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Oxygen Reduction on γ-Al_2O_3 Surfaces by Electron Transfer from Porphyrin-Like Complexes

Recent progress in heterogeneous catalysis with porphyrin-like complexes (*1*) has prompted us to make a direct spectroscopic investigation on the catalyst surface. Phthalocyaninato cobalt(II), supported on γ-Al_2O_3, is being investigated at present in order to understand the role of complexes of this type in oxidation processes, e.g., in hydrocarbon oxidation (*2*), and to investigate the relations between the chemisorbed

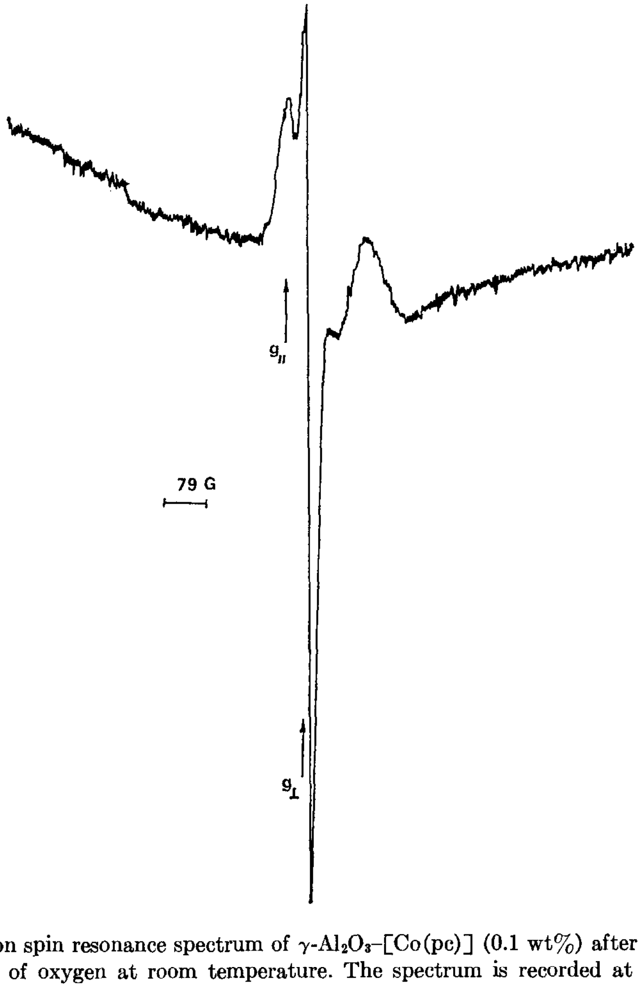

FIG. 1. Electron spin resonance spectrum of γ-Al_2O_3–[Co(pc)] (0.1 wt%) after oxygenation in 40 atm pressure of oxygen at room temperature. The spectrum is recorded at liquid nitrogen temperature.

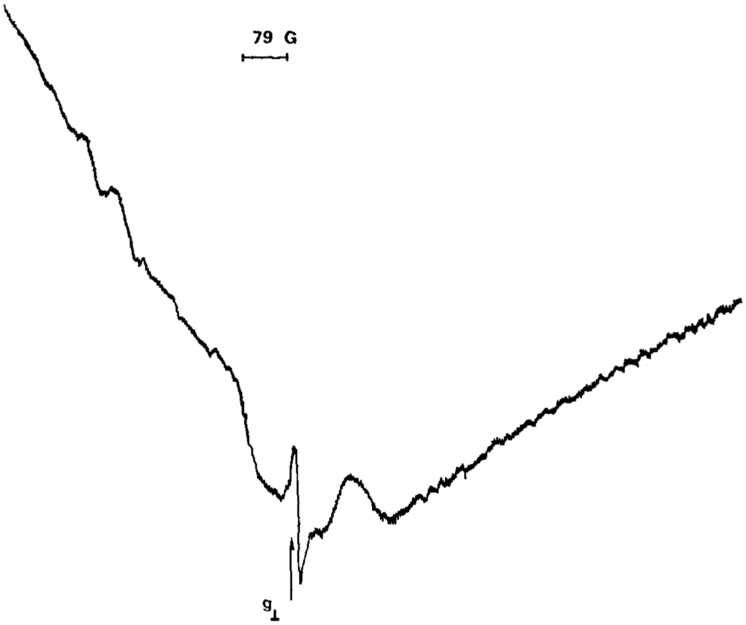

FIG. 2. Electron spin resonance of γ-Al_2O_3–[Co(pc)] (4 wt%) after oxygenation in 40 atm pressure of oxygen at room temperature. The spectrum is recorded at liquid nitrogen temperature.

species and the catalytic properties. It is well known that phthalocyaninato cobalt(II) [Co(pc)] gives 1:1 oxygen adducts where the unpaired electron of Co(II) is transferred to the O_2 molecule (*3*). The ease of electron transfer from cobalt has now also been verified in the solid state.

