JOURNAL OF CATALYSIS 30, 13–20 (1973)

Benzene Adsorption and Its Interaction with Carbon Monoxide on Alumina-Supported Platinum— An Infrared Spectroscopic Study

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Received November 14, 1972

Benzene and cyclohexane adsorption on Pt–Al_2O_3 samples of optimum platinum contents was investigated, and benzene π-complex formation on the surface was directly observed when these hydrocarbons were in contact with the catalyst. The surface π-complex formed after adsorption on Pt–Al_2O_3 sample had a considerable thermal stability, but reacted readily with hydrogen, and was removed by carbon monoxide subsequently adsorbed on the same sample. The direction of the change of the C–O stretching frequency of the carbon monoxide adsorbed in its linear form served as an indicator of the type of the bonds formed when some other co-adsorbate was present on the same sample. For example, the difference between π- and σ-bonded coadsorbants could be registered in this way.

INTRODUCTION

It is well known that the coordinative interaction of aromatic compounds in transition metal complexes is realized by means of the π-electrons of the hydrocarbon. The formation of a π-complex between aromatic hydrocarbons and metal and metal oxides during the catalytic reactions has been suggested in a number of papers in the field of heterogeneous catalysis (*1–5*); however, the direct evidence obtained by using physical methods was absent until recently.

Infrared spectroscopy has found wide application in the investigation of surface species formed upon adsorption of different gases and vapors onto supported metals. The ir spectrum of benzene adsorbed on a Pt–Al_2O_3 sample was recently observed (*6*). A comparison with the spectra of some bulk coordination compounds enabled the authors (*6*) to obtain direct evidence for π-complex formation.

The presence of definite adsorption bands make it possible to investigate some properties of this complex, such as its thermal stability and behavior during interaction with some other gases and vapors, which is the main purpose of the present study.

As is known from coordination chemistry, it is possible to obtain some arenmetaltricarbonyl complexes by replacing three CO molecules from hexacarbonyls of the respective metal (*7, 8*). The replacing of CO molecules by olefines in arenmetaltricarbonyl complexes has been also observed (*9*). Having in mind these data and the fact that the structures of surface compounds and relevant bulk compounds are similar [for example, benzene and carbon monoxide adsorbed on platinum (*6, 10*) on the one hand, and arene π-complexes and metal carbonyls on the other], it was of interest to study whether the reactions already observed with bulk coordination compounds also take place on the metal surface. For example, removal of preadsorbed benzene from the nickel surface by n-hexene was established recently by means of ir spectroscopy (*11*). The same reactions of mutual replacement of different hydrocarbons are well known in coordination chemistry (*12*).

In the present study, the interaction between carbon monoxide and benzene in an adsorbed layer on alumina-supported platinum was investigated in detail. In this way, information regarding the bonding of the adsorbed compounds with the surface was also obtained, proceeding from the manner of their interaction on the catalyst.

EXPERIMENTAL

The infrared cell, vacuum device, preparation and purification of hydrogen and CO used in the present study have been described elsewhere (*13*, *27*).

The samples were prepared by impregnating γ-Al_2O_3 (Degussa P110C1) with chloroplatinic acid solutions of such concentrations as to give from 2 to 9 wt% platinum after reduction. The powder was dried at 50°C and then pressed into thin pellets, 30 × 15 mm, weighing 200 mg. The reduction time was 6–10 hr, followed by evacuation for 2 hr. The residual pressure reached was 1×10^{-6} Torr.

The hydrocarbons and carbon monoxide were adsorbed at 35°C (the temperature of the sample when placed in the infrared beam).

The careful observation of all experimental conditions in the course of the preparation and treatment of the samples led to reproducible results regarding transmission in the spectral region used in the present work. The intensity of the bands of adsorbed benzene were the same for all samples when maximum coverage was reached.

The following abbreviations are used for the sake of brevity:

$(Pt\text{–}Al_2O_3)_{H_2}$ indicates evacuation of the cell in a stream of hydrogen had been carried out at room temperature after reduction.

