

An Infrared Spectroscopic Investigation on CO Adsorbed on Silica-Supported Vanadocene

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Vanadocene and $V(cp)(CO)_4$ in toluene solution have been adsorbed on SiO_2 and SiO_2/Al_2O_3 , respectively. The number of surface hydroxyl groups on these supports was varied by using two different temperatures of activation *in vacuo* (573 and 873 K). IR spectra indicated that vanadocene formed $V(cp)_2CO$ and/or $[V(cp)_2(CO)_2]^+$ when exposed to CO after sample evacuation at 298 and 373 K.

Reaction of $V(cp)_2$ with the support at 573 K yielded inorganic V(II) surface compounds on SiO_2 activated at 873 K and inorganic V(II) and V(III) surface compounds on SiO_2/Al_2O_3 activated at 573 K. Reaction at 773 K resulted in V(II) and V(III) species on the SiO_2 and mainly V(III) on the SiO_2/Al_2O_3 support. The oxidation states of vanadium were determined from the IR spectra of adsorbed CO. Vanadocene did not give any surface compounds on the SiO_2 support activated at 573 K. These results are explained by the different acidities of the surface silanol groups. Increased acidity leads to more complete reaction. $V(cp)(CO)_4$ cannot be bound to the supports used here by adsorption from toluene solution. Silica-supported vanadocene was not found to be active as a catalyst for ethylene polymerization.

Organometallic complexes supported on organic polymers¹ or inorganic oxides^{1,2} are frequently used and studied in chemical research. The main purpose, besides acquiring knowledge of their general chemical properties and surface chemistry, is often to apply the compounds to catalytic processes. Organometallics may be employed as such in homogeneous reactions and in supported form in heterogeneous catalytic reactions, as well as combined to exploit the properties of both types of catalysts. A lot of attention has been paid to compounds of metals in groups VIB–VIII B. Investigations on chemical and catalytic properties of supported compounds classified as true organovanadium compounds, however, have not been reported. Hucul and Brenner have made a temperature-programmed decomposition study of transition metal carbonyls, among them $V(CO)_6$, supported on alumina.³

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In order to obtain some knowledge within this unexplored field we have studied, by IR spectroscopy, general chemical and catalytic aspects of the behaviour of vanadocene [$V(cp)_2$; cp = cyclopentadienyl] and cyclopentadienyltetracarbonylvanadium [$V(cp)(CO)_4$] on two different supports. Vanadocene gives IR spectra with bands of low intensity;⁴ furthermore, some bands are located in a spectral region which is not accessible with the self-supporting disc technique used. Therefore, we have chosen to study the nature and coordinative unsaturation of the organovanadium species by recording their IR spectra in the presence of adsorbed CO.

Vanadocene is of particular interest because of its resemblance to chromocene, which supported on silica is commercially used in the manufacture of polyethylene.⁵ Vanadocene, however, has not been mentioned in this connection, although this 15-electron system could be expected to show catalytic activity. Vanadocene in benzene so-

lution has been reported to polymerize acetylene.⁶ Supported vanadium catalysts, however, are normally utilized in oxidation reactions.⁷ These oxide catalysts are often prepared by impregnation of the carrier with a solution of an inorganic vanadium compound. Organovanadium compounds may be an alternative for the preparation of well-dispersed vanadium surface compounds with catalytic activity and selectivity in oxidation reactions.

Experimental

Supports. Two supports have been studied. The first of these was SiO₂, Silica gel 60 ("Merck 7733"), with a surface area of 600 m² g⁻¹. It was further purified by treatment with concentrated HCl. The second support was SiO₂/Al₂O₃ (Degussa COK84) with 16–18% Al₂O₃ and a surface area of 170 m² g⁻¹; it was stirred with water and dried at 493 K before the experiments. Evacuation at different temperatures (573 and 873 K, respectively) was carried out to create a variation in the number of hydroxyl groups on the support surface. This activation procedure will be referred to in the text concerning the respective supports as "support/activation temperature in K".

