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FT-IR Spectroscopic Studies of Catalysts

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The role of FTIR spectroscopy in catalytic studies is briefly discussed and some typical examples are shown. IR spectra of weakly bound hydrogen on Pt/SiO₂ reveal surface heterogeneity. The hydrogen concentration on the surface is described by a Temkin isotherm. Adsorption of unsaturated C₆ ring compounds on hydrogen poor Pt/SiO₂ is essentially a self-hydrogenation process resulting in the formation of cyclohexane and carbon deposit on the metal surface.

Chemisorption of *n*-hexane and benzene on hydrogen-rich Ni/SiO₂ surface gives identical spectra under similar conditions. The same phenomenon is established for *n*-butane and benzene after chemisorption on the hydrogen-poor surface. The infrared and Raman spectra of C₆H₆ on Ni/SiO₂ suggested a symmetry lowering somewhere between C_{6v} and C_{3v} because of the non-planarity of C₆H₆ and the site symmetry of the surface.

INTRODUCTION

IR spectroscopic investigations of surface phenomena occurring on metal catalysts were pioneered by Eischens and Pliskin some thirty years ago.¹ Since their classical work the experimental techniques of IR spectroscopy have made remarkable progress and the method has become very popular and consequently widely utilized in the study of surface structures and reactions. With the advent of modern, computer-controlled Fourier-transform spectrophotometers it is relatively easy to overcome the difficulties caused by the severe optical conditions often encountered in such measurements, and as computer facilities are always at hand for digital data storing and post-processing, good-quality spectra can be produced within a reasonable time scale. On the other hand, in the last decades a number of other excellent surface probing methods (various electron spectroscopies and electron diffraction methods, inelastic neutron and atomic beam scattering, »surface enhanced« Raman and reflection-adsorption IR spectroscopies, etc.) have been developed which are able to offer very specific and detailed information on the structure of the surface species and often surpass the efficiency of FTIR spectroscopy, especially when submonolayer coverages on low-area samples have to be investigated. This means that the initial popularity of IR spectroscopy has somewhat weakened. However, from the point of view of heterogeneous catalysis (and some other »applied« sciences) the importance of IR studies can by no means be questioned.

EXPERIMENTAL

Preparation of the catalysts is described elsewhere.^{11,25} The infrared spectra were recorded using a Digilab FTS-20C Fourier spectrometer. Each record was typically 200 scans at 4 cm⁻¹ resolution. The single beam spectra of the samples were ratioed against those of the supported metal catalysts. A specially constructed evacuable and heatable cell was used for the FT-IR transmission measurements.²⁸

USE OF FTIR STUDIES IN CATALYTIC RESEARCH

The field of surface studies seems to be considerably polarized nowadays. At one extreme, in surface science, high-quality structural data are reported as having been obtained by special experimental methods (together with quantum chemical calculations) on »model« systems, *i. e.* clean, »well defined« surfaces (*e. g.* single crystals) and studied in ultrahigh vacuum, at low temperature, *etc.* At the opposite end, there are »practical« heterogeneous catalysis works with »classical« measurements (kinetics, product analysis, *etc.*) on poorly characterized, multiphase, dispersed systems (metal, support carbon deposit contamination, *etc.*) under high adsorbate pressures and generally at high temperatures. Thus, though catalysis is strongly needed for structural information, the application of surface science data to solve the problems of catalytic studies meets with difficulties because of the noncomparable conditions. Two typical problems are often encountered:

(i) The surface science methods are not applicable because, for example, a too high pressure is necessary.

(ii) The surface science results are not transferable to a given catalytic problem because the processes taking place are essentially different, or special effects (*e. g.* strong metal-surface interaction, support effects, *etc.*) should be taken into account.

In such cases IR spectroscopy usually offers a possible solution since it has high resolving power and, moreover, is suitable for studying diverse samples (single crystals, foils, films, powders or industrially preshaped catalyst pellets) by various optical setups best fitting the special requirements of the system under investigation (transmission, different reflection-absorption or emission measurements). There are no restrictions regarding high or low temperatures and the adsorbate pressures can range from UHV up to several kilobars.

