Preparations and Reactions of a Coordinatively Unsaturated Surface Compound of Nickel(II) on Silica Gel

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The preparation of a coordinatively unsaturated surface compound of nickel(II) on silica gel is described. CO, C_2H_4, NO and NO_2 are adsorbed by this compound at room temperature with an accompanying colour change. Stoichiometric measurements are explained on the basis that three (CO) or two ligands (CO, NO) can be adsorbed by one nickel(II) surface ion, which is thought to be connected to the silica gel by two oxygen ligands. The oligomerization of C_2H_2 to benzene is catalysed by this surface compound at room temperature, but the oligomerization of C_2H_4 to various hexenes was observed only at higher temperatures.

To date four divalent transition metal ions are known to bind to silica gel, presumably through two oxygen ligands. These are chromium(II),[1] manganese(II),[2] iron(II)[3] and cobalt(II).[4] A fifth member of this group, nickel(II), is described in this article.

In connection with investigations on the catalytic properties of metallic nickel on silica gel, surface compounds of nickel(II) have been described.[5] However, the samples had a rather high nickel content of 5 % or more (together with a relatively low pretreatment temperature of 500 °C) and so comparison to low-content samples as used in this work (less then 1 %) may prove difficult.

Low-content nickel(II) silica gels have been investigated by some authors.[6–10] The results[7–10] indicate that a coordinatively unsaturated surface compound of nickel(II) on silica gel may exist, but the attributed tetrahedral coordination[7] and the connection to the silica gel surface by three oxygen ligands[9,10] seems rather unlikely, compared with the properties of the other members of the group of surface compounds mentioned above.

EXPERIMENTAL

The experimental conditions were in general the same as those described in Refs. 3 and 4.

Nickel(II) samples were prepared according to Ref. 4 by impregnating silica gel "Merck 7733"[11] with nickel(II) chloride and were analysed, after destroying the silica gel with hydrofluoric acid, by dimethylglyoxime.[12]

RESULTS

After impregnation and drying at 120 °C in air the colour of the sample is light green (Fig. 1, Curve 1) due to $Ni(H_2O)_6^{2+}$ with O^h symmetry. After vacuum heat treatment at 200 °C the colour changes to yellow (Fig. 1, Curve 2), at 500 °C to brownish pink (Fig. 1, Curve 3) and at 1000 °C (Fig. 1, Curve 4) the sample has the same light green colour as after impregnation. Surprisingly, reflection spectra* of the sample vacuum heat treated at 1000 °C and that of the just impregnated and dried sample have the same two bands near 15 and 25×10^3 cm^{-1}. A third band near 7×10^3 cm^{-1} (Fig. 1, Curve 4) cannot be represented in Fig. 1, Curve 1 because of the intense water and SiOH bands (see note below).

Adsorption of C_2H_4 at room temperature to the sample with pretreatment at 1000 °C gives rise to a colour change to blue (Fig. 2, Curve 2), which, after evacuating the sample, changes to light violet blue (Fig. 2, Curve 3). This behaviour is strong evidence for a coordinatively unsaturated surface compound of nickel(II) on silica gel in this sample.

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* Two sharp peaks at 7.3 and 4.5×10^3 cm^{-1} belong to overtones or combination vibrations of the SiOH surface groups.
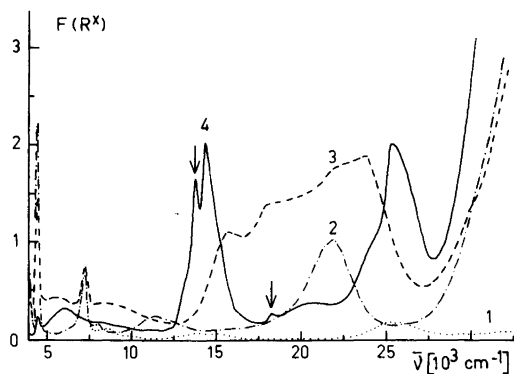
Fig. 1. Reflectance spectra of nickel-containing silica gel with vacuum heat treatment (10^{-2} Torr) at 1, 120 °C (air); 2, 200; 3, 500; 4, 1000 °C [0.6 % nickel(II)].

