Characterization of the Pt–C bond of CO adsorbed by small Pt particles in a NaX zeolite by IR diffuse reflectance spectroscopy

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The unusual properties of small (1–2 nm) Pt particles within a zeolite support are documented by diffuse reflectance infrared spectroscopy of the metal–carbon bond of linearly adsorbed CO. The wave number of the metal–carbon stretching frequency is found to be about 60 cm^{-1} higher compared to larger particles (2–3 nm) or to the bulk metal. The stronger bond is attributed to a negative charge on the small metal particles.

Keywords: CO chemisorption on Pt; carbon–Pt bond; IR diffuse reflectance spectroscopy

1. Introduction

Due to the narrow pore size distribution zeolites are unique supports for the preparation of metal dispersions with different though uniform sizes of the small metal particles under appropriate preparation procedures [1,2]. A common way to study their properties is the adsorption of CO as a molecular probe with IR control of the state of adsorbed species. The stretching frequency of the linear form of adsorbed CO was found to decrease with increasing dispersion of the platinum incorporated in the micropores of a faujasite matrix [3]. Similar effects in metal loaded zeolites were attributed to back donation of electrons resulting from the negative charging of small metal particles [4–7]. However, the C–O bond is not directly involved in adsorption. Therefore, its stretching frequency is rather insensitive to the nature and the state of the metal. More informative in this respect is certainly the Me–C stretching vibration that can be directly measured for CO adsorption on metal films and single crystals [8–11]. For supported metals the corresponding bands are hidden under intensive Me–O–Me bending modes of the oxide carriers. Therefore, for metal loaded zeolites the direct observation of the Me–C stretching vibrations was not yet reported.

Some new possibilities are provided in this context by the diffuse reflectance IR technique [12]. Due to the very high sensitivity it allows the observation of the combination of C–O and Me–C stretching bands that are about two orders of magnitude less intensive than the fundamental modes. The Me–C frequencies can then be easily obtained as the difference between the combination and the C–O stretching frequencies [11,12].

The aim of this paper is the application of this approach to the study of platinum loaded zeolites that have been investigated earlier in ref. [3].

2. Experimental

The Pt loaded NaX zeolite with a Si/Al ratio of 1.2 was prepared according to procedures described in refs. [2,13] by ion exchange with the tetraammine ion complex from aqueous solutions of the chloride. After ion exchange the samples were washed until complete removal of the chloride ions and dried at 353 K. The degree of ion exchange was equal to 10%.

The specimens were heated in flowing O_2 up to 673 K (5 K min^{-1}) followed by treatment in flowing hydrogen at 573 K for 1 h [13]. The mean diameter of platinum particles after such treatment as evaluated from electron micrographs was equal to 1–3 nm (fig. 1).

IR diffuse reflectance spectra were recorded according to ref. [12] at room temperature for the original samples in the form of a powder and for small grains (0.25–0.5 nm in diameter) made from powder by pressing and subsequent crushing. The aim of the latter preparation was to reproduce thin pressed pellets that were used before for measurements of transmittance IR spectra in ref. [3].

Before diffuse reflectance IR measurements the samples were additionally evacuated and reduced in IR cells at 570 or 628 K for 2 h under static conditions ($P_{H_2} = 1.3 \times 10^4$ Pa). Then they were again evacuated for 1 h at the same temperature. Under these conditions an Ostwald ripening of the samples can be expected [13].

CO adsorption was carried out at room temperature at the equilibrium pressure of 1.3×10^3 Pa. IR spectra were also recorded at this temperature either in CO atmospheres or after evacuation at 298 K and different elevated temperatures.

3. Results and discussion

Evolution of IR spectra of CO adsorbed by the granulated sample at different surface coverages is presented in fig. 2. In the fundamental region of the C–O stretching vibrations a band with the maximum at 2080 cm^{-1} with a low frequency