In the following, IR studies of the adsorption of some important molecules on Pt/SiO₂ and Ni/SiO₂ are discussed as an illustration of the situation outlined above.

WEAK HYDROGEN ADSORPTION

Since metal catalysts are activated in hydrogen, it is generally present on the surface. Moreover, the adsorbed hydrogen plays a substantial role in a number of heterogeneous catalytic reactions. Therefore, its structural characterization is of great importance but rather difficult because most of the surface probing experimental methods are insensitive to adsorbed hydrogen.²

On Pt surfaces, hydrogen is adsorbed in several different forms.³ After the completion of a strongly bound monolayer of H atoms, another, reversibly adsorbed, hydrogen appears if the gas pressure above the sample exceeds *ca.* 10⁻² Pa. This pressure is greater than that applicable for electron spec-

troscopies, but the system can be conveniently studied by IR spectroscopy.⁴⁻¹³ In the spectra (Figure 1.) adsorbed H and D give bands at 2120 cm^{-1} and 1520 cm^{-1} , respectively. These bands — by analogy with the spectra of transition metal hydride compounds — are assigned to the Pt—H(D) stretching of H(D) atoms coordinated to one surface metal atom only, and are therefore usually referred to an »on-top« hydrogen. (Strongly bonded H atoms are situated in bridge sites or in trigonal holes of the surface.) It would be reasonable to suppose molecular hydrogen adsorption, but in this case, in Figure 1, a third band of intermediate frequency should also be present because of the HD molecules produced in the exchange reaction between molecules adsorbed from the H_2/D_2 mixture.⁴ The derivative-shaped feature on the low frequency side of the 2120 cm^{-1} band is caused by the adsorbed carbon monoxide which is usually present as a contamination on the sample.^{6,7,11,12} The derivative shape indicates that the CO band frequency is increased by hydrogen adsorption.^{7,11} However, the shift is already observed during the formation of the strongly bound H monolayer, prior to the appearance of the on-top hydrogen, *i.e.* interaction occurs between the CO molecules and strongly bonded H atoms only.¹² The effect of the on-top hydrogen becomes more pronounced at high CO and H coverages resulting in a decrease of CO band frequency.⁴

Both Pt—H and Pt—D bands have an asymmetric shape indicating that they are composed of several overlapping components.¹³ The band fitting

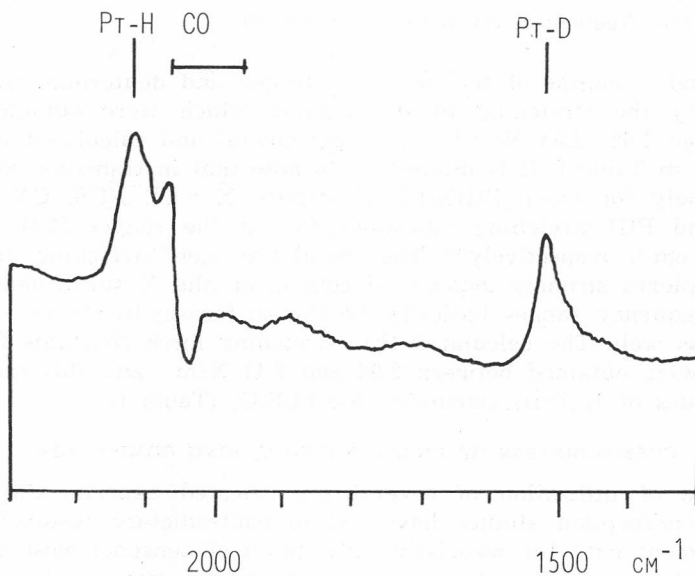


Figure 1. IR spectrum of 1:1 $\text{H}_2 + \text{D}_2$ mixture adsorbed on CO contaminated Pt/SiO₂. Pressure: 300 Pa.

procedure performed on the 2120 cm^{-1} band reveals the presence of (at least) three close lying Lorentz curves with peak frequencies at 2129, 2118, 2097 cm^{-1} . This refers to surface heterogeneity, *i. e.* all the hydrogen atoms are connected to the surface by essentially the same type of bonding, but the local environments of the metal atoms are different. However, in order to determine the adsorption site geometry, reflection measurements on single crystal surfaces would be necessary. On Pt/SiO₂ the band area (as a measure of surface concentration) linearly depends on the logarithm of H₂ pressure (Figure 2.), *i. e.* a Temkin isotherm is observed as further proof of the surface heterogeneity.¹³ However, in the case of Pt[Al₂O₃] a dissociative Langmuir isotherm was reported⁸ showing that a weak hydrogen adsorption is influenced by other effects as well (*e. g.* strong metal-support interaction).

