Inorganica Chimica Acta, 25 (1977) L115–L116
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

Electron Perturbing Effect of γ-Al_2O_3 Surface Centres on the Supported Phthalocyaninatocobalt(II) ([Co(pc)])

G. MERCATI and F. MORAZZONI

Istituto di Chimica Generale ed Inorganica, Centro C.N.R., Via Venezian 21, 20133 Milan, Italy

Received October 13, 1977

The electronic configuration of transition metal ions supported on various oxides has particular interest in view of explaining the catalytic properties frequently associated to these systems. Interaction between the transition metal ions and the oxide surface is in general difficult to investigate, because of the different geometrical sites available to the metal.

The cobalt ion which will be here considered is strongly coordinated by the phthalocyaninato tetradentate ligand, in a planar coordination geometry [1]. The supporting process on γ-Al_2O_3 [2] does not involve dramatic changes in this geometry, as the supported product, not the supporting material decides the stronger field around the metal. On the other hand a detailed analysis by diffuse reflectance spectra shows that relevant electronic perturbations derive to [Co(pc)] molecule from interaction with γ-Al_2O_3.

By impregnation of γ-Al_2O_3 (Ketjen grade A, 10 g) with a [Co(pc)] solution in n-butylamine (30 mg in 50 ml) and after solvent removal at room temperature, the monoadduct [(n-butylamine)phthalocyaninatocobalt(II)] ([Co(pc)(n-but)]) has been supported on γ-Al_2O_3. The nature of this product was confirmed by the diffuse reflectance spectrum, which is very similar to that of pure [Co(pc)(n-but)] obtained by concentrating a [Co(pc)] solution in n-butylamine. The sharp absorption band in the near infrared region (Fig. 1) is peculiar of the mono and bis adducts of [Co(pc)] and it was assigned to the $d_{x^2-y^2} \rightarrow d_{z^2}$ electronic transition [3]. In the case of the supported system γ-Al_2O_3[Co(pc)(n-but)], the energy of this transition reflects the interaction of [Co(pc)(n-but)] with the support through a shift to higher frequency with respect to unsupported [Co(pc)(n-but)]. Moreover the intensity of this band greatly increases by supporting, and it depends on the thermal pretreatment of γ-Al_2O_3 (Fig. 2).

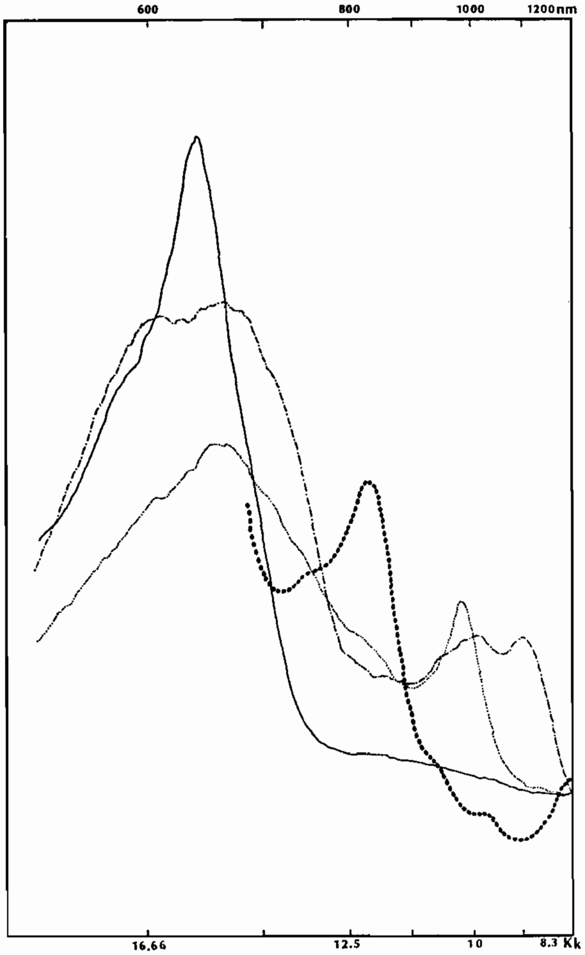

Fig. 1. Diffuse reflectance electronic spectra of ·········· [Co(pc)(n-but)], ∘∘∘∘∘ γ-Al_2O_3·[Co(pc)(n-but)], —— γ-Al_2O_3·[Co(pc)], – · – · – β[Co(pc)].

The support was pretreated at temperatures from 200 to 700 °C for 5 h, in N_2 fluidizing stream, before imbibition. The intensity trend of the band at 12.4 kK shows that interaction between [Co(pc)] and γ-Al_2O_3 is a function of the hydration degree of the surface, while the shift of energy suggests that an electron transfer from the filled $d_{x^2-y^2}$ cobalt orbital to the empty p orbitals of Al^{3+} could be responsible for the increased energy difference between $d_{x^2-y^2}$ and d_{z^2} orbitals. It can be observed that electronic changes of this kind were observed in the energy of d levels of some oxygen carrier cobalt complexes, whence their activity towards oxygen was partly derived [1]. The higher intensity of the $d_{x^2-y^2} \rightarrow d_{z^2}$ transition in the supported [Co(pc)(n-but)], with respect to [Co(pc)(n-but)] is hardly explainable owing to the mixed nature of the band.

