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Oxygen Chemisorption by γ-Al_2O_3 Phthalocyaninato Cobalt(II)

Influence of the Surface Species γ-Al_2O_3 on O_2^- Fixation

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The degree of hydration of the γ-Al_2O_3 surface governs (*a*) the type of interaction between phthalocyaninato cobalt(II), [Co(pc)], and γ-Al_2O_3; (*b*) the activation of [Co(pc)] towards O_2 reduction; (*c*) the fixation of O_2^- to Al^{3+} centres.

Thermal, spectroscopic and spectromagnetic analyses show that: (*a*) the complex [Co(pc)] interacts with the support, as expected for a basic molecule fixed to an acidic surface; (*b*) O_2 is reduced by the cobalt complex; (*c*) the initial stage of interaction between γ-Al_2O_3[Co(pc)] and O_2 is formation of the adduct [Co(pc)]O_2 on the γ-Al_2O_3 surface, followed by O_2^- fixation on the Al^{3+} centres. Competition exists between [Co(pc)] and Al^{3+} as for O_2^- coordination.

Formation of O_2^- on the surface of γ-Al_2O_3 phthalocyaninato cobalt(II), γ-Al_2O_3[Co(pc)], and fixation of [Co(pc)] to the Al^{3+} have been the subject of previous communications.[1, 2]

The mutual influence of the species [Co(pc)], O_2^-, —OH and n-butylamine, which are present on γ-Al_2O_3, is now discussed in order to clarify the relations between fixation of the superoxide anion and the surface groups of the alumina. Our hypothesis that O_2^- is formed by electron transfer from [Co(pc)], as well as the basic nature of this anion, are confirmed here.

EXPERIMENTAL

MATERIALS

Materials employed were γ-Al_2O_3 (Ketjen grade A) and n-butylamine (C. Erba). [Co(pc)] was prepared by reaction of $CoCl_2 . 6H_2O$ with phthalodinitrile, in quinoline. From the refluxed solution β[Co(pc)] precipitated at room temperature as blue crystals which were washed by acetone.

APPARATUS AND PROCEDURE

Elemental analyses were carried on a Hewlett-Packard 185 instrument, on samples of 6-8 mg, with a precision of 0.03 %, and by a Varian Techtron atomic absorption spectrophotometer. Thermogravimetric analyses (t.g.a.) were performed by a Dupont 950 thermal analyser; differential thermal analyses (d.t.a.) by a Dupont 900 instrument. Electronic

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diffuse reflectance spectra were recorded on a Beckman DK-2A spectrophotometer. Electron spin resonance (e.s.r.) spectra were recorded on a Varian E-9 spectrometer operating at X-band frequencies and the g values were evaluated by standardization with diphenylpycrylhydrazyl (DPPH). The samples ($\approx$ 200 mg) were placed in an e.s.r. tube connected to a vacuum line. Treatment of the samples with dry O_2 or dry H_2 was performed under the experimental conditions (time, pressure, temperature) specified below. Before recording the spectra all the samples were outgassed at room temperature for 30 min (10^{-2} mmHg).

PREPARATION AND CHARACTERIZATION OF THE SAMPLES

Two types of γ-Al_2O_3[Co(pc)] samples were prepared, which differed in the thermal pretreatment of γ-Al_2O_3. Type I: γ-Al_2O_3 grade A, without thermal pretreatment, was impregnated by a [Co(pc)] solution in n-butylamine. The amount of [Co(pc)] absorbed was 0.03-0.04 g/100 g Al_2O_3, where the quantities employed were 10 g of γ-Al_2O_3 and 50 cm^3 of a [Co(pc)] solution in n-butylamine (30 mg [Co(pc)] in 50 cm^3 of solvent), and the impregnation time was 12 h. The impregnated powders were finally dried by fluidizing in an N_2 stream at 200°C for 12 h. Type II: the support was pretreated at temperatures from 200 to 700°C for 5 h, by fluidizing γ-Al_2O_3 with N_2, at a stream rate such as to allow the radial temperature gradient of γ-Al_2O_3 to be negligible. The length of the thermal treatment was sufficient to reach a constant degree of hydration.[3] The degrees of impregnation and final drying were the same as for the type I samples. [Co(pc)]n-butylamine was obtained as a blue powder by slow evaporation of a [Co(pc)] solution in n-butylamine (% Co calc. 9.2, found 9.16; % n-butylamine calc. 11.33, found 11.4). T.g.a. results show that the base dissociates from the monoadduct [Co(pc)(n-butylamine)] between 85 and 135°C, leading to [Co(pc)]. Before final drying of the samples (type I and II), [Co(pc)] is present on γ-Al_2O_3 as the monoadduct [Co(pc)(n-butylamine)]; heating at 200°C in a N_2 stream removes the base from the cobalt coordination [*cf.* diffuse reflectance data in ref. (2)].

