An Infrared Spectroscopic Study of the Hydrogenation and Dehydrogenation of the Complexes of Aromatic Compounds and of Fullerene C_{60} with Silica-Supported Platinum

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An infrared spectroscopic study has been made of the surface complexes from the chemisorption of the aromatic compounds benzene, toluene, para-xylene (1,4-dimethylbenzene), mesitylene (1,3,5-trimethylbenzene), naphthalene, and anthracene, and also of fullerene C_{60}, on silica-supported platinum catalysts, and of their subsequent hydrogenation and dehydrogenation reactions. The complexes of the initial adsorbates with platinum can be hydrogenated under relatively low pressures of hydrogen (<1 atm) and then dehydrogenated to considerable degrees by evacuation even at ambient temperatures.

In the case of benzene the hydrogenated cyclohexane-like complex gives very extensive reversion to adsorbed benzene on evacuation. The surface complexes gradually diminish in amount during successive cycles of hydrogenation and dehydrogenation, with the generation of gas-phase cyclohexane. For the other compounds, except for C_{60}, the hydrogenation is also virtually (or actually) complete but the dehydrogenation is only partial and the surface complexes remain present during multiple cycles of hydrogenation and dehydrogenation. The room temperature spectra from the methyl-substituted benzenes under vacuum support chemisorption via methyl-group dissociation. For naphthalene and anthracene the spectra of stable partially dehydrogenated species are consistent with the rearomatization of only one end ring. For fullerene C_{60} the spectrum of the hydrogenated species suggests that a five-membered ring is in selective contact with the surface but that some adjacent six-membered rings are also hydrogenated. The hydrogenation and dehydrogenation processes are both slow but the rates, together with the extent of hydrogenation, increase with temperature. The hydrogenated spectra of the fullerene-based complex differ from those reported earlier for $C_{60}H_{18}$ and $C_{60}H_{36}$. © 2002 Elsevier Science (USA)

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INTRODUCTION

The study of the hydrogenation and dehydrogenation mechanisms of hydrocarbons on oxide-supported metals is of interest from fundamental and practical points of view. We record here infrared spectroscopic results from the initially adsorbed complexes, and after their hydrogenation and dehydrogenation reactions, from a range of aromatic molecules, including fullerene C_{60}, on silica-supported platinum.

Infrared spectroscopy has been the most widely used method of investigation of adsorbed species on finely divided surfaces. The results for hydrocarbons adsorbed on oxide-supported metals, and on their single-crystal-surface counterparts, have been reviewed recently (1, 2). There is however a lack of detailed published work on aromatic adsorbates. The chemisorption of benzene on Pt was investigated for the first time in (3). Follow-up studies of toluene, para-xylene (1,4-dimethylbenzene), and mesitylene (1,3,5-trimethylbenzene) were made in 1967 but have been only partially published [see Ref. 358 of (2)]. The more detailed results are published here together with recent results from the adsorption of the polynuclear aromatic molecules naphthalene and anthracene and of fullerene, C_{60}.

Following its prediction in 1970 (4) and discovery in 1985 (5) methods have been worked out for the macroscopic-scale production of fullerenes (6). Since then their derivatization, including hydrogenation, has become a wide field of investigation (7). The hydrogenation and dehydrogenation of fullerenes has been investigated using different chemical (8–13) and catalytic (14) methods. It was shown that C_{60} could be hydrogenated and dehydrogenated reversibly and envisaged that hydrogenated fullerene could be used for hydrogen storage (15). Catalytic methods make it possible to reduce the pressure and the temperature of the hydrogenation reaction. Hence the investigation of the mechanism of fullerene hydrogenation on adsorbent-supported metal catalysts is of great interest.

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EXPERIMENTAL

As adsorbents for the support of Pt particles the highly dispersed silicas Cab–O–Sil or Aerosil have been used for spectroscopic investigations.

For the investigation of benzene, toluene, p-xylene, and mesitylene complexes the silica-supported platinum sample was prepared by mixing 2.2429 g of Cab–O–Sil in 20 cm^3 of distilled water and 10 cm^3 of water containing 1.0354 g of $H_2PtCl_6 \, nH_2O$. The chloroplatinic acid contained about 40 wt% Pt. After stirring and the evaporation of water the sample after reduction contained ca. 16 wt% Pt. The disk, about 2.5 cm in diameter, was prepared by the compression of 0.11 g of silica plus hexachloroplatinic acid at 640 kg/cm^2. Before compressing the sample was dried at ca. 373 K in air. The disk was evacuated at ambient temperature and then at higher temperatures (gradually increasing to ca. 573 K). The color of the sample changed from yellow to black near 573 K.

The reduction of the sample was made under stationary conditions. To the evacuated sample after cooling hydrogen was added at 400 torr. Then the temperature was increased gradually up to ca. 573 K. After 20–30 min the sample was evacuated and a new portion of hydrogen was added under ~400 torr. This operation was repeated several times for 4–5 h. After reduction the sample was cooled under ~400 torr of hydrogen.

The hydrogen used was purified from traces of oxygen by passing the gas though a deoxo catalytic purifier and dried by $Mg(ClO_4)_2$ and P_2O_5 and liquid nitrogen traps. The spectra were registered with a Grubb Parsons GS2 double-beam infrared spectrometer in vacuum-tight cells with KBr windows.

For the investigation of naphthalene, anthracene, and fullerene C_{60}, the silica-supported Pt sample was prepared by mixing 1.875 g of Aerosil in 20 cm^3 of distilled water and 10 cm^3 of water containing 0.895 g of $H_2PtCl_6 \, nH_2O$. The disk, about 1 cm in diameter, was prepared by compressing 0.012 g of silica with hexachloroplatinic acid at about 600 kg/cm^2. The reduction of the sample was made after evacuation, first at ambient temperature and then at gradually increasing temperature up to 573 K, starting at 423 K under 60–100 torr and at 573 K under 400–700 torr of hydrogen.

Hydrogen from a hydrogen generator (Hewlett–Packard) was used without any purification. For registration of the spectra a Jasko FT-IR Spectrometer Model 610 was used together with a vacuum cell with quartz windows (16), which gave transmission down to 2000 cm^{-1}.

Pure samples of benzene, toluene, and p-xylene were received from the National Physical Laboratory. Mesitylene was a normal commercial sample but was distilled and fractionated at 437–438 K before being used. Naphthalene, anthracene, and carbon tetrachloride of commercial grades were used without additional purification. Fullerene C_{60} was purified by sublimation at 773 K in vacuum to remove traces of the toluene solvent.

The chemisorbed layers of benzene, toluene, p-xylene, and mesitylene on the surface of the platinum particles were produced by adsorption under 40, 15, 5, and 1.5 torr of the corresponding hydrocarbon vapor in the vacuum cell.

The chemisorbed layers of fullerene C_{60}, naphthalene, and anthracene were formed by adsorption from solutions in carbon tetrachloride. The solubility of C_{60} in CCl_4 is small (17), but it is enough to produce a chemisorbed layer of C_{60} for spectroscopic investigations. The pellets of the catalyst sample, after reduction by hydrogen and evacuation at ambient temperature, were placed for 24 h in these solutions. After washing by pure carbon tetrachloride the pellet was transferred to the optical vacuum cell for spectroscopic investigation.

