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CO-induced surface structural changes of Pt on oxide-supported Pt catalysts studied by DRIFTS

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Abstract

CO adsorption (0.01–10 Torr) on differently pretreated titania-, alumina-, and silica-supported 1 and 5% Pt catalysts was investigated by DRIFTS at 300 K. The three band structure observed in 0.01 Torr CO on reduced 1% Pt/oxide catalysts has been connected with the presence of monoatomic Pt^0 (2112–2106 cm^{-1}), Pt atoms on edges (2070 cm^{-1}), and kinked Pt atoms (2050 cm^{-1}). The increase of CO pressure caused the disappearance of the bands due to CO adsorbed on edged and kinked Pt atoms, and at the same time a band due to CO linearly (on top) adsorbed on smooth Pt facets appeared at 2058–2068 cm^{-1}. These features were regarded as consequences of surface Pt reconstruction. CO adsorption on reduced 5% Pt/oxide catalysts did not show the presence of edged and kinked Pt atoms, as only the bands due to CO adsorbed on monoatomic Pt^0 (2105–2109 cm^{-1}) and CO linearly (on top) adsorbed on smooth Pt facets (2066–2076 cm^{-1}) were observed. The intensity of the band due to CO adsorbed on monoatomic Pt^0 increased with time and CO pressure, which is probably characteristic for the disruption of Pt crystallites into Pt^0 with the help of CO.

Keywords: CO adsorption; Oxide-supported Pt catalysts; Surface structural changes of Pt; DRIFTS

1. Introduction

Numerous papers have been devoted to the (mainly infrared) spectroscopic study of the structural changes of noble metals supported on oxides during CO adsorption. It has been well documented that CO adsorption at 300 K and at lower temperatures led to the oxidative disruption of Rh [1–3], Ir [4], and Ru [5] crystallites supported on oxides resulting in the formation of metal carbonyl ($M^+(CO)_2$) surface species. The effect of CO at higher temperature (above 448 K) was reversed: reduction of M^+ sites and agglomeration of the resulting M^0 atoms caused the formation of metallic crystallites (reductive agglomeration) [1,4,5]. The reconstruction of metal particles due to CO adsorption was further strengthened by STM studies on $Rh/TiO_2(100)$ [6] and $Ir/TiO_2(100)$ [7] surfaces.

Despite the fact that the systems of CO/oxide-supported Pt and CO/Pt single crystal surfaces have been frequently studied by FTIR, HREELS, IRAS, and SFG, respectively, no unambiguous conclusion for the oxidative disruption–reductive agglomeration (in general, reconstruction) of Pt has appeared in the literature.

Most of the papers dealing with CO/Pt systems depicted only one band in the range of 2100–2000 cm^{-1}; this band was attributed to the linear (on top) CO adsorbed on Pt atoms surrounded by only Pt atoms (i.e., large Pt particles). The position of this band depended on the dipole–dipole interaction increasing with the surface coverage [8] or on the reduction degree of Pt [9].

An additional model explaining the observations made using infrared spectroscopy is the CO island formation model [10–13]. Based on the fact that the CO stretching frequency over a wide range of coverage on the surface of the supported Pt catalysts was constant, it was concluded that CO may exist in the form of closely packed islands on the catalyst surface.

In the range of 10^{-8}–2 Torr CO pressure only one band at 2057 cm^{-1} and a small shoulder at 2067 cm^{-1} were detected on the spectra of Pt/SiO_2 having a mean Pt particle size of 1.1 nm. These bands were attributed to CO adsorbed on corner Pt atoms. When the Pt particle size was greater, i.e., 4.2 nm, three bands at 2067, 2080, and 2090 cm^{-1} were ob-

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served under the same circumstances, which were assigned as CO adsorbed on edges (2067 cm^{-1}), CO molecules adsorbed on edge atoms, vibrating in-phase (2080 cm^{-1}), and the vibration of islands of CO adsorbed on (111) face atoms (2090 cm^{-1}), respectively [14].

The appearance of the bands due to symmetric and asymmetric stretchings of metal dicarbonyls during CO adsorption on corresponding oxide-supported noble metal catalysts has been connected with the oxidative disruption of Rh [1–3], Ir [4], and Ru [5]. Taking into account the great similarities of Pt with the above noble metals, the disruption of (at least small) Pt particles, i.e., the detection of Pt–carbonyl surface species, during CO adsorption has been strongly expected. (We note here that the same is valid for Pd.)

The studies of oxide-supported Pt catalysts, however, have been unsuccessful in this respect so far. This might be due to the fact that neutral Pt carbonyls containing only CO ligands are unknown or very unstable [15–17], and $Pt(CO)_4$ has only been prepared under low-temperature matrix isolation conditions [18].

The reductive carbonylation (400 Torr CO at 353 K) of $Pt(NH_3)_4{}^{2+}/NaY$ led to the formation of $[Pt_9(CO)_{18}]^{2-}$ located in the NaY zeolite, while the exposure of Pt^{2+}/NaY to 550 Torr CO at 298 K resulted in the synthesis of the $[Pt_{12}(CO)_{24}]^{2-}$ cluster in the NaY zeolite [19]. These dianions exhibited infrared bands only due to linearly and bridge-bonded CO (2086, 1898, 1836, and 1798 cm^{-1} for $[Pt_9(CO)_{18}]^{2-}$ and 2112, 1896, and 1841 cm^{-1} for the $[Pt_{12}(CO)_{24}]^{2-}$ cluster, respectively). Taking into account that $Pt(NH_3)_4{}^{2+}$ and Pt^{2+} were originally situated individually in the appropriate crystallographic positions of the zeolite framework, the formation of the above Pt clusters can be regarded as an agglomeration process.

