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Probing the early stages of polymerization of ethylene on a model chromium / silica catalyst by Fourier transform infrared spectroscopy

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The nature of the interaction of monomer, and the early stages of growth of oligomers of ethylene on a rather more uniform surface of Cr / SiO_2 catalyst than hitherto studied has been investigated by difference FTIR spectroscopy using C_2D_4 and C_2H_4 as reactants both with and without subsequent treatment of the catalyst with CO and THF. The active catalyst was prepared by reaction of vapour phase CrO_2Cl_2 with the vicinal hydroxyls of the silica surface. Three distinct kinds of methylene groups were detected. Arguments are given for assigning the peaks at 2935 and 2860 cm^{-1} to CH_2 groups directly bound to the active site and those at 2920 and 2850 to CH_2s in the growing chain well removed from the Cr. The peaks at 2160 and 2165 cm^{-1} are attributed to CD_2 groups hydrogen bonded to surface hydroxyls.

Keywords: Cr / SiO_2; ethylene polymerization; methylene groups; FT IR; Phillips catalyst

1. Introduction

Silica-supported chromium catalysts (of the so-called Phillips' type) for polymerization of ethylene have been studied for over thirty years because of their great industrial as well as intrinsic chemical importance [1]. But, in spite of intensive research, the structure of the active species and the reaction mechanism are still the subjects of lively debate. One of the reasons for the lack of progress stems from the non-uniformity of the samples – it is estimated [2,3] that only about 10% of the chromium is catalytically active. In this investigation we have endeavoured to overcome, in part, the intrinsic non-uniformities of the catalyst by grafting Cr(VI) ions from CrO_2Cl_2 [1,4,5] onto OH groups of the silica support, thereby producing better defined chromium sites. Difference FTIR spectra, over relatively short intervals of time, have been used to probe the progress of reaction at such sites.

2. Experimental

The catalysts were prepared by exposing the hydroxyl groups of silica gel (Aldrich, grade 643, 99%, surface area 300 m^2/g) to CrO_2Cl_2 vapour (Aldrich, 99.99%). In order to control the number of hydroxyl groups of the surface, a wafer of the silica was first outgassed (1×10^{-4} Torr) at 450°C for 30 min in an in situ cell. 1 Torr of CrO_2Cl_2 vapour was then admitted at room temperature (r.t.) for 2 min, followed by evacuation at r.t. and subsequently at 450°C. The concentration of chromium from chemical analysis was 0.63 wt% of the catalyst. This corresponds to one Cr atom for every ten Si atoms on the silica surface. IR spectra were monitored using a Perkin-Elmer FT-IR spectrometer (model 1725X). The catalysts were calcined in O_2 (15 Torr) at 650°C for 30 min and then reduced with CO (15 Torr) at 425°C for 15 min. The initial stages of the polymerization reaction of ethylene were allowed the take place at r.t., and the catalytic activities were monitored both by the decrease of ethylene pressure and the increase of the IR peaks in the CH_2 stretching vibration region of the spectrum.

3. Results and discussion

3.1. INTERACTION BETWEEN CrO_2Cl_2 AND HYDROXYL GROUPS OF SILICA

Fig. 1 shows the IR spectra of the OH stretching vibration region of pristine silica. Outgassing at 450°C left both isolated OH species at 3745 cm^{-1} and hydrogen-bonded ones (shoulder at lower frequencies) (see fig.1 (a)). When CrO_2Cl_2

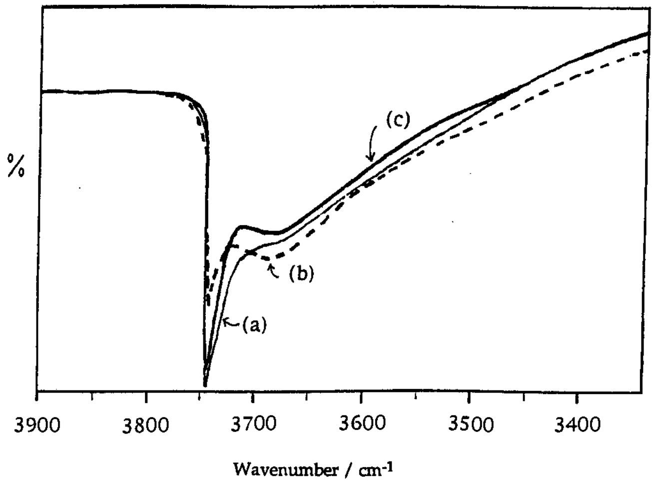

Fig.1. FTIR spectra of OH stretching vibration region of silica gel; (a) outgassed at 450°C for 30 min (——); (b) contacted with CrO_2Cl_2 followed by pumping away at room temperature (— — —); (c) followed by pumping away at 450° C (——).