The effect of carbon tetrachloride as solvent on chemisorption of polyaromatic hydrocarbons and fullerene C_{60} from solution on silica-supported Pt at ambient temperature (about 300 K) is so small that it was not possible to detect it and the concentration of chemisorbed polyaromatic hydrocarbons and C_{60} on the surface of Pt particles was enough for FT-IR spectroscopic measurements. However, at higher temperature (about 400 K) during hydrodechlorination of carbon tetrachloride by the Pt catalyst on the surface of Pt particles a surface Pt(II) species with Cl ligands appeared (18, 19).

RESULTS

Figure 1 gives an example of the results of a typical full range of spectroscopic measurements made for an adsorbed hydrocarbon, in this case benzene. Spectrum 1 is of the Pt/SiO$_2$ catalyst taken after its reduction in 400 torr of hydrogen at 573 K followed by cooling, and spectrum 2 is after evacuation at ambient temperatures. Spectrum 3 is taken after the introduction of 40 torr of benzene. It is seen that the characteristic absorption band of free silanol groups at 3750 cm^{-1} has been reduced in intensity and replaced by an additional broad absorption band, centered at ca. 3600 cm^{-1}, generated through hydrogen bonding of the OH group with the π electrons of the aromatic molecule. The strong and sharp absorptions at 3094, 3075, and 3038 cm^{-1} have wavenumbers and relative intensities closely similar to those of liquid benzene and are from benzene for the most part physically adsorbed on the surface of the silica support. The much weaker bands in the 3000- to 2800- cm^{-1} region are from a trace of cyclohexane in the gas phase resulting from hydrogenation by residual hydrogen in the Pt catalyst.

After evacuation at ambient temperature (spectrum 4) the strong bands from physical adsorption are removed and the silanol absorptions are thereby restored to their original profile. All that remains from the chemisorbed benzene on the Pt surface is a weak and broad absorption band at ca.
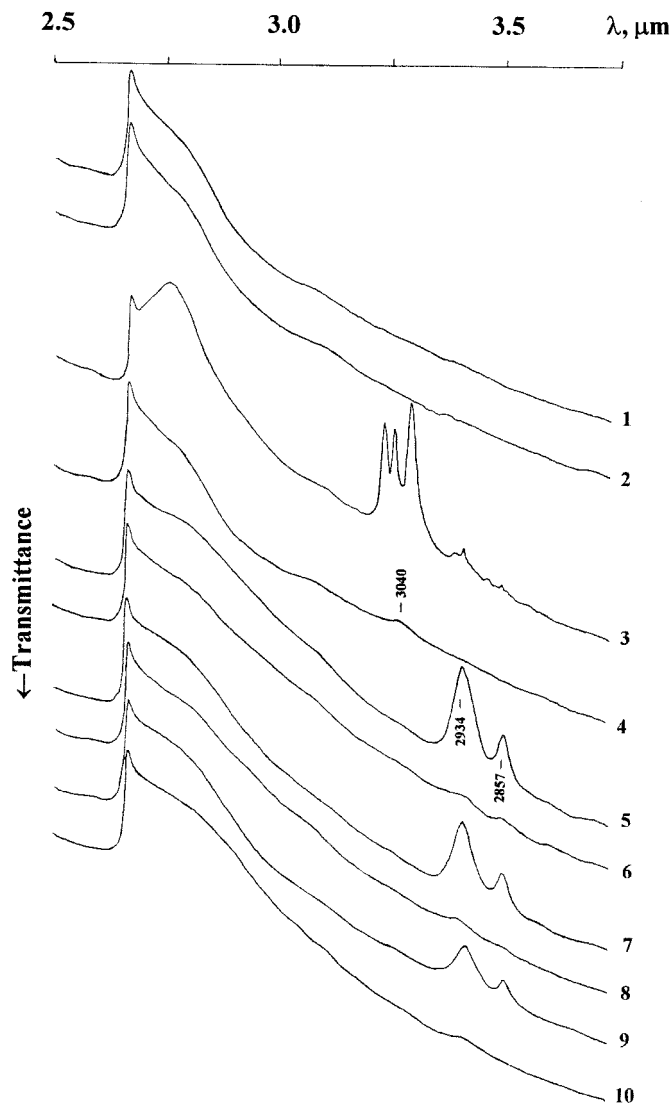
FIG. 1. Infrared spectra of silica-supported Pt after reduction at 573 K under 400 torr of H_2 and cooling up to ambient temperature (spectrum 1), after evacuation of hydrogen at ambient temperature (spectrum 2); after adsorption of benzene (spectrum 3) and evacuation at ambient temperature (spectrum 4), after hydrogenation of chemisorbed benzene on Pt at 293 K in gas phase under 400 torr of H_2 (spectra 5, 7, 9), and after dehydrogenation by evacuation at 293 K (spectra 6, 8, 10).

3040 cm^{-1} from CH bonds of the aromatic ring. Spectrum 5 was taken after filling the cell with 400 torr of hydrogen when the aromatic absorption was removed and replaced by absorptions at 2934 and 2857 cm^{-1}, characteristic of a CH_2-rich surface species. Reevacuation (spectrum 6) leads to weak residual absorption bands at ca. 2930 and 2860 cm^{-1} and a regrowth of the 3040-cm^{-1} aromatic absorption band (see later discussion). Repeated cycles of hydrogenation and dehydrogenation (spectrum pairs 7 and 8, 9 and 10) lead to a gradual reduction of intensities in the spectra as the adsorbate is slowly removed, presumably as gas-phase cyclohexane.

For the other hydrocarbons studied only the principal absorption bands, corresponding to the hydrocarbon absorption bands of spectra 4–6 of Fig. 1, are shown as figures at appropriate places under Discussion, with the positions of the absorption bands listed at the side (see Figs. 5, 6 and 9). Except for the cases of benzene, toluene, and C_{60}, there were negligible reductions of spectral intensities during repeated cycles of hydrogenation and dehydrogenation.

DISCUSSION

In terms of determining the structures of the species present after the chemisorption of hydrocarbons on metals, it is now well established that the experimental spectroscopic results from adsorption on metal single-crystal surfaces are of great help in interpreting the more complex spectra obtained from adsorption on oxide-supported metal catalysts (1, 2). This is particularly the case for chemisorption on (111) single-crystal surfaces and on the relatively abundant (111) facets on metal particles. In interpreting the present spectra use is also made of comparisons with the spectra from relevant species on Pt single-crystal surfaces, including their involvement in dehydrogenation or hydrogenation processes. Such spectra are obtained either by vibrational high-resolution electron energy loss spectroscopy (HREELS), by reflection–absorption infrared spectroscopy (RAIRS or IRRAS), where the resolution is higher or, more recently, by sum frequency generation (SFG).

