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MICROCALORIMETRIC AND FT–IR SPECTROSCOPIC STUDY OF BENZENE ADSORPTION ON α-Fe_2O_3 AND γ-Al_2O_3

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The adsorption of benzene at room temperature on α-Fe_2O_3 and on γ-Al_2O_3 powders was investigated by heat-flow microcalorimetry and FT–IR spectroscopy.

On iron oxide a chemisorption-combustion step is followed by a highly exothermic adsorption step, reversible at r.t.

Few combustion centres exist on alumina if reducing pretreatment is not carried out. Two reversible adsorption steps are subsequently observed and were interpreted as due to interaction with two different types of surface hydroxy groups.

Adsorption microcalorimetry is a powerful technique for the energetic characterization of solid surfaces, as well as for the thermodynamic description of solid-gas interface phenomena [1, 2].

Its coupling with qualitative techniques, such as surface spectroscopies, allows complete indications to be obtained, even when different surface interactions occur simultaneously.

We have undertaken the study, by adsorption calorimetry and Fourier transform infrared spectroscopy [3], of the adsorption of some hydrocarbons on metal oxides having different surface properties and chemical natures.

We report here the results of our investigation concerning the interaction of benzene with α-Fe_2O_3, which is a component of some hydrocarbon oxidation catalysts, and has already been the object of a joint calorimetric and spectroscopic study [4]. The results are compared with those obtained on γ-Al_2O_3, whose surface is well known [5] and which exhibits mainly an acid-base character.

Experimental

Crystalline α-Fe_2O_3 samples were obtained by thermal decomposition in vacuo of crystalline geothite (α-FeOOH) and were evacuated at 673 K for 30 min only, to avoid surface reduction. γ-Al_2O_3 was aluminium oxide C from Degussa (Frankfurt am Main) and was evacuated at 673 K for 2 h (10^{-5} Torr) before adsorption experiments.

Resulting surface areas were 40 and 100 m^2 g^{-1} for iron oxide and aluminium oxide, respectively. Microcalorimetric experiments were carried out using a Tian–Calvet heat flow calorimeter, equipped with a Setaram NV 724 amplifier nanovoltmeter and a Servotrace Sefram recorder. Cells and ramps were similar to those reported by Della Gatta et al. [6].

Two adsorption runs, both at 298 K, were performed. Run 2 was carried out on samples evacuated at 298 K before run 1, since desorption was terminated, as deduced from the stability of the calorimetric baseline.

FT–IR spectra were recorded using a Nicolet MX 1 Fourier transform spectrometer. Self-supporting pressed discs underwent the same pretreatment as for microcalorimetric measurements in the IR cell.

Results and discussion

a) Benzene/iron oxide system

The difference between the calorimetric and volumetric adsorption isotherms of benzene on α-Fe_2O_3 (Fig. 1), corresponding to run 1 and run 2, indicate that an irreversible chemisorption process takes place involving about 0.5 μmol m^{-2}. Successively, a reversible adsorption process is active, as deduced from the superimposition of the run 2 curve on that corresponding to run 1 if its origin is translated. However, the plot of the integral adsorption heat (Q^{int}) in Fig. 2 shows in the region of reversible adsorption two linear branches for both the first and the second admission runs. The change of slope is at about 1.8 μmol m^{-2} for run 1, and 1.2 μmol m^{-2} for run 2. The difference between these values corresponds approximately to the number of irreversibly adsorbed molecules. We can conclude that when 1.8 μmol m^2 is adsorbed, a further change in the adsorption mechanism takes place.

The differential adsorption heats (Q^{diff}) are 150–180 kJ mol^{-1} for the irreversible mechanism, about 100 kJ mol^{-1} for the first reversible step, and 40–35 kJ mol^{-1} for the second reversible step (Fig. 2). The last value is slightly higher than the condensation heat of benzene (33 kJ mol^{-1}).