vapour was admitted into the cell, the peak at 3745 cm^{-1} decreased and a new one appeared at 3685 cm^{-1} (fig. 1 (b)). When this sample was heated to 450°C in vacuo, desorption of some of the CrO_2Cl_2 occurred at about 420°C, the peak at 3745 cm^{-1} was completely restored and those at 3720 and 3600 cm^{-1}, which were assigned as to vicinal species [6], disappeared (shade in fig. 1). The changes visible in fig. 1 (b) are explicable in terms of chemisorption of the CrO_2Cl_2 on isolated OH groups. The amount of spectral shift from 3745 to 3685 cm^{-1} accords with that known [7] to occur upon the adsorption of electrophilic sorbates such as olefins on surface hydroxyl groups. Evidently CrO_2Cl_2 selectively reacts with vicinal OH groups at r.t. to bind to silica surface.

3.2. ACTIVITIES OF CO ADSORPTION AND ETHYLENE POLYMERIZATION

Reduced Cr/ SiO_2 catalysts are known [8] to adsorb CO at r.t. We found that the amounts of CO on the catalysts prepared from CrO_2Cl_2 were four times as much as on those prepared by a conventional method using chromium acetate. Activities for ethylene polymerization on the CrO_2Cl_2-treated silica showed enhancement compared with the acetate-treated variety, there being a roughly four-fold increase in line with increase in CO adsorption. These results differ from those in a previous work [4] where the CrO_2Cl_2 was deposited at 200°C in a flow of He and where no improvement in the activities was observed.

3.3. IR SPECTRA OF POLYMERIZATION OF ETHYLENE

Polymerization was carried out at r.t. by contacting ethylene gas (4 Torr) with the reduced catalysts. Fig. 2a shows the IR spectra in the C–H stretching vibration region. Each spectrum was taken after pumping away the gas phase C_2H_4 and subtracting the spectrum recorded before admission of the C_2H_4. Changes in both positions and shapes were observed over period as short as 30 s. To investigate these changes further the spectrum recorded at a time t_1 (say 10 s) was subtracted from that recorded at t_2 (say 20 s). In this way the growth of the polymer chain during each 10 s interval could be tracked (see fig. 2b). Polyethylene has been reported [9] to give peaks at 2919 and 2851 cm^{-1} for the antisymmetric and symmetric modes, respectively, in the C–H stretching vibration region. In our work the first pair of peaks appeared at 2930 and 2855 cm^{-1}, somewhat at higher frequencies and of greater breadth (fig. 2b (1)) than previously observed. Polymer chains which grew during the next 10 s showed shifts to lower frequencies and became slightly sharper (fig. 2b (2)). After 20 s of contact with ethylene the peaks began to appear at the normal positions (fig. 2b (3)), though the antisymmetric peak at 2920 cm^{-1} had a shoulder around 2890 cm^{-1}. Similar changes were more clearly visible when C_2D_4 was used instead of C_2H_4, the IR spectra of the C–D stretching vibration region corresponding to that shown in fig. 2b being as in fig. 3. The peaks during the first 10 s (fig.3 (a)) were at higher frequencies and broader in shape than those generated

