Diffuse reflectance IR study of noble metals supported on basic carriers.
Part I: Pt supported on Al–Mg hydrotalcite

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The state of metallic Pt supported on alumina–magnesia hydrotalcite was investigated using diffuse reflectance FT-IR spectra of adsorbed CO and terminal Pt hydrides formed upon hydrogen dissociative chemisorption on metal at room temperature. On hydrotalcite surface metallic Pt exists in three different forms, such as neutral and negatively charged metallic particles as well as slightly negatively charged clusters encapsulated between layers of support. Negative charging on Pt particles results in decrease of singleton frequency of linearly adsorbed CO by 70 $\mathrm{cm^{-1}}$ and frequency of Pt–H bond vibration by 50–100 $\mathrm{cm^{-1}}$. It was also established that negatively charged Pt is less sulfur resistant than neutral Pt particles.

Keywords: supported Pt, hydrotalcites, adsorption of CO, adsorption of hydrogen, Pt hydrides, DRIR spectroscopy, sulfur modification

1. Introduction

Noble metals supported on basic carriers are known to possess unusual catalytic properties. For instance, according to refs. [1,2], Pt stabilized in alkaline and alkaline-earth forms of L, X or Y zeolites is highly active and selective in hexane aromatization. Similar properties were reported for Pt, supported on amorphous basic MgO stabilized by alumina [3,4]. In both cases this was explained by negative charging resulting from electron density transfer from the surface basic oxygen of the carriers to supported metallic particles [5–7].

It was suggested in ref. [8], that the degree of the negative charging and, consequently, of the electronic modification of supported dispersed metals increases in parallel with the basicity of the carriers. Therefore, the use of oxides with variable basic properties could result in modification of catalytic and adsorption properties of supported metals in a desirable direction.

In this connection, hydrotalcites are of definite interest. These materials combine strong basic properties with high specific surface area and relatively high thermostability. The chemical composition of hydrotalcites is presented by the following formula:

$$(\mathrm{M}^{2+}_{1-x}\mathrm{M}^{3+}_{x}(\mathrm{OH})_2)^{x+}(\mathrm{A}^{m-}_{x/m})\cdot\mathrm{H_2O}\,,$$

where the role of bivalent cations $\mathrm{M^{2+}}$ is played by $\mathrm{Mg^{2+}}$, $\mathrm{Ca^{2+}}$, $\mathrm{Zn^{2+}}$ or $\mathrm{Ni^{2+}}$ ions, and that of trivalent cations by $\mathrm{Al^{3+}}$, $\mathrm{Fe^{3+}}$, $\mathrm{Cr^{3+}}$, etc. The charge-compensating anions A^{m-}, for instance $\mathrm{OH^-}$, $\mathrm{Cl^-}$, $\mathrm{NO_3^-}$, $\mathrm{CO_2^{2-}}$, $\mathrm{SO_4^{2-}}$, etc., are localized between the oxide layers. The basic properties of hydrotalcites can be changed either by the variation of cations and atomic $\mathrm{M^{2+}/M^{3+}}$ ratio or by the nature of charge-compensating anions A^{m-}.

In the present paper the state of dispersed metallic platinum supported on alumina–magnesia hydrotalcite was studied by diffuse reflectance FT-IR (DRIR) spectroscopy by means of carbon monoxide adsorption and dissociative adsorption of hydrogen as molecular probes. In addition, the DRIR technique was also used to characterise the modification of supported Pt particles by sulfur. The obtained results were compared with the data of the spectroscopic study of platinum supported on alumina.

2. Experimental

The hydrotalcite used here is a pure phase from the XRD pattern. It contains 8.8 wt% Al and 23.75 wt% Mg; after activation for 5 h at 450°C, the surface area is 200 $\mathrm{m^2/g}$ with the porosity centered at 2 nm. The 0.5% Pt supported on hydrotalcite and on γ-$\mathrm{Al_2O_3}$ with BET specific surface area of 180 $\mathrm{m^2/g}$ were prepared by impregnation with aqueous solution of $\mathrm{H_2PtCl_6}$. The air-dry samples were placed into a U-type quartz reactor supplied with a finger with a $\mathrm{CaF_2}$

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window transparent in the IR region. (During the subsequent thermal treatment this part of the reactor was kept at room temperature.) Then the samples were treated in flowing hydrogen for 2 h at 120°C followed by reduction in hydrogen flow at 400°C also for 2 h. The rate of temperature rise from 120 to 400°C was 5°C/min, while hydrogen flow velocity was equal to 60 ml/min. After reduction the samples were evacuated at 400°C for 1 h and cooled down to room temperature.