TABLE 1.—ELEMENTAL ANALYSES OF ORGANIC RESIDUES ON γ-Al_2O_3 . N-BUTYLAMINE (*a*) AND γ-Al_2O_3 . N-BUTYLAMINE[Co(pc)] (*b*) SAMPLES

pretreatment temperature /°C	atomic ratio *N*/*C* *a*	*b*
RT	0.15	0.15
200	0.12	0.18
300	0.20	0.20
350	—	0.22
400	0.24	0.22
500	0.24	0.21
600	0.23	0.21
700	0.22	0.20

INTERACTION OF γ-Al_2O_3 WITH [Co(pc)] AND WATER

D.t.a. analysis shows that Ketjen γ-Al_2O_3 grade A contains $\approx$ 25 % of water. Two endothermic processes were observed, of which the first (at 150°C) is probably related to physically absorbed water or to water capillary-condensed in γ-Al_2O_3 pores. The second process starts at 400°C and is related to the loss of chemisorbed water. Dehydration is a reversible process, and water absorption also occurs by air humidity. The presence of [Co(pc)] does not affect the aforementioned properties of γ-Al_2O_3. Therefore, it is possible to deduce that drying at 200°C in N_2 fluidizing stream removes physisorbed water from the surface of γ-Al_2O_3[Co(pc)] samples. These samples are therefore stocked in dried N_2 atmosphere.

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INTERACTION OF γ-Al_2O_3 WITH [Co(pc)] AND n-BUTYLAMINE

As expected, residual n-butylamine has been found on the dried samples of types I and II. Both the quantity and the type of chemical species depend on the degree of hydration of the oxide surface.[4, 5] As is well known, the interaction between the oxide centres and the amino-groups depends on the acidity of the γ-Al_2O_3 surface.[5, 6] Samples of Ketjen γ-Al_2O_3 grade A were impregnated for 12 h by n-butylamine, either after pretreatment at a temperature between 200 and 700°C, or without thermal pretreatment. n-Butylamine and γ-Al_2O_3 were in the ratio 30 cm^3 to 10 g. After filtration and drying at 200°C in an N_2 fluidizing stream for 12 h, elemental analysis shows that: (i) all samples, either pretreated or not, retain organic residues also after drying at 200°C; (ii) the composition of organic residues depends on the thermal pretreatment of γ-Al_2O_3; specifically the atomic ratio N/C increases with the pretreatment temperature and approaches that of n-butylamine (0.25) at 400-500°C. From 500 to 700°C the ratio decreases.

The properties of the solid so prepared are similar to those of samples γ-Al_2O_3[Co(pc)], which must be more properly defined as γ-Al_2O_3 . n-butylamine[Co(pc)]. The presence of the cobalt complex does not change the atomic ratio N/C, as shown in table 1.

INTERACTION OF γ-Al_2O_3 . n-BUTYLAMINE WITH [Co(pc)] AND [Co(pc)(n-BUTYLAMINE)]

The interactions between the surface groups of γ-Al_2O_3 and chemisorbed [Co(pc)] and [Co(pc)(n-butylamine)] have previously been investigated, with the help of diffuse reflectance analysis.[2]

E.S.R. ANALYSIS

γ-Al_2O_3

Ketjen γ-Al_2O_3 grade A (containing 300 p.p.m. Fe), either without thermal pretreatment or after activation at different temperatures up to 500°C, following the procedures for type II samples, shows stable resonance lines due to Fe^{3+} ($g = 4.05$).[7, 8] At higher field ($g = 2.003$) a lower intensity signal is detected and is ascribed to the parallel resonances of Fe^{3+} and to other impurities. After activation above 600°C the lower field signal decreases in intensity, whereas the one at higher fields disappears.