Circumstances where evacuation was carried out at 450°C are indicated by lack of parentheses and subscript.

$(Pt/Al_2O_3)_{CO,C_6H_6}$ indicates preadsorption of the sample compounds which are written as a subscript.

HT indicates hydrogen treatment of the preadsorbed sample compounds on the catalyst.

RESULTS AND DISCUSSION

Adsorption of Benzene and Cyclohexane on Pt–Al_2O_3

The experiments carried out with samples containing from 2 to 9 wt% showed that the Pt–Al_2O_3 (9 wt% Pt) samples were the most convenient for the purpose of this investigation. The size of the metal particles for samples containing 3 and 9 wt% Pt was determined by a chromatographic hydrogen–oxygen titration technique according to Kanazirev *et al.* (*14*), and it was found to be same in both cases: 23 Å. The mean particle size increased gradually when the contents of platinum was increased above 9 wt%. This could be used as an indication for preparing the best suited samples: increase in the platinum content within certain limits does not increase the size of the particles and only has as a result the desirable increase of the number of adsorption centers. This in particular means an increase in the intensity of the infrared bands arising from hydrocarbons adsorbed on Pt–Al_2O_3 samples.

The platinum particle size for a Pt–SiO_2 (3 wt% Pt) sample determined by the same method (*14*) was 65 Å. The larger value of the particle size in this case is a possible reason for the low band intensities in the 3000–3100 cm^{-1} region when benzene was adsorbed on Pt–SiO_2 samples (*15*).

In Fig. 1b the spectrum of benzene adsorbed on a Pt–Al_2O_3 (9 wt% Pt) sample is shown. The spectrum observed in this

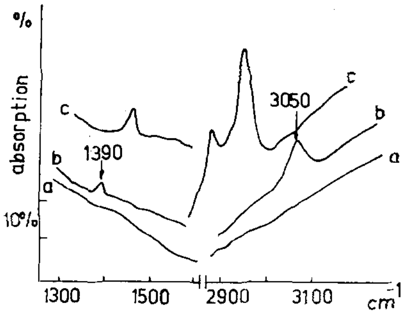


FIG. 1. Infrared spectra of a Pt–Al_2O_3 sample. (a) Background spectrum; (b) benzene added ($P_{C_6H_6}$ = 10 Torr) followed by evacuation to 1×10^{-5} Torr; (c) hydrogen added (P_{H_2} = 100 Torr).

case was explained in a preliminary paper (*6*). The bands depicted in Fig. 1b have considerably higher intensities in comparison with the bands previously observed (*6*).

The experiments carried out by using only samples prepared from a Al_2O_3 support unequivocally demonstrated that the presence of a single band at 3050 cm^{-1} in the ir spectrum of the $(Pt\text{–}Al_2O_3)_{C_6H_6}$ sample is due to the π-complex on the catalyst surface. In the ir spectrum of liquid benzene, there are three bands in the region of the aromatic C–H stretching vibrations: 3050, 3077, and 3099 cm^{-1}. The spectra of physically adsorbed benzene onto a Al_2O_3 pellet at different pressures are shown in Figs. 2b and c. It is seen that the three bands mentioned above could be simultaneously observed in spite of their negligible intensities (Fig. 2c). These bands disappeared immediately after evacuating the cell, hence, there was no benzene chemisorption on the support. The single band in the 3000–3100 cm^{-1} region which is observed for benzene chemisorbed on platinum is characteristic for "sandwich" complexes of transition metals: $Cr(C_6H_6)_2$, 3047 cm^{-1} (*17*); $Mo(C_6H_6)_2$, 3030 cm^{-1} $W(C_6H_6)_2$, 3012 cm^{-1}, $V(C_6H_6)_2$, 3062 cm^{-1} (*18, 19*).

