JOURNAL OF CATALYSIS **125**, 467–471 (1990)

Temperature Effects on the Infrared Spectrum of Carbon Monoxide Adsorbed by Supported Platinum

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Received March 27, 1990; revised May 15, 1990

When alumina-supported platinum with adsorbed carbon monoxide is heated to 200°C an infrared band at about 2000 cm^{-1} grows in and the main band at 2060 cm^{-1} decreases in intensity. When the sample is allowed to cool, the 2000 cm^{-1} band virtually disappears and the 2060 cm^{-1} band increases in intensity. The main band for CO adsorbed by silica-supported platinum at 2070 cm^{-1} decreases in intensity on heating and increases on cooling. The 2000 cm^{-1} band is absent on silica-supported platinum. We tentatively attribute this band to the C–O stretching vibration of linearly adsorbed CO which interacts with electron withdrawing sites on the support. The increase in the 2060 cm^{-1} (2070 cm^{-1} for Pt/SiO_2) band on cooling may be due to increasing dipolar interactions enhancing the intensity of high-frequency absorbers at the expense of low-frequency absorbers.

INTRODUCTION

In an earlier thermal desorption–infrared spectroscopic study of the adsorption of CO by alumina-supported platinum, we reported that a sample exposed to CO at room temperature and then heated under purge to 250°C revealed a band at about 2000 cm^{-1} which we attributed to the C–O stretching of CO linearly bound to sites which have no analogs on single crystals (*1*). Haaland had previously reported a similar band for a Pt/Al_2O_3 sample exposed to CO at 183°C, attributing it to CO bound to sites at steps (*2*). We now report that this band appears at elevated temperature and virtually disappears on cooling. The main band at about 2060 cm^{-1} increases in intensity on cooling. CO adsorbed by Pt/SiO_2 displays no band at 2000 cm^{-1}. Its main band at 2070 cm^{-1} displays behavior similar to that of Pt/Al_2O_3.

METHODS

Impregnated samples were prepared by dropwise addition of sufficient aqueous H_2PtCl_6 (Alfa) of the appropriate concentration to the support material to give incipient wetness while stirring thoroughly with a glass rod. Ion-exchanged Pt/SiO_2 was prepared by dropwise addition with constant mechanical stirring of a solution of 0.0992 g of $[Pt(NH_3)_4](NO_3)_2$ (Alfa) in 75 ml of water to a mixture of 10 g silica and 400 ml of water. Both the Pt-containing solution and the silica–water had been adjusted to a pH of 10 with aqueous ammonia. After the addition was complete, the mixture was allowed to stand with stirring for 2 hr. The solid was separated by vacuum filtration in a fritted funnel. With either technique, the damp solid was dried in a vacuum desiccator at room temperature and then stored in air until preactivated. Catalyst samples were preactivated in a reactor consisting of a vertical glass tube containing a fritted disk. Reactant gases passed upward through a bed of short glass tubes to facilitate preheating then through the frit and the sample, which was fluidized. Preactivated samples were stored in vials under air until used. The preparation of wafers for infrared studies was as described previously (*1*). The alumina was Degussa Aluminiumoxid C; the

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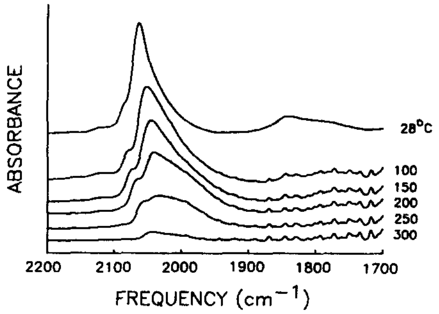

FIG. 1. Thermal desorption of CO from 0.3% Pt/Al_2O_3.

silica was Cab-O-Sil grade M-5 (Cabot). Both were donated by the manufacturers.

The equipment was identical to that used in our previous study, with the exception noted below (*1*). In essence, gases passed through a purification train and then into a quartz cell with KCl windows containing a self-supporting wafer of sample in a quartz holder. We modified the purification train by removing the supported manganese oxide traps from the helium and hydrogen lines and by adding a commercial OM-1 trap (Supelco) to the helium line.

The FTIR spectra we report result from coaddition of four scans, the collection of which took about 25 s. The previous paper describes the procedure for background subtraction (*1*). The sample area of the spectrometer was covered with plastic film to maintain the dry air purge. The gases, which were provided by Airco, were as follows: helium grade 5 (99.999%), hydrogen grade 4.5 (99.995%), carbon monoxide grade 4 (99.99%), and oxygen grade 2.6 (99.6%). Water, when used, was allowed to diffuse into the purge stream from a glass doser in the shape of a "T." An O-ring stopcock in the upright of the T isolated the water which was in the lower part of the upright. Purge gas flowed through the horizontal part of the T, which was connected to the gas switching system and the IR cell with ultra-Torr fittings (Cajon). The water was purified by distillation and ion exchange, then boiled in the doser and subjected to eight freeze–pump–thaw cycles. The doser was only used for the water dosing experiment. For the other experiments the switching system was connected directly to the IR cell.