Adsorption of CO yields a violet compound which changes colour after a few seconds to light gray blue (Fig. 3, Curve 2) and after evacuation to light yellow (Fig. 3, Curve 3). As in the case of adsorbed C_2H_4 the above-mentioned three bands, or in these cases band groups, seem to represent the spectra.

A green compound is the result of the adsorption of NO (Fig. 4, Curve 2). Remarkably there is a difference between the spectra when NO is added directly to the coordinatively unsaturated surface compound (Fig. 4, Curve 2) or when first CO is adsorbed and then displaced by NO (Fig. 4, Curve 3).

The coordinatively unsaturated nickel(II) compound and the water complex of this compound
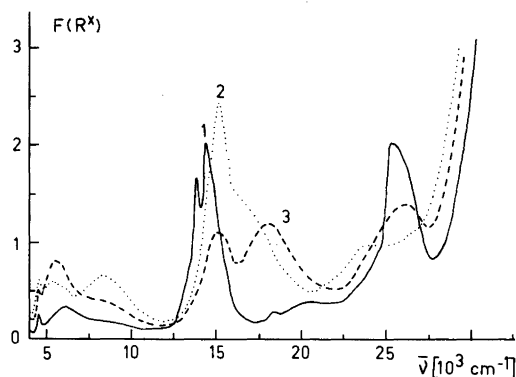

Fig. 2. Reflectance spectra of nickel-containing silica gel with vacuum heat treatment at 1, 1000 °C; 2, with adsorbed C_2H_4 at 760 Torr/20 °C; and 3, with adsorbed C_2H_4 at 1 Torr/20 °C.
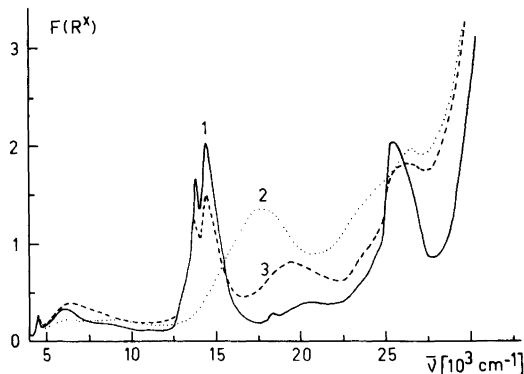

Fig. 3. Reflectance spectra as in Fig. 2 but with adsorbed CO at 2, 760 Torr/20 °C; and 3, 1 Torr/20 °C.
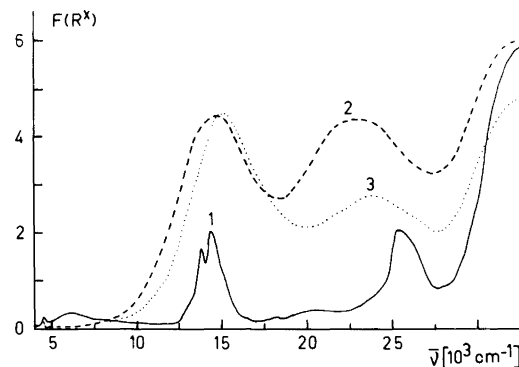

Fig. 4. Reflectance spectra as in Fig. 2 but with adsorbed NO at 2, 1 Torr/20 °C; and 3, 1 Torr/20 °C after displacing CO.
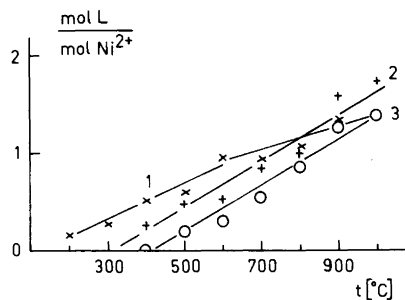

Fig. 5. Effect of the pretreatment temperature on the adsorption of NO and CO at 0 °C on the nickel-containing silica gel [0.6 % nickel(II); 1, NO/1 Torr; 2, CO/760 Torr; 3, CO/1 Torr].

