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FTIR evidence of the formation of platinum carbonyls from Pt metal clusters encaged in KL zeolite

A.Yu. Stakheev, E.S. Shpiro

N.D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Leninsky prospect 47, 117913 Moscow, Russia

N.I. Jaeger and G. Schulz-Ekloff

Institut für Angewandte und Physikalische Chemie, Universität Bremen, PF 330 440, D-28334 Bremen, Germany

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Reactivity of Pt metal clusters supported on KL zeolite toward CO was studied by FTIR spectroscopy. Investigation of the CO adsorption was performed within a wide CO pressure range (1–500 mbar). IR data on the CO adsorption at high pressure (500 mbar) suggest the transformation of the finest Pt particles into neutral Pt carbonyls ($(\text{Zeol-O:})_m\text{Pt}_x(\text{CO})_y$) stabilized by the basic oxygen atoms of the KL framework. The transformation is found to be readily reversible upon CO adsorption–desorption at room temperature (RT).

Keywords: platinum carbonyls; KL zeolite supported Pt; CO chemisorption on Pt; IR spectroscopy

1. Introduction

Numerous researchers have recently directed to the investigation of the Pt/KL catalytic system. This interest arose from the fact that the Pt/KL system demonstrates a unique activity and selectivity for *n*-hexane aromatization to benzene, which appears to be a result of a specific influence of the zeolite environment on Pt particles [1–4]. Evidence obtained from IR spectroscopy for the pronounced effect of the zeolite lattice on the electronic properties of the encaged metal particles is reported in refs. [5–8]. It was suggested that the zeolite matrix can act as electron donor and increase the electron density on the encapsulated Pt clusters, which, in turn, results in a marked downward shift of the stretching frequency of adsorbed CO. However, some distinct discrepancies are apparent in the spectra of CO adsorbed on Pt/KL obtained by different research groups. While IR-spectra reported by Kustov et al. [6], Kappers and Van der Maas [7] showed several sharp bands of linearly bonded CO in the region 2070–2000 cm^{-1}, spectra reported by

McVicker et al. [8] and Lane et al. [7] exhibited distinctly broader bands at frequencies as low as 1980–1960 cm^{-1} without a well-resolved structure. Kappers et al. [10] suggested that one of the possible reasons for these discrepancies is the amount of water present in the zeolite. However, another source of these disagreements might be the difference in the treatment conditions (CO pressure, duration etc.). McVicker et al. [8] and Lane et al. [9] applied CO adsorption at 10 and 8 Torr CO pressure respectively. On the other hand, Kustov et al. [6] and Kappers and Van der Maas [7] have carried out CO adsorption at atmospheric pressure in their experiments.

In order to resolve the discrepancies the transformation of the Pt/KL system upon CO adsorption has been studied at low (1 mbar) and elevated (500 mbar) CO pressure. The results obtained allow the interpretation that upon CO adsorption at elevated pressure (500 mbar) Pt metal clusters localized inside the channels of KL can be transformed into Pt carbonyls and that this transformation is found to be easily reversible.

2. Experimental

2.1. MATERIALS

1 wt% Pt/KL zeolite was prepared by incipient wetness impregnation of KL zeolite (Si/Al = 2.9) with an appropriate amount of $Pt(NH_3)_4Cl_2$ dissolved in distilled water. The sample was dried overnight at room temperature and calcined in flowing O_2 with the temperature ramped at a rate of 0.5 K/min from RT 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 298 K in a hydrogen flow and purging with Ar.

2.2. 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 0.5 K/min from 298 to 623 K with a hold at 623 K for 3 h, followed by cooling to 298 K. The ultimate vacuum in the cell was 1×10^{-6} mbar. Before measurements the sample was reduced in flowing hydrogen of 1 mbar 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 on the reduced Pt/KL sample were performed at 298 K in two steps at different CO pressures. At the first stage, CO was admitted with a pressure of 1 mbar in flowing mode under continuous evacuation, and spectra were taken every 2 min for about 1 h. Thereafter, the CO pressure was increased up to 500 mbar and the sample was kept in static CO for 1 h. Then, spectra were taken every 2 min under continuous evacuation for 3 h.

