

## UV/Vis Investigation of Cobalt(II) on Silica Gel

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The coordinatively unsaturated surface compound of cobalt(II) on silica gel has been investigated by several authors.<sup>1–6</sup> This surface compound is most likely coordinated to the silica gel surface by two oxygen ligands and can adsorb up to three CO or ethylene molecules at low temperatures.<sup>6</sup> It has also been found that two slightly different surface compounds of cobalt(II) exist.<sup>6</sup>

Recently, the author showed that chromium(III) on silica gel can be a very active catalyst for the polymerization of ethylene.<sup>7</sup> This catalyst can also be prepared by using a dinuclear chromium(III) complex for impregnation of the silica gel.<sup>8</sup> Such dinuclear complexes exist also with cobalt(III),<sup>9</sup> although cobalt(III) is generally less stable than chromium(III). It was therefore interesting to investigate whether a surface compound with cobalt(III) on silica gel is possible.

### Experimental

The cobalt(II) on silica gel samples were prepared by impregnating silica gel 60 (Merck 7733) with a solution of  $[\text{Co}(\text{H}_2\text{O})_6]\text{Cl}_2$ , drying the product at 393 K and heating in vacuum (10 Pa) to 1073 K. Substituting the last preparation step with treatment in an oxygen stream (fluidized bed) at 1073 K produced a slightly modified cobalt(II) surface compound. The cobalt concentration was 0.074% Co after heating and was fixed in the impregnation solution.

The UV/Vis diffuse reflectance spectra were recorded and recalculated with the Kubelka-

Munk function according to Ref. 10. The IR spectra were recorded as described previously.<sup>6,11</sup>

### Results and discussion

Fig. 1 shows reflectance spectra of the “normal” coordinatively unsaturated cobalt(II) surface compound, prepared by vacuum heat treatment at 1073 K, before and after CO adsorption (spectra A and B). Spectra C to H in Fig. 1 were recorded after removing CO by stepwise evacuation. The spectrum of the coordinatively unsaturated cobalt(II) surface compound consists of 4 bands at 6500, 14700, 16600 and 41500  $\text{cm}^{-1}$  (spectrum A). A small shoulder at 20000  $\text{cm}^{-1}$  is visible. After adsorption of CO at 293 K and 100 kPa two new bands were observed at 13200 and 20200  $\text{cm}^{-1}$ , together with a small sharp band at 14300  $\text{cm}^{-1}$  and a shoulder at 22300  $\text{cm}^{-1}$  (spectrum B). The bands at 6500 and around 41000  $\text{cm}^{-1}$  had increased intensity. On removing the CO by evacuation, the intensity of all bands decreased again, especially those at 6500, 13200 and 20200  $\text{cm}^{-1}$ . The latter two bands shifted to 13800 and 19700  $\text{cm}^{-1}$ , respectively (spectrum E in Fig. 1). As spectrum H shows, the CO can be desorbed nearly completely and the original spectrum A regained.

Fig. 2 shows the spectra of the cobalt(II) surface compound after adsorption of  $\text{C}_2\text{H}_4$ . Ethylene adsorbed at 293 K and 100 kPa gave rise to bands at 12900, 19300 and 43000  $\text{cm}^{-1}$ , together with shoulders at 14100 and 21000  $\text{cm}^{-1}$  (spectrum B). The band at low wavenumber was now

