Co-adsorption of acetone and CO on Cu-ZSM-5: an in situ FTIR study

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The adsorption of acetone and its co-adsorption with CO were studied on a solid state ion exchanged Cu-ZSM-5 catalyst using in situ Fourier transform infrared (FTIR) spectroscopy. The C–O stretching vibrational band of adsorbed acetone at Cu^{1+} is centered at 1671 cm^{-1}, red-shifted by 48 cm^{-1} in comparison to that in the gas phase. Adsorbed acetone at the Cu^{1+} site does not eliminate the adsorption of CO onto the same cationic center (and vice-versa); however, the strength of the CO binding is suggested to be weaker to the $\{Cu[(CH_3)_2CO]\}^+$ center than to the adsorbate free Cu^{1+} site and is manifested by a 28 cm^{-1} red-shift in the C–O stretching frequency of adsorbed CO in the former complex in comparison to the latter complex. The position of the C–O stretching vibrational band of adsorbed acetone blue-shifts by about 20 cm^{-1} as a result of the presence of CO on the cationic center. The changes in the C–O stretching vibrational frequencies of the absorption features of the two adsorbate molecules can be rationalized by the changes in the electronic environment at the Cu^{1+} adsorption center.

Keywords: Cu-ZSM-5, CO, acetone, adsorption, infrared spectroscopy

1. Introduction

In heterogeneous catalytic reactions the number of chemically different molecules (both reactants and products) possibly present in the system under study is, in most cases, large. To understand the coordination chemistry relevant to molecular catalysis adsorption studies on prospective materials have been most frequently carried out with single adsorbates. The results of these adsorption studies with single adsorbates may be an oversimplification of a complex chemical system due to the strong and potentially competitive interactions of different molecules with the same adsorption site. For example, in the selective catalytic reduction of NO_x with hydrocarbons in the presence of excess oxygen a multitude of different molecular species are present simultaneously which can strongly interact with Cu^{1+} sites of the Cu-ZSM-5 catalyst. Adsorption studies on this specific catalyst material with single adsorbates are abundant in the literature [1–6]. Recently, a number of studies have been carried out in the presence of two or more adsorbates and some interesting differences have been suggested to have catalytic importance [7–14].

In our previous study on the co-adsorption of acetonitrile and CO on Cu-ZSM-5 we have shown how the adsorption of one adsorbate affects the adsorption and the infrared spectroscopic characteristics of the second adsorbate on the same Cu^{1+} adsorption center [15,16]. Variations in both the electronic and steric environments around the adsorption center have been suggested to be important factors in altering adsorption properties of the second interacting molecule with the adsorption site. The presence of adsorbed acetonitrile at Cu^{1+} site reduces the strength of the $Cu^{1+} \cdots CO$ bond, which is manifested in the large red-shift of the C–O stretching frequency of adsorbed CO on the acetonitrile covered sample as compared to that on the clean Cu-ZSM-5. Furthermore, the adsorption of CO onto $[Cu(CH_3CN)_n]^{1+}$ ($n = 1$ or 2) complexes also alters the C–N stretching frequency of adsorbed CH_3CN. Herein the co-adsorption of $(CH_3)_2CO$ and CO on a solid state ion exchanged Cu-ZSM-5 catalyst is examined and the similarities and differences with respect to acetonitrile and CO coadsorption in constrained geometry environments (zeolites) are discussed.

Of pragmatic importance is the observation [17,18] that water soluble oxygenated organic compounds (e.g., alcohols, aldehydes, ketones, or ethers) serve as reductants for NO_x reduction in the place of simple alkenes such as propene. Therefore, the spectroscopic charcterization of clean well defined Cu samples with the coadsorbates acetone and CO was examined to provide further insight into how Cu centers (predominately Cu^{1+}) coordinate potential reactants. Futhermore, it has been noted that in the catalytic combustion chemistry of CuH-ZSM-5 in the presence of propene and oxygen, small amounts of CO are produced. The spectroscopic results described herein clearly indicate a rich and complex coordination chemistry occurring at temperatures below where combustion chemistry occurs and indicate plausible chemical complexes present under specific conditions.

2. Experimental

The experiments performed in this study were carried out on a solid state ion exchanged Cu-ZSM-5 catalyst. The parent Na-ZSM-5 material was obtained from PQ Corporation. This material was initially ion exchanged for 3×8 h with a 0.1 mol/ℓ NH_4F solution at 350 K. After room temperature filtration and drying at 373 K the ammonium form was decomposed at 870 K to obtain the H-ZSM-5 material which then was used for the preparation of Cu-ZSM-5 catalyst. The solid state ion exchange was carried out in a quartz reactor connected to a vacuum line. Cuprous chloride, in stoichiometrically excess amount (relative to the number of Brønsted sites), was placed on the bottom of the reactor tube and separated from the H-ZSM-5 sample by a thin layer of quartz wool. The reactor was first heated in vacuum overnight at 400 K to remove most of the water present in the system. The reactor then was slowly heated up to 800 K. At this temperature CuCl has sufficiently high vapor pressure for the reaction with the OH groups of the zeolite. The reactor was kept at this temperature for an hour and then the sample was cooled back to room temperature under constant pumping. The resultant Cu-ZSM-5 has the following elemental ratios: $Si/Al = 27$; and $Cu/Al = 2.2$. The high Cu/Al ratio shows that besides the Brønsted acidic protons of bridging hydroxyls some of the terminal silanol groups reacted with CuCl as well. Extensive details regarding the gas phase preconditioning treatments and IR characterization of the solid state ion exchanged Cu-ZSM-5 sample are contained in refs. [16,19]. Experimental IR characterization and critical comparisons with more conventional aqueous ion exchanged Cu-ZSM-5 samples are also contained therein. Experimental IR characterization of the solid state exchanged Cu-ZSM-5 sample indicates no hydroxyl groups present (either silanol or Brønsted sites). Reversibility of all adsorption/desorption processes described in this paper was ascertained by examining the C–O stretching region following periodic experimentation. Reproducibility in the C–O stretching intensities and positions attests to the lack of carbonaceous buildup either at the Cu centers or in pore regions that might block access to such centers. Furthermore, all vibrational features relating to acetone and CO coadsorption were reproducible in intensity and position following multiple repetitive sequential experiments on the same mounted sample.

