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Fourier Transform–Infrared Study of the Adsorption of Unsaturated and Aromatic Hydrocarbons on the Surface of α-Fe_2O_3

II. Benzene

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Benzene adsorption on α-Fe_2O_3 in the temperature range 300–673 K has been studied. Two different molecular adsorbed forms can be distinguished due to their spectroscopic behavior and the different equilibrium pressures needed for their formation. The more stable form, in which the benzene molecule is π-bonded on exposed metal cations, slowly transforms at room temperature into combustion products. This process is inhibited by the presence on the surface of the second form of adsorbed benzene.

INTRODUCTION

In the preceding paper we have observed π-bonding, room temperature slow combustion, and high temperature partial oxidation of ethylene on the surface of α-Fe_2O_3 (*1*). The adsorption sites have been identified as exposed iron cations (*1*).

Interaction of the aromatic π-electron system would be involved in the mechanisms of selective dehydrogenation of ethylbenzene (*2*) and nonselective oxidation of benzene (*3*) on iron oxide catalysts. However, very few data are reported in the literature about adsorption of aromatics on transition metal oxides (*4, 5*).

We have now studied by FT–ir spectroscopy the interaction of benzene with α-Fe_2O_3 with the aim to identify adsorption sites and conditions, if they are, of partial or total oxidation of this very stable molecule.

EXPERIMENTAL

Sample preparation and pretreatments, and experimental conditions were the same as reported in Part I (*1*).

Benzene and benzene-d_6 were hyperpure products from Carlo Erba (Milan, Italy) and were purified by several freeze–pump–thaw cycles.

Experimental work was performed with a Nicolet 6000 C Fourier Transform Infrared Spectrometer at the Stazione Sperimentale per i Combustibili (San Donato Milanese, Italy).

RESULTS AND DISCUSSION

(*a*) *Infrared Spectra after Adsorption at Room Temperature*

Figure 1 shows the spectrum of an "oxygen-rich" (*6*) α-Fe_2O_3 sample at increasing times of contact with 1.33×10^3 N m^{-2} of benzene vapor, in the region 2000–1100 cm^{-1}. We can observe the immediate appearance of new bands at 1979, 1839, 1481, 1403, and 1178 cm^{-1}, for which assignments are given in Table 1. This species, which will be called benzene I, shows a significant enhancing of the frequencies corresponding to $\nu_5 + \nu_{17}$, $\nu_{10} + \nu_{17}$, and $\nu_5 + \nu_{16}$ combination vibrations, all composed by out-of-plane deformation vibrations. By increasing the time of contact we can also observe (i) a progressive perturbation of the bands, observed in the region 1350–1250 cm^{-1} in the starting haematite sample (*6*); (ii) a progressive intensification of a new band centered at 1620 cm^{-1}. During these transfor-

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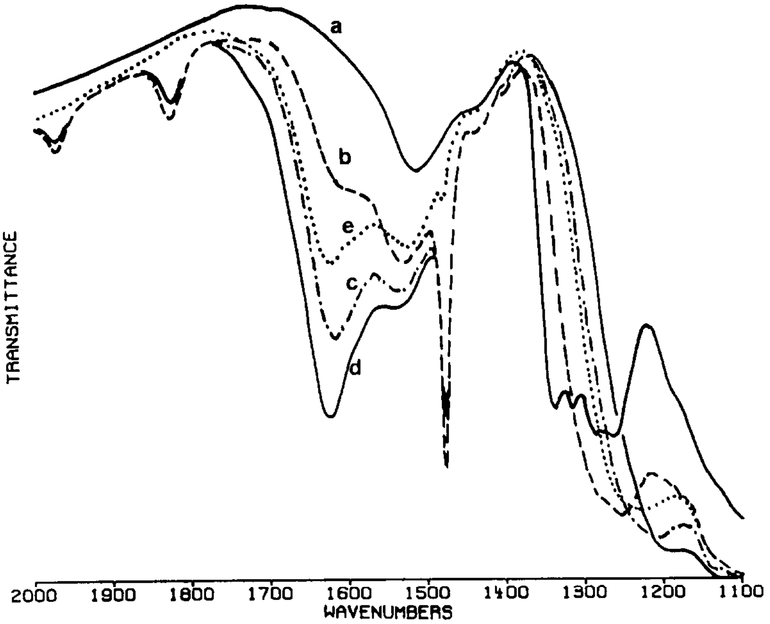

FIG. 1. Infrared spectra of benzene adsorbed on α-Fe_2O_3: (a) "oxygen-rich" α-Fe_2O_3 disk; (b)–(d) after contact with benzene vapor at 1.33×10^3 N m^{-2} at room temperature (r.t.) (b) 5 min, (c) 10 min, (d) 4 h; (e) sample d degassed at r.t. for 30 min.

mations the intensities of the bands connected with adsorbed benzene decrease very slowly.