TABLE I
Platinum-Hydrogen Stretching Frequencies and Calculated Force Constants

Compound	ν (PtH) (cm^{-1})	ν (PtD) (cm^{-1})	K (PtH) Ncm^{-1}	Remarks
Pt/SiO ₂	2129	1526*	2.62	(a)
	2118	1519*	2.59	(a)
	2097	1504*	2.54	(a)
<i>trans</i> -[PtH(OCN)(PEt ₃) ₂]	2234	1589	2.93	(b)
<i>trans</i> -[PtHCl(PEt ₃) ₂]	2230	1610	2.83	(b)
<i>trans</i> -[PtH(NCS)(PEt ₃) ₂]	2195	1571	2.79	(b)
<i>trans</i> -[PtH(CN)(PEt ₃) ₂]	2072	1504	2.41	(b)

* Predicted (calculated) band components of the asymmetric shape experimental band at 1520 cm^{-1} .

(a) This work.

(b) Experimental frequencies are taken from Ref. 23.

The bond strengths of the on-top hydrogen and deuterium can be characterized by the stretching force constants which were obtained in the narrow range $2.62\text{--}2.54\text{ Ncm}^{-1}$. The experimental and calculated results are summarized in Table I. It is interesting to note that in transition metal complexes, namely for *trans*-[PtHX(PEt₃)₂] (where X = Cl, NCS, CN or OCN), the PtH and PtD stretching vibrations fall in the ranges 2234—2072 and 1610—1504 cm^{-1} , respectively.²³ The metal-hydrogen stretching frequencies for Pt complexes strongly depend, of course, on the X substituent, but the observed frequency ranges basically fit the surface-hydrogen or -deuterium vibrations as well. The calculated PtH stretching force constants for the Pt complexes were obtained between 2.93 and 2.41 Ncm^{-1} and this range involves the values of K (PtH) calculated for Pt/SiO₂ (Table I).

CHEMISORPTION OF UNSATURATED C₆ RING COMPOUNDS

In spite of utilization of several sophisticated experimental methods, benzene chemisorption studies have led to contradictory results.¹⁴⁻²¹ There is an agreement with the associative adsorption of benzene; most of the studies reported that the ring plane was parallel to the metal surface,¹⁴⁻¹⁹ while others concluded that the adsorbed layer consisted of molecules inclined to the metal plane.²⁰ In the former case it was supposed that the C—H bonds