The adsorption experiments were carried out in a home-built IR cell mounted into the sample compartment of a Mattson Cygnus 100 FTIR spectrometer. The IR cell consisted of a turbomolecularly pumped 275″ conflat six-way cross equipped with KBr vacuum windows and connected to a gas manifold for fast and accurate gas introduction. The sample was mounted vertically into the cell on a double wall stainless steel rod which in turn was attached to a linear motion that enabled us to move the sample in and out of the IR beam. The powder zeolite sample itself was pressed onto a tungsten grid and attached to a special stainless steel sample holder. The temperature of the sample was monitored by a chromel/alumel thermocouple spot-welded to the top center of the tungsten grid. The sample holder then attached to the rod via ceramic feed throughs. This experimental arrangement allowed sample heating to 1200 K and cooling to ~ 110 K. The ultimate attainable base pressure using this pumping arrangement in the IR cell was 1×10^{-7} Torr.

Acetone (Aldrich) was used as received after multiple freeze–pump–thaw cycles. Research purity CO (Matheson) was stored in a glass bulb at 77 K (liquid nitrogen) to eliminate contamination originating from transition metal carbonyls present even at this supplied purity level.

3. Results and discussion

All the adsorption experiments were carried out on a solid state ion exchanged Cu-ZSM-5 catalyst (the same source material previously used in the CH_3CN/CO coadsorption study [16]) in order to eliminate the IR absorption interference originating from the adsorption of $(CH_3)_2CO$ on residual H^+ and Cu^{2+} sites ubiquitous in aqueous ion exchanged CuH-ZSM-5 catalysts. The results of the CO and NO adsorption experiments indicated that the material used herein contains exclusively well dispersed Cu^{1+} sites [16]. Only one sharp absorption feature at 2157 cm^{-1} is observed upon CO adsorption followed by evacuation at room temperature, characteristic of the C–O stretching vibration of a singly bound CO molecule on Cu^{1+}. The only absorption features detectable at the onset of NO adsorption were the ones representing the N–O stretching vibrational features of Cu^{1+} adsorbed mono- (1811 cm^{-1}) and dinitrosyl (1734 and 1824 cm^{-1}) species. Only trace ($< 0.1\%$) amounts of Cu^0 and Cu^{2+} sites were detected in the reduced Cu-ZSM-5 sample [16]. An IR spectral series of adsorbed acetone on Cu-ZSM-5 is shown in fig. 1 obtained with increasing $(CH_3)_2CO$ partial pressure at 300 K sample temperature. At low acetone partial pressure there is only one, sharp absorption feature at 1671 cm^{-1} characteristic of the C–O stretching vibration of adsorbed acetone. The symmetric and asymmetric bending vibrational modes of the CH_3 groups of adsorbed acetone are located at 1372 and 1420 cm^{-1}, respectively. In a recent work, Hoost et al. [14] reported 1682 cm^{-1} for the C–O stretching vibration of adsorbed acetone at Cu^{1+} in a Cu,H-ZSM-5 sample prepared by aqueous ion exchange). This is 11 cm^{-1} higher than observed here for acetone at Cu^{1+} in a Cu-ZSM-5 system, measured at the same sample temperature. This frequency difference is suggested to arise from the presence of protons in the aqueous ion exchanged catalyst sample of ref. [14], which also strongly adsorbs acetone. The overlap between these two absorption features may well explain the higher frequency observed in that study. In our catalyst sample the only adsorption sites present are Cu^{1+} ions, therefore we conclude that the C–O stretching frequency of Cu^{1+} adsorbed acetone molecules is centered