The adsorption of 500 mbar CO at 300 K on 1% Pt/KL zeolite (reduced at 673 K) caused the appearance of well-resolved bands at 2068, 2031, and 2008 cm^{-1}, which were connected with the formation of neutral Pt_xCO_y stabilized by the oxygen atoms in the framework of the KL zeolite [20]:

$$(\text{Zeol-O:})_m - Pt_xCO_y.$$

It should be pointed out that the formation of the above surface species proved to be reversible: after a relatively short evacuation time (28 min) at 300 K the characteristic bands disappeared and only a broad absorption at around 2000 cm^{-1} remained in the spectrum, which was also obtained during the adsorption of 1 Torr CO on the same sample and assigned to linearly bonded CO on larger Pt particles. Unfortunately the accurate assignments of the bands at 2068, 2031, and 2008 cm^{-1} were not given.

EXAFS study of the Pt/K-LTL zeolite (reduced at 573 K) before and after CO adsorption at 300 K revealed that the coordination number of Pt decreased from 4.2 to 2.2 and the Pt–Pt distance diminished from 0.274 to 0.267 nm due to CO adsorption [21]. Based on these data it has been stated that the very small platinum metal particles (consisting of five to six atoms) formed during pretreatment were completely decomposed and transformed to platinum carbonyl clusters. The coordination parameters pointed to a structure of $[Pt(\text{linear-CO})_3]$ stabilized by the zeolite walls.

Adsorption of CO (10^{-1} Pa) at 300 K on 0.5% Pt/ZSM-5 reduced at 573 K resulted in the appearance of two bands at 2124 and 2091 cm^{-1}. An increase of the reduction temperature to 823 K led to the disappearance of both bands and to the appearance of a band at 2082 cm^{-1}. On the sample with higher metal loading (1% Pt/ZSM-5 reduced at 623 K) adsorption of CO led to the appearance of the 2082 cm^{-1} band, which shifted to lower wavenumbers and split into two bands (2070 and 2050 cm^{-1}) upon thermodesorption up to 573 K. At the same time a band at 2123 cm^{-1} was clearly detected [22]. The thermally stable 2123 and 2092 cm^{-1} bands were attributed to the symmetric and asymmetric stretchings of $Pt^{\delta+}$–$(CO)^2$ species and the band at 2082 cm^{-1} was assigned to CO adsorbed on the Pt cluster. As the intensity of the 2123 cm^{-1} band increased with adsorption time and CO pressure on 1% Pt/ZSM-5, this might be attributed to CO adsorbed on monoatomic Pt in the hidden sites of the ZSM-5 structure.

SFG studies of CO adsorption on platinum single crystal surfaces under high CO pressure and room temperature [23–25] showed a decreasing on top peak superimposed on a broad shoulder with increasing pressure. The broad shoulder around 2040–2000 cm^{-1} was suggested [24] to be associated with the formation of a carbonyl binary complex on a platinum surface under high CO pressure. A similar conclusion was published on high pressure CO adsorption on polycrystalline Pt foil [25]. The revisited SFG study of a CO/Pt(111) system, however, showed only the presence of on top CO between 10^{-7} and 500 mbar and at 160–400 K [26]. It has been pointed out that the disappearance of the on top CO peak and other SFG features was due to the gas-phase absorption [27].

Taking into account the (sometimes contradictory) pieces of information collected above, as a continuation of our former studies, a more detailed DRIFTS investigation on the CO-Pt/support interaction seemed to be necessary.

2. Experimental

The oxide-supported Pt catalysts were prepared by incipient wetting of TiO_2 (Degussa, P25), Al_2O_3 (Degussa), and SiO_2 (Cab–O–Sil) with an aqueous solution of $H_2PtCl_6 \times 6H_2O$ (Reanal). For preparation triple-distilled water was used. The metal contents were 1 and 5 wt%. All materials were of analytical grade. After impregnation the samples were dried in air at 373 K.

The powdered catalysts were placed in the sample holder of a CHA-CHC DRIFTS chamber (Harrick), which was connected with an all-metal vacuum and gas handling system routinely capable of producing 5×10^{-7} Torr pressure. O_2, H_2, and CO were of high commercial purity (Linde).

The pretreatments of the catalysts were performed in the DRIFTS chamber. Three different pretreatments were applied: (i) the sample was evacuated at 573 K for 2 h; (ii) the catalyst was heated (10 K/min) from 300 to 573 K in O_2 (10 Torr), and kept in O_2 for 1 h at this temperature and then it was evacuated for 30 min at 573 K, and the sample was cooled to the temperature of the adsorption; and (iii) the catalyst was heated (10 K/min) from 300 to 573 K in H_2 (10 Torr), and kept in H_2 for 1 h at this temperature and then it was evacuated for 30 min at 573 K, and the sample was cooled to the temperature of the adsorption. The dispersity of the samples was calculated on the basis of the amount of chemisorbed hydrogen (determined from isothermal H_2 adsorption at 300 K) with a surface stoichiometry of Pt:H = 1:1.

DRIFT spectra were recorded at 300 K by a Genesis (Mattson) FTIR spectrometer with a wavenumber accuracy of $\pm 4\ \text{cm}^{-1}$. Any other adsorption temperature will be mentioned in the text. Typically 136 scans were collected. The actual spectrum was ratioed by the spectrum of pretreated samples, the result of which was transformed to the Kubelka–Munk function. The sample compartment and the spectrometer were purged with water- and CO_2-free air produced by a Whatman purge gas generator to eliminate the disturbing effects of H_2O and CO_2 in the infrared beam.

3. Results

3.1. Pt/TiO_2

The adsorption of 0.01 Torr CO at 300 K on differently pretreated 1% Pt/TiO_2 resulted in the spectra depicted in Fig. 1A. The spectrum of the sample evacuated at 300 K (not shown) displayed a sharp band at 2128 cm^{-1} and a shoulder at 2092 cm^{-1}. When the sample was oxidized at 573 K, CO adsorption caused the appearance of a band at 2075 cm^{-1}. This band appeared at a lower wavenumber, at 2058 cm^{-1}, on the sample evacuated at 573 K. The adsorption of 0.01 Torr CO on 1% Pt/TiO_2 reduced at 573 K caused the appearance of the bands at 2106, 2070, and 2050 cm^{-1} (three band structure) and an absorption at around 1850 cm^{-1}.