The presence of the 1390-cm^{-1} band in the ir spectrum of the $(Pt\text{–}Al_2O_3)_{C_6H_6}$ sample (Fig. 1b) presents more evidence for π-complex formation on the catalyst surface. The stretching C–C vibration of the benzene ring at 1485 cm^{-1} appears at 1430 cm^{-1} in the $Cr(C_6H_6)_2$ ir spectrum (*17*) and in the spectra of $Mo(C_6H_6)_2$, $W(C_6H_6)_2$, and $V(C_6H_6)_2$ at 1425, 1412, and 1415 cm^{-1} respectively (*18, 19*).

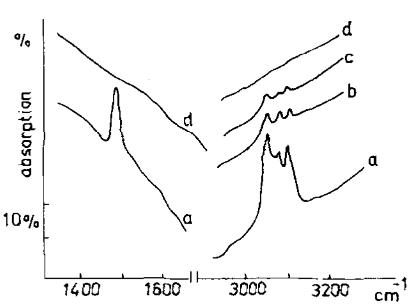


FIG. 2. Infrared spectrum of Al_2O_3 sample together with the gas phase in the cell. (a) After addition of C_6H_6 ($P_{C_6H_6}$ = 0.5 Torr); (b) and (c) after subsequent evacuation of small portions of benzene; (d) immediately after connection of the ir cell with the vacuum pump.

The absence of bands in the ir spectrum when benzene was adsorbed on some other samples (Ni/SiO_2, for example) (*20, 21*) could again be explained with recourse to the ir spectra of coordination compounds. From the spectra presented in the papers of Fritz and coworkers (*18, 19*), it is seen that both the absolute and relative intensities of the bands in the 1300–1500 cm^{-1} regions are different depending on the nature of the central metal atoms. Hence, it is possible that the band intensities are not sufficient to be observed in some cases, even when particle size and the amount of adsorbed benzene are the same for the different samples.

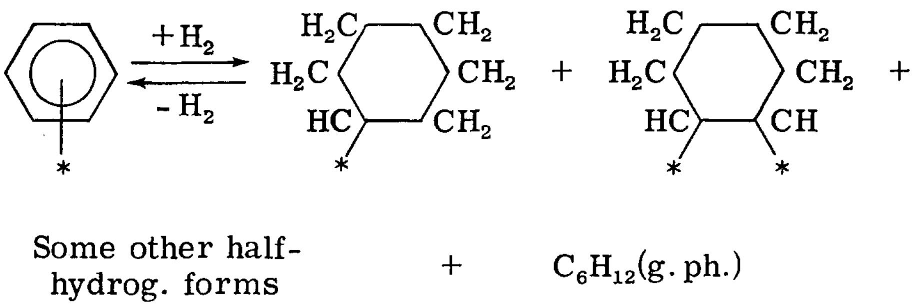
The band at 2270 cm^{-1} appears after C_6D_6 adsorption on $Pt\text{–}Al_2O_3$. The intensity of this band, however, is considerably lower than the intensity of the 3050-cm^{-1} band due to the lower extinction coefficient of the stretching C–D vibration in comparison with that of the stretching C–H vibration. The 2270-cm^{-1} band disappeared rapidly when C_6H_6 was added into the cell containing a $(Pt\text{–}Al_2O_3)_{C_6D_6}$ sample, and a band at 3050 cm^{-1} appeared immediately. This observation may result from simple displacement of adsorbed C_6D_6 by C_6H_6 present in large excess or by rapid H–D exchange between the large amount of light benzene with a small amount of preadsorbed C_6D_6.

The suggestion that cyclohexane is dissociatively adsorbed on supported nickel, platinum, and palladium (*15, 20*) was directly demonstrated by investigation of C_6H_{12} adsorption on $Pt\text{–}Al_2O_3$. In Fig. 3 the spectrum of a $Pt\text{–}Al_2O_3$ after addition of cyclohexane into the infrared cell is shown. The bands characteristic for adsorbed benzene immediately appeared, and their intensities did not change when the contact time between cyclohexane and catalyst was increased or after evacuation of the cell (Fig. 3c), which indicates that the dissociative adsorption of C_6H_{12} proceeds very rapidly and irreversibly.

