

NOTE

Evidence for Monatomic Platinum Species in H-ZSM-5 from FTIR Spectroscopy of Chemisorbed CO

Numerous studies have been carried out regarding the preparation and characterization of small metal particles entrapped in zeolite matrices. The zeolite framework not only imposes a steric constraint, but also strongly affects the intrinsic properties of encaged metals. Brønsted acid sites in the acidic forms of zeolites (Y, ZSM-5) were shown to act as electron acceptors and decrease the electron density on the metal (1-7).

The reduction of Pt^{2+} by hydrogen, a standard procedure following the ion exchange of the zeolite mostly with $\text{Pt}[(\text{NH}_3)_4]^{2+}$, leads to the interaction of the protons formed with the metal particles. In the metal-proton adducts the positive charge of the protons is shared with the metal (4, 8). The existence of a positive charge on the metal particles has been verified by different methods. A shift in the binding energy of X-ray photoelectrons to higher values is indicative of $\text{Pt}^{\delta+}$ (9). Moreover, positively charged metal particles exhibit higher catalytic activity in hydrogenation (10-12) and hydrogenolysis (7, 10, 12, 13). FTIR spectroscopy of CO chemisorbed on supported Pt catalysts has shown that stretching frequencies and relative intensities of the CO bands are sensitive to oxidation state (15, 16), particle size (17-23), and metal-support interaction (23, 24), and can serve as a powerful tool for the characterization of the electronic state of supported metal particles.

Recently it has been shown that zeolite protons can stabilize Pt in atomic form in Pt/H-mordenite (25). These species have been characterized by very unusual stretching vibration frequencies (2123 cm^{-1}) in the IR spectra of chemisorbed CO. In the following it will be shown that isolated platinum atoms located in different positions of the ZSM-5 framework can be detected and characterized by CO chemisorption.

Pt/H-ZSM-5 samples containing 0.5 and 1 wt% of Pt were prepared from H-ZSM-5 zeolite (Si/Al = 23). Platinum was introduced via ion exchange in a dilute solution (0.01 M) of $\text{Pt}[(\text{NH}_3)_4]\text{Cl}_2$ with a zeolite slurry in deionized water (200 ml g^{-1} of zeolite) for 24 h at room temperature. The sample was dried overnight at ambient temperature than calcined in flowing O_2 (flow rate $1000\text{ ml min}^{-1}\text{ g}^{-1}$) with a heating rate of 0.5 K/min to 673 K and held there for 2 h. Thereafter the sample was purged with Ar, followed by cooling to 300 K. Reduction was carried out in

flowing H_2 with the temperature ramped at a rate 8 K/min from 300 K to the desired value with a hold at this temperature for 2 h, followed by cooling to 300 K in a hydrogen flow and purging with Ar. The 0.5% Pt/ZSM-5 sample was reduced at 573 and 823 K in order to study the effect of the reduction temperature on the final catalyst structure. The sample containing 1 wt% of Pt was reduced at 623 K.

The Fourier transform infrared spectra were recorded on a Bio-Rad single beam FTIR spectrometer in the range of $400\text{--}4000\text{ cm}^{-1}$ with a resolution of 2 cm^{-1} . The self-supported wafers of the reduced Pt/H-ZSM-5 sample with a thickness of approximately $5\text{--}7\text{ mg/cm}^2$ were mounted in a cell connected to a turbomolecular pump and to a gas handling system. The sample was evacuated overnight starting with a temperature program (0.5 K/min) from 300 to 623 K, a hold at 623 K for 3 h followed by cooling to 300 K. The ultimate vacuum in the cell was $1 \times 10^{-4}\text{ Pa}$. Before measurements samples were reduced again in flowing hydrogen of $1 \times 10^{-3}\text{ Pa}$ at 573 or 623 K for 30 min. After reduction, background spectra were measured in 10 K intervals heating at a rate of 2.5 K/min.