Organovanadium compounds. V(cp)₂ was prepared by reaction of NaC₅H₅ with VCl₃, followed by sublimation.⁸ V(cp)(CO)₄ was prepared from V(cp)₂, CO and Na-sand, with sublimation of the product.⁹ The organometallic compounds were kept under nitrogen and handled by standard Schlenk procedures.

IR measurements. A self-supporting disc

(~3 cm²) of the carrier was placed in the IR cell previously described.¹⁰ A toluene solution of the organovanadium compound was drawn into a syringe from which the air had been removed with a stream of nitrogen. When blowing nitrogen through the cell via one of the vacuum couples, the disc could be reached by a teflon hose connected to the syringe through the second vacuum couple of the cell. The solution was thereafter carefully splashed on the disc. The vanadium content of the toluene solution was chosen so that the vanadium concentration of the disc was around 1% V. Spectra were recorded on a Perkin Elmer 580B IR spectrophotometer. The scan time was around 30 min. All programming of the instrument and treatment of the spectra were carried out via a PE 3600 data station. A CO pressure of 10 kPa (80 torr) was used in the adsorption studies. A twin-peaked absorption band centered around 2143 cm⁻¹ in the spectra recorded under CO is due to gaseous carbon monoxide.

Results

The identification of species and the assignment of bands require some IR data from the literature. These data on well characterized compounds are collected in Table 1. We do not report any data for V(cp)(CO)₄. This compound showed no reaction with or on the support. Spectra indicated only physisorption, and it sublimed at a slightly elevated temperature (373 K).

Reaction with SiO₂/873 at 298 K. CO adsorption on vanadocene/SiO₂/873 after evacuation at ambient temperature gives rise to several bands in the carbonyl stretching region (Fig. 1). With the

Table 1. Literature data on carbonyl stretching frequencies in vanadium carbonyl complexes.

Species	Solvent	$\nu(\text{CO})/\text{cm}^{-1}$	Ref.
V(cp) ₂ CO	Toluene	1881	18
[V(cp) ₂ (CO) ₂] ⁺ I ⁻	Nujol	2036, 1988	18
[V(cp) ₂ (CO) ₂] ⁺ I ₃ ⁻	Nujol	2040, 2000	19
V ₂ (cp) ₂ (CO) ₅	Mineral oil	2009, 1955, 1910, 1871, 1832	20
V(CO) ₆	Cyclohexane	1976	21
K ⁺ V(CO) ₆ ⁻	Acetone	1860	21
V(cp)(CO) ₄	Nujol	2020, 1950, 1920, 1890	22
V(III)-CO _{ads} /SiO ₂		2187, 2173	13