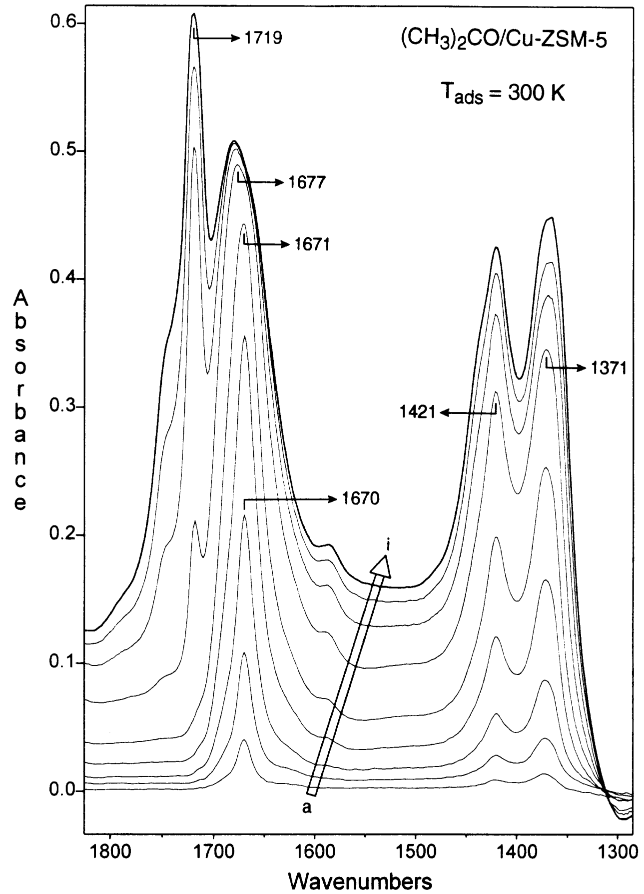

Fig. 1. IR spectra: acetone adsorption on Cu-ZSM-5 at 300 K. Spectra were collected at increasing partial pressure of acetone. Partial pressures of acetone (in Torr) were: a) 0.010; b) 0.021; c) 0.045; d) 0.096; e) 0.138; f) 0.302; g) 0.73; h) 1.81; and i) 1.83.

at 1671 cm^{-1}, which is 48 cm^{-1} red-shifted in comparison to the C–O stretching frequency of 1719 cm^{-1} observed in the gas phase. Hoost et al. [14] assigned the 1377 and 1420 cm^{-1} absorption bands to "carboxylate stretchings" although it is evident that these features are the symmetric and asymmetric bending vibrational modes of the CH_3 groups in adsorbed $(CH_3)_2CO$ molecules [20, and references cited therein]. Increasing the partial pressure of acetone results in an absorption feature at 1719 cm^{-1} characteristic of gas phase acetone and its intensity increases with acetone pressure. Concomitantly, with the appearance of the gas phase acetone feature, the C–O stretch of Cu^{1+} bound acetone significantly broadens and shifts toward higher wavenumbers. At the highest acetone partial pressure studied (~ 5 Torr) this feature has a maximum at 1681 cm^{-1}. Broadening of this band is caused, in part, by the overlap between the C–O features of gas phase and adsorbed $(CH_3)_2CO$, but in addition, the development of a new adsorption complex containing two adsorbed $(CH_3)_2CO$ molecules is suggested. This complex exists only in the presence of excess gas phase acetone. These observations suggest that the adsorption of acetone on the Cu^{1+} centers of a Cu-ZSM-5 catalyst follows the same step-by-step adsorption pattern as seen previously for the adsorption of CH_3CN [16], CO [21] and NO [21,22]. In the present case, however, only two adsorption complexes of Cu^{1+} with acetone, namely $\{Cu[(CH_3)_2CO]\}^{1+}$ (at low acetone pressures) and $\{Cu[(CH_3)_2CO]_2\}^{1+}$ (at high acetone pressures) are suggested to be present. The $\{Cu[(CH_3)_2CO]\}^{1+}$ complex forms readily and it is stable toward room temperature evacuation, while the $\{Cu[(CH_3)_2CO]_2\}^{1+}$ complex exists only in the presence of excess gas phase acetone with the second complexing acetone molecule desorbing upon evacuation from the IR cell.

The co-adsorption of acetone and CO on the Cu^{1+} sites of Cu-ZSM-5 was conducted in two series of separate experiments. In the first series of measurements the Cu-ZSM-5 sample with an initial saturation coverage of acetone (excess gas phase acetone pumped from IR cell) at 320 K was given increasing exposures of CO (CO remaining in cell) and IR spectra were periodically acquired. The IR spectra series are displayed in fig. 2. Panel A of fig. 2 shows the C–O stretching region of acetone, while panel B displays the C–O stretching vibrational region of adsorbed CO. The C–O absorption feature of the adsorbed $(CH_3)_2CO$/Cu-ZSM-5 sample is located at 1671 cm^{-1} (spectrum a). The introduction of a small aliquot of CO onto the $(CH_3)_2CO$ saturated Cu-ZSM-5 sample results in the appearance of an IR absorption band at 2129 cm^{-1}, representative of a C–O stretch from CO coordinated at Cu^{1+} centers which already have one $(CH_3)_2CO$ in their coordination sphere. Concomitant with the appearance of this new band the C–O stretching vibrational feature of adsorbed acetone also changes. Its intensity decreases and a shoulder on the high frequency side of this band appears. As the CO partial pressure increases the 1671 cm^{-1} C–O stretching vibrational band of adsorbed acetone gradually converts into a new band, positioned at 1688 cm^{-1}. The interconversion of these two bands is clearly indicated by the isosbestic point seen at 1677 cm^{-1}. The new feature at 1688 cm^{-1} arises from the C–O stretch of the acetone ligand from a Cu^{1+} complex containing both CO and $(CH_3)_2CO$ ligands in its coordination sphere. The position of the C–O stretch of the adsorbed CO in the $\{Cu[(CH_3)_2CO]CO\}^{1+}$ complex is 28 cm^{-1} red-shifted relative to that of the acetone free $[Cu(CO)]^{1+}$ complex. This result indicates that adsorbed acetone on the Cu^{1+} sites notably modifies the bonding interaction between Cu^{1+} and CO. In the simplest approximation, the binding interaction between Cu^{1+} and $(CH_3)_2CO$ is formed through charge donation from the lone pair electrons of the oxygen atom in the acetone molecule toward the positively charged Cu^{1+} center. As a result of this charge donation and bonding interaction, the Cu^{1+} center becomes partially positively charged and therefore, the incoming CO molecule experiences at the Cu atom an electron charge density and valence bonding which