The samples were exposed to CO: (i) at 10^{-1} Pa for 15 min in flowing mode under continuous evacuation; (ii) at $3 \times 10^4\text{ Pa}$ for 15 min in static mode; (iii) at $3 \times 10^4\text{ Pa}$ for 2 h in static mode; (iv) at stepwise increased CO pressure in static mode: 10^2 Pa for 15 min; for 30 min; and for 1 h; $3 \times 10^4\text{ Pa}$ for 15 min; for 30 min; and for 1 h. Each CO adsorption was followed by temperature-programmed desorption, which was carried out at 2.5 K/min up to 623 K and spectra were taken in 10 K intervals starting at 300 K.

Adsorption of carbon monoxide on 0.5% Pt/ZSM-5 reduced at 573 K results in the appearance of two bands at 2124 and 2091 cm^{-1} (Fig. 1). Increase of the reduction temperature for this catalyst to 823 K leads to the disappearance of both bands in the IR spectra of adsorbed CO and appearance of a narrow symmetric band at 2082 cm^{-1} (Fig. 2).

On the sample with higher metal loading (1% Pt/ZSM-5) adsorption of carbon monoxide at low CO pressure results in the appearance of a band at 2082 cm^{-1} (Fig. 3) similar to that obtained for 0.5% Pt/ZSM-5 reduced at high temperature (Fig. 2). Upon thermodesorption this band significantly shifts toward lower frequency and splits into two

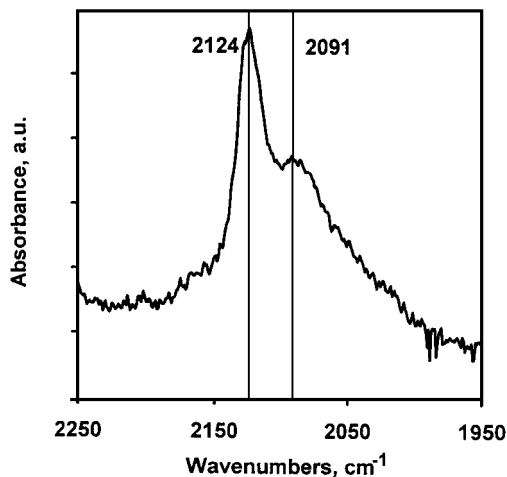


FIG. 1. FTIR spectrum of CO adsorbed at 10^{-1} Pa for 15 min on 0.5% Pt/ZSM-5 reduced at 573 K.

components (at ~ 2070 and 2050 cm^{-1} , respectively). At the same time a weak band initially present as a shoulder at 300 K appears at 2123 cm^{-1} .

Figure 4 shows the spectra obtained after adsorption at increased CO pressure and time (up to 3×10^4 Pa and 2 h, respectively). The curve-fitting analysis of these spectra reveals the presence of five bands in the initial spectra at 2053 , 2082 , 2092 , 2123 , and 2157 cm^{-1} (Fig. 5).

The bands at 2123 and 2092 cm^{-1} appear to be very stable under thermodesorption compared with the bands at 2082 and 2053 cm^{-1} . The elimination of the bands at 2082 and 2053 cm^{-1} starts already at 323 K and is completed between 523 and 573 K. The intensity of the bands at 2123 and 2092 cm^{-1} does not change up to 573 K. The curve-fitting analysis clearly indicates that the initial apparent decrease in the intensity between 323 and 473 K is entirely attributed

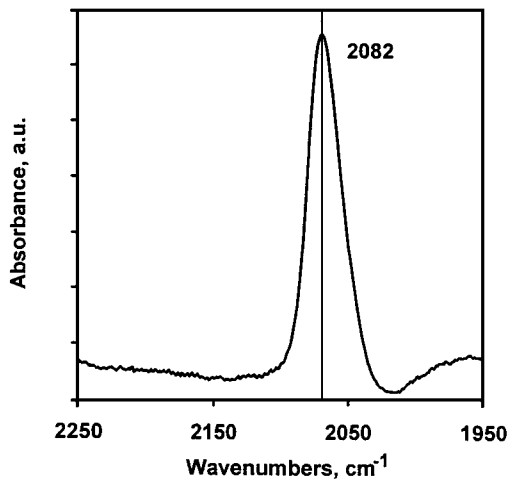


FIG. 2. FTIR spectrum of CO adsorbed at 10^{-1} Pa for 15 min on 0.5% Pt/ZSM-5 reduced at 823 K.