γ-Al_2O_3 . n-BUTYLAMINE

Impregnation of γ-Al_2O_3 samples with n-butylamine, followed by drying at 200°C, does not change the e.s.r. spectra (fig. 1). Reduction with dry H_2 (200 mmHg) at 200°C for 3 h leads to the disappearance of all resonances. After contacting with dry O_2 (200 mmHg) at room temperature for 10 min, all resonances are restored.

γ-Al_2O_3 . n-BUTYLAMINE[Co(pc)]

Samples of type I and type II, treated with H_2 (200 mmHg) at 200°C for 3 h, do not show any resonance lines. After contacting with dry oxygen (200 mmHg) at room temperature for 10 min, type I samples show resonance lines similar to those of γ-Al_2O_3 . n-butylamine samples (*cf.* room temperature spectra in fig. 1 and 2). On the other hand, type II samples show two different kinds of resonance lines together with the signals of the γ-Al_2O_3 impurities (fig. 2). The lines at lower fields ($g_1 = 2.045$, $g_2 = 2.034$) have lower intensity and become clearly visible in the samples prepared by γ-Al_2O_3 pretreated at temperatures between 350 and 500°C. The lines at higher field coincide with those of the γ-Al_2O_3 impurities ($g_3 = 2.003$), but differ from the latter by their asymmetrical shape. In samples pretreated at 500°C the g_1 lines disappear and at 600-700°C no resonance lines were observed.

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By considering that g_2 and g_3 lines are coincident in their field and shape with the $g_{\parallel}$ and $g_{\perp}$ of O_2^- in ref. (1) and (9), we assign these lines to O_2^- fixed on Al^{3+} centres. The most probable suggestion for the g_1 lines is that they belong to the parallel resonances of O_2^- fixed on Al^{3+} centres of different acid strengths from the former.[10, 11] The Al^{3+} centres corresponding to lower field resonances should have lower acidity, in agreement with the trend of $g_{\parallel}$ values against the positive charge on the metal [12] and in accordance with the disappearance of those lines by increasing the surface acidity of γ-Al_2O_3. Attribution of the g_1 lines to O_2^- anion fixed to a cation of quite different ionic charge (for example Co^{2+}) can be excluded by their field value.[12] Surprisingly the lines of O_2^-, though weaker, are also present in the spectra of γ-Al_2O_3 . n-butylamine (500°C, fig. 1), after O_2 contact. Some of the impurities of Ketjen γ-Al_2O_3 grade A could have an effect similar to that of the supported [Co(pc)].

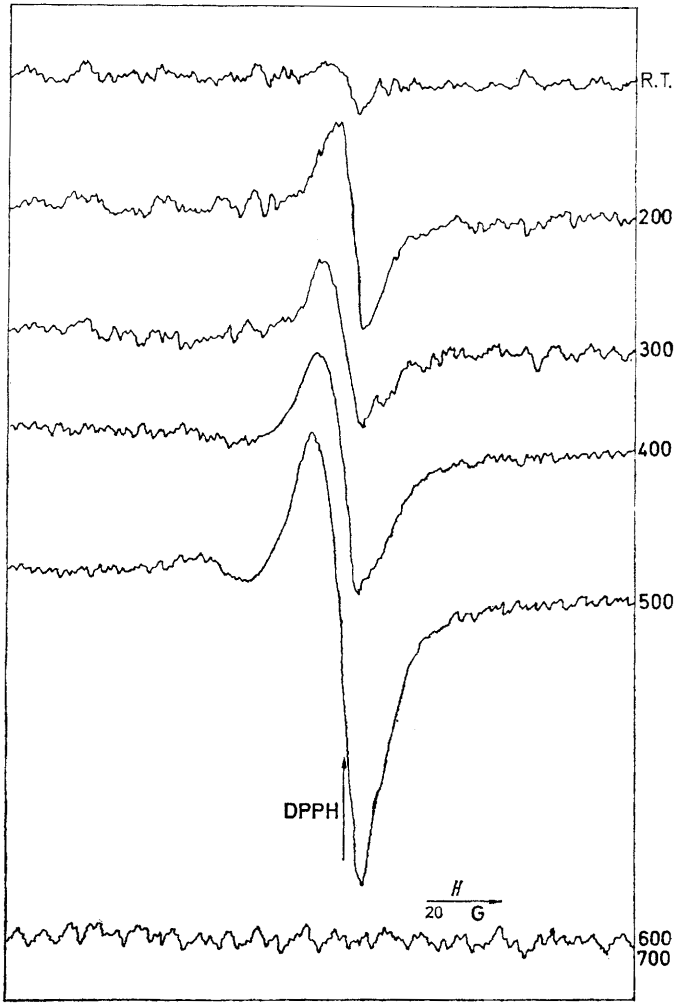

FIG. 1.—E.s.r. spectra, recorded at +100°C, of γ-Al_2O_3 pretreated at the indicated temperatures (right).