DRIR measurements were carried out directly in the reactor used for reduction. For this purpose the part of the sample powder was poured from the U-tube to the finger with CaF_2 window and the reactor was transferred to the diffuse reflectance attachment for IR measurements which was similar to that one described in refs. [9,10]. The consequent DRIR measurements were carried out with a Nicolet Impact-410 FT-IR spectrophotometer at room temperature.

Adsorption of CO and H_2 on the reduced catalysts was carried out at 20°C and the equilibrium pressures of the gases were equal to 20 and 30 Torr, respectively. The gradual decrease of the metal surface coverage with adsorbed CO was performed by subsequent evacuation of the samples at elevated temperatures. The obtained IR spectra were converted into Kubelka–Munk units. For this purpose the reflection ability of the samples at 4000 cm^{-1} was chosen equal to 0.7.

Sulfidation of the reduced catalysts was performed by treatment at 400°C for 1 h in a flowing $H_2 + H_2S$ mixture containing 100 ppm of H_2S. Carbon monoxide was prepared by decomposition of $W(CO)_6$.

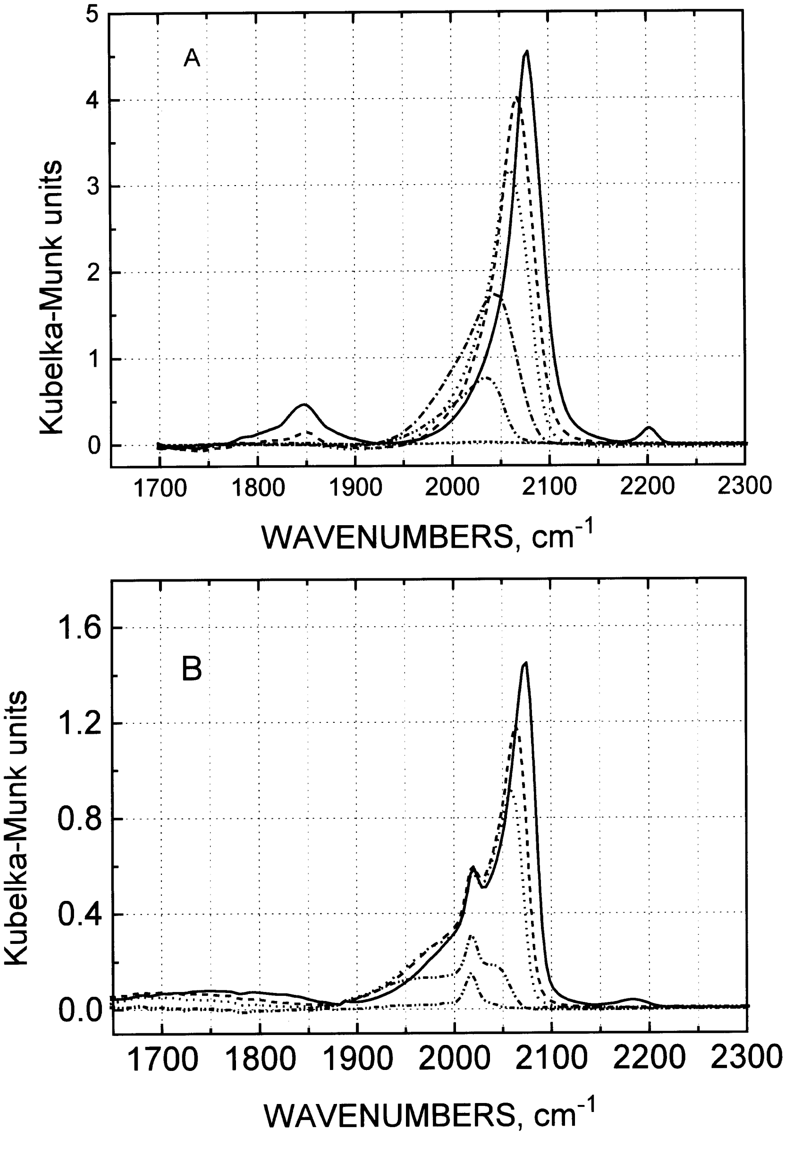

Figure 1. DRIR spectra of CO adsorbed on reduced Pt/alumina (A) and on Pt/hydrotalcite (B) samples at equilibrium CO pressure at 20 Torr (——) or after evacuation of preadsorbed CO for 0.5 h at 20°C (- - -), 100°C (· · ·), 200°C (– · –) and 300°C (– · · –). The measurements were carried out at room temperature.