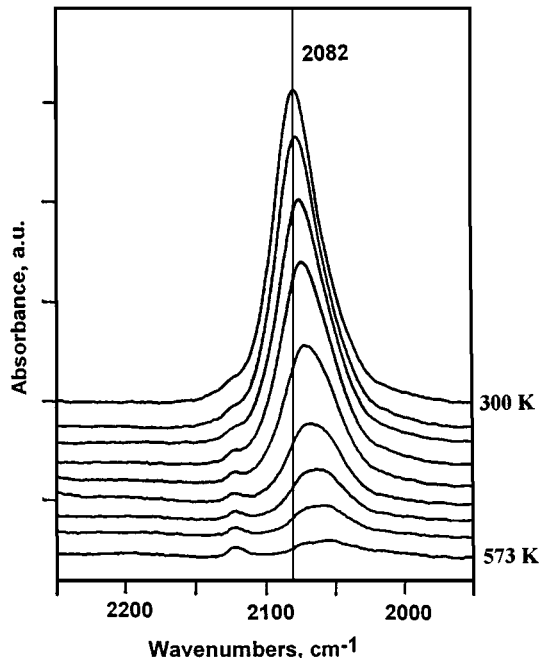


FIG. 3. FTIR spectra upon thermal desorption following CO adsorption at 10^2 Pa for 15 min on 1% Pt/ZSM-5 reduced at 623 K: 300 K (top spectrum), 343, 363, 393, 423, 453, 483, 523, and 573 K.

to the elimination of the band at 2082 cm^{-1} . The bands at 2123 and 2092 cm^{-1} remain in the spectra even after desorption at 623 K and continuous desorption at this temperature is required for their complete elimination.

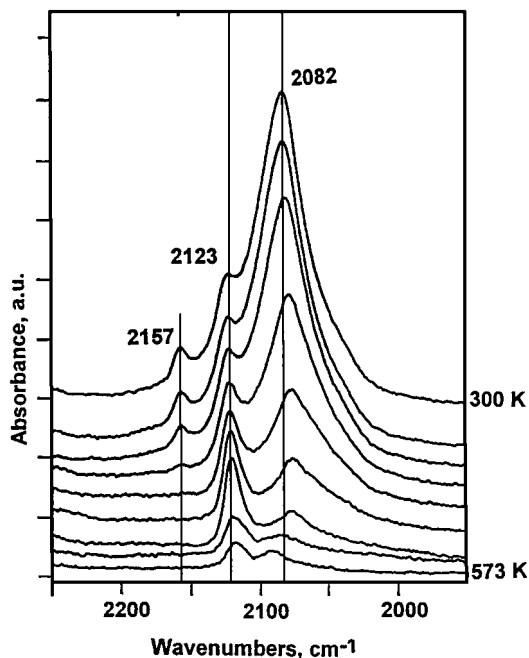


FIG. 4. FTIR spectra upon thermal desorption following CO adsorption at 3×10^4 Pa for 2 h on 1% Pt/ZSM-5 reduced at 623 K: 300 K (top spectrum), 343, 363, 393, 423, 453, 483, 523, and 573 K.