Figure 2 shows the same spectral region during contact with increasing pressures of benzene vapor. At 2×10^3 N m^{-2} pressure both the higher frequency combinations split, with lower frequency components at 1964 and 1821 cm^{-1}. These become predominant at 2.66×10^3 N m^{-2}, when also the $\nu_5 + \nu_{16}$ absorption is shifted to 1395 cm^{-1} (Fig. 2d) and ν_{19} is observed at 1479 cm^{-1}.

TABLE 1

Vibrational Frequencies (cm^{-1}) of Benzene Adsorbed on Haematite

Benzene ads. on α-Fe_2O_3		Liquid	Assignments (Ref. (7))	Notes
I	II			
3093	3089	3091	ν_{20}	Fermi resonance
3071	3069	3072	$\nu_{18} + \nu_{19}$	
3039	3038	3036	$\nu_1 + \nu_6 + \nu_{19}$	
2328	2327	2328	$\nu_{10} + \nu_{19}$	
2211	2210	2214	$\nu_9 + \nu_{18}$	
1979	1964	1960	$\nu_5 + \nu_{17}$	
1839	1821	1815	$\nu_{10} + \nu_{17}$	
	1755	1755	$\nu_6 + \nu_{15}$	
1481	1479	1479	ν_{19}	
1403	1395	1393	$\nu_5 + \nu_{16}$	
	1346	(1346)	ν_3	Inactive in D_{6h} symmetry
1178	1178	(1178)	ν_9	Raman active in D_{6h} symmetry
1036	1036	1036	ν_{18}	

Comparison of spectra reported in Figs. 1 and 2 indicates that at higher benzene vapor pressures the band at 1620 cm^{-1}, due to a transformation product, remains less intense. Moreover, at higher pressures only the two higher frequency bands of the adsorbent in the region 1350–1250 cm^{-1} are perturbed while a band at 1346 cm^{-1} reappears, not detected with benzene-d_6, possibly due to the activation of ν_3, usually inactive, on the second adsorbed species of C_6H_6 (benzene II). This second species, responsible also for the components at 1964, 1821, and 1395 cm^{-1}, is formed at higher pressures, is quickly desorbed by brief evacuation and is not formed by transformation of benzene I. An overview of all the

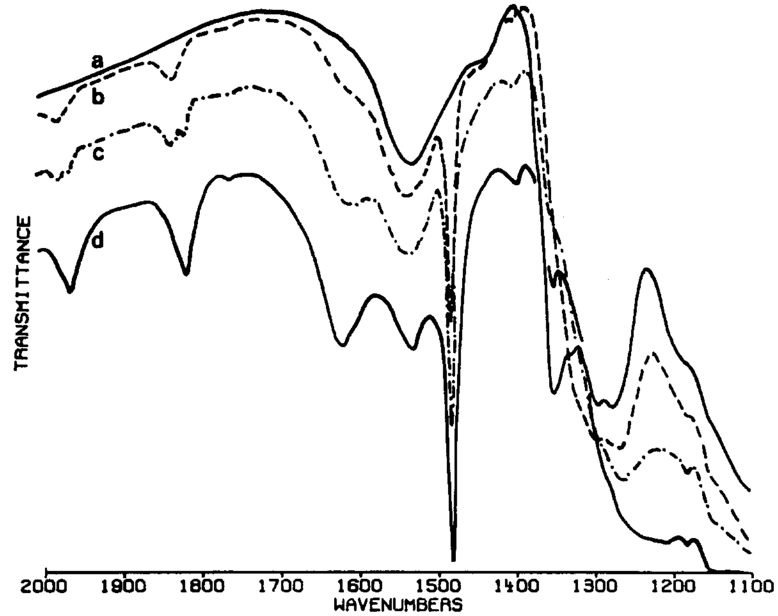

FIG. 2. Infrared spectra of benzene adsorbed on α-Fe_2O_3: (a) "oxygen-rich" α-Fe_2O_3 disk; (b)–(d) after short contact with benzene vapor at r.t., (b) 1.33×10^3 N m^{-2}, (c) 2×10^3 N m^{-2}, (d) 2.66×10^3 N m^{-2}.

available spectral range indicates some changes in the intensities of the single bands of adsorbed benzene, where, in particular, the intensity ratio of ν_{19} and ν_{20} is reversed with respect to the liquid.

