

THE IR SPECTRA OF BENZENE AND CYCLOHEXANE ADSORBED ON CO-PRECIPITATED NICKEL-ALUMINA AEROGEL

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The absorption spectra $4000-1100\text{ cm}^{-1}$ of benzene $-d_0$, benzene $-d_6$, and cyclohexane adsorbed at room temperature from gaseous phase on a powdered $\gamma\text{-Al}_2\text{O}_3\text{-Ni}$ (23 wt.%) aerogel were measured, before and after treatment with hydrogen or deuterium. The influence of hydrogen atmosphere in the infrared cell and of its evacuation on the spectra of adsorbates was studied, together with the effect of temperature of the catalyst. The results were confronted with the published spectra of such compounds like bis-arene-metals and monoarene metal complexes. From the phenomenological point of view, the surface species were classified as the spectrally detected complexes (in the presence of hydrogen, 10^1-10^2 Torr) and the so-called "vacuum" complexes. The latter did not manifest itself in the studied region though they are the precursors of the former. Spectral behaviour of the "vacuum" complexes is explained as follows: all the C—H bonds of the adsorbed benzene molecule are hydrogen-bonded to particles of nickel under reduced pressures of hydrogen (10^{-1} Torr or less). A bonding interaction of adsorbates with alumina was not considered.

The infrared spectrum of silicagel (Aerosil) pressed discs impregnated with nickel, reduced in hydrogen and evacuated, has not been changed by sorption of benzene¹⁻³. After introduction of hydrogen into the infrared cell, two absorption bands (2850 and 2930 cm^{-1}) immediately appeared in the spectrum of the catalyst with the adsorbate. These two bands were assigned to cyclohexane formed on the surface by hydrogenation of the adsorbate¹⁻³. After evacuation of hydrogen from the cell the bands disappeared; this was the evidence for physical sorption of cyclohexane, because an additional introduction of hydrogen into the cell did not lead to their repeated appearance in the spectrum of the catalyst. The sorbed cyclohexane, cyclohexene, 1,3- or 1,4-cyclohexadienes¹ showed an analogous behaviour after sorption, before and after treatment with hydrogen. Alkenes sorbed on a nickel impregnated silicagel behaved differently. After evacuation and re-introduction of hydrogen into the cell, they could be again detected as adsorbates in the spectrum⁴⁻⁷, likewise *o*-xylene, and *cis*- or *trans*-1,2-dimethylcyclohexanes². After hydrogen treatment of these cyclic hydrocarbons the formation of partially hydrogenated surface species occurred. These species, which could not be desorbed by evacuation, were detected in the region of the C—H stretching vibration. However, on the basis of EPR-spectra³, it was concluded that also in the case of benzene sorbed on Ni—SiO₂, some adsorbate remained on the surface after hydrogen treatment and evacuation. The residual species could not be desorbed, and at room temperature they were not detected in the infrared spectrum³. As to the sorption mechanism

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of the compounds with six-membered carbon ring, Palazov and coworkers¹⁻³ assumed that with cyclohexane the dissociative chemisorption occurs with the fission of at least one C—H bond on each carbon atom. Cyclohexane sorbed in this way forms a surface complex which is identical with that of chemisorbed benzene. Benzene itself is chemisorbed as a π -complex. After introduction of hydrogen into the cell, the physically adsorbed cyclohexane is always formed by hydrogenation of individual surface complexes.

Unlike the authors¹⁻³ we used a co-precipitated Ni-Al₂O₃ aerogel catalyst. The small size of microcrystallites made it possible to avoid pressing of the solid. As another important factor, the influence of temperature of the catalyst on adsorbates was investigated in the presence of hydrogen or after its evacuation. The aim of this work was to study the behaviour of the six-membered carbon ring in hydrocarbons adsorbed on Ni—Al₂O₃ in respect to mechanism of hydrogenation and hydrogenolysis studied in our laboratory⁸⁻¹¹.

EXPERIMENTAL

Chemicals. Benzene (thiophene free; Lachema, Brno) had infrared spectra (liquid, gas) in accordance with the published ones¹². Benzene-*d*₆ (U.S.S.R.) was the solvent used in NMR spectroscopy. The content of benzene-*d*₀ in it was less than 5 mol.% according to IR-spectra. Cyclohexane (spectrograde; Lachema, Brno) did not contain detectable amount of benzene (220—300 nm, 1 cm cell); its IR-spectrum was identical with the published one¹⁴. Isooctane (Lachema, Brno) had the IR-spectrum identical with that of the standard¹³. All hydrocarbons were dried with an activated molecular sieve Linde 5A before use. Gaseous deuterium was generated by electrolysis of about 30% solution of NaOD in D₂O in an electrolyser with nickel electrodes. Heavy water (U.S.S.R.) contained, according to its IR-spectrum and the published one¹⁵, about 1—3 mol.% of H₂O. Mass spectrometric analysis of the gaseous product of the electrolysis in vol.%: 93.3 D₂, 6.4 HD, 0.3 N₂, eventual traces of O₂ ranged in 10⁻². Hydrogen and deuterium were introduced into the vacuum line through a palladium deoxo-catalyst tube and a cooling trap filled with glass balls, cooled to the temperature of liquid nitrogen.

