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Preparation and Reactions of a Coordinatively Unsaturated Surface Compound of Cobalt(II) on Silica Gel

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The preparation of a coordinatively unsaturated surface compound of cobalt(II) on silica gel is described. This surface compound adsorbs easily CO, C_2H_4, NO or H_2O at room temperature with an accompanying colour change. Stoichiometric measurements of the complex formation showed that two ligands can be adsorbed by one cobalt ion, which is thought to be connected to the silica gel surface by two oxygen ligands. Reactions catalysed by this cobalt(II) surface compound are the oxidation of CO with O_2 (air) and the oligomerization of C_2H_2. Polymerization of C_2H_4 was not observed.

Since Krauss and Stach [1] described a coordinatively unsaturated surface compound of chromium(II) on silica gel and stated that this compound is the polymerization center of the widely used Phillips process [2] for polymerization of ethylene, there has been some interest in surface compounds of transition metal ions, mainly those of chromium(II).[3–5]

Although some papers deal with cobalt(II) on silica gel a coordinatively unsaturated surface compound of this ion, comparable to that of chromium(II) has not been observed. The adsorption of different cobalt(II) complexes on ion exchanged silica gel was investigated by Burwell, Jr. *et al.*[6] Subsequently Anderson [7] described the change in the coordination sphere of cobalt(II) adsorbed on silica gel due to heat treatment up to 500 °C. Investigations of Kazansky *et al.*[8] yielded surface compounds which adsorbed water or ammonia but gave only labile surface complexes of olefins.

EXPERIMENTAL

Silica gel "Merck 7733" was purified by heating in distilled water to 95 °C and additional washing with distilled water. After drying at 150 °C in air for 3 h a solution of the cobalt(II) salt in water was added and the silica gel dried at 120 °C in air. The impregnated silica gel was heated in a quartz tube under vacuum and afterwards handled with exclusion of moisture and air.

Gravimetric measurements were carried out with the samples placed in a Schlenck tube equipped with a teflon stopcock. When the amount of adsorbed gas was measured after evacuating no correction was necessary for physisorbed gas. At a pressure of 760 Torr the correction was calculated from identical argon measurements assuming the physisorption of argon to be the same as that of CO. The error of the stoichiometric relation ranged from 5 to 10 % depending on the amount of adsorbed gas.

Cobalt(II) was analysed by dissolving the silica gel in a boiling solution of sodium hydroxide, acidifying the solution by hydrochloric acid after cooling, replacing the silica gel by filtering and determining the absorption at 630 nm of the thiocyanate complex in acetone. The error was within 2 %.

IR spectra were obtained on powdered samples mixed with paraffin oil under argon and placed between plates of calcium fluoride. The measurements were performed with a Perkin-Elmer 221 spectrophotometer and were accurate to within ± 2 cm^{-1}.

RESULTS

After impregnation, the silica gel is light pink but changes colour at 100 °C under vacuum to blue due to the change from $Co(H_2O)_6^{2+}$ to $Co(H_2O)_4^{2+}$ (with O_h and T_d symmetry at the Co^{2+} ion, respectively). This reaction is reversed by treatment with water as shown by the use of such silica gel as moisture indicator. Heating of the impregnated silica gel to tem-

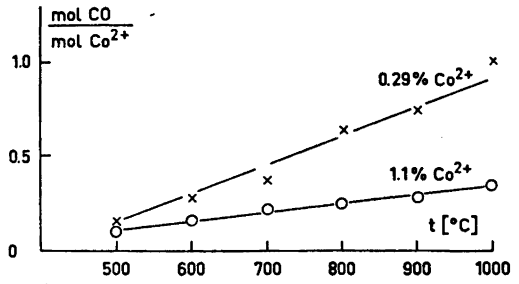


Fig. 1. CO adsorption at 0 °C/1 Torr on samples impregnated with cobalt(II) chloride *versus* temperature of the vacuum heat treatment (1 Torr).

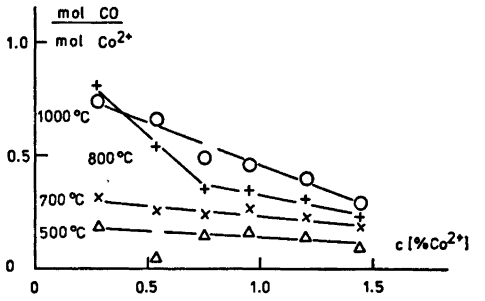


Fig. 2. CO adsorption at 0 °C/1 Torr on samples impregnated with cobalt(II) acetate *versus* cobalt content. Different temperatures of vacuum heat treatment (1 Torr) as indicated.

peratures between 300 and 500 °C under vacuum results in an almost irreversible colour change to blue. This is due to the bonding of a cobalt(II) ion to the silica gel surface with loss of acid formed by the former anion of the cobalt salt and a proton from silanol groups at the surface. The hydrochloric or acetic acid so formed can be collected in a cold trap.

