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The effect of water on the infrared spectra of CO adsorbed on Pt / K L-zeolite

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The effect of water on the infrared spectrum of adsorbed CO has been studied for a Pt / K L-zeolite sample. The red shift of the CO spectra and the intensity transfers to lower frequency bands observed with increasing uptake of water are attributed to an increased electron density of the metal particles. Adsorption of CO under "wet" conditions results in an increase in the ratio of integrated intensities of bridged to linear CO species, consistent with an increase in the electron density on the metal particles. It is proposed that the water molecules associated with the zeolite cations modify the metal–support interaction via the zeolite lattice.

Keywords: Pt / K L-zeolite, effect of water on adsorbed CO, infrared spectra of CO on zeolite

1. Introduction

Since the pioneering work of Eischens and co-workers [1–4], the infrared spectrum of CO adsorbed on supported metal catalysts has been used to infer information about metal–support interaction [5–11]. It was also appreciated by Eischens and co-workers that the chemisorption of CO on supported metal particles can be strongly influenced by the experimental conditions, i.e., the effect of CO coverage, and the resulting dipolar coupling. More recently it has been demonstrated [12,13] that exposure to higher partial pressures of CO may lead to the breaking up of small metal particles, and the formation of metal–carbonyl species. Therefore the infrared spectrum of CO adsorbed on supported metal particles can be strongly influenced by the experimental conditions. In the present study, we were particularly interested in the effect of water on the infrared spectrum of CO adsorbed on zeolite-supported metal particles.

Kappers et al. [14,15] have recently proposed a cation–dipole interaction between CO adsorbed on Pt / K L-zeolite and the K^+ cations present in the main channel. The authors observed that when CO, adsorbed under "wet" conditions, was heated in an inert gas to 200°C, it resulted in the appearance of a peak at ~ 1940 cm^{-1}, which they attributed to a cation–dipole interaction. They proposed that under "wet" conditions the water was adsorbed on the cations, thereby shielding the adsorbed CO from interacting with the cations, and that the appearance of the new band on heating to 200°C was as a result of the removal of water, thereby exposing the cation to the CO molecule. However, in recent research in our laboratory [16] it was observed that heating of CO adsorbed (in the absence of water) on zeolite-supported platinum in an inert gas, in the absence of water, led to a redistribution of CO stretching frequencies similar to that observed by Kappers et al. [14,15]. A similar effect has also been reported in previous studies [6,8,10]. In this context, it is necessary to clarify what we mean by redistribution, as there are two kinds of redistribution of the adsorbed CO molecules that can be encountered. In the first case, the CO uptake is a fraction of the saturation uptake, usually on the more accessible sites, and the thermal redistribution results in a more homogeneous distribution of the adsorbed CO (while maintaining the low CO coverage to eliminate dipole–dipole coupling). In the second case, as is the case in the present study, saturation uptake of CO is followed by thermal treatment in an inert gas (or vacuum), to redistribute the adsorbed CO. In this case, the appearance of new bands [6,8,10,16] may be due to the population of energetically favorable sites, which have an activation energy barrier to adsorption. Therefore, the equilibration of a saturation uptake of CO at higher temperatures (100–400° C), in inert gas or vacuum, results in both a redistribution of adsorbed CO, and a reduction in the integrated intensity caused by net desorption of adsorbed CO [6,8,16].

In the present study, we have proceeded to investigate the effect of water on the infrared spectrum of CO adsorbed on a Pt / K L- zeolite sample, after room temperature saturation uptake of CO, and after equilibrating this adsorbed CO at higher temperatures in helium.

2. Experimental

The catalyst used in the study was a 3.67 wt% Pt / K L-zeolite that was prepared by ion-exchange, calcined in oxygen at 300°C, reduced in hydrogen at 400°C, passivated in air at room temperature (RT), and then back-exchanged with K^+ to exchange for protons generated upon reduction. The preparation method has been described in detail elsewhere [17]. Infrared spectra of zeolite-supported metal catalysts prepared by ion-exchange show a Brønsted acid OH stretching band at ~ 3650 cm^{-1} [9,17]. The infrared spectrum of the OH stretching region [17] confirms that the back-exchange is successful in removing the Brønsted acidity generated during reduction, and this sample was chosen so as to have a cation content similar to the Pt/K L-zeolite samples used by Kappers et al. [14,15] in their experiments, which were prepared by impregnation of the platinum precursor. The X-ray absorption near edge structure (XANES) indicates that all of the metal is reduced [18]. The first metal–metal shell coordination number determined from the X-ray absorption fine structure (XAFS) was ~ 5 [18], corresponding to approximately 10–12 atom metal clusters. Also the XAFS chi functions for the ion-exchanged and back-exchanged samples are very similar and do not show any contributions from K^+ backscattering [18], indicating that the K^+ cations are not directly associated with the metal particles.