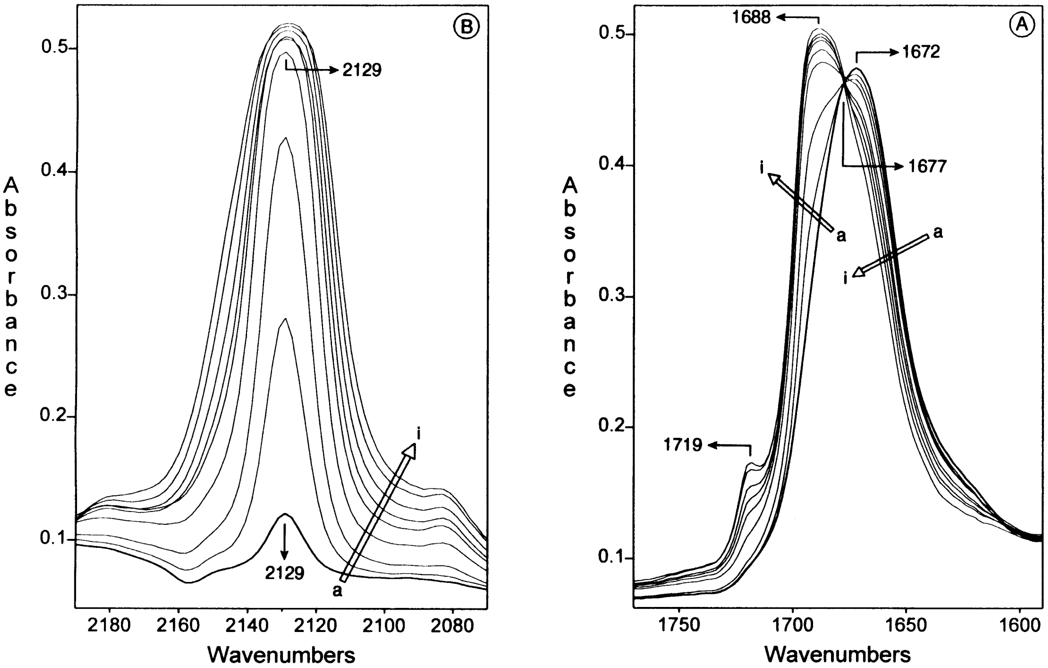

Fig. 2. IR spectra: CO adsorption on an acetone saturated Cu-ZSM-5 sample at 300 K. Spectra in the C–O stretching vibrational region of adsorbed acetone (A) and CO (B) are displayed at increasing CO partial pressure. Partial pressures of CO (in Torr) were: a) 0.005; b) 0.016; c) 0.030; d) 0.058; e) 0.122; f) 0.209; g) 0.66; h) 1.48; and i) 6.03.

are between those characteristic for Cu^{1+} and Cu^{0}. The specific C–O stretching frequencies (in italic print) of adsorbed CO are offered in support of this observation: ($[\mathrm{Cu}(\mathit{CO})]^0$ (2108 cm^{-1}) < ($\{\mathrm{Cu}[(\mathrm{CH_3})_2\mathrm{CO}](\mathit{CO})\}^{1+}$ (2129 cm^{-1}) < $[\mathrm{Cu}(\mathit{CO})]^{1+}$ (2157 cm^{-1}).

It is also interesting to compare the changes in the C–O stretching frequency shift in adsorbed acetone and C–N stretching frequency shift in adsorbed acetonitrile as a consequence of CO coadsorption at the same Cu^{1+} center. As seen previously [15,16], the C–N stretching frequency of Cu^{1+} bound acetonitrile molecules red-shifts upon adsorption of CO while herein the C–O stretching frequency of adsorbed acetone blue-shifts as a result of CO coadsorption. These observations suggest that the adsorption of CO onto the Cu^{1+} centers affects the C–N stretching frequency of adsorbed acetonitrile and the C–O stretching frequency of adsorbed acetone in differing ways. While the C–N bond in the acetonitrile molecule becomes weaker as CO adsorbs onto the same adsorption center, the C–O bond in the acetone strengthens as a consequence of CO adsorption. These results are suggested to be the consequences of differing rehybridization and binding of acetonitrile and acetone onto Cu^{1+} sites. The C–O stretching frequency changes of adsorbed CO show the same trends for both the acetonitrile and acetone containing complexes. In both cases a large red-shift is observed (i.e. weakening of the C–O bond as the Cu^{1+} centers accept electron charge density from either the acetonitrile or acetone molecules).