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No resonance corresponding to β[Co(pc)] ($g_\perp = 2.94$, $g_\parallel = 1.89$) or to its adduct with n-butylamine ($g_\perp = 2.32$) has been observed. Consequently, it follows that [Co(pc)] on γ-Al_2O_3 is in an electronic situation different from the β form and more similar to that of the α form (no resonance).

As metallic phthalocyanines have been used as heterogeneous catalysts for the propylene oxidation under high pressure,[13a, b] it was interesting to analyse the spectra of samples of types I and II after treatment with oxygen at pressures from 5 to 40 atm at room temperature. Generally no significant modification in the e.s.r. spectra was observed. Some modifications were only observed in the spectrum of a type II sample (with the support pretreated at 300°C) after subjecting the sample to oxygen at 40 atm (fig 3). The changes consist of well-resolved resonance lines at fields lower than the free electron signals. Their position ($g = 2.098$) and the hyperfine pattern ($A = 6.12 \times 10^4$ cm^{-1}) suggest assignment to the parallel resonances of O_2^-, fixed to

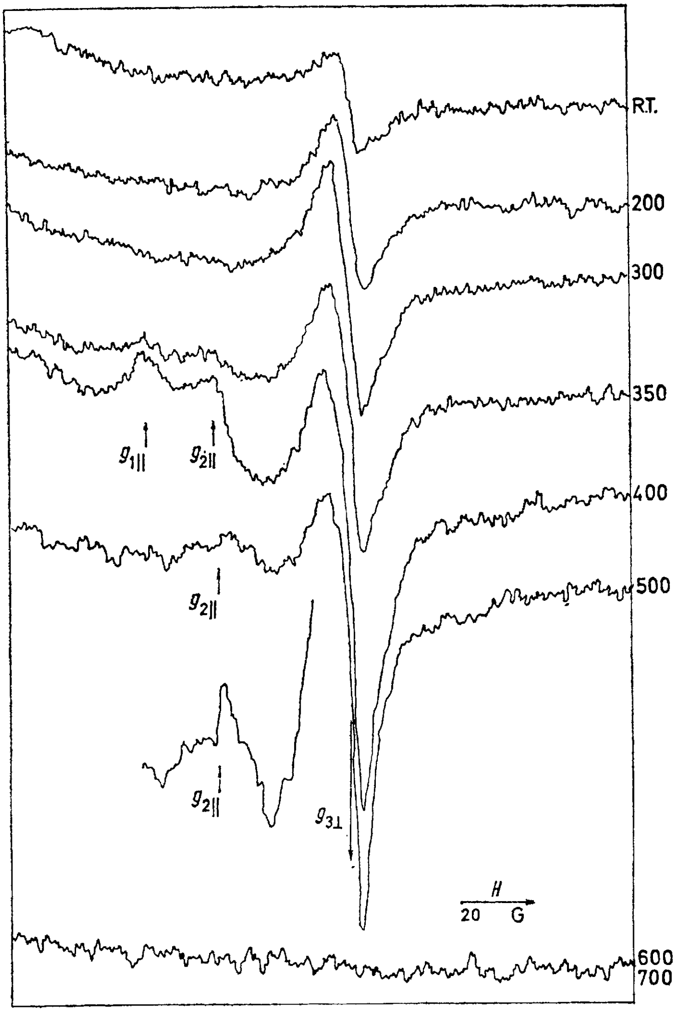

FIG. 2.—E.s.r. spectra, recorded at −100°C, of γ-Al_3O_3[Co(pc)]. The temperature of thermal pretreatment is indicated on the right.

