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Ion–dipole interactions between adsorbed CO and support cations in Pt / K-LTL

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The adsorption of carbon monoxide on a non-acidic Pt/K-LTL catalyst has been studied by diffuse reflectance and transmission IR spectroscopy. The CO spectrum is strongly dependent on the experimental conditions. Adsorption on the small Pt clusters in the presence of water gives linear-CO bands between 2060 and 1990 cm^{-1} and a bridging-CO band around 1800 cm^{-1}. In the absence of water, the linear bands are red shifted to about 1940 and 1720 cm^{-1}, respectively. The frequency shift is attributed to an ion–dipole interaction between adsorbed CO and support cations. The ion–dipole interaction is screened by the adsorbed water leading to a smaller red shift in the CO stretching frequency.

Keywords: Infrared spectroscopy; DRIFT; FT-IR; CO adsorption; Pt/K-LTL zeolite; ion–dipole interaction; bifunctional promotion; water contamination

1. Introduction

Infrared spectroscopic studies of adsorbed carbon monoxide as molecular probe have contributed substantially to the understanding of metal catalysts. The assignment of CO absorption bands is complicated by the effects of particle size, dipolar coupling, CO–support interactions and electronic changes in the metal structure which are reflected in the shift of CO stretching frequency from its gas-phase value [1–15].

The electronic properties of supported metal clusters are thought to be influenced by the composition of the support and by the presence of promoter ions

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[16–20]. Previous infrared studies indicate that zeolite acid sites withdraw electrons from small metal particles making them electron-deficient, whereas metal clusters supported in basic zeolites are electron-rich [21–25]. Early infrared work on Pt/LTL catalysts by Besoukhanova et al. [26] and a recent study by Larsen and Haller [27] showed that the positions of the CO bands are influenced by the type of the exchanged alkali and alkaline earth cations. Based on these results, both authors concluded that platinum in K-LTL is electron-rich. Both studies, however, were complicated by the fact that not all Pt particles were inside the zeolite channels.

Lane et al. [28] and Kustov et al. [29] have also investigated the CO infrared spectra of highly dispersed Pt/K-LTL zeolite with transmission FT-IR spectroscopy. The IR spectra reported by Kustov et al. showed several sharp, linear-CO bands in the region between 2070 and 2000 cm^{-1}, while the FT-IR spectra reported by Lane et al. showed fewer and broader linear-CO bands, at frequencies as low as 1960 cm^{-1}. A recent DRIFT (diffuse reflectance infrared Fourier-transform) spectrum [30] of the same Pt/K-LTL catalyst used by Lane et al. [28] also gave broad linear-CO bands, but at frequencies similar to those reported by Kustov et al. [29]. The reasons for these differences in the infrared spectra were not understood.

In this study, additional experiments have been carried out in order to resolve the discrepancy between the data obtained by transmission FT-IR and DRIFT. The results show that the presence or absence of water strongly affects the stretching frequency of adsorbed CO. We conclude that the contradictory data reported in the literature are due to the presence of traces of water in the sample.

2. Experimental

2.1. SAMPLE PREPARATION

The K-LTL zeolite was obtained from Linde. Excess alkali was reduced by water wash until the pH of the wash solution was 9.5. The Pt (1.2 wt%) was loaded by impregnation using tetraamineplatinum(II)nitrate followed by drying at 120°C.

2.2. DRIFT SPECTROSCOPY

Infrared spectra were recorded on a Perkin-Elmer 1720X FT-IR equipped with a DTGS detector and were averaged over 256 scans at 4 cm^{-1} resolution. The in situ measurements were performed in a diffuse reflectance accessory ("Collector", Barnes Analytic) equipped with a standard controlled environment chamber (Spectra-Tech, model 0030-103). The reflectance from a neat catalyst sample relative to the open beam throughput, with the dome and (self-pressed) KBr windows in place was about 2%R at 2000 cm^{-1}.

The CO spectra were corrected for the catalyst background, and when necessary also for the CO gas phase. The actual sample temperature during in situ pretreatment was measured with a micro-thermocouple in contact with the powdered sample. The spectral data are presented as the diffuse absorbance ($-\log(R/R_0)$) analogous to absorbance used for transmission experiments. Spectral subtraction and integrated intensity calculations were performed on a Perkin-Elmer 3600 data station.