Figure 3 shows that also for perdeuterobenzene adsorption two species are successively formed (Table 2); in this case the first formed species is again characterized by an enhancement of the frequencies due to the combinations of out-of-plane vibrations, observed, very weak, at 1640, 1472, and 1184 cm^{-1}. However, d_6-benzene II more clearly shows a remarkable lowering of ν_{20} and ν_{19} fundamental frequencies (asymmetric CD and CC stretchings) to 2271 and 1326 cm^{-1}.

Adsorption of both benzene and benzene-d_6 reversibly shifts surface OH's (Fig. 4), more weakly in the case of C_6D_6 (from 3670–3640 to 3600 cm^{-1}) than in the case of C_6H_6 (to 3590 cm^{-1}). However, broad adsorptions are formed near 3300 and 2550 cm^{-1}, that grow in parallel with the band at 1620 cm^{-1}, due to benzene and perdeuterobenzene transformation on the surface, respectively. The spectrum of C_6H_6 in the region 3100–3000 cm^{-1} appears practically unperturbed by adsorption, although at higher coverages a higher complexity of this region can be noticed (Fig. 4).

(*b*) *Molecular Adsorption of Benzene*

The ir spectrum of adsorbed benzene I, showing, as already cited, an enhancement of the out-of-plane vibrational frequencies, indicates that there is an interaction with an electron-withdrawing center nearly perpendicular to the ring. The extent of the enhancement on α-Fe_2O_3 is more pronounced than those observed after contact with a stronger H-bonding donor such as silica (*8*) or with a Brønsted acidic adsorbent such as H-Y-Zeolite (*9*). However, it is smaller than that measured on the Lewis form and on Na- and Ca-exchanged Y-Zeolites (*9*), where interaction with surface cations appears to be well founded. These considerations, together with the experimental observation of the perturbation of the bands in the region 1350–1250 cm^{-1}, in the same way as occurs with several basic molecules (*6*,

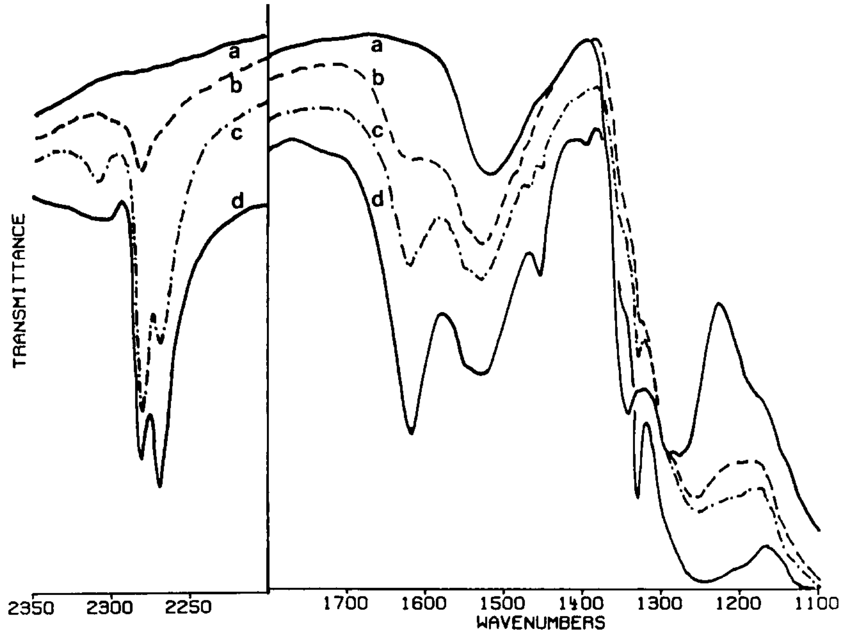

FIG. 3. Infrared spectra of benzene-d_6 adsorbed on α-Fe_2O_3: (a) "oxygen-rich" α-Fe_2O_3 disk; (b)–(d) after short contact with benzene-d_6 vapor at r.t.: (b) 1.33×10^3 N m^{-2}, (c) 2×10^3 N m^{-2}, (d) 2.66×10^3 N m^{-2}.

10), indicate that formation of benzene I takes place on rather strong Lewis acidic centers. This is confirmed by the observation that no benzene adsorption is detected on wet surfaces, where water poisons Lewis acid sites.

