

SURFACE COMPOUNDS OF TRANSITION METALS, XII.\*  
COORDINATION STATE OF CHROMIUM(II) AMINE COMPLEXES IN CO REDUCED  
PHILLIPS CATALYSTS: A VISIBLE AND NEAR INFRARED SPECTROSCOPIC STUDY

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Surface chromium (II) on silica is coordinated by two  $\equiv\text{SiO}$  groups in cis position. Adsorption of ammonia and amines leads to stable  $(\equiv\text{SiO})_2\text{CrL}_2$  and further to unstable  $(\equiv\text{SiO})_2\text{CrL}_4$ ; reflection spectra suggest pseudo square planar and pseudo octahedral structures respectively for these complexes. Formation of the six-coordinate species depends on the type of the amine.

Поверхностный хром (II) на окиси алюминия координирован в положении цис двумя группами  $\equiv\text{SiO}$ . Адсорбция аммония и аминов приводит к образованию стабильного  $(\equiv\text{SiO})_2\text{CrL}_2$  и нестабильного  $(\equiv\text{SiO})_2\text{CrL}_4$ ; на основе спектров отражения для этих комплексов полагается псевдоквадратноплоская и псевдооктаэдрическая структура, соответственно. Образование соединений с координационным числом шесть зависит от типа амина.

## INTRODUCTION

After reduction with CO, Phillips catalysts contain Cr(II) surface compounds /2/ which include the catalytically active sites in the polymerization of ethylene /3, 4/. The coordination state of these — coordinatively unsaturated — surface

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species (c. u. s. ) is therefore of central interest with respect to the polymerization mechanism. Recently we have shown for a silica supported catalyst by means of TG analysis and optical spectroscopy that at least 3 coordination sites per  $\text{Cr}^{2+}$  are available for the adsorption of the strong electron donor  $\text{NH}_3$ , leading to surface complexes with the ratios  $\text{NH}_3/\text{Cr}^{2+} = 2$  and  $4 \pm 1$  respectively /5/. In this work we report the spectroscopic data in more detail. Using diffuse reflectance spectroscopy we have studied the adsorption of ammonia, monomethylamine (mma), dimethylamine (dma), trimethylamine (tma), ethylenediamine (en) and pyridine (py).

### EXPERIMENTAL

Sample preparation and chemical analysis were described earlier /5/. The experimental data in this work were as follows: Cr content 0.35% (applied by impregnation of silica "Merck 7733" with  $\text{CrO}_3$  in  $\text{H}_2\text{O}$ ); activation ( $\text{O}_2$ ), reduction ( $\text{CO}$ ), desorption of  $\text{CO}$  (Ar) at  $500^\circ\text{C}$ , oxidation number 2.1 - 2.2. Gases were dried and freed from  $\text{O}_2$  by passing through columns with Na and  $\text{Cr}^{2+}/\text{SiO}_2$  catalyst; liquids were refluxed over Na in an argon stream for several hours prior to fractionation. Adsorption and desorption were carried out at various temperatures in a fluidized bed reactor using argon as carrier gas with variable partial pressures of the respective ligand. Conventional Schlenk-tube techniques were applied to operate reactor and cuvette (quartz tube, 2 cm diameter) under argon. Diffuse reflectance spectra were recorded at room temperature against a silica standard calcined at  $1000^\circ\text{C}$  and sealed under argon.