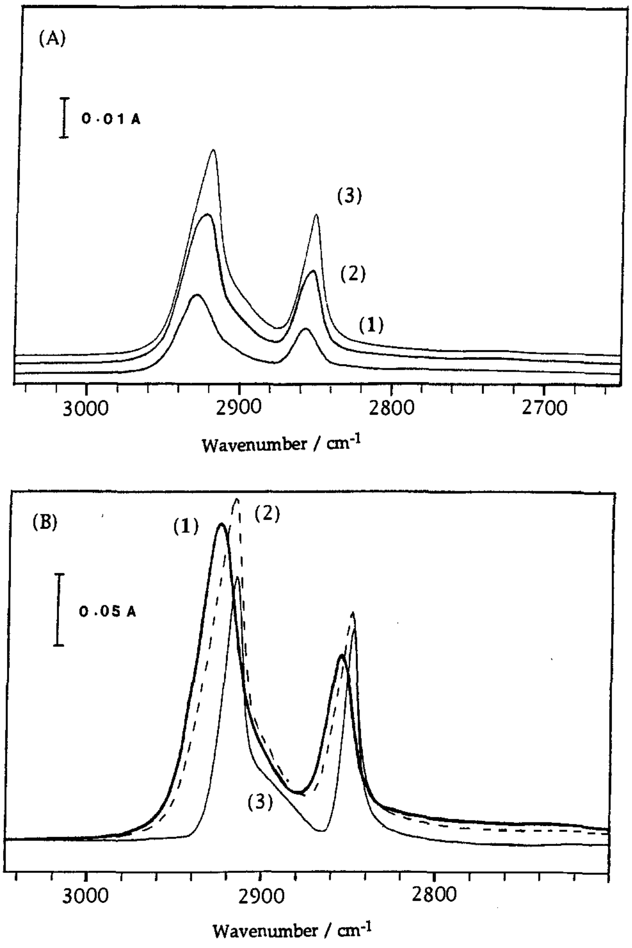

Fig.2. (a) FTIR spectra of the CH stretching vibration region of the reduced catalysts after C_2H_4 (4 Torr) was admitted for; (1) 10 s; (2) 20 s; (3) 30 s; (b) FTIR difference spectra of a; (1) same as a(1) (——); (2) subtraction of a(1) from a(2) (– – –); (3) subtraction of a(2) from a(3) (——).

during the third 10 s interval (fig.3 (b)), which appeared at 2195 and 2090 cm^{-1} with additional peaks at 2160 and 2065 cm^{-1}. Peak separations were more clear cut in the C–D than in the C–H region, particularly for the symmetric stretching frequencies.

It is reasonable to suppose that a methylene group next to a low valent chromium would be influenced by the presence of the chromium and exhibit a distinct difference in the IR spectrum from that of methylene groups in the middle of the chains. The pair of peaks at 2931 and 2860 cm^{-1} has been reported by Spoto et al. [10] in the case of chromium in silicalite, where these bands were observed as shoulders of 2920 and 2850 cm^{-1} and assigned as CH_2 species more directly bonded to or influenced by the catalytic centre, which dominates in the short hydrocarbon

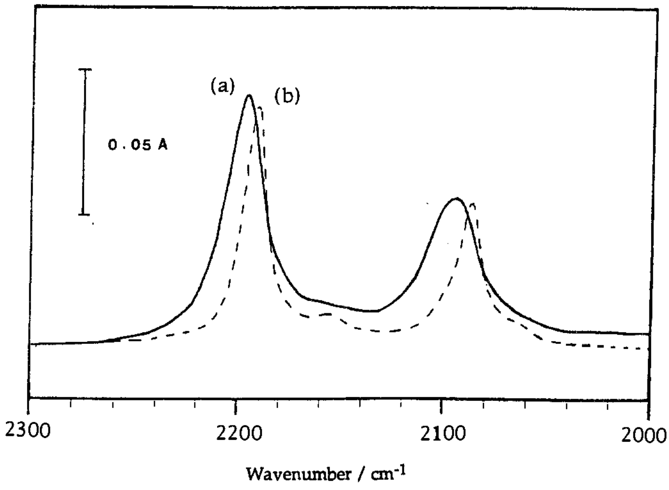

Fig.3. FTIR difference spectra of CD stretching vibration region of the reduced catalyst; (a) after C_2D_4 (4 Torr) was admitted for 10 s (——); (b) subtraction of a spectrum for 20 s from one for 30 s (– – –).

chains. In order to distinguish the methylene groups juxtaposed to the chromium site from those far away from it, per-deuterated ethylene was admitted to the sample which had first been used in the polymerization of C_2H_4. As new C_2D_4 inserts between α-carbon and chromium metal bond, the CH_2 initially neighbouring the metal ion is displaced into the middle of polymer chains. Fig.4 shows an IR difference spectrum before and after C_2D_4 admission to the sample which had $(CH_2)_n$ polymer chains. The pair at 2935 and 2860 cm^{-1} shifted to the normal position at 2920 and 2850 cm^{-1}, respectively. And the disappearance of the peaks at higher fre-