Catalyst. According to lighter colour on their edges, the obtained plates of co-precipitated aerogel catalyst¹⁶ did not appear to be homogeneous in respect to the content of nickel. Due to their fragility and impossibility to cut them, the plates were crushed to powder and mechanically homogenized. After complete reduction at 350°C, the aerogel contained 23 wt.% of nickel and 67 wt.% of Al₂O₃. X-ray analysis of this powdered aerogel (exposed to air) showed the lines typical for NiO and γ -Al₂O₃ only.

The thickness of the powder layer between the two NaCl plates was 2 mm so that with bulk weight of about 50 mg/cm³, approximately 10 mg of the sample was in each 1 cm² of the cross-section of the incident beam. The sample was purified between succeeding experiments by one hour oxidation in pure oxygen (1 atm, 520°C), followed by reduction in a stream of hydrogen at 350°C for 3—5 h. The hydrogen was then evacuated to 10⁻³—10⁻⁴ Torr at the same temperature in time as short as possible.

Instruments. The infrared spectra (3600—1100 cm⁻¹) were measured on double-beam Beckman IR-7 and Zeiss (Jena) UR-20 spectrophotometers, increasing 2—3 times the standard slit program. Attenuation of the reference beam was carried out with the aid of a mechanical beam attenuator with variable transmission. The monochromator of IR-7 was purged with dry air. The infrared cell used was already described¹⁷. For compensation, an evacuated 10 cm gas cell (NaCl) was placed in the reference beam.

Procedures. The samples of hydrocarbons were sealed under purified nitrogen into glass balloons. The weights of samples (about 250 mg) were chosen so that at a given volume of the cell (about 400 cm^3), the pressure of the gaseous hydrocarbons would reach the saturated vapor pressure at 25°C (about 95–100 Torr for C_6H_6 , C_6D_6 , C_6H_{12})¹⁸. After contacting the vapours for 10 minutes with the catalyst, the gaseous phase was either evacuated or the condensable products were frozen and the remaining gas (N_2) was evacuated to 10^{-4} – 10^{-5} Torr. The vacuum line of common design was attached to a diffusion pump filled with methylphenylsilicone oil. The hydrogen treatment of the adsorbate was carried out always at room temperature and at pressures between 10^1 – 10^2 Torr. Hydrogen from the cell was evacuated to 10^{-5} – 10^{-6} Torr, unless otherwise stated. After each measurement of the spectrum of the catalyst, either the spectrum of the gaseous phase or the spectrum of the evacuated cell was recorded, respectively.

RESULTS

The influence of pretreatment (elimination of a surface carboxylate and crushing of the sample) of $\text{Ni-Al}_2\text{O}_3$ aerogel on its transmission in the infrared region was described elsewhere¹⁶. The spectrum of the powdered aerogel after reduction with hydrogen and following evacuation at 350°C is in Fig. 1A. In the region of the O—H stretching vibration¹⁹ the following bands of isolated OH groups of γ -alumina appeared: 3675 (sharp), 3710–3725 (shoulder), and 3765 (shoulder) cm^{-1} . During reduction of the catalyst with deuterium, the OH groups changed to the OD groups. Instead of the mentioned bands, the new ones were recorded: 2725 (sharp), 2735 (shoulder, and 2750 (broad) cm^{-1} (Fig. 1B). Moreover, the spectra A and B (Fig. 1) show another two very weak bands at 1210 and 1280 cm^{-1} which were not identified. These two bands remained in the spectrum of the nickel catalyst after oxidation-reduction pretreatment¹⁶, and after sorption of benzene. In the 2400 – 2300 cm^{-1} region, there appears a negative absorption by atmospheric CO_2 , which was caused by a small improper balance of both beams and detectable after the ordinate scale expansion. This fact could have a certain influence on the spectrum of benzene- d_6 in the 2300 to 2200 cm^{-1} region as it will be discussed later.

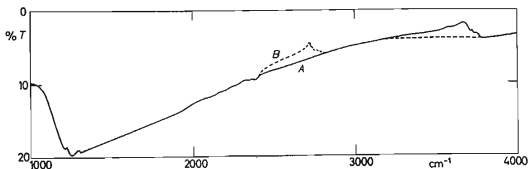


FIG. 1

IR Spectrum of Powdered $\text{Ni-Al}_2\text{O}_3$ Aerogel

After reduction with: A H_2 at 350°C and evacuation at the same temperature, B deuterium at the same conditions.