Benzene

The spectrum from the chemisorbed species from benzene adsorbed on Pt/SiO_2, illustrated in Fig. 1, spectrum 4, shows only a single broad and weak absorption near 3040 cm^{-1}, from aromatic vCH bond-stretching modes. It should be recalled that such modes are expected to be very weak because the undissociated benzene C_6 skeleton lies flat on the surface of most metals, including Pt(111) (2). The metal-surface selection rule (MSSR) as applied to infrared and to the principal features in on-specular electron energy loss spectra only allows the observation of those vibrational modes with dipole changes that are perpendicular to the surface (20, 21). It has been shown that the same considerations are qualitatively important in interpreting the spectra from species on larger metal particles (22). Aromatic vCH absorptions for flat-lying rings therefore principally acquire intensity due to polarization of the molecule resulting from π bonding to the surface, leading to a slight out-of-plane distortion of the CH groups from parallelism to the surface.

After addition of gas-phase hydrogen two strong absorptions bands, at 2934 and 2857 cm^{-1}, are present (Fig. 1, spectrum 5), clearly from the presence of CH_2 groups such as occur in a cyclohexane ring, together with a vPtH

absorption (not illustrated) at 2130 cm^{-1}. A proportion of the hydrogenated benzene appears in the gas phase as cyclohexane; the rest remains more strongly linked to the surface, as is shown by the very slow decrease of intensities from the adsorbed species during subequent dehydrogenation and then rehydrogenation cycles (Fig. 1, spectra 6–9).

Dehydrogenation of the CH$_2$-rich adsorbed species by prolonged evacuation (Fig. 1, spectrum 6) leads to weak residual absorptions near the same positions, together with the reemergence of a weaker form of the 3040-cm^{-1} absorption band from adsorbed benzene. The latter, as studied by Takenaka and co-workers, is more clearly shown in Ref. (3), where intermediate stages were studied and compensation was carried out for the sloping backgrounds; these spectra are conveniently reproduced as Fig. 10 of Ref. (2). The residuals after dehydrogenation, which recur with gradually reduced intensities during repeated dehydrogenation and then rehydrogenation cycles, show that full dehydrogenation is a slow process at room temperature.

Haaland earlier made a somewhat similar study at room temperature on Pt/Al$_2$O$_3$, but starting with adsorbed cyclohexane rather than benzene (23). Similar cyclohexane-like spectra were obtained after rehydrogenation, which also only slowly decreased in intensity during dehydrogenation/rehydrogenation cycles. As no absorptions were recorded during the dehydrogenation cycles (equivalent to Fig. 1, spectra 6, 8, and 10) it was considered that the retained species was a C$_6$ cyclic carbonaceous species. After the evacuation of hydrogen in our and Takenaka and co-worker's spectra two weak absorptions bands, near 2940 and 2850 cm^{-1}, are retained from residual CH$_2$ groups but the removal of the major fraction of intensity from the CH$_2$ groups is accompanied clearly by the regrowth of the, necessarily weak, aromatic vCH absorptions.

The impression is that each hydrogenated species which dehydrogenates to adsorbed benzene does so completely once the process has commenced. An earlier study by Takenaka showed that the dehydrogenation process was slow and took on the order of an hour under evacuation. He also showed that in the continued presence of hydrogen gas the CH$_2$-rich species was stable to about 500 K but regenerated on cooling to room temperature (24). In view of this temperature stability of the CH$_2$-dominated species, and of its substantial recovery on the readmission of hydrogen after a period of prolonged pumping, it seems probable that it is bonded to the surface either as a cyclohexyl or, at most from the simplicity of the spectrum, as a 1,2-substituted cyclohexane group, i.e., adsorbed cyclohexene. However the latter seems to be ruled out by the fact that at 295 K, cyclohexene on Pt(111) in the presence of 100 torr of gas-phase hydrogen, as studied by SFG (25), gives a much more complex spectrum than Fig. 1, spectrum 5.

A cyclohexyl group could be attached to the surface through an axial or equatorial C–Pt bond with respect to the cyclohexane ring; steric considerations suggest that equa-

torial bonding is more likely, with the cyclohexyl ring orientated at a considerable angle with respect to the metal surface. This could account for the absence in the spectra of the very broad "soft-mode" absorption bands in the region of 2700–2600 cm^{-1} that occur at low temperatures from undissociated cyclohexane on Pt(111) (26, 27). Such absorptions are interpreted as arising from a substantial hydrogen-bonding-type interaction between axial CH bonds of the molecule and the metal surface. The residual species after prolonged pumping may be associated with a minor fraction of bonding sites, such as at edges or corners of the crystallites, or on (100) rather than (111) facets, where dehydrogenation of cyclohexyl is more difficult because adjacent metal sites are less accessible for the transferred adsorption of hydrogen atoms. Repeated rehydrogenation/dehydrogenation cycles lead at room temperature to the gradual loss of the hydrogenated chemisorbed species, presumably as cyclohexane.

In (28–33) adsorption and desorption of cyclic hydrocarbons on Pt metal crystal were investigated by a combination of different methods, including thermal desorption mass spectrometry (TDS) and HREELS, for an understanding of the mechanisms of a hydrocarbon conversion reaction on Pt catalysts. Adsorbed cyclic hydrocarbons easily desorb from the surface of Pt crystal on heating to about 220–230 K, which means the desorption of physically adsorbed molecules. At higher temperature there are drastic changes in HREELS spectra, showing the formation of chemisorbed complexes with Pt, which at higher temperatures (above 300 K) are destroyed, and benzene as a dehydrogenation product evolves. If stopped at about 300 K, it is probable that on the surface of the Pt crystal complexes will exist which can gain and lose hydrogen, as was demonstrated in Fig. 1, and also in (23).

Toluene

Avery studied the adsorption of toluene on Pt(111) at 350 K using HREELS and concluded that its spectrum, in the vCH region of a medium absorption band at 3010 and a weaker companion at 2940 cm^{-1}, could be interpreted in terms of σ bonding to the surface via methyl-group dissociation to give a surface benzyl group (34). The latter conclusion was supported by thermal desorption measurements which showed that at that temperature one hydrogen per adsorbed toluene molecule had been lost on adsorption. Earlier work with HREEL spectra, which lacked the thermal desorption data, had assumed the presence of intact methyl groups (35, 36). Avery also postulated additional π bonding of the adsorbed species to the surface via the phenyl group. This conclusion was based, in conjunction with the MSSR, on the strong out-of-plane CH absorptions of the aromatic ring, implying that the latter is approximately parallel to the surface. The weak spectrum of the chemisorbed species on Pt/SiO$_2$ (Fig. 2a) agrees well with
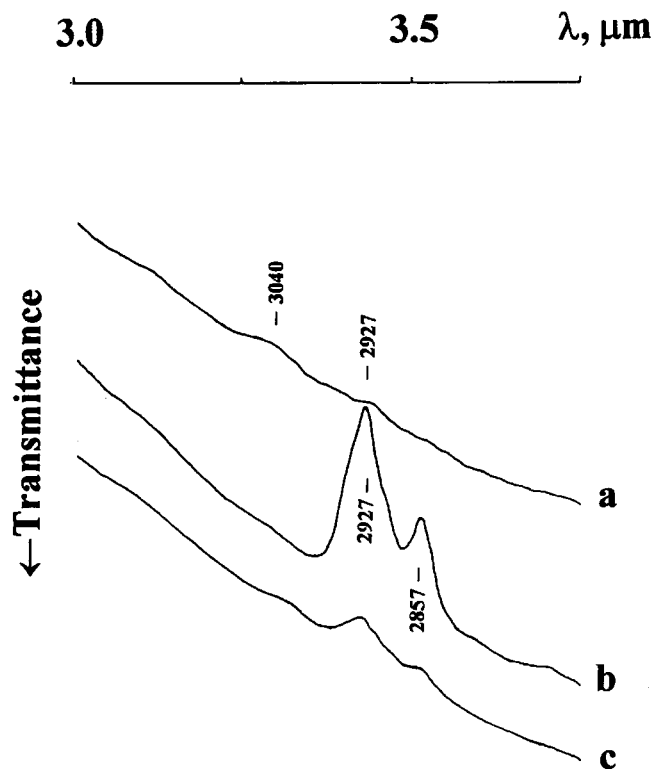
FIG. 2. Infrared spectra of silica-supported Pt–toluene complexes (a) before, (b) after hydrogenation of chemisorbed toluene on Pt at 293 K in gas phase under 400 torr of H_2, and (c) after dehydrogenation by evacuation at 293 K.