## RESULTS AND DISCUSSION

On the silica support most of the surface  $\text{Cr}^{2+}$  if not all is bound by  $2 \cong \text{SiO}$  groups, derived from vicinal surface hydroxyls /6/. Additional ligands in question would be oxygen ligands as well, so a weak ligand field with  $\text{Cr}^{2+}$  in a quintet high spin state is to be expected. In a cubic ligand field the  $^5\text{D}$  ground term would split into two terms allowing one electronic transition ( $^5\text{T}_{2g} \leftarrow ^5\text{E}_g(\text{O}_h)$ ;  $^5\text{E} \leftarrow ^5\text{T}_2(\text{T}_d)$ ). According to the Jahn-Teller theorem, however, a degenerate ground state is not stable in a  $d^4$  system and will split into its components, giving rise to asymmetric or split absorption bands and lower coordination symmetry, i. e. an octahedron with 6 identical ligands will be tetragonally distorted. The theory is fully confirmed by X-ray structures /7, 8/ and the spectroscopic data for bulk and dissolved  $\text{Cr}^{2+}$  aqua and amine complexes /9, 10/. In the spectral region characteristic of d-d transitions our samples exhibit two broad absorption bands at 12.9 and  $\sim 8.3$  kK (spectrum 1; the CT transition at ca. 31 kK and the narrow peaks due to vibrations of support and ligand will not be discussed here). Stepwise adsorption and curve analysis of the corresponding spectra using Gaussian components show that both transitions belong to the same center. Provided that these absorptions belong to d-d transitions indeed, we may rule out a tetrahedral coordination, which was proposed by Kazanskii et al. /11/: For tetrahedral coordination with O-ligands, only one transition at about 6 kK would be expected, using the relationship  $\Delta(\text{T}_d) = 4/9 \Delta(\text{O}_h)$  and the hexaaqua ion as reference. The validity of this argument is proved for  $\text{Cr}^{2+}$  in a ZnS host lattice /12/.

Prior to further interpretation of the spectra we have to mention the role of  $\text{Cr}^{3+}$  which is also present in 10 – 20% of the overall Cr. Its formation is due to hydrolysis of the  $\text{Si-O-Cr}^{6+}$  bonds during activation and subsequent thermal decom-

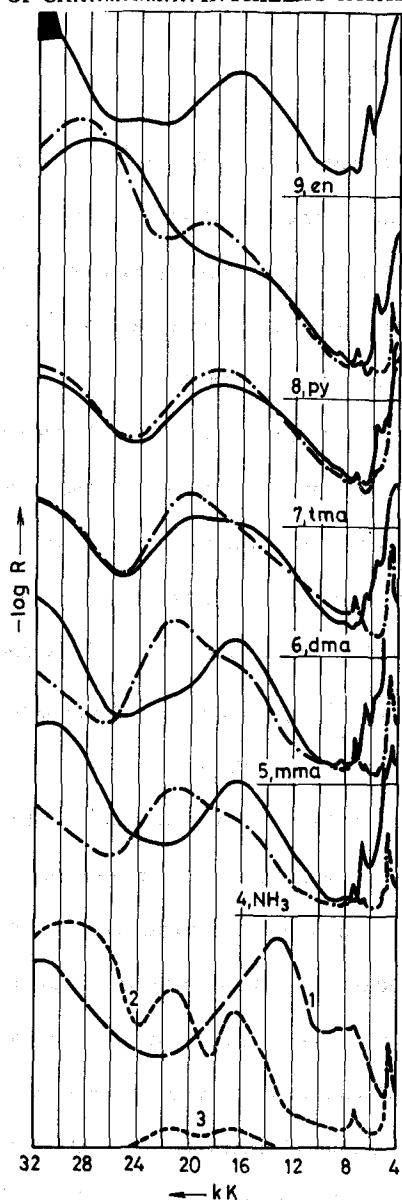


Fig. 1. Reflectance spectra of a silica supported Phillips catalyst (0.35 wt.% Cr)  
 (1)  $\text{CrO}_3/\text{SiO}_2$  reduced in CO at  $500^\circ\text{C}$ :  $\text{Cr}^{2+}$  c. u. s., (2)  $\text{CrO}_3/\text{SiO}_2$  after  
 treatment in  $\text{H}_2\text{O}/\text{Ar}$  at  $500^\circ\text{C}$ :  $\text{Cr}^{3+}$ ; (3) estimated fraction of (2) in (1)  
 in the d-d region; (4)-(9) adsorption complexes of  $\text{Cr}^{2+}$   
 a) -.- desorbed at  $100 - 150^\circ\text{C}$  in an Ar stream after saturation,  
 b) — saturated adsorption

