Electronic state and location of Pt metal clusters in KL zeolite: FTIR study of CO chemisorption

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Electronic state and location of Pt metal clusters supported on KL zeolite are studied by FTIR spectroscopy of adsorbed CO. Investigation of the CO adsorption was performed within the wide CO pressure range (from 4×10^{-3} to 10^2 Pa) and supplemented by the study of the CO desorption at elevated temperature. Comparison of the data on CO adsorption and desorption at increased temperature reveals the existence of two groups of Pt particles in the sample. The first group of the particles is localized on the outer surface of the zeolite microcrystals and in the near surface region; they exhibit CO bands at 2060–2050 cm^{-1} close to those of Pt supported on conventional supports. The particles of the second group are encaged inside zeolite channels and their electronic structure is presumably strongly perturbed by the zeolite framework. CO adsorbed on the Pt particles of this group exhibits coverage dependent bands at frequencies in the range 1960–1920 cm^{-1}. The marked downward shift of the νCO band is attributed to the increase of electron density on these particles.

Keywords: Pt / KL zeolite; CO chemisorption on Pt; IR spectroscopy; electron microscopy

1. Introduction

Numerous studies have been carried out on the preparation and characterization of small metal particles entrapped in a zeolite matrix. Zeolite framework not only imposes a steric constraint for reacting molecules, but also strongly affects the intrinsic properties of encaged metals. Brønsted acid sites in the acidic forms of zeolites Y and ZSM-5 were shown [1–7] to act as electron acceptors and to decrease the electron density on the metal. Positively charged metal particles exhibit higher catalytic activity in hydrogenation [8–10] and hydrogenolysis [7,8,10,11] as well as stronger resistance to sulphur poisoning [12–14]. However, it was suggested that the framework of basic zeolites could act like an electron donor and increase the electron density on the metal clusters. Formation of "electron-rich" metal particles was proposed on the basis of IR, EXAFS and catalytic data [15–19].

A very intriguing system is Pt supported on basic KL zeolite. Due to the remarkable activity and selectivity in *n*-hexane aromatization [20–22] this catalyst attracts much attention. The high aromatization activity of the catalyst [16,23–25] was ascribed to both geometric (channeling of reactant) and electronic effects.

The electronic effect of the KL lattice was manifested in competitive hydrogenation of a benzene–toluene mixture [17] and in the IR spectra of adsorbed CO [16,18,19,23,26–29]. Generally, a prominent downward shift of 100–120 cm^{-1} of the CO stretching vibration frequency was observed with respect to Pt/SiO_2. IR study of CO adsorption on Pt/KL by Besoukhanova et al. [16] and Larsen and Haller [18] showed that the position of the CO bands is the function of the type of exchanged alkali and alkaline earth cations. Both groups of authors concluded that platinum in KL zeolite is electron-rich.

However, a number of aspects remains unexplained. (1) No attempts have been made by now to estimate the frequency of the singleton CO (i.e., free of dipole–dipole coupling) adsorbed on Pt/KL. This value should provide more reliable information on the electronic state of the metal particles [30]; it is also diagnostic of the interaction between Pt particles and zeolite carrier. (2) As shown in many papers, the IR spectra of CO adsorbed on Pt/KL exhibit abnormally broad bands. Thus, the FWHM of the bands attributed to linear CO adsorbed on Pt/KL is 120–150 cm^{-1}, while the FWHM of the bands of CO on other supports including zeolites is 30–50 cm^{-1}. The origin of this anomalous behaviour is not clear. (3) The mechanism of the possible donation of an electron density from the zeolite support to platinum particles also remains obscured.

To elucidate these questions we have carried out a thorough FTIR investigation of CO adsorption on Pt/KL catalyst applying several approaches, which were not employed up to now for investigation of this system: (1) CO adsorption over wide range of CO pressure from 4×10^{-3}–10 Pa; (2) examination of temperature-programmed desorption of CO from the sample and extrapolation of the CO frequences obtained to zero coverage.

It will be shown in the following that this set of experiments enables one (1) to suggest the existence of two groups of Pt particles distinguished by the location, particle size and interaction with the zeolite support and (2) to make different environments of the metallic particles responsible for altered CO band positions.