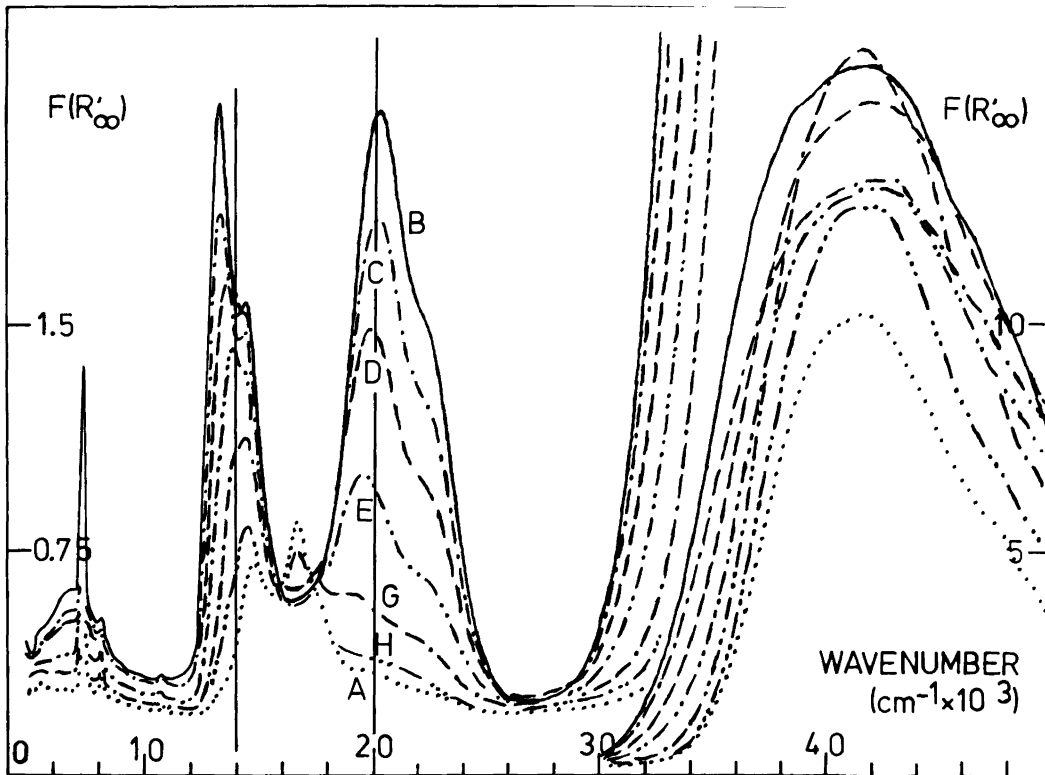


Fig. 1. Diffuse reflectance spectra of 0.074 % cobalt(II) on silica gel prepared by vacuum heat treatment at 1073 K. Spectrum A: vacuum (10 Pa), B: CO, 100 kPa, C: CO, 10 kPa, D: CO, 1 kPa, E: CO, 100 Pa, G: CO, 1 Pa, H: 1 Pa for 15 min.

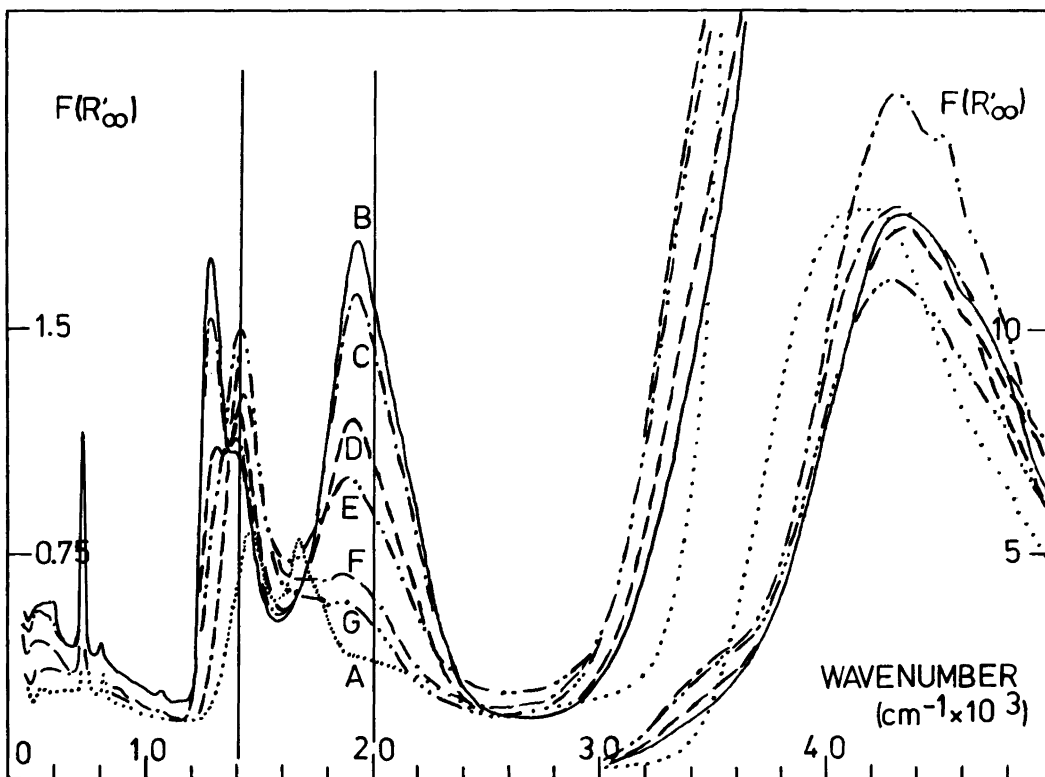


Fig. 2. Reflectance spectra of cobalt(II) on silica gel as used in Fig. 1, but with adsorbed ethylene. Notation as in Fig. 1.