3. Results and discussion

3.1. CO adsorption

The evolution of the DRIR spectra of carbon monoxide adsorbed on the aluminum oxide and hydrotalcite supported samples after subsequent evacuation at room and elevated temperatures is shown in figures 1A and 1B, respectively. The expanded-scale spectra for the intermediate temperatures of desorption are additionally displayed in figures 2A and 2B.

Adsorption of CO on the alumina-supported sample at the equilibrium pressure of 20 Torr results in the appearance of three bands with maxima at 1845, 2080 and 2200 cm^{-1}. According to refs. [11,12], the first two bands correspond to the bridging and linear forms of CO adsorption on supported Pt particles, respectively, while the maximum at 2200 cm^{-1} represents CO adsorbed on coordinatively unsaturated Al^{3+} cations of the support.

After evacuation at temperatures above 100°C the bands at 1845 and 2200 cm^{-1} disappear, while the intensity of the band at 2080 cm^{-1} decreases and its maximum is shifted to lower wavenumbers. This effect has been traditionally explained by the weakening of the lateral interaction between the linearly adsorbed CO molecules at lower metal surface coverage. The singleton frequency of this linear form of adsorption obtained after CO desorption at 300°C is equal to 2035 cm^{-1}. This is somewhat lower than the value reported for Pt/alumina catalysts in refs. [11,13] but coincides with the figure obtained by the isotopic dilution method with use of the ^{12}CO + ^{13}CO mixtures in ref. [14].