the HREEL spectrum, with the aromatic vCH absorption band at 3040, and with the vCH_2 symmetric absorption band at ca. 2927 cm^{-1}, with the latter probably being in Fermi resonance with a $2\delta CH_2$ overtone at ca. 2850 cm^{-1}. The vCH_2 asymmetric mode would have its dipole change approximately parallel to the surface and is therefore not observed. The value of 2927 cm^{-1} is too low to correspond to the MSSR-allowed out-of-plane component of the vCH_3 asymmetric mode that should dominate the vCH region from an intact toluene molecule adsorbed parallel to the surface.

Hydrogenation (Fig. 2b) leads to a spectrum similar to that obtained from benzene hydrogenation, with strong absorption bands at 2927 and 2857 cm^{-1} but with additional shoulders at ca. 2945 and ca. 2900 cm^{-1}. The first and stronger of the shoulders is probably from the vCH_2 symmetric mode from the CH_2 group bonded to metal and the cyclohexyl ring; the second weak one could be from the lone CH group of the cyclohexyl ring attached to carbon. Although the 2945-cm^{-1} band could alternatively be from a methyl group (see the case of mesitylene, discussed below) the slow reduction in the intensity of the spectrum with pumping is consistent with a rehydrogenated species bonded to the surface (but see later discussion).

The spectrum after dehydrogenation by evacuation (Fig. 2c) shows a partial regrowth of the aromatic vCH

absorption at 3040 cm^{-1} together with residuals of the aliphatic absorptions at the slightly different positions of 2934 and 2864 cm^{-1}. As postulated in the benzene case, this suggests slightly different adsorption sites for the residual hydrogenated species. Also, again as in the benzene case, the hydrogenated species are only very slowly removed from the surface (presumably as gas-phase methylcyclohexane) during repeated dehydrogenation/rehydrogenation cycles.

Para-Xylene (1,4-Dimethyl Benzene)

The initially chemisorbed species on metal particles (Fig. 3a) once again gives a weak spectrum, with absorption bands at 3040, 2948, 2920, and 2874 cm^{-1}. The 3040-, 2920-, and 2874-cm^{-1} absorptions correspond to similar absorptions in the toluene case and indicate bonding to the surface through dissociation of at least one methyl group. On the basis of thermal desorption measurements Wilk et al. concluded that para-xylene on Pt(111) had lost two hydrogen atoms at the somewhat higher temperature of 370 K and hence that the chemisorbed species was bonded to the surface via dissociation of both CH_3 groups (37). Unfortunately their vCH HREEL spectrum was poorly resolved. The 2948-cm^{-1} band could be from the vCH_3 asymmetric absorption of a proportion of still-intact methyl groups, as
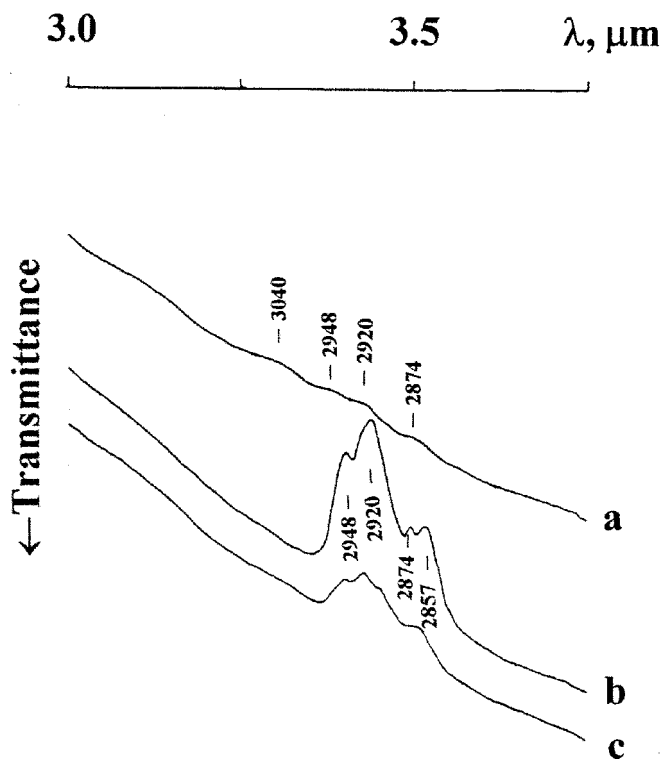

FIG. 3. Infrared spectra of silica-supported Pt–p-xylene complexes (a) before, (b) after hydrogenation of chemisorbed p-xylene on Pt at 293 K in gas phase under 400 torr of H_2, and (c) after dehydrogenation by evacuation at 293 K.

discussed in the case of toluene. With the benzene ring parallel to the surface the component of the otherwise doubly degenerate vCH_3 asymmetric mode that is perpendicular to the surface should be strongly allowed by the MSSR. The vCH_3 symmetric mode of a methyl group attached to an aromatic ring, expected near 2930 cm^{-1} (38, 39), should at the best be very weak on this criterion.

After hydrogenation (Fig. 3b) there is less ambiguity in spectral interpretation, as the bands at 2948 and 2874 cm^{-1}, which are additional to the vCH_2 modes from the rest of the cyclohexane ring at 2920 and 2857 cm^{-1}, are as expected from the vCH_3 asymmetric and symmetric modes, respectively, of a methyl-substituted cyclohexyl group at an angle to the metal surface. It seems probable that, as assumed in the toluene case, the hydrogenated species remains bonded to the surface by dissociation of one of the initial CH_3 groups of para-xylene.

After pumping the residuals are more substantial in this case, again with a similar profile but slightly different positions (2955, 2934, 2914, and 2860 cm^{-1}) with respect to the spectrum of the fully hydrogenated species (Fig. 3c). Any corresponding aromatic vCH absorption is very weak. This time there is little or no reduction in intensities during successive rehydrogenation/dehydrogenation cycles.

Mesitylene (1,3,5-Trimethyl Benzene)

After evacuation to reveal the spectrum of the species chemisorbed on Pt the spectrum (Fig. 4a) shows absorptions at 3040, 2971, 2927, and 2870 cm^{-1}, with the 2971-cm^{-1} band, clearly from an undissociated methyl group, attached to the aromatic ring. It seems that bonding by dissociation of one methyl group leaves those in *meta* substitution in positions that are difficult for bonding to the surface by further methyl dissociation.