The acetone/CO co-adsorption experiment was also conducted in the reverse order, the Cu-ZSM-5 sample was first saturated with CO followed by evacuation and then acetone was gradually introduced onto CO$_a$/Cu-ZSM-5. The resulting IR spectral series are shown in fig. 3 for the C–O stretching region of acetone (panel A) and that of adsorbed CO (panel B). The IR spectrum after CO saturation shows a main feature centered at 2157 cm^{-1} (CO singly bound to Cu^{1+} centers) and a low intensity band at 2108 cm^{-1} (CO adsorbed onto residual trace Cu^{0} sites). Introduction of a small amount of acetone onto the CO saturated Cu-ZSM-5 sample induces two new small features to appear in the C–O stretching region of adsorbed acetone at 1671 and 1692 cm^{-1}, the former having higher intensity. These two features represent the C–O stretches of adsorbed acetone in the $\{\mathrm{Cu}[(\mathrm{CH_3})_2\mathrm{CO}]\}^{1+}$ and $\{\mathrm{Cu}[(\mathrm{CH_3})_2\mathrm{CO}](\mathrm{CO})\}^{1+}$ complexes, respectively. Room temperature evacuation of the CO saturated Cu-ZSM-5 sample results in the desorption of a fraction of adsorbed CO from the Cu^{1+} sites, leaving behind a small number of adsorbate free Cu^{1+} centers. Acetone preferentially adsorbs on these adsorbate free Cu^{1+} centers, although not exclusively (even at the lowest acetone pressure studied acetone adsorption onto $[\mathrm{Cu}(\mathrm{CO})]^{1+}$ complexes is clearly evident). With increases in acetone partial pressure the higher frequency band (1692 cm^{-1}) preferentially gains intensity and at high acetone pressures (~ 2 Torr) the low frequency feature (1671 cm^{-1}) is present only as a shoulder on the more intense high frequency band. Concomitant to the intensity increase of the high frequency band, its peak position gradually shifts toward lower wavenumbers, primarily due to the overlap of the

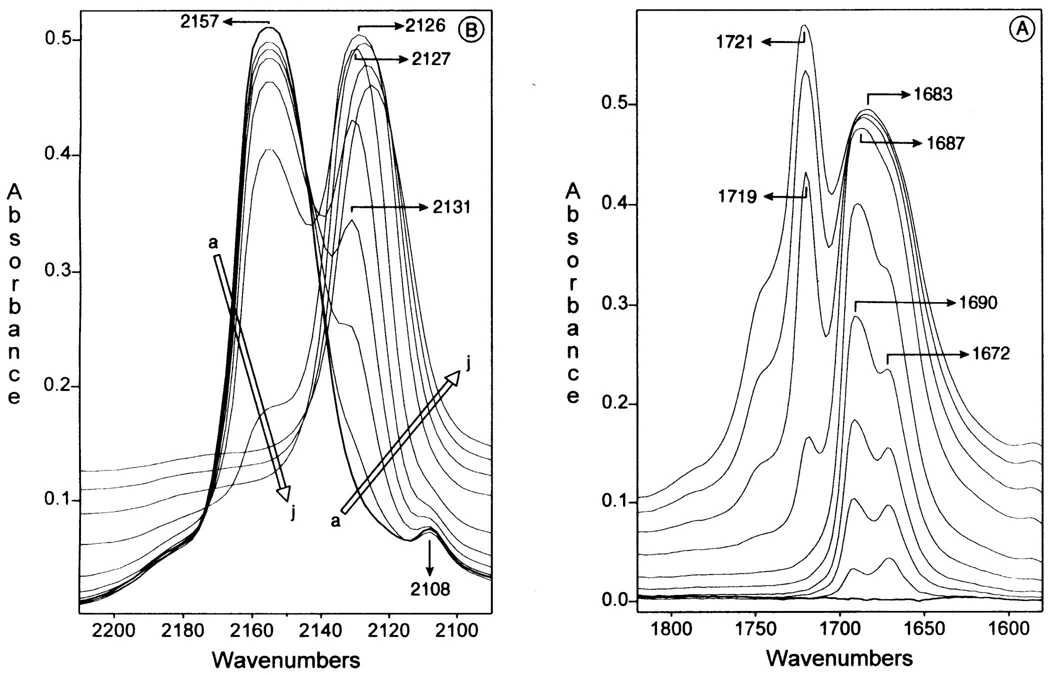

Fig. 3. IR spectra: acetone adsorption on a CO saturated Cu-ZSM-5 sample at 300 K. The C–O stretching vibrational regions of adsorbed acetone (A) and CO (B) are shown as a function of increasing acetone partial pressure. Partial pressures of acetone (in Torr) were: a)< 0.0001; b) 0.016; c) 0.029; d) 0.041; e) 0.065; f) 0.107; g) 0.271; h) 0.484; i) 1.28; and j) 1.68.

absorption bands. At the highest acetone pressure studied (~ 5 Torr) this peak has a maximum at 1683 cm^{-1}. At these acetone partial pressures, gas phase acetone is observed at 1719 cm^{-1}. In the C–O stretching region of adsorbed CO the interconversion of the 2157 cm^{-1} band into the 2129 cm^{-1} feature indicates the disappearance of the $[Cu(CO)]^{1+}$ complex and the formation of the $\{Cu[(CH_3)_2CO](CO)\}^{1+}$ complex. The 2129 cm^{-1} feature reaches its maximum intensity as the 2157 cm^{-1} band completely disappears. Further addition of acetone into the IR cell results in a drop of the intensity of the 2129 cm^{-1} band and a shift toward lower frequencies. At high acetone pressures in the absence of gas phase CO, acetone displaces adsorbed CO at the Cu^{1+} center, while the desorbed CO is not able to find an empty adsorption site again due to its relative low concentration in the adsorbate gas mixture. This is a possible manifestation of either the competitive adsorption processes or also a very slow approach to equilibrium.