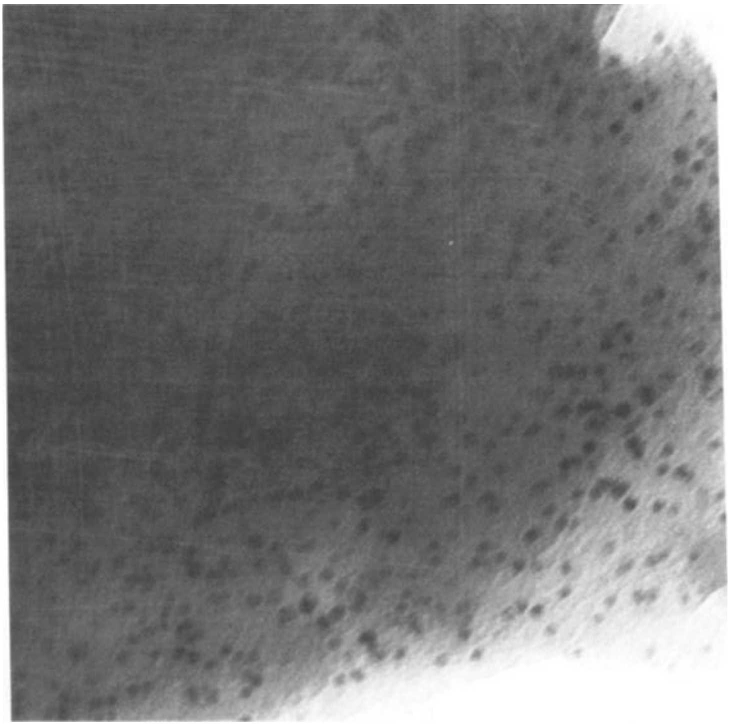

Fig. 1. Transmission electron micrograph of Pt dispersed in a NaX matrix (1 mm = 1.8 nm).

shoulder appears in CO atmosphere (fig. 2a). Both of them belong to linear forms of CO adsorption and are similar to the spectra previously reported for alkaline earth forms of platinum loaded zeolites [3–7].

The successive sample evacuation for 20 min at 470 K (b) and 620 K (spectrum c) results in a decrease of the CO adsorption and shifts both the main band and the shoulder towards lower frequencies. This is a common feature of carbon monoxide adsorption on metallic platinum connected with the decrease of dipole–dipole coupling between the adsorbed molecules at a low surface coverage [8]. The positions of the bands at the lowest surface coverage (those of singletons) are the characteristics of isolated CO molecules and therefore can be used for the comparison of different supported platinum catalysts. For the sample under consideration they are equal to 2045 and 1970 cm^{-1} (fig. 2c) indicating two different kinds of CO adsorption. According to refs. [4,6,7] the lower C–O stretching frequency should be attributed to CO linearly adsorbed by negatively charged small Pt particles, while the high frequency band can be assigned to CO adsorption on larger Pt particles with properties only slightly different from those of massive platinum foils or films.

The intensity of CO bands for the powdered sample is much higher due to the more intensive light scattering (fig. 3). In the presence of gaseous CO the positions

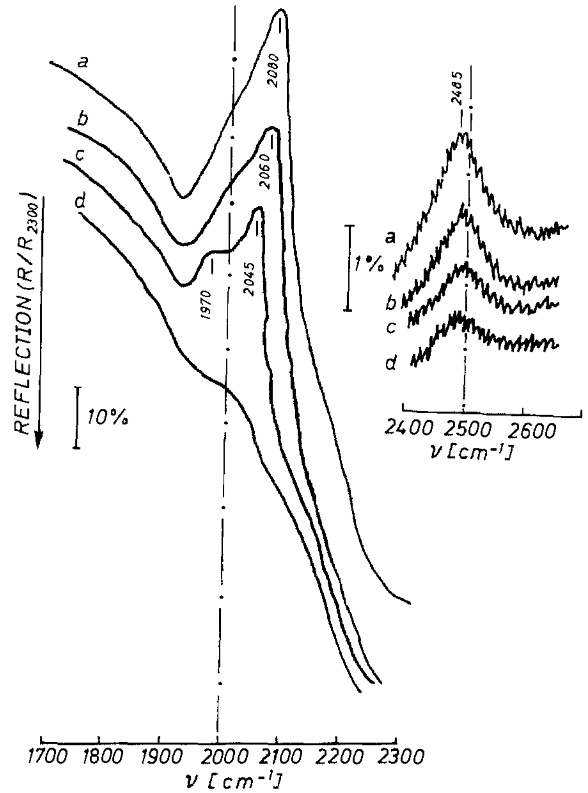

Fig. 2. IR diffuse reflectance spectra of CO adsorbed on granulated Pt/NaX zeolite ($\alpha = 10\%$) in the fundamental C–O stretching and $\nu_{CO} + \nu_{Pt-C}$ combination regions (inset). (a) $P_{CO} = 1.3 \times 10^3$ Pa, (b) after evacuation at 470 K for 20 min, (c) subsequent evacuation at 620 K for 20 min, (d) the background.

of the maxima in the fundamental region can be only estimated (a), however, at lower surface coverages the resolution is improved (spectra b and c). In addition, an intense band at 1700–1800 cm^{-1} connected with bridging forms of adsorbed CO is also observed both in the presence of gaseous CO and after evacuation at 470 K.

At a higher temperature of evacuation the bridging form is desorbed, while the intensity of the linear form decreases several times and two bands with maxima at 1970 and 2020 cm^{-1} can clearly be distinguished (spectrum (c) in fig. 3).

The remarkable difference between the spectra of CO adsorbed on granulated and powdered samples is the reversal of the ratio between the low frequency and high frequency band intensities. Indeed, for the crushed pellets, the high frequency band predominates indicating the lower platinum dispersion. This could be due to some sintering in the course of the additional treatment in hydrogen, which may have led to an increasing fraction of the larger (2–3 nm) particles. This spectrum practically coincides with the transmittance spectra of the pellet reported earlier in ref. [7].

