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ETHYLENE POLYMERIZATION ON CHROMOCENE SUPPORTED ON γ-Al_2O_3: AN FT-IR INVESTIGATION

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Summary

Interaction of chromocene (from the gaseous phase) with the isolated surface hydroxyl groups of γ-Al_2O_3 generates a quantitative hydrolysis reaction which leads to the formation of the coordinatively unsaturated $Al^{3+}CrCp$ surface species (A).

Anchored mononuclear species A can react further with excess chromocene to give the polynuclear $Al^{3+}CrCp\cdots CpCrCp$ species (B).

Species A provide active sites for ethylene polymerization, in which chain initiation probably involves the formation of a metallocyclic structure.

Introduction

Chromium-based ethylene polymerization catalysts are usually prepared by reacting oxide surfaces either with chromic acid (Phillips catalyst) or with organometallic precursors (mainly chromocene, $Cr(Cp)_2$: Union Carbide catalyst) [1 - 3].

During the interaction of $Cr(Cp)_2$ with a silica surface, sequential hydrolysis reactions occur involving silanols [2, 3]:

$$\gt Si{-}OH + Cr(Cp)_2 \rightarrow CpH + \gt Si{-}O{-}CrCp \text{ (isolated silanols)} \qquad (1)$$

$$2\gt Si{-}OH + Cr(Cp)_2 \rightarrow 2CpH + (\gt Si{-}O)_2Cr \text{ (vicinal silanols)} \qquad (2)$$

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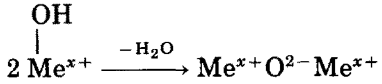
Since high degrees of surface hydroxylation do not favour maximum polymerization activity, reaction (2) is considered to lead to a surface centre exhibiting minimal catalytic activity. This is a particularly strange observation because a Cr^{II} species doubly anchored to the surface via siloxane bridges is thought to be the active centre of the Phillips catalyst [4].

However, despite this discrepancy, it is important to stress that on both silica and other oxides the surface OH groups are commonly regarded as the main (if not the only) sites where chromium active species can be anchored. Although this is probably true for silica (even if a small fraction of distorted and reactive siloxane bridges does exist on samples subject to high degrees of dehydroxylation at high temperature) [5], the same has not necessarily been verified for other oxides. For example, with ionic solids such as MgO, Al_2O_3, etc., it is known that surface dehydroxylation *in vacuo* at high temperature gives rise to the species $Me^{x+}O^{2-}$ according to the following scheme:



$$2\,\overset{\overset{\text{OH}}{|}}{\text{Me}}{}^{x+} \xrightarrow{-H_2O} Me^{x+}O^{2-}Me^{x+} \qquad (3)$$

Such species are both coordinatively unsaturated and ionic. Thus they can behave as Lewis acids (Me^{x+}) and Lewis bases (O^{2-}), and can react with incoming organometallic species via a nucleophilic or an electrophilic mechanism [5 - 7].

In this paper, we describe the interaction of $Cr(Cp)_2$ from the gaseous phase with highly dehydroxylated γ-Al_2O_3 and the subsequent formation of surface centres active in ethylene polymerization. The polymerization reaction has been followed against time by means of FT–IR spectroscopy.

Experimental

The γ-Al_2O_3 utilized in this study has been prepared by thermolysis at 1173 K of ammonium alum (Koch-Light: 99.97%) (specific surface area: 170 $m^2\,g^{-1}$). To achieve activation, the γ-Al_2O_3 powder in the form of self-supporting compressed discs was fired at 1073 K under dynamic vacuum conditions (10^{-5} Torr). To eliminate residual sulphate impurities, the sample was then reduced by heating three times in hydrogen at 1073 K (for 10 min on each occasion) and finally activated by heating *in vacuo* at the same temperature for 30 min.

The $Cr(Cp)_2$ (Strem Chemicals) was dosed on to the sample from the gaseous phase by direct sublimation at room temperature. IR spectra were recorded in the transmission mode using a Brucker 48 IFS spectrometer.