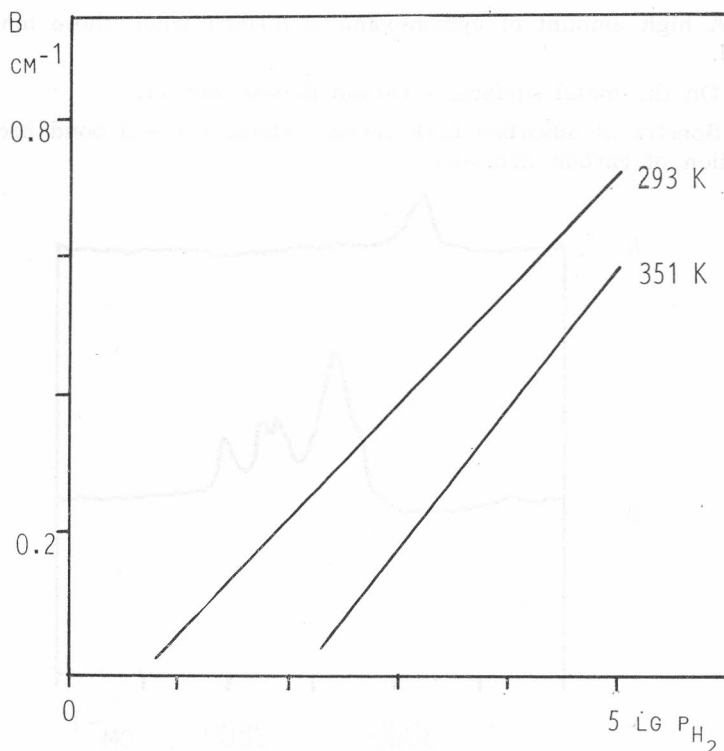


Figure 2. Pressure dependance of the adsorbed hydrogen band intensity. Pressure unit: Pa.

were bent out from the molecular plane. It has also been suggested that the ring can be distorted: it has alternating shorter and longer C—C bonds, *i. e.* similar to the »Kekule-benzene«.^{14,19}

a) Benzene on Pt/SiO₂

In the IR spectra of benzene adsorbed on Pt/SiO₂ only weak C—H bands are seen above 3000 cm⁻¹ (Figure 3). The low frequency limit in such measurements is 1300 cm⁻¹ since below that value the support completely absorbs the infrared energy. Moreover, in the sense of the »metal surface selection rule«²² the observable vibrations are only those which have a change in the dipole moment component perpendicular to the metal surface. Thus, because of the presence of the C—H stretchings and the absence of the characteristic in-plane C—C stretching bands around 1600—1500 cm⁻¹, it could really be proved that benzene chemisorption is associative, parallel to the surface and the C—H bonds are bent away from the surface. The results of other experiments, however, indicate that the situation is more complicated and thus make this conclusion questionable. These are summarized as follows:^{11,21}

(i) Cyclohexene, cyclohexadienes and benzene give identical spectra under comparable conditions.

(ii) A high amount of cyclohexane is formed when these molecules are adsorbed.

(iii) On the metal surface, a carbon deposit develops.

(iv) Spectra of adsorbed C_6D_6 reveal extensive C—D bond breaking (hydrogenation of carbon deposits).

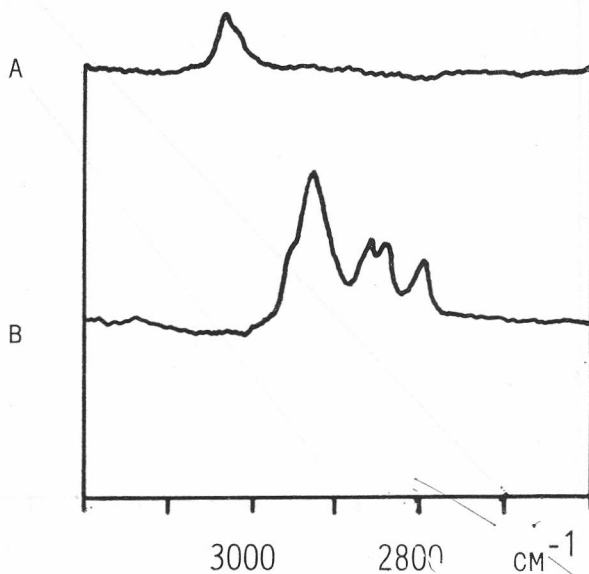


Figure 3. IR spectra of chemisorbed benzene on Pt/SiO₂

A — 34 Pa vapour introduced and evacuated;

B — after introduction of 40 Pa hydrogen.

Taking into account the results mentioned above a different interpretation seems more reasonable.¹¹ The adsorption of C_6 ring compounds follows essentially the same process and it is a dissociation resulting in the formation of a saturated product (cyclohexane) which is desorbed and the surface becomes covered by a strongly bound carbon deposit. The presence of aromatic or mainly olefinic C—H bands can be explained by supposing that on defect sites, crystallite edges, kinks, *etc.* the dehydrogenation is not complete on the surface.

