

On the Catalytic Activity of Mononuclear and Dinuclear Chromium(II)-A Surface Species on Silica Gel

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As can be shown from low-temperature spectra of adsorbed CO at 2184 cm^{-1} on mononuclear chromium(II)-A, this surface compound is partially converted by repeated oxidation/reduction cycles (at 800 and 350 °C, respectively) into the dinuclear surface species with the typical low temperature triplet from bridging CO molecules at 2120, 2100 and 2035 cm^{-1} . Low-temperature CO IR spectra recorded before (CO removed again at 300 °C in vacuum) and after short polymerization with ethylene show that only the dinuclear species is polymerization active. Previously, it was shown that in certain chromium(II)-B samples (oxidation at 500 °C, reduction at 350 °C) which also contain some chromium(II)-A exclusively as the mononuclear species, only the chromium(II)-B species polymerizes. These results show that at low oxidation temperatures (500 °C) mainly mononuclear chromium surface species are formed, and that with higher oxidation temperatures (up to 800 °C) dehydroxylation and a conversion to dinuclear species take place.

The question of whether the catalytically active sites of the Phillips catalyst [Chromium(VI) on silica gel]¹ for polymerization of ethylene consist of mononuclear or dinuclear [chromium(II)] surface compounds has been investigated by several research groups. Shortly after the first publications on the active chromium(II) surface compound by Krauss and Stach²⁻⁴ in 1968, Hogan⁵ proposed a “monochromate (possibly dichromate)” structure on the basis of gravimetric measurements on chromium(VI) catalysts in relation to unimpregnated silica gel. However, similar measurements on the chromium(II)/SiO₂ catalyst were later published by Hierl and Krauss.⁶ Here, mononuclear structures were proposed for the chromium(II) species on silica gel oxidized at 500 °C.

Meanwhile, the chromium(II) species on silica gel was found to consist of three subspecies, which were denoted A, B and C. Chromium(II)-A was identified as the active site of the Phillips catalyst, where the chromium(II) has only two oxygen ions as ligands and therefore has the coordination number two.⁷⁻¹⁰ The chromium(II) species B and C have as a third ligand a hydroxyl group^{7,8} or a siloxane group^{9,10} from the silica gel, respectively. On the basis of low-temperature CO IR spectra of the chromium(II)-A surface compound and other results, which were interpreted as due to bridging CO ligands, the Italian group concluded that the chromium(II)-A surface species must be dinuclear.^{9,10} More elaborate results and interpretations were later published by the present author.^{11,12} On the basis of a postulated initiation mechanism for the polymerization it was proposed that only the dinuclear chromium(II)-A species should be catalytically active, while a mononuclear chromium(II)-A species should be inactive.¹²

In the beginning of the eighties, McDaniel published

results from impregnation studies¹³⁻¹⁶ with chromic acid and chromyl chloride, and did not find evidence for dinuclear chromium(II)-A species. An investigation of the chemiluminescence spectrum during the oxidation of chromium(II) to chromium(VI) by oxygen by Morys *et al.*¹⁷ provided evidence for a mononuclear chromium(II)-A surface species.

In a recent paper¹⁸ on the polymerization mechanism of the chromium(III) and chromium(II)-B surface species the author found evidence for the mononuclear chromium(II)-A surface species, which in contrast to chromium(II)-B and chromium(III) showed no catalytic activity. The preparation conditions for this sample were changed slightly from those for a “normal” chromium(II)-B catalyst: instead of oxidation and reduction at 500 °C, the reduction temperature had been lowered to 350 °C. This change yielded a small amount of chromium(II)-A together with the chromium(II)-B.

In order to obtain more conclusive evidence for a catalytically inactive mononuclear chromium(II)-A the chromium(II)-A catalysts were studied again with an improved experimental design, and the results are presented below.

Experimental

The chromium concentration of the silica gel (60, Merck 7733) was 0.5 %. Discs with a diameter of 2 cm were pressed at 500 kg cm^{-2} from the powdered catalyst. The discs were positioned on a quartz holder (which gives a better reproducibility of the disc position than the previous one made of platinum wire) and placed in an IR cell described previously.¹⁹ The samples were heated to 800 °C [Chromium(II)-A] or 500 °C [Chromium(II)-B], alternating

between vacuum and oxygen (oxidation), and were reduced with CO at 350 °C. The IR spectra were recorded on a Nicolet 20SXC FTIR spectrometer. The resolution was set to 2 cm^{-1} and 512 spectra were accumulated.