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the Co^{2+} centres. The values of the magnetic parameters indicate electronic differences between the oxygen adduct with cobalt in the γ-Al_2O_3 system and the one observed in [Co(pc)] base solution ($g_{\parallel} = 2.061$, $A_{\parallel} = 14.84 \times 10^4$ cm^{-1});[14] in γ-Al_2O_3[Co(pc)]O_2 cobalt carries a lower total positive charge, while the unpaired electron of the metal is more localized on the oxygen. By oxygenation the lines at $g = 2.003$ loose their symmetrical shape, thus confirming a positive interference of the oxygen superoxide $g_{\perp}$ signals on the impurity lines. By considering the ratio deducible from ref. (14) between $A_{\parallel}$ and $A_{\perp}$ values, an $A_{\perp}$ value of $\approx 3 \times 10^4$ cm^{-1} is expected in the present case. Such a splitting is too small to be resolved.

All properties revealed by the e.s.r. investigation reported here strongly relate to γ-Al_2O_3 Ketjen grade A, and it cannot be excluded that small variations in the

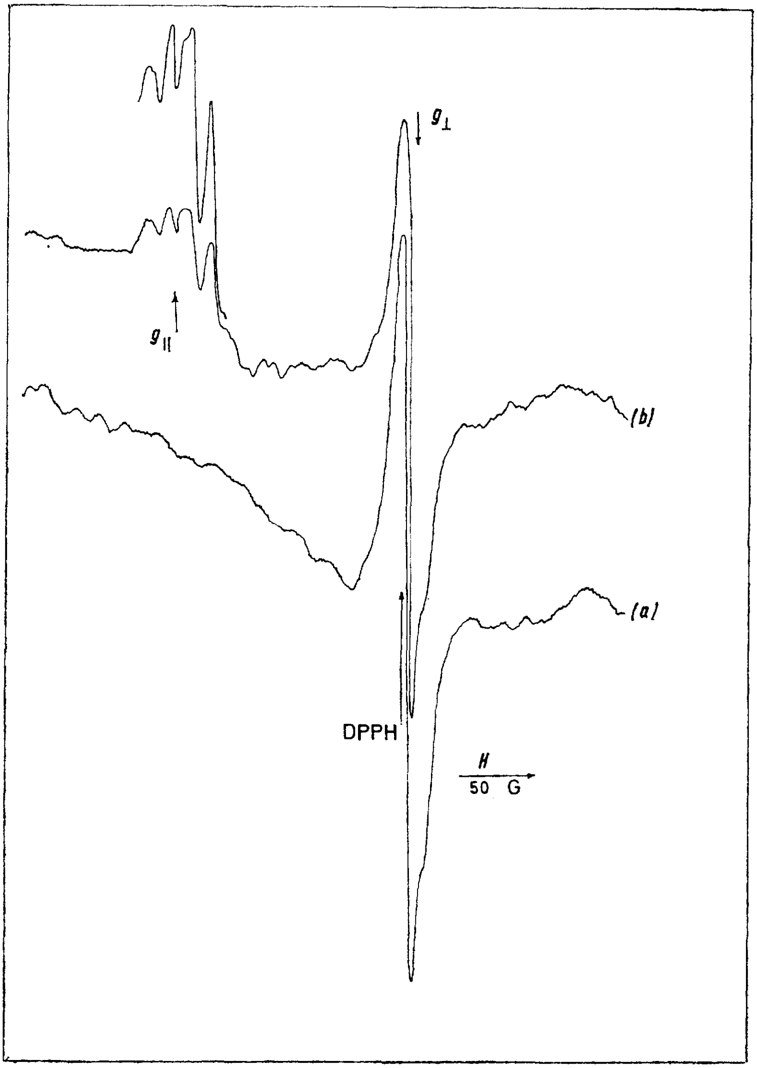

FIG. 3.—E.s.r. spectra, recorded at −100°C, of γ-Al_2O_3[Co(pc)] obtained by γ-Al_2O_3 pretreated at 300°C. (a) Before oxygenation; (b) after oxygenation by oxygen at room temperature and 40 atm.

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impurities on the surface of different alumina samples cause considerable variations in the absorption of oxygen molecules; the use of this type of γ-Al_2O_3 is imposed in view of the correlations with the catalytic activity.[13c]

DISCUSSION

The experimental results suggest relations between: (i) the composition of the organic residue in type I and II samples and the thermal pretreatment of γ-Al_2O_3; (ii) thermal pretreatment and chemisorption of [Co(pc)]; (iii) thermal pretreatment and oxygen fixation to surface species.