The increase of CO pressure to 10 Torr resulted in a shoulder at 2105 cm^{-1} and only one band between 2100 and 2000 cm^{-1} on samples pretreated at 573 K (Fig. 1B). The position of the latter band depended on the pretreatment: it appeared at 2078 cm^{-1} on the oxidized sample, at 2070 cm^{-1} on the evacuated sample, and at 2067 cm^{-1} on the reduced sample. On the reduced sample a band at 1843 cm^{-1} was also detected. The 2184 cm^{-1} band is due to CO adsorbed on TiO_2, as Ti^{4+}–CO [28].

The three band structure (2106, 2070, and 2052 cm^{-1}) appeared already after 1 min adsorption of 0.01 Torr CO at 300 K on reduced 1% Pt/TiO_2 and could be detected even after 180 min adsorption time. While the intensities of the bands at 2070 and 2052 cm^{-1} were practically constant for 180 min, the intensity of the 2106 cm^{-1} band increased with time (Fig. 2A).

When the adsorption temperature was higher, at 543 K, the same spectral features were registered as at 300 K. (Spectra were taken at 543 K in this experiment.) The three band structure (2112, 2073, and 2044 cm^{-1}) formed in the first minute of CO adsorption (0.01 Torr) and remained for 180 min even at 543 K (Fig. 2B).

In the following experiments the effect of CO pressure was investigated on reduced Pt/TiO_2 catalysts at 300 K. In 0.01 Torr CO the three band structure was observed on 1% Pt/TiO_2. In higher CO pressure (0.1–10 Torr), however, only one band appeared in the range of 2100–2000 cm^{-1}, the

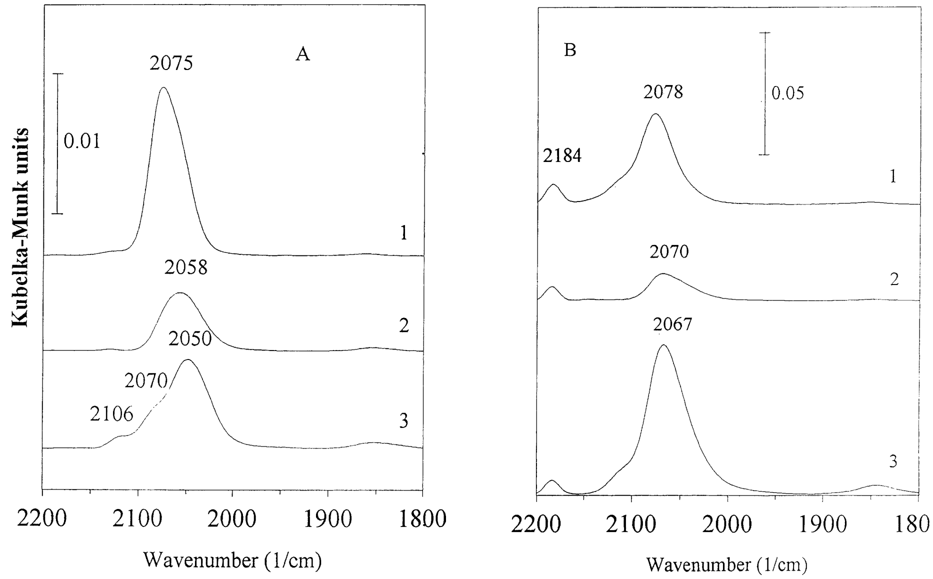

Fig. 1. Spectra of CO adsorbed on differently pretreated 1% Pt/TiO_2 at 300 K. (A) 0.01 Torr CO; (B) 10 Torr CO. Adsorption time was 15 min. 1, oxidized at 573 K; 2, evacuated at 573 K; and 3, reduced at 573 K.

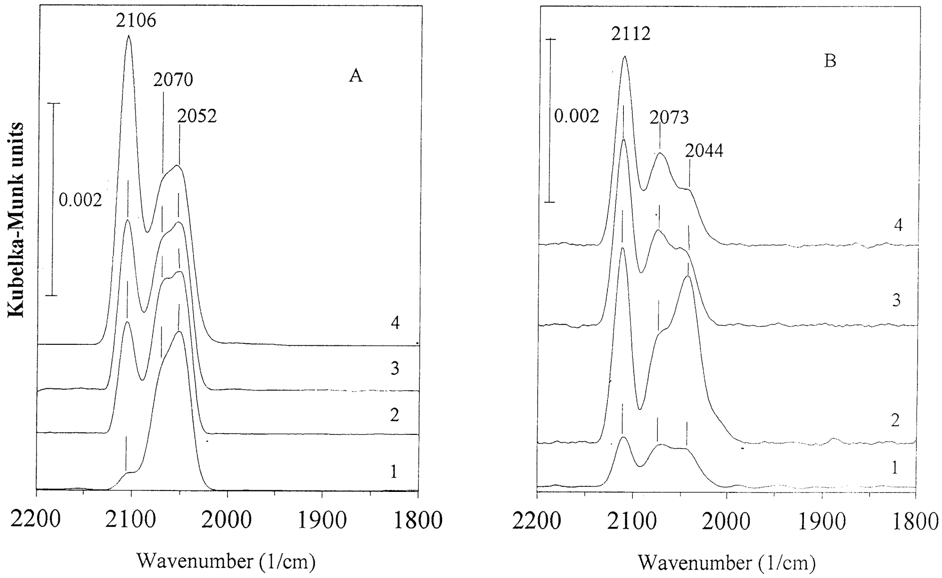

Fig. 2. Spectra due to the adsorption of 0.01 Torr CO on reduced 1% Pt/TiO_2 as a function of adsorption time: (A) at 300 K; (B) at 543 K. 1, 1 min; 2, 60 min; 3, 120 min; and 4, 180 min.