2.1. Transmission Fourier transform infrared (FTIR) spectroscopy of adsorbed CO

The infrared measurements were performed using a MIDAC M-series FTIR spectrometer operating at a resolution of 2 cm^{-1}. Transmission FTIR spectra were obtained using a self-supported wafer (18 mg/cm^2), by co-averaging 256 scans ($\sim$ 10 min total scan time). The infrared cell was connected to a gas flow manifold. The gases used were ultra high purity (UHP) grade helium and hydrogen, which were further purified using an Oxysorb purifying trap (Supelco) and an OMI-2 indicating–purifying trap (Supelco), and a 1000 ppm CO in helium blend (Scott Specialty Gases) which was purified by flowing through a 5A molecular sieve trap (Supelco) to remove water and CO_2 impurities. Water vapor was admitted through a 3 O-ring stopcock (Ace Glass, Inc.) to a T-junction from where it was carried to the cell by the gas flow (figure 1). This arrangement enabled us to introduce reproducible amounts of water to the cell, and to shut off the water vapor supply during the experiment (complete purge of the dead volume took less than 1 h). Peak positions were determined using the second-derivatives technique described by Kappers and van der Maas [19]. Second-order derivatives were calculated using a 15-point Savitzky–Golay derivative function [20].

The sample was heated in flowing hydrogen to 400°C and rereduced at this temperature for 30 min (the heating rate used throughout was 5 K/min). The flow was then switched to helium (for 1 h, at 400°C) and then cooled to RT. The flow was switched to the CO/He blend until saturation adsorption was reached ($\sim$ 30 min). The flow was then switched to helium and the cell was purged in helium for 30 min. The water vapor was admitted by opening the stopcock and the evolution of the CO spectrum with increasing uptake of water in the zeolite was followed. The water vapor supply was then shut off, and after a short purge period, the catalyst was heated to 200°C in helium flow, equilibrated at this temperature for 30 min, then cooled to RT. The evolution of the redistributed CO spectrum with increasing uptake of water (at RT) was then followed. The procedure was repeated for an equilibration temperature of 350°C after re-adsorbing CO at RT.

2.2. Adsorption of CO under "wet" conditions

The catalyst was first cleaned by treating in hydrogen at 300°C for 30 min, followed by purging in helium at this temperature for 1 h (temperature-programmed desorption of hydrogen [16] indicates that the chemisorbed hydrogen is removed at this temperature), and then cooled to RT. The adsorption of CO under "wet" conditions was then investigated. The stopcock was opened and the water vapor was admitted in helium (until the water bending vibration peak at 1632 cm^{-1} was the same intensity as in the first wet spectrum), then the gas flow was switched to the CO/He blend and the infrared spectrum of CO was recorded after saturation of the surface in the "wet" gas blend.

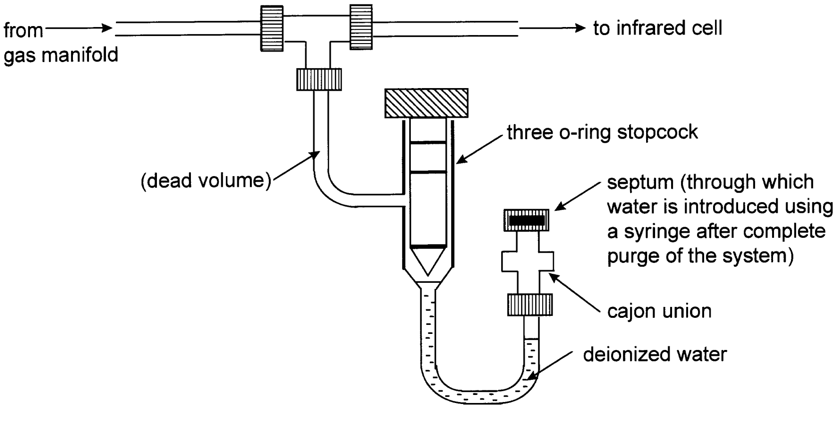


Figure 1. Schematic of the water dosing apparatus.