2. Experimental

2.1. MATERIALS

Pt/KL zeolite was prepared by incipient wetness impregnation of KL zeolite with an appropriate amount of $Pt(NH_3)Cl_2$ dissolved in distilled water. The sample was dried overnight at 298 K and calcined in flowing O_2 at a flow rate of 1000 ml/min with the temperature ramped at a rate of 0.5 K/min from 298 to 673 K with a hold at 673 K for 2 h. Thereafter the sample was purged in Ar, followed by cooling to 298 K. Reduction was carried out in flowing H_2 with the temperature ramped at a rate 8 K/min from 298 to 673 K with a hold at 673 K for 2 h, followed by cooling to room temperature in flowing hydrogen and purging with Ar.

2.2. TRANSMISSION ELECTRON MICROSCOPY

TEM was carried out with a Philips EM 420 T electron microscope (LaB_6 filament) operated at 120 kV. The catalyst was ground to a fine powder, deposited on a copper grid coated with a carbon film and dispersed on the grid ultrasonically.

2.3. FTIR MEASUREMENTS

The Fourier transform infrared spectra were recorded on a BIO-RAD single beam FTIR spectrometer in the range of 400–4000 cm^{-1} with a resolution of 2 cm^{-1}. The self-supported wafers of the reduced Pt/KL sample (without binder) with a thickness of approximately 5–7 mg cm^{-2} were pressed and mounted in a cell connected to a turbomolecular pump and to a gas handling system. The sample was evacuated overnight with the temperature ramped at a rate of 0.5 K/min from RT to 623 K with a hold at 623 K for 3 h, followed by cooling to RT. The ultimate vacuum in the cell was 1×10^{-4} Pa. Before measurements the sample was rereduced in flowing hydrogen of 102 Pa at 623 K for 30 min. After reduction background spectra were measured ramping the temperature at 2.5 K/min in 10 K intervals.

Adsorption experiments were performed at RT in several steps at different CO pressures. At the first stage, CO was admitted at a pressure of 4×10^{-3} mbar in flowing mode under continuous evacuation, and spectra were taken every 2 min for 25 min. Thereafter, the CO pressure was increased up to 10^2 Pa and spectra were taken every 2 min for 0.5 h. Temperature-programmed desorption measurements were performed ramping the temperature at 2.5 K/min from RT to 623 K, the spectra were taken every 10 K.

3. Results

3.1. TEM

TEM measurements performed for Pt/KL reduced at 723 K showed that most of the Pt particles are hardly detectable at magnifications as high as 500000 (fig. 1, reduced to 75% of the original size). A few clusters with diameter < 1 nm are uni-

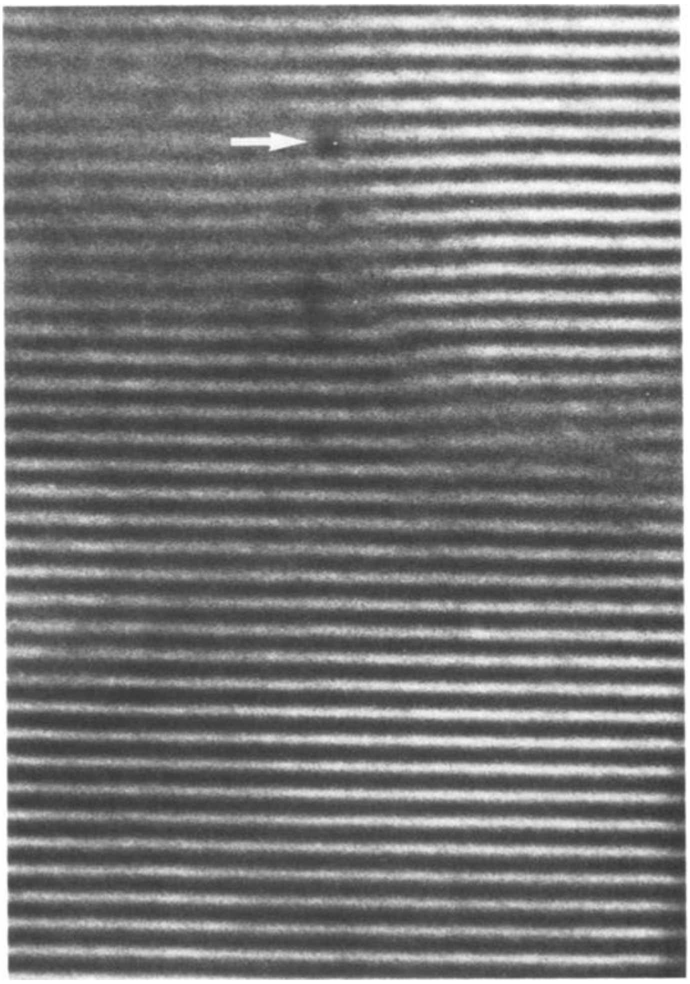

Fig. 1. Electron micrograph of 1 wt% Pt/KL sample. A Pt particle is marked by an arrow.

formly distributed within the zeolite structure. Only very few particles have dimensions exceeding 5 nm located on the external surface.