Hydrogenation of the chemisorbed aromatic species leads (Fig. 4b) once again to a strong spectrum with absorptions at 2950, 2934, and 2913 cm^{-1}, plus a tail of overlapping absorptions down to near 2800 cm^{-1}, and is consistent with expectation for a 1,3,5-trimethylcyclohexyl group bound to the surface by dissociation of one CH_3 group. The strong and sharp absorption at 2950 cm^{-1} is clearly from the methyl groups attached to the cyclic aliphatic ring and, as expected, it is stronger than in the analogous spectrum derived from para-xylene. The principal 2934- and 2913-cm^{-1} absorption bands are from CH_2 groups and the poorly resolved region below 2900 is as expected from aliphatic CH, CH_3, and CH_2 groups, in that order (38, 39). Considerable residual absorption bands at 2963, 2934, and ca. 2860 cm^{-1} are retained after pumping (Fig. 4c), together possibly with a weak 3040-cm^{-1} aromatic vCH absorption band.

Naphthalene

The initial spectrum, derived from the chemisorption of naphthalene from carbon tetrachloride solution at ambient
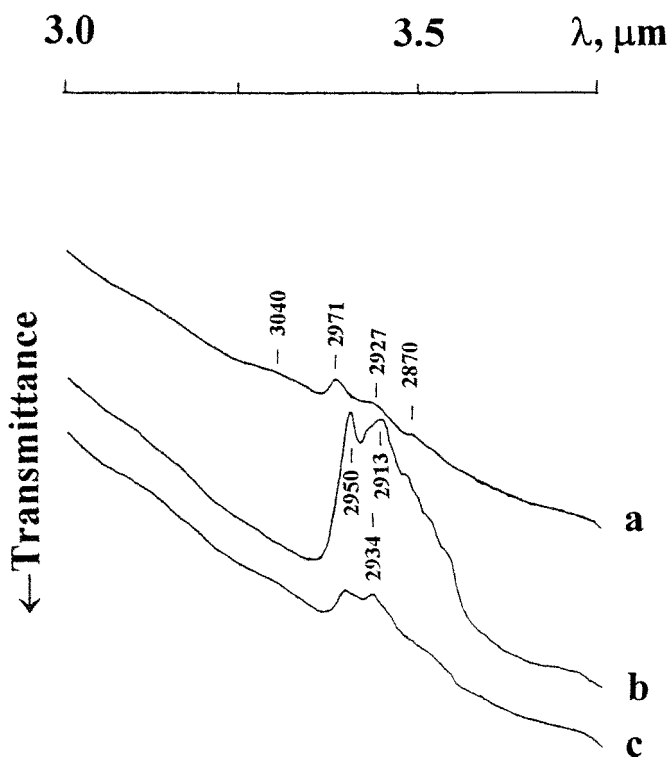

FIG. 4. Infrared spectra of silica-supported Pt–mesitylene complexes (a) before, (b) after hydrogenation of mesitylene chemisorbed on Pt at 293 K in gas phase under 400 torr of H$_2$, and (c) after dehydrogenation by evacuation at 293 K.

temperature followed by evacuation, is shown in Fig. 5a. There are two absorption bands, at 3077 and 3057 cm^{-1}, from aromatic vCH absorptions. The additional very weak bands at 2977, 2932, and 2862 cm^{-1} are probably from a trace of hydrogenation originating in residual hydrogen on the Pt catalyst.

On hydrogenation, carried out with 600 torr of hydrogen for 30 min at 323 K, with the latter temperature being chosen to accelerate the process, once again a CH_2-rich spectrum is obtained (Fig. 5b). On dehydrogenation, by evacuation for 30 min at the same temperature, substantially weakened CH_2 absorptions are left with somewhat different profiles and the reemergence of the 3071-cm^{-1} band can be clearly seen (Fig. 5c).

Comparison of the spectra of Figs. 5b and 5c with analogous spectrum pairs from the substituted benzenes shows a number of differences. The after-dehydrogenation spectrum for the naphthalene case is both relatively stronger and more altered in profile with respect to the hydrogenated spectrum than is the case for benzene and its methyl-substituted derivatives. These differences are most probably related to the consideration that naphthalene has two aromatic rings, with the possibility that only one of these is restored to aromatic status on dehydrogenation. If, as seems probable, during hydrogenation the hydrogen
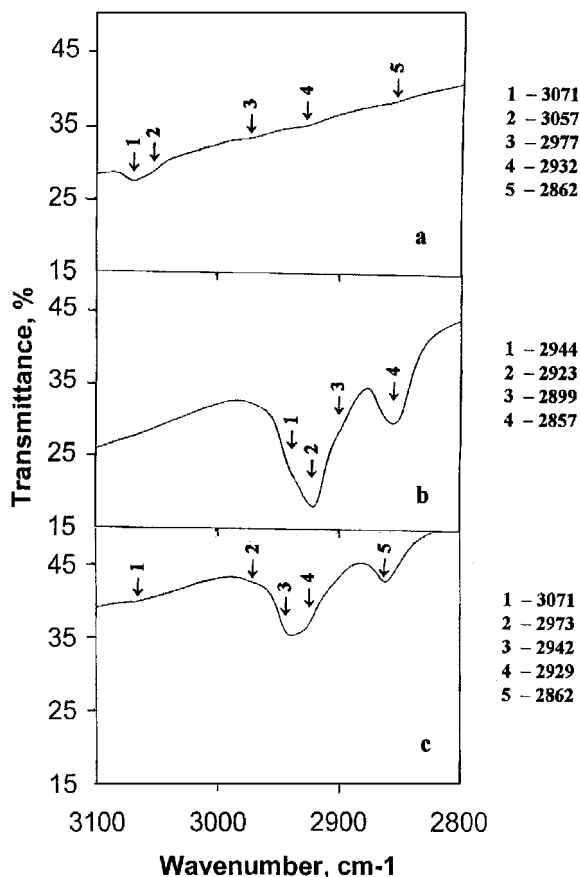
FIG. 5. Infrared spectra of silica-supported Pt–naphthalene complexes (a) before, (b) after hydrogenation of at 323 K in gas phase under 750 torr of H_2 for 30 min, and (c) after dehydrogenation by evacuation at 323 K for 30 min.

atoms add to the same side of the flat-lying naphthalene molecule, then the *cis*-decalin (or *cis*-decalin-like) product so formed would have the two mean planes of the saturated C_6 rings oriented at a considerable angle with respect to each other. The observed spectral profile after hydrogenation is closely similar to that of *cis*-decalin and agrees somewhat better with the *cis* than *trans* form as the possible product (40). In the *cis*-decalin case possibly only one of the C_6 rings, that with the more parallel orientation with respect to the surface, could dehydrogenate to form an aromatic ring, causing the second ring, with a pair of CH_2 groups forced away from the surface for steric reasons, to resist dehydrogenation. Such a situation provides a reasonable interpretation of Fig. 5c on the grounds of a ring-strain explanation of the higher-than-normal 2942-cm^{-1} value of the absorption band from the remaining CH_2 groups. On this picture the simplifying assumption that all the saturated CH bonds absorb with equal intensity leads to the expected ratio of integrated intensities for the aliphatic absorptions after and before dehydrogenation of 8/18, i.e., 0.44. This compares reasonably with the measured ratio of 0.38 ob-

tained by weighing the cutout paper spectra recorded in absorbance.