[Co(pc)] was supported by dripping a solution of this complex in *n*-butylamine onto γ-Al_2O_3 (Ketjen Grade A; surface area $S = 317$ m^2/g; pore volume $v = 0.49$ ml/g; mean pore diameter $d = 4v/S = 62$ Å) which had been previously heated to 600°C for 2 hr. The solid was fluidized by a stream of nitrogen at 65°C throughout the dripping, to remove the *n*-butylamine from the catalyst. Complete removal of the solvent was carried out by heating to 200°C for 12 hr in a stream of dry nitrogen. The quantity of [Co(pc)] on the support, analyzed by atomic absorption spectrophotometry has been limited to about 0.1 wt%, that is about 10^{-2} monolayer, assuming (*4*) [Co(pc)] has a cross section of about 150 Å^2 (mean diameter $\simeq$15 Å). The supported [Co(pc)] assumes the α structure, as proved by electronic reflectance spectra (*5*).

Appropriate quantities of the catalyst were oxygenated with dry oxygen at various pressures from 5 to 40 atm and the samples were analyzed by e.s.r. spectroscopy. The spectra recorded at room and at liquid nitrogen temperature, showed the resonance lines illustrated in Fig. 1, whose intensities increase on increasing the oxygen pressure. Oxygenation of γ-Al_2O_3 and pure [Co(pc)] does not give esr signals.

The resonance lines, obtained only for the system γ-Al_2O_3–[Co(pc)], clearly show a large amount of chemisorbed O_2^-. The g values, $g_\parallel = 2.034$, $g_\perp = 2.003$, are in agreement with those found when O_2^- has been adsorbed on triply charged cations (*6*). A reasonable hypothesis is that the superoxide anion is bonded to Al^{3+} centers. In fact no oxygen adduct of a cobalt(II) complex shows the metal to be in the +3 oxidation state, nor the complete absence of a Co–O_2 covalent bond (*7*). Particularly (*3*, *5*) [Co(pc)(pyridine)O_2] gives resonances with $g_{\parallel} = 2.06$, $g_{\perp} = 2.02$, $A_{\parallel} = 14.8$ ($\mathrm{cm}^{-1} \times 10^4$), $A_{\perp} = 7.05$ ($\mathrm{cm}^{-1} \times 10^4$), and shows that also when the electron transfer to O_2 molecule is high the g values are in agreement with those found for a +2 oxidation state. Hyperfine interaction with the nucleus is still clearly detectable. The esr spectrum of γ-Al_2O_3–[Co(pc)] is in accordance with that of O_2^- obtained from the adsorption of O_2 on Al_2O_3, under ^{60}Co irradiation (*8*). It may be concluded that in γ-Al_2O_3–[Co(pc)] samples there is no evidence that the O_2^- species is bonded to cobalt; however, the presence of the metal complex on the surface is indispensable in forming the chemisorbed anion.

An electron transfer from the transition metal complex to oxygen is the origin of the O_2^- which is then fixed to Al^{3+} centers. The availability of these centers on the surface is a required condition for the O_2^- chemisorption. In fact, when the amount of [Co(pc)] is increased to 4 wt% (see Fig. 2), the intensity of the superoxide esr lines is greatly lowered; when pure [Co(pc)] is oxygenated, as mentioned above, no significant resonance lines are observed. When Al_2O_3 is substituted by SiO_2 (Ketjen, F II), no O_2^- species has been detected after oxygenation of SiO_2–[Co(pc)] samples. An associative interaction between Co(II) and Al^{3+} is required for the formation and the chemisorption of O_2^-.

The strength of the chemisorption is very high. Indeed, thermal treatment *in vacuo* at 200°C for 3 hr does not remove the oxygen, and only chemical reduction with hydrogen at 200°C for 3 hr may remove O_2^- from the surface; similar behavior has been found for O_2^- chemisorbed on silver (*9*). This is probably the first example of an electron transfer process from a prophyrin-like complex to be confirmed with direct evidence. Other systems involve electron transfer from transition metal ions (*10*, *11*).

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