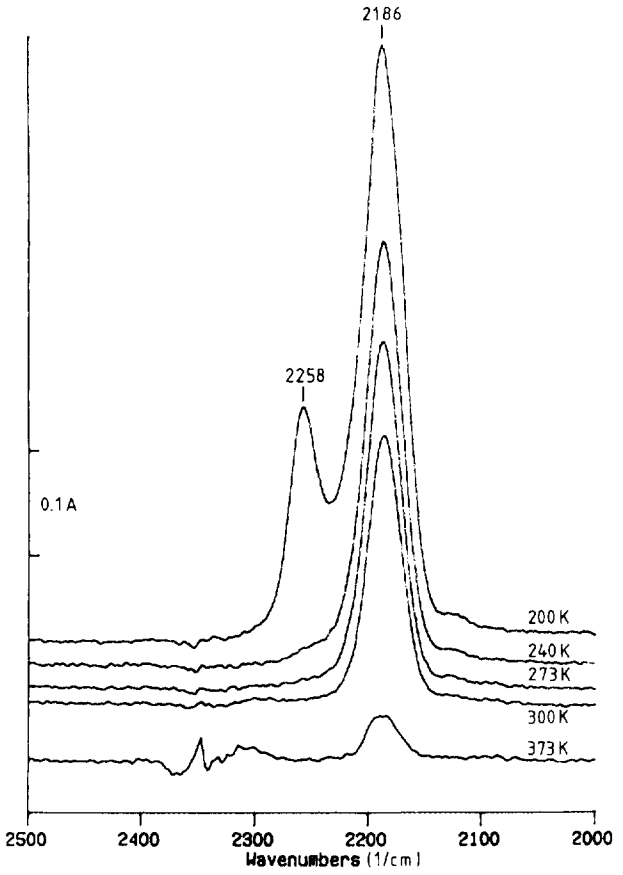

FIG. 10. Infrared spectra of 2% $CuCl_2/SiO_2$ following HNCO adsorption at 200 K and subsequent degassing at different temperatures.

copper. At present we can not propose an explanation for this feature.

4.4. NCO on Cu/ZSM-5

For oxidized Cu/ZSM-5, we also identified the two absorption bands at 2182 and 2202 cm^{-1}, which we attributed above to NCO adsorbed on Cu^{2+} and Cu^{+}, respectively. In addition, the band due to Al^{3+}–NCO was also observed at rather low temperatures. The 2300 cm^{-1} band indicative of the formation of Si–NCO was detected first at 373 K. The spectral feature at 2206 cm^{-1} dominated the spectrum for the partially oxidized sample containing mainly Cu^{1+} ions (Fig. 6). A weak band at 2227–2230 cm^{-1} due to Cu°–NCO was also detected, indicating the presence of metallic copper.

An interesting feature of the Cu-ZSM-5 sample reduced at 673 K is that the absorption band attributed to NCO bonded to Cu metal for Cu/SiO_2 did not appear following the adsorption of HNCO at 200–300 K. Instead, we obtained bands at 2200–2206 and 2260–2264 cm^{-1}. The appearance of the band at 2200–2206 cm^{-1} indicates that a considerable fraction of the Cu^{1+} is stabilized in ZSM-5 and escapes reduction at 673 K, which is in harmony with the behavior of Cu/ZSM-5 catalyst. As regards the 2260–2264 cm^{-1} band, an obvious explanation is that it belongs to the Al^{3+}–NCO species. The most probable reason for the lack of the band due to Cu°–NCO is that the reduction of Cu-ZSM-5 produced large Cu crystallites, the adsorption capacity of which is very low, particularly in comparison with other adsorption sites also present (26). In accord with this when the reduction temperature was lowered to 548 K the strongest band at 300–373 K was at 2240 cm^{-1} (Fig. 5), which we ascribe to NCO bonded to the copper metal.

