

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

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The preparation of a coordinatively unsaturated surface compound of iron(II) on silica gel is described. CO, C₂H₄, NO and O₂ are adsorbed by this surface compound at room temperature with colour change. Stoichiometric measurements are explained on the basis that one (CO, C₂H₄) or two ligands (NO) can be adsorbed by one iron(II) surface ion, which is thought to be connected to the silica gel by two oxygen ligands. The oligomerization of C₂H₄ to benzene is catalysed at room temperature, but polymerization of C₂H₄ was not observed.

Up to now two coordinatively unsaturated surface compounds have been observed, which consist of transition metal ions on silica gel with the oxidation number two and which are thought to be connected to the silica gel surface by two oxygen ligands. These are the surface compounds of chromium(II)¹ and cobalt(II).² In this article a third member of the group is described and its properties are compared with those of the known compounds.

EXPERIMENTAL

When not explicitly mentioned below, the experimental conditions were in general the same as those described in Ref. 2.

For impregnation a solution of iron(II) chloride in water was added to the purified silica gel "Merck 7733" and dried at 120 °C in vacuum. The impregnated silica gel was heated in a quartz tube under vacuum to a final pressure of 10⁻² Torr at the special temperature mentioned below. These operations were performed with exclusion of air.

Iron(II) was analysed after oxidation to iron(III) with peroxodisulfate solution in water by determining the absorption at 458 nm of the

thiocyanate complex in dilute hydrochloric acid. The error was within 2 %.

The reflectance spectra were recorded at room temperature on a Beckman DK 2 spectrophotometer equipped with a reflectance attachment. Magnesium oxide was used as a reference sample and the absorbance was calculated according to the Kubelka-Munk function.³

RESULTS

Vacuum heat treatment of the impregnated silica gel up to 1000 °C changes the colour of the samples only in a minor respect from nearly white to light grey, while water and, between 200 and 500 °C, hydrochloric acid are lost. The reflectance spectra* of selected samples with pretreatment temperatures of 200, 500 and 1000 °C show only small peaks in the NIR region (Fig. 1); for instance after vacuum heat treatment at 1000 °C two maxima at 7.6 and 12.0 kK are observed. If CO or C₂H₄ are added (20 °C/760 Torr) to a sample with such a pretreatment the colour changes to blue green or blue, respectively, and comparably intense bands are observed in the reflectance spectra (Fig. 2). This behaviour is thought to be strong indication of a coordinatively unsaturated surface compound of iron(II) on silica gel.

Adding water to this compound does not change the colour significantly (Fig. 2/3). Exposure of the coordinatively unsaturated compound to air or O₂ changes the colour immediately to brown (Fig. 2/4), but the colour

* Two sharp peaks at 7.3 and 4.5 kK belong to overtones or combination vibrations of the SiOH surface groups.

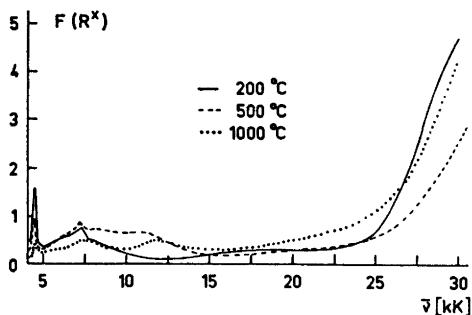


Fig. 1. Reflectance spectra of iron-containing silica gel with vacuum heat treatment at 200, 500 and 1000 °C, respectively [0.7 % iron(II)].

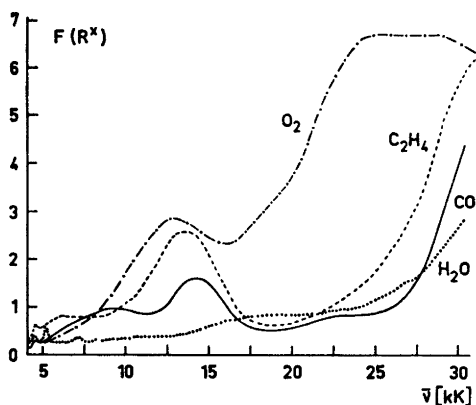


Fig. 2. Reflectance spectra of iron-containing silica gel [0.7 % iron(II), pretreatment: 1000 °C] with CO , C_2H_4 , O_2 and H_2O , respectively, adsorbed at 20 °C.