Further vacuum heating changes the colour to light blue and results in production of the coordinatively unsaturated cobalt(II) surface compound, which can be detected by adsorption of CO. Fig. 1 shows the adsorption of CO, determined by gravimetric measurements, for samples with different vacuum heat treatments. Adsorption of CO also gives rise to a colour change ranging from violet to brown [9] depending on the amount of adsorbed CO.

As shown in Figs. 2 and 3 the cobalt concentration has a great influence with respect to the percentage of the cobalt(II) surface compound compared to the total analysed cobalt. This effect may be due to the different cobalt content of the silica gel particles resulting from chromatographic separation during the impregnation. This can result in the formation of small crystals of cobalt(II) salts on the surface during the heat treatment which cannot react as coordinatively unsaturated surface compounds.

The CO is released when heated under vacuum to 100 °C, restoring the coordinatively unsaturated surface compound. C_2H_4 replaces CO and gives a colour change to red violet, but is not bonded more strongly than CO. Polymerization of C_2H_4 was not observed. Both ligands are replaced when exposed to water with change of colour to blue.

To determine the stoichiometric relation between the ligands and the cobalt(II) surface compound, adsorption of NO was examined (colour change to brown). For this purpose NO is better suited than CO because it is adsorbed more strongly and so ensures that all coordinatively unsaturated surface sites have adsorbed ligands. As shown in Fig. 4, at low cobalt content two NO ligands are adsorbed per cobalt(II) ion but this ratio decreases with rising cobalt content due to the effect discussed previously. Adsorption of CO at 760 Torr is equal to the adsorption of NO under vacuum. CO and C_2H_4 adsorption under vacuum is lower than both NO and CO at 760 Torr, but is greater than a ratio of one ligand per cobalt ion at low cobalt content. Comparison of Figs. 2 and 4 reveals the influence of the vacuum

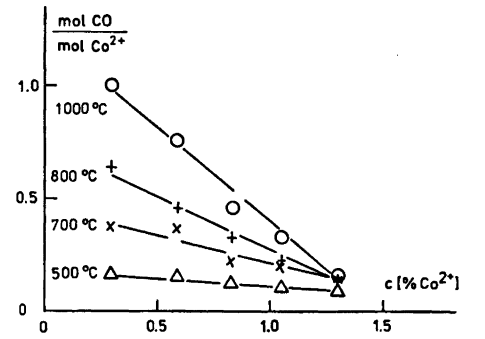


Fig. 3. The same as Fig. 2 but with samples impregnated with cobalt(II) chloride.

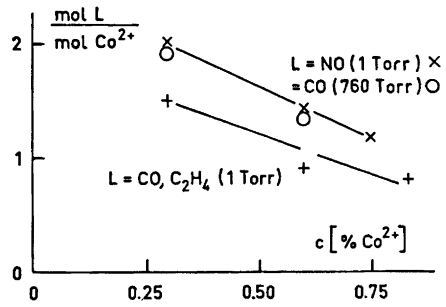


Fig. 4. NO, CO and C_2H_4 adsorption on samples impregnated with cobalt(II) chloride *versus* cobalt content. Vacuum heat treatment (10^{-2} Torr) at 1000 °C.

during the heat treatment on the amount of adsorbed ligands: with a higher vacuum the yield of the coordinatively unsaturated cobalt(II) surface compound increases.

Adsorbed NO is not stable against O_2(air), but reacts to form adsorbed NO_2. The surface compound is then blue brown and is destroyed by water. Adsorption of N_2, CO_2 and O_2 was not observed.

If the complex between water and the coordinatively unsaturated cobalt(II) surface compound is heated under vacuum, adsorption of CO at 0 °C begins after temperature treatment higher than 400 °C. After this temperature treatment roughly 1.3 mol H_2O per cobalt is still adsorbed, which is within error just the same as shown for adsorbed NO in Fig. 4 for a sample with the same cobalt content (0.59 %). The temperature of 400 °C fits well with results shown in Fig. 1 which means that in both cases the same reaction takes place. If the samples, which have adsorbed water, are heated in vacuum to temperatures used in the preparation, the coordinatively unsaturated compound is regained.

IR spectra of adsorbed CO and NO are shown in Figs. 5 and 6, with adsorbed CO exhibiting two peaks at 2184 and 2170 cm^{-1} and NO at 1875 and 1797 cm^{-1}. No frequency shift was observed on samples with different cobalt(II) content (0.29, 0.59, 0.83 % Co). Only slight differences of the intensities were observed due to different cobalt contents.