RESULTS

Figure 1 shows a typical set of thermal desorption infrared spectra for CO adsorbed by 0.3% Pt/Al_2O_3. We had preactivated this sample in oxygen for 3.5 hr at 300°C and in hydrogen for 3 hr at 300°C. After activating the sample *in situ* for 2 hr in flowing oxygen at 300°C followed by 2 hr in flowing hydrogen at 300°C, we cooled the sample under helium purge, admitted flowing CO at 1 atm at room temperature, purged with helium, and recorded these spectra as the temperature increased. The main band at 2060 cm^{-1} shifts to lower frequency and broadens as the temperature increases. By about 200°C it is quite clear that there is an overlapping band at about 2000 cm^{-1}. This band becomes more prominent relative to the 2060 cm^{-1} band at higher temperature.

Figure 2 shows the results of the same experiment performed on 0.3% Pt/SiO_2 prepared by ion exchange. We had preactivated this sample in oxygen for 2 hr at 300°C and in hydrogen for 2 hr at 200°C. The *in situ* activation consisted of heating to 205°C in flowing helium followed by 2 hr treatment in flowing hydrogen at 205°C. The main band at 2070 cm^{-1} decreases and shifts to lower frequency as the temperature increases. In

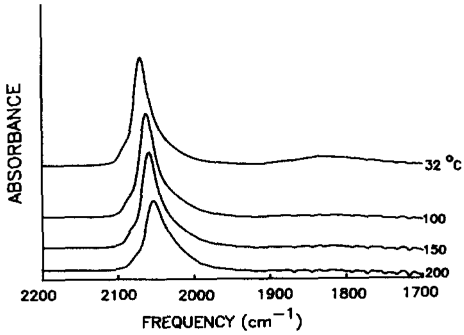

FIG. 2. Thermal desorption of CO from 0.3% Pt/SiO_2.

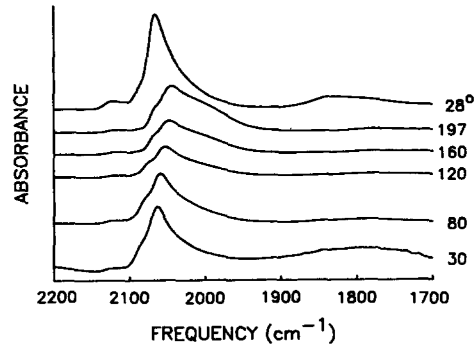

FIG. 3. CO adsorbed at room temperature by 0.3% Pt/Al_2O_3 followed by heating to 200°C and cooling.

this case there is no 2000 cm^{-1} band evident at 200°C. A 0.3% Pt/SiO_2 catalyst prepared by impregnation displayed similar results.

Figure 3 shows spectra of 0.3% Pt/Al_2O_3 preactivated and *in situ* activated as above. We exposed the sample to CO at room temperature, rapidly heated it under helium purge to 200°C, held it briefly at 200°C, then cooled it to room temperature. At 200°C the spectrum resembles the 200°C spectrum in Fig. 1. Upon cooling, the 2060 cm^{-1} band and the bridge bands gain in intensity and the 2000 cm^{-1} band decreases in intensity. Upon returning to room temperature the spectrum resembles that which was taken immediately after CO exposure, although there seems to be slightly more tailing of the 2060 cm^{-1} band to low frequency.

We considered the possibility that the behavior of the 2000 cm^{-1} band could be due to adsorption of traces of water from the purge gas. Upon heating, this water would desorb giving rise to band growth, and upon cooling, more water would adsorb, causing the band to decline in intensity. To test this, we exposed an activated sample of Pt/Al_2O_3 to CO at 40°C, purged with helium, then opened a water doser in the purge line. We then heated the sample to 200°C and allowed it to cool under wet purge. The spectra were essentially identical to those of Fig. 3, which were taken under nominally dry conditions.

Figure 4 shows spectra of impregnated 0.3% Pt/SiO_2, preactivitated and *in situ* activated as above, exposed to CO at room temperature, heated under purge to 197°C, and allowed to cool. The intensity of the main band decreases and the frequency increases with cooling until 70°C, whereupon the intensity begins to increase and the frequency remains constant.

All of the samples show a shoulder at high frequency, typically at about 2080 cm^{-1}.

DISCUSSION

The three key observations which we have made are the reversible appearance of the 2000 cm^{-1} band on Pt/Al_2O_3 upon heating, the absence of this band on Pt/SiO_2, and the increase in the intensity of the main (2060 cm^{-1} or 2070 cm^{-1}) band upon cooling.