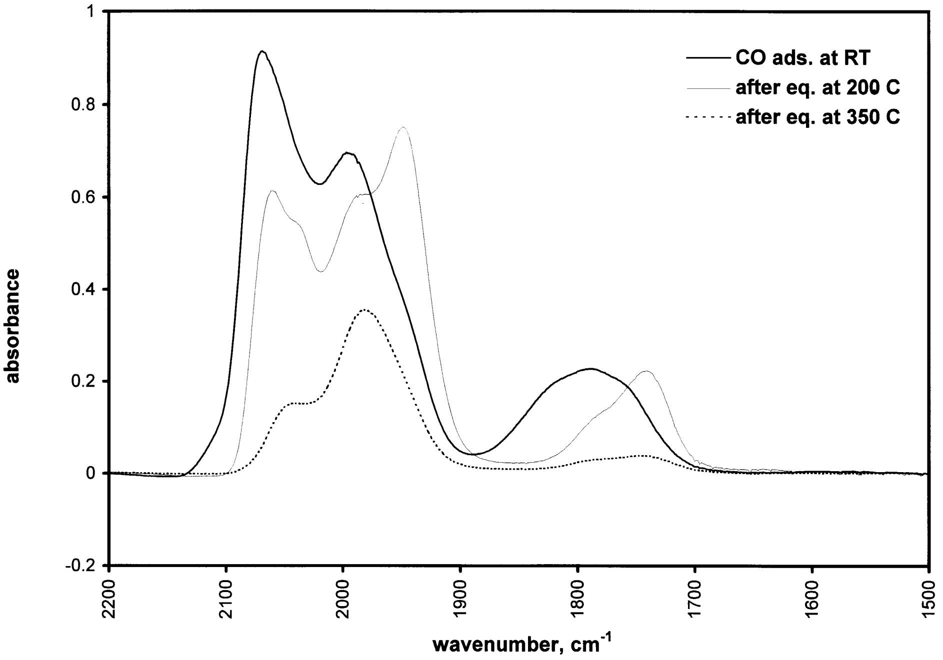


Figure 2. Equilibration of CO adsorbed at room temperature at 200 and 350°C in dry helium for 30 min.

2.3. Estimation of water uptake

To estimate the amount of water corresponding to the highest uptake, the catalyst was cleaned (as described previously) and then water vapor was introduced to reach the highest uptake (as determined by the intensity of the water bending vibration peak at 1632 cm^{-1}). The pellet was weighed with this water content and then again after heating to 200°C in air for 1 h. Note: Because the pellet was exposed to the atmosphere during weighing, the water content determined is considered an approximate value only.

3. Results

Figure 2 shows the effect of equilibration of CO in dry helium at different temperatures (after RT exposure

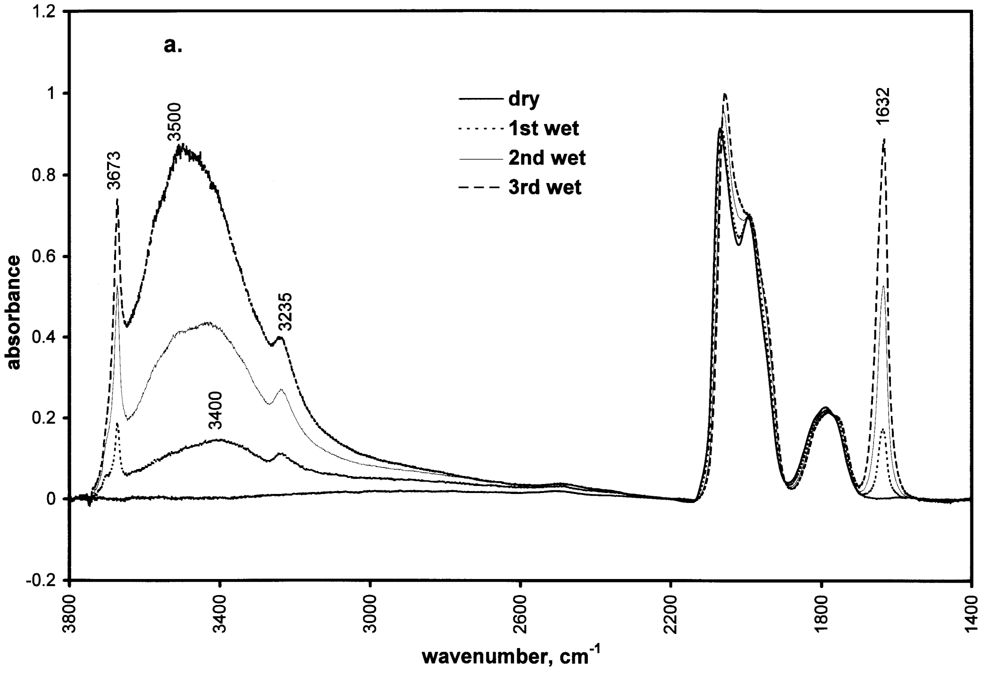


Figure 3. Evolution of the CO adsorption spectrum with increasing uptake of water by exposure to "wet" helium: (a) after CO adsorption at room temperature, (b) after equilibration in helium at 200°C for 30 min, (c) after equilibration in helium at 350°C for 30 min. (Continued on next page.)

to "wet" helium). It is observed that the equilibration of CO at 200°C increases the intensity of the peak at $\sim 1940\ \mathrm{cm}^{-1}$. The spectrum obtained after equilibration of the sample (after RT exposure to "wet" helium) at 200°C is identical to that obtained after equilibration at 200°C without any introduction of water [16], and is therefore due to a redistribution of adsorbed CO. This effect was mistakenly attributed to the effect of water removal and a proposed interaction of CO with a cation by Kappers et al. [14,15]. Figures 3a, 3b and 3c show the effect of water on the infrared spectrum of CO adsorbed at RT, equilibrated at 200°C, and equilibrated at 350°C, respectively. Figure 4 shows the same spectra in the region of the CO stretching frequency. Figure 5 shows the calculated second derivatives of the absorbance spectra in figure 4a. The peak positions of the different CO bands (corresponding to the negative lobes of the second derivative function [19]) are reported in table 1. In all three cases, a red shift of the CO bands and intensity transfer from higher frequency bands to lower frequency