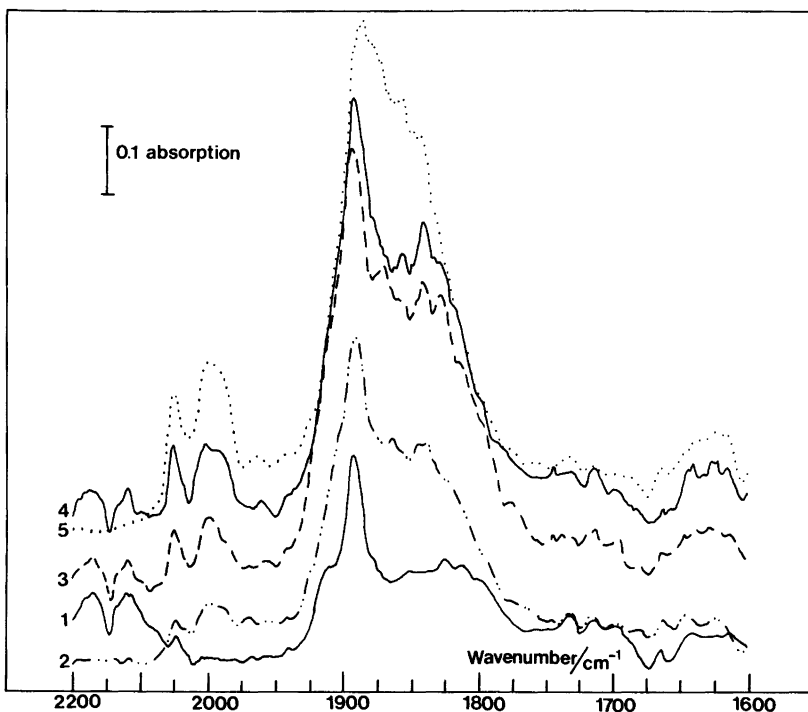


Fig. 1. IR spectra of CO adsorbed on vanadocene/SiO₂/873. Spectrum 1: after evacuation at 298 K and exposure to 10 kPa CO, 2: after evacuation of CO immediately after the first spectrum was recorded, i.e. CO exposure for 30–40 min, 3: renewed CO exposure, 4: same as 3 but after 2 h, 5: same as 4 but removal of gaseous CO by evacuation.

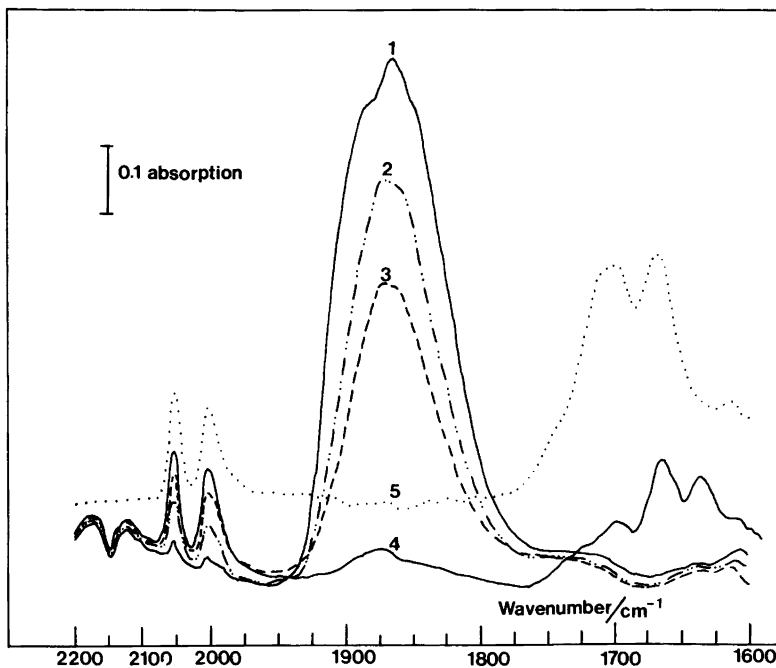


Fig. 2. IR spectra of CO adsorbed on V(cp)₂/SiO₂/573 after evacuation at 298 K. Spectrum 1: immediately after inlet of CO, 2: after CO exposure for 2 h, 3: after 4 h, 4: after 6 h, 5: after 22 h and vacuum.

help of data from Table 1 we make the following assignments: The 1890 cm⁻¹ band arises from V(cp)₂CO physisorbed on the silica surface. After a while, bands at 2048 and 1998 cm⁻¹ become more prominent (Fig. 1: 2-3). These we suggest to originate from a [V(cp)₂(CO)₂]⁺...O-Si structure. From the relative intensities (taken as absorbance times full width at half maximum) of the symmetric and asymmetric CO modes, the angle between the CO ligands (2θ) in this compound can be calculated.¹¹ These calculations require some estimations, since it is difficult to draw an unambiguous baseline in the spectra used for the calculations. The results should therefore be regarded as approximations and not exact determinations of the angle as can be deduced from X-ray diffraction data. We think that these calculations, however, show some interesting trends and are therefore worth reporting.