UV/Vis/NIR diffuse reflectance spectra were recorded on a Hitachi (Perkin-Elmer) 330 spectrometer with an integrating sphere. All samples were manipulated in such a way that contact with air was excluded. The spectrometer was controlled from an Atari 1040 ST computer using a home-made program compiled in 2.0 GFA Basic. The program corrected the spectra at 875 nm (detector change) and at 350 nm (lamp change), recalculated the spectra according to the Kubelka-Munk function,²⁰ and converted them from wavelength into wavenumber spectra.

Results

Fig. 1 shows low temperature ($-145\text{ }^{\circ}\text{C}$) CO IR spectra of samples oxidized at 800 °C and reduced with CO at 350 °C. Spectrum A was recorded after the first oxidation/reduction and spectrum B after an additional two oxidation/reduction cycles. The low-temperature triplet of CO IR bands at 2120, 2100 and 2035 cm^{-1} is prominent in both spectra, and in spectrum B it has such a high intensity that the conversion from transmittance to absorbance yields infinite (unreliable) values (transmittance close to zero). This triplet has been assigned to CO stretching vibrations from three CO molecules bridging two chromium(II) surface cations from a dinuclear surface compound.^{10,11}

The well known room temperature triplet of CO IR bands at 2190, 2185 and 2180 cm^{-1} is to a large extent converted to the low temperature triplet on cooling with liquid nitrogen.^{10,11} The interpretation for this conversion is that terminal CO ligands are replaced by bridging CO ligands. However, a weak band at 2184 cm^{-1} is not con-

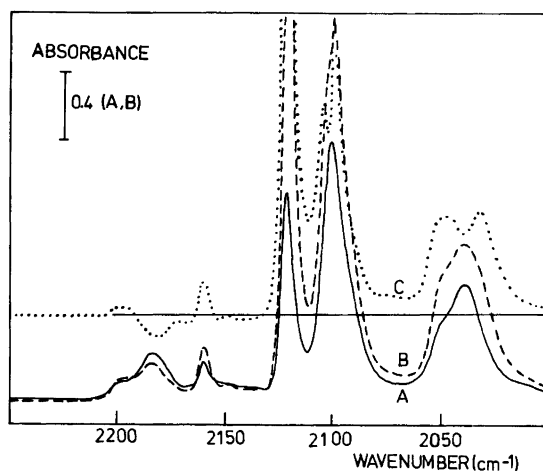


Fig. 1. FTIR spectra of CO adsorbed at low temperatures on chromium(II)-A samples. Spectrum A after the first oxidation (800 °C, O_2)/reduction (350 °C, CO) treatment. Spectrum B after two additional oxidation/reduction cycles. Spectrum C is the difference spectrum (spectrum A minus spectrum B).

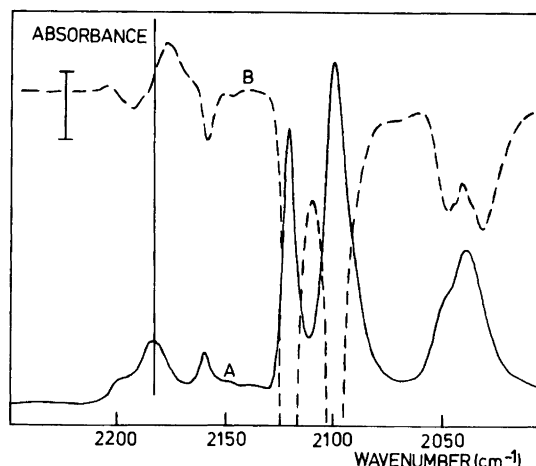


Fig. 2. FTIR spectra of CO adsorbed at low temperatures on chromium(II)-A samples (oxidation at 800 °C, O_2 , reduction at 350 °C, CO). Spectrum A as for spectrum A in Fig. 1. Spectrum B is the difference spectrum for the CO IR spectrum after short polymerization with ethylene minus the spectrum before short polymerization. Negative bands are from CO species removed by the polymerization, positive bands are from those newly formed.

verted at low temperatures (Fig. 1, spectra A and B). This band was previously interpreted¹¹ as arising from terminal CO on the dinuclear chromium(II) surface compound at low temperatures, adsorbed simultaneously with the three bridging CO ligands.¹¹