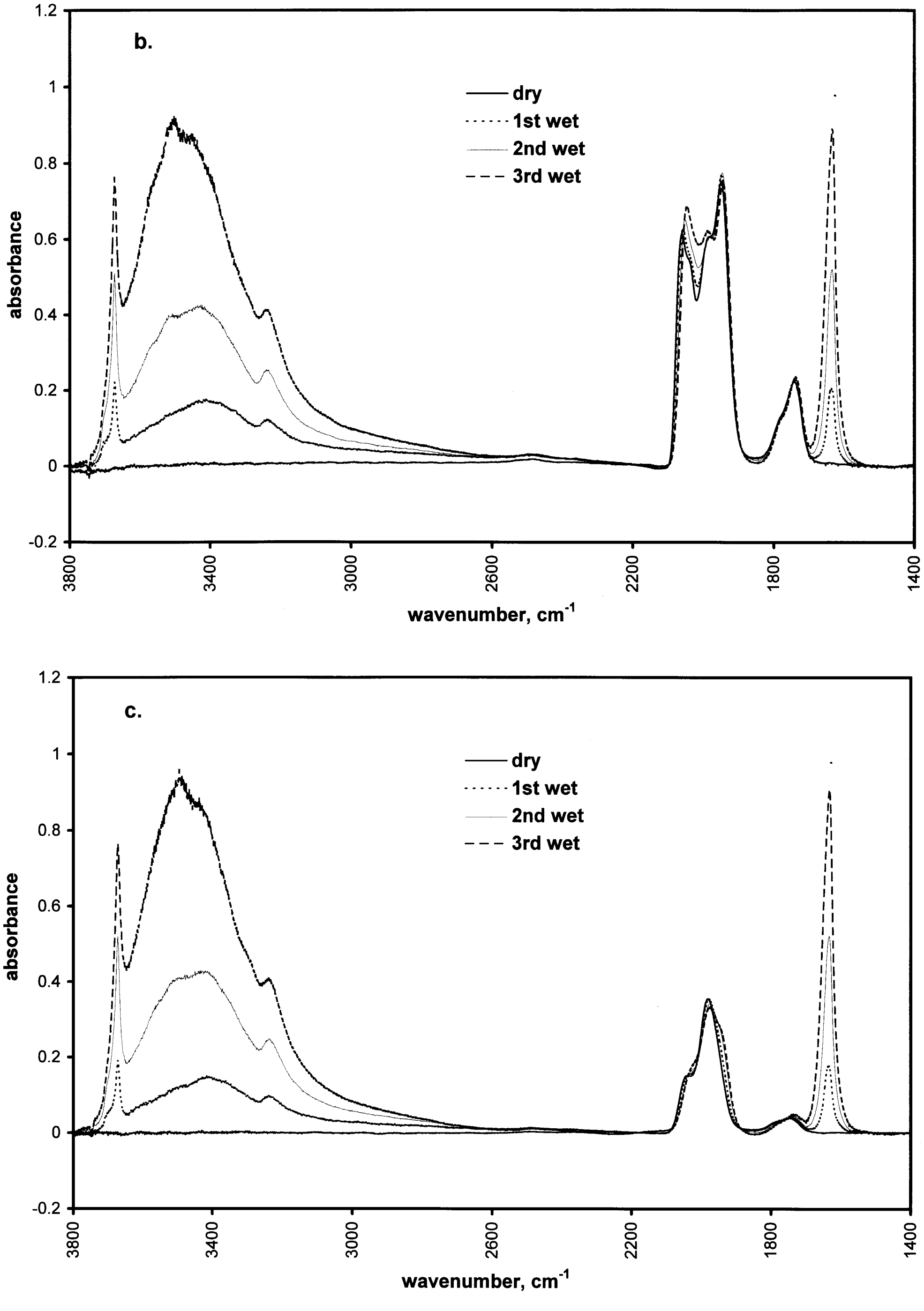


Figure 3. (Continued.)