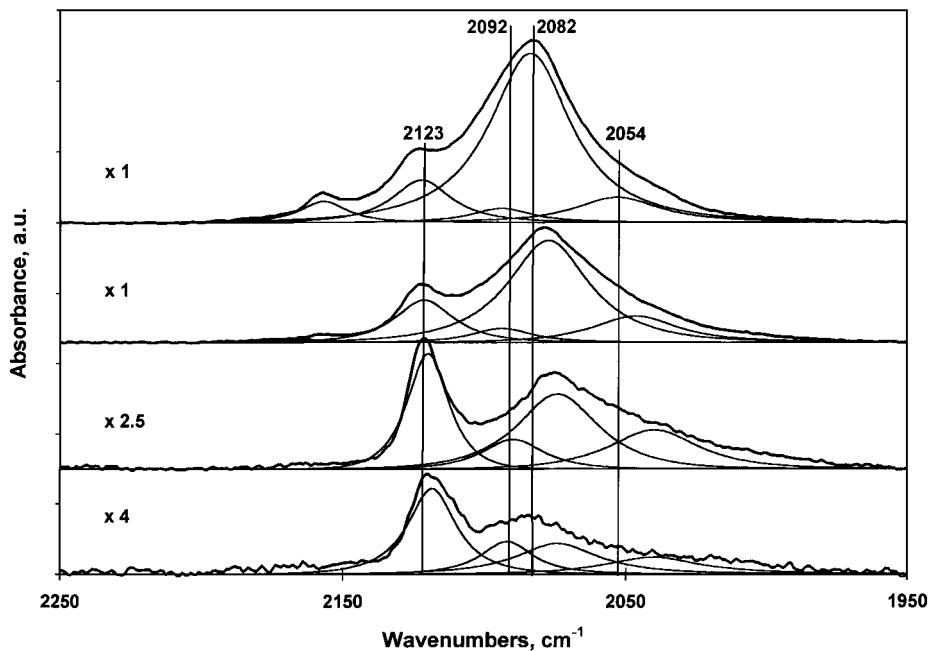


FIG. 5. Curve-fitting analysis of the FTIR spectra obtained upon thermal desorption of the CO from 1% Pt/ZSM-5 reduced at 623 K: 300 K (top spectrum), 423, 483, and 523 K.

Moreover, upon increasing the CO adsorption time at 3×10^4 Pa to 2 h a new band at 2157 cm^{-1} arises. However, this band shows lower stability and can be easily removed even upon evacuation at room temperature.

It is noteworthy to compare the variations of the positions of the bands at 2082 and 2123 cm^{-1} upon thermodesorption. The dependences of their positions on the intensity are depicted on Figs. 6 and 7, respectively. The band at 2082 cm^{-1} shifts significantly toward lower frequency. Extrapolation of the CO stretching vibration frequency to zero coverage gives the value of 2075 cm^{-1} . The variation of the band position at 2123 cm^{-1} is depicted in Fig. 7. Unlike the band at 2082 cm^{-1} the position of this band remains almost unaltered. The band shifts only slightly by $2\text{--}3 \text{ cm}^{-1}$.

The bands at 2056 and 2092 cm^{-1} exhibit a similar behavior (Fig. 5). While the band at 2056 cm^{-1} shifts by $\sim 15 \text{ cm}^{-1}$, the position of the band at 2092 cm^{-1} is practically unchanged.

After complete thermodesorption of the adsorbed CO (Figs. 4 and 5) the 1% Pt/ZSM-5 sample was re-exposed to CO with a stepwise increase in CO pressure and time for elucidation of the effect of these factors. The results are presented in Fig. 8. Clearly, the intensity of the band at 2123 cm^{-1} increases with increasing the time and pressure of the adsorption.

Afterward, adsorbed CO was removed by thermodesorption, and the sample was exposed again to CO under conditions corresponding to the initial step of the adsorp-

tion (10^2 Pa for 15 min). This treatment completely restores the initial spectrum (Fig. 8, spectrum 1).

For the discussion of the possible assignment of the bands in the spectra of Pt/ZSM-5 several groups of bands can be discerned on the basis of their characteristics and their behavior upon thermodesorption.