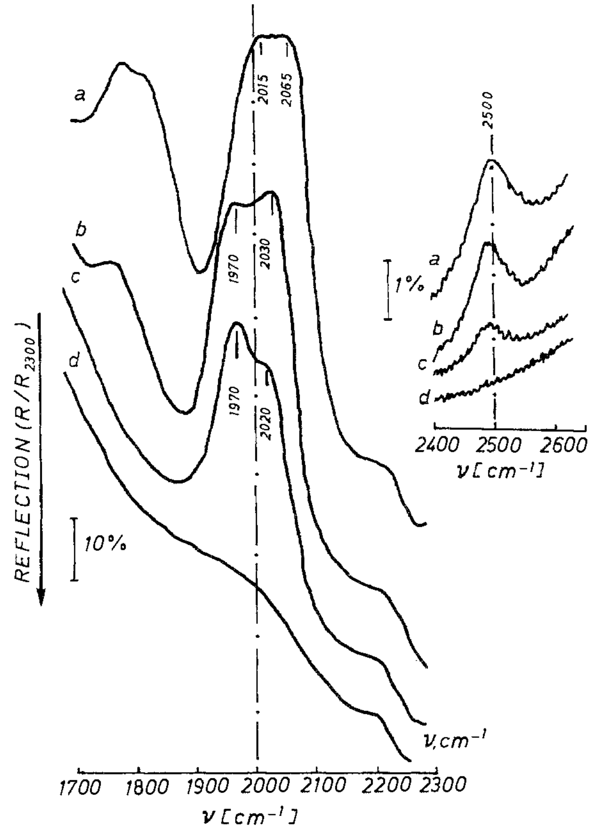

Fig. 3. IR diffuse reflectance spectra of CO adsorbed on powdered Pt/NaX zeolite ($\alpha = 10\%$) in the fundamental C–O stretching and $\nu_{CO} + \nu_{Pt-C}$ combination regions (inset). (a) $P_{CO} = 1.3 \times 10^3$ Pa, (b) after evacuation at 470 K for 20 min, (c) subsequent evacuation at 620 K for 20 min, (d) the background.

The spectra of the same granulated and powdered samples in the combination $\nu_{CO} + \nu_{Pt-C}$ region (2400–2600 cm^{-1}) are represented in the right parts of figs. 2 and 3 (note that their intensity is much lower). In both cases, only the single unresolved combination bands with the maximum at about 2500 cm^{-1} for the powdered or at 2485 cm^{-1} for the granulated samples are observed. Their positions are the same both in CO atmosphere and after desorption at 573 K in contrast to the behavior of the fundamental CO stretching vibrational frequencies that shift to lower frequency with decreasing surface coverage. This is in agreement with the results reported in refs. [11,12] where the frequency of the combination mode has been shown not to depend on dipole–dipole coupling between adsorbed CO molecules. Hence, for the lowest surface coverage, the combination frequencies are equal to the sum of the singletons of the stretching vibrations of isolated adsorbed CO molecules and the Me–C stretching vibrations. The frequencies of the latter can then be obtained as the difference of the combination frequencies and the singletons.

The corresponding values for low frequency forms of CO adsorption on powdered and granulated samples are equal to 515–530 cm^{-1}. This is about 60 cm^{-1} higher than the value of 460–470 cm^{-1} reported in refs. [8,10,11] for the $\nu_{\mathrm{Pt-C}}$ stretching frequency of CO linearly adsorbed on the Pt(111) single crystal face or on Pt films. Thus, our results confirm the unusual properties of the very small Pt particles encapsulated in the micropores of the zeolite matrix.

On the other hand, for the high frequency linear forms of CO adsorption the differences between the combination frequencies and the singletons are less. For the powdered sample, the corresponding value is equal to 480 cm^{-1}, while for granulated sample to $\nu_{\mathrm{Me-C}} = 440\ \mathrm{cm}^{-1}$. Both of them are close to the Pt–C frequency reported earlier for massive platinum and Pt single crystal and confirm the assignment of the corresponding bands to the bigger platinum particles.

4. Conclusion

We show that CO molecules linearly adsorbed on small platinum particles with dimensions of 1–2 nm encapsulated in the cavities of NaX zeolite show a Pt–C stretching frequency higher by about 60 cm^{-1} compared to massive platinum and consequently are more strongly bonded to the Pt surface. This effect is also accompanied by the lower CO stretching frequency. The stronger binding should be attributed to the higher extent of back donation of electrons from the small Pt particles t the adsorbed CO molecules compared to larger particles or to bulk platinum. This finding is consistent with the concept of negatively charged small platinum particles in zeolites earlier postulated in refs. [4–7]. The presence of small Pt particles with unusual properties and the larger particles with properties closer to the bulk metal is in agreement with histograms which can be derived from fig. 1. Their proportion depends on the pretreatment conditions.

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