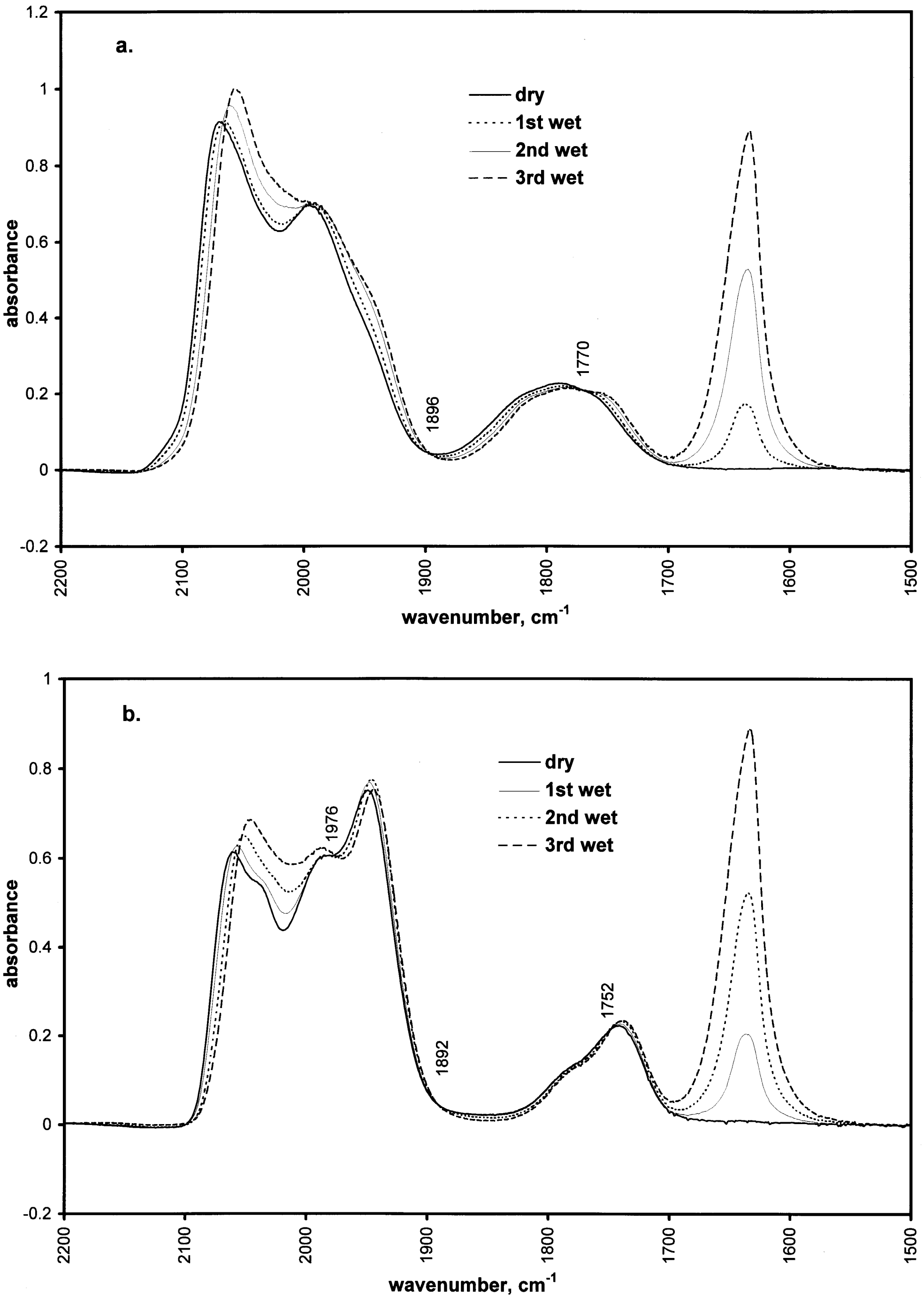


Figure 4. Evolution of the CO adsorption spectrum with increasing uptake of water by exposure to "wet" helium (in the region of CO stretching frequencies): (a) after CO adsorption at room temperature, (b) after equilibration in helium at 200°C for 30 min, (c) after equilibration in helium at 350°C for 30 min. (Continued on next page.)

bands is observed with increasing uptake of water. The isosbestic points are at about the same frequencies in all three cases (see figure 4). The intensity transfer from higher frequency bands to lower frequency bands with increasing water uptake can be seen from the second derivative of the absorbance spectra, for example, in figure 5. Both the red shift of the CO bands and the transfer of CO band intensity to lower frequency bands with increasing water uptake are consistent with increased electron density of the metal particles (see below). The intensity of the peak at ~ 1940 cm^{-1} is seen to increase with increasing water uptake, indicating that it was incorrectly assigned as resulting from a cation–dipole interaction [14,15].

3.1. Adsorption of CO under "wet" conditions

Figure 6 compares the infrared spectrum of CO

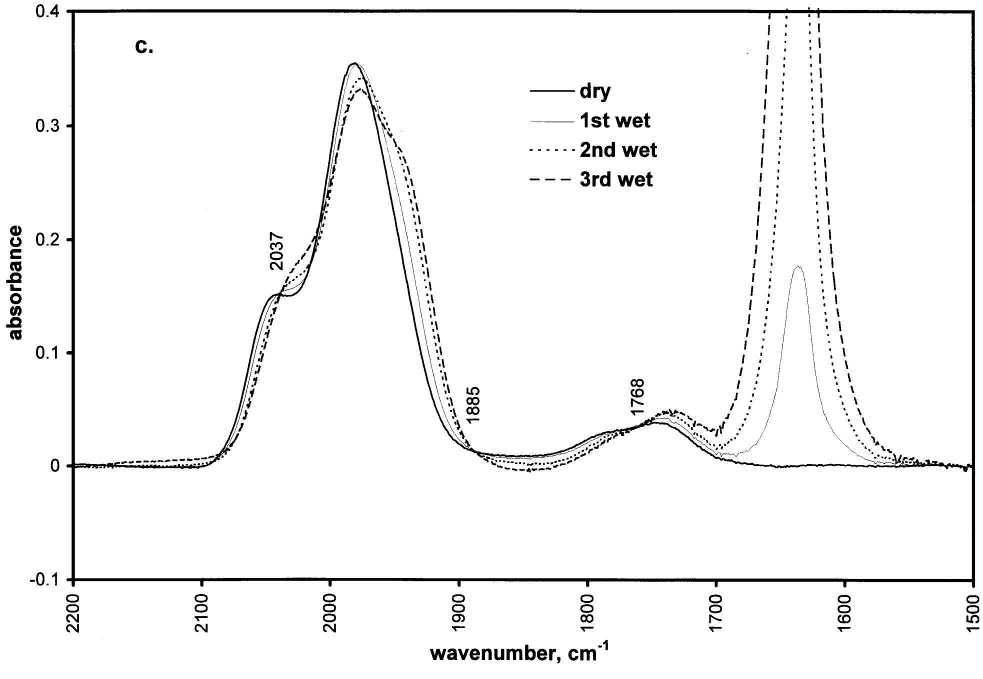


Figure 4. (Continued.)