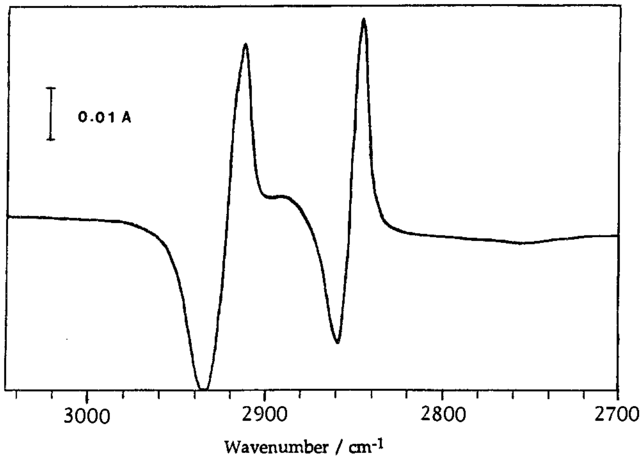

Fig.4. FTIR difference spectrum before and after C_2D_4 admission to the sample which had $(CH_2)_n$ polymer chain.

quencies as a result of the ensuing polymerization shows that these peaks are indeed due to the methylene neighbouring chromium sites. These shifts rationalise the changes seen in fig. 2b. The broad peaks of the first 10 s in fig. 2b (1) may consist of two kinds of methylene species. There is a pair at 2935 and 2860 cm^{-1} which is attributable to the CH_2 directly bound to the chromium, as well as the normal pair at 2920 and 2850 cm^{-1}; and, after the initiation reaction is complete, only the latter pair grows in intensity, as shown in fig. 2b (3).

3.4. INFLUENCE OF ADSORBATES ON POLYMER CHAINS

The influence of CO adsorption on polymer chains has been reported [8,11,12] by several groups to give rise to an increase in intensity at 2926 and 2855 cm^{-1} and a decrease at 2750 cm^{-1}. The results we observed were, however, decrease at 2935, 2861 and 2750 cm^{-1} and increase at 2920 and 2850 cm^{-1}. These shifts were reversible by desorption of CO. The same magnitude of shifts was observed on CD_2 polymer when tetrahydrofuran (THF) was admitted (THF did not desorb at room temperature). These results suggest that when the electron donors (CO and THF) adsorb on chromium the influence of the chromium upon its immediate neighbouring methylene is nullified. In other words a methylene group situated next to a Cr ion may be influenced by the empty d-orbital of the transition metal-ion, thereby causing a shortening of the C–H bond.

When all IR spectra were taken, gas phase ethylene was evacuated. But if there is ethylene present, it should adsorb on chromium sites and the peaks at 2935 and 2861 cm^{-1} should not appear. As polymerization continues in an ethylene atmosphere, it was difficult to compare two spectra with and without gas phase ethylene. Fig. 5 shows the IR spectrum of the difference before and after evacuating gas-

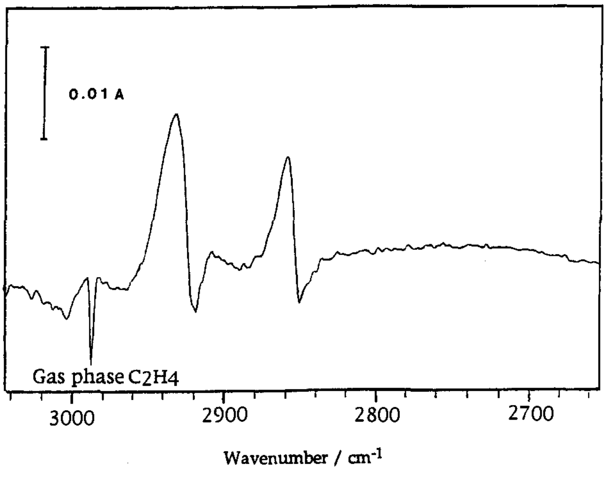

Fig.5. FTIR difference spectra of CH stretching vibration region before and after gas-phase C_2H_4 was evacuated after 30 min of polymerization.

phase C_2H_4. The negative peaks around 2990 cm^{-1} arise because of the presence of gas phase C_2H_4. Though the decrease of the peaks at 2920 and 2850 cm^{-1} is compensated with polymer growth, as mentioned above, the observed increases at 2935 and 2861 cm^{-1} support the idea that adsorption on ethylene on Cr neutralizes the influence upon the methylene next to the Cr.