Further experiments involving co-adsorption of acetone and CO on the Cu^{1+} sites of Cu-ZSM-5 were conducted in which the second adsorbate was introduced onto the catalyst sample partially covered with the first adsorbate. Initially a CO saturated Cu-ZSM-5 sample was prepared and subsequently annealed at 550 K for 30 s under evacuation. The resulting sample produced a fractional CO coverage of ~ 70%. (Approximate fractional coverages were determined by ratioing the integrated intensity of the adsorbate feature obtained after annealing to that obtained at saturation. This procedure assumes that the IR absorption cross section of the characteristic vibration is constant over the entire coverage range.) The IR spectral series obtained during the adsorption of acetone on the 70% CO covered Cu-ZSM-5 sample is shown in fig. 4. The prominent absorption band at 2157 cm^{-1} again is characteristic of the C–O stretching vibrations of CO adsorbed at Cu^{1+} centers. Introduction of the first small acetone exposure onto the sample does not change this feature; however, absorption bands characteristic of the adsorbed acetone molecules appear. The sharp band at 1671 cm^{-1} corresponds to the C–O stretch of acetone adsorbed at Cu^{1+} centers. This is the same feature discussed previously for the adsorption of acetone on the adsorbate free Cu-ZSM-5 sample. The incoming acetone molecules first bind to the adsorbate free Cu^{1+} centers. With increasing acetone partial pressure, a shoulder on the high frequency side of this band appears and its intensity gradually increases. Concomitantly, the adsorbed CO feature interconverts with the band at 2129 cm^{-1}. The explanation for these observations is straightforward. Acetone is suggested to first adsorb onto the Cu^{1+} sites having no coordinated CO, resulting in the development of the absorption feature at 1671 cm^{-1}. This band, however, does not reach its maximum intensity before the other C–O stretching vibrational feature of adsorbed acetone develops. With increasing acetone partial pressure the intensities of the C–O stretches of the two acetone species in different coordination environments increase simultaneously. Energetically the two adsorption sites for acetone adsorption are not sufficiently different to obtain exclusive site filling. Parallel with the development of a

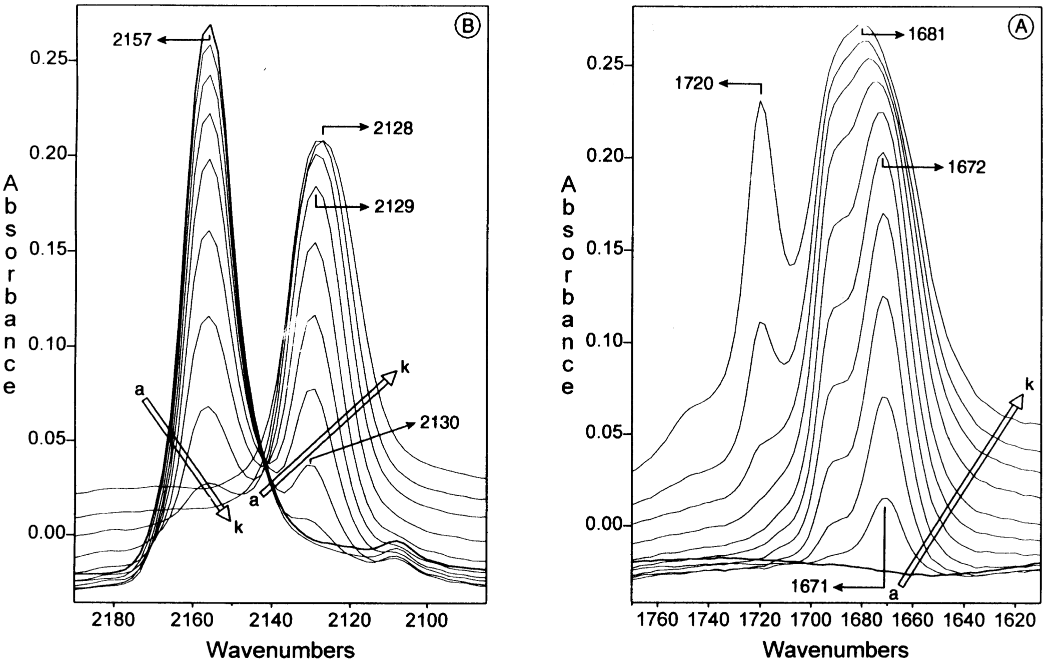

Fig. 4. IR spectra: acetone adsorption on a partially CO covered Cu-ZSM-5 at 300 K $\Theta_{CO} \sim 70\%$). The C–O stretching vibrational regions for adsorbed acetone (A) and CO (B) are displayed with increasing acetone partial pressure. Partial pressures of acetone (in Torr) were: a)< 0.0001; b) 0.075; c) 0.139; d) 0.203; e) 0.261; f) 0.335; g) 0.458; h) 0.723; i) 0.938; j) 1.36; and k) 2.50.

shoulder at ~ 1690 cm^{-1} the feature characteristic of the $[Cu(CO)]^{1+}$ adsorption complex gradually disappears and the 2129 cm^{-1} band, characteristic of the $\{Cu[(CH_3)_2CO](CO)\}^{1+}$ mixed ligand Cu^{1+} complex develops. Evacuation of the acetone saturated sample results in the significant decrease of the intensities of both the 2129 cm^{-1} band and the shoulder at ~ 2190 cm^{-1}, but even after the limited evacuation both features are still present with notable intensities.