adsorbed under "wet" conditions to the spectrum of CO adsorbed in the absence of water with subsequent uptake of water (from figure 2). The increased intensity for the bridging CO species for the former is consistent with theoretical calculations by Van Santen [21] that suggest that the ratio of bridging to linearly adsorbed CO increases with increasing electron density of the metal particles.

3.2. Estimation of water uptake

The amount of water corresponding to the highest uptake was determined as 6.1 wt% of the dry zeolite weight. From the integrated intensities of the water bending vibration peak, the water contents corresponding to the two lower uptakes of water were estimated as 1.1 and 3.2 wt% of the dry zeolite weight, respectively.

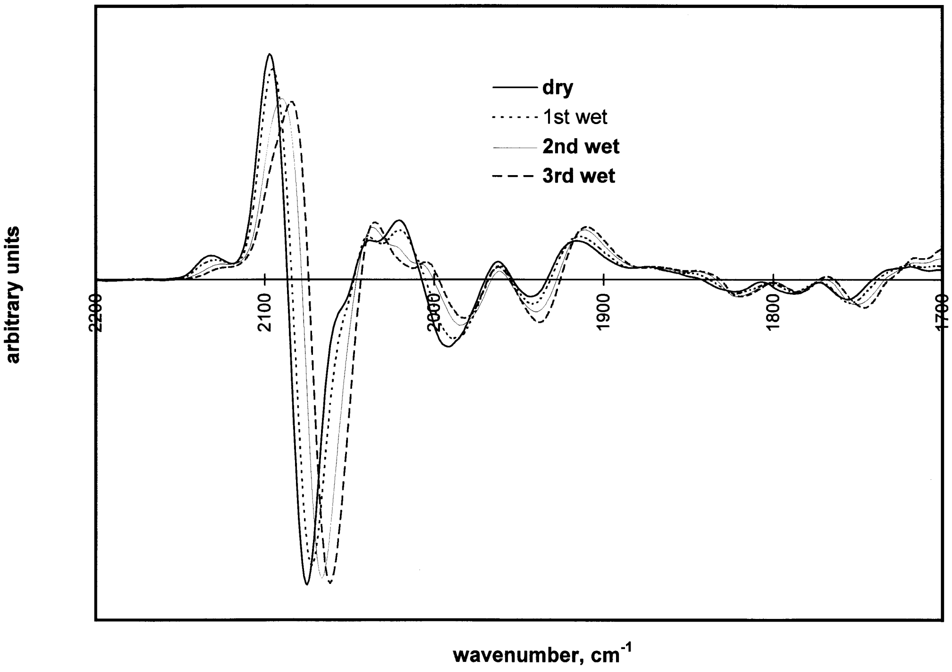


Figure 5. Second-order derivatives of the absorbance spectra for increasing uptake of water after CO adsorption at room temperature (figure 4a), using a 15-point Savitzky–Golay derivative function.

Table 1

Spectrum	Peak positions (cm^{-1})							
after CO adsorption at RT								
before addition of water	2075	–	1992	1943	1823	1788	1756	–
1st wet spectrum	2072	–	1988	1942	1823	1788	1754	–
2nd wet spectrum	2067	–	1985	1940	1822	1786	1751	–
3rd wet spectrum	2062	–	1983	1939	1821	1784	1747	–
after equilibration at 200° C								
before addition of water	2066	2036	1992	1944	–	1788	1739	–
1st wet spectrum	2062	2034	1991	1944	–	1787	1737	–
2nd wet spectrum	2057	–	1989	1943	–	1786	1736	–
3rd wet spectrum	2053	–	1987	1941	–	1785	1735	–
after equilibration at 350° C								
before addition of water	2051	–	1985	–	–	1787	1740	–
1st wet spectrum	2048	–	1983	1942	–	1783	1740	1727
2nd wet spectrum	2043	–	1981	1940	–	1783	1740	1727
3rd wet spectrum	2039	–	1981	1938	–	1782	1740	1727

4. Discussion

It is observed that increasing the water uptake results in both a red shift and a transfer of intensity from higher frequency CO bands to lower frequency bands. Also, the CO adsorbed under "wet" conditions shows an increased intensity for the bridging CO peaks. These effects are consistent with an increase in the electron density of the metal particles with increasing water uptake [21,22].