At the end of this section, some features concerning the interaction between hydrogen and benzene in an adsorbed layer on Pt–Al_2O_3 will be briefly discussed:

a. Absorption bands in the region of the stretching CH_2 and CH_3 vibrations were not observed when benzene was adsorbed on a $(Pt–Al_2O_3)_{H_2}$ sample, i.e., preadsorbed hydrogen does not hydrogenate benzene adsorbing on this sample. Further experiments did show, however, that adsorption of benzene on a hydrogen-covered surface displaces hydrogen into the gas phase without any reaction.

b. After HT of benzene adsorbed on Ni–SiO_2 (under the same experimental conditions as those ones used in the present study), the former was completely hydrogenated, and cyclohexane formed during this treatment passed into the gas phase or remained physically adsorbed on the catalyst (*20, 21*). In the present study, however, it was established that, after the first HT of the $(Pt–Al_2O_3)_{C_6H_6}$ sample at 35°C, only about 40–50% of the preadsorbed benzene was fully hydrogenated. In contrast to Ni–SiO_2, the benzene residue remaining on the Pt–Al_2O_3 catalyst after HT presented half-hydrogenated forms, as in the case of *n*-hydrocarbons (*15, 21*). These half-hydrogenated forms were converted again into chemisorbed benzene after evacuation of the hydrogen and cyclohexane (formed during the HT) from the cell. After a second treatment, the bands at 2850 and 2925 cm^{-1}, characteristic for cyclohexane, appeared again (Fig. 1c), but of lower intensity (about 40–50%) in comparison to the bands already observed after the first HT. Schematically, the procedures described above can be presented in the following manner:



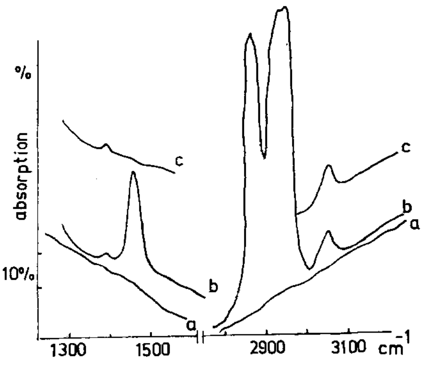


FIG. 3. Infrared spectra of Pt–Al_2O_3 sample together with the gas phase in the cell. (a) Background spectrum of the catalyst sample; (b) cyclohexane added ($P_{C_6H_{12}} = 1$ Torr); (c) after evacuation of the gas phase.

Formation of monoadsorbed half-hydrogenated forms on nickel and the predomination of multiply-bonded forms on platinum is one of the most possible explanations for the difference in the behavior of benzene when $(Ni–SiO_2)_{C_6H_6}$ and $(Pt–Al_2O_3)_{C_6H_6}$ samples were treated with hydrogen (Scheme I). It is reasonable to assume that the rate of desorption of the monoadsorbed half-hydrogenated forms is higher in comparison with the multiply-adsorbed ones.

Thermal Stability of the Surface π-Complex of Adsorbed Benzene

The thermal destruction of the surface π-complex of benzene adsorbed on Pt–Al_2O_3 catalyst took place at comparatively elevated temperatures. In Fig. 4 the intensity of the 3050-cm^{-1} band (which is proportional to the amount of π-complexed adsorbed benzene) as a function of the temperature is shown. The area under the

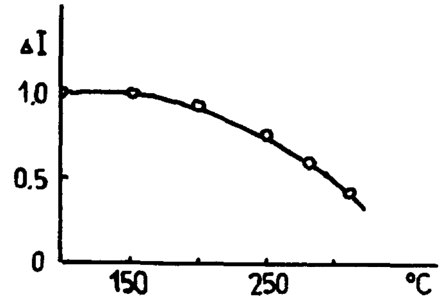


FIG. 4. Intensity of the 3050-cm^{-1} band vs temperature. ΔI is defined by the following ratio: $\Delta I = (I_{10}/I_0)$, where I_0 is the area under the 3050-cm^{-1} band of the $(Pt\text{–}Al_2O_3)_{C_6H_6}$ sample at 35°C; I_{10} is the area under the same band after heating the sample under vacuum at the definite temperature for 10 min.