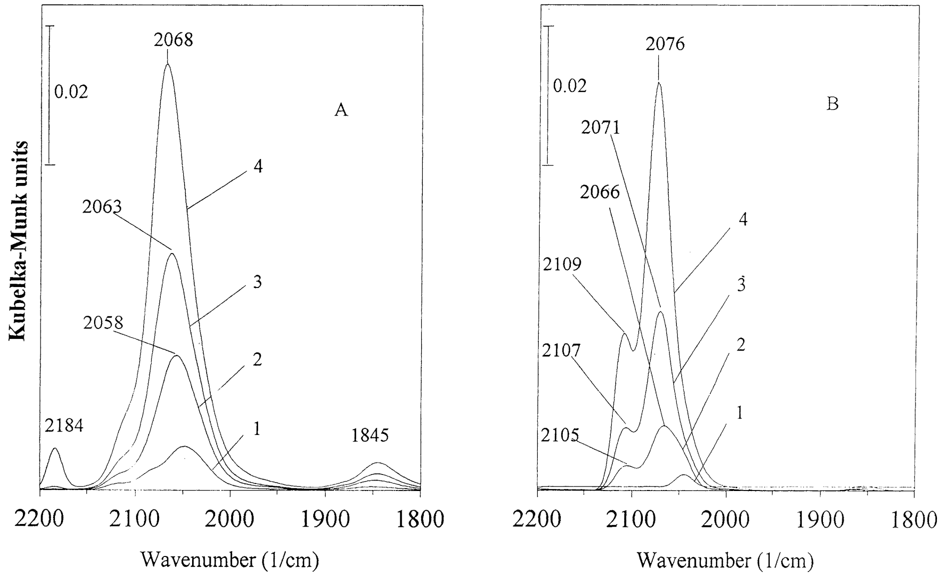

Fig. 3. Spectral changes due to the effect of CO pressure changes at 300 K on (A) reduced 1% Pt/TiO_2; (B) reduced 5% Pt/TiO_2. Adsorption time was 15 min. 1, 0.01 Torr; 2, 0.1 Torr; 3, 1 Torr; and 4, 10 Torr.

position of which depended on the CO pressure applied: it was registered at 2058 cm^{-1} in 0.1 Torr CO and shifted to 2063 cm^{-1} (1 Torr) and to 2068 cm^{-1} (10 Torr) (Fig. 3A).

Upon increasing the Pt content to 5%, the three band structure was not observable in 0.01 Torr CO; only a small band at around 2050 cm^{-1} could be detected. As the CO pressure increased to 0.1 Torr, two bands at 2105 and 2066 cm^{-1} appeared. The positions of these bands shifted to higher wavenumbers with a further increase of CO pressure (Fig. 3B). In 10 Torr CO they appeared at 2109 and 2076 cm^{-1}.

When the reduced 1% Pt/TiO_2 sample was kept in 10 Torr CO at 300 K, an intense band at 2065 cm^{-1} was displayed in the spectrum after 1 min adsorption time. In addition to this band a shoulder at 2109 cm^{-1} and a small band at 1845 cm^{-1} appeared at the same time. With the increase of the adsorption time the 2065 cm^{-1} band shifted continuously to higher wavenumbers: after 20 h it was detected at 2072 cm^{-1}. The intensities of the bands at 2109 and around 1840 cm^{-1} increased with an increase of the adsorption time (Fig. 4A).

The same experiment (10 Torr CO at 300 K) on reduced 5% Pt/TiO_2 led to the appearance of the bands at 2109, 2074, and 1845 cm^{-1}. Their intensities increased with the increase of the adsorption time; their positions, however, proved to be stable even after 20 h adsorption (Fig. 4B).

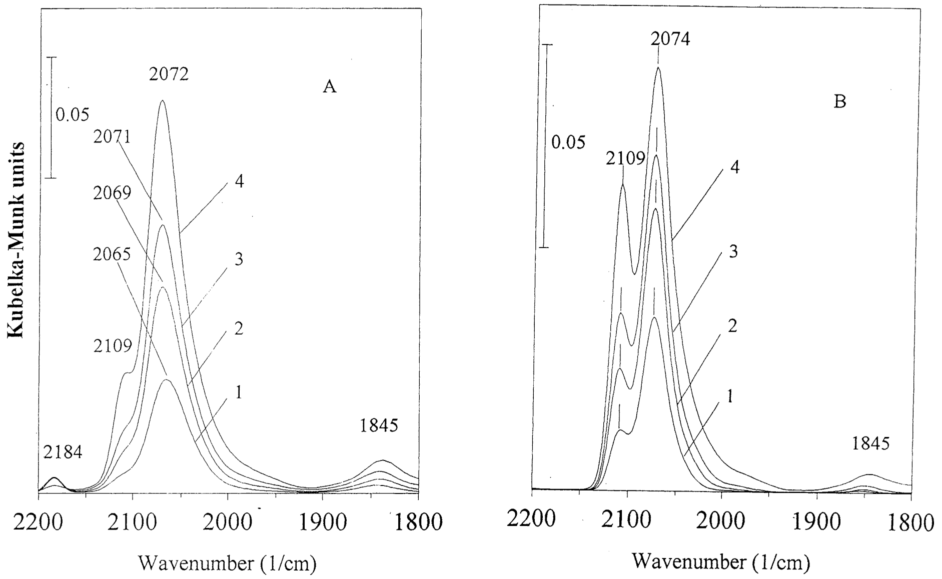

Fig. 4. Spectra due to the adsorption of 10 Torr CO at 300 K as a function of adsorption time on (A) reduced 1% Pt/TiO_2; (B) reduced 5% Pt/TiO_2. 1, 1 min; 2, 60 min; 3, 180 min; and 4, 20 h.