The DRIFT cell was connected to a flow-system suited to mix purified gases at atmospheric pressure with a controlled flow-rate of up to 100 ml/min. The tubes from the system to the cell were Impolene PP (Imperial Eastmann), lines in the unit (including gas-cylinders) were stainless steel, except the carbon monoxide lines and fittings, which were brass and copper.

The gases were of high purity; 10% O_2/Ar (O_2, 4.5N; Ar,5.0N), 10% H_2/Ar (H_2, 5.0N; Ar, 5.0N), Ar (5.0N) and CO (4.7N, in Al-cylinder), all supplied by Hoekloos Laboratories. Argon and hydrogen were passed through "Oxysorb" and "Hydrosorb" traps, oxygen and carbon monoxide through a "Hydrosorb" trap (all Messer Griesheim).

The following in situ procedure was used to reduce the samples: (i) heating in argon flow at 3°C/min to 150°C and kept at 150°C for 16 h, (ii) cooling to room temperature and reduction in a 10% H_2/Ar mixture at a rate of 5°C/min to 300°C, and (iii) cooling to room temperature in a stationary atmosphere of H_2/Ar. No attempt was made to remove adsorbed hydrogen from the metal surface. A background spectrum was taken at room temperature in a stationary atmosphere of H_2/Ar before switching to carbon monoxide. To obtain infrared data in the presence of water, CO spectra were first taken after 20 s or 1 min CO flow and additional purging at room temperature with Ar in order to remove gaseous CO. To obtain spectra in the absence of water, the samples were then heated in argon flow at 20°C/min up to 200°C and cooled to room temperature in a stationary atmosphere of argon.

2.3. TRANSMISSION FT-IR SPECTROSCOPY

The vacuum manifold and infrared cell assembly were evacuated to a pressure less than 10^{-4} Torr. The sample was then re-reduced in situ by admitting hydrogen to a pressure of 50 Torr, followed by heating to 300°C for 1 h. After reduction, the hydrogen was evacuated to less than 10^{-4} Torr for 15 min at 300°C. The sample was cooled to room temperature and lowered into the infrared beam. The transmission spectra were recorded on a Nicolet 740 at a spectral resolution of 4 cm^{-1} for all spectra.

Following reduction and evacuation, research grade CO (99.999%) was admitted from a glass bulb to a pressure of 8.0 Torr at ambient temperature, after which the CO spectrum was collected. The background (reference) spectrum was digitally subtracted from the CO absorbance spectrum. A second spectrum was obtained by simultaneously admitting 8.0 Torr CO and 1.0 Torr H_2O to a freshly reduced sample.

3. Results

3.1. DRIFT SPECTROSCOPY

Adsorption of carbon monoxide at room temperature immediately after reduction gives a complex spectrum as shown in fig. 1a. The absorption bands between 2100 and 1700 cm^{-1} can be attributed to CO chemisorbed onto reduced Pt clusters. The CO species, which are linearly bonded to Pt atoms absorb between 2100 and 1875 cm^{-1}, whereas the broad overlapping bands between 1875 and 1700 cm^{-1} are due to bridged CO species (bonded to two or more Pt atoms). The linear-CO band shows maxima at 2049, 2031, 2010 and 1990 cm^{-1}. The broad bridge-CO band consists of two overlapping bands with maxima at 1820 and 1770 cm^{-1}.