The difference spectrum C in Fig. 1, which was calculated by subtracting spectrum A from spectrum B, discredits, however, such an interpretation. The only negative band is at 2183 cm^{-1} , and several positive bands are near those of the low temperature triplet. The interpretation is simple: a chromium(II) surface species has been transformed to the dinuclear species on several (two in this case) additional oxidation/reduction cycles. The CO IR "rest band" at 2184 cm^{-1} is now interpreted as arising from terminal CO adsorbed on the mononuclear chromium(II) surface species. It should be noted that the weak band at 2200 cm^{-1} in spectrum C, arising from CO on chromium(III) surface compounds,¹¹ is also positive. This implies that the new dinuclear chromium(II) species is not formed by reduction of chromium(III). One should also notice in the difference spectrum C the splitting of the two bands around 2100 and 2035 cm^{-1} into bands at 2102.2, 2097.61 cm^{-1} and 2045.76 and 2029.13 cm^{-1} . A band at 2158.76 and a small band at 2147.02 cm^{-1} also increase together with the low-temperature triplet.

We now turn to the most interesting question of whether the mononuclear chromium(II) species polymerize ethylene or not. Fig. 2, spectrum B, shows the difference between the IR spectrum of the CO adsorbed at low temperature on the chromium catalyst after short polymerization at 100 °C for 15 sec and 22 Torr ethylene pressure and the CO IR spectrum at low temperature before the short polymerization (this CO was removed again at 300 °C in

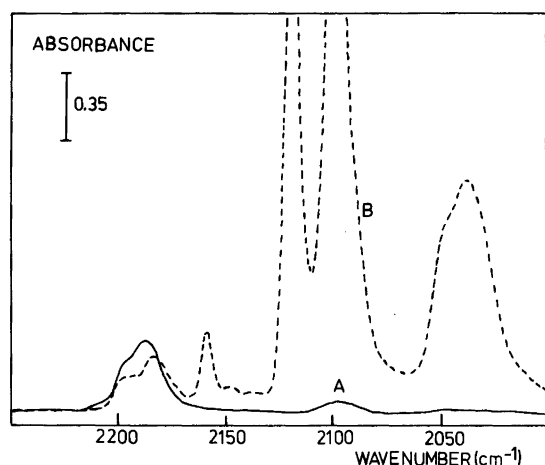


Fig. 3. FTIR spectrum (A) of CO adsorbed at low temperature on a chromium(II)-B sample (oxidation at 500 °C, reduction at 350 °C). Spectrum B the same as spectrum B in Fig. 1.

vacuum). This means that negative bands are from sites removed by the polymerization and positive bands from sites newly formed. As noted previously,²¹ the low-temperature CO triplet shows negative bands together with splitting of the 2035 cm⁻¹ band (2045.27 and 2029.16 cm⁻¹) and the (negative) band at 2158.28 cm⁻¹.

One additional negative band appears at 2193 cm⁻¹, which correlates with CO on a chromium(II)-C surface species¹¹. This indicates that also this species is polymerization active.

The most important feature in spectrum B is, however, that no change occurs at the position where the IR bands due to CO adsorbed on the mononuclear chromium(II)-A species are found (2184 cm⁻¹). This means that the mononuclear chromium(II)-A species is indeed present in a chromium(II)-A catalyst (high oxidation temperature of around 800 °C, reduction at 350 °C with CO), but is not, in contrast to the dinuclear species, polymerization active. The only positive band at 2176.8 cm⁻¹ arises from CO adsorbed on the polymerizing ("living") catalyst site.^{21,22}

As Fig. 3, spectrum A shows, using a lower oxidation temperature (500 °C) than in the above case and the same reduction temperature (350 °C) yields low temperature CO IR spectra with nearly no bands from the low temperature triplet. Only a weak band at 2098 cm⁻¹ is seen. On the other hand, the shoulder at 2184 cm⁻¹ is clearly visible in contrast to spectra²³ from chromium(II)-B sample with a reduction temperature of 500 °C. However, comparing spectrum A and B in Fig. 3 it can be seen that the intensity of the low-temperature band at 2184 cm⁻¹ is considerably higher in the case of spectrum B. This means that on increasing the oxidation temperature, much more mononuclear chromium(II)-A species is formed after reduction at the same temperature (350 °C).