It is also reasonable to suppose that the carbonaceous overlayer has an ordered structure, especially in those cases when ordering is preferred by the common hexagonal symmetry of the C_6 rings and the metal, *e.g.* on the (111) faces. If this is so, the model explains those discrepancies reported in Ref. 20. The surface carbon concentration measured by Auger spectroscopy was much higher (on Pt(111)) than the one calculated from the LEED structures if associative benzene adsorption was assumed. With dehydrogenated rings much denser structures can be constructed having carbon concentration in good agreement with that reported in Ref. 20.

b) Benzene on Ni/SiO₂

Slightly different behaviour was observed in the study of benzene adsorption on a silica supported nickel catalyst.^{24,25} Two different Ni/SiO₂ catalysts were investigated: one with high hydrogen contamination (»hydrogen rich«), the other with low hydrogen contamination (»hydrogen poor«).

Very strong and total hydrogenation of the aromatic ring was established on a hydrogen rich Ni/SiO₂ surface at room temperature and low pressures. The weak IR bands in the 2850—2970 cm⁻¹ region (Figure 4B) suggest that benzene is chemisorbed with the loss of its aromatic character and without formation of a pi-complex like in the case of organometallic sandwich type molecules. A detailed study of the CH stretching bands showed that the formation of aliphatic hydrocarbon(s) is similar to the structure developed by the chemisorption of *n*-hexane under identical conditions. The observed frequencies are summarized and approximately assigned in Table II.

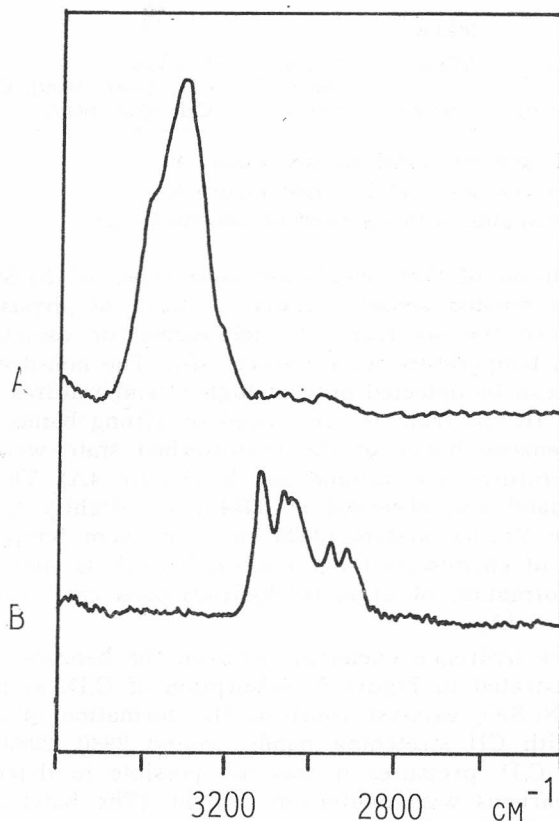


Figure 4. IR spectra of chemisorbed benzene on Ni/SiO₂

A — 2 kPa vapour introduced and evacuated at 350 K.

B — 1.2 Pa vapour introduced and evacuated at 300 K.

Ni/SiO₂ catalyst with 5% Ni on Cab—O—sil; prepared from Ni(NO₃)₂ at 710 K under stream of H₂ and cooling to 300 K under H₂ (hydrogen rich). The hydrogen poor catalyst was cooled under vacuum.

Adsorption of C_6H_6 on a »hydrogen poor« Ni/SiO₂ catalyst at low pressures led to the formation of aliphatic hydrocarbon(s) similar to those of the chemisorption of *n*-propane under similar conditions. The observed bands and their assignments are presented in Table II.

TABLE II

IR Spectra of Chemisorbed Aliphatic Hydrocarbons Formed from Benzene at 300 K

Ni/SiO ₂ /H ₂ (1)	<i>n</i> -C ₆ H ₁₄ on Ni/SiO ₂	Ni/SiO ₂ / vacuum (2)	<i>n</i> -C ₂ H ₁₀ on Ni/SiO ₂	Assignment
2962 vs	2960 vs	2960 vs	2960 vs	CH ₃ asym. stretch
2925 vs	2925 vs	2920 sh	2940 sh	CH ₂ asym. stretch
		2898 s	2890 sh	
		2882 s	2880 m	
2874 m	2874 m			CH ₃ and CH ₂ sym. stretch
2860 m, w	2857 m			
		2840 w		
	2770 vw	2775 w	2760 w	2 × 1380
— (3)	1465 m	— (3)	1468 w	CH ₃ asym. bend, CH ₂ scissoring
1380 sh	1380 w, m	(1405 w)	1380 w	CH ₃ sym. bend

Remarks: (1) Hydrogen rich catalysts (see Figure 4).