The transmission of the catalyst reduced and evacuated at 350°C was not markedly influenced by residual pressure of hydrogen or deuterium in the range 10^{-6} –1 Torr. The introduction of these gases into the cell at pressures 10^1 – 10^2 Torr lowered, however, the transmission of the sample at room temperature by about 10–20% of the original value; the bands of isolated OH groups decreased, too. During evacuation of the gases, the original overall transmission of the catalyst was reached almost immediately. The bands of isolated OH groups became more pronounced.

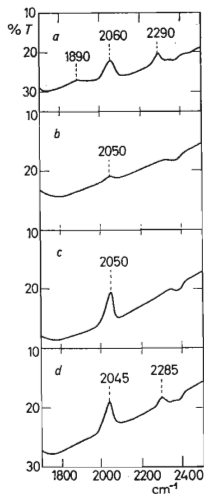
System Ni (H₂)-C₆D₆-H₂

The spectrum of the catalyst with the adsorbate was identical with the spectrum of the catalyst evacuated after reduction with hydrogen. Besides the bands presented in Fig. 2a, a small band at 1333 ± 3 cm⁻¹ immediately appeared in the spectrum of the catalyst after introduction of hydrogen (30–220 Torr) into the cell. Prolonged contact with hydrogen at higher pressures brought about a shift of the band from 2060 to 2025 cm⁻¹ only. In the gaseous phase, some traces of desorbed C₆D₆ were detectable. Even after 15 hours' contact of the catalyst with hydrogen, no bands of the adsorbate were detected in the region of the C—H stretching vibration (3100 to 2800 cm⁻¹) and therefore we conclude that sorption of C₆D₆ does not involve dissociation of C_{arom}-D bonds¹. Further it follows that on the surface neither a partially deuteriated cyclohexane was formed. After a short-time evacuation of hydrogen from the cell the bands at 1333, 1890, and 2290 cm⁻¹ immediately disappeared, while with the 2050 cm⁻¹ band only its intensity was lowered (Fig. 2b). After additional introduction of hydrogen (30 Torr), the intensity of the 2050 cm⁻¹ band immediately reached the original value (Fig. 2c). The band at 2290 cm⁻¹ together with the very weak band at 1333 cm⁻¹ appeared not sooner then after some hours of contact and the band at 1890 cm⁻¹ did not appear at all (Fig. 2d).

FIG. 2

Infrared Spectra of the Surface Complex of Benzene-d₆ after Treatment with H₂ under Various Conditions

The spectrum of the catalyst with the adsorbate: *a* immediately after the introduction of H₂ (30 Torr) into the cell, *b* after 1 h evacuation down to $5 \cdot 10^{-4}$ Torr, *c* immediately after the re-introduction of 30 Torr H₂ into the cell, *d* as *c*, after 20 h.



The successive evacuation of hydrogen brought about a disappearance of the 2290 cm^{-1} and 1333 cm^{-1} bands and a weakened absorption at 2050 cm^{-1} . Re-introduction of hydrogen (30 Torr) immediately increased the 2050 cm^{-1} band to the original value.

A lowering of the intensity of the 2050 cm^{-1} band was dependent on the duration of evacuation of hydrogen. The complete disappearance of the band was accomplished after three hours' evacuation to $2 \cdot 10^{-5}$ Torr. After re-introduction of hydrogen (220 Torr) the band at 2050 cm^{-1} immediately appeared again, however, with lowered intensity while the bands at 2290 and 1333 cm^{-1} appeared after some hours of contact.

In the spectra¹⁴ of cyclohexane- d_{12} the frequencies 2083 cm^{-1} (Raman-active, polarized, very strong, A_{1g} fundamental) and 2289 cm^{-1} (infrared-active, strong, A_{2u} fundamental) can be found which roughly correspond to the bands at 2050 and 2290 cm^{-1} , regardless the symmetry and activity of the corresponding vibrations. These two frequencies were assigned¹⁴ to the stretching vibrations of C—D bonds in the CD_2 group. However as to their relative intensity, both bands of the adsorbate behaved independently during evacuation and introduction of hydrogen into the cell. Therefore, the bands cannot be associated with vibrational motions of the CD_2 group. For this reason the adsorbate cannot be described as cyclohexane- d_{12} , regardless the otherwise inevitable speculations about its formation in the system $C_6D_6-H_2$. Hence it follows: the formation of physically adsorbed cyclohexane¹ is not applicable to our case. It is clear from Fig. 1 that the negative absorption by atmospheric CO_2 causes a lowering of the intensity of the 2290 cm^{-1} band. However, this fact cannot substantiate any explanation of the independent behaviour of both bands at 2050 and 2290 cm^{-1} .