3.5. INTERACTION OF POLYMER CHAINS WITH OH GROUPS

A pair of the lowest frequencies were clearly observed in the case of C_2D_4. These peaks became more pronounced as the polymer chain grows as seen in fig. 6, which shows the difference spectra of 3 – 2, 4 – 3 and 5 – 4 min contact with C_2D_4. The shifts of 3745 to 3695 cm^{-1} in the OH stretching vibration region have been well characterized by Jozwiak et al. [12] as the result of interaction with polymer chains.

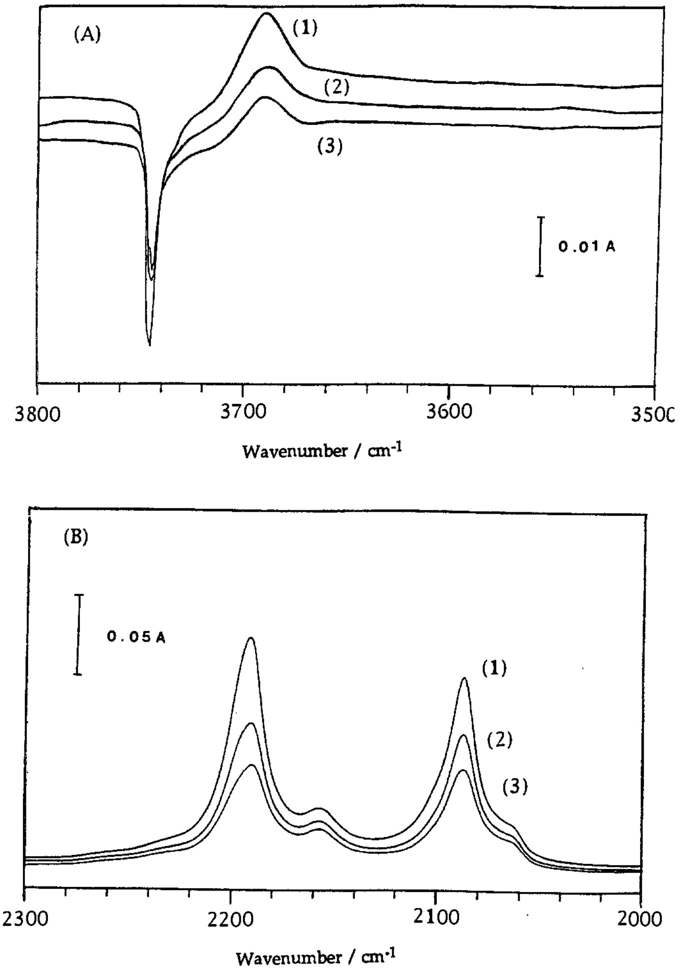

Fig.6. FTIR difference spectra of the reduced catalyst after 4 Torr of C_2D_4 was admitted; (1) a spectrum taken at 2 min was subtracted from one at 3 min (3 – 2 min); (2) 4 – 3 min; (3) 5 – 4 min.

It seems that such interaction does not result in any change in the methylene region of the spectrum. The amounts of increase both at 2160 and 3695 cm^{-1} in fig.6, however, were in good accord with one another, and the direction of shift of the methylene group from the normal position to lower frequencies is accounted for by hydrogen-bonding. It is plausible, therefore, to conclude that the methylene species at 2160 and 2065 cm^{-1} are those that are hydrogen-bonded with the surface hydroxyl groups of the silica gel.

4. Conclusion

Silica-supported chromium catalysts have been industrially used for producing polyethylene. Non-uniformity of the chromium sites prepared by the conventional impregnation method has caused inconsistent results among many researchers. As the vapour of CrO_2Cl_2 selectively reacted with vicinal OH groups of the silica surface, the environment of chromium atoms was more uniform, and the activity of the sample for the polymerization reaction was improved four-fould.

When the polymerization reaction was carried out only for a few tens of seconds, IR bands of methylene group showed clear shoulders at higher frequencies. These shoulders were assigned to methylene groups neighbouring chromium ions, which increased only for the first twenty seconds. The shift to the normal absorbance frequencies upon admitting adsorbates such as CO or THF confirmed the assignment. Another methylene group was observed when C_2D_4 was polymerized, which was assigned to be hydrogen-bonded with the surface hydroxyl groups.

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