Anthracene

The set of Figs. 6a–c is analogous to that from naphthalene, although the spectra were obtained under the slightly different experimental conditions of 373 K for the hydrogenation and dehydrogenations to speed up the processes, and hydrogenation was in 700 torr of hydrogen. In Fig. 6a the prominent 3077- and 3032-cm^{-1} absorption peaks are clearly from vCH modes from aromatic rings, with the weak 2982-, 2937-, and 2861-cm^{-1} peaks again attributable to residual hydrogenation on the Pt catalyst. Figure 6b has a profile such as would be expected from a CH_2-rich completely hydrogenated product. The quite strong spectrum obtained after dehydrogenation (Fig. 6c) has a profile similar to that in the naphthalene case, suggesting that dehydrogenation has been confined to one or two aromatic rings. A considerable degree of restoration of aromatic character is shown by the 3074-cm^{-1} absorption. Possibilities for partial dehydrogenation are that one end ring (as with naphthalene), one middle ring, two adjacent rings, or two end rings
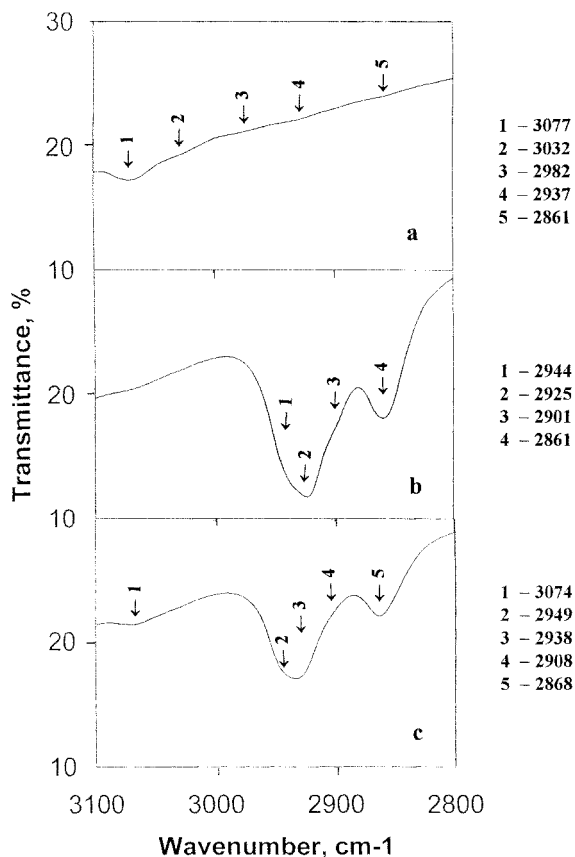

FIG. 6. Infrared spectra of silica-supported Pt–anthracene complexes (a) before, (b) after hydrogenation at 373 K in gas phase under 750 torr of H_2 for 30 min, and (c) after dehydrogenation by evacuation at 373 K for 30 min.

are aromatized. In comparison with a fully hydrogenated species with 24 aliphatic CH bonds, these various possibilities would retain respectively 14, 16, 8, and 4 such CH bonds, with predicted ratios for the integrated intensities of dehydrogenation/hydrogenation of 0.58, 0.67, 0.33, and 0.17. The measured ratio is 0.50, favoring one end-ring aromatization, as was the case for naphthalene, and for which a similar explanation can be envisaged. Once again the *in situ* hydrogenation and dehydrogenation process does not lead to appreciable intensity losses after repeated reaction cycles.

An Alternative Scenario

Implicit in the above spectral interpretations has been the fact that the extremely slow removal of the hydrogenated species on pumping implies that the saturated cycloalkane species are chemisorbed through residual carbon–metal bonds to the platinum surface rather than physisorbed. However in all cases the spectra of these species are consistent with the presence of fully hydrogenated products. There is a possible alternative explanation for the lack of removal of fully hydrogenated cycloalkanes from the catalyst.

The diffusion of larger molecules through the pores of a catalyst disk is a slow process. It is known that by 290 K hydrogen chemisorbed on platinum is driven off into the gas phase under vacuum (41). This hydrogen will be pumped out more rapidly than the hydrocarbons, leaving bare platinum particles, which at this temperature are capable of dehydrogenating the cycloalkanes to the corresponding aromatic or semiaromatic products (42). If even the first steps of the latter multistep processes are competitive in speed with the diffusion of fully hydrogenated cycloalkanes, in effect the latter species would remain trapped within the catalyst. The lack of "soft-mode" hydrogen-bonding-like vCH absorptions from the six-membered alkane rings, which in the absence of σ bonding will presumably lie flat on the platinum surface, could under these conditions be attributed to the absence of such an interaction with a platinum surface that is also hydrogen covered by contact with the gas-phase hydrogen; the single-crystal studies where soft-mode absorptions are observed are all carried out on hydrogen-free surfaces in ultra-high vacuum.

In the case of Haaland's study (23), where the fully hydrogenated species would be cyclohexane, his use of alumina as the support enabled the spectrum to be measured down to 1100 cm^{-1} and its simplicity in this region also would be entirely consistent with cyclohexane as the adsorbent. A better distinction between the possibilities of cyclohexane or the less symmetrical cyclohexyl group could be made with Pt(111) if RAIRS were used to cover the complete vibrational range. Unlike HREELS, which requires high vacuum conditions, RAIRS is a technique which can be carried out in the presence of a gas phase such as hydrogen. Equally it could be used to check whether in fact soft-mode absorptions are absent when cyclohexane

is adsorbed on hydrogen-covered Pt(111). For an oxide-supported platinum catalyst an alternative test would be to carry out the pumping well below room temperature, where the reductive and therefore retentive activity of the platinum would be lessened by the retention of chemisorbed hydrogen. Whatever is the actual situation, it is clear that the spectra are monitoring steps in the *in situ* catalytic hydrogen-dependent equilibra between aromatic and cycloalkane rings.

Fullerene, C_{60}

It was natural to ask whether fullerene, with its aromatic character, would exhibit similar dehydrogenation/rehydrogenation spectroscopic behavior. Because of the very low vapor pressure of C_{60} once again adsorption was carried out from carbon tetrachloride solution.