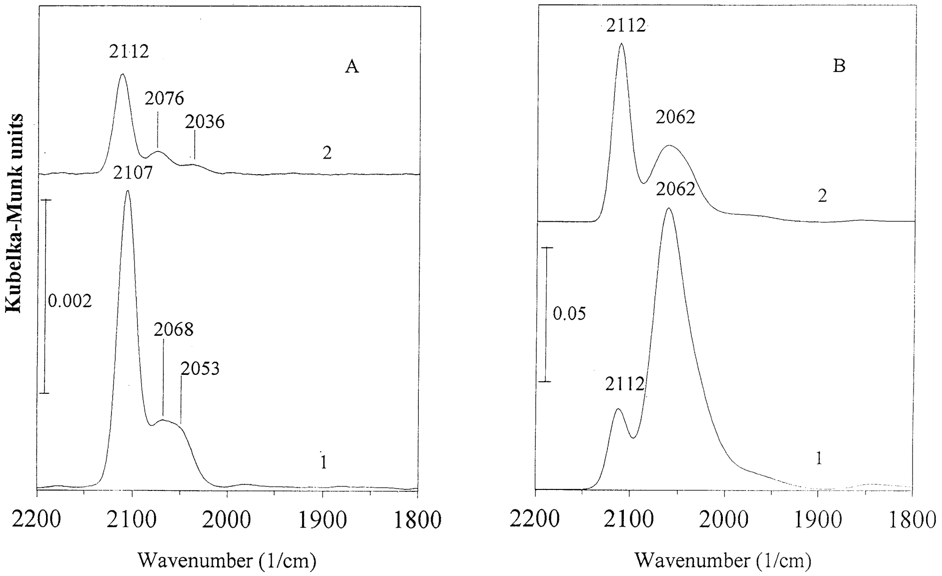

Fig. 5. Spectra recorded (A) on reduced 1% Pt/TiO_2 after adsorption of 0.01 Torr CO for 180 min and evacuation at 300 K (1) and at 543 K (2); (B) on reduced Pt/TiO_2 catalysts after adsorption of 10 Torr CO for 20 h and evacuation at 300 K: 1% Pt/TiO_2 (1) and 5% Pt/TiO_2 (2).

It is worth mentioning that the three band structure did not appear in these experiments.

The three band structure remained on the spectra when the sample (1% Pt/TiO_2) was evacuated at the adsorption temperatures after 0.01 Torr CO adsorption at 300 and 543 K, respectively (Fig. 5A). It is noteworthy that the evacuation at both temperatures resulted in a dominant band at 2107 cm^{-1} (300 K) and at 2112 cm^{-1} (543 K), and small bands at 2068 and 2053 cm^{-1} at 300 K, and at 2076 and 2036 cm^{-1} at 543 K.

Stable bands at 2112 and 2062 cm^{-1} were observed in the spectra of both the 1 and 5% Pt/TiO_2 due to evacuation at 300 K after the adsorption of 10 Torr CO for 20 h at 300 K (Fig. 5B). It is interesting that the intensity of the 2062 cm^{-1} band reduced in a greater extent on 5% Pt/TiO_2, as on 1% Pt/TiO_2.

3.2. Pt/SiO_2 and Pt/Al_2O_3

The three band structure (2107, 2069, and 2045 cm^{-1}) appeared in the spectra of reduced 1% Pt/SiO_2 due to the adsorption of 0.01 and 0.1 Torr CO at 300 K, respectively (Fig. 6A). With the further increase of CO pressure the 2069 cm^{-1} band became dominant. When the sample was kept in 10 Torr CO at 300 K for 20 h, only the band at 2069 cm^{-1} could be detected, which shifted to 2058 cm^{-1}

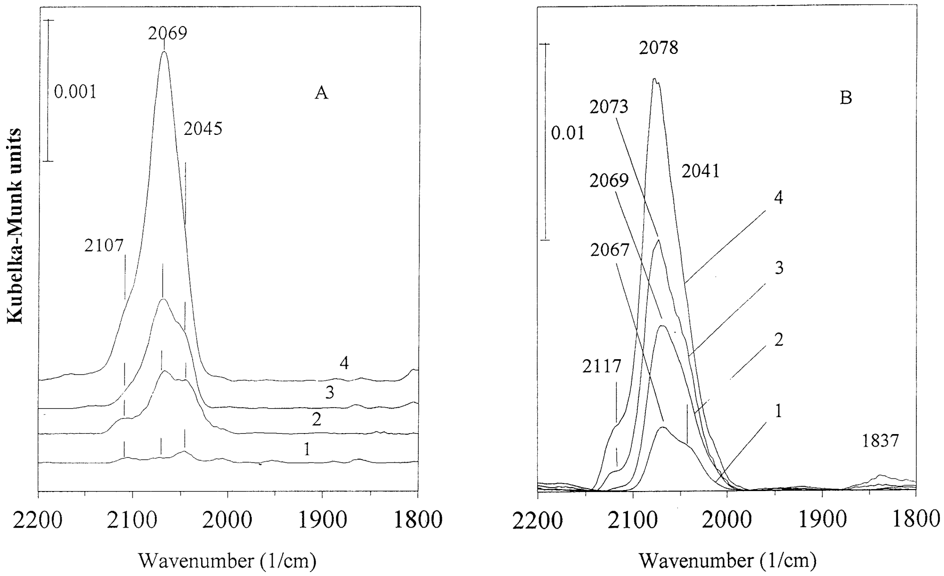

Fig. 6. Spectral changes due to the effect of CO pressure changes at 300 K on (A) reduced 1% Pt/SiO_2; (B) reduced 5% Pt/Al_2O_3. Adsorption time was 15 min. 1, 0.01 Torr; 2, 0.1 Torr; 3, 1 Torr; and 4, 10 Torr.

and diminished on the effect of subsequent evacuation at 300 K.

The features registered on reduced 1% Pt/Al_2O_3 were different from the above: the adsorption of 0.01 Torr CO at 300 K resulted in the appearance of two bands at 2067 and 2041 cm^{-1}. With the increase of CO pressure the intensity of the 2067 cm^{-1} band increased and shifted to higher wavenumbers (in 10 Torr CO it appeared at 2078 cm^{-1}). The 2041 cm^{-1} band could not be resolved in 0.1–10 Torr CO. A shoulder at 2117 cm^{-1} and a band at 1837 cm^{-1} developed in 1 and 10 Torr CO (Fig. 6B). The positions of the 2117 and 2078 cm^{-1} bands were unchanged when the sample was kept in 10 Torr CO at 300 K for 20 h; their intensities, however, increased with increasing adsorption time. On the effect of subsequent evacuation at 300 K the intensities of both bands diminished and they shifted to lower wavenumbers (to 2116 and 2067 cm^{-1}).