Differences in behaviour of the samples in chemisorption processes depend on the thermal conditioning. This effect was not considered in our previous communication,[1] where the experimental conditions involved heating for 2 h only, without a fluidizing stream of nitrogen. Consequently, the behaviour reported in ref. (1) for the samples heated at 600°C cannot be compared with that of the samples reported in the present paper at the same temperature.

As to (i), the surface of γ-Al_2O_3 is covered by physisorbed and chemisorbed water, the latter being bonded to Al^{3+} centres.[3] The coverage depends on the temperature of pretreatment [3] and the main species present on dehydrated γ-Al_2O_3 are: Al^{3+} (Lewis acid centre), O^{2-} (Lewis basic centre), —OH (Brønsted acid centre). Acidity and basicity of these centres also depend on the nature of their environment.[10] The elemental analyses, reported in table 1, indicate that [Co(pc)] does not interfere with the system γ-Al_2O_3 . n-butylamine. Consequently, interaction of n-butylamine with the surface in samples of type I and II can be assumed to be as described by Morimoto *et al.*[5] for the system γ-Al_2O_3 . n-butylamine. In the absence of thermal pretreatment, the base is mainly fixed to Brønsted centres as the n-butylammonium ion; after thermal pretreatment fixation occurs on Al^{3+} as molecular n-butylamine.[5] Hydroxyl group, as expected, cannot be substituted by n-butylamine.

The different composition of organic residues on samples of type I and II is explained in terms of differences in chemisorptive properties of the nitrogen of n-butylamine. In type I samples the bond to Brønsted centres does not directly involve the nitrogen in a bond to Al^{3+}; apparently, it can be more favourably removed from the surface as NH_3 by drying at 200°C. The decomposition process of n-butylamine [15] is clearly favoured. The processes

$$\begin{tikzcd}
 & \frac{1}{2}(C_4H_9)_2NH+\frac{1}{2}NH_3 \\
C_4H_9NH_2 \arrow[ur] \arrow[dr] & \\
 & C_4H_8+NH_3
\end{tikzcd}$$

both lead to a decrease in the atomic ratio N/C with respect to the value of n-butylamine. As the decomposition rates depend on H_2O, which inhibits the *trans*-alkylation,[14] it is suggested that the surface of γ-Al_2O_3 not thermally pretreated favours the decomposition to olefin.

Thermal pretreatment above 500°C does not favour the fixation of butylamine, as observed by MacIver *et al.* for ammonia, due to the rapid decrease of the number of acid centres.[6]

As far as point (ii) is concerned, the presence of different centres on the surface of γ-Al_2O_3 should affect the chemisorption of [Co(pc)], either with regard to the electronic structure of the cobalt or the electronic distribution over the phthalocyaninato ligand.

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We have shown [2] that the electronic transition $d_{x^2-y^2} \rightarrow d_{z^2}$, visible in the spectrum of the samples γ-Al_2O_3[Co(pc)(n-butylamine)], shifts to higher frequency with respect to pure [Co(pc)(n-butylamine)] and we have suggested that the increase in the energy difference between $d_{x^2-y^2}$ and d_{z^2} orbitals could be due to the influence of the filled non-bonding $d_{x^2-y^2}$ orbital, in a π back-donation to Al^{3+} centres. Now we observe, as an independent and confirming proof, that both intensity of this band and acid strength of the γ-Al_2O_3 surface increaes with the temperature of thermal pretreatment. Thermal activation increases the number of Al^{3+} centres [6] which are π-acceptors.

The increase in the energy difference between $d_{x^2-y^2}$ and d_{z^2} orbitals can be also