3050-cm^{-1} peak was used as a measure of the band intensity. A new portion of benzene was adsorbed before heating the $(Pt\text{–}Al_2O_3)_{C_6H_6}$ sample at a definite temperature.

It is seen (Fig. 4) that even at about 150°C the intensity of the 3050-cm^{-1} band was almost unaltered, which gives evidence for the considerable thermal stability of the benzene π-complex formed on the alumina-supported platinum surface. The desorption of benzene was assumed to be the rate-controlling step when cyclohexane was dehydrogenated on supported platinum (*22*). The experiments in the present study showing the considerable stability of the π-complex on the platinum surface are consistent with Kraft and coworkers' (*22*) assumption concerning the rate-controlling step of the above-mentioned reaction. The cyclohexane adsorption proceeds at room temperature (Fig. 3 and above) and obviously with lower activation energy and cannot be regarded as a rate-controlling step of the dehydrogenation.

Benzene Adsorption on $(Pt\text{–}Al_2O_3)_{CO}$ Samples

It is well known from the chemistry of complex compounds that the ir bands of one ligand are usually shifted by the effect of other ligands. In this way, the direction of the C–O stretching vibration may be taken as an indicator of the character of interaction between different coadsorbants and the metal surface.

Figure 5b depicts the spectrum of CO adsorbed on a $Pt\text{–}Al_2O_3$ sample when the surface coverage was about 20–30%. The spectrum shown in Fig. 5c was observed after benzene adsorption onto the same sample. The intensity of the 3050-cm^{-1} band was the same as in the case when C_6H_6 was adsorbed on a bare platinum surface (see, for example, Fig. 5c and Figs. 1b and 3c).

The bands characteristic for adsorbed benzene did not appear after benzene and cyclohexane adsorption on a $(Pt\text{–}Al_2O_3)_{CO}$ sample with which maximum CO coverage was achieved and no carbon monoxide present in the gas phase. According to elementary considerations, it follows that C_6H_6 and CO cannot be adsorbed at the same time on the same metal atom. Thus, it seems likely that the observed shift in CO frequency when benzene is coadsorbed arises from interaction induced through the metal.

Coadsorbed benzene produces shift of the carbon-oxygen frequency that may be predicted from what is known about the adsorption of the two compounds. According to contemporary conceptions, two types of interaction participate in bonding between carbon monoxide and transition metals upon adsorption: donor-acceptor and dative. As-

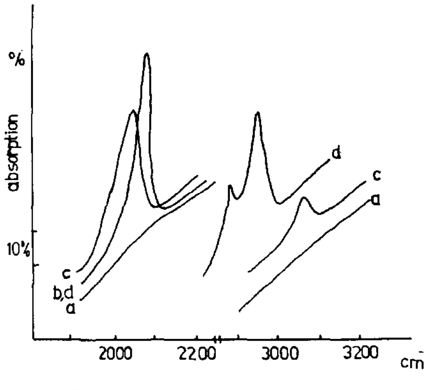


FIG. 5. Infrared spectra of $Pt\text{–}Al_2O_3$ sample. (a) Background spectrum; (b) after adsorption of CO; (c) after addition of C_6H_6 ($P_{C_6H_6} = 1$ Torr) and subsequent evacuation of the gas phase; (d) hydrogen added ($P_{H_2} = 100$ Torr).

suming that the σ-component of the metal-carbon bond is constant, the decrease of the C–O stretching frequency should be caused by the electrons donated from the metal to the CO molecules, since they are entering an antibonding orbital of the carbon monoxide (*23*). Therefore, the shift due to the coadsorption has to be attributed to an increase in the *d*-electron density in the surface metal atoms when benzene is adsorbed on the $(Pt–Al_2O_3)_{CO}$ sample, i.e., benzene is an electron-donating coadsorbate. The donating ability of benzene adsorbed on nickel and platinum has been experimentally established by work function measurements (*24*, *25*).