(2) Hydrogen poor catalyst (see Figure 4).

(3) Overlapping with ν_{19} band of adsorbed C_6H_6 .

Further addition of C_6H_6 yields, on both types of Ni/SiO₂ catalysts, IR bands of weakly bonded benzene similar to those of physisorbed C_6H_6 . Our attempts to record the spectrum of chemisorbed or associatively adsorbed benzene at room temperature were unsuccessful. The non-dissociative adsorption of benzene can be detected only at higher temperatures because at room temperature the IR spectrum is overlapped by strong bands of the physisorbed benzene. Benzene bands of the chemisorbed state were observed only at higher temperatures, *i. e.* around 350 K (Figure 4A). The main aromatic CH stretching band was observed at 3034 cm⁻¹, slightly higher than those obtained for the Pt/SiO₂ system (3028 cm⁻¹) at room temperature. The CH stretching band of chemisorbed benzene on Ni/SiO₂ is shown in Figure 4A. Traces of the formation of aliphatic hydrocarbons can also be detected at 350 K (see Figure 4A).

The intensive hydrogen exchange between the benzene ring and surface hydrogen is illustrated in Figure 5. Adsorption of C_6D_6 at low pressures on hydrogen rich Ni/SiO₂ catalyst confirms the formation of surface aliphatic hydrocarbons with CH stretching bands around 2980, 2960 and 2925 cm⁻¹. Even at higher C_6D_6 pressures it was not possible to detect any bands of aliphatic hydrocarbons with deuterium content. (The band at 2290 cm⁻¹ belongs to the physisorbed C_6D_6 .)

Free benzene belongs to the D_{6h} symmetry group. Weak perturbations (physisorption, chemisorption) caused by symmetry lowering can successfully be detected by vibrational spectroscopy. As a result of chemisorption, among other effects some infrared inactive vibrations might become active or considerable shifts of some frequencies might be observed.

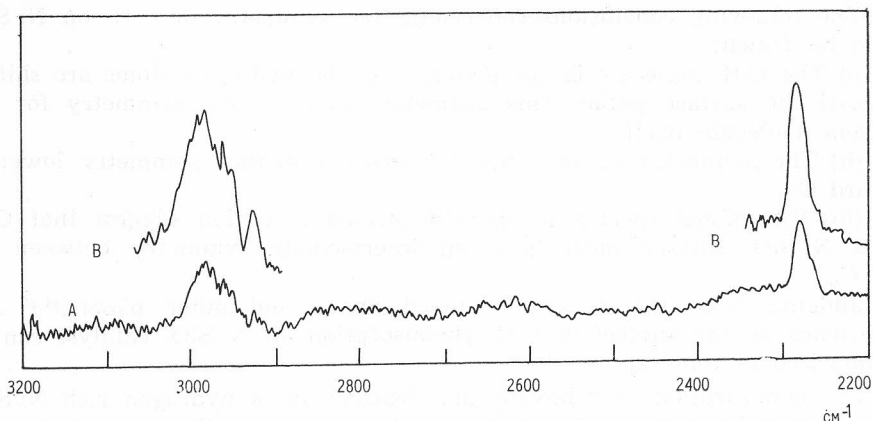


Figure 5. IR spectrum of adsorbed C_6D_6 on Ni/SiO_2 3.7 kPa vapour introduced and evacuated. (Catalyst: see Figure 4) A — original spectrum, B — scale expanded and smoothed spectrum.