(both are light green) can not be visually distinguished.

As shown before for other members of this group of surface ions[3,4] the adsorption of CO rises with increasing temperature of the vacuum heat treatment (Fig. 5). In contrast to the adsorption of NO, which shows a deviation from linearity and crosses the CO adsorption line, the latter does increase linearly when either 760 or 1 Torr are applied (Fig. 5).

The group behaviour is also apparent when the "concentration effect"[3,4] is investigated (Fig. 6), which causes samples with lower metal content to show higher ligand per metal ion ratios during adsorption of various ligands. The best results are nearly three molecules CO per nickel(II) ion at 0.3 % nickel(II) content. NO is, as is also known for chromium(II),[13] iron(II)[3] and cobalt(II),[4] at low metal ion concentrations adsorbed with a ratio of two molecules per metal ion. The same ratio is observed here with nickel(II) for CO under 1 Torr pressure. No difference in the stoichiometric ratio between NO and the nickel(II) surface ion was observed if NO was adsorbed directly by the surface ion or if CO was first adsorbed and then displaced by NO.

The "concentration effect" is explained on the basis that with rising concentration more nickel(II) ions build small metal oxide or chloride crystals which cannot react as coordinatively unsaturated compounds. With this in mind the stoichiometric ratios at low nickel(II) concentrations are thought to be the "real" values. Referring to the spectra
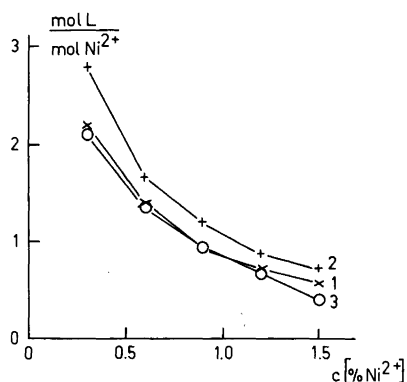

Fig. 6. Adsorption of NO and CO at 0 °C on nickel-containing silica gel with different nickel(II) concentrations (pretreatment: 1000 °C/10^{-2} Torr; 1, NO/1 Torr; 2, CO/760 Torr; 3, CO/1 Torr).

above, this gives a ratio for CO/760 Torr of three to one and for CO/1 Torr of two to one.* The latter ratio is thought to be valid also for the NO spectra. C_2H_4 displaces CO and so is bonded somewhat more strongly. This points to nearly the same or somewhat higher stoichiometric ratios at conditions similar to those of the reflectance spectra.

Adsorption of N_2 or O_2 was not detected. In contrast to the chromium(II)−NO[14] and iron(II)−NO[3] complexes the nickel(II) surface compound does not react with O_2 to yield NO_2-complexes. However, NO_2 is adsorbed to give a light green colour.

After adsorption of C_2H_2 at 760 Torr and 20 °C oligomerization to benzene (detected by mass spectrometry) was observed. A corresponding reaction with C_2H_4 was observed only at temperatures higher than 70 °C at 760 Torr together with a colour change to yellow. As products of this reaction four different hexenes were detected. In Ref. 6 butenes were reported for this reaction, but the preparation of the nickel catalyst was different there. At temperatures higher than 250 °C the colour of the sample changed to black (deposition of carbon or reduction to nickel(O)) and various C_4 and C_3 molecules were detected together with C_2H_6 and the above-mentioned hexenes.

Heating the coordinatively unsaturated nickel(II) compound in a stream of CO gave rise to a colour change to black at temperatures higher then 250 °C and metallic nickel (mirror) was deposited on the glass walls (a glass column was used as the sample container). This points to the reduction of nickel(II) to $Ni(CO)_4$, which decomposed later on the hotter glass walls.