The spectra of 5% Pt/SiO_2 and 5% Pt/Al_2O_3 samples displayed only one band at 2062 and 2066 cm^{-1}, respectively, due to the adsorption of 0.01 Torr CO at 300 K. The intensity of these bands increased with increasing CO pressure; no other bands, however, could be observed.

4. Discussion

The different pretreatments of the 1% Pt/TiO_2 sample led to an unexpected result: the oxidation and the evacuation at 573 K resulted in the appearance of one band between 2100 and 2000 cm^{-1}, which resembles well the band assigned to linearly bonded (on top) CO on Pt crystallites (formed during reduction) (Fig. 1A). The shifts of this band to higher wavenumbers with the increase of CO pressure from 0.01 to 10 Torr (Fig. 1B) seems to strengthen further the above similarity. When the sample was evacuated at 300 K (not shown) after 10 Torr CO adsorption, the above band shifted to lower wavenumbers, which is also similar to the behavior of on top CO surface species.

The possible explanation of these infrared features, indirectly that of the formation of Pt crystallites during oxidation and evacuation at 573 K, might be based on the extended electron transfer from titania to platinum ions. The electronic interaction between titania and metal supported by titania was first supposed and demonstrated more than three decades ago [29]. The easy electron transfer from titania to the supported metals has been recently demonstrated in some catalytic systems [30–32]. This would result in the reduction of Pt^{n+} ions to Pt^0 atoms, and then Pt atoms agglomerate to Pt crystallites producing quasi-uniform adsorption sites for CO adsorption. It should be noted, however, that no measurable H_2 adsorption (i.e., no detectable Pt dispersity) was experienced at 300 K on oxidized or on evacuated 1% Pt/TiO_2.

The most striking feature obtained in this work was the detection of a three band structure (similarly to that observed on supported Rh) in low CO pressure at 300 K on 1% Pt/TiO_2 reduced at 573 K (Fig. 1A). This structure remained in 0.01 Torr CO at 300 and 543 K for longer time (Figs. 2A and 2B). The band slightly above 2100 cm^{-1} (2106 cm^{-1} at 300 K, 2112 cm^{-1} at 543 K) has grown with adsorption time at both temperatures independent of the two other bands at 2100–2000 cm^{-1}, showing that the bands in the three band structure should belong to different adsorbed CO species. Thus the classical assignment of the three bands observed in the case of supported Rh ($\sim$ 2100 and $\sim$ 2030 cm^{-1} are due to symmetric and asymmetric stretchings of $Rh^{+1}(CO)_2$ and $\sim$ 2060 cm^{-1} is due to on top CO) [1] is not applicable to supported Pt.

In other experiments the development of the band at slightly above 2100 cm^{-1} was dependent also on the CO pressure (Figs. 3A and 3B) and on the Pt content (comparison of Figs. 3A and 3B and Figs. 4A and 4B, respectively). This band was stable and dominant in the spectra recorded after evacuation at 300 and 543 K, respectively (Fig. 5A).

A plausible assignment of this band would be that it might belong to CO adsorbed on (at least partially) oxidized Pt ($Pt^{\delta+}$) sites. The oxidation of originally reduced Pt atoms may have occurred by oxygen generating from CO dissociation on titania-supported Pt samples. There are no data, however, which would demonstrate the occurrence of CO dissociation at 300 K on Pt/TiO_2 catalysts. After a more effective oxidation (at 573 K in O_2), on the other hand, no band at slightly above 2100 cm^{-1} appeared in CO adsorption (Figs. 1A and 1B). The assignment of this band to CO adsorption on Pt ions seems to be also unlikely, because the adsorption of CO on these sites was found to be very weak [33,34], which is in contrast to the high stability of this band found on evacuation at 543 K (Fig. 5A). All these suggest that this band cannot be assigned to $Pt^{\delta+}$–CO surface species.

A more convincing interpretation can be obtained by taking into account the assignment of the 2123 cm^{-1} band which appeared in CO adsorption on Pt-mordenite [35] and on Pt/ZSM-5 [22]. The 2123 cm^{-1} band was attributed to CO adsorbed on monoatomic Pt^0 in the case of Pt-mordenite [35]. As the band at 2123 cm^{-1} was easily detected on Pt/ZSM-5 only when conditions known to favor the formation of atomically dispersed metal species were used, i.e., low metal loading and low reduction temperature, this assignment for the 2123 cm^{-1} was also applied to this sample [22]. The band at 2123 cm^{-1} could be detected in the highly loaded Pt/ZSM-5 only upon extended CO adsorption at elevated pressure. In the latter case the 2123 cm^{-1} band was attributed to CO adsorbed on Pt^0 atoms in hidden sites of the ZSM-5 structure, which are not readily accessible for CO.

Spectral features similar to those observed on Pt/ZSM-5 were registered in the present study: the band at 2112–2106 cm^{-1} appeared immediately after admission of CO to Pt/TiO_2 and this band developed slowly at higher CO pressure. Based upon the above the 2112–2106 cm^{-1} band observed on Pt/TiO_2 can tentatively be assigned to CO adsorbed on monoatomic Pt^0. Its immediate appearance may refer to the possibility that after reduction at relatively low temperature (573 K) a part of the platinum exists in the form of Pt^0 atoms. The slow increase in the intensity of this band with adsorption time and CO pressure, on the other hand, may reflect a slow surface process due to CO adsorption, which is probably the disruption of Pt crystallite (especially in the case of higher—5%—Pt loading) into Pt^0 atoms with the help of CO.