The first Q^{diff} values are much higher than those measured during benzene adsorption on hydroxylated silica (52 kJ mol^{-1} [7]), where a rather strong hydrogen-bonding interaction is foreseen. This indicates that a strong chemisorptive or reactive adsorption mechanism takes place. These results agree very well with those obtained by FT–IR spectroscopy. In fact, at low coverages, the vibrational spectra show only small shifts of surface hydroxy groups, still present on the surface under our operating conditions [4], and a significant perturbation of the two combination bands of adsorbed benzene, situated between 2000 and 1800 cm^{-1} (Fig. 3). These bands, observed at 1979 and 1839 cm^{-1}, compared to the values of 1960 and 1815 cm^{-1} measured for the liquid, have been shown to be the most sensitive to the strength of the adsorption bond [3]. These features have been interpreted [8] as due to a π-bonding interaction with exposed cations. This species is progressively oxidized on

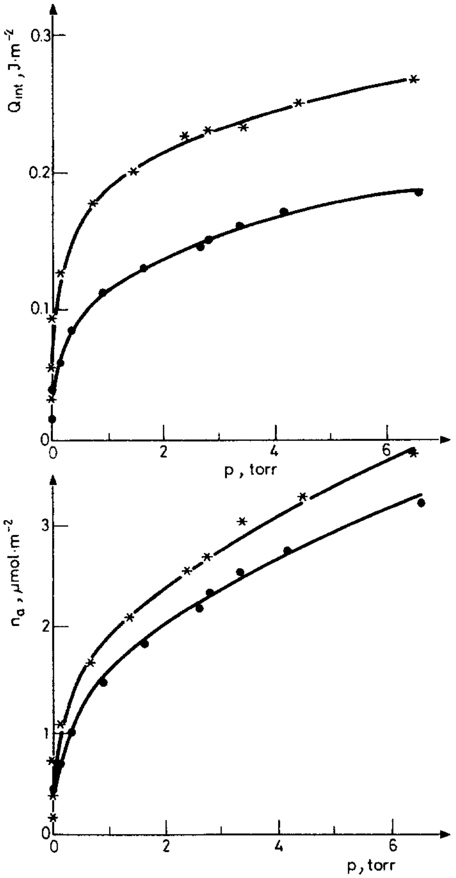

Fig. 1 Calorimetric (above) and volumetric (below) adsorption isotherms of benzene/iron oxide system, corresponding to run 1 (*) and run 2 (•) experiments

the surface, to produce carbonates and water, as deduced from the growing of a band at 1620 cm^{-1} (Fig. 3d) and by broadening of the OH stretching bands near 3400 cm^{-1}. The first step of benzene adsorption on α-Fe$_2$O$_3$ may then be interpreted as a highly exothermic adsorption-combustion mechanism.

At higher coverages, the spectroscopic features of adsorbed benzene change, as deduced from the splitting of the above combination bands (Fig. 3c) to form components of frequencies similar to those for the liquid. However, the shift of the ν_{19} fundamental vibration (more clearly observed using C_6D_6 [8]) shows that this second species is strongly perturbed, probably being chemisorbed.

This conclusion, given as a hypothesis in ref. [8], is strongly supported by the calorimetric data, the high Q^{diff} value of 100 kJ mol^{-1} being a clear indication of chemisorption.

Examination of the shapes of the curves confirms the above conclusions. In fact, the heat emission peaks corresponding to the irreversible adsorption step are signifi-

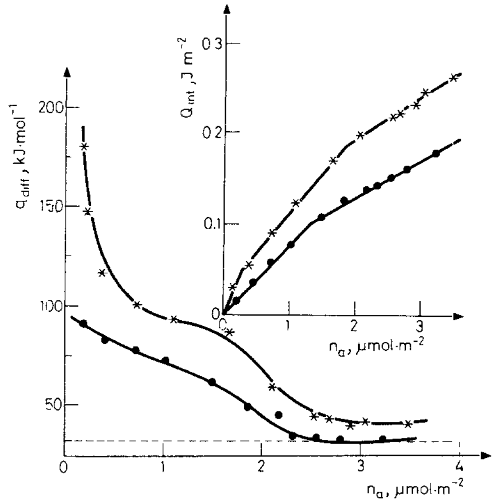

Fig. 2 Differential and integral adsorption heats of benzene/iron oxide systems, corresponding to run 1 (*) and run 2 (●) experiments