IR spectra of CO adsorbed by the coordinatively unsaturated surface compound of nickel(II) on silica gel show only one very strong signal at 2042 cm^{-1}. On occasion two additional very weak signals at 2132 and 2192 cm^{-1} can be observed (Fig. 7). At these conditions (1 Torr/20 °C) the stoichiometric ratio is thought to be two molecules CO per metal surface ion (see above).

On heating this sample in vacuum at higher temperatures (50 and 100 °C) only the decrease of the signal at 2042 cm^{-1} was observed, but no increase in the intensities of the other two signals. This points to a direct breakdown of the CO com-

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* The slight temperature difference between the stoichiometric measurements and the spectra (20 °C) introduces a small error.
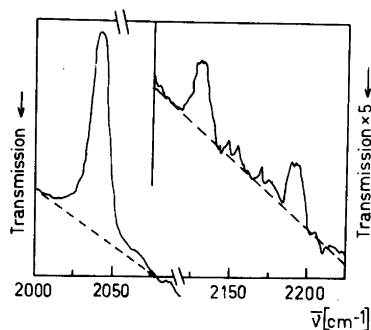
Fig. 7. IR spectrum of adsorbed CO at 20 °C/1 Torr [nickel(II) content: 0.6 %, pretreatment: 1000 °C/ 10^{-2} Torr].

plex without the other two CO complexes being involved as intermediate compounds. Samples with 1.5 % nickel and a pretreatment temperature of 500 °C showed a somewhat stronger band at 2192 cm^{-1}.

IR spectra of NO adsorbed by the nickel(II) surface compound show two signals at 1832 and 1878 cm^{-1} (Fig. 8, Curve 1). Again a difference can be seen between IR spectra when NO is directly adsorbed by the surface compound (Fig. 8, Curve 1) or when CO is adsorbed by the surface compound and then displaced by NO (Fig. 8, Curve 2). Under these conditions (1 Torr/20 °C) the stoichiometric ratio of NO per metal ion is thought to be two to one. Calculation of the angle between the two NO molecules according to Ref. 15 gives a value between 95 and 100°. IR bands at 1842 and 1872 cm^{-1} were reported for the deep green $Ni(NO)_2Cl_2$.[16] By comparison with the analogous compound of $Pd(NO)_2Cl_2$[17,18] a tetrahedral structure can be assigned to $Ni(NO)_2Cl_2$ and also (a distorted one)
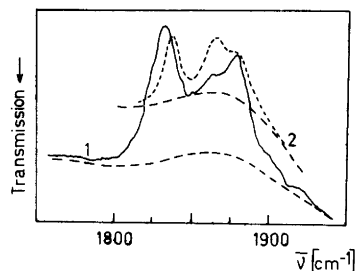

Fig. 8. IR spectra of adsorbed NO: 1, directly adsorbed; 2, after displacing CO [nickel(II) content 0.6 %; pretreatment 1000 °C, 10^{-2} Torr].

to the NO complex of the nickel(II) surface compound on silica gel. This is an important indication of four ligands around the nickel(II) surface ion, which then directly leads to the conclusion that the nickel(II) surface ion is bonded to the silica gel surface by two oxygen ligands.