Fig. 4 shows diffuse reflectance spectra of one sample after different preparation procedures. The first procedure was oxidation and reduction at 500 °C (spectrum not

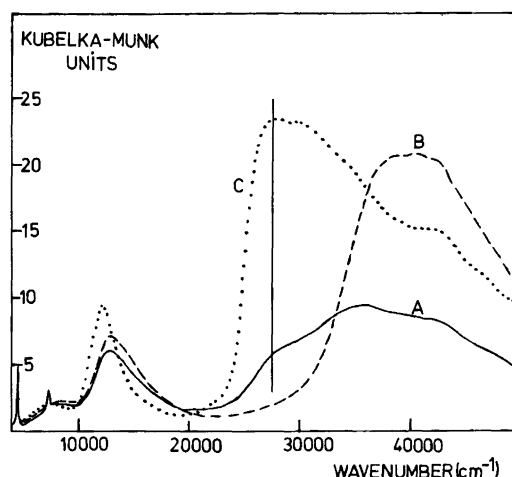


Fig. 4. Diffuse reflectance spectra of (A) a sample after oxidation at 500 °C and reduction at 350 °C; (B) with following oxidation and reduction at 500 °C each; (C) after a further two oxidation/reduction cycles at 800 °C and 350 °C, respectively.

shown), the second was oxidation at 500 °C and reduction at 350 °C (Spectrum A in Fig. 4), the third was oxidation/reduction at 500 °C (Spectrum B), the fourth was oxidation at 800 °C and reduction at 350 °C (not shown), and the last (fifth) was the same as the fourth preparation procedure (spectrum C).

Spectrum A (reduction at 350 °C) shows a general shift of the peaks to lower wavenumber compared to spectrum B (reduction at 500 °C) from 8770 to 8190 cm⁻¹, 12 960 to 12 790 cm⁻¹, 37 960 to 35 550 cm⁻¹ and a new band at 27 480 cm⁻¹ (vertical line in Fig. 4). The latter band is also found in spectrum C and obviously belongs to the chromium (II)-A species. The two other peaks in spectrum C are at 7520 and 12 130 cm⁻¹.

Difference spectra in Fig. 5 of spectrum A minus spec-

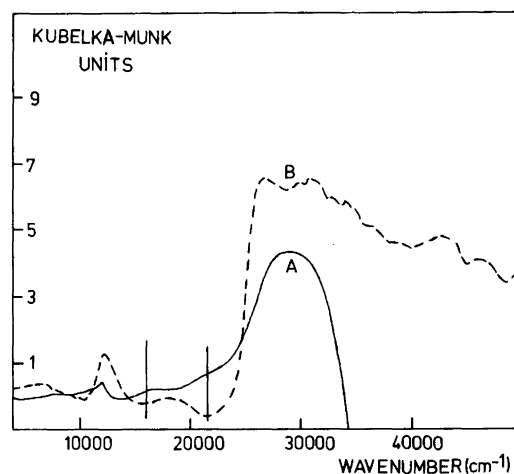


Fig. 5. Difference diffuse reflectance spectra of (A) spectrum A minus spectrum B from Fig. 4 and (B) spectrum C from Fig. 4 minus the spectrum from the first oxidation/reduction cycle at 800 and 350 °C.

trum B in Fig. 4 (spectrum A in Fig. 5), and spectrum C in Fig. 4 minus the spectrum after the fourth preparation procedure (not shown) (spectrum B in Fig. 5) show positive bands from a chromium(II)-A species around 7000, 12 000 and 28 000 cm^{-1} . Two bands at 16 600 and 21 600 cm^{-1} (vertical lines in Fig. 5) show up in the difference spectrum A as positive bands and in the spectrum B as negative bands. In both cases this means that after one more preparation cycle some chromium(III) has been converted to chromium(II). From Figs. 4 and 5 and the above results it may be concluded that all three bands at 7500, 12 000 and 28 000 cm^{-1} belong to the chromium(II)-A species, and that no differences in these UV/Vis spectra are observed for the mononuclear and the dinuclear chromium(II) surface species. This contrasts with a previous interpretation by the present author.²⁴

Discussion

The above results show again the uniqueness of the low temperature CO IR spectra of chromium(II) in silica gel. There is no other plausible interpretation than the assumption of the formation of bridging CO molecules on chromium(II). A similar conversion of terminal CO to bridging CO is known for the dimeric cobalt carbonyl $[\text{Co}_2(\text{CO})_8]$.²⁵ However, the CO IR bands in this case are observed at much lower wavenumbers.