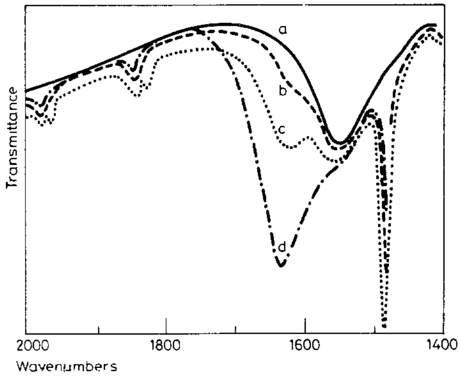

Fig. 3 FT—IR spectrum during benzene adsorption on α-Fe_2O_3. a) α-Fe_2O_3 activated disc, b) and c) in contact with increasing benzene pressures (2 min), d) after prolonged contact with benzene vapour (1 h at 1 Torr)

cantly broader than those corresponding to the first reversible step. Both times of half-deviation ($t_{1/2}$) and times of return to the baseline (t_0) are about two-thirds in the reversible region compared to those measured during the irreversible adsorption step.

This unusual behaviour cannot be explained by successive adsorption on sites of decreasing strength. It may be interpreted as due to the superimposition of a slow exothermic phenomenon (combustion) on the simple adsorptive act during the first adsorption step.

The third step may be attributed to a rather weak physisorptive interaction, possibly on surface OH's, mainly on the basis of its Q^{diff} value, which is lower than that observed for hydrogen-bonding interaction on hydroxylated silica [7].

Minor changes in the evolved heats during the reversible steps between run 1 and run 2 may be due to the presence of oxidation products on the surface.

According to the data reported by Marimoto and co-workers [9], under our operating conditions the surface would be highly dehydroxylated. The amount of OH groups still present on the surface may be evaluated to be about 1.5 μmol m^{-2} [9]. Under these conditions, more than 90% of the cationic sites exposed on the (0001) face of α-Fe_2O_3, which may be considered to be the predominantly exposed plane in our sample [4], would be available for chemisorption. We can deduce that about 5% of the exposed cation sites are able to cause benzene combustion, while another 10% remain available for reversible adsorption.

b) Benzene/alumina system

A qualitative examination of the microcalorimetric data indicates that, in the case of the benzene/alumina system too, different adsorption mechanisms occur (Figs 4 and 5).

A small number of molecules (about 0.2 μmol m^{-2}) are apparently involved in an irreversible chemisorptive step, which evolves a heat amount only slightly smaller

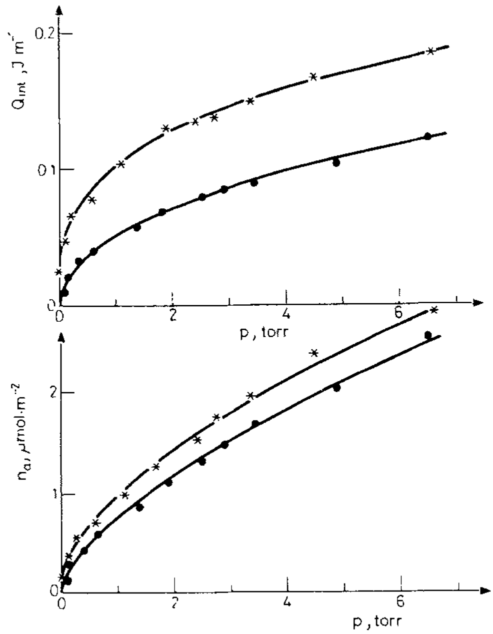

Fig. 4 Calorimetric (above) and volumetric (below) adsorption isotherms of benzene/alumina system, corresponding to run 1 (*) and run 2 (•) experiments

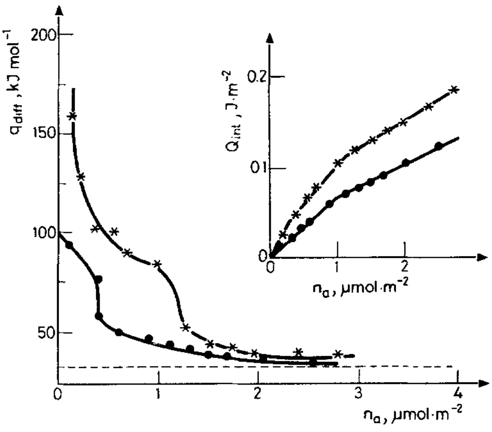

Fig. 5 Differential and integral adsorption heats of benzene/alumina system, corresponding to run 1 (*) and run 2 (•) experiments

than that observed on Fe_2O_3 (160 kJ mol^{-1}). Two different reversible steps, corresponding to values of about 8 and 45 kJ mol^{-1}, are observed successively, both involving about 0.5 µmol m^{-2}, and they are followed by a step showing a heat evolution only slightly higher than that of benzene condensation heat.