The remaining bands in the spectrum are due to adsorbed carbon dioxide and water species, present as contaminants in the gas-feed. The sharp peak at

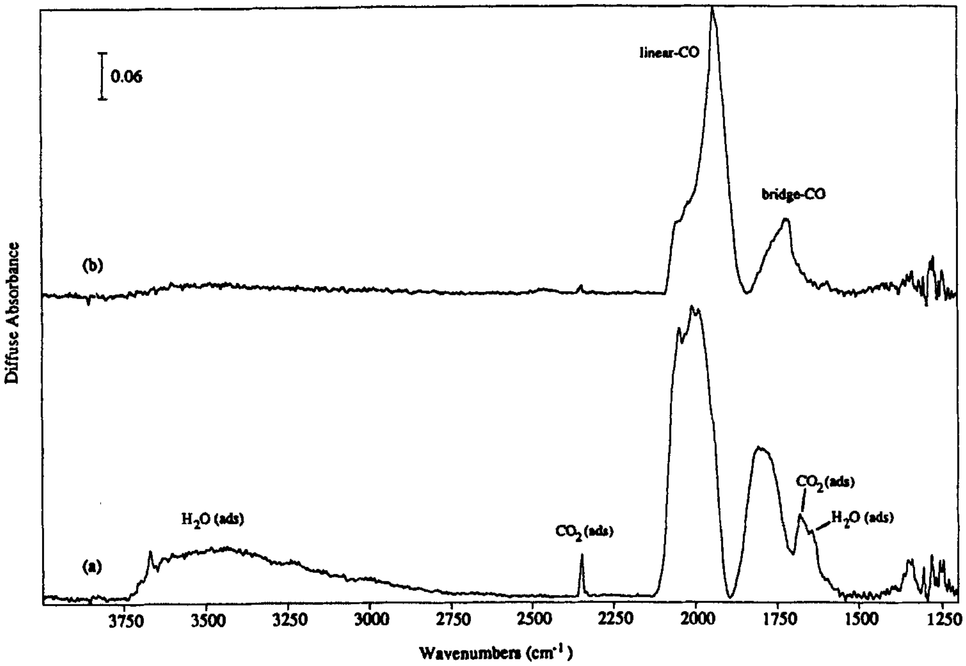

Fig. 1. DRIFT spectra of adsorbed CO on Pt/K-LTL zeolite reduced at 300°C for 4 h after saturation in CO gas-phase and (a) purge with Ar at room temperature and (b) purge with Ar at 200°C. The spectra have been corrected for CO gas-phase and catalyst background.

2346 cm^{-1} is due to physisorbed CO$_2$ [31]. The bands at 1678 and 1350 cm^{-1} are attributed to (bidentate) carbonate species formed by chemisorption of CO$_2$ onto the zeolite surface [32]. The presence of water contamination can be deduced from a weak band in the water bending region at 1643 cm^{-1} and the peaks in the OH stretching region, which are assigned to H$_2$O molecules with the oxygen coordinated to the framework cations [33]. The sharp 3673 cm^{-1} peak is the stretching mode of the non-bonded hydrogen atom of water. The other hydrogen of the water molecule, hydrogen-bonded with framework oxygen, gives rise to the broad band at 3450 cm^{-1}.

Heating the previous sample in argon at 200°C for 5 min changes the Pt–CO absorption spectra. The bands ascribed to the presence of water and carbon dioxide have disappeared (fig. 1b). In the absence of CO$_2$ and H$_2$O, the linear-CO band is observed at 1942 cm^{-1} with a shoulder at 1930 cm^{-1} and weak absorptions occur between 2100 and 2000 cm^{-1}. The absorption band due to bridging-CO also shifts to a lower frequency, i.e. 1718 cm^{-1}.

An argon flow at room temperature partially restores the CO absorptions above 1960 cm^{-1}, as is shown in figs. 2b and 2c (fig. 2a is the same as fig. 1b). With the