The angle 2θ in the dicarbonyl complex is calculated to be around 115° under CO atmosphere (Fig. 1: 3, 4), but increases to around 125° after evacuation (Fig. 1: 5). The absorption band

around 1840 cm⁻¹ (Fig. 1: 2-4) might be due to semi-bridging CO linking adjacent organovanadium compounds together. This peak position is close to the value reported by Cotton *et al.* for semi-bridging carbonyls in V₂(cp)₂(CO)₅.²¹ Alternatively, the 1840 cm⁻¹ band might also be assigned to V(CO)₆⁻ (Table 1), cf. reaction at 373 K.

Reaction with SiO₂/573 at 298 K. V(cp)₂ on SiO₂/573 after vacuum treatment at room temperature also forms the species V(cp)₂CO and [V(cp)₂(CO)₂]⁺ with CO, as seen from the presence of the broad band at 1862 cm⁻¹ and the more resolved peaks at 2051 and 2000 cm⁻¹, respectively (Fig. 2). However, there are no spectral features between 2200 and 1700 cm⁻¹ other than those arising from these two species. Note that the carbonyl stretching band of the monocarbonyl complex shifts to lower wavenumbers with increase in the number of silanol groups on the support (cf. the Discussion section). One also observes that the 1862 cm⁻¹ peak slowly vanishes.

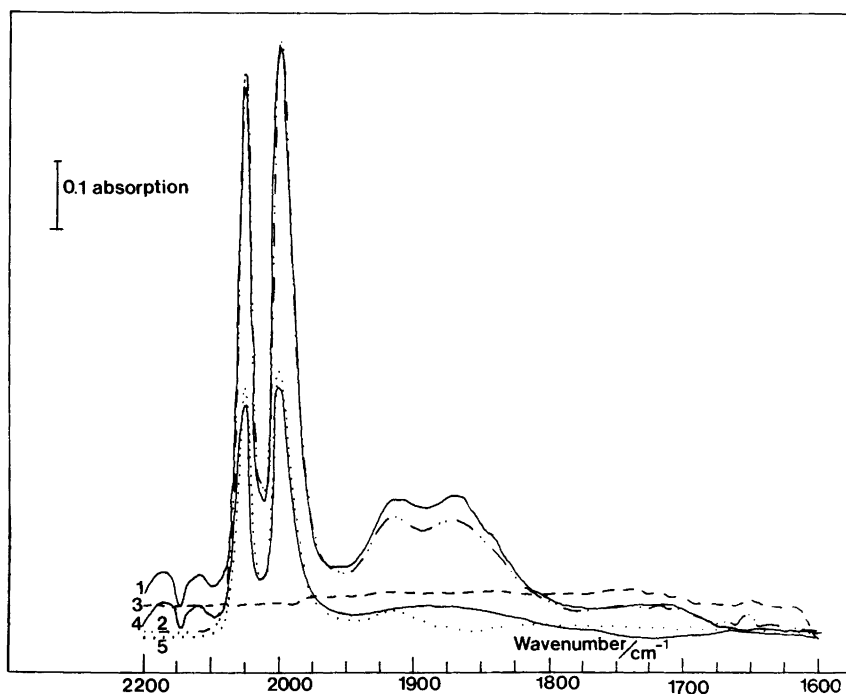


Fig. 3. IR spectra of CO adsorbed on V(cp)₂/SiO₂/Al₂O₃/573 after evacuation at 298 K. Spectrum 1: after evacuation of gaseous CO, 3: vacuum treatment of the sample at 373 K, 4: same as 3 but under CO, 5: removal of gaseous CO by evacuation.

This is interpreted as arising from transformation of $V(cp)_2(CO)$ species to $[V(cp)_2(CO)_2]^+$. There is also a shift with time towards higher wavenumbers for this band. The angle between the two CO ligands in the dicarbonyl complex, 2θ , has been calculated to be $95\text{--}100^\circ$. The absorptions below 1700 cm^{-1} (Fig. 2: 4, 5) most likely arise from $R\text{--}C=O$ species formed by reaction between CO and decomposition products of the cp ligands.