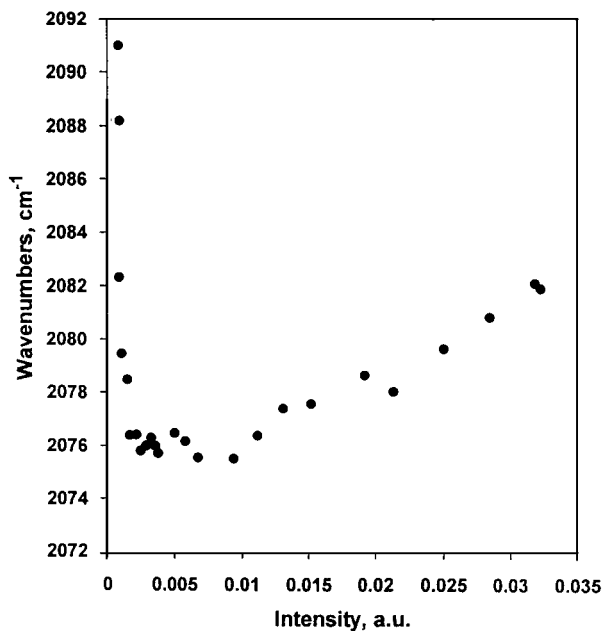


FIG. 6. Dependence of the position of the band at 2082 cm^{-1} on its intensity in the course of CO thermodesorption.

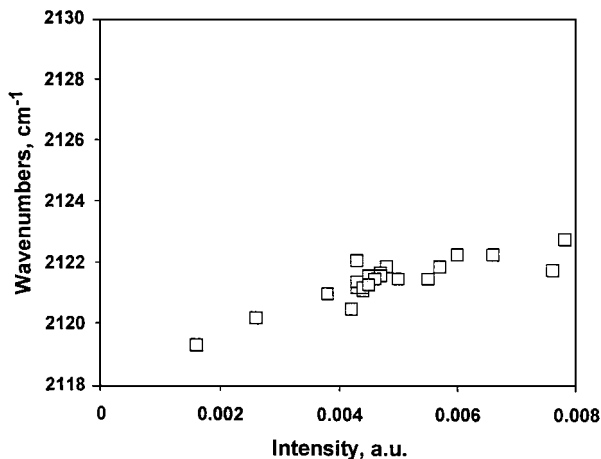


FIG. 7. Dependence of the position of the band at 2123 cm^{-1} on its intensity in the course of CO thermodesorption.

(i) The Band at 2157 cm^{-1}

This band was observed only in the 1% Pt/ZSM-5 sample. The band is very weak and can be easily removed by evacuation at room temperature. In agreement with recent literature this band can be attributed to CO adsorbed on Pt ions (26, 27). The low intensity of the band indicates that only a trace amount of Pt remains unreduced in 1% Pt/ZSM-5 sample.

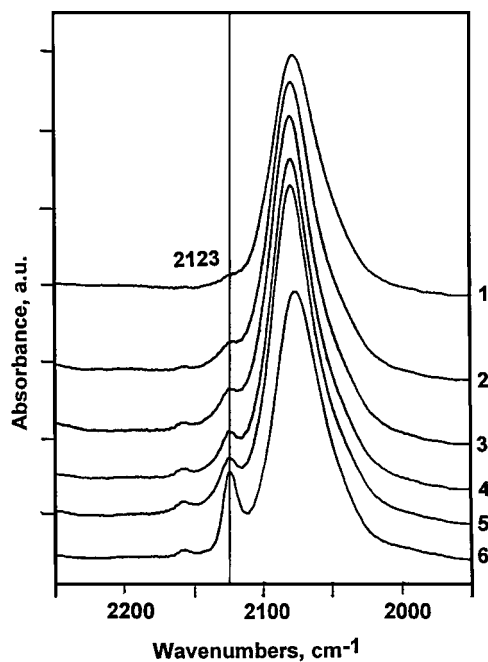


FIG. 8. Variation of the CO spectra upon CO adsorption at ambient temperature and increased time and pressure on 1% Pt/ZSM-5 reduced at 623 K: CO adsorption at 10^2 Pa (1) for 15 min (top spectrum); (2) 30 min; (3) 1 h; $3 \times 10^4\text{ Pa}$ (4) 15 min; (5) 30 min; (6) 1 h.