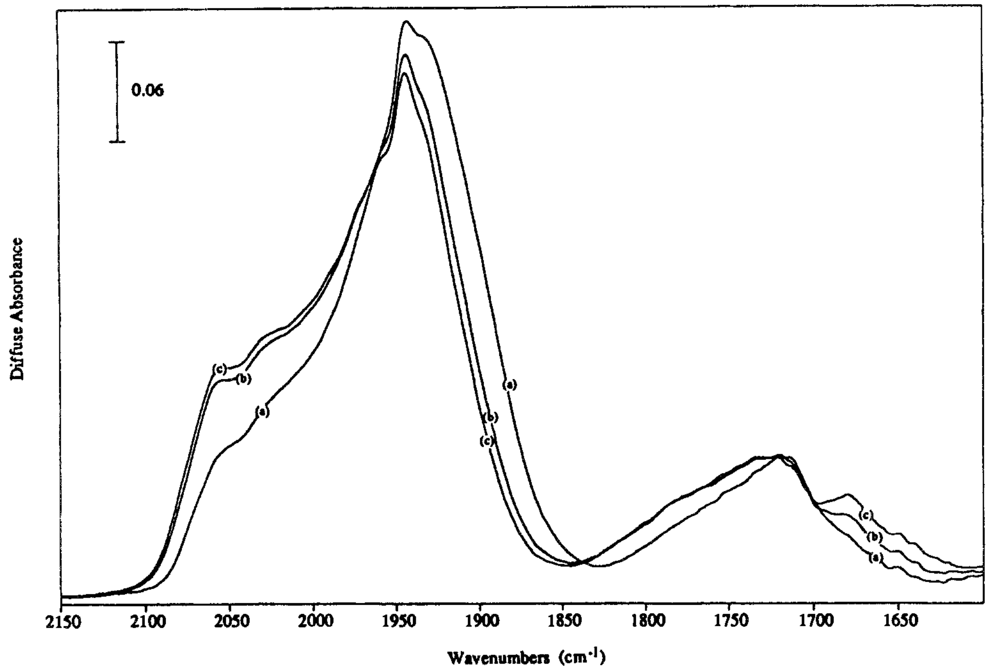

Fig. 2. DRIFT spectra of adsorbed CO on Pt/K-LTL zeolite reduced at 300°C for 4 h after (a) saturation in CO gas-phase and purge with Ar at 200°C, (b) purge with Ar at room temperature for 10 s, and (c) purge with Ar at room temperature for 2 min. The spectra have been corrected for CO gas-phase and catalyst background.

growth of the CO bands over 1960 cm^{-1}, the species absorbing around 1900 cm^{-1} disappear at the same time. The presence of an isosbestic point at 1960 cm^{-1} indicates conversion of the 1900 cm^{-1} bands into those above 1960 cm^{-1}. Flowing argon at room temperature re-introduces carbon dioxide and water, as can be observed clearly in the difference spectra presented in fig. 3. Bands due to OH species are observed again at 3673 and 3450 cm^{-1}. These hydroxyl bands were also observed after the first admission of argon following reduction (fig. 1a). Addition of H_2O and CO_2 does not fully restore the original spectra. Re-admission of CO at room temperature produces an infrared spectrum similar to that shown in fig. 1a, indicating that the metal particles have not been changed by heating to 200°C.

3.2. TRANSMISSION FT-IR SPECTROSCOPY

The infrared spectra of adsorbed CO on Pt/K-LTL reduced and evacuated at 300°C are presented in fig. 4. The spectrum taken after adsorption of CO (8 Torr) and H_2O (1 Torr) in fig. 4A is similar to fig. 1a obtained under flowing He contaminated with H_2O and CO_2. The band at 1637 cm^{-1} is assigned to the O–H deformation of adsorbed H_2O. The absorption spectrum taken after exposure to dry CO (fig. 4B) is similar to that obtained by DRIFT after drying in Ar at 200°C, fig. 1b.