Reaction with $SiO_2/Al_2O_3/573$ at 298 and 373 K. The behaviour of vanadocene on the SiO_2/Al_2O_3 carrier differs from that on silica. By introducing alumina, one obtains surface hydroxyl groups which are more acidic than those on pure silica. From IR spectra showing the 2047 and 1999 cm^{-1} bands (Fig. 3: 1, 2), it is clear that mainly the dicarbonyl species is present on the support surface (Table 1). Only a minor proportion of the monocarbonyl complex is present. The CO mode for this complex has, for unknown reasons, become split into two components at 1870 and 1915 cm^{-1} (Fig. 3: 1–2, Table 1).

Elevated temperature (373 K) and vacuum lead to loss of CO from the dicarbonyl complex formed at 298 K (Fig. 3: 3). Note also that there is no IR absorption due to vanadocene in the discussed region. Renewed exposure to CO regenerates only $[V(cp)_2(CO)_2]^+$ (Fig. 3: 4, 5). The angle 2θ has been calculated to be $102\pm 1^\circ$ for this cation on silica/alumina, a value similar to that found for $SiO_2/573$.

Reaction with $SiO_2/873$ at 373 K. The behaviour of vanadocene on $SiO_2/873$ differs from that on SiO_2/Al_2O_3 in that the monocarbonyl complex is clearly formed on contact with CO after vacuum treatment at 373 K (Fig. 4, Table 1). The shift of the carbonyl stretching band from 1890 (Fig. 1) to 1870 cm^{-1} is explained by assuming that the physisorbed species no longer are affected by residual toluene. The dicarbonyl complex is now readily detectable immediately after CO exposure by bands at 2047 and 1997 cm^{-1} (Fig. 4: 1), in contrast to what was found for the sample when evacuated at ambient temperature (Fig. 1: 1). Somewhat surprising is the peak at 1976 cm^{-1}

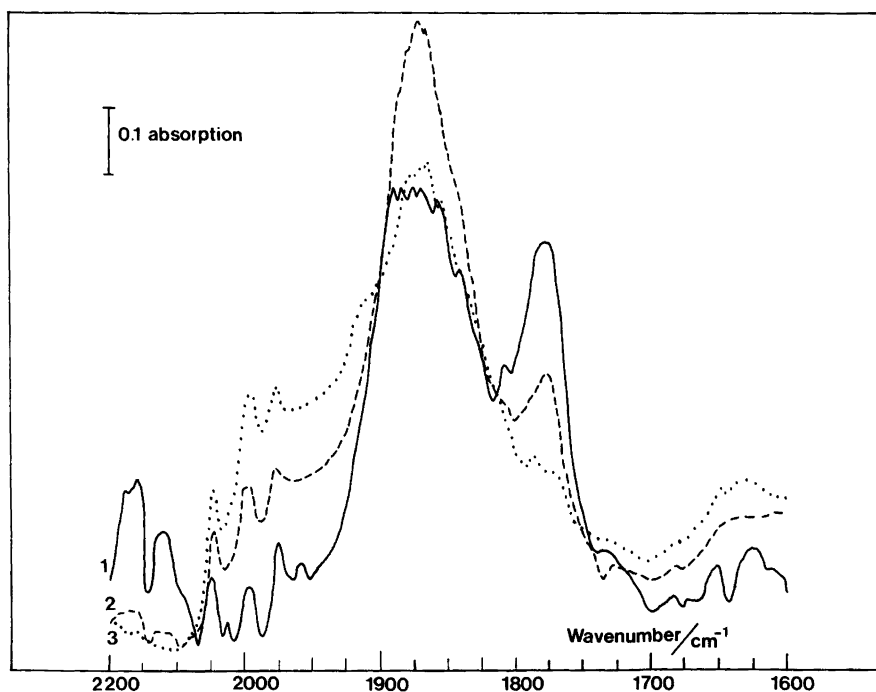


Fig. 4. IR spectra of CO adsorbed on $V(cp)_2/SiO_2/873$ after evacuation at 373 K . Spectrum 1: immediately after CO exposure, 2: same as 1 but after 15 h, 3: same as 2 but after removal of gaseous CO by evacuation.