The angles between the two ligands were calculated from the intensities of the IR absorptions according to Beck *et al.*[10] The values from Figs. 5 and 6 for adsorbed CO are nearly 90° and for adsorbed NO 110°. For the latter, both the IR absorptions [11] and their intensities agree remarkably well with those of $(Co(NO)_2Cl)_2$:[10] 1860 and 1795 cm^{-1}, angle 112°. On the basis of this comparison the symmetry of the complex between NO and the coordinatively unsaturated cobalt(II) surface compound is thought to be pseudo tetrahedral.

Catalysed reactions. In contrast to adsorbed C_2H_4, adsorbed CO reacts with O_2(air), revealing the light blue colour of the coordinatively unsaturated surface compound. However, at room temperature this reaction is quite slow: it takes about half an hour for full conversion of the adsorbed CO. Between 50 and 100 °C

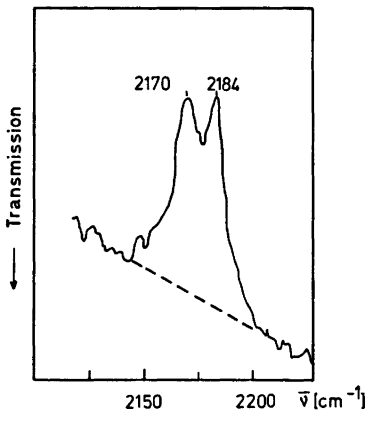


Fig. 5. IR spectrum of adsorbed CO. Samples as used in Fig. 4 (0.59 % Co).

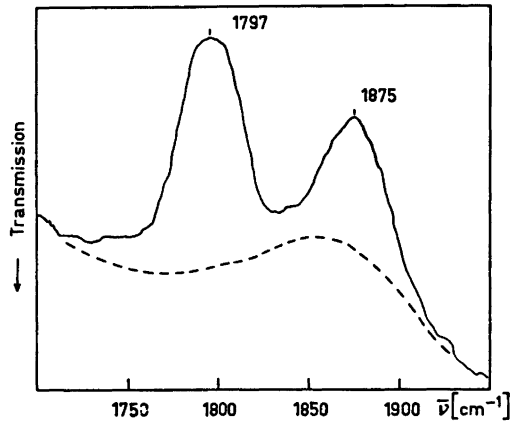


Fig. 6. IR spectrum of adsorbed NO. Samples as used in Fig. 4 (0.59 % Co).

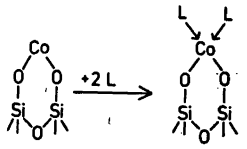
(760 Torr) the conversion time decreases to some minutes and the evolved CO_2 was easily identified with barium hydroxide solution and by means of IR spectrophotometry.

Adsorbed C_2H_2 changes the colour of the cobalt(II) surface compound to pink, almost like C_2H_4, but reacts, in contrast to C_2H_4, easily at 25 °C to give a brown product. By means of mass spectroscopy benzene was detected as the main reaction product, but higher oligomers were also present.

DISCUSSION

A comparison of the heat treatment of the impregnated silica gel as described by Kazansky *et al.*[8] with that used in this work, reveals that the temperatures used by Kazansky (500 and 700 °C) were too low and could only give poor yields of the coordinatively unsaturated cobalt(II) surface compound (see Fig. 1).

The structure of the coordinatively unsaturated cobalt(II) surface compound may be approached in the following way. The angle between the two NO ligands (110°) and comparison with the structure of $[Co(NO)_2Cl]_2$ [10] is strong evidence for a pseudo tetrahedral structure with symmetry C_{2v}. The angle of the two adsorbed CO molecules (90°) would lead to a pseudo square planar or distorted pseudo tetrahedral configuration with symmetry C_{2v}. Further evidence for such a structure is gained by the colour (blue) and the stoichiometric relation between water and cobalt(II) (1.3:1)* of the water complex with the cobalt(II) surface compound. Thus on the basis that the structure of the water complex is pseudo tetrahedral (the same colour as the blue $Co(H_2O)_4^{2+}$ complex) the cobalt ion must be bonded to the silica gel surface by two oxygen ligands. This is confirmed by the formation of hydrochloric or acetic acid during the vacuum heat treatment up to 500 °C of the impregnated samples.



The structure and the reaction with ligands of the coordinatively unsaturated cobalt(II) surface compound on silica gel is schematically shown.

This model is the same as that of the coordinatively unsaturated surface compound of chromium(II) on silica gel reported by Krauss.[12] The comparison of both compounds in Table 1 reveals some common behaviour, but two main differences are obvious: the chromium(II) compound is easily oxidized by O_2 to chromium(VI) while the similar co-

* In view of the cobalt concentration influence discussed above, the real value is thought to be 2:1.