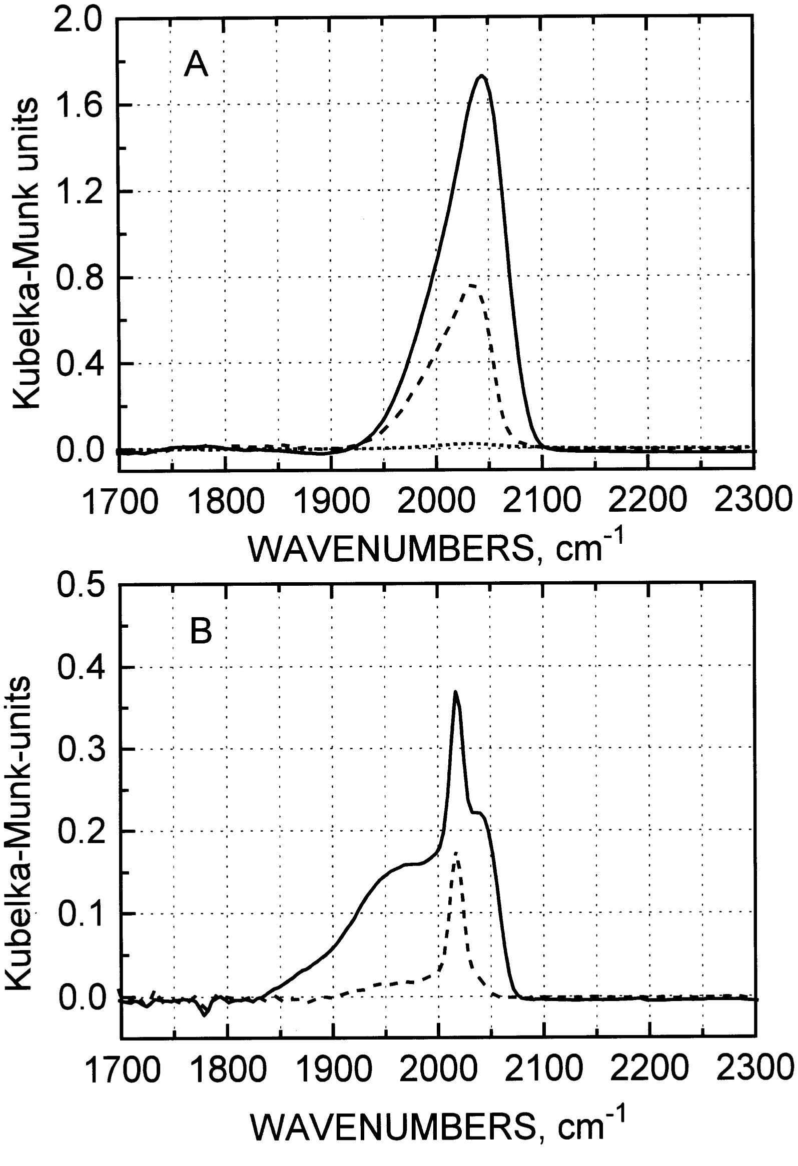

Figure 2. Expanded DRIR spectra of CO adsorbed on reduced Pt/alumina (A) and Pt/hydrotalcite (B) after evacuation of preadsorbed CO for 0.5 h at 200°C (——) and 300°C (- - -). The spectra were measured at room temperature.

The spectra of CO adsorbed on the Pt/hydrotalcite sample are different in several respects (figures 1B and 2B). Firstly, the stretching frequency of CO adsorbed on coordinatively unsaturated Al^{3+} cations of the support of 2180 cm^{-1} is somewhat lower than for the corresponding form of CO adsorption on Al^{3+} ions of the aluminum-supported sample of 2200 cm^{-1}. (The maximum at 2180 cm^{-1} also appears in the spectrum of CO adsorbed on Pt-free hydrotalcite dehydrated at 400°C.)

Secondly, the bridging form of CO adsorption on the hydrotalcite-supported platinum is represented by a broad low intense band which is shifted to the lower frequencies of 1700–1800 cm^{-1} as compared with the corresponding maximum at 1845 cm^{-1} for CO adsorbed on the Pt/alumina sample. In addition, this bridging form of CO adsorption is thermally more stable than for alumina-supported Pt, since after evacuation of the sample at 100°C the intensity of the corresponding band remains almost unchanged. (After such treatment the maximum of the band was by 80 cm^{-1} shifted to the lower frequency.)

The difference between the linear forms of CO adsorption on hydrotalcite- and aluminum oxide-supported platinum samples is the strongest. Indeed, after CO adsorption at room temperature the corresponding band for the Pt/hydrotalcite sample is well resolved in two lines with maxima at 2020 and 2075 cm^{-1} (figure 1B). Evacuation at 200°C results in even a stronger difference, since the band from the linear forms of CO adsorption on the Pt/hydrotalcite sample is clearly resolved into three different lines (figure 2B), with the maximum at 2017 cm^{-1} and shoulders at 1965 and 2035 cm^{-1} (figure 2B), while for Pt/alumina such treatment results only in a low-frequency shift of the maximum of the band of linear form of adsorption from 2075 to 2035 cm^{-1} (figure 2A).

The shoulders at 1965 and 2035 cm^{-1} most likely represent low-frequency singletons of CO linearly adsorbed on metallic Pt. Both types of these linear complexes possess a lower thermal stability than those resulting from CO adsorption on Pt/alumina, since the corresponding bands completely disappear from the spectrum after sample evacuation at 300°C.

The strongest form of CO adsorption on Pt/hydrotalcite is represented by the narrow band at 2020 cm^{-1}. Both the intensity and position of this line remain almost unchanged after evacuation of preadsorbed CO even at 300°C. At higher temperature of evacuation (350°C) this band decreases in intensity and is slightly shifted toward 2012 cm^{-1}. Such shift resulting from CO desorption probably also indicates a linear form of CO adsorption on metallic Pt. Thus, the supported metallic Pt particles exist on the hydrotalcite carrier in three different forms which correspond to singleton frequencies of linearly adsorbed CO of 1965, 2012 and 2035 cm^{-1}.

The singletons with a low stretching frequency were earlier reported for CO adsorption on Pt supported on different basic carriers. For instance, for Pt in basic NaX and NaY zeolites the corresponding frequency was equal to 1963 cm^{-1} [15]. This is close to the value of 1965 cm^{-1} obtained in this study. For Pt supported on MgO stabilized by alumina the singleton frequency of 1945 cm^{-1} is even lower [7]. Such strong decrease of the stretching frequencies of adsorbed CO was explained by a negative charging of platinum particles due to electron density transfer from basic oxygen atoms of the carriers. This interpretation is supported by spectroscopic study of CO adsorption on the negatively charged Pt electrodes [16] as well as by results of quantum chemical calculations [17,18]. By analogy, one may also accept the similar explanation for the low singleton frequency of 1965 cm^{-1} obtained in this study. The negative charging of the hydrotalcite-supported Pt particles also agrees with a lower thermal stability of linear Pt–CO complexes together with a stronger CO adsorption in bridging form as compared with the Pt/alumina sample. The extent of such negative charging of Pt/hydrotalcite is most likely close to that for Pt in NaX zeolite, but somewhat lower than for Pt supported on MgO stabilized by alumina.