3.2. CO ADSORPTION MEASUREMENTS

Adsorption of carbon monoxide at low CO pressure results in the appearance of a very broad band in the region 1600–1900 cm^{-1}, which can be attributed to the linearly bonded CO, and the band near 1850 cm^{-1} which can be attributed to the bridged CO. Fig. 2 shows the variation of the spectra upon CO admission at 4×10^{-3} Pa. Initially CO adsorption at the low pressure results in the appearance of a high frequency band (HFB) near 2050 cm^{-1}. This band gradually grows upon

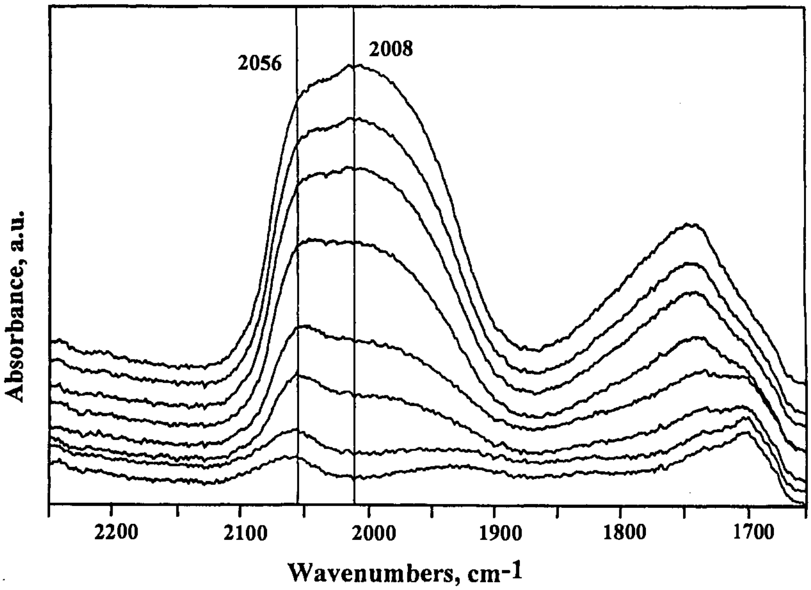

Fig. 2. Variation of the CO spectra upon adsorption at 4×10^{-5} mbar; time of adsorption: 3 min (bottom spectrum), 5 min, 7 min, 13 min, 15 min, 19 min, 25 min.

CO adsorption. Moreover, after several minutes the band at lower wavenumbers near 2000–1980 cm^{-1} (low frequency band (LFB)) arises in the spectra. Following CO admission leads to the predominant growth of this band. Its intensity gradually increased during CO adsorption and after 20–30 min of the adsorption the LFB dominates in the spectra. Upon adsorption at higher CO pressure (10^2 Pa) the LFB/HFB intensity ratio increases and at the end of the adsorption the LFB becomes the principal band in the spectra (fig. 3).

Dependence of the integral intensity of linear bonded CO on the adsorption time is depicted in fig. 4. As is evident from the figure, saturation of the Pt surface with CO is reached by the end of the adsorption.

Fig. 5 shows the variation of the spectra of adsorbed CO upon desorption at increased temperature. Initially, desorption results in the preferential elimination of the HFB. In the course of further desorption of the LFB diminishes and shifts downward. The dependence of the LFB frequency on the integral intensity is depicted in fig. 6. As can be inferred from the figure extrapolation to zero coverage gives a value of the frequency of 1920–1918 cm^{-1}.