4.5. Comparison of the Behavior of NCO on Cu and Pt Metals

The adsorption of HNCO has previously been investigated on SiO_2-supported Pt and Rh (14, 17). NCO bonded to the metals has been identified by means of IR spectroscopy at as low as 200 K. In this case, the NCO gave an absorption band at 2185–2195 cm^{-1}. With elevation of the temperature, a fraction of the NCO migrated from the metal onto the SiO_2, while another fraction decomposed to N_2 and CO. Above 300 K, no NCO was detected on the metals by IR spectroscopy (14, 17). In the present case, NCO bonded to Cu metal proved to be much more stable; it disappeared completely only above 473 K. The higher stability of NCO on supported copper accords with the results obtained following HNCO adsorption on metal single-crystal surfaces (Cu(111) (32), Pt(110) and (111) (33,

TABLE 2

The Positions of the Asymmetric Stretch of NCO Following the Adsorption of HNCO on Supported Copper

Sample	Pretreatment	Location of NCO band (cm^{-1})	Adsorption sites
Cu/SiO_2	(T_R = 673 K)	2230–2240	Cu°
		2300	Si^{4+}
Cu/SiO_2	(T_{OX} = 573 K)	2180–2185	Cu^{2+}
		2300	Si^{4+}
Cu-ZSM-5	Si/Al = 40.0	2200–2205	Cu^{1+}
	(T_R = 548 K)	2230–2240	Cu°
		2250–2255	Al^{3+}
		2300	Si^{4+}
Cu-ZSM-5	Si/Al = 40.0	2206	Cu^{1+}
	(T_{evac} = 1123 K)	2225	Cu°
		2254–2263	Al^{3+}
		2300	Si^{4+}
Cu-ZSM-5	Si/Al = 40.0	2180–2185	Cu^{2+}
	(T_{OX} = 573 K)	2200	Cu^{1+}
		2250–2260	Al^{3+}
		2300	Si^{4+}
$CuCl_2/SiO_2$	T_{evac} = 300 K	2185–2190	Cu^{2+}

TABLE 3

The Positions of the Asymmetric Stretch of NCO Following the Adsorption of HNCO on Various Supports

Sample	Origin and pretreatment	Location of NCO band (cm^{-1})	Adsorption sites	Refs.
TiO_2	Degussa P 25 (150 m^2/g)	2210	Ti^{4+}	(13, 14)
Cr_2O_3	$(NH_4)_2Cr_2O_7$	2212	Cr^{3+}	(22)
MgO	DAB 6 (170 m^2/g)	2223	Mg^{2+}	(13, 14)
Al_2O_3	Degussa P 110/1 (100 m^2/g)	2260 2255	Al^{3+}	(13, 14) Present study
SiO_2	Cab-O-Sil (200 m^2/g)	2300	Si^{4+}	(13, 14) Present study
SiO_2	Aerosil (240 m^2/g)	2300	Si^{4+}	Present study
ZSM-5	Si/Al = 40.0	2300 2260	Si^{4+} Al^{3+}	Present study
ZSM-5	Si/Al = 13.8	2300 2260	Si^{4+} Al^{3+}	Present study

34), and Rh(111) (35)) under UHV conditions. NCO on Cu existed even at 493 K, while it decomposed totally on Pt and Rh at around room temperature.

CONCLUSIONS

(i) HNCO adsorbs dissociatively on H-ZSM-5 at 200–300 K to give an absorption band at 2260 cm^{-1}, attributed to Al-NCO. At higher temperatures, above 373 K, formation of the Si–NCO species, characterized by an absorption band at 2300 cm^{-1}, is favored. (ii) The presence of Cu in ZSM-5 provides additional adsorption sites for HNCO adsorption. New bands are produced at 2180–2185, 2200–2210, and 2230–2240 cm^{-1}. These bands are attributed to the asymmetric stretches of Cu^{2+}–NCO, Cu^{+}–NCO, and Cu°–NCO species, respectively. (iii) NCO bonded to Cu metal clusters exhibits a significantly higher stability than those observed for Pt metals.

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