If our sample with the adsorbate was heated to 100°C for 15 minutes while continuously evacuating, the 2050 cm^{-1} band lowered its intensity and after raising the temperature to 200°C it vanished. After introduction of hydrogen (30 Torr), this band immediately appeared but its intensity was markedly lower than before heating the sample. The bands at 2290 and 1333 cm^{-1} were not detected even after some hours of contact of hydrogen with the catalyst. However, it cannot be decided whether very weak intensity is the cause or that the corresponding adsorbate cannot exist on the surface at the given conditions at all.

Heating of the sample with the adsorbate to 100°C (for 15 minutes) in the atmosphere of 30 Torr H_2 (all condensable gases were continuously frozen down) led to a decrease of the 2290 cm^{-1} band, to the disappearance of the 1333 cm^{-1} band while the 2050 cm^{-1} band was shifted to 2020 cm^{-1} without changing its intensity; the band at 1890 cm^{-1} remained unchanged. Heating to 200°C (other conditions as in the previous case) led to the disappearance of the 2290 cm^{-1} band, to a lowering of the 2020 cm^{-1} band and the absorption at 1890 cm^{-1} was almost depressed. In the region of the stretching C—H vibration a very weak, broad band appeared with ma-

ximum between $2850-60\text{ cm}^{-1}$ as well as a more intense band at 2930 cm^{-1} . Both bands disappeared by overnight freezing of the gaseous phase. The bands at 2870 and 2935 cm^{-1} (cyclohexane) and a very small band at $2170-80\text{ cm}^{-1}$ revealed after evaporation of the together condensed products from the two experiments. The very small band could correspond to the CHD groups of partially deuterated cyclohexane ring as it follows from the comparison with the Raman spectrum of cyclohexane- d_1 (point group of symmetry C_s , cf.²⁰).

Heating of our sample with the adsorbate to 110°C in the atmosphere of 220 Torr H_2 for 15 minutes or 75 minutes (without condensation of desorption products) led to a lowering of the bands at 2295 and 1333 cm^{-1} . The 2025 cm^{-1} band was not changed (Fig. 3a). The gaseous phase contained only the desorbed C_6D_6 (2290 cm^{-1}). Heating to 205°C (1 h, other conditions as in the previous case) led to a lowering of the intensity of the band which shifted from 2025 cm^{-1} to 2040 cm^{-1} . The change in intensity was so marked that the band was lower than the band at 2290 cm^{-1} . Consequently, in the C—H stretching region appeared a weak absorption at 2870 and $2930-40\text{ cm}^{-1}$, the latter being more intense (Fig. 3b). The gaseous phase contained mostly C_6H_{12} and CH_4 (3020 and 1320 cm^{-1} , ref.²¹,

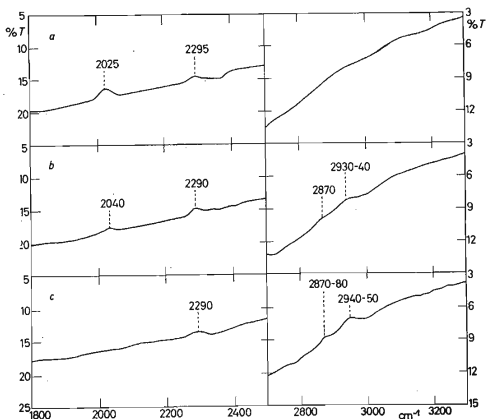


FIG. 3

Infrared Spectra of the Surface Complex of Benzene- d_6 after Heating the Catalyst in H_2 Atmosphere (220 Torr) Measured at Room Temperature

a After 75 min at 110°C , b 60 min at 205°C , c 60 min at 300°C .

cf. also¹) and traces of C_6D_6 and C_6H_6 (671 cm^{-1}). After heating the sample to 300°C for one hour, the 2040 and 1333 cm^{-1} bands disappeared, only a weakened absorption at 2290 cm^{-1} remained, while the bands at $2870-80\text{ cm}^{-1}$ and $2940-50\text{ cm}^{-1}$ (more intense) became pronounced (Fig. 3c). The gaseous phase had the same composition as in the case of 205°C . Evacuation of gaseous phase caused the disappearance of all bands of the adsorbate from the spectrum of the catalyst. Repeated introduction of hydrogen (220 Torr) immediately led to appearance of a small band at 2030 cm^{-1} which, after heating the sample in hydrogen to 300°C , vanished. In the gaseous phase no traces of desorbed products were detected.

Survey of our spectral observations in another experiments with benzene and cyclohexane is given in Table I.