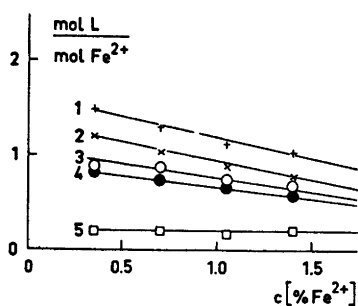


Fig. 3. Adsorption of NO , CO , C_2H_4 and O_2 at 0 °C on iron-containing silica gel with different iron(II) concentrations (pretreatment: 1000 °C). Curve 1, NO , 1 Torr; 2, CO , 760 Torr; 3, C_2H_4 , 1 Torr; 4, CO , 1 Torr; 5, O_2 , 1 Torr.

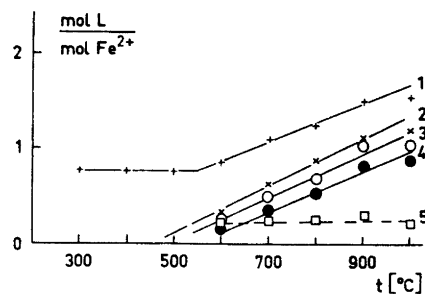


Fig. 4. Effect of pretreatment temperature on the adsorption of NO , CO , C_2H_4 and O_2 at 0 °C on the iron-containing silica gel [0.35 % iron(II)]. Curves 1 – 5, see legend to Fig. 3.

change is reversed again to light grey if water is added or if the compound is in contact with moisture. After a few days exposure to air this sample becomes yellow, obviously due to the oxidation to iron(III). If NO is added to the coordinatively unsaturated surface compound the colour becomes black and changes again, if O_2 is added, to yellow.

NO and O_2 react also with samples pretreated only at temperatures between 200 and 500 °C but in this case the colours are different (NO : green) and with O_2 , addition of water gives a yellow sample.

Gravimetric determination of the ligand/iron(II) ratio (Fig. 3) shows the same concentration effect as was observed with cobalt(II) on silica gel,* with the difference that O_2 is adsorbed to the same relative amount at all concentrations. Up to 90 % of this O_2 can be removed by heating the sample to 300 °C under vacuum. On the basis of Fig. 3 the stoichiometric ratio of CO or C_2H_4 to iron(II), under conditions similar to those at which the reflectance spectra were recorded (20 °C, 760 Torr, 0.7 % iron(II)), is assumed to be 1:1.* From the corresponding ratio of 1.5:1 for adsorbed NO at low iron concentrations at least half of the iron(II) surface ions are thought to have each two molecules NO adsorbed. Adsorbed CO , C_2H_4 or NO can be removed under the same conditions as O_2 .

Investigation of the pretreatment temperature effect (Figs. 4 and 5) showed that adsorp-

* However, the application of lower temperatures at the same pressure may lead to a ratio of 2:1 or even higher.

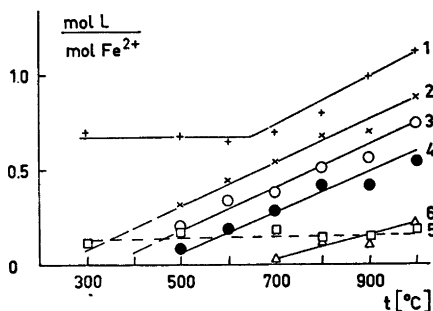


Fig. 5. The same as Fig. 4 but with different iron content [1.05 % iron(II)]. Curves 1–5, see legend to Fig. 3. Curve 6, N_2 , 760 Torr.

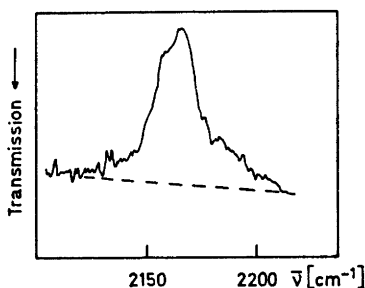


Fig. 6. IR spectrum of adsorbed CO [iron(II) content: 0.7 %, pretreatment: 1000 °C].

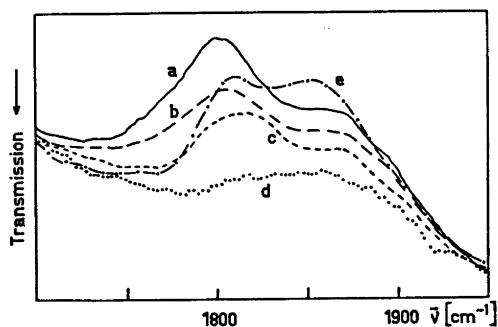


Fig. 7. IR spectra of adsorbed NO [iron(II) content: 0.7 %; a, b, c, d; pretreatment at 1000 °C; e: pretreatment at 300 °C] evacuated at a: 20, b: 100, c: 200, d: 400, e: 20 °C.

tion of CO and C_2H_4 at 0 °C begins when pretreatment temperatures of about 400 °C are used, while N_2 adsorption (Fig. 5) begins only after pretreatment at temperatures higher than 600 °C and is obviously much weaker than that

of CO or C_2H_4 . The NO adsorption decreases with decreasing temperature of the pretreatment to only approximately half of its value at 1000 °C and then remains constant from 500 down to 200 °C. The stoichiometric ratio of NO to iron(II) is then rather 1:1. No effect of the pretreatment temperature on the O_2 adsorption was observed (Fig. 5).