The spectra show also that the chromium(II) ions in the mononuclear surface compound and those in the dinuclear species are electronically quite similar: terminal CO is bonded with similar frequencies, and the electronic spectra show no differences beyond the experimental error.

The Phillips catalyst is essentially chromium(VI) on silica gel. During the various oxidation treatments in our experiments at 800°C, followed by reduction at 350°C, the amount of the mononuclear chromium(II) surface compound decreases. It is concluded that the conversion of surface monochromate to surface dichromate is rather slow compared to the dehydroxylation of the silica gel: otherwise the chromium(II)-B species would still be present. During the activation of the industrial catalyst by oxygen or dry air at temperatures between 400 to 900°C, at the lower temperatures monochromate with surrounding hydroxyl groups will predominate, and on reduction with CO (or ethylene in the industrial polymerization) form mononuclear chromium(II)-A, -B and chromium(III) species. After activation at the higher temperatures many surface silanol groups will be removed and most of the monochromate will be converted to dichromate. On reduction with CO (or ethylene), mainly dinuclear chromium(II)-A, -C and (few) chromium(III) species are then formed.

Medium activation temperatures will give rise to mixtures of the two extreme situations.

The dinuclear chromium(II)-A, -C and chromium(III) species are polymerization active, and will lead, after high temperature activation, to a mixed product from these catalytically active species [mainly from chromium(II)-A and chromium(III)]. Chromium(II)-B, which is mononuclear, can be oxidized by the hydroxyl ligand (and ethylene) to an active chromium(III) species, and therefore the low temperature activated catalysts will show only polymers produced by chromium(III).

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References

1. Clark, A., Hogan, J. P., Banks, R. L. and Lanning, W. C. *Ind. Eng. Chem.* **48** (1956) 1152.
2. Krauss, H. L. and Stach, H. *Inorg. Nucl. Chem. Lett.* **4** (1968) 393.
3. Krauss, H. L. and Stach, H. *Z. Anorg. Allg. Chem.* **366** (1969) 34.
4. Krauss, H. L. and Stach, H. *Z. Anorg. Allg. Chem.* **366** (1969) 280.
5. Hogan, J. P. *J. Polym. Sci. A-1* **8** (1970) 2637.
6. Hierl, G. and Krauss, H. L. *Z. Anorg. Allg. Chem.* **415** (1975) 57.
7. Rebenstorf, B. *Thesis*, Freie Universität Berlin, Berlin (West) 1975.
8. Krauss, H. L., Rebenstorf, B. and Westphal, U. *Z. Anorg. Allg. Chem.* **414** (1975) 97.
9. Zecchina, A., Garrone, E., Ghiotti, G., Morterra, C. and Borello, E. *J. Phys. Chem.* **79** (1975) 966.
10. Zecchina, A., Garrone, E., Ghiotti, G. and Coluccia, S. *J. Phys. Chem.* **79** (1975) 972.
11. Rebenstorf, B. and Larsson, R. *Z. Anorg. Allg. Chem.* **478** (1981) 119.
12. Rebenstorf, B. and Larsson, R. *J. Mol. Catal.* **11** (1981) 247.
13. McDaniel, M. P. *J. Catal.* **67** (1981) 71.
14. McDaniel, M. P. *J. Catal.* **76** (1982) 17.
15. McDaniel, M. P. *J. Catal.* **76** (1982) 29.
16. McDaniel, M. P. *J. Catal.* **76** (1982) 37.
17. Morys, P., Görges, U. and Krauss, H. L. *Z. Naturforsch. B* **39** (1984) 45.
18. Rebenstorf, B. *Z. Anorg. Allg. Chem. In press.*
19. Rebenstorf, B. and Larsson, R. *Z. Anorg. Allg. Chem.* **453** (1979) 127.
20. Kubelka, P. and Munk, F. *Z. Techn. Phys.* **12** (1931) 595.
21. Rebenstorf, B. *J. Mol. Catal.* **345** (1988) 263.
22. Rebenstorf, B. *J. Catal. In press.*
23. Hoepfl, R. *Thesis*, Universität Bayreuth, F. R. G. 1981.
24. Rebenstorf, B. *Z. Anorg. Allg. Chem.* **531** (1985) 41.
25. Purcell, K. F. and Kotz, J. C. *Inorganic Chemistry*, W. B. Saunders Company, Philadelphia, PA 1977, p. 858.

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