To illustrate these phenomena the CH stretching bands for chemisorbed benzene are summarized in Table III. The most intensive infrared band can be assigned to the ν_{20} infrared active mode of e_{1u} species and the high frequency Raman line at 3060 cm^{-1} can be reasonably interpreted as the ν_1 mode of a_{1g} species. The appearance of ν_2 and ν_7 modes in the infrared spectra as weak shoulders and the presence of ν_{20} band in the Raman spectrum suggest that the original D_{6h} symmetry of free benzene is substantially lowered. According to the surface selection rules²² the in-plane CH stretching modes of C_6H_6 are allowed in the case of nonplanarity of benzene. The nonplanar benzene belongs to C_{6v} symmetry group, but for this point group the ν_7 band is not active in IR spectrum.

TABLE III

CH Stretching Bands of Chemisorbed C_6H_6 on Supported Metal Catalyst

Pt/SiO ₂ ^a infrared (cm ⁻¹)	Ni/SiO ₂ ^b infrared (cm ⁻¹)	Ni/SiO ₂ ^c Raman (cm ⁻¹)	Approximate Assignment (d)
3070 vw	3053 sh	3060 s	ν_2 (a_{1g})
3028 s	3043 s	3040 s	ν_{20} (e_{1u})
3018 sh	3020 sh	3016 w	ν_7 (e_{2g})

^a See Figure 3A; ^b See Figure 4A; ^c Ref. 26.

(d) Benzene modes are taken from Ref. 27.

The surface enhanced Raman spectrum of chemisorbed benzene and deuterated benzene showed a number of forbidden additional bands which were attributed to symmetry lowering produced by the site symmetry of the surface. It was suggested that in an adsorbed state on Ni/SiO_2 the benzene molecule belongs to C_{3v} symmetry group.²⁶ The C_{3v} symmetry involves four IR and Raman active CH stretching bands which is in agreement with experimental observation.

The following conclusions concerning the symmetry of C_6H_6 on Ni/SiO_2 could be drawn:

(i) The C_6H_6 molecule is not planar, e.g. the hydrogen atoms are shifted towards the surface plane. This geometry refers to C_{6v} symmetry for the benzene molecule itself.

(ii) The symmetry of the surface causes a further symmetry lowering toward C_{3v} .

(iii) Vibrational spectra in the CH stretching region suggest that C_6H_6 on a Ni/SiO_2 surface must have an intermediate symmetry between C_{6v} and C_{3v} .

Judging from the results discussed above and other papers,^{24,25} our experience on the subject of C_6H_6 chemisorption on Ni/SiO_2 catalyst can be summarized as follows:

(i) Chemisorption of *n*-hexane and benzene on a hydrogen rich Ni/SiO_2 surface gave identical spectra under similar conditions. The same is true of *n*-butane and benzene adsorption on a »hydrogen poor« surface.

(ii) As a result of ring opening and strong hydrogen exchange the most active sites of a Ni/SiO_2 catalyst are occupied by aliphatic hydrocarbons and possible carbon deposits at the beginning of the exposure to a low pressure of C_6H_6 .

(iii) If the activity for ring opening and benzene cracking are compared, it can be concluded that the Ni/SiO_2 catalyst is more active than the Pt analogue.

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SAŽETAK

FT-IR spektroskopski studij katalize

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Ukratko se raspravlja uloga FI-IR spektroskopije u katalitičkim istraživanjima, te se daju tipični primjeri. Infracrveni spektri slabo vezanog vodika na Pt/SiO₂ otkrivaju nehomogenost površine. Koncentracija na površini opisuje se Temkinovom izotermom. Adsorpcija spojeva s nezasićenim šesteročlanim prstenom na površini Pt/SiO₂ siromašnoj vodikom u biti je samohidrogenacijski proces, koje rezultira talogom cikloheksana i ugljika na metalnim površinama.

Kemisorpcija *n*-heksana i benzena na površinama Ni/SiO₂ bogatima vodikom daje identične spektre pod sličnim uvjetima. Ista pojava utvrđena je za *n*-butan i benzen na površinama siromašnim vodikom. Infracrveni i Ramanovi spektri C₆H₆ na Ni/SiO₂ upućuju na sniženje simetrije, nešto između C_{6v} i C_{3v}, koja je posljedica neplanarnosti C₆H₆ i položajne simetrije površine.