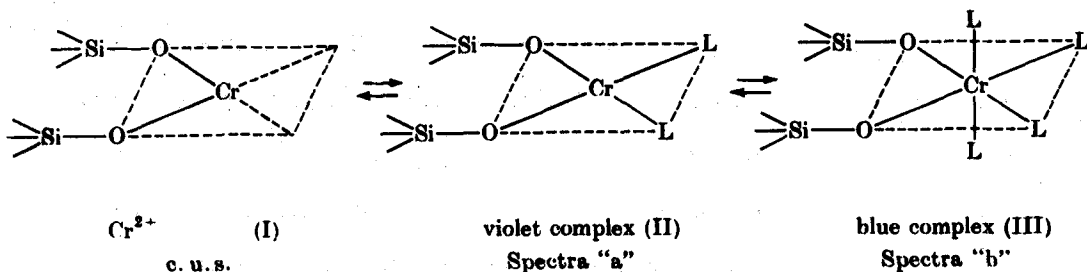
position. Accordingly, treatment of an activated sample with an  $H_2O/Ar$  stream at  $500^\circ C$  for several hours forms a greenish  $Cr^{3+}$  product. Besides a slight asymmetry, the spectrum (sp. 2) is identical with that of bulk  $Cr_2O_3$  and not affected by the adsorption of  $NH_3$ . Hence we may consider  $Cr^{3+}$  as a small and negligible component (sp. 3) in the  $Cr^{2+}$  spectra.

With stepwise adsorption of  $NH_3$  now, the  $Cr^{2+}$  spectrum slowly changes and a new absorption band at 20.8 kK is finally established (sp. 4a) which corresponds to an  $NH_3/Cr^{2+}$  ratio of 2/5/. This violet complex is completely stable up to  $150^\circ C$  in an Ar stream. From the marked asymmetry we may conclude again that the central ion is not in a cubic ligand field. Further adsorption to final saturation does not result in a continued shift to higher frequencies as one might expect. On the contrary a large reverse shift does occur ( $\lambda_{max} = 16.3$  kK, sp. 4b). This phenomenon is typical for  $d^4$  and  $d^9$  systems and generally known as "pentaamine effect" /13/. Without going into details of structural discussion /13/ we may state that this effect is observed if an additional (or stronger) ligand enters the axial position in a planar (or distorted octahedral) ligand field; the axial bonds are markedly weakened. The lability of the blue complex which starts to decompose in Ar at room temperature and in  $NH_3$  at  $50^\circ C$  is obviously correlated to that effect. Though the TG measurements indicate a range from 3 to 5 for the  $NH_3/Cr^{2+}$  ratio and though one ligand would be sufficient to produce the "pentaamine effect", we think that two additional  $NH_3$  molecules coordinate in the violet complex. The unusual magnitude of the reverse shift ( $\Delta \bar{\nu} = 4.5$  kK compared to 2.2 kK in  $[Cr en_2 Br_2]^{2+} \rightleftharpoons [Cr en_3]^{2+}$  for example /10/ and the increased symmetry of the absorption band support this view. We rule out further the formation of  $[Cr(NH_3)_6]^{2+}$  in a detectable amount, as its spectrum /15/ is not compatible with sp. 4b.

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At desorption temperatures of 450 – 500 °C the spectrum of the starting material is obtained again. The adsorption is fully reversible if good flow conditions and short heating times are applied. Accordingly, the desorbed samples show the same polymerization activity as the original  $\text{Cr}_{\text{C. u. s.}}^{2+}$ , whereas the violet and the blue complexes are absolutely inactive.

We now can propose the following reaction scheme in agreement both with the experimental data above and the general features of the coordination chemistry of  $\text{Cr}^{2+}$



Weak interaction of (I) with other easily replaceable surface groups cannot be completely excluded.

With the exception of "en", the adsorption scheme applies to the amines as well, but to a varying degree. We find the formation of (III) (sp. 5 – 8b) the more restricted the more bulky ligands we use. In the case of "tma" even (II) is not fully established as spectra and TG results ( $\text{tma}/\text{Cr}^{2+} = 1.2 - 1.8$ ) indicate. Surprisingly, all attempts to prepare the intermediate (II) of "en" have failed. By adsorption, (III) is obtained only which cannot be desorbed to (II) at elevated temperatures without massive decomposition to  $\text{Cr}^{3+}$ . We ascribe this enhanced stability to the chelate

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effect with a bidentate ligand. Up to now we have spoken in terms of uniform  $\text{Cr}^{2+}$  c. u. s. sites. This simplification does not affect the principal conclusions drawn above, but it must be kept in mind that the  $\text{Cr}^{2+}$  centers represent a distribution with respect to various properties, depending on the conditions of catalyst preparation /16/. The spectral changes in the aliphatic amine series which seem to be due primarily to steric reasons will thus provide a new means for the study of the distribution of the  $\text{Cr}^{2+}$  centers over a topology parameter.

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