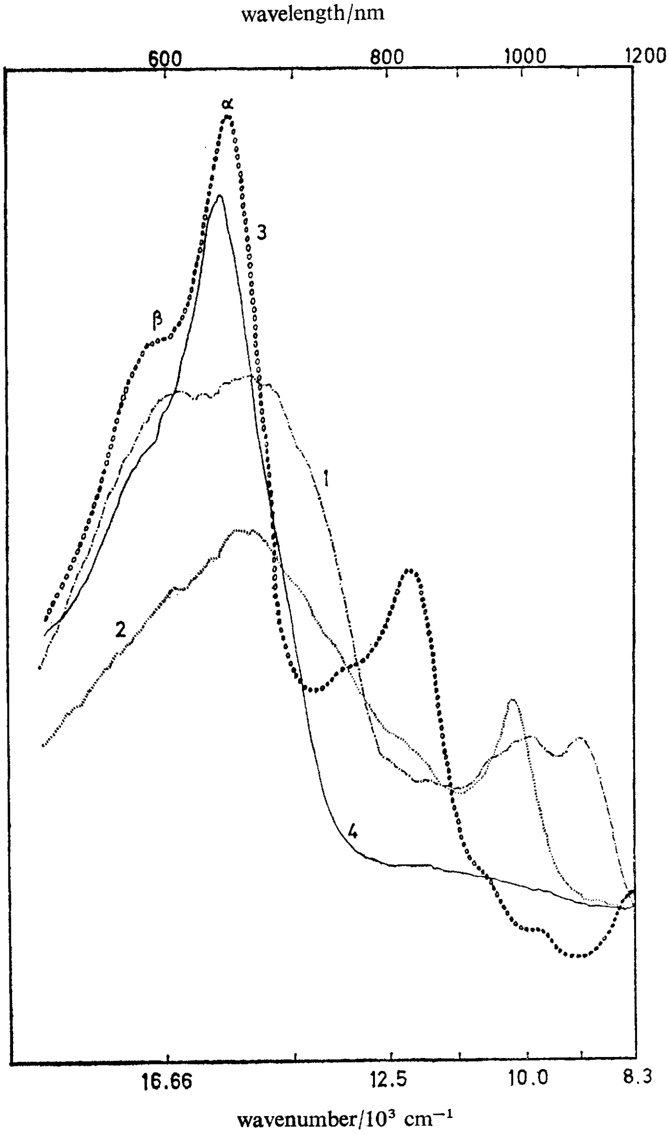

FIG. 4.—Electronic diffuse reflectance spectra: (1) [Co(pc)], (2) [Co(pc)(n-butylamine)], (3) γ-Al_2O_3[Co(pc)(n-butylamine)], (4) γ-Al_2O_3[Co(pc)] obtained from (3) on drying.

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related to a higher localization of the unpaired electron in the d_{z^2} orbital. This localization promotes the oxygen absorption, as O_2^-.[16] This kind of activation can also be extended to supported [Co(pc)]. Stabilization of the $d_{x^2-y^2}$ orbital can also occur in the tetracoordinated complex, as this orbital is not directly involved in the interaction with the coordinated n-butylamine.

Supported [Co(pc)] should also have the possibility of interacting with the oxide dianion (Lewis base). Specifically O^{2-} could take the place of the removed n-butylamine in the coordination field of cobalt. However, apparently the perturbation by O^{2-} is not strong enough to affect the near infrared region, because no new bands related to pentacoordinated cobalt have been observed in γ-Al_2O_3[Co(pc)] with respect to [Co(pc)].

An important indication of the perturbing action of γ-Al_2O_3 on [Co(pc)] may be derived from the spectral changes in the region of $\pi \rightarrow \pi^*$ phthalocyaninato transitions. The D_{4h} symmetry of the system is lost by interaction with the support centres; consequently, the physical basis for the selection rules for the vibrational structure of the electronic $\pi(a_{1u}) \rightarrow \pi^*(e_g)$ transition weaken and the forbidden component 0–0 (α) increases in intensity with respect to the 0–1 (β) (fig. 4).

Interactions between nitrogen atoms of phthalocyaninato and Al^{3+} of the support are suggested in those cases where phthalocyaninato acts as a Lewis base and between nitrogen atoms and —OH groups when phthalocyaninato acts as a Brønsted base. The relative impact of these interactions should be related to the distribution of Al^{3+} and —OH on the surface of γ-Al_2O_3. It is improbable that the perturbation of the π system can be symmetrical over the eight nitrogen atoms of phthalocyaninato. Consequently, it is difficult to find two samples with identical relative intensity of the vibrational components of the electronic transition. This is especially true if we consider that e.s.r. data indicate that the acidity of a specific centre is different for different neighbours. Perturbation of the relative intensity of the vibrational components of the $\pi \rightarrow \pi^*$ transition could also result from interaction of cobalt with the O^{2-} anion. This effect is related to the decrease in symmetry of [Co(pc)] from D_{4h} to C_{4v}. The same trend has been observed in the spectra of the solids [Co(pc)] and [Co(pc)(n-butylamine)] (fig. 4).