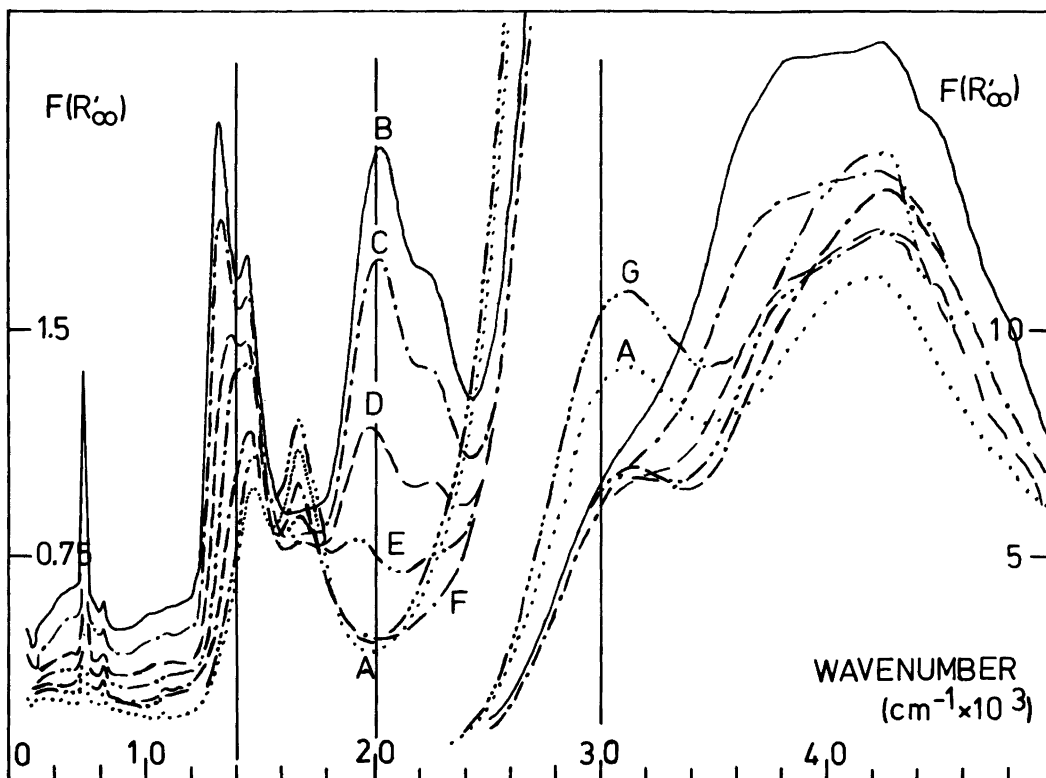


Fig. 3. Reflectance spectra of cobalt(II) on silica gel prepared by heating in an oxygen stream at 1073 K. The spectra show the adsorption of CO. Notation as in Fig. 1.

very broad and it was difficult to determine the exact position, which may have been around 4000 to 5000  $\text{cm}^{-1}$ . On desorbing ethylene, the bands at 12900 and 19300  $\text{cm}^{-1}$  decreased, while a band at 14100  $\text{cm}^{-1}$  first increased strongly (spectrum E in Fig. 2) and thereafter decreased also (spectrum F and G). This latter observation is a clear indication that the ethylene is desorbed stepwise. In other words, two ethylene molecules are adsorbed at room temperature and normal pressure, one of which is desorbed on evacuation. This is also valid for CO, but in contrast to ethylene, where not all  $\text{C}_2\text{H}_4$  is desorbed (spectrum G in Fig. 2), all CO is desorbed from the cobalt(II) surface compound (spectrum H in Fig. 1).

Heating the dried samples in an oxygen stream at 1073 K changed the spectrum of the coordinatively unsaturated cobalt(II) surface compound in only one respect: a new band at 31000  $\text{cm}^{-1}$  was observed (spectrum A in Fig. 3). The

intensity of this band decreased on adsorption of CO, but its position seemed not to be affected (spectra B to F in Fig. 3). The intensity of this band was regained after desorption of CO (spectrum G in Fig. 3). On adsorption of ethylene, a similar behaviour was observed (spectra not shown here).