Results and discussion

The blank spectrum of γ-Al_2O_3 treated at 1073 K (Fig. 1) exhibits residual OH stretching bands at 3800, 3750 and $\approx$ 3700(sh) cm^{-1}. On the basis

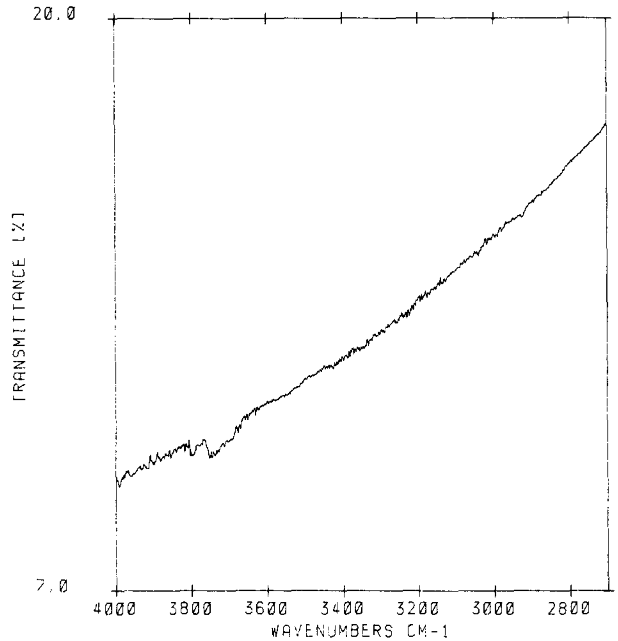
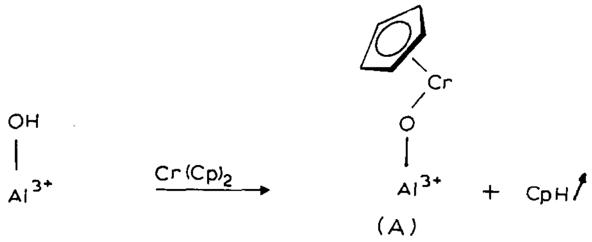


Fig. 1. Blank IR spectrum of γ-Al_2O_3 activated at 1073 K showing the OH bands remaining after such treatment.

of the abundant data in the literature [8], the concentration of residual OH groups has been estimated as *ca.* 0.4 OH per 10 nm^2. This means that such groups are all *isolated* and that the major fraction of the surface is fully dehydroxylated.

The effect of dosing increasing amounts of $Cr(Cp)_2$ from the gaseous phase is shown in Fig. 2 (difference spectra). The following should be noted: (i) the bands arising from the residual OH groups gradually diminish (in fact, they appear as negative peaks) and then disappear; and (ii) peaks associated with both fundamental (3100 - 3090 cm^{-1}) and overtone and combination modes (marked with asterisks in Fig. 2) associated with the cyclopentadienyl ring [9 - 11] appear simultaneously. As shown in the inset, an initial proportionality exists between the overall decrease in the integrated intensity of the OH modes and the increase in intensity of the peak at 3090 cm^{-1} [strongest ν(CH) mode of the Cp^- ring] [9 - 11]. This means that over this range of coverage, the hydrolysis reaction:



(4)

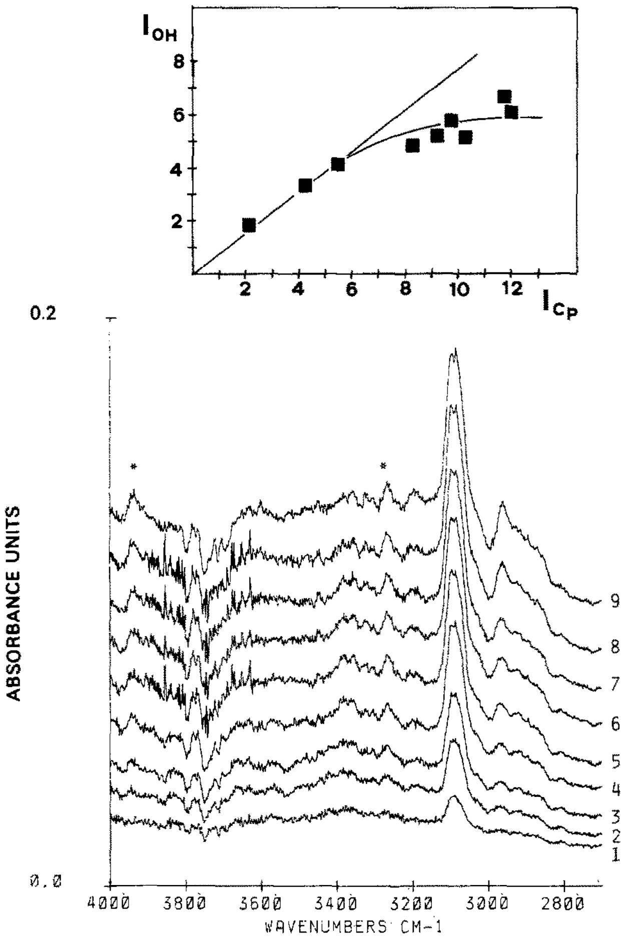
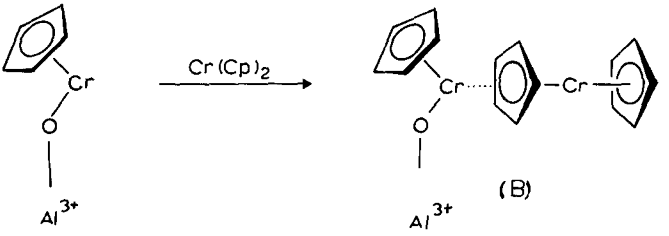