The desorption measurements at room temperature were followed by temperature-programmed desorption measurements. TPD was performed by ramping the temperature at 2.5 K/min from RT to 623 K. The spectra were taken every 10 K. The adsorption–desorption cycle was repeated four times in order to study the reversibility of the transformation of different CO/Pt species.

3. Results

The variation of the integral intensity of the linear CO band with the time of adsorption at 1 mbar CO pressure is depicted in fig. 1. As can be inferred from fig. 1, after CO adsorption for 20–25 min saturation of the Pt surface is achieved. It is not possible to increase the amount of chemisorbed CO significantly beyond this coverage. By the end of the adsorption a spectrum specific for CO adsorbed on Pt/KL zeolite [5] was detected. The spectrum consists of a very broad band around 2000 cm^{-1} typical for linearly bonded CO, and the band near 1750 cm^{-1}, which can be attributed to the bridged CO (fig. 2, spectrum 1).

Adsorption at high CO pressure (500 mbar) and removal of gas phase CO by evacuation for 2 min results in a strong five-fold increase of the integral intensity of the spectrum (fig. 2, spectrum 2). Moreover, several sharp, well-resolved bands appear at 2130, 2068, 2031, and 2008 cm^{-1}. The band at 1800 cm^{-1}, attributed earlier to bridged CO, also narrows and shifts to higher wavenumbers.

CO evacuation at room temperature leads to a decrease in the intensity of the

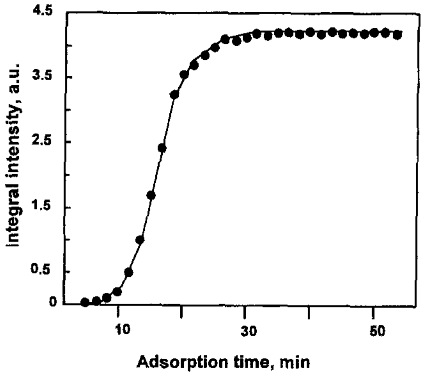

Fig. 1. Time dependence of the integral intensity of linearly bonded CO in the course of CO adsorption at 1 mbar CO pressure. Pressure of adsorption was adjusted during the first 10 min.

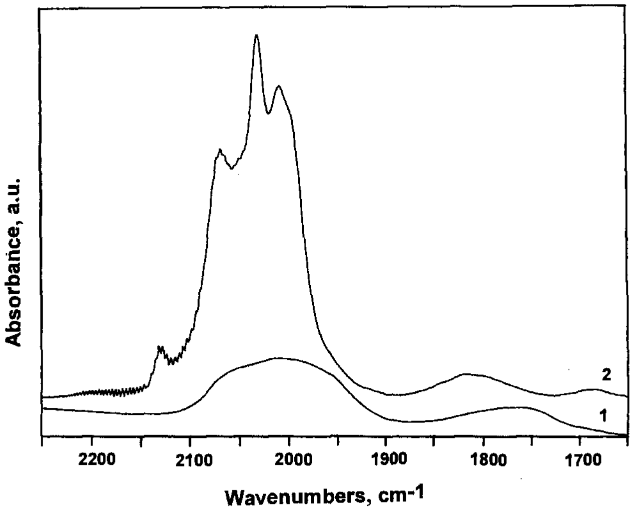

Fig. 2. FTIR spectra of CO adsorbed on freshly reduced Pt/KL: (1) after CO adsorption at 1 mbar; (2) after CO adsorption at 500 mbar and removal of gas phase CO by evacuation for 2 min.

new bands without variations of their positions (fig. 3). Furthermore, a new band around 1928 cm^{-1} arises in the course of evacuation and disappears upon further evacuation. It should be noted that, although the new peaks are readily eliminated during the period of desorption at room temperature, even a 2 to 3 h desorption does not fully restore the spectrum observed following the treatment of 1 mbar (fig. 1, spectrum 1). The band of the bridged CO remains shifted toward higher