The second type of negatively charged Pt on hydrotalcite is probably connected with a singleton frequency of linearly adsorbed CO of 2012 cm^{-1}. This value is lower than that of CO adsorbed on Pt/alumina and, therefore, also indicates a small negative charging of Pt. Such form of CO adsorption possesses unusual properties, since despite the CO adsorption is rather slow the resulting linear Pt–CO complexes are very stable. The literature data concerning similar properties of Pt supported on other basic carrier are absent. To our mind, the appearance of such unusual Pt is most likely connected with peculiarities of the hydrotalcite structure. Perhaps the corresponding Pt particles are encapsulated between layers of hydrotalcite resulting in slow diffusion of CO toward metallic adsorption sites as well as a low rate of CO desorption at elevated temperatures. Such supported Pt particles could be also additionally specifically modified by charge-compensating anions A^{m-}. However, these suggestions are certainly quite tentative and need additional confirmation from the study of Pt supported on hydrotalcites of different chemical compositions.

The rest of the supported Pt, similar to that supported on alumina, is connected with a singleton frequency of linearly adsorbed CO equal to 2035 cm^{-1}. The corresponding linear form of CO adsorption is, however, somewhat less thermally stable than for Pt/alumina whereas the band from bridging species with maxima at 1845 cm^{-1} is absent.

3.2. H_2 adsorption

The difference in the state of Pt particles supported on alumina and hydrotalcite is also clearly evident from IR spectra of terminal Pt hydrides resulting from dissociative adsorption of hydrogen at room temperature.

The corresponding data are shown in figures 3A and 3B, respectively.

At an equilibrium pressure of hydrogen equal to 35 Torr the DRIR spectrum of Pt/alumina hydrides represents a slightly asymmetric absorption band with the maximum at 2100 cm^{-1}. Evacuation of hydrogen at room temperature decreases the intensity of the band while its maximum shifts to 2085 cm^{-1}. Since the decrease of platinum surface coverage with chemisorbed hydrogen is not accompanied by variation of the Pt–H frequency [19], this indicates the presence of two different terminal surface Pt hydrides with stretching frequencies of Pt–H bonds of about 2100 and 2085 cm^{-1}. This is consistent with earlier observations of two different terminal Pt hydrides with stretching frequencies of 2105 and 2055 cm^{-1} [20] or of 2120 and 2060 cm^{-1} [21], for high-loaded Pt/Al catalysts, which were explained by the existence of surface Pt atoms in two different environments. In our case the frequency difference of Pt–H bonds for these hydrides is equal only to 15 cm^{-1}. This is considerably less than the value of 40–50 cm^{-1} reported for the bigger supported platinum particles and most likely indicates more uniform metallic sites of hydrogen chemisorption in dilute platinum/alumina catalysts than those found at higher metal loadings.

In contrast to Pt/alumina, the adsorption of hydrogen at room temperature with an equilibrium pressure of 35 Torr on the Pt/hydrotalcite sample results in the band with a maximum at 2035 cm^{-1} (figure 3B1). The second type of adsorbed hydrides with the maximum at 2000 cm^{-1} remains in the spectrum after hydrogen evacuation at room temperature (figure 3B2). Both these