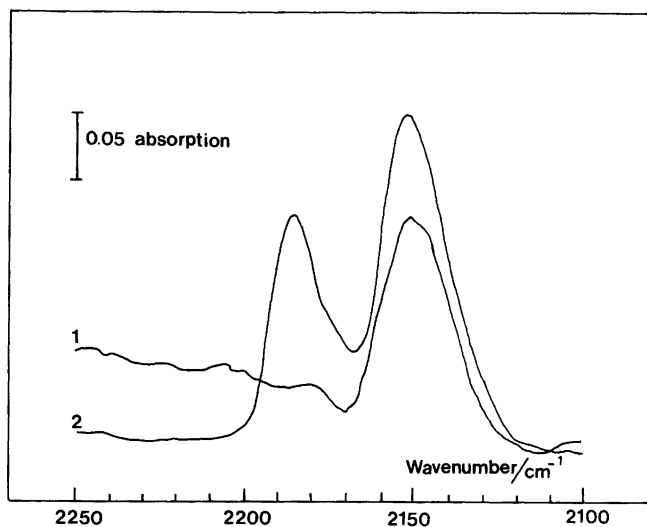


Fig. 5. IR spectra of CO adsorbed on products from $V(cp)_2$ on $SiO_2/873$. Spectrum 1: after evacuation at 573 K, 2: after evacuation at 773 K.

(Fig. 4), which we suggest to originate from $V(CO)_6$. The reaction producing the hexacarbonyl might proceed via $V(cp)(CO)_4$, which gives rise to the bands at 2030 and 1959 cm^{-1} and the broadening of the 1870 cm^{-1} band (Fig. 4: 1, Table 1). A broad band around 1870 cm^{-1} might very well also contain a contribution from $V(CO)_6^-$. A metal hexacarbonyl complex has previously been found in an organometal–silica system.¹² CO adsorbed in a bridging position between surface compounds is suggested to cause the 1776 cm^{-1} absorption (Fig. 4: 1–2). The shift from the previously (Fig. 1: 2–4) suggested semi-bridging to bridging CO indicates a shorter distance between the organovanadium compounds than is the case after a lower temperature of evacuation (Fig. 1: 2–4).

Reactions of $V(cp)_2$ with the supports at 573 and 773 K. A further increase in evacuation temperature has different consequences for the supported vanadocene for the samples. $V(cp)_2/SiO_2/573$ does not show any spectral evidence of remaining vanadium surface compounds after vacuum treatment at 573 K.

The spectra of $V(cp)(CO)_4$ showed no bands besides those due to physisorbed complexes on any support employed in this study. Elevated temperature of evacuation led to sublimation of the tetracarbonyl complex, the orange compound being observed on the windows of the IR cell.

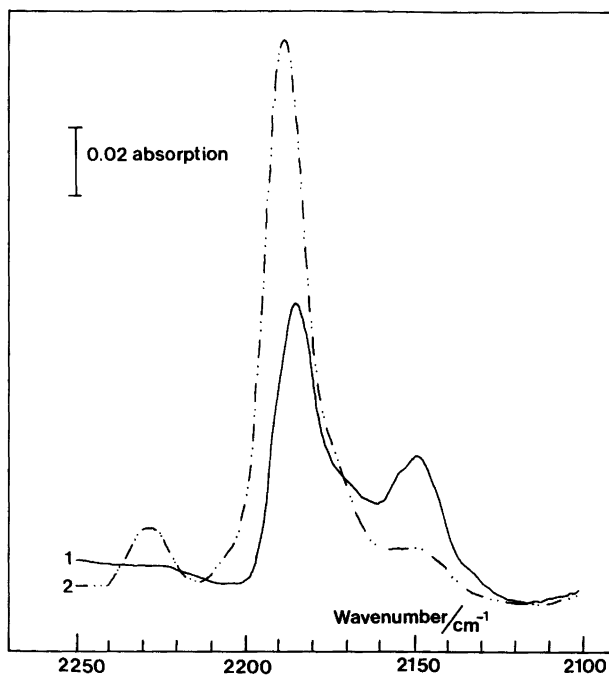
Reaction with $SiO_2/873$. Vacuum treatment of $V(cp)_2/SiO_2/873$ at 573 K produces inorganic vanadium surface compounds, i.e. compounds not containing organic ligands. The vanadium compounds have no spectral features in the region 2100–1700 cm^{-1} , but are characterized by an IR CO absorption band at 2150 cm^{-1} (Fig. 5: 1).