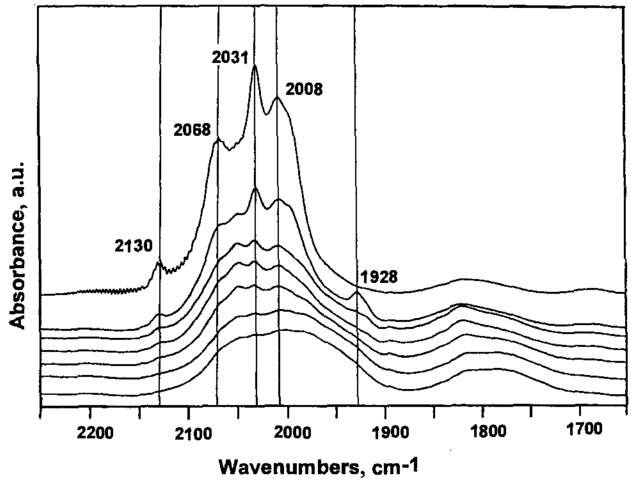

Fig. 3. Variation of FTIR spectra of CO adsorbed on Pt/KL at 500 mbar upon CO evacuation at room temperature. Evacuation time: 2 min (top spectrum), 4 min, 6 min, 8 min, 28 min, 2 h, 3 h. The top spectrum corresponds to spectrum 2 of fig. 2.

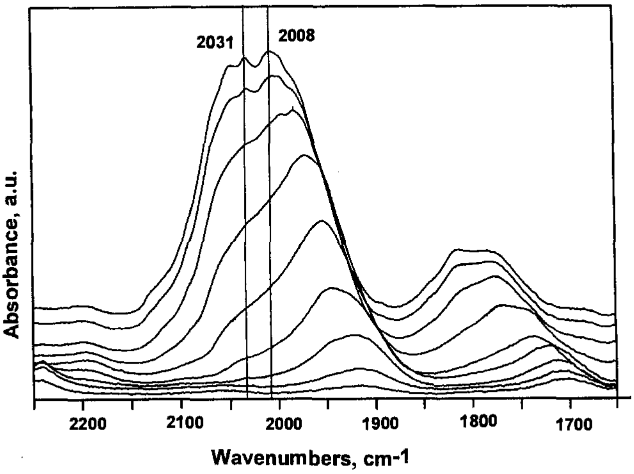

Fig. 4. Thermal desorption CO spectra: RT (top spectrum), 343 K, 373 K, 423 K, 473 K, 523 K, 573 K, 623 K, 623 K after 40 min.

wavenumbers and a certain amount of the newly formed Pt entities (characterized by the bands at 2068, 2031, and 2008 cm^{-1}) is retained in the sample.

Variations of CO spectra in the course of temperature-programmed desorption are depicted in fig. 4. As may be inferred from fig. 4, the removal of the aforementioned newly formed Pt species can clearly be observed during the temperature program already at 373 K.

Repeated treatments of the sample with CO at 500 mbar result in similar spectra. Only after four adsorption–desorption cycles some irreversible changes are observed in the spectra (fig. 5). The intensity of the most distinct bands decreases, however, their positions are not changed. Interestingly, after four adsorption–desorption cycles a noticeable modification is observed of the spectrum obtained

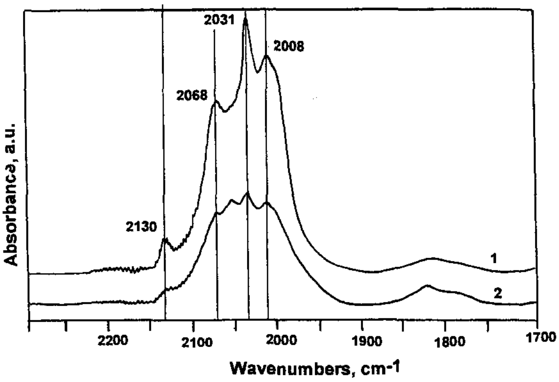

Fig. 5. FTIR spectra of CO adsorbed on Pt/KL at 500 mbar: (1) initial sample; (2) after four adsorption–desorption cycles.

upon low-pressure CO adsorption as compared to that recorded at the beginning of the adsorption–desorption experiments (fig. 6). The shoulder at higher frequency (~2060 cm^{-1}) becomes more pronounced. Furthermore the whole spectrum narrows and shifts toward higher wavenumbers.