DISCUSSION

The three bands observed in reflectance spectra of the sample with vacuum heat treatment at 1000 °C and that of the just impregnated and dried sample are in good agreement with the electronic spectra of octahedral nickel(II) complexes,[13] which have three spin-allowed transitions from the $^3A_{2g}$ state to the $^3T_{2g}$, $^3T_{1g}(F)$ and $^3T_{1g}(P)$ excited states, respectively $[(7-13) \times 10^3, (11-20) \times 10^3,$ and $(19-27) \times 10^3$ $cm^{-1}]$. Two spin-forbidden transitions, ^1E_g $[(11-14) \times 10^3$ $cm^{-1}]$ and $^1T_{2g}[(18-21) \times 10^3$ $cm^{-1}]$, are often observed. These are evident in the spectrum of the sample with vacuum heat treatment at 1000 °C (Fig. 1/4, near 14 and 18×10^3 cm^{-1}) (arrows). This indicates that the above spectrum arises from nickel(II) ions. However, as will be shown below, the actual symmetry must be C_{2v} and the actual coordination number is thought to be only two in the case of the sample with vacuum heat treatment at 1000 °C.

A model for the coordinatively unsaturated transition metal ions on silica gel with oxidation- and coordination-number two has been proposed before.[19,4] The reactions which may occur during the vacuum heat treatment were discussed in Refs. 3 and 4 and can be applied also to the nickel(II)/silica gel system.

Comparing the IR absorptions of the CO complexes with other coordinatively unsaturated surface compounds reveals a strong difference to the one observed above at 2042 cm^{-1} for nickel(II). So for chromium(II) a band at 2186,[20] for iron(II) at 2165[3] and for cobalt(II)[4] two bands at 2170 and 2184 cm^{-1} were observed and ascribed to CO metal ion ratios of 2:1 or 1:1 [iron(II)]. These bands all have higher wavenumbers than gaseous CO (2143 cm^{-1}). Only the very weak band at 2192 mentioned above would fit compared with the CO complexes of the other three surface compounds. High content nickel/silica gel systems[5] have a strong CO band near 2195 cm^{-1} after vacuum heat treatment at 500 °C and show bands near 2130 and 2050 cm^{-1} after reduction with hydrogen at that temperature. Consequently the IR bands are assigned to surface

compounds of nickel(II), nickel(I) and nickel(O), respectively.

Two arguments suggest that this explanation will not explain the observations stated above for the CO complex of the nickel(II) surface compound: 1, If $Ni(CO)_4$ is produced, it should leave the silica gel surface under vacuum and higher temperature (100 °C). This was not observed. Also $Ni(CO)_4$ was not detected in the gas phase above the samples under vacuum by mass spectrometry; 2, Nickel(0) is a d^{10} electronic system, which means that it has no allowed $d-d$ transitions and so should show no bands below 25×10^3 cm^{-1} [$Ni(CO)_4$ is colourless]. However, the spectra of CO adsorbed at the nickel(II) surface compound show bands in this region.

With four ligands, two oxygen ligands from the silica gel surface and two CO ligands, around the surface metal ion, three different configurations are possible: 1, tetrahedral; 2, *cis* square-planar (Fig. 12a); 3, *trans* square-planar (Fig. 12b). It is a well-established law of ligand field theory that the separation of the energy states in tetrahedral com-
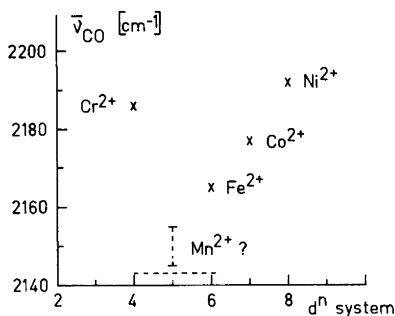
plexes is 4/9 of the separation in octahedral complexes.[21] So if the CO complexes had tetrahedral configurations the bands of the electronic spectra should be shifted to lower wavenumbers. This is not observed for the CO complexes of chromium(II),[22] iron(II)[3] and cobalt(II)[23] surface compounds on silica gel, so that only the two square-planar configurations are left.