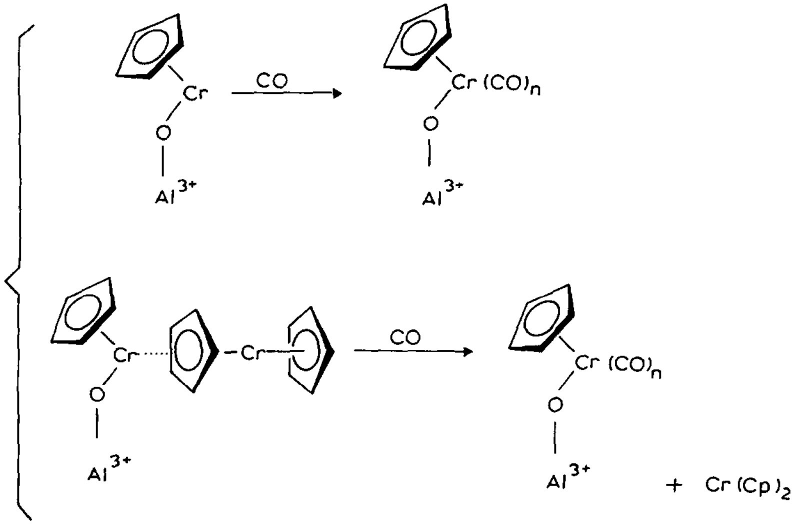
Fig. 2. Difference spectra obtained with increasing doses (1 - 9) of $Cr(Cp)_2$ (from the gaseous phase) on γ-Al_2O_3 activated at 1073 K (the asterisks indicate overtone and combination bands of cyclopentadienyl rings). Inset: plot of the integrated intensity of the OH bands *versus* the intensity of the Cp^- band at 3090 cm^{-1} (arbitrary units).

occurs quantitatively with the formation of the isolated coordinatively unsaturated surface $Al^{3+}CrCp$ species (A). The CpH hydrocarbon fragment probably does not completely leave the surface and is partially re-adsorbed either as a dimer (a stable, well-known product) or in a polymeric form (since the Al^{3+}—CrCp centre formed in reaction (4) can polymerize olefins) (see below). Indeed, the IR absorption at 2965 - 2900 cm^{-1}, which is suggestive of saturated —CH_n— ($n = 2, 3$) groups, could well be ascribed to minor amounts of dimeric and/or polymeric species. It is noticeable that the intensity of this absorption peak (generally weak or very weak) changes from one sample to another without any appreciable alteration being observed in the catalytic properties of the $Cr(Cp)_2/\gamma$-Al_2O_3 system. On the basis of the results obtained with the similar $Cr(Cp)_2/SiO_2$ system (Union Carbide catalyst) [12], and from simple chemical considerations, it is possible to suggest that the coordinatively unsaturated species A cannot survive in the presence of excess $Cr(Cp)_2$ (because of the complexing ability of the Cp^- ligand) and that they readily undergo further transformation according to the scheme:



(5)

in which the cyclopentadienyl ring of the incoming (excess) $Cr(Cp)_2$ molecule acts as a weak π-ligand and saturates the coordination vacancies of the anchored Cr^{II} species B. In fact, once the hydroxyl groups are totally consumed, the peaks associated with the cyclopentadienyl ring continue to grow in intensity (inset of Fig. 2) because of adsorption of $Cr(Cp)_2$ on previously anchored species (and, eventually, on the dehydrated parts of the alumina surface). Of course, the relative concentration of the surface complexes A and B will depend critically upon the total quantity of $Cr(Cp)_2$ dosed on to the surface. Complexes A and B can react with other ligands either by insertion (complex A) or displacement (complex B) reactions. For example, if CO is contacted with the surface (spectra not reported for sake of brevity), two strong peaks associated with carbonyl groups develop instantaneously at