(ii) The Bands at 2082 and 2056 cm^{-1}

The frequencies of these bands correspond to the frequencies of CO linearly adsorbed on supported Pt particles ($2060\text{--}2080\text{ cm}^{-1}$). The bands are relative easily removed upon thermodesorption and demonstrate the behavior characteristic of CO molecules adsorbed on the surface of metal particles (Figs. 4–6). Thus, they exhibit the typical coverage-dependent shift upon thermodesorption, which is due to elimination of dipole–dipole interaction with decrease in surface coverage. Primet *et al.* (20, 28) showed that the frequency obtained by extrapolation of the thermodesorption data to zero coverage corresponds to the frequency obtained from isotopic dilution experiments, and that this value might be considered as the singleton frequency free of dipole–dipole coupling. Upon thermodesorption the band at 2082 cm^{-1} shifts to 2074 cm^{-1} (Fig. 6). The band at 2056 cm^{-1} shifts to 2045 cm^{-1} (Fig. 5). Comparison of these frequencies with those obtained in the course of similar experiments for Pt/ Al_2O_3 (2052 cm^{-1} (20)) and Pt/NaY (2060 cm^{-1} (28)) shows that the band at higher frequency is shifted markedly toward a higher wavenumber by $15\text{--}23\text{ cm}^{-1}$. This band can be attributed to small Pt particles inside the zeolite channels: the increase in the stretching vibration frequency of CO adsorbed on these particles results from the decrease of the electron density on the particles due to the interaction with strong Brønsted sites of highly acidic HZSM-5 zeolite (5, 8, 9).

The band at 2056 cm^{-1} can be attributed to the particles on the outer zeolite surface. The electronic structure of these particles remains almost unaltered and the adsorbed CO exhibits the lower frequency, typical for Pt supported on a support with low acidity (*vide supra*).

(iii) The Bands at 2123 and 2092 cm^{-1}

The most intriguing features in the spectra are the bands at 2123 and 2092 cm^{-1} . Upon thermodesorption these bands do not exhibit the coverage-dependent shift typical for CO adsorbed on a Pt metal surface (Figs. 4, 5, and 7). The slight shift by $2\text{--}3\text{ cm}^{-1}$ can be attributed to the temperature dependence of the stretching vibration. In addition, their intensities appear to be a function of CO adsorption time and pressure (Fig. 8). Interestingly, in the 0.5% Pt/ZSM-5 sample reduced at lower temperature these bands are the main bands in the spectrum, while the high-temperature reduction converts them to the band at 2082 cm^{-1} (Figs. 1 and 2). Several alternative interpretations should be considered for the careful assignment of these bands.

(i) They can be assigned to CO adsorbed on Pt sites with high coordination numbers. It was demonstrated that the CO stretching vibration frequency increases with increasing coordination numbers of the Pt sites (see Table 1) (21, 29, 30). Thus, CO adsorption on Pt(111) faces results in the peak at $2090\text{--}2100\text{ cm}^{-1}$ (29). However, these peaks

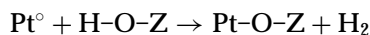
TABLE 1
Unusual CO Bands in the IR Spectra of Pt Catalyst