The most relevant spectral features of benzene II are the lowerings of the in-plane vibration frequencies ν_{19} and ν_{20}, and possibly the activation of ν_3. These perturbations are similar (although smaller in extent) than those observed when benzene coordinates on a reduced metal center, as on di-benzene–chromium and analogs (*11*) and on species adsorbed on metals (*12*). Moreover, the measured shifts on adsorbed C_6D_6, although small, cannot be justified, in our opinion, by a simple H-bonding interaction. It seems probable, then, that benzene II is also adsorbed on a metal center, possibly reduced or sterically hindered. The *d* character of metal centers on α-Fe_2O_3 would justify the formation of π-bonded forms, not observed on the more acidic Al_2O_3 (*12*).

TABLE 2

Vibrational Frequencies (cm^{-1}) of Benzene-d_6 Adsorbed on Haematite

Benzene-d_6 ads. on α-Fe_2O_3		Liquid	Assignments (Ref. (*7*))	Notes
I	II			
	2390	2385	$\nu_3 + \nu_{19}$	Fermi resonance
2283	2270	2281	ν_{20}	
		2269	$\nu_1 + \nu_{19}$	
1640	1623	1619	$\nu_5 + \nu_{17}$	
1472	1451	1453	$\nu_{10} + \nu_{17}$	
1329	1326	1330	ν_{19}	
1185	1185	1181	$\nu_5 + \nu_{16}$	
812	812	812	ν_{18}	

The perturbation of surface OH's would be due to interaction of some benzene hydrogens with the nonbonding orbitals of hydroxylic oxygens, so justifying the small isotopic effect previously observed.

(*c*) *Reactivity of Adsorbed Benzene at Room Temperature*

Absorptions in the 3300-cm^{-1} region and at 1620 cm^{-1}, which progressively appear at

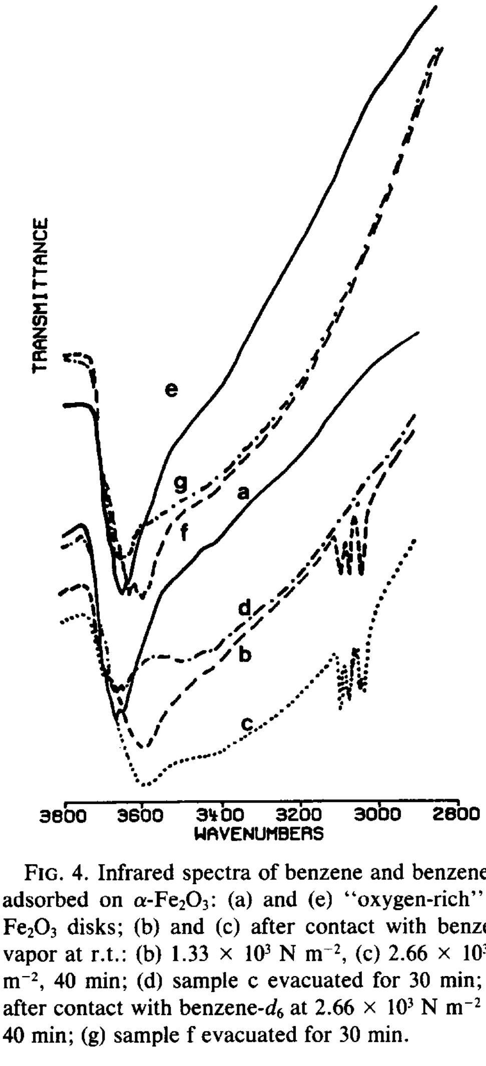

FIG. 4. Infrared spectra of benzene and benzene-d_6 adsorbed on α-Fe_2O_3: (a) and (e) "oxygen-rich" α-Fe_2O_3 disks; (b) and (c) after contact with benzene vapor at r.t.: (b) 1.33×10^3 N m^{-2}, (c) 2.66×10^3 N m^{-2}, 40 min; (d) sample c evacuated for 30 min; (f) after contact with benzene-d_6 at 2.66×10^3 N m^{-2} for 40 min; (g) sample f evacuated for 30 min.

increasing times of contact (Figs. 1 and 4), can be assigned to adsorbed water and bidentate carbonates as in the case of ethylene combustion, detected in the same conditions. A comparison of the trends of the intensities of the ν_{19} band of adsorbed benzene and of the 1620-cm^{-1} band of carbonates and water indicates that greater and increasing amounts of combustion products are observed when only benzene I is present. This would indicate that benzene II, present on the surface at higher vapor pressures, inhibits benzene I combustion possibly by hindering the conformation needed for its oxidation or by blocking the electron transfer from active sites. No bands due to compounds other than benzene are observed in the gas phase after treatments of Figs. 1, 2, and 3. By short duration heating at 673 K of a sample previously treated as in Fig. 1e, i.e., one which only shows the band at 1620 cm^{-1}, CO_2 is detected in the gas phase through its PR band centered at 2340 cm^{-1}.