In Fig. 9 the position of the IR bands from the CO complexes with the surface compounds (Cr, 2186; Fe, 2165; Co, 2177 (arithmetic mean value of 2170 and 2184), Ni: 2192 cm^{-1}) are shown *versus* the number of d electrons. With the assumption that the wavenumber of the gaseous CO can be used as the base line, this figure resembles the variation of the ligand field stabilisation energy when drawn for different d electron systems surrounded by a square-planar ligand field.[24]

In Fig. 10a the splitting of the d orbitals as derived from Fig. 9 (base line: gaseous CO) is shown. Again a correspondence with the diagram of the d orbitals split by a square-planar ligand field as shown in Refs. 21 and 24 can be seen. The fact that the manganese(II) surface compound binds the CO molecules only very weakly[2] can be explained by the d^5 electronic system of manganese(II) and so fits well in the above figures.

The assumption that the CO frequency can be used as a quantitative measure of the bond strength between the CO molecules and the surface compound is supported by Fig. 11. From preliminary adsorption measurements[23] it can be concluded that the IR absorption of CO adsorbed by the

Fig. 9. IR absorptions of CO adsorbed by transition metal ion surface compounds *versus* number of d electrons of the metal ions.

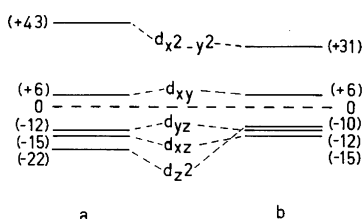*Fig. 10* . Splitting of d orbitals derived from Fig. 9 with the baseline at a, 2143 cm^{-1} and b, 2155 cm^{-1}. The numbers in brackets are the relative distance from zero in cm^{-1}.
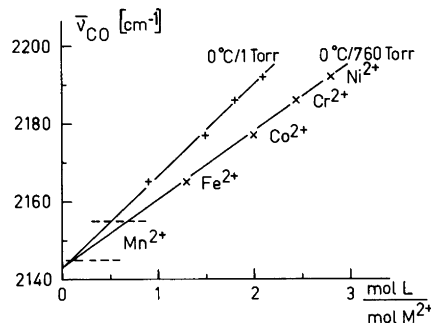

Fig. 11. IR absorptions of CO adsorbed by transition metal ion surface compounds *versus* ratio of adsorbed CO per metal ion (metal content: around 0.3 %). Fe, Co and Ni see Refs. 3, 4 and this paper. Chromium content: 0.3 %, oxydation number: 2.2, preparation see Ref. 34, absorption of CO see Ref. 23).
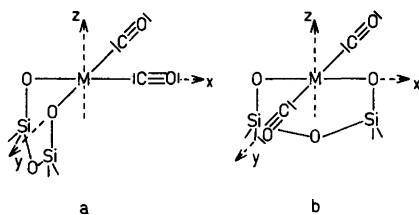
Fig. 12. Model of CO complexes with the transition metal ion surface compounds for a, *cis* and b, *trans* square-planar configuration.

manganese(II) surface compound may lie between 2145 and 2155 cm^{-1}. With the latter value Fig. 10b is redrawn from Fig. 10a, but no substantial difference can be seen between the two figures.

Referring to Fig. 12a a deformation of the (not drawn) d_{xy}, d_{xz} and the d_{yz} orbitals can be assumed on the basis of the electronegativity difference of the oxygen ligands and the metal ions. Together with the low electronegativity difference between the metal ion and the carbon of CO and the relatively high positive charge of two compared with other metal carbonyls this may lead to an electron decrease for the d_{xy}, d_{xz} and the d_{yz} orbitals oriented towards the CO molecules. This can explain why weak or no back donation at all from the metal to the CO is observed with chromium(II), [manganese(II)], iron(II) and cobalt(II) if one assumes a *cis* square-planar configuration.