| Catalyst | Pretreatment of the reduced catalyst | Wavenumber (cm ⁻¹) | Assignment | Comments | Ref. |
|--|--|--------------------------------|---|--|------------|
| Pt/SiO ₂ | — | 2090 2100 | CO on Pt(111) terraces | The CO band frequency is found to be higher on the Pt sites with higher coordination numbers. | 21, 29, 30 |
| 6.2% Pt/Al ₂ O ₃ | CO oxidation by O ₂ | 2123 2092 | CO on PtO CO on Pt ⁺¹ | The bands are almost invisible in the reduced catalyst and become more pronounced under reaction conditions (excess of O ₂). | 15 |
| 5% Pt/Al ₂ O ₃ | Heating under 100 Torr O ₂ at 323 K for 1 h | 2120 2090 | $\begin{array}{c} \text{O} \\ \diagup \\ \text{Pt} \\ \diagdown \\ \text{CO} \end{array}$ | Upon oxidation the band at 2090 cm ⁻¹ appears. Further oxidation leads to the diminution of this band and appearance and growth of the band at 2120 cm ⁻¹ . | 20 |
| Pt-Cr/HZSM-5 | No pretreatment | 2120 2092 | Pt ^{δ+} -CO Pt-CO | | 43 |
| 0.5–5% Pt/Mor | No pretreatment | 2123 2092 | -O-H...Pt ^{δ+} -CO Pt-CO | The bands arise and grow upon increase in the reduction temperature in the range 323–573 K. Reduction at 773 K leads to the disappearance of these bands and appearance of the band at 2082 cm ⁻¹ . | 25 |
| 1% Pt/HZSM-5 | No pretreatment | 2123 } 2092 } 2082 } | Pt ₁ ^{δ+} -(CO) ₂ Pt(cluster)-CO | | This work |

were observed only for relatively large Pt particles (~4 nm) which do not fit inside the ZSM-5 structure and should be located on the outer surface. In this case, these sites should be occupied first during adsorption due to higher adsorption energy (30), and better accessibility. This is at variance with the experimental fact that these bands appear only after prolonged adsorption at elevated CO pressure (Fig. 8). Moreover, the absence of the coverage-dependent shift for these bands (Figs. 4, 5, and 7) also contradicts this assumption.

(ii) The appearance of these bands may be also attributed to CO adsorption on partially reduced Pt ions (see Table 1). However, careful XPS study of the 0.5% Pt/ZSM-5 sample (31) containing a maximum relative amount of these species (Fig. 1) indicated that the platinum in this sample is completely reduced.

(iii) The possible reoxidation of Pt metal particles by zeolite protons should be taken into account:



This process has been reported for small metal particles or supported carbonyls (32–35). However, exhaustive investigation of this process by Sachtler *et al.* (32, 33) indicates that the reoxidation of Pt atoms by zeolite protons proceeds only at high temperature (~450°C).

(iv) Another alternative to be considered is the reoxidation of Pt by zeolite protons induced by the extended

CO treatment. This process has been reported repeatedly for Rh-containing catalysts (35, 36). The promoting effect of CO on the Rh reoxidation is related to the formation of the stable Rh(CO)₂⁺ carbonyl:



However, similar Pt carbonyls are not stable (36–38) and there is no effect of the adsorbed CO on the platinum reoxidation by zeolite protons, as reported by Sachtler and Zhang (39).

The existence of reoxidized Pt can be also ruled out based on the result that after readsorption of CO at 10² Pa for 15 min, following CO adsorption at 3 × 10⁴ Pa and its complete desorption, the initial spectrum (Fig. 8, spectrum 1) is completely restored without pronounced bands at 2123 and 2092 cm⁻¹. In addition, the assignment of the bands at 2123 and 2092 cm⁻¹ to CO adsorption on Pt ions seems to be unlikely, because the adsorption of CO on these sites was found to be very weak (26, 27) which is in contrast to the high stability of these bands found upon thermodesorption (Figs. 4 and 5).

The most convincing explanation so far has been proposed by Zholobenko *et al.* (25) in the case of Pt-mordenite. The authors assigned the band at 2123 cm⁻¹ to CO adsorbed on monatomic Pt⁰ species. This interpretation appears to be the most plausible for Pt/ZSM-5 and provides a conceivable interpretation of the experimental data. Indeed,

the band at 2123 cm^{-1} is easily detected on Pt/ZSM-5 only when conditions known to favor the formation of atomically dispersed metal species are used, i.e., low metal loading and low reduction temperature. When the Pt loading and/or the reduction temperature increases, the band at 2082 cm^{-1} typical for CO adsorbed on Pt particles becomes predominant (compare Fig. 1 and Figs. 2 and 3).