The occurrence of irreversible chemisorption of benzene on alumina is rather surprising, and has not been cited in previous experimental work [10–12]. FT–IR spectra of benzene on our γ-Al_2O_3 sample (Figs 6 and 7) show that irreversibly adsorbed compounds are indeed formed during the first step of benzene adsorption. They are characterized (Fig. 6) by bands at 1650, 1440 and 1230 cm^{-1}, which correspond to those of surface bicarbonate ion on aluminas [13]. A combustion step, limited to a few strongly active sites, also seems to take place on γ-Al_2O_3 under our experimental conditions.

Apart from this first, fast phenomenon, benzene adsorption on alumina is completely reversible at r.t., and reversibly shifts the bands due to surface hydroxy groups (Fig. 7b–d). In agreement with ref. [12], we observed the progressive formation of two broader bands at 3590 cm^{-1} and 3640 cm^{-1}, due to the slower and smaller shift of the band observed at 3690 cm^{-1} after adsorption. This interpretation contradicts that of Scokart and Rouxhet [12] and, in principle, would also contradict the acidity scale implicit in the Knözinger and Ratnasamy model of the surface OH groups on alumina [5]. However, it agrees better with our calorimetric data, which indicate a relatively strong H-bonding interaction (Q^{diff} = 85 kJ mol^{-1}) followed by a much weaker one (Q^{diff} = 45 kJ mol^{-1}). We ascribe the first phenomenon to the shift of 140 cm^{-1} of the band at 3730 cm^{-1} on the clean surface, and the second to the smaller and slower shift of the band at 3690 cm^{-1} ($\Delta\nu$ = 50 cm^{-1}).

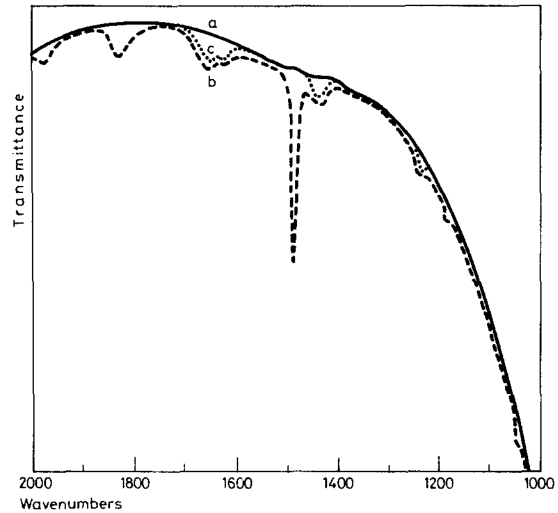

Fig. 6 FT–IR spectrum (2000–1000 cm^{-1}) of γ-Al_2O_3 disc: a) after pretreatment, b) after benzene adsorption (3 Torr), c) after following evacuation at r.t.

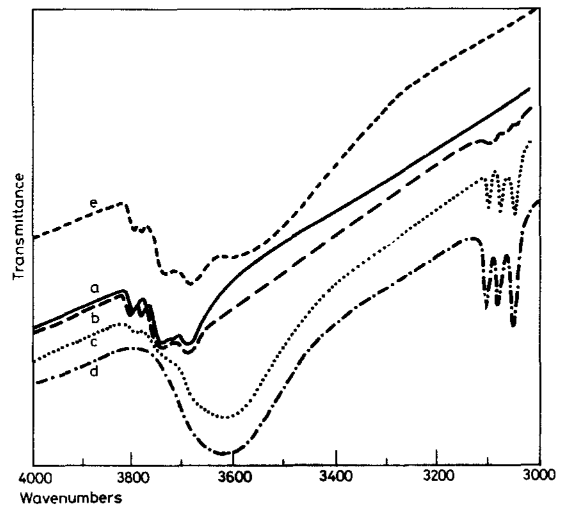

Fig. 7 FT–IR spectrum (4000–3000 cm^{-1}) during benzene adsorption on γ-Al_2O_3: a) after pretreatment, b)–d) in contact with increasing benzene pressures (2 min up to 3 Torr), e) after following evacuation at r.t.

