

Room-temperature Polymerisation of Ethylene on a TiO₂ (Anatase) Surface; Infrared Spectroscopic Evidence for an Alkylidene-Ti⁴⁺ Polymer End-group and for a 'Hydrogen-bonding' Type of Interaction of CH Bonds of the Polymer Chain with the Oxide Surface

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An infrared spectroscopic study of the spontaneous polymerisation of ethylene on a sulphate-containing TiO₂ (anatase) sample shows evidence for an alkylidene surface end-group of the polymer and for substantial perturbation of CH₂ groups of the polymer chain by interaction with the oxide surface.

Zecchina and colleagues¹ have reported an infrared spectroscopic study of ethylene polymerisation over a chromia/silica catalyst which included the observation of a weak and broad absorption centred near 2750 cm⁻¹. This band was assigned to the ν(CH) vibration of a =CH end-group of the polymer located at the surface of the catalyst with the structural formula Crⁿ⁺=CH-[CH₂]_n-Me. The latter formulation is consistent with the chemical expectation based on a previously proposed polymerisation mechanism.²

We have found that a TiO₂ (anatase) sample (hydroxy-free but with covalently bonded surface sulphate³) acts as a spontaneous ethylene polymerisation catalyst at room temperature. Figure 1 shows infrared spectra resulting from the interaction of ethylene with anatase after the gas phase

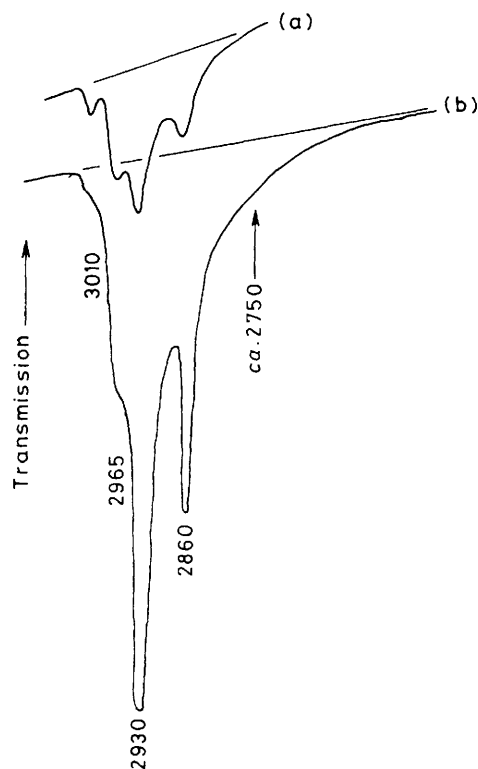


Figure 1. Infrared spectra in the ν(CH) bond-stretching region of polymers obtained from the interaction of gaseous ethylene with a TiO₂ (anatase) sample with 7% sulphate as SO₃ and of area 106 m² g⁻¹. (a) Initial stage of polymerisation (7 Torr C₂H₄ for 2 min and evacuation) and (b) later stages of polymerisation (7 Torr C₂H₄ for a total of 37 min).

had been pumped off. At very low coverages, and hence low mean chain-lengths, [Figure 1(a)] the spectra show bands at 2930 and 2860 cm⁻¹ due to CH₂ groups, at 2965 cm⁻¹ due to methyl groups, probably from the free end of the polymer chain, and a weak band at 3010 cm⁻¹ which can very reasonably be assigned to the proposed Mⁿ⁺=CH- end-group involving an sp² hybridised carbon atom. Figure 1(b) shows that as the polymer chain grows, the anomalous low frequency band observed by Zecchina *et al.*¹ at ca. 2750 cm⁻¹ appears, ultimately with much greater relative intensity with respect to the methylene bands at 2930 and 2860 cm⁻¹ than in the former case.¹ Furthermore, its intensity grows with the chain length. We have also observed this broad band when n-hexane is physically adsorbed on the anatase surface. Post-adsorption of CO on the anatase-polymer system weakens the ca. 2750 cm⁻¹ band and increases the methylene bands as described by Zecchina *et al.* but without, in our case, corresponding observable changes in the ν(OH) region.¹

The low-frequency, intensity, and breadth of the ca. 2750 cm⁻¹ band are collective phenomena of the type commonly observed in an infrared spectrum when an X-H bond suffers hydrogen bonding. We therefore propose an alternative assignment for this band that is based on such a perturbation of CH groups along the polymer chain, probably through interaction with the electron-deficient Ti⁴⁺ ions on the surface of the anatase. This is schematically represented in Figure 2.

In our infrared spectrum of the polymer on anatase the ratio between the intensities of the two methylene ν(CH) stretching bands when the ca. 2750 cm⁻¹ band is present is different from that in the spectra of normal polyethylene. This implies the presence of an additional band near 2900 cm⁻¹ which can be assigned to the free-CH of the 'hydrogen bonded' CH₂ group in our scheme (see Figure 2).

CH bonds in saturated alkyl groups are not normally thought to participate in hydrogen bonding. However a similar phenomenon has recently been observed, and a similar interpretation offered, for the adsorption of cyclohexane on Pt(111) and Ni(111) single crystals.⁴ Also infrared spectroscopic⁵ and crystallographic studies⁶ have led to the recognition of C-H...M interactions within a few organometallic compounds. The present observation seems to provide the first record of such an interaction on an oxide surface of

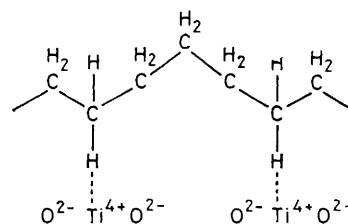


Figure 2

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catalytic interest. Brookhart and Green⁷ have recently coined the term 'agostic' to describe substantial mutual interactions between metal atoms and adjacent CH bonds. We suspect that a distinction can be made on infrared spectroscopic grounds between (a) linear or near-linear C-H...M interactions which give low frequency, strong (per CH), and broad $\nu(\text{CH})$ absorptions of the hydrogen-bonding type as in this case and in some of the earlier examples cited,⁴ and (b) non-linear M-CH interactions, where the MCH angle is near to 90°, which Schrock *et al.*⁸ have shown in tantalum complexes to give low frequency, weak and *sharp* $\nu(\text{CH})$ absorptions.

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