A decrease of the CO stretching frequency has been observed in $C_6H_6–Cr(CO)_3$ in comparison to $Cr(CO)_6$ and has been explained by a π-donating ability of the benzene ring (*26*). However, it was already mentioned that the coadsorption of CO and C_6H_6 on one and the same platinum atom is impossible, therefore it is reasonable to assume that the interaction on the metal surface was affected by the delocalized *d*-electrons participating in the π-bonding formation during benzene adsorption on the $(Pt–Al_2O_3)_{CO}$ sample.

The band frequency of the stretching CO vibration shifted from 2020 cm^{-1} to 2070 cm^{-1} after HT of the $(Pt–Al_2O_3)_{CO,C_6H_6}$ sample (Fig. 5d), i.e., it nearly reached its normal value for a bare surface: 2075 cm^{-1}. It was recently established that hydrogen does not change the band form and frequency of CO adsorbed on $Pt–Al_2O_3$ in its linear form (*27*)[1]. Consequently, the observed effect of restoration of the frequency of the 2075-cm^{-1} band after HT was not due to hydrogen coadsorption and is connected with the change in the bond between benzene and platinum surface.

The conversion of π-bonded benzene into σ-bonded half-hydrogenated forms appears to account for the disappearance of the effect of coadsorption of C_6H_6 on the CO stretching frequency after HT of the $(Pt–Al_2O_3)_{CO,C_6H_6}$ sample (scheme I). On this assumption, it follows that when a σ-bond is realized on the surface the *d*-electrons which are localized on the individual metal atoms take a participate more in bond formation, and thus the mutual influence through the metal becomes less pronounced.

The frequency of the 2070-cm^{-1} band [recorded after HT of a $(Pt–Al_2O_3)_{CO,C_6H_6}$ sample] decreased again after evacuation of the hydrogen and shifted to 2050 cm^{-1}; thus, it did not achieve the initial decreased value obtained after benzene adsorption on a $(Pt–Al_2O_3)_{CO}$ sample: 2020 cm^{-1}. This observation can be readily explained, having in mind that about 50% of the initial amount of adsorbed benzene was fully hydrogenated to cyclohexane and went into the gas phase after HT of the $(Pt–Al_2O_3)_{CO,C_6H_6}$ sample (see Scheme I and above).

It should be noted that the effects observed in the catalyst-coadsorbed benzene and carbon monoxide/hydrogen system studied in the present work are not in conflict with the existence of a transition between π- and σ-bonds depending on experimental conditions, proposed before by Shopov and Palazov (*21*) for catalyst-adsorbed hydrocarbon/hydrogen systems.

The fact that the 3050-cm^{-1} bands appearing when benzene was adsorbed on bare platinum and also in the case of a surface partially covered with CO (a coverage of about 20–30%) have like intensities shows that benzene was not adsorbed on the entire metal surface and occupied only definite centers. Further work is however necessary to settle the exact value of the area of this "inactive" part. For the time being, it can only be estimated that at least 20–30% of the platinum surface accessible for CO adsorption does not adsorbed benzene.

As could be expected, the shift of the band of the CO stretching vibration was also observed after cyclohexane adsorption on a $(Pt–Al_2O_3)_{CO}$ sample (20–30% coverage with CO), and it had the same value as with coadsorbed benzene.