(6)

1896 and 1788 cm^{-1} (intensity ratio ≈ 0.25). On the basis of the IR spectra of the homogeneous $M(Cp)_m(CO)_n (m = 1, 2;\ n = 2, 3)$ analogues [13], and from the results obtained with the $Cr(Cp)_2/SiO_2$ system [12], these bands may be assigned to the symmetric and asymmetric modes of a polycarbonyl structure formed according to the reaction sequence (6). Isotopic $^{12}CO/^{13}CO$ substitution experiments to determine the exact stoichiometry of these complexes are at present in progress.

In a similar manner to CO, insertion and substitution reactions involving NO also lead to compounds of a polynitrosyl nature [12].

With suitable pressure conditions, despite its weaker complexing ability C_2H_4 should also give insertion and displacement reactions with complexes A and B. However, in this case the product is *not* a π-complex of ethylene but a transformation product, *i.e.* a living polymeric $-(CH_2)_n-$ chain. In fact,

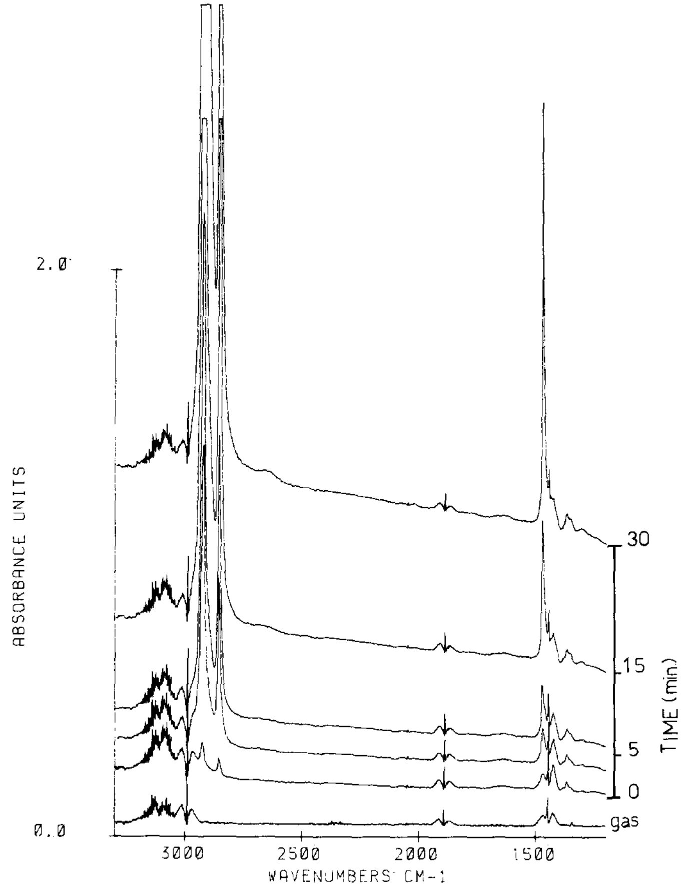
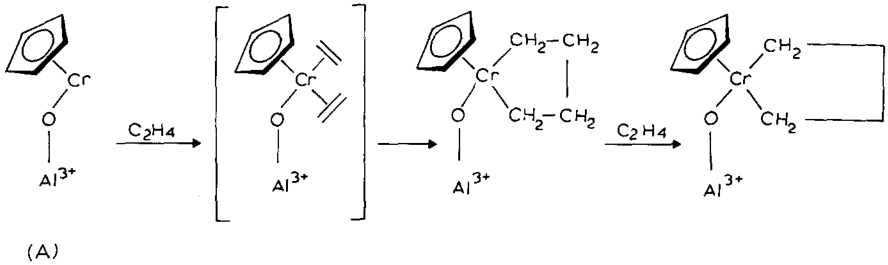
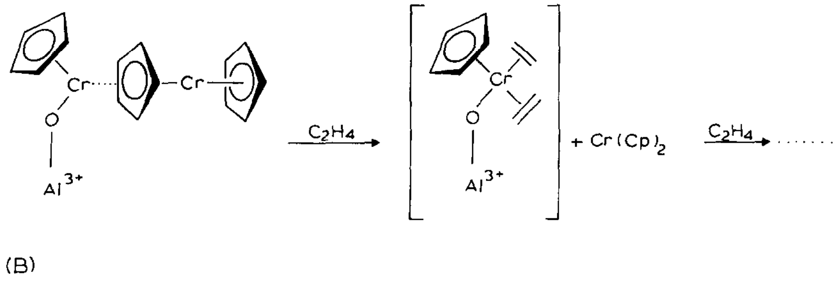