Gravimetric measurements showed also that adsorbed NO reacts at room temperature with O_2 to give adsorbed NO_2 with an accompanying colour change from black to yellow. The same reaction was observed with chromium(II) on silica gel.⁴

CO adsorbed by the coordinatively unsaturated iron(II) surface compound (pretreatment temperature: 1000 °C) shows an IR absorption band at 2165 cm^{-1} (Fig. 6). NO adsorbed by the same surface compound has two bands at 1802 and 1870 cm^{-1} (Fig. 7a and b) when evacuated (1 Torr) at 20 or 100 °C before the IR measurements and two bands at 1815 and 1865 cm^{-1} when evacuated at 200 °C (Fig. 7c). Evacuation at 400 °C desorbs all NO and gives the baseline (Fig. 7d). The fact that two IR bands exist also at higher evacuation temperatures (100 and 200 °C) is an indication that either two NO molecules or none are adsorbed. On this basis the angle between the two NO molecules can be calculated according to Beck *et al.*⁵ from the intensities of the IR absorptions. This calculation gives a value of approximately 130° for a sample with adsorbed NO evacuated at 20 °C.

If a low pretreatment temperature (300 °C) is used for the preparation of the sample, adsorbed NO gives two IR bands at 1810 and 1855 cm^{-1} (Fig. 7e) possibly due to two different adsorption sites and not to two adsorbed NO molecules at one iron(II) surface ion.

As in the case of cobalt(II)² and in contrast to chromium(II)¹ C_2H_4 is not polymerised by the coordinatively unsaturated iron(II) surface compound at room temperature and 760 Torr pressure. C_2H_2 is oligomerised to benzene by all three surface compounds.

DISCUSSION

In general the model for the reactions during the preparation of the coordinatively unsaturated cobalt(II) surface compound² applies also to the iron(II) surface compound. During the

impregnation the hexaaquo iron(II) ion is physisorbed at the silica gel surface and subsequently loses water when heated to 200 °C in vacuum to give the tetraaquo ion. Between 200 and 500 °C the anion combines with a proton from a silanol surface group to give hydrochloric acid. The iron(II) ion is bonded to the silica gel surface by two oxygen ligands and two water molecules are left adsorbed to the iron, which is now four coordinated with pseudo square planar or more exactly C_{2v} symmetry. During heating to 1000 °C the adsorbed water is lost to give the coordinatively unsaturated iron(II) compound with the coordination number two and C_{2v} symmetry.

Both the four coordinated compounds have free coordination sites where NO or O₂ can be adsorbed. However, only the two coordinated surface compounds can adsorb CO, C₂H₄ and, very weakly, N₂.

This model for the coordinatively unsaturated surface compound of iron(II) is the same as that proposed for chromium(II)⁶ and cobalt(II),² so there should be a number of comparable properties. For instance all three compounds adsorb CO or C₂H₄ at room temperature and 760 Torr with, in the case of CO, an IR vibration at higher wave-numbers than gaseous CO. This is an indication of electron donation from the CO coupled with weak back donation from the metal and is caused by the relatively high oxidation number of the metal ion. Perhaps the siloxane bond between the silica gel surface and the metal ion is also influencing this.

All three surface compounds bind C₂H₄ a little stronger than CO and adsorb two molecules NO at room temperature which have two IR absorptions at lower wave-numbers than the gaseous NO. The oligomerization of C₂H₂ to benzene was mentioned before.

Beside this general correspondence between the three surface compounds there are some special similarities in the reflectance spectra of chromium(II)⁷ and iron(II) compounds. Both the coordinatively unsaturated surface compounds absorb at 7.6 and 12.0 kK, after adsorbing one molecular CO per metal ion they both have maxima at 8.7 and 13.8 kK and also the reflectance spectra after adsorption of one molecule C₂H₄ or in the case of chromium(II) of an olefin⁸ equal each other.

This astonishing behaviour can easily be understood by applying the electron hole formalism of ligand field theory, which predicts that a d^4 electronic system [chromium(II)] should have comparable spectra to a d^6 system [iron(II)]. However, there is a difference in the stability of the ligand adsorption, which is for instance expressed by the weaker N₂ adsorption of iron(II) compared to chromium(II) and which is the cause of the difference in the IR spectra of adsorbed CO [chromium(II): 2186 cm⁻¹; iron(II): 2165 cm⁻¹].

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