4. Discussion

The discussion of the unconventional behavior of the Pt/KL sample upon high pressure CO adsorption will concentrate on the following observations:

(1) a five-fold increase in the integral intensity of the linear CO band after adsorption at 500 mbar CO compared to that obtained after CO adsorption at 1 mbar;

(2) appearance of the new narrow and well-resolved bands;

(3) their reversible appearance–disappearance upon CO adsorption–desorption at room temperature;

(4) the absence of a noticeable frequency shift of the new bands, which might be expected as a result of a variation of the dipole–dipole coupling in the course of the CO desorption from Pt surface;

(5) the loss of the reversibility of the spectra after several adsorption–desorption cycles.

It is difficult to explain a five-fold increase in the linear CO band integral intensity and the appearance of the well-structured new bands upon adsorption at elevated CO pressure in terms of ordinary CO chemisorption on a Pt surface. The results obtained for low-pressure CO adsorption indicate that saturation of Pt surface with CO is achieved at 1 mbar CO. Thus, an additional adsorption of a considerable amount of CO on the metal surface at elevated pressure is doubtful. One

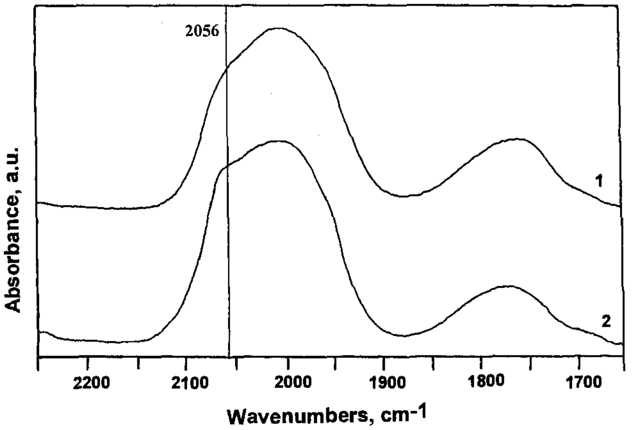

Fig. 6. FTIR spectra of CO adsorbed on Pt/KL at 1 mbar: (1) initial sample; (2) after four adsorption–desorption cycles at 500 mbar.

can also assume the additional adsorption of a minor amount of CO resulting in an appearance of adsorbed CO species with higher extinction coefficient. Kappers et al. ascribed, for example, different bands in similar spectra to various Pt sites having different coordination numbers [7]. Indeed, integral intensities of CO adsorbed on steps and kinks were found to be high [11–13]. Such sites are characterized by a high energy of adsorption and should be occupied first during the initial stages of adsorption even at low pressure. Desorption from these sites is hampered due to the higher adsorption energy and should proceed at higher temperature. However, the formation of very weakly adsorbed CO species could be observed, which are readily eliminated upon evacuation at ambient temperature. The absence of a coverage-dependent shift also disagrees with the suggestion that the newly formed bands correspond to CO adsorbed on the Pt surface. Adsorption of CO on a zeolite carrier can be ruled out as it normally occurs at liquid nitrogen temperature. Furthermore, a similar behavior was not observed for a Pd/KL sample prepared using the same parent zeolite but containing larger metal particles [14].

