FTIR STUDY OF BENZENE CHEMISORPTION ON Pt/SiO2

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ABSTRACT

Infrared spectra of chemisorbed benzene suggest that under "hydrogen free" conditions the surface reaction is essentially a self hydrogenation process resulting in the formation of cyclohexane and a deposit of strongly bound overlayer of C_6 rings what have lost practically all their hydrogens. C_6D_6 adsorption reveals that H (D) atoms are in fact highly mobilized as H-D exchange in the adsorbed layer and spill-over of D atoms to the support are also observed. Another weakly bound surface species is also found that has non-planar, distorted structure and can be easily hydrogenated. The cabonaceous deposit formed initially by dehydrogenation can probably be compressed into a planar, close packed monolayer and since it adsorbs reversibly hydrogen, it likely forms a catalitically active surface in those reactions involving hydrogen transfer.

INTRODUCTION

Benzene chemisorption on transition metals is of great practical and theoretical importance. Accordingly, several studies of its structural properties have been performed by different experimental methods on Pt surfaces. However, results still seem somewhat contradictory.

Vibrational spectroscopies on Pt(111) and Pt(110) single crystal surfaces (refs. 1-3), Raney-Pt (ref. 4) and Pt/SiO₂ (refs. 5-7) concluded in associative adsorption with the ring plane parallel to the surface. However, the appearance of CH stretchings in the adsorbed state suggested that either the CH bonds are bent out of the molecular plane, or another distortedly adsorbed form also exists on the surface. On the other hand, it was suggested by LEED and Auger spectroscopic measurements (ref. 8) that surface layer consists of planar molecules inclined to the surface, since the surface carbon concentration was much higher than that allowed by parallel adsorption.

In this report IR spectra of adsorbed benzene is discussed with special attention to the problems outlined above.

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METHODS

The Pt/SiO₂ catalyst containing 16% w/w of the metal was prepared by impregnating Cabosil HS5 silica with a H_2PtCl_6 solution. The dried catalyst was pressed into thin pellets, calcined in air at 720 K and reduced in hydrogen flow at 620 K in the adsorption cell. After completing the reduction, samples were evacuated at the reduction temperature and allowed to cool down in vacuum. Though samples pretreated such manner are often referred to as "hydrogen free", it was found that those still contained a substantial amount of strongly chemisorbed hydrogen (ca. 30% of a monolayer) (ref. 9). The average metal particle size was found to be 6.5 nm (calculated from CO chemisorption data measured on samples pretreated under the conditions), same thus the "metal-particle surface selection rule" should be taken into account (ref. 11). As a consequence, only those vibrations having a dynamic dipole moment component perpendicular to the surface can be observed on the spectra.

Adsorption was performed at room temperature. The infrared cell and vacuum system were constructed of stainless steel and have been described elsewhere (ref. 10). Infrared spectra were measured on a Digilab FTS-20C Fourier-transform spectrophotometer at a nominal resolution of 4 cm⁻¹, between 4000 and 1300 cm⁻¹. At lower frequencies no useful spectra could be recorded because of the strong infrared absorption of the support.

RESULTS AND DISCUSSION

Introduction of benzene vapour to the sample results in spectrum of Fig. 1a. It is similar to that of benzene physisorbed on the metal-free SiO_2 support except the 2800-3000 cm⁻¹ region where the strong CH₂ bands of gas phase and adsorbed cyclohexane indicate hydrogenation. No CH₃ bands are seen, hence no cracking or ring opening occurs. Upon evacuation all the bands disappear except a small, asymmetric one at 3040 cm⁻¹ (Fig. 1b). All these phenomena can be explained by simple adsorption (in accordance with earlier reports), i.e. first benzene is hydrogenated by residual surface hydrogen, then it is adsorbed associatively parallel to the surface. H atoms are slightly bent out of the plane of the carbon ring, thus CH stretchings acquired a small dipole moment change component perpendicular to the surface. Hence, in the sense of the metal-particle surface selection rule (ref. 11), they appear as low intensity bands above 3000 cm⁻¹.