Vacuum treatment at 773 K yields V(III) species [structure (c) in Scheme 1] with an IR CO absorption band at 2185 cm^{-1} ¹³ (Table 1), besides the compounds giving rise to the band around 2150 cm^{-1} (Fig. 5: 2).

Reaction with $SiO_2/Al_2O_3/573$. Similar compounds must exist on the surface of $V(cp)_2/SiO_2/Al_2O_3$ after vacuum treatment at 573 K, as indicated by the IR CO bands at 2148 and 2184 cm^{-1} , respectively (Fig. 6: 1). The latter band arises from CO adsorbed on V(III) surface compounds.

The IR spectrum of the sample evacuated at 773 K (Fig. 6: 2) has a shoulder at 2149 cm^{-1} . The major IR features arise from CO adsorbed on V(III) (2188 cm^{-1}) and on Al(III) (2228 cm^{-1}). The adsorption on aluminium ions of the surface means that the vanadium coverage is less than one monolayer, i.e. less than 0.1% of the vanadium originally adsorbed on the disc is left.

Fig. 6. IR spectra of CO adsorbed on products from $V(cp)_2$ on $SiO_2/Al_2O_3/573$. Spectrum 1: after evacuation at 573 K, 2: after evacuation at 773 K.



Catalytic activity

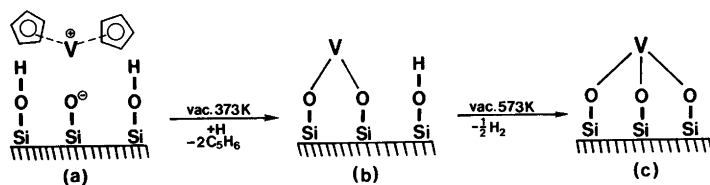
As previously mentioned, vanadocene is analogous to chromocene, which is used for catalytic polymerization of ethylene.⁵ However, we have found that vanadocene supported on $SiO_2/873$, evacuated at 298 and 373 K, respectively, is not active for the polymerization of ethylene (298 K, 60 kPa C_2H_4). Nor does the addition of Al^{3+} to the support before introduction of $V(cp)_2$ confer any catalytic activity to the system. However, there was a minor decrease in the ethylene pressure over the sample during the experiments. An explanation for this might be the formation of a $V(cp)_2C_2H_4$ complex analogous to the complex with CO discussed above. To our knowledge, $V(cp)_2C_2H_4$ is not described in the literature, although compounds of the type $V(cp)_2(C_2H_2R_2)$ are known.¹⁴

The vanadium surface species formed by evacuation and calcination in air of the samples at elevated temperature (773 K) will be investigated for their catalytic activity in toluene oxidation. The results of this investigation will be reported later.

Discussion

The spectra of $V(cp)(CO)_4$ adsorbed on the studied supports revealed nothing besides physisorbed complexes. Sublimation occurred when evacuation was performed at 373 K. The stability of this 18-electron species and its lack of vacant coordination positions have most likely eliminated the possible reaction routes under the described conditions.