Similar effects (reversible appearance–disappearance of highly structured spectra upon CO adsorption at high pressure and following desorption) were observed by Kubelkova et al. [15] and Bein et al. [16] for the Ni/Y system and was explained in terms of Ni-carbonyl formation upon treatment in CO at elevated pressure. Formation of Ni carbonyls is a well-known reaction and their detection in a zeolite is not surprising. The appearance of Pd carbonyls upon treatment in CO was found by Sachtler et al. [17,18] for Pd/NaY zeolite. Spectral features analogous to those found in our work were observed by FTIR: appearance of intense highly structured bands upon CO adsorption at atmospheric pressure, their ready elimination upon purging in Ar, and the reversibility of the processes. Although the $Pd_x(CO)_y$ carbonyl is not known in inorganic chemistry, its formation was tentatively attributed to the stabilizing effect of the zeolite environment.

The facts discussed above suggest that the unusual spectra of CO adsorbed on Pt/KL samples at elevated pressure and their variations upon desorption can be ascribed to the formation of Pt carbonyls followed by their ready decomposition. This hypothesis provides a consistent interpretation for the observed variations of the CO bands. The formation of Pt-carbonyl species leads to the drastic transformation of the Pt/CO stoichiometry resulting in the increase of band intensity and the appearance of a well-defined structure inherent to the spectra of metal carbonyls. The absence of the coverage-dependent shift during CO evacuation is also conceivable, assuming that band disappearance reflects the decomposition of Pt carbonyls rather than CO desorption from the metal surface.

Some additional evidence for the formation of the Pt carbonyls in KL zeolite might be inferred from the comparison of the IR data with those obtained on Pt/KL samples by Kustov et al. [6] and Kappers et al. [7]. The adsorption of CO in refs. [6,7] was carried out at comparable pressures. The data reported for linearly adsorbed CO are summarized in table 1. There is a remarkable matching in the frequencies of the bands reported in different papers. The frequencies of the principal

Table 1
IR data on CO stretching vibration frequencies reported for different Pt systems

Pt system	CO stretching vibration frequencies (cm^{-1})					Ref.
Pt/KL	2063		2034	2015	1996	[7]
	2066	2051	2031	2008	1998	[6]
	2068	[a]	2031	2008	[a]	this work
$Pt(CO)_4$	2053					[32]
$Pt(CO)(Ph_3P)_3$	1930					[29]
$Pt(CO)_2(Ph_3P)_2$	1990, 1948					[29]
$Pt_3(CO)_3(Ph_3P)_4$	1839, 1784					[29]
$Pt_4(CO)_5(Et_3P)_4$	1980, 1875, 1845, 1785, 1755					[29]

[a] These bands appear in the course of CO evacuation (see fig. 3).

bands coincide with an accuracy of 2–3 cm^{-1} which is quite unusual for IR data on conventional CO adsorption on the surface of Pt reported by different authors. The formation of molecular complexes with a particular stoichiometry could explain the remarkable matching of the frequencies of four CO bands observed in three different papers (table 1).

The formation of neutral Pt carbonyls in zeolite has not been reported. However, the formation of anionic carbonyl complexes [19], which can also be prepared within a faujasite matrix [20–24], has to be considered. It can be ruled out since the IR spectra for bridged and linearly bonded CO are quite different compared to those observed in this work. Moreover, their formation is a very slow process [24] and their decomposition was found to be completely irreversible [25,26]. It is therefore assumed that the spectra can be interpreted by the reversible formation–decomposition of neutral $Pt_x(CO)_y$ species in analogy to those observed for Pd/Y and Ni/Y zeolite.

Two major factors may facilitate the formation from small metal clusters encapsulated inside the KL zeolite.

(1) It is well known that the free energy of small metal clusters is significantly higher than that of bulk metal and that they are highly reactive. The reason for that is the smaller number of bonds per metal atom in the clusters compared to the bulk metal. Gingerich et al. demonstrated experimentally that the atomization energy for Pt_2 is only 340–360 kJ/mol [27,28], which is significantly lower compared to that of bulk metal (570 kJ/mol [29]). Moreover, for small metal clusters the strength of the single Me–Me bond may be lower than that in the bulk metal. According to a calculation performed by Baetzold [30,31], in the case of transition metal clusters containing less than 15–20 atoms the average bond energy per atom can be 2 to 3 times lower than for bulk metal. The energy passes through a minimum for particles containing 6–10 atoms, and reaches the values specific for bulk metal for clusters consisting of 20–30 atoms. Taking into account that several studies performed on Pt/KL zeolite [5,32,33] have shown that Pt particles encaged in this zeo-