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Further experiments, however, reveal a more complicated process. IR spectrum of adsorbed C_6D_6 is shown on Fig. 1c. It is seen that upon introduction of perdeutero-benzene to a fresh Pt/SiO₂ sample - besides the CD stretching of adsorbed C_6D_6 (denoted as =C-H on Fig. 1c.) - bands of other deuterium and hydrogen vibrations appear indicating that D atoms are in fact highly mobilized and several concurrent reactions take place on the surface. Presence of CD₂ bands reveals self-deuteration, the



Fig. 1. A - IR spectrum of adsorbed benzene with 53 Pa vapour in the cell; B - spectrum of chemisorbed benzene, gas phase evacuated; C - IR spectrum of adsorbed perdeutero-benzene with 34 Pa vapour in the cell.

unsaturated CH band above 3000 cm^{-1} refers to H-D exchange in adsorbed molecules and the OD band shows that D atoms spilled over to the support as well. (The feature of derivative shape around 2000 cm^{-1} is caused by adsorbed CO present as a contamination on the metal surface.)

If H_2 is added to chemisorbed benzene the 3040 cm⁻¹ band disappears and CH₂ bands are seen but no hydrocarbon is observed in the gas phase (Fig. 2a.). Evacuation and repeated addition of hydrogen result in disappearance and reappearance of the CH₂ bands, respectively. Such cycles can be performed several times without degradation of the spectra. The 3040 \rm{cm}^{-1} band is not observed any more after the first H2 introduction. It shows that the surface is covered with carbon deposit which can reversibly take up or release a substantial amount of hydrogen but cannot be removed as a saturated hydrocarbon under such conditions. If benzene is introduced again to samples already covered by carbon deposit, the 3040 $\rm cm^{-1}$ band has higher intensity than after the initial adsorption (Fig. 2b.). This can be explained supposing that the band is actually caused by those molecules adsorbed on edges, kinks, defect sites, etc. of the surface and have a distorted, non-planar structure because not all their carbon atoms can be bonded to the surface and therefore not all the hydrogen atoms have been removed.



Fig. 2. IR spectra of chemisorbed benzene in the C-H stretching region. A - difference spectrum; negative band: 34 Pa benzene introduced and evacuated; positive bands:after introduction of 40 Pa hydrogen.

B - 34 Pa benzene is chemisorbed on carbon contaminated surface. (cf. band intensity with that of the negative band on Fig. 2.A)

CONCLUSIONS

IR spectra of adsorbed C_6H_6 and C_6D_6 clearly show that, instead of associative adsorption, chemisorbed benzene is dehydrogenated on the Pt surface. Detached hydrogen atoms can enter into different reactions but it is reasonable to suppose that finally they are used up e.g. in cyclohexane molecules. Hence the metal surface remains covered with a strongly hydrogen deficient carbonaceous deposit which cannot be removed by hydrogen addition at room temperature. This process probably does not cause catalyst deactivation, since the carbon deposit is able to adsorb substantial amount of hydrogen. Hence it is likely active at least in surface reactions involving hydrogen transfer. In addition to those molecules that could reach the metal surface with all their carbon atoms (and therefore have lost all their hydrogens) another form of benzene is adsorbed on particle edges and defect sites that likely has non-planar, distorted structure. This surface species is less strongly bound and can be easily removed by hydrogen in the form of cyclohexane. On the other hand, no structures like surface phenyl groups were found since such structures should have intensive bands in the region characteristic of the ring vibrations of monosubstituted benzene compounds (below 1700 cm⁻¹).

This model can also explain some contradictions observed earlier. LEED and Auger measurements (ref. 8) on Pt(111) showed a metastable benzene which was rearranged into a denser, stable structure upon pumping. However, the surface carbon concentrations (37 and 46 C-atom/nm², respectively) were higher than that of the densest structure which could be depicted supposing associative adsorption (11 C-atom/nm²). According to the present results this problem is easily solved, since by compression of the dehydrogenated C₆ rings a graphite-like structure (40 C-atom/nm²) or even a close packed hexagonal structure (50 C-atom/nm²) can be formed on Pt(111). Obviously, these considerations refer only to the possible geometries of the carbonaceous layer but present measurements offer no experimental evidences concerning their reality.

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