A UV band similar to that above for cobalt(II) was observed for the chromium(II) surface compound<sup>12</sup> around 3000  $\text{cm}^{-1}$ . The latter was interpreted as arising from a metal-metal bond of a dinuclear chromium(II) surface compound. In addition, the IR spectra of CO adsorbed on the chromium(II) surface compound at low temperatures showed decreasing bands at wavenumbers higher than the stretching vibration (2143  $\text{cm}^{-1}$ ) of the CO gas molecule, while 3 new bands appeared at lower wavenumbers. This observation was interpreted as a conversion of terminal CO to bridging CO and is regarded by the author to

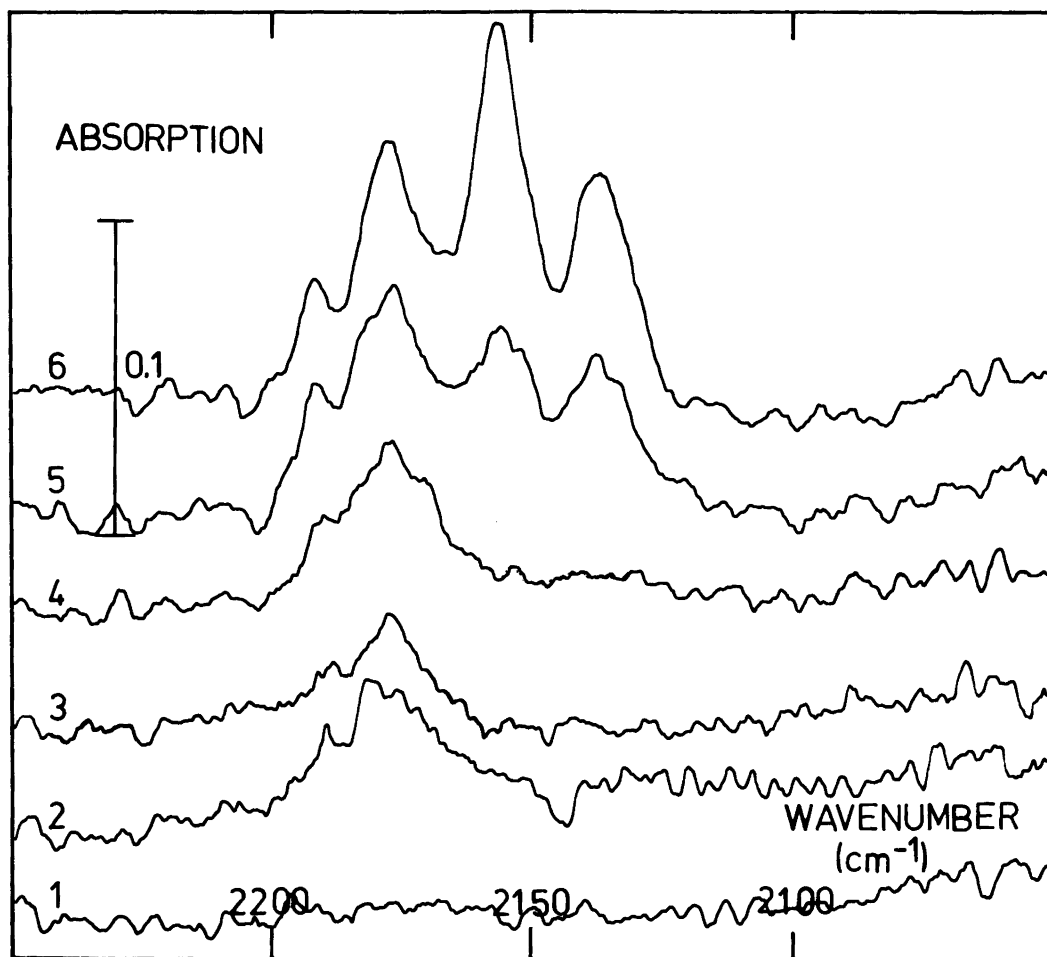


Fig. 4. IR spectra of CO adsorbed on cobalt(II) on silica gel prepared as in Fig. 3. Spectrum 1: Vacuum, 1 Pa, 2: CO, 100 Pa, 3: CO, 1 kPa, 4: CO, 10 kPa, 5: CO, 10 kPa, 200 K, 6: CO, 100 Pa, 130 K.

be proof of the presence of the above-mentioned dinuclear chromium(II) surface compound.

As Fig. 4 shows, a similar decrease in the intensity of the bands at 2192 and 2178  $\text{cm}^{-1}$  was not observed in the case of the cobalt(II) surface compound prepared by heating in an oxygen stream. In addition, no new IR bands were observed below 2140  $\text{cm}^{-1}$ . The two bands at 2156 and 2138  $\text{cm}^{-1}$  at low temperature are from CO adsorbed on Si-OH groups and from CO aggregates.<sup>6</sup> In conclusion, the CO IR spectra at low temperatures gave no indication of a dinuclear cobalt(II) surface compound. The UV band from cobalt(II) at 31000  $\text{cm}^{-1}$  in Fig. 3 might therefore

be due to a slight configurational change of the cobalt(II) surface compound, also giving rise to two slightly different series of CO IR spectra observed previously.<sup>6</sup>

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SHORT COMMUNICATION

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