In the experiments mentioned above, sorption of benzene was always accompanied by interaction of the sorbed benzene with the surface $\text{OH}(\text{OD})$ groups of γ -alumina. The character of this interaction turned out to be identical for all four systems studied. For both benzene $-d_0$ or $-d_6$ the sorption caused a lowering of the sharp band at 3765 or 2725 cm^{-1} , respectively, in the region of lower wave numbers remained only one broad shoulder $3740-20$ or $2760-40\text{ cm}^{-1}$, respectively. Moreover, in the case of C_6D_6 -alumina(OH), a new very weak band appeared at 2720 cm^{-1} which is evidence for a little deuterium exchange likewise in the case of C_6H_6 -alumina(OD) when a very weak band was observed at $3680-50\text{ cm}^{-1}$. The bands of hydroxyl groups maintained their shape and intensity during another changes of experimental conditions with the exception of the case of evacuation at 350°C . From this it can be concluded that benzene, as to the hydroxyl groups, caused the same changes like gaseous hydrogen or deuterium.

$\gamma\text{-Al}_2\text{O}_3/\text{Ni}$ (43 wt.%) Catalyst for Hydrogenolytic Dealkylation

Preparation of this catalyst for measurements in the infrared region by pressing was described elsewhere¹⁶. The sample after reduction and evacuation was practically transparent only in the region $2500-1100\text{ cm}^{-1}$. Introduction of hydrogen (30–760 Torr) into the cell narrowed the region of its transparency to $2200-1200\text{ cm}^{-1}$. Sorption of 2,2,4-trimethylpentane $-d_0$ and $-d_{18}$, cyclohexane, benzene $-d_0$ and $-d_6$ resp. was studied. No bands of the adsorbates were detected in the spectrum of the catalyst, neither before nor after hydrogen treatment. Products of interaction between the catalyst and the hydrocarbons were observed only in gaseous phase after hydrogen treatment in some cases: a partial deuterium exchange was proved with isooctane $-d_{18}$, formation of cyclohexane with benzene $-d_0$, and with benzene $-d_6$ the presence of partially deuteriated cyclohexane and of cyclohexane $-d_0$. After evacuation of gaseous phase and after repeated introduction of hydrogen, no bands were recorded in the spectra of new gaseous phase at all.

TABLE I
Survey of Spectral Observations with Benzene and Cyclohexane (cm^{-1})

Experiment	System		
	$\text{C}_6\text{D}_6\text{-H}_2$	$\text{C}_6\text{D}_6\text{-D}_2$	$\text{C}_6\text{H}_6\text{-H}_2$
1. After sorption of the hydrocarbon on the evacuated catalyst	no absorption bands of the adsorbed benzene were observed		
2. After introduction of the gas into the cell	1 333 ^b , 2 290 ^c 1 890 2 050	1 333 ^b , 2 290 ^c 1 890 2 020	1 490 ^b , 3 100—3 050 ^d 2 870 2 940
3. After evacuation of the gas	all absorption bands of the adsorbate disappeared, the band at 2 050 as the last		
3a. Re-introduction of H_2 or D_2	immediat. 2 050, 1 333; 2 290 later	immediat. 2 050, 1 333; 2 290 later	flat max. at 2 900
4. Heating of the catalyst with the adsorbate during evacuation	all absorption bands of the adsorbate disappeared, the band at 2 050 as the last (200°C)		
4a. Re-introduction of H_2 or D_2	immediat. 2 050	immediat. 2 050	—
5. Heating of the catalyst with the adsorbate in H_2 or D_2	deuterium exchange, see text	only 2 050 remained	1 490, 3 065—3 055 2 870 2 940

DISCUSSION

According to Peri⁶ even after a strong reduction with hydrogen, silicagel impregnated with nickel can contain nickel ions the presence of which lowers the wave number of the band of isolated surface OH groups to 3620 cm^{-1} . In comparison with the spectrum of γ -alumina aerogel¹⁹, we also observed that the position of the strongest band of isolated OH groups of our sample is shifted (3675 cm^{-1}). Therefore we assumed that in our reduced sample were present the nickel ions in the aerogel network. Despite this fact, the term nickel atom instead of nickel ion will be used for the assumed centres of sorption in the following text.

Assignment of Bands of the Adsorbate after Hydrogen Treatment

The 2290 cm^{-1} band of the adsorbate was accompanied (experiments 2 and 3a, Table I) by a less intense band at 1333 cm^{-1} . This couple of bands corresponds

TABLE I
 (Continued)

System $C_6H_6-D_2$	Type of the benzene surface complex	System $C_6H_{12}-H_2$
	vacuum π -complex	no band ^a
1 490 ^b , 3 100–3 040 ^d 2 955 } —	s.d. ^e π -complex s.d. ^e σ -complex	weak 2 870 ^f medium 2 940 ^f
—	vacuum π -complex vacuum σ -complex	both bands weakened but did not disappear
—	s.d. ^e σ -complex s.d. ^e π -complex	both bands increased intensity
—	vacuum π -complex vacuum σ -complex	both bands weakened
—	s.d. ^e σ -complex	—
—	s.d. ^e σ - and π -complexes	both bands increased intensity ^g