The chief characteristics of the 2000 cm^{-1} band are that it is present on Pt/Al_2O_3, absent on Pt/SiO_2, and that it grows in intensity at elevated temperature and disappears when the temperature is lowered. It seems to persist on purging at least as well as the 2060 cm^{-1} band. So far as we know, this band was first reported by Haaland (*2*), who assigned it to linear CO adsorbed at steps. In the light of single crystal studies, which report that CO on steps absorbs at frequencies in the range of 2065 to 2095 cm^{-1} (*3*, *4*), this assignment seems unlikely. Our observation that water deliberately added to the purge gas does

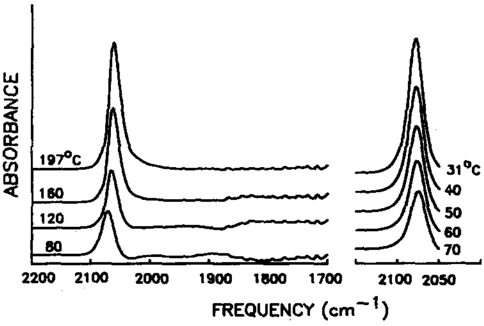

FIG. 4. CO adsorbed at room temperature by 0.3% Pt/SiO_2 followed by heating to 200°C and cooling.

not cause a decrease in the intensity of the 2000 cm^{-1} band at 200°C indicates that contamination of the sample with water is not the cause of the observed temperature effects. One possible explanation for this band is that it is due to linear CO (on Pt) which interacts in some way with the support. This would account for the presence of this band on the alumina-supported sample and its absence on the silica-supported sample and on unsupported platinum. We also have some preliminary results which suggest that the 2000 cm^{-1} band is relatively less prominent on Pt/Al_2O_3 samples with higher platinum loadings. This is consistent with a support effect. The temperature behavior of this band is of considerable interest. We might imagine that the CO in sites giving rise to the 2000 cm^{-1} band is in a higher energy state than that giving rise to the other bands. At room temperature most of the CO would be in the lower energy state, but at higher temperature a significant fraction could be in the higher energy state. This increased energy does not seem to be due to a lower adsorption energy, because this species is at least as tightly bound as the other linear forms. We can speculate that the 2000 cm^{-1} band arises from partial transfer of electrons from the C–O binding molecular orbitals to acceptor sites on the support. This would weaken the C–O bond and hence lower its stretching frequency without much affecting the adsorption energy. Thus the total energy of the adsorbed molecule would be higher than that of a molecule which did not interact with the support in this way. It is possible to make a rough estimate of the difference between the energy for the 2000 cm^{-1} state and the other linear states. If, without making any quantitative claims, we suppose that the amount of CO in this state at 200°C is 10 times as great as it is at 25°C, then a simple two-level statistical approach would estimate the energy difference as 15.5 kJ/mol. This is about 1.5% of the thermodynamic bond energy for gas phase CO.

This model seems to account for our observations and it gives an energy separation which is not ridiculous. It may account, at least in part, for the well-known broadness of the linear CO band on Pt/Al_2O_3 as compared to that on Pt/SiO_2. Thus it warrants further testing.

The increase of the main (2060 cm^{-1} or 2070 cm^{-1}) band with cooling seems best explained by dipolar interactions. While it is plausible that on Pt/Al_2O_3 some of the recovery of the 2060 cm^{-1} band is due to conversion of the 2000 cm^{-1} form on cooling, this cannot be the case on Pt/SiO_2 which exhibits no 2000 cm^{-1} band. One of the effects of dipolar interactions between two vibrators whose frequencies are close is to increase the effective absorptivity of the higher frequency vibrator at the expense of the lower frequency vibrator (*5*). If we imagine that there are potentially coupled vibrators with a range of frequencies representing the main band, then increased coupling would enhance the highest frequency at the expense of the lower parts of the range. This may account for the apparent enhancement of the main band upon cooling, especially in the case of Pt/SiO_2. As the temperature decreases, coupling may become more important, perhaps because of a decrease in wagging, rocking, frustrated translation, and similar motions. As a result, the highest frequency absorption is enhanced. The loss at lower frequency would be spread out over a range of frequencies, and hence would be lost in the baseline. This interpretation finds support in the behavior of the 2070 cm^{-1} band frequency for Pt/SiO_2 on cooling, as shown in Fig. 4. A similar phenomenon involving intermolecular coupling between the C–O stretching vibration and other modes, called vibrational dephasing, has been observed to cause a decrease in frequency and an increase in bandwidth for linear CO adsorbed by Ru(001) (*6*). Vibrational dephasing can be expected to make a contribution to the observed results.

ACKNOWLEDGMENTS

This work was supported, in part, by West Chester University. We thank Dr. R. P. Eischens and Dr. R. Pitchai for helpful comments and encouragement.

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