The peak at ~ 1940 cm^{-1} (which was proposed to result from a cation–dipole interaction [14,15]) appears to be a bridging carbonyl species. It is observed that the intensity of this peak increases with increasing water uptake (see figure 5). Even in the case of the spectra after equilibration at 350°C, when this species is not initially present, it appears with the uptake of water (figure 4c). The integrated intensity between 2100 and 1900 cm^{-1} increased with increasing water uptake, while the integrated intensity between 1900 and 1700 cm^{-1} remained almost constant, or showed a slight decrease (see table 2). This is consistent with the assignment of this peak to a bridge bonded species, because an increase in the electron density of the metal particles is expected to cause a shift from linear to bridge bonded CO species [22]. The intensity of the peak at ~ 1940 cm^{-1} increased when

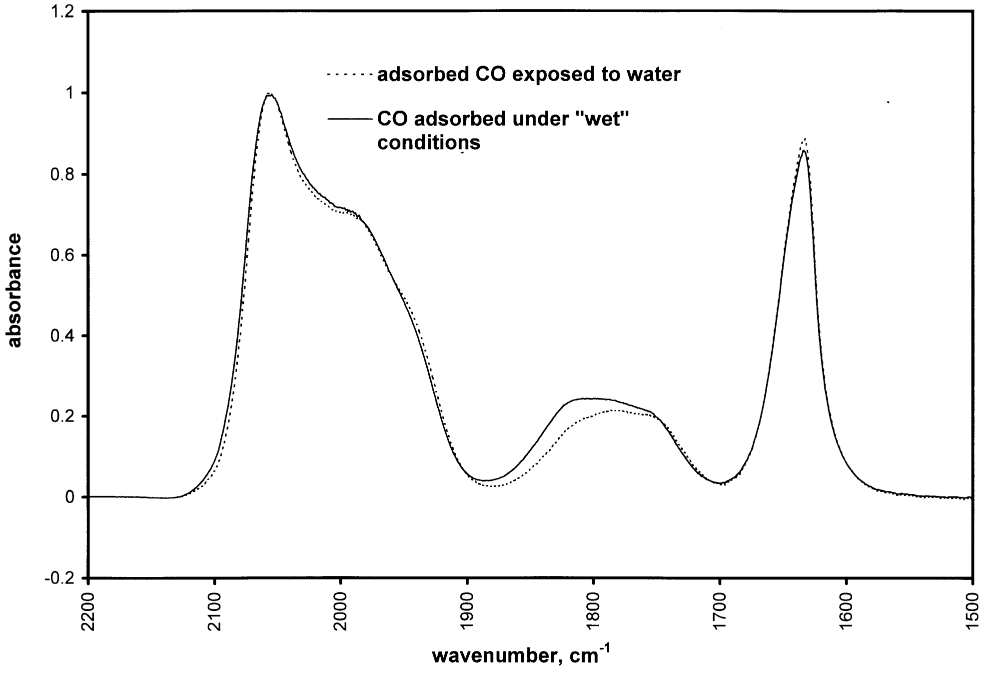


Figure 6. Comparison of the infrared spectrum of CO adsorbed in the absence of water and subsequently exposed to water vapor, with that of CO adsorbed under "wet" conditions.

equilibrated at 200°C, but becomes negligible after equilibration at 350°C, suggesting that this adsorbed CO species has an activation energy barrier to adsorption, but the adsorption strength is less than that of linear bonded CO species. This is also consistent with the potential energy surface and CO site exchange behaviour reported by Schweizer et al. [23], for CO adsorbed as linear (on top) and bridged species on Pt(111).

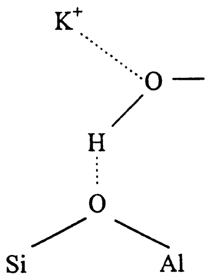
Two additional factors need to be considered in this discussion. The first of these is the effect of water on the dipole–dipole coupling. The phenomenon of dipole–dipole coupling has recently been reviewed by Hollins and Pritchard [24,25]. In the earliest treatment of dipole–dipole coupling by Hammaker, Francis and Eischens [26], the oscillating molecules were assumed to interact via their through-space dipolar fields. Subsequent refinements have accounted for the role of the metal in modifying this field [27], electronic polarization effects [27,28] and changes in the effective absorption coefficient of the adsorbate [29,30]. Coupling between identical species results in a shift of the absorption band to higher frequencies and a reduction in the molecular absorption coefficient as the number of interacting molecules increases. A third effect arises when there are more than one species (i.e. species having different singleton frequencies). There is then observed a characteristic transfer of intensity from the band due to the lower frequency species to that due to the higher frequency species [25]. Therefore, the red shift of the CO bands and the intensity transfer to the lower frequency bands with increasing water uptake may also be caused by a reduction in the dipole–dipole coupling of the different CO species. By equilibrating the adsorbed CO at 350°C we have attempted to depopulate the adsorbed CO species (the integrated intensity of the linear bonded species is ~ 29% of that after adsorption of CO at room temperature). However, as can be seen from table 1, the red shift of the linear CO species is about the same in both cases. This suggests that the observed changes in the CO adsorption spectrum are not due to changes in the dipole–dipole coupling (assuming that equilibration at 350°C causes a random distribution in sites and the break-up of any CO islands).