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[1] It was reported before (*28*) that the frequency of the band of the stretching C–O vibration had decreased about 40 cm^{-1} after hydrogen adsorption on a $(Pt/Al_2O_3)_{CO}$ sample. However, Eischens (*29*) reported recently that the decrease of the frequency of this band was only about 5 cm^{-1}. The reasons for these discrepancies were explained in a previous paper (*27*).

Adsorption of CO on $(Pt\text{–}Al_2O_3)_{C_6H_6}$ Samples

The spectra in Fig. 6 demonstrate the bands observed after addition of different portions of CO onto a $(\text{Pt–Al}_2\text{O}_3)_{\text{C}_6\text{H}_6}$ sample (a maximum coverage with benzene was achieved). It is worth noting that, if the ir spectrum was immediately recorded after the addition of a definite portion of CO, the band of linearly-adsorbed carbon monoxide (2075 cm^{-1}) appeared at 2060 cm^{-1} but after 15 min it was further displaced downwards about 20–30 cm^{-1}. The spectra shown in Fig. 6 were taken 30 min after the addition of definite portions of CO on a $(\text{Pt–Al}_2\text{O}_3)_{\text{C}_6\text{H}_6}$ sample, i.e., when the shift of the band position had stopped. This is an interesting experimental fact which shows that the CO adsorption occurs initially on weaker adsorption sites and subsequently on stronger ones. The latter are ordinary sites made stronger by the presence of preadsorbed benzene. Probably stronger sites become occupied by migration of adsorbed CO molecules rather than by CO molecules coming directly from the gas phase. The relatively large size of the benzene molecules and corresponding steric hindrance makes this explanation acceptable. In addition, the mechanism of benzene displacement from the surface by adsorbed CO molecules is more probable than the interaction between adsorbed benzene and CO from the gas phase.

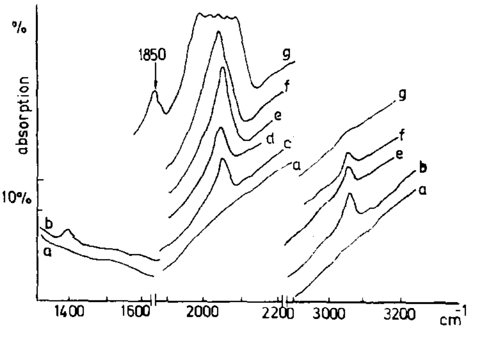

FIG. 6. Infrared spectra of $\text{Pt–Al}_2\text{O}_3$ sample. (a) Background spectrum; (b) after adsorption of C_6H_6; (c), (d), (e), (f), and (g) after subsequent adsorption of small portions of carbon monoxide (spectra were recorded 30 min after CO addition).

The intensity of the 3050-cm^{-1} band, used as an indicator regarding the changes of the coverage of the $(\text{Pt–Al}_2\text{O}_3)_{\text{C}_6\text{H}_6}$ sample with benzene, gradually decreased after adsorption of different CO portions and disappeared when the maximum coverage with CO was achieved, indicating that pre-adsorbed benzene was completely removed. The removal of the preadsorbed benzene is consistent with the π-complex character of benzene adsorption, since this process is much more possible on the provision that there is no previous dissociation of hydrogen atoms upon adsorption. Otherwise, hydrogen atom (or atoms) should be attached to the adsorbed benzene molecule before desorption, which takes place with difficulty when CO is introduced into the cell containing a $(\text{Pt–Al}_2\text{O}_3)_{\text{C}_6\text{H}_6}$ sample.

At the beginning of this paper, we mentioned some examples in which the CO ligands in arenmetalcarbonyls were displaced by benzene or olefines (*7–9*). As was shown above, however, the reverse was true on the platinum surface. Hence, in spite of the existence of a number of similarities between adsorbent–adsorbate bonds and the bonds in bulk coordination compounds, some specific properties of the surface manifest themselves in the catalyst–adsorbate systems.

ACKNOWLEDGMENTS

The author is extremely grateful to Mrs. J. Neinska and Mr. V. Kanazirev for determining the particle size of the catalyst samples used in the present study.

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