Fig. 3. Spectra recorded at increasing contact time showing the polymerization of ethylene (60 Torr) in the presence of the $Cr(Cp)_2/\gamma$-Al_2O_3 system. The spectrum of ethylene (gas phase) is also reported for comparative purposes.

if C_2H_4 is dosed at 60 Torr pressure on to the sample reacted with $Cr(Cp)_2$ (Fig. 2), the spectra depicted in Fig. 3 are obtained. These spectra are time-dependent and exhibit the characteristics bands associated with a polyethylene chain [$\nu_{\mathrm{asym}}(CH_2)$ and $\nu_{\mathrm{sym}}(CH_2)$ at 2918 and 2851 cm^{-1}; $\delta(CH_2)$ at 1472 and 1465 cm^{-1}] whose intensities increase very rapidly with time. The growth of the bands at 2918 - 2851 cm^{-1} is strictly proportional (at constant pressure) to the contact time. This means that the number of polymerizing centres remained constant during the polymerization interval investigated (30 min). It is most noticeable that, under the experimental conditions employed, no indications of methyl and/or vinyl terminating groups were observed in the spectra. Since the terminal methyl groups in linear C_nH_{2n+2} hydrocarbon molecules give rise to absorption peaks which can be clearly identified even when $n = 20 - 40$, we conclude that the systems studied in this work involved living chains with *no* end groups. Not only is the living nature of the polymeric chain demonstrated by the absence of end groups (vinyl or methyl), but the following experiment also supports this view. Thus, if at any stage during the polymerization process the pressure of C_2H_4 is reduced to zero, the IR bands visible at 2918 - 2851 cm^{-1} cease to grow immediately. Their growth can however be completely restored by the introduction of ethylene back into the system at its initial pressure. The absence of any change in the number of polymerizing centres in the system supports the suggestion of living chains. Indeed, the results described here are very similar to those obtained with the $Cr(Cp)_2/SiO_2$ system [12] and indicate the following sequence of reactions:



(7)



(8)

whereby chain initiation consists of the formation of a metallocyclic structure while propagation corresponds to the insertion of ethylene into the metallocyclic ring. Determination of the structural units in the polymeric chain (by IR spectroscopic investigation of the macroscopic samples after exposure to air) has already been reported in ref. 2. The primary coordination complex of ethylene, obtained either by insertion into complex A or displacement of $Cr(Cp)_2$ from complex B, cannot be distinguished by IR spectroscopy because of its rapid attachment to the metallocyclic structure. Such insertion of ethylene into the metallocyclic ring would be favoured by simultaneous ring slippage involving transformation of Cp^- from an η^5 to an η^3 configuration [14].

Reaction (8) probably only operates at high ethylene pressures, because only under these conditions can the weak ethylene ligand displace the blocking $Cr(Cp)_2$ group. With the experimental conditions employed in this work (low ethylene pressure and at room temperature), reaction (7) will predominate. This is demonstrated by the observation that samples with low amounts of adsorbed $Cr(Cp)_2$ lead to the polymerization of ethylene at higher rates than those with a large excess of $Cr(Cp)_2$.

In conclusion, sites at which complex A is situated are the primary centres where ethylene polymerization occurs. However, the mechanistic details of chain initiation and growth are less well defined and deserve further investigation. As far as the presence of $Cr(Cp)_2$ adsorbed on totally dehydroxylated parts of the γ-Al_2O_3 surface is concerned, the IR spectra reported do not provide unequivocal information even at the highest coverages studied. In particular, the peculiar IR observations reported for the $Mg(Cp)_2/MgO$ system [6] were not apparent in this case, leading to the conclusion that the adsorption of $Mg(Cp)_2$ occurs dissociatively on the $Mg^{2+}O^{2-}$ coordinatively unsaturated ion pairs.

Acknowledgements

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