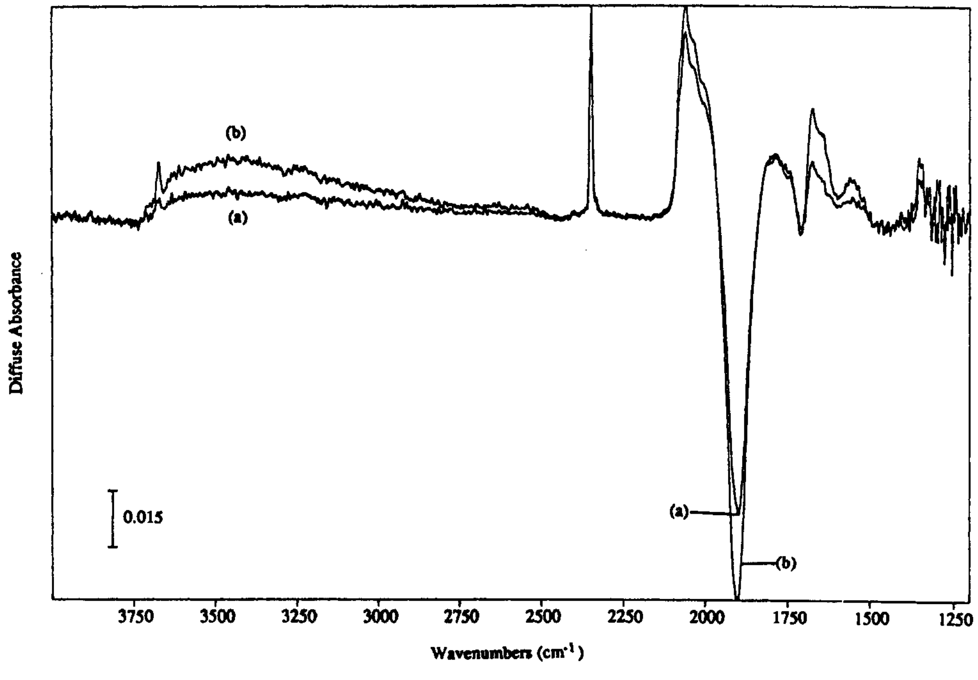

Fig. 3. DRIFT difference spectra of (a) fig. 2b minus 2a and (b) fig. 2c minus 2a.

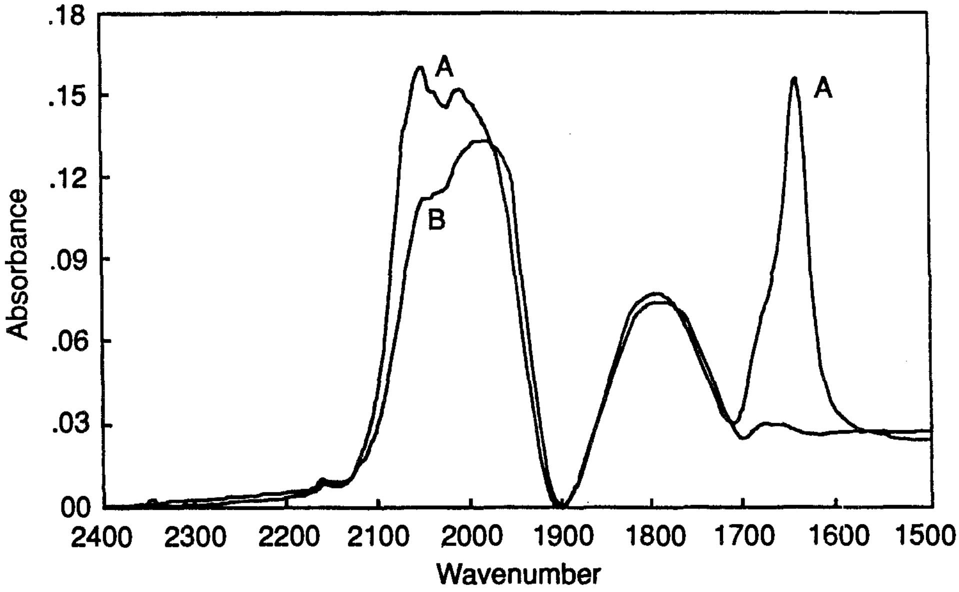

Fig. 4. Transmission FT-IR spectra of adsorbed CO on Pt/K-LTL zeolite reduced at 300°C for 1 h and evacuation at 300°C after (A) admission of 8 Torr CO and 1 Torr H_2O simultaneously at ambient temperature, and (B) admission of 8 Torr CO. The spectra have been corrected for CO gas-phase and catalyst background.