4. Discussion

Adsorption of CO at 10^2 Pa results in the appearance of a very broad band in the region 2060–1900 cm^{-1}. This situation is quite general for IR spectra of CO adsorbed on Pt/KL. Comparing the spectra reported in refs. [18,19,23,26–29] we

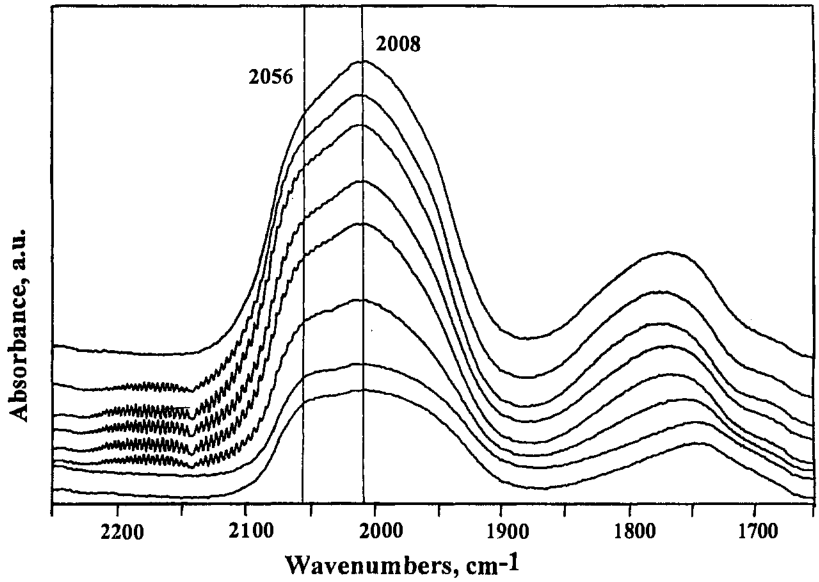

Fig. 3. Variation of the CO spectra upon adsorption at 1 mbar; total time of adsorption: 25 min (bottom spectrum), 27 min, 29 min, 31 min, 33 min, 39 min, 49 min, 53 min.

can conclude that in all papers the observed peak of adsorbed CO is enormously broad (100–200 cm^{-1}). Taking into consideration that the natural bandwidth of CO adsorbed on Pt supported on conventional supports is about 50 cm^{-1} we can assume that the observed bands are so broad, because they comprise a variety of bands corresponding to CO molecules adsorbed on sites with different environments: particles with different locations in zeolite matrix and varied degree of

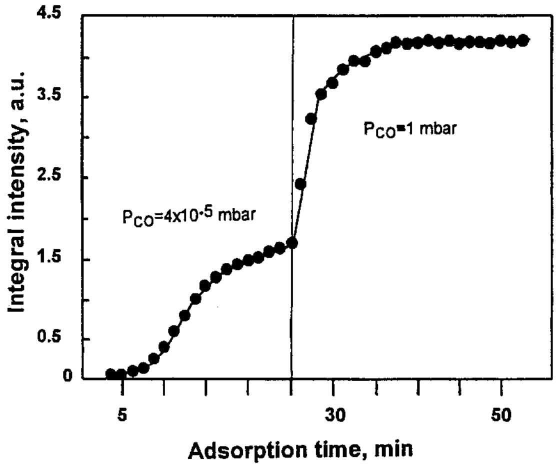

Fig. 4. Time dependence of the integral intensity of linear bonded CO upon CO adsorption at different CO pressures.

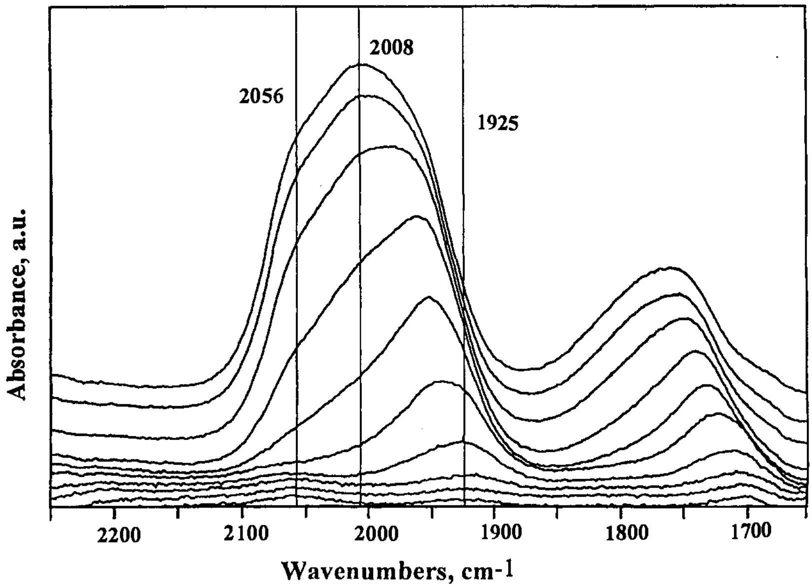

Fig. 5. Thermal desorption CO spectra: 298 K (top spectrum), 343 K, 373 K, 443 K, 473 K, 523 K, 573 K, 573 K (after 20 min), 573 K (after 40 min).