An important argument in favor of monatomically dispersed Pt is the constancy of the band position at 2123 cm^{-1} during thermodesorption of CO (Figs. 4, 5, and 7) and the low value of the band half-width (Fig. 5). Presumably, in low-loaded samples reduced at low temperature, the major part of Pt exists as isolated Pt atoms. The high wavenumbers of adsorbed CO indicate that Pt is strongly electron deficient, and exists probably as $[\text{Pt}-\text{H}_{\text{zeol}}]^+$ adducts (25).

This is confirmed by a density functional model cluster study (40) according to which an experimentally observed shift of 20 cm^{-1} of the band at 2123 cm^{-1} relative to the stretching frequency of the free CO molecule (2143 cm^{-1}) can be assigned to electron-deficient Pt atoms anchored to the zeolite by one or two acidic hydroxyl group.

The assignment of the band at 2123 cm^{-1} provides the following tentative interpretations of the appearance of the band at 2092 cm^{-1} .

(i) As can be seen from the data obtained (Figs. 1, 4, and 5) the appearance of the band at 2123 cm^{-1} is always accompanied by the band at 2092 cm^{-1} . Similar results were obtained by Zholobenko *et al.* (25). Chemisorption data obtained by these authors for samples with a high relative concentration of Pt in atomic dispersion have shown a CO : Pt ratio markedly greater than 1. It can therefore be assumed that coordinatively highly unsaturated Pt atoms are able to coordinate 2 CO molecules forming a dicarbonyl. This has already been suggested by Bischoff *et al.* (27). The dicarbonyl species might be responsible for the appearance of the second band in the spectra of CO adsorbed on isolated Pt atoms. In this case the band at 2092 cm^{-1} would correspond to the asymmetric and the band at 2123 cm^{-1} to the symmetric vibration of the dicarbonyl. The ratio of the intensities of the asymmetric and the symmetric bands (Figs. 1 and 5) of $I_{\text{as}}/I_{\text{sym}} < 1$ is indicative of a OC-Pt-CO bond angle of less than 90° (41). Of course, the unambiguous assignment of the bands at 2123 and 2092 to Pt dicarbonyl requires ^{13}C - ^{12}C isotopic dilution experiments and further experimental investigation of the reported phenomena is needed.

(ii) As an alternative the Pt atoms located in two different positions in the zeolite structure has to be considered. According to Yakovlev *et al.* (40) CO adsorbed on Pt atoms anchored in a four ring with two bridging hydroxyls could account for a further red shift and thus for the frequency observed at 2092 cm^{-1} . This would also explain why the formation of the two bands is always observed simultaneously.

Interestingly, the band at 2123 cm^{-1} can be detected in the highly loaded 1% Pt/ZSM-5 only upon extended CO adsorption at elevated pressure. Note that the increase in CO adsorption time and pressure leads to a steady increase in the intensity of the bands (Fig. 8). The band at 2091 cm^{-1} is still screened by the strong band at 2082 cm^{-1} . The following tentative explanation may be given for these observations. For the low-loaded sample reduced at low temperature, the majority of the Pt atoms are localized in the main channels and easily accessible for CO adsorption (Fig. 1). However, increase in reduction temperature and/or metal loading results in the formation of Pt particles in the main channels, which exhibit spectra characteristic of CO adsorbed on a Pt surface (Figs. 2 and 3). For 1% Pt/ZSM-5 the monatomic species become visible only upon extended CO adsorption at elevated pressure and the band at 2123 cm^{-1} might thus be attributed to Pt atoms located in hidden sites of the ZSM-5 structure, which are not readily accessible for CO. This slow development of the band appears to be a transport limited process. It was demonstrated (42) that metal ions can be localized not only in the main channels of the ZSM-5 structure, but also inside the polyhedron formed by 6-, 5-, and 4-membered rings. Probably, after reduction of 1% Pt/ZSM-5 a fraction of the Pt atoms remains in these hidden positions. These positions are less accessible for CO molecules and a longer exposure time at elevated CO pressure is required for an interaction of Pt species in these positions with CO.

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