No intermediates are obtained in benzene I oxidation to carbonates; this may be due to their rate of formation being smaller than that of decomposition.

(*d*) *Adsorption at Higher Temperatures*

Contact of the haematite surface with benzene at temperatures intermediate between 300 and 673 K does not cause significant changes in the spectra: increasing amounts of CO_2 and H_2O are observed. Isotopic exchange of OH's is complete after contact with benzene-d_6 at 573 K for 20 min; in these conditions there is a single PR band in the gas phase centered at 3061 cm^{-1} which can be assigned to a partially deuterated species formed by isotopic exchange, probably C_6D_5H.

If contact is maintained at 673 K for more than 30 min, surface reduction causes complete loss of transmittance of the samples, and CO_2 is observed in great amounts in the gas phase. Disks reduced in benzene can be reoxidized in oxygen at 673 K, but these samples show an intense sharp band, without rotational components, at 2355 cm^{-1}, which resists evacuation and which is due to trapped CO_2 molecules formed by oxidation of carbonaceous material deposited during high temperature contact.

If contact at 673 K is carried out for brief times the spectrum collapses in the region below 1350 cm^{-1} as for vacuum treatment at the same temperature (*6*), due to a faster partial reduction (Fig. 5). In these conditions bands are observed at 1567, 1550, 1464, 1445, 1243, 1135, and 1040 cm^{-1}. The same treatment in C_6D_6 causes the formation of bands at 1546, 1532, 1408, 1392, and 1128 cm^{-1}. These bands are certainly due to

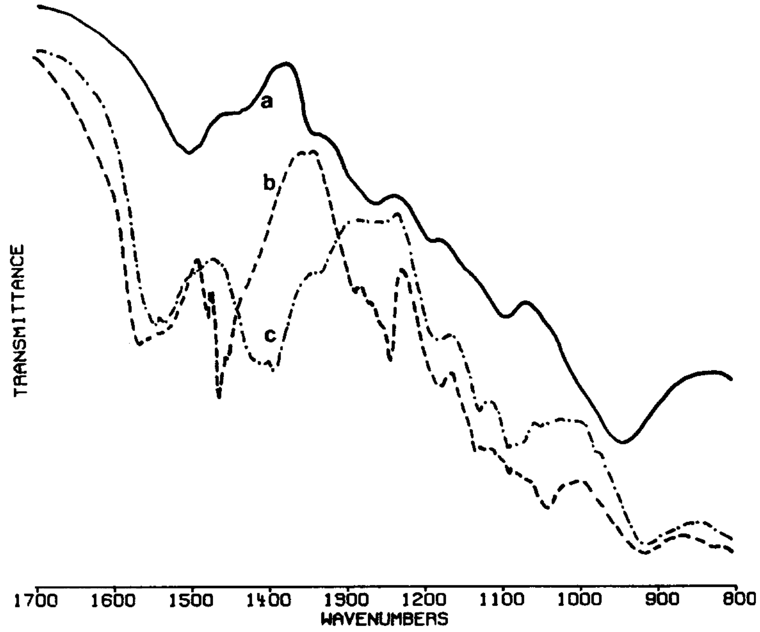

FIG. 5. Infrared spectra of α-Fe_2O_3 disks heat-treated at 673 K: (a) 1 h under evacuation, (b) 20 min in 3.33×10^3 N m^{-2} of benzene, (c) 20 min in 3.33×10^3 n m^{-2} of benzene-d_6.

transformation products of benzene, which however are further oxidized to CO_2 which leaves the surface. They do not correspond to bands of C_1 or C_2 oxidized fragments, and must be due to species again containing CH (or CD) bonds, as indicated by their isotopic shift. The position and number of these bands seem to indicate aromatic character. However, we were not able to identify these species with more certainty.

CONCLUSIONS

This work has shown that benzene adsorbs on α-Fe_2O_3 in two different π-bonded forms coordinated on surface metal centers. One of these species is the first step of a slow combustion which starts already at room temperature.

Only traces of unidentified partial oxidation products are observed after contact for short times at 673 K.

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