metal–zeolite interactions, particles of different shapes etc. Indeed, considering the spectra measured during adsorption–desorption experiments, we can discern at least two distinct groups of the Pt particles. CO adsorption on the first group of the particles results in the appearance of the HFB exhibiting a frequency similar to that observed for Pt supported on conventional carriers. The band of carbon mon-

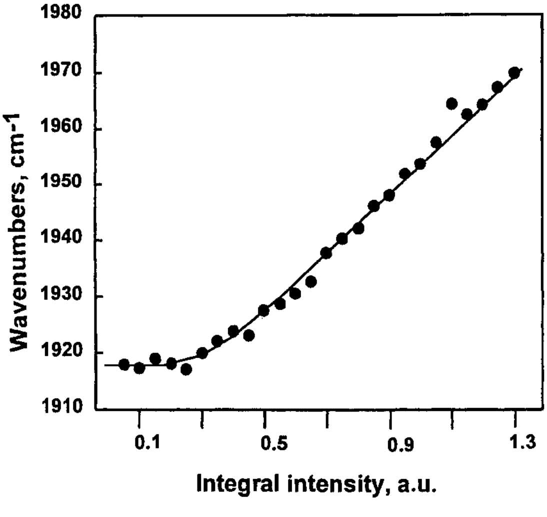

Fig. 6. Dependence of the linear bonded CO frequency (LFB) on the integral intensity in the course of thermal desorption.

oxide adsorbed on the Pt particles of the second group is considerably shifted towards lower wavenumbers by 100–150 cm^{-1}.

Unambiguous conclusions on the nature of these two populations can be inferred from the observed succession of CO adsorption–desorption on these particles. In the course of CO admission CO adsorbs initially on the particles of the first group, followed by adsorption on the particles of the second group. CO evacuation upon increasing temperature primarily results in preferential CO desorption from the particles of the first group, followed by the desorption π from the particles of the second group. Two different assumptions can be proposed to explain the difference in desorption behaviour of the two types of Pt sites.

The first is based on the difference in the heats of CO adsorption between the particles of the two groups. Indeed, the frequencies of CO adsorbed on the two groups of Pt particles differ radically. The frequency changes are traditionally explained by variation of $d–2\pi^*$ backdonation in the Me M–Co bond, which in turn alters, although indirectly, the strength of Me–C bond. Under this assumption, one can expect that the initial CO admission would result in the fast CO adsorption on the more tightly bound state, and slow CO desorption from this state with temperature increase. This contradicts, however, the experimental observations. The HFB at 2050 cm^{-1} appears first upon primary CO admission, but it is eliminated definitely more readily than the LFB in the course of thermodesorption.

We therefore assume that the observed sequence in adsorption–desorption on the two different metal sites is mainly due to their different locations rather than due to the difference in heat of CO adsorption. We suggest that the first group of the particles is localized in the near surface region of the zeolite microcrystals and outside. Carbon monoxide adsorbs on the particles located outside the zeolite first due to their higher accessibility. The properties of the particles are not modified significantly by metal–zeolite interaction; therefore, the CO frequency is close to that observed for CO on platinum supported on conventional carriers (2060–2050 cm^{-1}, HFB). The Pt particles of the second group are localized inside zeolite channels. Therefore, CO molecules reach these particles later. Zeolite lattice alters the parameters of CO adsorption causing a significant decrease in the frequency of carbon monoxide (LFB). Upon evacuation at increased temperature, CO desorption from the second group of the particles is inhibited due to intensive readsorption of CO molecules inside the channels before escaping to the outside. This effect appears to cause the apparent stability of CO exhibiting the LFB. These conclusions agree with those inferred from the data published by Besoukhanova et al. [16]. Although their spectra were poorly resolved compared to our experiment, they were able to discriminate at least three groups of platinum particles in KL on the basis of the bands of CO adsorbed. The HFB at 2075 cm^{-1} was ascribed to particles located on the outer surface. This band was no longer observed after poisoning the outer surface with sulphur containing molecules. Two other bands at 2060 and 2000 cm^{-1} have been assigned to the CO adsorbed on more dispersed Pt sites both located inside the zeolite but in different environments.