4. Discussion

The results from this study indicate that the infrared spectrum of adsorbed CO on Pt/K-LTL is strongly dependent on the experimental conditions, specifically, the presence of water in the catalyst. Based on these results, one can now understand the differences in spectra reported earlier [28–30]. For example, the DRIFT spectrum in fig. 1a (after CO adsorption in the presence of H_2O) is similar to the transmission FT-IR spectrum reported by Kustov et al. [29], and Kappers and Van der Maas [30]. By contrast, the transmission FT-IR spectrum reported by Lane et al. [28], obtained in the absence of H_2O, is similar to the DRIFT spectrum in fig. 1b. The spectral differences can be understood by realizing that the gases in flow experiments contain, typically, traces of water and carbon dioxide which contaminate the zeolite gradually. Traces of water, therefore, play a crucial role in the determination of the frequency of absorbed CO.

CO frequency shifts of approximately 15 cm^{-1} to *lower* energy have been reported for Pt/Al_2O_3, resulting from electron donation from H_2O to Pt [26]. However, on Pt/K-LTL there is a *blue* shift of at least 60 cm^{-1}, i.e. a frequency shift in opposite direction than can be explained by the adsorption of H_2O, a Lewis base, on the surface Pt atoms.

We believe that the observed shifts in the CO stretching frequency are to be explained by an ion–dipole interaction between the adsorbed CO and potassium ions in the zeolite channels [14,15,28]. Under dry conditions, the oxygen of the CO interacts directly with the potassium cations of the support, fig. 5a. Direct interaction of the oxygen atom of linear-CO with an alkali cation increases the adsorption energy and decreases the stretching frequency [35–37]. This is also in agreement with theoretical data [38]. Van Santen [39] has named the presence of direct electrostatic interaction between cation and CO adsorbate "bifunctional promotion".

We propose that H_2O adsorbs on the potassium ions, fig. 5b, screening the ion–dipole interaction and resulting in a higher CO stretching frequency. It is well known that small amounts of water strongly coordinate with cations present in zeolites [40–42]. The screening of the ion–dipole interaction by adsorbed H_2O requires that the K^+ ions must be nearby the platinum particles [43]. The potassium ions may be located at E sites [42] or may be alkali, present as 10% excess over the ion exchange capacity, within the zeolite pores.

The large shift to lower CO stretching frequencies considered in this paper and attributed to ion–dipole interactions should not be confused with a possible metal–support interaction in the Pt/K-LTL catalyst. It has been argued that the platinum clusters are electron-rich as a result of an increase in the platinum d-band density of states by electron donation from the basic LTL support [25–27]. This particular influence alone should be hidden in the CO spectrum observed in fig. 1a, as a red-shift of $\tilde{\nu}_{CO}$ compared to Pt/SiO_2. The interaction between the metal particles and the oxide support is not likely to be strongly affected by adsorbed H_2O. We, therefore, conclude that the large shifts of CO to lower frequency in Pt/K-LTL are due to ion–dipole interaction in addition to possible contributions from electron donation from the basic support.

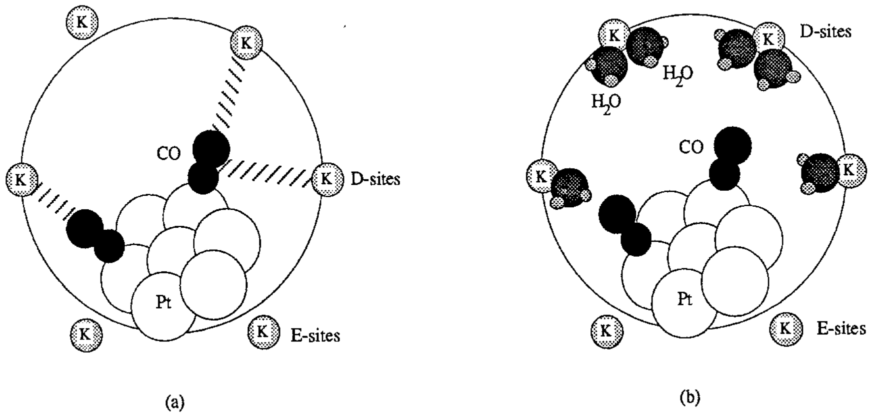

Fig. 5. Schematic representation of a cross-section of a Pt/K-LTL zeolite channel showing (a) the ion–dipole interaction in the absence of water, and (b) screening of the ion–dipole interaction by adsorbed water.

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