At the lowest CO pressure applied here (0.01 Torr) two other bands at about 2070 and 2050 cm^{-1} appeared in the spectra of 1% Pt/TiO_2 reduced at 573 K (Fig. 2A), the intensities of which did not change appreciably at 300 K in increasing adsorption time. Although the difference of their positions ($\Delta\nu = \sim 20$ cm^{-1}) is too low in comparison with that for Rh^+–$(CO)_2$ ($\Delta\nu = \sim 70$ cm^{-1}), their intensity ratio is near unity, which would permit their assignment to Pt^+–$(CO)_2$ surface species. The fact that these bands could be observed in CO (0.01 Torr) adsorption at 543 K contradicts this assignment, as 543 K would be high enough for reduction of Pt^+ sites by CO. More probably, these bands may belong to CO adsorbed on Pt atoms with different coordination numbers (i.e., Pt atoms on edges and on kinked Pt atoms). According to the spectral features observed, the edged and kinked Pt atoms are stable on 1% Pt/TiO_2 even at relatively high temperature and at low CO pressure.

Interestingly, these bands disappeared with the increase of CO pressure at 300 K (Fig. 3A); only one band at 2058 cm^{-1} appeared in 0.1 Torr CO, which shifted to higher wavenumbers with the further increase of CO pressure. This behavior is very characteristic for CO linearly (on top) adsorbed on a well-ordered Pt surface and is explained by dipole–dipole interaction [8]. The appearance of the band at 2058–2068 cm^{-1} already at 300 K due to increasing CO pressure suggests the occurrence of agglomeration or reconstruction of surface Pt atoms. The disappearance of the 2070 and 2050 cm^{-1} bands in higher CO pressure favors the possibility that edged and kinked Pt atoms transform to Pt atoms in more ordered position; i.e., they become parts of different smooth Pt crystalline facets (reconstruction). At the same time the increase of the Pt crystallite size can also be expected (agglomeration).

The bands due to CO adsorbed on edged and kinked Pt atoms did not appear on 5% Pt/TiO_2 in 0.01 Torr CO (Fig. 3B). Only one band due to linearly adsorbed CO (2066–2076 cm^{-1}) was detected in the range of 2100–2000 cm^{-1}, the characteristics of which were the same as that of the 2058–2068 cm^{-1} band observed on 1% Pt/TiO_2. This observation permits the conclusion that the reductive pretreatment (at 573 K) of 5% Pt/TiO_2 resulted in the formation of Pt crystallites with well-ordered facets containing no edged and kinked Pt atoms.

The dispersity reduced 1 and 5% Pt/TiO_2 (29 and 20%); consequently the particle sizes calculated [36,37] from the dispersity values (3.09 and 4.48 nm) were not considerably different. Thus, the difference in the particle size alone would not account for the different spectral features observed on the above catalysts. It is very possible that the heights of the particles are bigger in the case of 5% Pt/TiO_2, which may be more favorable in the formation of nearly ideal Pt facets (no disturbing effect of the support). It has been demonstrated [38–40] that the differences obtained in CO adsorption on Pt/Al_2O_3 and Pt/SiO_2 catalysts could be due to the different shapes and morphologies of Pt crystallites on alumina and silica formed during the reduction.

Once Pt facets (without edged and kinked Pt atoms) formed, they proved to be stable at 300 K in 10 Torr CO for a longer time (Figs. 4A and 4B). No new bands besides the absorptions due to CO adsorbed on monoatomic Pt (2109 cm^{-1}) and on smooth Pt facets (2074–2072 cm^{-1})

appeared even after 20 h. This observation is in contrast with the phenomenon detected on supported Rh, where Rh crystallites of appropriate size suffered oxidative disruption at 300 K in 10 Torr CO [1].

It can be supposed that the small bands at ~ 2070 and $\sim 2050\ \mathrm{cm}^{-1}$ were simply mismatched by the intense band at 2066–2076 cm^{-1}; thus no surface rearrangement occurred, as has been stated above. After a short evacuation at 300 K, however, only the bands at 2112 and 2062 cm^{-1} were detected; no traces of the bands due to CO adsorbed on edged and kinked Pt atoms were observed (Fig. 5B). These features strengthen further that the appearance of the 2066–2076 cm^{-1} band is really due to the surface rearrangement of Pt atoms.

Data similar in many respects to the features observed on 1% $\mathrm{Pt/TiO_2}$ were obtained on 1% $\mathrm{Pt/SiO_2}$ and on 1% $\mathrm{Pt/Al_2O_3}$ catalysts (Figs. 6A and 6B). A slight difference was detected on $\mathrm{Pt/Al_2O_3}$, where the 2117 cm^{-1} band (CO adsorbed on monoatomic Pt^0)—as a consequence of the reductive disruption of Pt crystallites—appeared only after the disappearance of the bands (2069 and 2041 cm^{-1}) due to CO adsorbed on edged and kinked Pt atoms. This might be connected with the finding that the Pt particle size was smaller (1.14 nm) on $\mathrm{Al_2O_3}$ than on $\mathrm{TiO_2}$ (3.09 nm), and originally no monoatomic Pt^0 atoms are available after reduction at 573 K.

In this work a low reduction temperature was chosen to avoid the strong metal support interaction (SMSI) phenomenon on $\mathrm{Pt/TiO_2}$. For better comparison the same reduction process was applied to $\mathrm{Pt/SiO_2}$ and $\mathrm{Pt/Al_2O_3}$ catalysts. With the increase of the reduction temperature, larger Pt particles without monoatomic Pt^0 atoms should form, which are more stable against the reconstruction effects of CO than the Pt particles formed during the pretreatment applied here. With all probability this would explain the fact that no infrared features due to surface rearrangement of Pt due to CO adsorption have been previously detected in most of the works dealing with this topic.

The above statements were made solely on the basis of DRIFTS experimental results. Evidences for further strengthening the surface rearrangement of Pt of this type on supported Pt catalysts can be expected from other sophisticated methods.