^a The vacuum σ -complex of cyclohexane, ^b the C—C skeletal vibration, ^c the C—D stretching vibration, ^d the C—H stretching vibration, ^e s.d. means spectrally detected, ^f the spectrally detected σ -complex of cyclohexane + physisorbed cyclohexane, ^g benzene or cycloalkenes were never observed in the gaseous phase during the experiments with cyclohexane.

to the two most intense absorption bands in the infrared spectra^{12,22} of liquid and gaseous C_6D_6 in the 4000–1100 cm^{-1} region. These absorptions were assigned to the stretching vibration of the C—D bonds (at 2280 cm^{-1}) and to the coupled²³ stretching and in-plane deformation vibrations of the carbon ring (at 1330 cm^{-1}). Both frequencies, ν_{20} and ν_{19} , are fundamental ones belonging to the symmetry species E_{1u} . (Notation of the vibrations of the benzene molecule is according to Wilson²³.) The same couple of bands was observed by us in the system $C_6D_6-D_2$, the analogous couple 3060, 1490 cm^{-1} for C_6H_6 molecule we observed in the experiments with H_2 and D_2 . With regard to the fact that the adsorbate in the

systems with C_6D_6 could not be eliminated solely by evacuation at room temperature, we assumed that the interaction with the surface is stronger than in cases of physical adsorption. A comparison with complexes of benzene and transition metals offers the possibility of an assumption of a π -dative bond between the surface and benzene molecules¹.

However, from the insignificant changes in positions of maxima of both couples of the bands of the adsorbate 2290, 1333 cm^{-1} and 3060, 1490 cm^{-1} , compared with free C_6H_6 and C_6D_6 molecules, it follows that this π -interaction of benzene with the surface is weaker than in cases of chemical compounds of the type bis-benzene-metal (*e.g.* V, Cr, Mo, W)²⁴, bis-(benzene- d_6)-Cr (see^{24,25}), or of half-sandwich complexes with one arene ligand. With these relatively very stable molecules a lowering by some tens of cm^{-1} of the benzene frequencies ν_{20} and ν_{19} can be observed.

Sorbed benzene after hydrogen treatment presumably retains its local symmetry D_{6h} although a lowered symmetry cannot be excluded, *e.g.* D_{3h} (plane cyclohexatriene). The overall symmetry of surface π -complexes is then further lowered to C_{6v} or C_{3v} . The half-sandwich complexes are then closer as model compounds to the assumed surface π -complex with some lower symmetry (*e.g.* benzene-metal-tricarbonyl).

It remains to explain why some absorption bands of the adsorbate were not found in the spectrum after hydrogen treatment of the sample, *i.e.* the frequencies attributable to vibrations which should become infrared-active due to lower symmetry of the surface complex²¹. Firstly, these are the vibrations of the bonds C_{arom} -(H, D): stretching $\nu_2(A_{1g} \rightarrow A_1$ for C_{6v} and C_{3v}), stretching ν_7 and in-plane deformation ν_9 (both $E_{2g} \rightarrow E$ for C_{3v}) and secondly, the vibrations of the carbon skeleton: stretching $\nu_8(E_{2g} \rightarrow E$ for C_{3v}) and $\nu_{14}(B_{2u} \rightarrow A_1$ for C_{3v}). From the absence of the frequencies ν_7 , ν_8 , ν_9 , and ν_{14} (active for C_{3v} only) in the spectrum, it could be concluded that the surface complex belongs to the point group of symmetry C_{6v} . However the absence of ν_2 (active for both C_{3v} and C_{6v}) in the spectrum indicates that such a decision between the two possibilities is farfetched. Very weak intensity of these bands cannot be excluded as the cause for their absence, which is in harmony with the published infrared spectra of $C_6H_6Cr(CO)_3$ (ref.²⁷), $C_6H_6Mo(CO)_3$ (ref.²⁸), and of their deuterioanalogues. The mentioned compounds evidently have the symmetry C_{3v} and the considered frequencies ν_2 , ν_7 , ν_8 , ν_9 , and ν_{14} are really infrared-active but their absorption bands are classified as weak ones. Therefore we only assume in the following that the sorbed benzene molecule retains its aromatic character in a π -dative bond with the surface and further, the plane benzene molecule is parallel to the surface. For this model we choose the term "spectrally detected π -complex of benzene with the surface".

Now, it remains to assign the 2050 cm^{-1} band of the adsorbate observed in both systems C_6D_6 -(H_2 or D_2). Difficulties with elimination of the band from the spectrum of the catalyst indicate a greater stability of a corresponding adsorbate, in comparison with the bands of the π -complex of benzene. This includes heating during

evacuation as well as heating in atmosphere of H_2 or D_2 . As the 2050 cm^{-1} band lies on lower limit of the interval for frequencies of saturated C—D bonds., we believe that this band is associated with a σ -complex of benzene with the surface, in which the six-membered carbon ring has lost its aromatic character.* Despite the lack of information about the number of bonds with the surface, we think that existence one C—D band only indicates²⁹ a high local symmetry of the saturated ring, *e.g.* D_{3d} or D_{6h} . Another band at 1890 cm^{-1} which accompanied the 2050 cm^{-1} band can now be assigned to the saturated C—D bonds which rest in an interaction with the catalyst, *i.e.* they form a kind of deuterium bridge.