As to the shift of the $\pi \rightarrow \pi^*$ transition to higher energy, on passing from β[Co(pc)] to γ-Al_2O_3[Co(pc)], this is probably due to increased back-donation of the d_{yz} cobalt orbital to the $\pi^*(e_g)$ orbitals of the ligand phthalocyaninato;[17, 18] the weight of the $e^4b_{2g}^2a_{1g}$ configuration, in the ground state, probably increases with respect to $e^3b_{2g}^2a_{1g}^2$, as a result of the interaction of cobalt with the γ-Al_2O_3 surface centres (Al^{3+} and O^{2-}).

As regards point (iii), the O_2 molecule can generally accept π electrons from a donor centre, thus acting as an acid; simultaneously it can donate σ electrons, acting as a base. An example of this behaviour is the large class of the oxygen carrier complexes,[19] where O_2 accepts electrons and donates electrons to the same centre. In our case, the cobalt centres should act as π donors, Al^{3+} centres as σ acceptors, and one process should be favoured with respect to the other, depending on the presence of different species on the γ-Al_2O_3 surface and on the pressure of the contacting O_2. The result shown in fig. 3 for a sample on γ-Al_2O_3 pretreated at 300°C and contacted with O_2 at 40 atm suggests that the oxygen molecule, in these conditions, interacts with the cobalt centres, probably as a superoxide anion. This means that activation of cobalt successfully competes with the acidity of Al^{3+}, the activating factors being the interaction of the $d_{x^2-y^2}$ orbital with Al^{3+} empty orbitals and the interaction of O^{2-} with cobalt, besides the high number of O_2 molecules in contact with the surface.

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After pretreatment of γ-Al_2O_3 at higher temperatures, the Al^{3+} centres appear to be electron-attracting enough to remove O_2^- from the cobalt. It is reasonable to suppose that the acidity of Al^{3+} centres changes with the temperature of pretreatment, depending on the electronic properties of the neighbouring groups. The two signals of type II samples, pretreated at 350 and 400°C, are due to O_2^- bonded to two different types of Al^{3+} centres, with the signal at lower field corresponding to a centre with lower effective charge. For thermal pretreatment at 500°C only one type of centre, identical to the one observed on ^{60}Co-irradiated γ-Al_2O_3,[9] is present; at this temperature also the impurities in Ketjen grade A lattice successfully act as an electron carrier to O_2, by a mechanism which is not considered in this paper.

The type I samples are not active in oxygen chemisorption, probably because the presence of —OH on the surface hinders the activation of [Co(pc)] by O^{2-} and by Al^{3+}; moreover, O_2^- species, if any, cannot fix to Al^{3+}, owing to the presence of more strongly bonded —OH.

The inability of type II samples, pretreated at temperatures higher than 500°C, to fix O_2^-, confirms the basic nature of the superoxide anion, and comparison with ammonia absorption suggests a basic strength comparable with that of a weak base.[6]

CONCLUSIONS

Activation of [Co(pc)] in the system γ-Al_2O_3[Co(pc)] has the same origin as in the liquid phase. The ease of oxygen absorption is probably still related to an increased weight of the $(x^2-y^2)^2(yz, yz)^4(z^2)$ configuration in the ground state of cobalt in [Co(pc)], due to σ donation of O^{2-} to the metal and/or to π back-donation from the cobalt $d_{x^2-y^2}$ orbital to Al^{3+}. The —OH group does not activate the oxygen absorption on cobalt, according to the behaviour of the oxygen carrier complexes of cobalt, whose carrier function is hindered by coordination to hydroxo ion.[20] The formation of O_2^- probably needs activated [Co(pc)]. However, the Al^{3+} centres present compete with cobalt for the oxygen fixation; the choice between cobalt and aluminium should be the result of competition between two opposite tendencies, and the process of oxygenation can be considered " cooperative–competitive " between Co^{2+} and Al^{3+}. Clearly this effect is strongly related to the nature of the γ-Al_2O_3 surface. In general the activation of metal ions in the solid state is different from that in solution; in our case it is probable that the stable structure of [Co(pc)] favours an electronically active cobalt species very similar in solution [12] and in the solid state, with only a change in the activator group. On the other hand, e.s.r. results show that the acidity of the cobalt centre in the oxygen adduct γ-Al_2O_3[Co(pc)]O_2 is lower than the acidity of cobalt in [Co(pc)(base)]O_2 and more similar to that occurring in oxygenation of tetrasulphonate phthalocyaninato cobalt(II), in solution without a coordinating base.[21]

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