5. Conclusions

1. It was demonstrated that Pt crystallites with flat Pt surfaces, edged and kinked Pt atoms, and monoatomic Pt^0 may exist on reduced Pt/oxide catalysts of low Pt loading.
2. This structure is stable up to at least 543 K in low CO pressure.
3. The increase of CO pressure caused the disappearance of edged and kinked Pt atoms (*smoothing* of the Pt surface) and the increase of the surface concentration of individual Pt^0 atoms (disruption).
4. On reduced Pt/oxide catalysts of higher Pt loading, Pt crystallites with flat Pt surfaces and monoatomic Pt^0 atoms can be found. No edged and kinked Pt atoms formed during reduction.
5. The surface concentration of monoatomic Pt^0 (the extent of disruption) increased with increasing time and CO pressure at 300 K on Pt/oxides of higher Pt loading.

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References

[1] F. Solymosi, M. Pásztor, J. Phys. Chem. 89 (1986) 4783; F. Solymosi, M. Pásztor, J. Phys. Chem. 90 (1986) 5312.

[2] M. Primet, J. Chem. Soc. Faraday I 74 (1978) 2570; M. Primet, J.C. Védrine, G. Naccache, J. Mol. Catal. 4 (1978) 411.

[3] C.A. Rice, S.D. Worley, C.W. Curtis, J.A. Guin, A.R. Tarrer, J. Chem. Phys. 74 (1981) 6748.

[4] F. Solymosi, É. Novák, A. Molnár, J. Phys. Chem. 94 (1990) 7250.

[5] F. Solymosi, J. Raskó, J. Catal. 115 (1989) 107.

[6] A. Berkó, G. Ménesi, F. Solymosi, J. Phys. Chem. 100 (1996) 17732; A. Berkó, F. Solymosi, J. Catal. 183 (1999) 91.

[7] A. Berkó, F. Solymosi, J. Phys. Chem. B 104 (2000) 10251.

[8] F. Stoop, F.J.C. Toolenaar, V. Ponec, J. Catal. 73 (1982) 50.

[9] C. Hippe, R. Lamber, G. Schultz-Ekloff, U. Schubert, Catal. Lett. 43 (1997) 195.

[10] N.W. Cant, R.A. Donaldson, J. Catal. 71 (1981) 320.

[11] D.M. Haaland, F.L. Williams, J. Catal. 110 (1982) 319.

[12] Y.-E. Li, D. Boecker, R.D. Gonzalez, J. Catal. 110 (1988) 319.

[13] P.T. Fanson, W.N. Delgass, J. Lauterbach, J. Catal. 204 (2001) 35.

[14] R.K. Brandt, M.R. Hughes, L.P. Bourget, K. Truszkowska, R.G. Greenler, Surf. Sci. 286 (1993) 15.

[15] S.C. Tripathi, S.C. Srivastava, R.P. Mani, A.K. Shrimal, Inorg. Chim. Acta 17 (1976) 257.

[16] F.R. Hartley, in: G. Wilkinson (Ed.), Comprehensive Organometallic Chemistry, Vol. 6, Pergamon, Oxford, 1978, p. 471.

[17] D.M. Roundhill, in: G. Wilkinson (Ed.), Comprehensive Coordination Chemistry, Vol. 6, Pergamon, Oxford, 1978, p. 351.

[18] E.P. Kündig, D. McIntosh, M. Moskovits, G.A. Ozin, J. Am. Chem. Soc. 95 (1973) 7234.

[19] G.-J. Li, T. Fujimoto, A. Fukuoka, M. Ichikawa, Catal. Lett. 12 (1992) 171.

[20] A.Yu. Stakheev, E.S. Shpiro, N.I. Jaeger, G. Schulz-Ekloff, Catal. Lett. 34 (1995) 293.

[21] B.L. Mojet, D.C. Koningsberger, Catal. Lett. 39 (1996) 191.

[22] A.Yu. Stakheev, E.S. Shpiro, O.P. Tkachenko, N.I. Jaeger, G. Schulz-Ekloff, J. Catal. 169 (1997) 382.

[23] X. Su, P.S. Cremer, Y.R. Shen, G.A. Somorjai, J. Am. Chem. Soc. 119 (1997) 3994.

[24] X. Su, P.S. Cremer, Y.R. Shen, G.A. Somorjai, Phys. Rev. Lett. 77 (1996) 3858.

[25] H. Harle, U. Metka, H.-R. Volpp, J. Wolfrum, Phys. Chem. Chem. Phys. 1 (1999) 5059.

[26] G. Rupprechter, T. Dellwig, H. Unterhalter, H.-J. Freund, J. Phys. Chem. 105 (2001) 3797.

[27] K.Y. Kung, P. Chen, F. Wei, Y.R. Shen, G.A. Somorjai, Surf. Sci. 463 (2000) L627.

[28] K. Hadjiivanov, Appl. Surf. Sci. 135 (1998) 331.

[29] F. Solymosi, Catal. Rev. 1 (1967) 233.

[30] J. Raskó, F. Solymosi, J. Phys. Chem. 98 (1994) 7147.

[31] J. Raskó, Catal. Lett. 56 (1998) 11.

[32] J. Raskó, Z. Szabó, T. Bánsági, F. Solymosi, Phys. Chem. Chem. Phys. 3 (2001) 4437.

[33] K. Klier, Langmuir 4 (1988) 13.

[34] H. Bischoff, N.I. Jaeger, G. Schulz-Ekloff, L. Kubelkova, J. Mol. Catal. 80 (1993) 95.

[35] V.L. Zholobenko, G.-D. Lei, B.T. Carvill, B.A. Lerner, W.M.H. Sachtler Jr., Chem. Soc. Faraday Trans. 90 (1994) 233.

[36] T.E. White, Catal. Rev.-Sci. Eng. 117 (1973) 8.

[37] J. Sárkány, University thesis, Szeged, 1977, p. 50.

[38] J. Sárkány, R.D. Gonzalez, Appl. Catal. 4 (1982) 53.

[39] J. Sárkány, R.D. Gonzalez, Ind. Eng. Chem. Prod. Res. Dev. 22 (1983) 548.

[40] J. Sárkány, R.D. Gonzalez, Appl. Catal. 5 (1983) 85.