To explain small changes in the spectra of Aerosil-supported Pt in the region of absorption bands of surface silanol groups ($\sim$3750 cm^{-1}) after adsorption of C_{60} from solution in CCl_4 the adsorption of C_{60} from solution on pure fumed silica was investigated. A spectrum from the interaction of fullerene with silica alone, pretreated by evacuation at 723 K, is shown in Fig. 7. Figure 8 illustrates the size of the fullerene molecules, ca. 1 nm
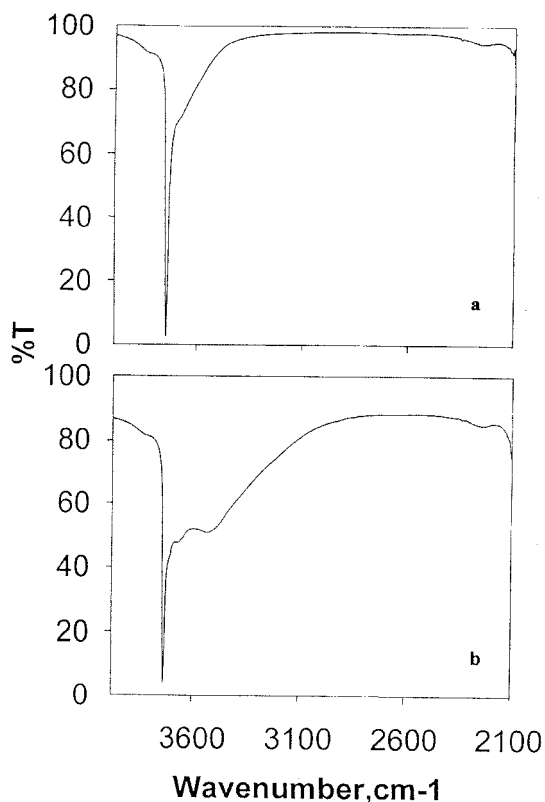
FIG. 7. IR spectra of fumed silica evacuated at 723 K (a) before and (b) after adsorption of fullerene C_{60} from a carbon tetrachloride solution and evacuation at ambient temperature.
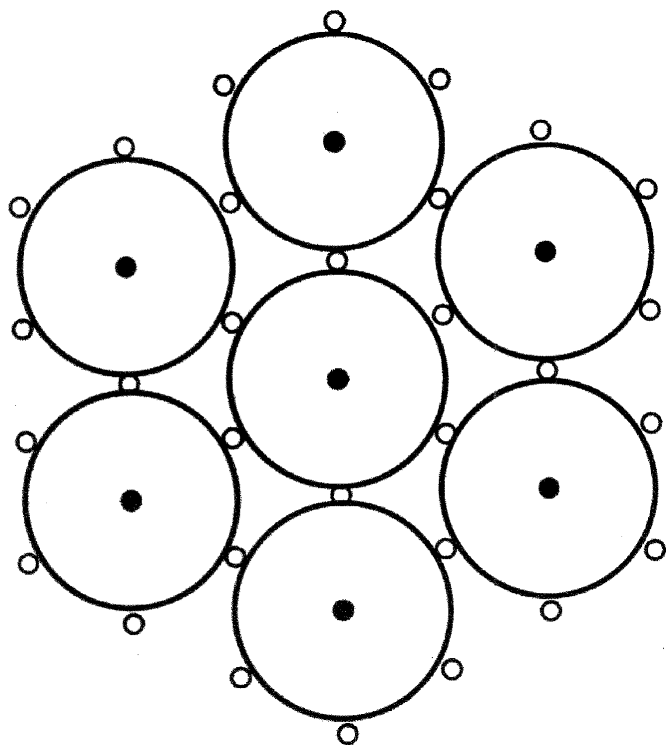
FIG. 8. Schematic view of silica surface with an adsorbed C_{60} monolayer. The average distance between surface free silanol groups of silica (small open and closed circles) is 0.54 nm. Large circles are fullerene C_{60} molecules ~1nm in diameter.

(43), relative to the estimated average spacing of free OH groups, about 0.54 nm, for a silica surface pretreared under vacuum at this temperature (44). The latter figure is similar to the value of 0.52 nm from a mica layer on which monolayer adsorption of C_{60} was studied by electron microscopy (45). The decrease of about 12% in the optical density of the free OH absorption after C_{60} adsorption (Fig. 7) is in reasonable agreement with expectation. The hydrogen bonding of the free OH groups to the π electron system gives a new absorption maximum, at ca. 3540 cm^{-1}. The band shift of 210 compared with 127 cm^{-1} for benzene provides an estimate of 4.34 kcal/mol (18.16 kJ/mol) (46) for the strength of the hydrogen-bonding interaction. However the fullerene molecule could present five- or six-membered rings for hydrogen-bonding purposes, and a long absorption tail to lower wavenumbers suggests the presence of a proportion of stronger hydrogen bonds.

Figure 9 shows the usual three spectra for fullerene adsorbed on Pt: before hydrogenation, after hydrogenation at 343 K under 750 torr of hydrogen for 2 h, and after dehydrogenation by evacuation at 343 K for 2 h. In Fig. 9a there is of course no vCH absorption, but the general relationship between Figs. 9b and 9c is similar to those from naphthalene and anthracene.

The interpretation of the latter two spectra is not straightforward but some suggestions can be made. Hydrogenation

could lead to CH groups around five- and/or six-membered rings. Although in fullerene itself all carbon sites are chemically equivalent and involve participation in one five-membered and two six-membered rings, this ceases to be the case when hydrogenation starts on a particular ring. The mean values between the wavenumbers of the coupled vCH$_2$ asymmetric and symmetric modes for the spectra of cyclopentane and cyclohexane are 2908 and 2885 cm^{-1} (38). These values may be assumed to be approximately correct for such modes of lone CH groups in situations of similar degrees of ring strain; greater strain, as in C_{60}, is expected to lead to higher values. It is therefore reasonable to attribute the higher wavenumber absorption at 2939 cm^{-1} after dehydrogenation (Fig. 9b) to CH bonds around five-membered rings, and the multiple peaks below 2895 cm^{-1} to hydrogenation around six-membered rings.

The metal surface selection rule requires that intensity be only derived from modes with vibrational dipole changes that are perpendicular to the metal surface. This implies that whichever of the five- or the six-membered rings is π bonded to the surface and becomes hydrogenated, it will show only a single vCH absorption, i.e., for the mode in

1 – 2939	
2 – 2919	
3 – 2888	
4 – 2880	
5 – 2871	
6 – 2858	
7 – 2845	
8 – 2820	

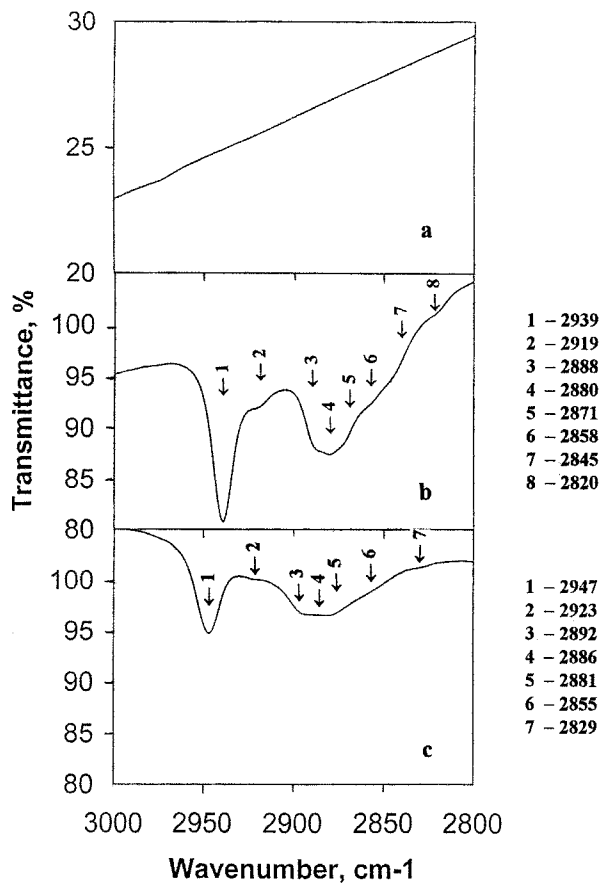|	
1 – 2947	
2 – 2923	
3 – 2892	
4 – 2886	
5 – 2881	
6 – 2855	
7 – 2829	