A third ligand in the z direction can use partly electrons from the deformed d_{xz} or d_{yz} orbitals for back donation and so may have wavenumbers below that of gaseous CO.[20,25]

Referring to Fig. 12b a deformation of the d_{xy} and the d_{xz} orbitals may be assumed, with only weak deformation of the d_{yz} orbital. The two CO ligands can now share the two electrons, each receiving one in the case of a d^8 electronic system [nickel(II)], assuming a splitting as shown in Fig. 10a. This provides for a back donation and can explain the observed CO stretching frequency of 2042 cm^{-1}. That this back donation is only observed for the nickel(II) surface compound may be due to the half filled d_{yz} orbital in the case of the other four metal ions and to the smaller ion radius of the nickel(II).[24]

A *trans* square-planar configuration for the nickel(II) CO complex explains also the fact that only one IR signal is found. Fig. 11 supports the assumption that the actual energies of the *cis* and the *trans* square-planar configuration are not very different. The two IR signals for CO adsorbed by the cobalt(II) surface compound support on the other hand a *cis* square-planar configuration. The single IR absorption for the CO complex with iron(II) may be explained by the stoichiometry of one CO molecule per metal ion.[3]

On samples with high nickel content and low pretreatment temperatures a transformation from a *cis* to a *trans* square-planar configuration may be prevented.

The model of a *cis* or *trans* square-planar configuration may also help to explain the rather complicated IR spectra of CO adsorbed by the surface compound of chromium(II).[20] As stated above the peak of this signal is at 2186 cm^{-1} but two shoulders are also observed at 2181 and 2191 cm^{-1}. After evacuation the main signal decreases but the shoulders remain nearly unchanged.

The IR band with the peak at 2186 cm^{-1} may be assigned to a CO complex with a *trans* square-planar configuration because the peak was recorded under conditions (40 Torr/CO pressure) where two CO molecules are bonded to the chromium(II) surface compound (Fig. 11). The two bands at 2191 and 2181 cm^{-1} may be assigned to a *cis* square-planar configuration and can be compared with those of the cobalt(II) surface compound[4] at 2184 and 2170 cm^{-1}: The two signals have in both cases nearly equal intensities, which means an angle of 90° between the two CO ligands according to Ref. 15 and the splitting in each case, 10 and 14 cm^{-1}, is very similar.

It is known that of the total amount of the chromium(II) surface compound only 5 to 20 %[26-28,30] reacts as the catalytic center of the polymerization of C_2H_4, which is thought to be the catalytic reaction of the Phillips process.[29] Now the intensity of the two IR bands at 2191 and 2181 cm^{-1} is just around 20 % of the total intensity when the peak at 2186 cm^{-1} has its highest intensity.[20] On this basis the chromium(II) surface compound which forms the CO complex with the two IR bands may be the precursor of the catalytic center for the polymerization of C_2H_4, which may start with the oxidative cyclo-addition of two C_2H_4 molecules.

The missing link between the CO complex and the starting mechanism of the polymerization, the C_2H_4 adsorption with the formation of a *cis* square-planar complex with the chromium(II) surface compound, although yet not proved, is easy to imagine as C_2H_4 complexes are known with all five metal ion surface compounds on silica gel.[2-4,30]

The model for the coordinatively unsaturated transition metal ions on silica gel with the oxidation- and coordination-number two implies that four ligands can be adsorbed to raise the coordination number of the metal ion to six. Four different types of ligands can be distinguished by their behaviour during adsorption:

1. Ligands with stoichiometric ratios of one molecule to one metal ion, for instance chelate ligands.[31]

2. Ligands with stoichiometric ratios of 2:1, for example NO.

3. Ligands with the stoichiometric ratio of up to three to one or even four to one such as CO (or C_2H_4). With these ligands a more or less linear increase in the ligand/metal ion ratio is observed with decreasing temperature and increasing pressure.[30]

4. Ligands with the stoichiometric ratio of up to 4:1 such as H_2O or NH_3[32] but with a discrete step at the 2:1 ratio.

After adsorbing less than four ligands the free coordination sites can be occupied by other ligands to yield mixed ligand complexes. This is especially well-established for NO as the first two ligands and various other ligands adsorbed thereafter, such as CO, H_2O, NH_3 etc.[33] (but not NO).

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