Coadsorption experiments on partially covered Cu^{1+} centers were also conducted in the reverse order. The acetone partial coverages were prepared by slowly annealing (under vacuum) an acetone saturated Cu-ZSM-5 sample up to progressively higher temperatures. Carbon monoxide was then gradually introduced into the cell and IR spectra recorded after each CO dose as the system reached equilibrium. The series of CO adsorption experiments were carried out on the 75, 42, 28 and 18% acetone relative coverage Cu-ZSM-5 sample at room temperature. The results obtained from the 75 and 18% acetone covered samples are displayed in figs. 5 and 6 , respectively. The spectrum of the 75% acetone covered Cu-ZSM-5 sample shows one C–O stretching vibrational absorption feature centered at 1671 cm^{-1} for the Cu^{1+} bound acetone molecules. Introduction of a small CO aliquot into the IR cell ($P \approx 0.001$ Torr) results in the appearance of two absorption bands characteristic of the C–O stretching vibrations of the CO ligands in the $[Cu(CO)]^{1+}$ (2157 cm^{-1}) and $\{Cu[(CH_3)_2CO](CO)\}^{1+}$ (2130 cm^{-1}) complexes. The former band is more intense in this spectrum than the latter one, suggesting the preferential adsorption of CO on the adsorbate free Cu^{1+} sites. As soon as the C–O stretching vibrational feature of adsorbed CO in the mixed ligand Cu^{1+} complex appears, the intensity of the C–O stretching vibrational feature of acetone bound to Cu^{1+} centers decreases and a shoulder develops on its high frequency side. Evidently, the formation of the $\{Cu[(CH_3)_2CO](CO)\}^{1+}$ complex results in a reduction in the number of $\{Cu[(CH_3)_2CO]\}^{1+}$ complexes present in the catalyst sample. Conversion of $\{Cu[(CH_3)_2CO]\}^{1+}$ into the $\{Cu[(CH_3)_2CO](CO)\}^{1+}$ complex is indicated by the interconversion of the 1671 cm^{-1} band into the 1691 cm^{-1} feature. Increasing the CO pressure increases the C–O intensity in the mixed complex rapidly, while the acetone free Cu^{1+} bound C–O feature is constant at its maximum. At high CO pressures (~ 2–5 Torr) the CO band of the mixed complex broadens significantly, possibly indicating the formation of mixed ligand complexes containing more than one CO molecules. Spectrum b of fig. 6 demonstrates CO adsorbing exclusively onto acetone free Cu^{1+} centers upon the introduction of the first small CO aliquot onto the 18% acetone covered Cu-ZSM-5 sample. This is indicated by the development of a sharp absorption feature at 2157 cm^{-1} and the complete absence of a band at 2130 cm^{-1}. Concomitantly, there is no change either in the position or in the intensity of the C–O stretching band of Cu^{1+} bound acetone molecules. As the partial pressure of CO increases the 2157 cm^{-1} band rapidly gains intensity and an absorption feature develops at 2130 cm^{-1}. Parallel to these changes, the 1671 cm^{-1} band gradually converts into the 1691 cm^{-1}

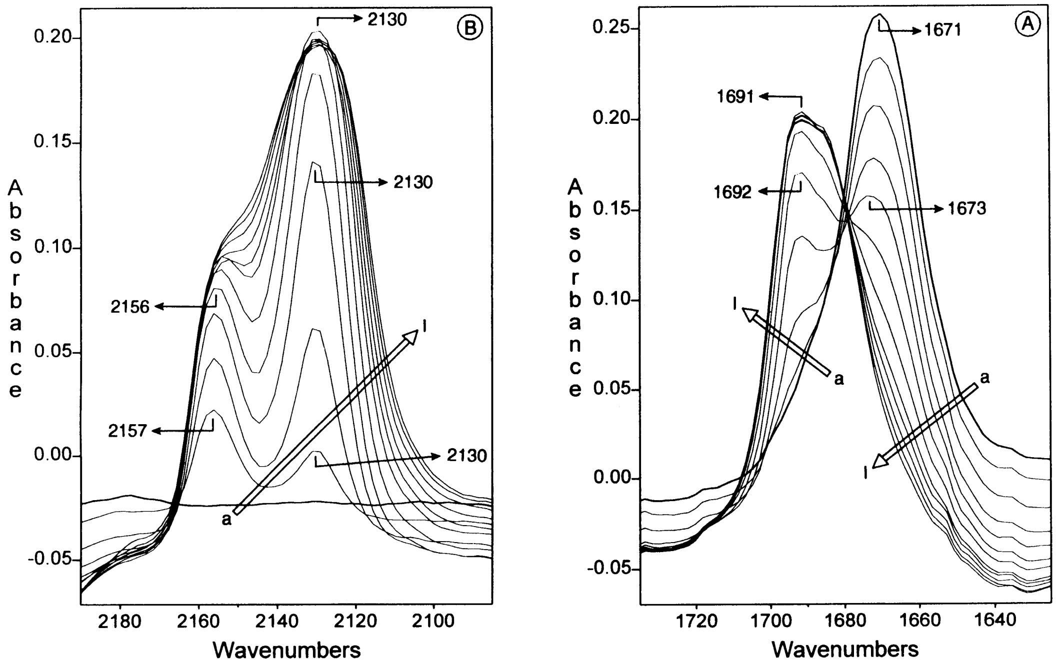

Fig. 5. IR spectra: CO adsorption on a partially acetone covered Cu-ZSM-5 sample at 300 K[$\Theta_{(CH_3)_2CO}$ ~ 75%]. The C–O stretching vibrational regions of adsorbed acetone (A) and CO (B) are shown as a function of increasing CO pressure. Partial pressures of CO were: a) < 0.0001; b) 0.011; c) 0.019; d) 0.035; e) 0.050; f) 0.078; g) 0.113; h) 0.184; i) 0.278; j) 0.725; k) 1.57; and l) 2.05.