The perturbation of γ-Al_2O_3 on [Co(pc)] molecule is clear also in the absence of n-butylamine. On drying γ-Al_2O_3·[Co(pc)(n-but)] at 200 °C in N_2 fluidizing stream for 12 h, the band at 12.4 kK disappears, in agreement with the loss of n-butylamine from the unsupported monoadduct between 85 and 135 °C. [Co(pc)] lies on γ-Al_2O_3 in small amount (0.03–0.04 g/100 g), and the near infrared bands of the complex have too low intensity to be

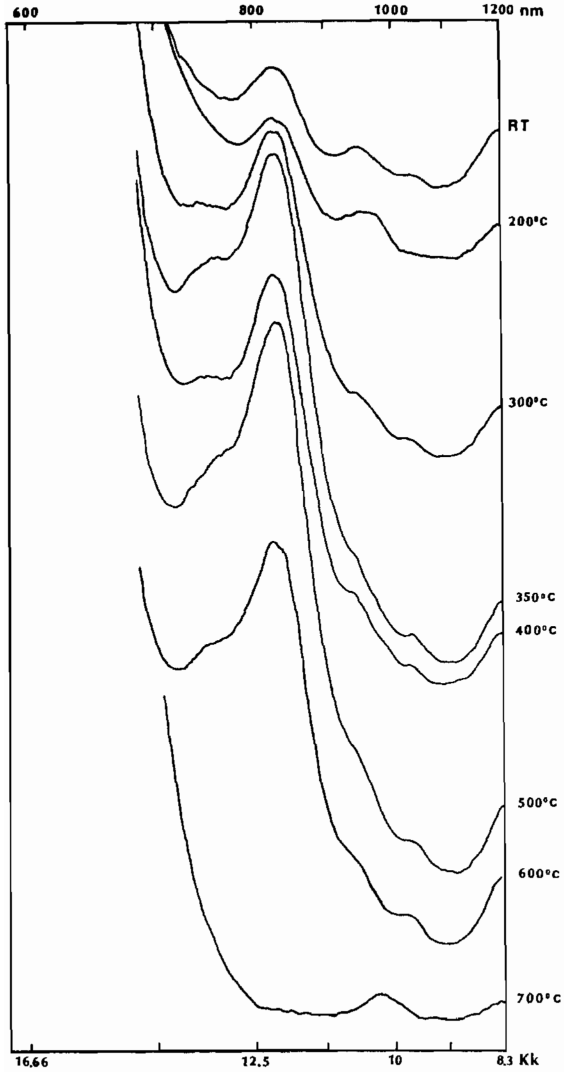

Fig. 2. Diffuse reflectance variations of γ-Al_2O_3·[Co(pc)-(n-but)] for various activation pretreatments of γ-Al_2O_3.

observed in these conditions [3a]. However, in the visible region, the phthalocyanine absorption band [5] $\pi(a_{1u}) \rightarrow \pi^*(e_g)$ shows changes in energy and in the fine structure associated to the supporting of [Co(pc)]. The energy increase with respect to α or β[Co(pc)] and the relative intensity of the two vibrational components become also very different (Fig. 1). It can be suggested that the shift of frequency depends on better back donation $d_\pi(e_g) \rightarrow \pi^*(e_g)$, due to the increased weight of the $e^4b_1^2a_1$ configuration in the ground state. The axial interaction between Co^{2+} and O^{2-} surface anions of the support and/or an interaction between the filled $d_\pi(e_g)$ of Co^{2+} and the empty p orbitals of Al^{3+} should provide this change.

The increase in intensity of the forbidden vibrational component (that at lower frequency) of the electronic $\pi(a_{1u}) \rightarrow \pi^*(e_g)$ transition shows that the D_{4h} symmetry of the phthalocyaninato has been removed by supporting. This effect very probably derives from the asymmetric interaction of the nitrogens of the phthalocyaninato and the surface centres of γ-Al_2O_3 (Al^{3+}, Lewis interaction; OH^-, Broensted interaction).

The properties reported in this paper suggest that the diffuse reflectance analysis is sensitive to the electronic changes of the supported metal complexes and that, by this method, the electronic investigation can be performed directly on the catalytic system.

Acknowledgments

The authors thank C.N.R. for financial support.

References

1 J. M. Robertson, "Organic Crystals and Molecules", Cornell University Press, New York (1953).
2 F. Campadelli, F. Cariati, P. Carniti, F. Morazzoni and V. Ragaini, *J. Catal.*, *44*, 167 (1976).
3 a) F. Cariati, D. Galizzioli, F. Morazzoni and C. Busetto, *J. Chem. Soc. Dalton*, 556 (1975).
b) F. Cariati, F. Morazzoni and C. Busetto, *J. Chem. Soc. Dalton*, 496 (1976).
4 C. Busetto, F. Cariati, P. Fantucci, D. Galizzioli and F. Morazzoni, *J. Chem. Soc. Dalton*, 1712 (1973).
5 P. S. Braterman, R. C. Davies and R. J. P. Williams, *Adv. Chem. Phys.*, *7*, 380 (1964).