As it was noted¹⁶, the preparation of the nickel catalyst included elimination of a surface carboxylate from the aerogel. With regard to the use of methanol in the preparation, it could be the surface formate. Greenler's paper³⁰ about formation of the surface carboxylates on alumina from methanol and ethanol, however, did not state presence of any bands in the stretching C—H or C—D region. In the Raman spectra of deuterioformates a line at 2120 cm^{-1} is assigned³¹ to the C—D stretching vibration. From these facts it follows that even traces of a surface deuterioformate can be excluded as a cause of the absorption at 2050 cm^{-1} .

In the infrared spectra of $(C_6H_6)_2$ and $(C_6D_6)_2Cr$ a band at 2045 cm^{-1} was observed²⁴ but only for solutions in CS_2 . Assignment of the band was not tried²⁴ though this absorption was one of the most intense ones. The band was also observed by Snyder²⁵ who proposed³² to ascribe it to CS_2 molecules forming a charge-transfer complex with the solute.

From the analysis of the infrared spectra of transition metal hydrides it follows^{33,34} that the band of the stretching metal-hydrogen vibration lies in the $2240\text{--}1700\text{ cm}^{-1}$ region regardless the nature of ligand (π -cyclopentadienyl²⁹ and ²⁹/or³⁴ carbonyl). Our experiments with C_6D_6 excluded such an assignment of the 2050 cm^{-1} band to the Ni—H bond. In one case H_2 was used, in the other D_2 . The band attributable to the Ni—D bond should be at lower wave numbers²⁹, $1700\text{--}1200\text{ cm}^{-1}$.

We carried out preliminary tests with sorption of CO on our Ni-aerogel. In accordance with the published data³⁵ we observed the unresolved doublet, typical for CO on Ni. However, appearance of the bands of adsorbed CO was independent on introduction of H_2 into the cell; also the elimination of adsorbed CO by evacuation was in general much easier than the elimination of our adsorbate characterized by the 2050 cm^{-1} . Therefore, we exclude the adsorbed CO as the species responsible for the mentioned absorption. The same reasons hold in our case for the adsorbed N_2 (near 2000 cm^{-1} , *cf.*³⁶).

The couple of bands $2050, 1890\text{ cm}^{-1}$ could be equivalent in the systems with C_6H_6 to another couple $2940, 2870\text{ cm}^{-1}$. Unfortunately, this region is covered by the bands of physisorbed or gaseous cyclohexane. Moreover, the transmission of our sample is very low at these wave numbers so that the resolution of bands is badly worsened.

Nature of Benzene Surface Complex before Hydrogen Treatment

After benzene was sorbed on $\gamma\text{-Al}_2\text{O}_3\text{--Ni}$ aerogel no bands of the adsorbate were found in the spectrum of the catalyst. Difficulties with detection of absorption bands

* Such a "mysterious, saturated" band near 2900 cm^{-1} is found in the infrared spectra of some π -cyclopentadienyl metals despite the aromatic character of the ring²⁹.

corresponding to vibrations of the C—(H, D) bonds of the adsorbate can be explained by a strong hydrogen bonding. According to our assumption, aromatic C—(H, D) bonds interact with nickel atoms surrounding the sorption centra for the aromatic ring π -system. For simplicity, this surface compound will be called* the "vacuum π -complex of benzene". In other words, we assume formation of a complex which in general⁶ is similar to the so-called metal atom cluster compounds. Existence of such complexes for other ligands has been already proved, *e.g.* the trinuclear tris-(π -cyclopentadienylnickel)dicarbonyl³⁸. In an analogous manner, it is possible to consider a "vacuum σ -complex" formed on evacuated nickel catalyst by dissociative chemisorption of cyclohexane. The symmetry of this surface complex will be again C_{6v} or *e.g.* C_{3v} , independently of whether the carbon ring is planar or puckered. An interaction of C—H bonds with the surface through hydrogen bonding is analogous to that in the vacuum π -complex. Absence of absorption bands arising from vibrations of the saturated carbon ring can be explained by the opacity of Al_2O_3 at lower wave numbers. The only one, very intense band of the vibrating carbon skeleton of free cyclohexane molecule is found in the Raman spectrum (A_{1g} , polarized) at 1156 cm^{-1} . This wave number lies, however, on the transmission edge of our sample. Presumably for this reason the mentioned band was not observed although the corresponding vibration should be infrared-active for both symmetries of the surface complex ($A_{1g} \rightarrow A_1$ for C_{6v} or C_{3v}).