$V(cp)_2$, in contrast to $V(cp)(CO)_4$, is a 15-electron system and should therefore be more reactive. Coordination to a suitable surface site can take place by displacement of the cp ligands. However, no reaction between $V(cp)_2$ and $SiO_2/573$ was observed. The relatively large number of silanol groups, approximately 80% of a completely hydroxylated surface, probably prevents reaction with this carrier by holding vanadocene at a distance from the surface at which reaction is not possible. The angle 2θ in the dicarbonyl complex was calculated to be $95-100^\circ$, which is considerably lower than the $115-125^\circ$ found for $SiO_2/873$. In fact, crystallographic data for $[V(cp)_2(CO)_2]B(C_6H_5)_4$ ¹⁵ indicate a



Scheme 1.

OC–V–CO angle of 92°. This means that the dicarbonyl complex on SiO₂/573 with an angle around 100° is not distorted to the same extent as the same complex on SiO₂/873 (2θ around 120). The absence of bridging or semi-bridging carbonyls (Fig. 2), suggested to be present on SiO₂/873, may be indicative of a less ordered surface structure, i.e. physisorption instead of defined positions of bonding. Note also that the carbonyl stretching frequency for V(cp)₂CO on SiO₂/573 initially appeared at 1862 cm⁻¹. This means a shift to lower energy of 28 cm⁻¹ relative to the same complex on SiO₂/873. This can be interpreted as implying that more electron density from vanadium is available for back-donation on SiO₂/573, while the corresponding electron density is used instead for interaction with the surface on SiO₂/873.

Vanadocene did react with SiO₂/873. Vanadium in a low-valent state was bound to this support, which has a relatively small number of silanol groups (approximately less than 50% of a completely hydroxylated surface). The calculated value of 2θ (from Fig. 1: 115–125°) indicates that the organovanadium compound ([V(cp)₂(CO)₂]⁺) is located closer to the surface than on SiO₂/573. By analogy, we assume that this also holds for V(cp)₂. This closeness and the accompanied distortion of the complex is an argument for why a reaction is possible. However, the acidity of the silanol groups, i.e. the ability to create ⁻O-centres, is also assumed to be an important factor. A decrease in the number of silanol groups is expected to increase the acidity of the remaining silanol groups.¹⁶ The reaction with a surface site probably proceeds through a cationic intermediate [structure (a) in Scheme 1]. It seems clear that cationic organovanadium species ([V(cp)₂(CO)₂]⁺) are formed on the silica surface under mild conditions (10 kPa CO). The 14-electron system V(cp)₂⁺ has been described,¹⁷ and might participate in the reaction route. The surface compounds formed by evacuation at 573 K

are proposed to be V(II) species [structure (b) in Scheme 1]. This is concluded from the known IR bands of CO adsorbed on V(III)/SiO₂¹³ and the general fact that these IR bands shift to lower wavelengths with decreasing oxidation state of the metal. To our knowledge, CO adsorption on inorganic V(II) surface compounds has not previously been reported. Further evacuation at 773 K yields a V(III) species [structure (c)] which has been characterized previously.¹³

A reaction also took place between vanadocene and SiO₂/Al₂O₃/573. The surface compounds formed are suggested to be analogous to those shown in Scheme 1. Vanadocene reacts with SiO₂/Al₂O₃ although its distance from the surface (estimated from 2θ ~ 102°) is similar to a distance that was unfavourable for reaction on SiO₂/573. However, the hydroxyl groups on SiO₂/Al₂O₃ are more acidic than those on silica, thereby creating more ⁻O-groups that are assumed to interact and react with vanadocene. The negative centre will make it easier to form and stabilize cations on the surface, as seen in the spectra in Fig. 3. The reaction pathway to vanadium surface compounds on SiO₂/Al₂O₃ is even more probable to involve ionic intermediates. The formation of V(III) after employing only 573 K and vacuum also reflects the more acidic nature of these hydroxyl groups.

A difference between the reaction of Cr(cp)₂ with silica and the reaction of V(cp)₂ with the same support is that chromocene loses one cp ligand more easily, forming an organochromium surface oxide. Vanadocene is, in contrast, more stable in reaction with silica, and a cp ligand is lost only under more severe conditions.

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