Table 1. Comparison of the chromium(II) and cobalt(II) coordinatively unsaturated surface compounds on silica gel.

	Chromium(II) [3–5]	Cobalt(II)
Oxygen ligands from the silica gel surface	2	2
Stoichiometry of ligand adsorption	2, 3, 4,	2, ?,
Possible ligands	N_2, CO_2, CO, C_2H_4, H_2O, NO (and others)	CO, C_2H_4, NO, H_2O
IR absorptions at 20 °C[a]		
for adsorbed CO	2186 cm^{-1}	2184, 2170 cm^{-1}
for adsorbed NO	1865, 1747 cm^{-1}	1875, 1797 cm^{-1}
Oxidation with O_2	easily to Cr^{6+}	none
Polymerization of C_2H_4	rapid reaction	none
Oligomerization of C_2H_2	yes	yes

[a] IR data for chromium(II) were taken from Zecchina *et al.*[4]

balt(II) compound does not react in this way, and the chromium(II) polymerizes C_2H_4 extremely well while cobalt(II) gives a stable complex with adsorbed C_2H_4. This comparison may give some further argument for an oxidative cycloaddition of two C_2H_4 molecules as the first step of the polymerization of C_2H_4 by a coordinatively unsaturated chromium(II) surface compound on silica gel.[14]

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REFERENCES

1. Krauss, H. L. and Stach, H. *Inorg. Nucl. Chem. Lett. 4* (1968) 393.
2. a. Clark, A., Hogan, J. P., Banks, R. L. and Lanning, W. C. *Ind. Eng. Chem. 48* (1956) 1152; b. Clark, A. *Catal. Rev. 3* (1969) 145.
3. a. Hogan, J. P. *J. Polym. Sci. 8* (1970) 2637; b. Hierl, G. and Krauss, H. L. *Z. Anorg. Allg. Chem. 402* (1973) 113; c. Krauss, H. L. and Rebenstorf, B. *Z. Anorg. Allg. Chem. 402* (1973) 263; d. Krauss, H. L. and Weisser, B. *Z. Anorg. Allg. Chem. 412* (1975) 82; e. Krauss, H. L., Rebenstorf, B. and Westphal, U. *Z. Anorg. Allg. Chem. 414* (1975) 97; f. Krauss, H. L., Rebenstorf, B., Westphal, U. and Schneeweiss, D. In Delmon, B., Jacobs, P. A. and Poncelet, G., Eds., *Preparation of Catalysts*, Elsevier, Amsterdam 1976, p. 149.
4. a. Zecchina, A., Garrone, E., Ghiotti, G., Morterra, C. and Borello, E. *J. Phys. Chem. 79* (1975) 966; b. Zecchina, A., Garrone, E., Ghiotti, G. and Coluccia, S. *J. Phys. Chem. 79* (1975) 972; c. Zecchina, A., Garrone, E., Morterra, C. and Coluccia, S. *J. Phys. Chem. 79* (1975) 978; d. Zecchina, A., Garrone, E., Ghiotti, G. and Coluccia, S. *J. Phys. Chem. 79* (1975) 984.
5. a. Yermakov, Yu. and Zakharov, V. *Adv. Catal. 24* (1975) 173; b. Kugler, E. L., Kokes, R. J. and Gryder, J. W. *J. Catal. 36* (1975) 142; c. Kugler, E. L. and Gryder, J. W. *J. Catal. 36* (1975) 152.
6. Burwell, Jr., R. L., Pearson, R. G., Haller, G. L., Tjok, P. B. and Chock, S. P. *Inorg. Chem. 4* (1965) 1123.
7. Anderson, Jr., J. H. *J. Catal. 28* (1973) 76.
8. a. Brotikovskii, O. I., Shvets, V. A. and Kazanskii, V. B. *Kinet. Katal. 13* (1972) 1342, Engl. 1198; b. Borovkov, V. Yu. and Kazanskii, V. B. *Kinet. Katal. 13* (1972) 1356, Engl. 1217; c. Kazansky, V. B., Borovkov, V. Yu. and Zhidomirov, G. M. *J. Catal. 39* (1975) 205.
9. UV/VIS spectra will be published elsewhere.
10. Beck, W., Melnikoff, A. and Stahl, R. *Chem. Ber. 99* (1966) 3721.
11. Connelly, N. G. *Inorg. Chim. Acta Rev. 6* (1972) 47.
12. Krauss, H. L. *Proc. Int. Congr. Catal. 5th, 1972, 1* (1973) 207.
13. Rebenstorf, B., *Diss.*, Freie Universität Berlin, Berlin 1975.

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