FIG. 9. Infrared spectra of silica-supported Pt–C_{60} complexes (a) before, (b) after hydrogenation of at 343 K in gas phase under 750 torr of H$_2$ for 2 h, and (c) after dehydrogenation by evacuation at 343 K for 2 h.

which all the CH bonds stretch or contract in phase. The other neighboring type of ring, if also hydrogenated, will be at an angle with respect to the surface and then several of its vCH modes will become active. The spectrum with a single strong absorption at 2939 cm^{-1} therefore suggests that the five-membered ring retains parallelism with respect to the surface after hydrogenation and that additional hydrogenation occurred around, presumably adjacent, six-membered rings. In a HREELS study of C$_{60}$ adsorbed on Pt (111) (47) Swami *et al.* showed that the molecule retains its identity up to 300 K and that a change in wavenumber of an absorption band at 548 cm^{-1} of the parent molecule to 526 cm^{-1} on adsorption implies strong electron donation from the metal, perhaps by two electrons, and a high heat of adsorption. Under these circumstances a selective pattern of adsorption between the five- and six-membered rings would not be surprising. Our results after hydrogenation suggest that five-ring adsorption is preferred.

This time repeated hydrogenation and then dehydrogenation cycles do lead to the gradual removal of the adsorbed fullerene, together with a selective removal of the 2939-cm^{-1} absorption band attributed above to hydrogenated five-membered ring, relative to an adjacent absorption at 2919 cm^{-1}. The infrared spectra of complexes of C$_{60}$ with hydrogen of formulas C$_{60}$H$_{36}$ and C$_{60}$H$_{18}$ have absorptions at 2912, 2850, 2831 and 2917, 2854, 2835 cm^{-1}, respectively (13) and are notably different from those of the surface complexes.

Dehydrogenation is once again a slow process at 295 K and the spectrum obtained after 2 h of pumping compared with before (Fig. 9c) shows a measured integrated intensity ratio of 0.53, together with band shifts to higher wavenumbers. The latter are probably caused by additional saturated ring strain, as the degree of unsaturation encroaches on the hydrogenated areas. The time scales and extents of the hydrogenation and dehydrogenation processes at different temperatures were monitored through the intensities of the 2939- and 2947-cm^{-1} absorption bands, respectively, and are depicted in Fig. 10. It is seen that both the extent and rate of hydrogenation increases with temperature, indicating a gradual growth of CH bonds over the surface of the fullerene molecules. The spectral data obtained for the curves labeled 343 and 373 K were obtained after short-term cooling to 295 K, i.e., ambient temperature.

Some information about structure and the arrangement of chemisorbed complexes of aromatic compounds (benzene, naphthalene, and anthracene) on the surface of platinum crystals was obtained by scanning tunneling electron microscopy (48, 49). Although in these works the arrangement of aromatic molecules on Pt in hydrofluoric acid solution was investigated the main conclusion may be applicable to formation of adsorption layers of naphthalene and anthracene on Pt in carbon tetrachloride solution, which was used in present work.
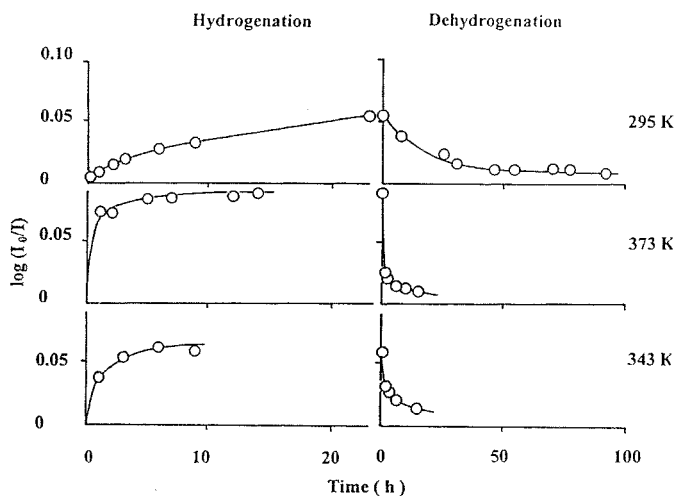

FIG. 10. Kinetics of Pt–C$_{60}$ complex hydrogenation in gas phase under 660–700 torr of H$_2$ and dehydrogenation by evacuation at different temperatures. The concentration of hydrogenated complexes is proportional to log I_0/I at 2939 cm^{-1}.

In accordance with the high-resolution images it was proposed that the binding of aromatic molecules of benzene, naphthalene, and anthracene with Pt (111) on adsorption is made in such a way that the molecules were centered above Pt atoms with their aromatic rings at two-fold bridge sites (48, 49).

Moreover in (50) chemisorption of benzene on Pt(III) was studied by a diffuse low-energy electron diffraction method (LEED) and it was shown that benzene on Pt(III) adsorbs across two-fold bridge sites. In addition, the benzene ring is found to be distorted.

Thus chemisorption of aromatic hydrocarbons as well as fullerene C$_{60}$ on the surface of Pt is not dissociative with hydrocarbon fragment formation through C–C bond breaking at temperatures under investigation, but the formation of strong π complexes of aromatic compounds with the metal surface takes place. This is supported by scanning tunneling microscopy (STM) (48, 49) and diffuse low-energy electron diffraction (LEED) (50) methods, which provide direct information on coordination of adsorbed molecules to atoms of metallic surfaces. Fullerene C$_{60}$ molecules on a Pt(III) surface decompose only at 850 K (51).

CONCLUSIONS

All the aromatic and polynuclear aromatic hydrocarbons studied, including fullerene C$_{60}$, form strong chemisorbed π complexes with silica-supported platinum. Infrared spectroscopy has enabled the monitoring of the slow hydrogenation and subsequent dehydrogenation processes that occur *in situ* on the surface of the catalyst. In all cases the overall removal of the hydrocarbon from the surface is a slow process and survives multiple cycles of hydrogenation and dehydrogenation. With the exception of C$_{60}$, where

comparison data are not available, all the spectra of the surface-hydrogenated species resemble those of the fully hydrogenated products, but these species are little removed by pumping at ambient temperature. Future experimental spectroscopic tests are suggested for distinguishing between a fully hydrogenated product and one covalently bonded to the Pt surface. In the cases of naphthalene and anthracene the pathways of hydrogenation and dehydrogenation differ in that the latter process is interrupted by a very stable intermediate species in which rearomatization occurs on only one end ring.

The complexes of C_{60} with the Pt surface can be hydrogenated and dehydrogenated even at ambient temperature. The rates of the slow hydrogenation and dehydrogenation processes increase with temperature, as does the extent of hydrogenation.

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