As confirmation, the value measured for the silica/benzene system are both intermediate ($Q^{diff} = 53$ kJ mol^{-1} [7]; $\Delta\nu = 120$ cm^{-1} [12]). The number of benzene molecules involved in the interaction with surface OH's (1 μmol m^{-2}) is of the same order, but smaller than the number of surface OH's present on aluminas evacuated at

673–773 K as reported in ref. [5] (3–8 μmol m^{-2}). This may indicate that several OH's interact with a single benzene molecule.

c) Comparison of iron oxide/benzene and alumina/benzene systems

Iron oxide is known to be an active catalyst for the combustion of hydrocarbons. In particular, it is reported to be highly active and unselective in benzene oxidation [14].

We have found that our samples cause the slow combustion of other unsaturated hydrocarbons, such as ethylene [8], propylene and butadiene [3], even at r.t. This effect has also been reported by other authors for transition metal oxides [15, 16], including Fe_2O_3 [17], as well as for metals on which atomic oxygen is adsorbed [18].

This behaviour may be related to the ability of iron cations, either Fe^{3+} or Fe^{2+}, to bond strongly unsaturated hydrocarbons, making available *d* electrons for π-back-bonding. The proposed adsorption structure is similar to that found for benzene adsorbed on bulk [19] and supported [10] metals.

The results we report here indicate that only some of the sites able to adsorb benzene cause the successive slow combustion. They may differ from the others in their own oxidation state or in the availability of active oxygen in their vicinity.

The heat evolved during the second step is only slightly higher than that measured for benzene adsorption on NaX and NaY zeolites [20], where an interaction with cations similar to that we have proposed has been identified [11].

The physisorption on surface hydroxy groups plays a minor role on this oxide, possibly due to their low acidity [4].

The presence of a combustion mechanism on γ-Al_2O_3 may be considered more surprising. However, the formation of oxidation products on aluminas even at r.t. has been reported frequently. As an example, contradictory results have been reported on the formation of carbonates from CO [21, 22, 13]. It is very likely that the oxidation ability of some alumina preparations depends on the amount of transition metal impurities, and on the pretreatment as well. If reducing pretreatment is carried out (treatment with hydrogen or high-temperature evacuation for several hours), these sites become reduced and surface oxidation reactions are no longer observed.

On the other hand, the formation of bicarbonates was mentioned by Haaland [10] in a spectroscopic study of the adsorption of benzene on alumina-supported platinum. In our sample we may observe the presence of a relevant amount of Fe_2O_3 impurities (0.2%), which may be concentrated more on the surface than in the bulk. Due to the similarity of the evolved heats, we may propose that the combustion sites on alumina are surface iron cations.

Apart from this oxidative step, our work confirms that benzene adsorbs rather strongly on alumina, on surface hydroxy groups. The differential adsorption heats we measured for the stronger H-bonding interaction are similar to the measured by Kiselev et al. for adsorbed benzene on aluminium-containing aerosil gels [23].

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Zusammenfassung — Die Adsorption von Benzol an α-Fe_2O_3- und γ-Al_2O_3-Pulvern bei Raumtemperatur wurde mittels Wärmefluß-Kalorimetrie und FT–IR-Spektroskopie untersucht. Beim Eisenoxid folgt auf dem Chemisorptions-Verbrennungs-Schritt ein bei Raumtemperatur reversibler, stark exothermer Adsorptionsschritt. Aluminiumoxid besitzt einige Oxydationszentren, sofern keine reduzierende Vorbehandlung erfolgt. Zwei aufeinanderfolgende reversible Adsorptionsschritte treten auf und werden der Wechselwirkung mit zwei verschiedenen Typen von Oberflächenhydroxylgruppen zugeschrieben.

Резюме — Методом микрокалориметрии теплового потока и ИК спектроскопии с фурье преобразованием исследована при комнатной температуре адсорбция бензола на α-Fe_2O_3 и γ-Al_2O_3. В случае окиси железа стадия хемисорбция—горение сопровождалась последующей высокотемпературной стадией адсорбции, обратимой при комнатной температуре. На образцах окиси алюминия, не подвергнутых предварительной обработке, существует несколько центров горения. Последовательно наблюдались две обратимые стадии адсорбции, которые были объяснены как результат взаимодействия с двумя различными типами поверхностных гидроксильных групп.