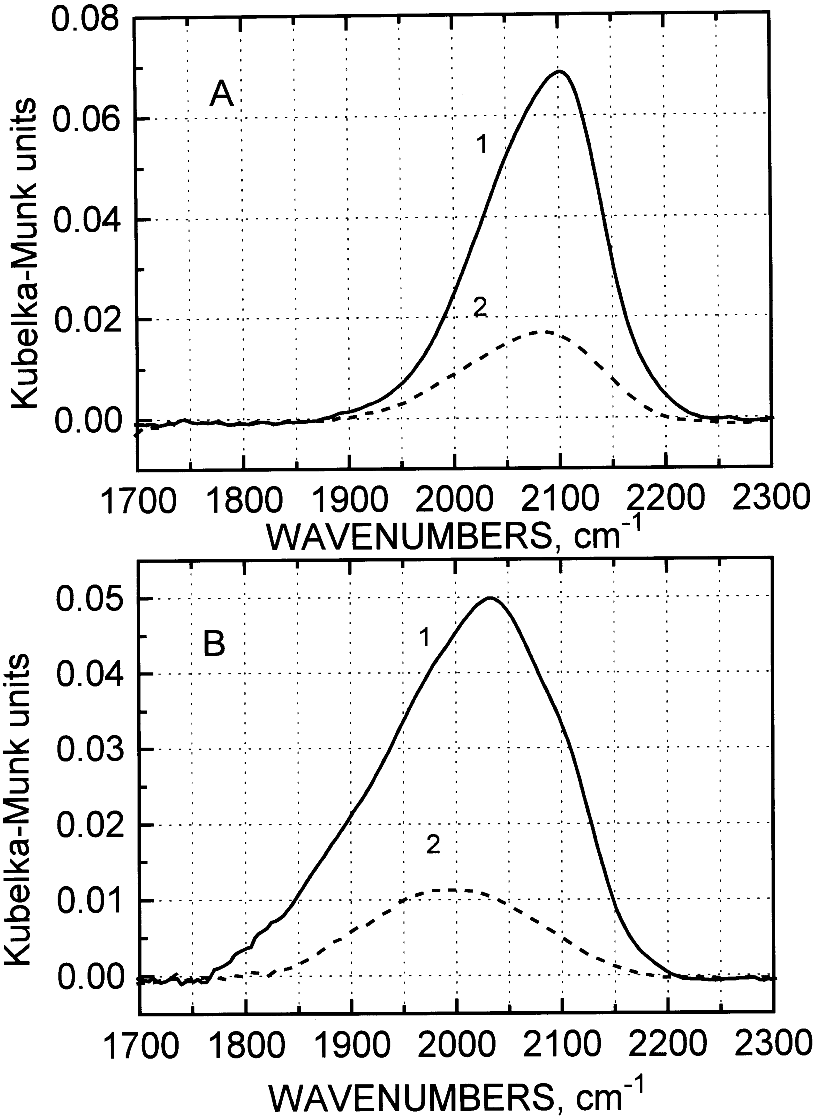

Figure 3. DRIR spectra of terminal Pt hydrides resulting from hydrogen adsorption at room temperature on Pt/alumina (A) and Pt/hydrotalcite (B) catalysts. The spectra were measured at room temperature at H_2 equilibrium pressure of 35 Torr (1) or after evacuation of preadsorbed hydrogen for 0.5 h at room temperature (2).

bands should be attributed to the hydrides resulting from dissociative hydrogen adsorption on negatively charged platinum particles. The corresponding Pt–H stretching frequencies for the negatively charged Pt particles are by 50–100 cm^{-1} lower than for the surface hydrides on the Pt/alumina sample. However, this is not connected with weakening of Pt–H bonds, since the corresponding DRIR bands were more difficult to be removed by evacuation than those from hydrides with higher stretching frequencies. A similar phenomenon was also reported earlier for Pt/alumina catalysts with higher metal loading [20].

3.3. Sulfur modification

The negative charging of supported Pt particles is known to decrease their sulfur resistance [22,23]. Therefore, we investigated DRIR spectra of CO adsorbed on sulfided Pt/alumina and Pt/hydrotalcite contacts. The corresponding spectra are depicted in figures 4A and 4B.

In presence of 20 Torr of CO the intensity of the bands from the linear form of CO adsorption on sulfided samples is several times less intense than those for the freshly reduced sample, while the positions of the maxima at 2075–2080 cm^{-1} are slightly shifted to the lower frequency, most likely due to partial dilution of adsorbed CO molecules by sulfur atoms. Subsequent evacuation of preadsorbed CO at elevated temperatures results in a further decrease of intensity of the adsorption bands, while the adsorption maxima are shifted to the singleton frequency of linearly adsorbed CO of 2055 cm^{-1}. Such