A second consideration is the location of the water molecules within the zeolite, i.e., whether it is associated with the zeolite cations or coadsorbed on the metal particles. Studies of the coadsorption of CO and water on Pt(111) surfaces [31,32] and Pt thin films [33] have observed similar shifts to lower frequency of the CO bands with small amounts of water coadsorbed, and band suppression at higher water uptakes. These effects have been attributed to either a coadsorbate induced change of the adsorption sites and/or electronic screening of dynamic dipole moments of vibrational modes by the coadsorbed water [32]. The polarizability of the coadsorbed water molecules results in a screening of the dynamic dipole moment of the adsorbed CO [30,32], leading to a decrease in the intensity of the CO stretching bands. However, in the present study, the intensity of the CO bands increased with increasing water uptake (see table 2). In single-crystal studies of water adsorbed on Pt(111), the water molecules were desorbed intact at temperatures < 200 K [34,35]. Also, from figure 6 it is seen that the adsorption of CO under "wet" conditions leads to similar (in fact, slightly higher) CO uptake than CO adsorbed in the absence of water. These results suggest that water is not coadsorbed on the metal particles (although trace amounts of water coadsorbed, either dissociatively or undissociatively, cannot be completely ruled out). Breck [36] has reported water uptakes (g of water/g of dehydrated K L-zeolite) of 0.132, 0.147 and 0.197 at water vapor pressures of 4, 10 and 22 Torr,

Table 2

Spectrum	Integrated intensities		
	2100–1900 cm^{-1}	1900–1700 cm^{-1}	OH bending vibration at 1632 cm^{-1}
after CO adsorption at RT			
before addition of water	108.7	25.6	–
1st wet spectrum	109.9	24.9	6.0
2nd wet spectrum	112.1	24.4	19.1
3rd wet spectrum	113.7	24.0	35.5
after equilibration at 200° C			
before addition of water	95.8	17.1	–
1st wet spectrum	97.0	16.9	7.3
2nd wet spectrum	97.9	16.7	19.1
3rd wet spectrum	98.8	16.4	36.5
after equilibration at 350° C			
before addition of water	32.0	3.8	–
1st wet spectrum	33.2	3.8	6.3
2nd wet spectrum	34.2	3.6	19.1
3rd wet spectrum	34.7	3.4	37.5

respectively. The water content at the different uptakes (0.011, 0.032 and 0.061) was much less than the (expected) equilibrium uptake. As shown in figure 3, the water uptake gave rise to peaks at 3673, 3235 and 1632 cm^{-1}, and a broad peak which shifted in position from ~ 3400 to ~ 3500 cm^{-1} with increasing uptake of water. Early infrared studies of water adsorbed on zeolite X [37,38] suggested that the water molecules are inserted between the cation and the zeolite lattice, interacting with the cation through the oxygen atom [37,39], and interacting with lattice oxygen through one of the hydrogen atoms, i.e,



The bands observed for K X-zeolite [37] and K Y-zeolite [40] are almost identical to the bands observed in the present study, therefore, we can assign the observed peaks as follows. The sharp peak at 3674 cm^{-1} can be assigned to the OH stretch of the free hydrogen atom, the peaks at ~ 3450 and 3240 cm^{-1} can be assigned to the stretching modes of the hydrogen bonded to the lattice oxygen, and the peak at ~ 1632 cm^{-1} can be assigned to a water bending vibration. This assignment also supports the observed parallel development of all four bands with increasing uptake of water. Therefore, we conclude that the water is most probably associated with the cations in the zeolite lattice [36,39]. This suggests that the water associated with the zeolite cations changes the metal support interaction, resulting in an increase in the electron density of the metal particles. From table 1, it can be seen that even the lowest uptake of water caused a red shift of ~ 4 cm^{-1}. This can have important consequences in the characterization of metal particles supported in zeolites by the infrared of adsorbed CO, as the effect of trace amounts of water may very well depend on both the number and type of cations present, and therefore may complicate the interpretation of the infrared spectra of CO adsorbed on the metal particles.

5. Conclusions

The effect of water on the infrared spectrum of CO adsorbed on Pt/K L-zeolite has been studied. The peak at ~ 1940 cm^{-1}, which was previously attributed to cation–dipole interaction, was found to be due to the redistribution of the adsorbed CO species on the Pt clusters upon heating to 200°C, and is proposed to be due to a bridging CO species. The red shift of the CO spectrum and the intensity transfers to lower frequency bands with increasing uptakes of water are attributed to an increased electron density on the metal particles. Consistent with this interpretation, adsorption of CO under "wet" conditions increases the ratio of the integrated intensities of bridged to linear species. The water contents at the different uptakes were much less than the equilibrium uptake of water, suggesting that the water was associated with the zeolite cations. Therefore, it is proposed that water molecules associated with the zeolite cations modify the metal–support interaction via the zeolite lattice. The presence of trace amounts of water can, therefore, complicate the interpretation of the infrared spectra of adsorbed CO, especially over zeolite-supported metal catalysts.

Acknowledgement

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