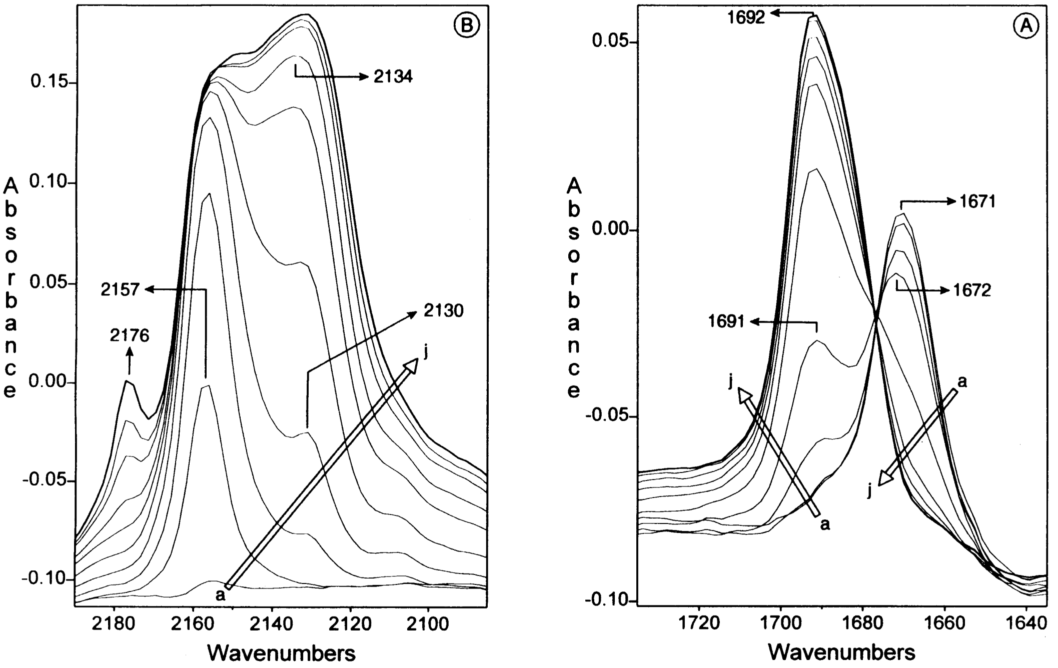

Fig. 6. IR spectra: CO adsorption on a partially acetone covered Cu-ZSM-5 sample at 300 K[$\Theta_{(CH_3)_2CO}$ ~ 18%]. The C–O stretching vibrational regions of adsorbed acetone (A) and CO (B) are shown as a function of increasing CO partial pressure. Partial pressures of CO (in Torr) were: a) < 0.0001; b) 0.016; c) 0.035; d) 0.062; e) 0.110; f) 0.209; g) 0.413; h) 1.16; i) 2.14; and j) 2.22.

feature. At high CO pressure (< 10 Torr) the formation of $[Cu(CO)_2]^{1+}$ complexes is seen and indicated by both the development of an IR band at 2176 cm^{-1} and the shifting of the 2157 cm^{-1} feature toward lower frequencies [16,22].

In practical terms the coadsorption and coordination of both CO and oxygenated molecules does occur at Cu^{1+} sites within the ZSM-5 host and is manifest in the notable frequency shifts and rehybridization of the coordinated molecules. At sufficiently low temperatures (below combustion) the close proximity of the coordinated molecules lends considerable insight into viewing possible transition states for chemical reactions such as the selective reduction of NO_x. This insight furthers our understanding of plausible multiple coordination environments in the presence of NO and selected hydrocarbons. To some extent preliminary experiments [19, and references cited therein] have identified transient species present under in situ conditions that may have significant reactivity and implications for actual catalyst design and use. Clearly however, further work on examining coadsorbates at temperatures sufficiently low or on time scales sufficiently short that relevant transient coordinated complexes can be inferred from experimental data will have an impact on our ability to design catalysts beyond the conventional Edisonian approach to discovery.

4. Conclusions

Coadsorption of CO and acetone at Cu^{1+} centers in ZSM-5 leads to frequency shifts in the primary C–O vibration of each adsorbate that are measured in the absence of the other adsorbate. These shifts reflect an increasing electron withdrawal from the Cu^{1+} center and the appearance of a more "reduced" Cu^{1+} center. Adsorbed acetone does not eliminate the adsorption of CO at the same site and vice-versa. The adsorption and coadsorption behavior were observed to be reversible over the temperature and pressure regimes of 300–550 K and 0.001–10 Torr, respectively. The formation of the mixed complex $\{Cu[(CH_3)_2CO](CO)\}^{1+}$ is inferred from spectroscopic evidence and the binding of CO in such a species is weakened by the presence of the coadsorbed $(CH_3)_2CO$.

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