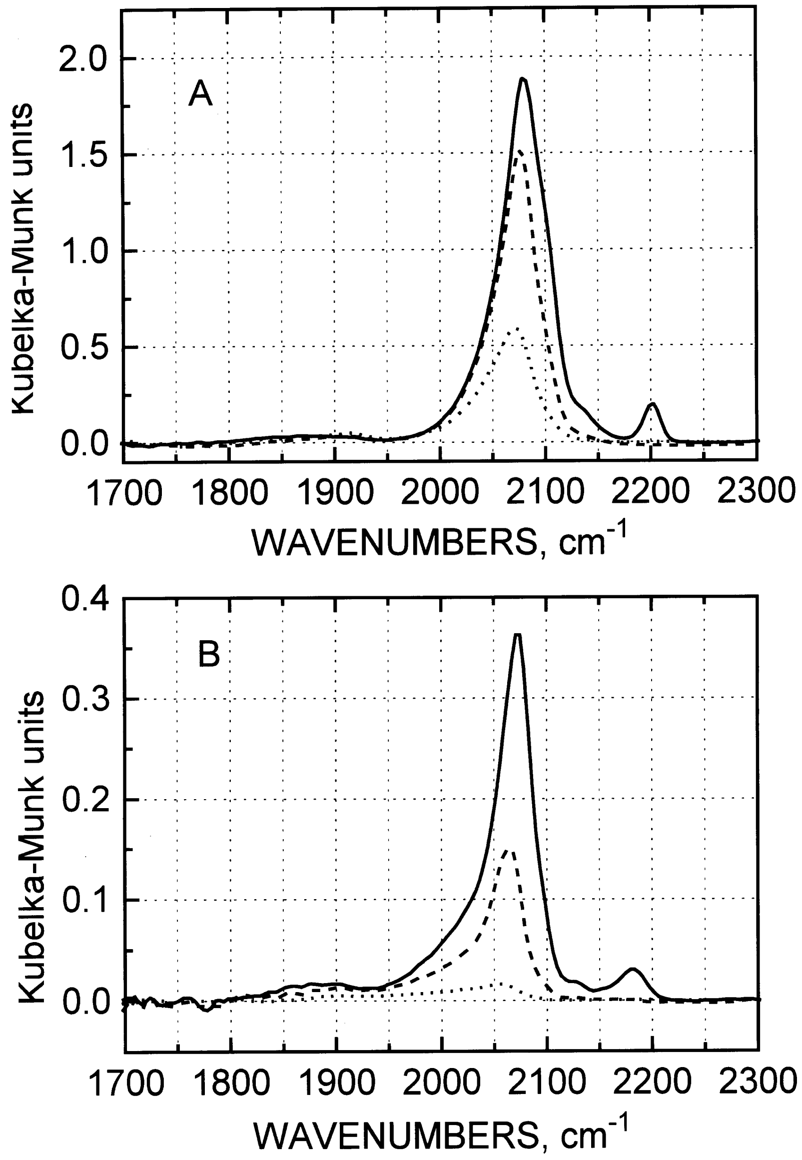

Figure 4. DRIR spectra of CO adsorbed on sulfided Pt/alumina (A) and Pt/hydrotalcite (B) samples at equilibrium CO pressure of 20 Torr (——) or after evacuation of preadsorbed CO for 0.5 h at 20°C (- - -) and 100°C (· · ·). The measurements were carried out at room temperature.

linear form of CO adsorption on sulfided catalysts is thermally less stable, since the corresponding bands were completely removed in vacuum already at 200°C. On the other hand, the singleton frequency at 2055 cm^{-1} higher than for Pt/alumina (at 2035 cm^{-1}) indicates a positive charging of sulfided Pt most likely due to electron density transfer toward chemisorbed sulfur [24]. It is also remarkable, that according to the spectral data the state of sulfided Pt in both alumina and hydrotalcite supported catalysts becomes similar. This most likely results from a complete poisoning of the negatively charged Pt by adsorbed sulfur. Thus, on the surface of the sulfided hydrotalcite remain accessible only the most sulfur resistant platinum particles with properties similar to Pt/alumina.

4. Conclusions

The hydrotalcite-supported metallic Pt exists in several different forms. One part of the supported Pt particles is similar to those supported on aluminum oxide. Another part of metallic Pt is negatively charged while its spectral features are similar to those of Pt stabilized in alkaline forms of X and Y zeolites. The stretching Pt–H frequency of terminal hydrides resulting from dissociative hydrogen chemisorption at room temperature on such negatively charged supported Pt particles is noticeable lower than that of hydrides on "neutral" Pt supported on alumina. The surface of negatively charged Pt particles becomes less sulfur resistant than that of supported neutral Pt crystallites.

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