Influence of Hydrogen on the Spectrum of Adsorbates

In accordance with the views on complexes of transition metals in low oxidation state^{38,39} we assumed an interaction of our catalyst (after reduction in hydrogen and evacuation) with the adsorbate in such a way that nickel attacks the antibonding π -orbitals of benzene molecule. A non-localized interaction is the condition for hydrogen bonding between nickel and the adsorbate, *i.e.* for formation of the vacuum π -complex of benzene. Interaction of our catalyst with hydrogen atmosphere ($10^1 - 10^2$ Torr) is apparent from the lowering of the overall transmission of our sample. Hydrogen, which can act as electron donor³⁹, influences after sorption electronic properties of metals on supports³⁵, either in the molecular³⁹ or the atomic form³⁵. Existence of the Ni—H bond has not yet been proved by infrared spectroscopy with nickel impregnated catalysts. Despite this, it is assumed that dissolution³⁵ of hydrogen in nickel leads to the formation of a surface hydride⁴⁰. However, hydrides which are considered as the catalytically active component in a reaction should exhibit

* From general properties of hydrogen bond it follows: the corresponding infrared absorption band markedly increases its half-band width, so that a broad, diffuse band is often difficult to detect. Low values of maximum absorptivities by aromatic or tertiary C—H bonds in free molecules cannot serve themselves as evidence¹ because the π - or σ -complexes observed by us contain just these bonds³⁷.

some specific stability³⁹: Assuming a low stability of nickel hydride hydrogen would be poorly soluble in nickel catalyst. On the other hand, a high stability (*i.e.* the possibility to detect the Ni—H bond in the infrared) would mean a lowered ability for a reaction with organic substrates. The formation of the hydride recalls higher oxidation state of nickel³⁹, of its coordination number^{38,39}, and due to this, of the geometry³⁸ of its surface complexes in comparison with zero-valent metallic nickel. Despite the fact, that only a half-space is available for the formation of a surface complex, a pyramidal π -complex could correspond to a higher coordination number of nickel, *e.g.* 6, with regard to the benzene molecule functioning as tridentate ligand^{41,42}. As the cause of extinction of hydrogen bonding in the vacuum π -complex, we suppose the gaseous hydrogen influencing electronically the used catalyst. The difference between the two π -complexes of benzene, the spectrally detected complex and the vacuum one, should consequently involve a change of the interaction with nickel⁴³. It is possible that the elimination of hydrogen bonding is accompanied by a change in the distance nickel atom — centre of the ring, *i.e.* by some restriction of back-bonding. The ability to transform the vacuum π -complex of benzene into the spectrally detected π -complex can be ascribed to the hydrogen dissolved in nickel. After evacuation of hydrogen from the cell (experiment 3) at room temperature of the catalyst not all the bands of the adsorbate disappeared from the spectrum. A possible explanation is that evacuation at this temperature removed only a portion of the dissolved hydrogen. Only the increased temperature of the catalyst (experiment 4: evacuation at 200°C) led to the disappearance of the last band of the adsorbate (2050 cm^{-1}) from the spectrum, but did not lead to the elimination of the σ -complex from the surface. Its existence was immediately apparent after the re-introduction of hydrogen into the cell (experiment 4a). From this fact we conclude that the increased temperature caused liberation of dissolved hydrogen from the catalyst, *i.e.* conditions for the hydrogen bonding between the adsorbate and the surface were renewed. On the contrary, the presence of hydrogen atmosphere, prior to the introduction of benzene — d_0 into the cell, preserved any observable sorption of benzene at room temperature⁴⁴. Furthermore, when a mixture of 90 Torr C_6H_6 and 210 Torr H_2 was in 40 hours' contact with the catalyst and then it was evacuated, no bands of adsorbate after introduction of hydrogen (760 Torr) were detected even after some hours. The hydrogen treatment of the adsorbates was consequently accompanied by desorption of products into the gaseous phase. Along with original benzene mainly cyclohexane was observed, either as the product of hydrogenation or of deuterium exchange. Increased temperature of the catalyst relieved the desorption and at temperatures above 300°C a cracking was also observed (CH_4 , CD_4).

From all these facts we conclude that the surface compounds assumed and proved in this work can be incorporated into the reaction scheme of catalytic hydrogenation of benzene to cyclohexane. Consequently, we point out that these reaction intermediates need not be the only ones as well as the most important ones⁴⁵.

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Note added in proof: During revision of this manuscript, new papers dealing with the presented or related subjects appeared. Erkelens and coworkers⁴⁶ observed with silica-supported nickel that benzene is chemisorbed without loss of its aromatic character and not by formation of a π -complex as with organometallic complexes. In the case of silica-supported platinum, Shopov and Palazov⁴⁷ proved a π -bond formation in sorption studies of benzene. Formation of this bond on nickel surface was predicted by these authors on the basis of quantum-mechanical calculations⁴⁸.

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