lite are extremely small and presumably contain only 5–6 atoms. It can be expected that a substantial fraction of the Pt particles inside the KL zeolite is highly reactive toward CO. Lower Pt–Pt bond energy for these clusters facilitates the disruption of Pt–Pt bonds followed by the formation of CO bonds in the course of Pt-carbonyl formation.

(2) At present, it can only be speculated on a possible structure of the Pt carbonyl. Pt carbonyls containing only CO ligands are unknown or very unstable [34–36] and $Pt(CO)_4$ has only been prepared under low-temperature matrix isolation conditions [37]. However, the substitution of CO ligands by PPh_3 leads to a stable product due to σ-donor action of the PPh_3 ligands [34]. Taking into account that oxygen atoms in the framework of KL zeolite exhibit strong basic properties, it can be assumed that they may act as σ-donor ligands and stabilize species of the following structure:

$$(\text{Zeol-O:})_m\text{Pt}_x(\text{CO})_y$$

Evidence for this interaction can be inferred from EXAFS data which indicate that small platinum particles are coordinated with framework oxygen of the zeolite. The existence of a Pt–O bond was found both for Pt-HZSM-5 and Pt/KL [32,33] with a distance of 2.06–2.14 Å. Recently, in an EXAFS study of Pt/KL a Pt–O bond length of 2.04 Å has been reported [38]. These distances are comparable to the Pt–P distance (2.25 Å) reported for platinum complexes containing phosphine ligands [39], if we take into consideration the smaller radius of the O atom.

A tentative explanation for the reversibility of Pt-carbonyl formation–decomposition upon CO admission–evacuation can be forwarded. Sheu et al. [17,18] attributed by easy release of CO from a Pd-carbonyl complex upon purging with an inert gas at room temperature to the substitution of a CO ligand by zeolite protons. However, KL zeolite does not contain any appreciable amount of Brønsted acid sites. It is therefore assumed that the reversibility of the Pt-carbonyl formation reflects the competition between the formation of strong Pt–CO and Pt–Pt bonds. The comparable energies of the bonds make the formation of PT carbonyl strongly dependent on the CO partial pressure.

In the framework of our hypothesis the temporary appearance of the band around 1928 cm^{-1} can also be explained. This band corresponds to the intermediate product of $(\text{Zeol-O:})_m\text{Pt}_x(\text{CO})_y$ during decomposition. The partial removal of CO ligands leads to an increase of the electron density on the Pt atom and to an decrease of the stretching vibration frequency of the remaining CO molecules [34].

The irreversible decrease in the intensity of the new bands after several adsorption–desorption cycles accompanied by the alteration of the spectra of CO adsorbed at low pressure (1 mbar) can be now better understood. Metal-carbonyl species exhibit high mobility inside zeolite microcrystals, which can lead to the redistribution and agglomeration of the metal [40]. Taking into account that the band at 2050–2060 cm^{-1} in the spectrum obtained after low-pressure adsorption is associated with CO adsorbed on bigger Pt particles localized in the near-surface region [5], it can be assumed that the growth of this band and the shift of the whole spectrum to higher frequency reflects the agglomeration of the Pt both on the outer surface and inside the channels. This agglomeration presumably occurs mainly in the course of thermodesorption at elevated temperature. Pt particle growth proceeds at the expense of the finest particles which are reactive toward Pt-carbonyl formation and decreases the concentration of Pt carbonyls.

5. Conclusion

Data on the CO adsorption at elevated pressure allow for a first time to propose the transformation of Pt metal clusters encaged in the channels of KL zeolite into neutral Pt carbonyls. It is presumed that the basic oxygen atoms of the zeolite framework can act as σ-donor ligands and stabilize the Pt carbonyls.

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