Accepting the assumption concerning the location of the particles of the second group inside the channels, it is noteworthy to discuss the possible role of metal-support interaction for this Pt population, which presumably leads to the remarkably low frequency of the adsorbed CO.

Extrapolation of the linear CO stretching vibration frequency to the zero coverage gives the value of 1920 cm^{-1}. Primet et al. [31,32] showed that the frequency obtained by the 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. Comparison of this frequency with those obtained for other Pt systems enables to conclude that the stretching vibration frequency of CO adsorbed on Pt/KL is shifted significantly toward lower wavenumbers by 120–150 cm^{-1}.

To correlate this shift with the electronic state of the Pt particles we should also take into consideration the variation of the CO frequency with particle size, because our TEM results indicate that the Pt particles inside zeolite channels appear to be extremely small (<1 nm). The significance of this factor for supported catalysts was demonstrated repeatedly [33–37]. Kappers et al. [26] suggested the correlation of the CO frequency with Pt coordination number. This correlation was revised in ref. [33]. Extrapolating the results summarized in ref. [33] to low coordination numbers we can roughly estimate a possible shift of the adsorbed CO due to the size effect to be 60–80 cm^{-1}. Thus, we can conclude, that the dramatic shift of CO frequencies compared to that observed for other Pt samples is not entirely due to a size effect but reflects the significant effect of the zeolite framework on the electronic state of Pt particles.

To explain this shift different possible mechanisms were proposed.

(1) Direct interaction of the oxygen atom of linear bonded CO with alkali cation leads to a decrease in the stretching frequency. Van Santen [38] has named the direct electrostatic interaction between cation and CO adsorbed as "bifunctional promotion". Lane et al. [28] showed that the presence of potassium results in the appearance of an additional band near 1970 cm^{-1}. However, this band cannot be entirely attributed to the electrostatic interaction, because no correlation was found between potassium concentration and the intensity of the band at 1970 cm^{-1}.

(2) The interaction of Pt particles with strongly basic oxygen atoms of the zeolite framework [37,38] leads to the increase of the electron density on Pt particles [34,39]. Enhanced back-donation from the d-orbitals of an electron-rich metal cluster into the antibonding $2\pi^*$-MO of carbon monoxide results in the additional downward shift.

(3) The negative charge of the zeolite framework oxygen polarizes the electron gas of the platinum particles [40]. The positively charged pole of the resulting dipole particle is directed towards the zeolite framework whereas the negatively charged

pole points to the free space of the zeolite cage. The CO molecules, which will be chemisorbed at the electron-rich domain of the platinum crystallites, exhibit downward shifts.

(4) The CO-covered platinum clusters change their structure during heating [41]. It is proposed that the new structure is one in which the carbon monoxide molecules insert into spaces between the framework atoms of the L zeolite. However, the authors point to the speculative nature of this explanation.

It is supposed that several factors can play a significant role. We assume that the potassium ions affect the electron density on the Pt particles even in the case of interaction between oxygen atoms of zeolite framework and Pt particles, albeit indirectly. Indeed, results of the earlier work of Barthomeuf [39] and that of the recent study of Huang et al. [42] indicate that the strength of basic sites depends on the nature of the cation and increases in the order Li>Na>K>Rb. Therefore, we suggest that considering the influence of the potassium on the Pt particles properties we should take into account its "direct effect" (bifunctional promotion) and "indirect effect" (increase of the basicity of the oxygen atoms). In the forthcoming paper we intend to present some evidence for the interaction between oxygen atoms and Pt particles.

5. Conclusion

The combination of CO adsorption experiments within a wide pressure range with CO desorption measurements at RT and elevated temperature provides valuable information on the location of Pt particles in KL zeolite and their electronic structure. A minor part of the particles locates on the outer surface of the zeolite microcrystals and in the near surface region. CO adsorption on these particles results in the appearance of a CO band at 2050–2020 cm^{-1}. The major part of the Pt metal clusters is encaged in the zeolite structure as very fine particles. The interaction of CO with these clusters is strongly perturbed by the zeolite matrix, which leads to the prominent shift of the adsorbed CO band down to 1960–1920 cm^{-1}. The development of the relative intensities of the bands in the spectra can be explained by the kinetics of the adsorption on the particles located within the zeolite channels.

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