FTIR investigation of ethylene coordination and polymerization on reduced Cr/SiO_2 catalyst

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FTIR spectroscopy was applied to study the initial steps of ethylene polymerization on reduced chromia–silica (0.5 wt% Cr/SiO_2). To decrease the speed of the reaction small doses of gas were introduced to the catalyst in each run and C_2D_4 was used to confirm band assignments. At the initial steps of the reaction only ethylene molecules coordinated to probably Cr_A^{2+} cations were observed. The concentration of such complexes was estimated to be about 50% of the total amount of Cr atoms in the sample. The FTIR spectrum of the polymer formed at the initial doses of C_2H_4 (when $[C_2H_4] \approx [Cr]$) was found to be slightly different from that formed after excess ethylene was introduced onto the catalyst ($[C_2H_4] > [Cr]$).

Keywords: Ethene [74-85-1]; polymerization; chromium [7440-47-3]

1. Introduction

Ethylene polymerization on chromia–silica catalyst was studied recently by Ghiotti et al. [1] using the IR technique on CO prereduced 0.5% Cr/SiO_2. IR spectroscopy was shown to be useful to study the kinetics of the process and some features of the growing polymer such as interaction with the surface and coordination with Cr cations. However, due to very fast polymerization it was not possible to understand the initial steps of the reaction as the strong absorption bands (AB) of the polymer in CH_2 stretching and bending regions masked weak AB of initially formed products. In order to overcome the difficulty in this study an attempt was made to inhibit fast polymerization by using very small doses of ethylene and following changes in the FTIR spectrum.

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2. Experimental

The CrO_3/SiO_2 catalyst (0.5 wt% of Cr) was prepared by impregnation of SiO_2 (Aerosyl Degussa, surface area ≈ 330 m^2/g) with an aqueous solution of CrO_3. The dried powder was pressed into pellets (about 0.02 g/cm^2) containing $\approx 3 \times 10^{18}$ Cr atoms. These pellets were contained in golden frames and put into a conventional quartz vacuum cell having a finger for IR measurements with KBr windows.

The standard pretreatment and reduction procedure described thoroughly in ref. [2] included calcination in vacuum at slowly increasing temperature up to 750°C, oxidation in dry O_2 at 550°C and reduction in CO at 350°C. Water and CO_2 formed during pretreatment and reduction were eliminated by liquid N_2 trapping. After reduction CO was outgassed at 200°C.

The cell with the reduced catalyst was transferred to a Bruker-48 FTIR instrument and connected to a vacuum line allowing all subsequent adsorption–desorption experiments to be carried out in situ. The spectra were recorded with 4.0 cm^{-1} resolution and 256 accumulating scans.

A 500 cm^3 flask with two valves and a known volume between them (0.5566 ± 0.0004 cm^3 as calibrated with Hg) was used to introduce equal successive doses of ethylene on the catalyst. The system allowed operation with such small doses of gases as of 5×10^{17} molecules each.

"Matheson" high purity grade O_2, CO, C_2H_4 and C_2D_4 were used in this study. Olefins were purified by repeated freeze–pump–thaw cycles.

3. Results and discussion

Fig. 1 (curves 1–10) represents changes in the baseline corrected spectra of reduced catalyst upon chemisorption of ten successive doses of ethylene. Each spectrum was recorded after complete adsorption of a dose so that the residual pressure of gas phase ethylene was a few Pa (after about 10 min). The first dose gave rise to a couple of AB at about 3000 ± 2 and 1448 ± 2 cm^{-1}. They continued growing up to the point (curve 2) where the number of adsorbed ethylene molecules corresponded approximately to 50% of the total number of Cr atoms in the sample and then seemed to be saturated. Already after the second dose the spectrum showed new AB developing at about 2927 ± 2, 2855 ± 2, 1469 ± 2 and 1461 ± 2 cm^{-1}, AB at 2927 cm^{-1} being slightly asymmetric at higher wavenumbers particularly in the first stages (curves 2–6). These AB increased in intensity upon chemisorption of new doses and additional features appeared in the spectrum, i.e. AB at about 1369 ± 2 and 1354 ± 2 cm^{-1}. One can also notice that apparently the intensity of the 1461 cm^{-1} component did not increase after the first stages so that the ratio of intensity between 1469 and 1461 cm^{-1} AB was growing with dosing.

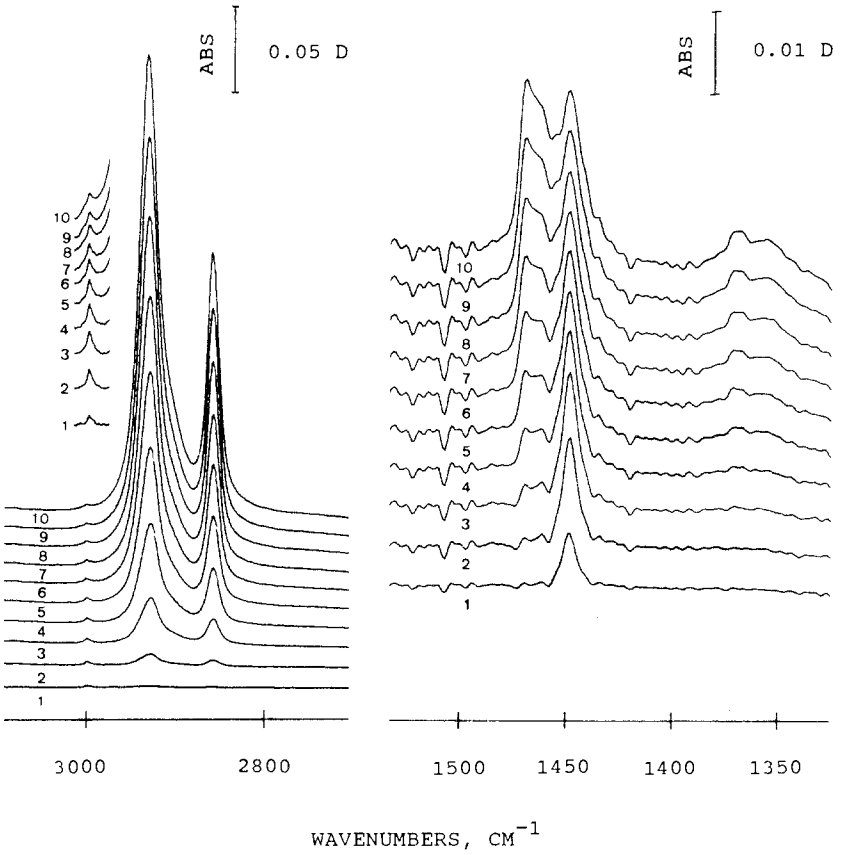

Fig. 1. FTIR spectra of successive ten doses of C_2H_4 (4.3×10^{17} molecules each) chemisorbed on the surface of reduced 0.5% Cr/SiO_2 (2.6×10^{18} Cr atoms in the sample). Background of reduced sample was subtracted, spectra 2–10 were shifted. The region about 3000 cm^{-1} is shown being expanded ten times.

Taking into account data published in the literature on the IR spectra of polyethylene [3] and results by Ghiotti et al. [1], the AB continuously growing with ethylene dosing may be assigned to the growing chains of a polymer. However, two AB at about 3000 and 1448 cm^{-1} show behavior different from these AB of polyethylene. It is interesting to point out that Ghiotti et al. [4] observed AB of coadsorbed CO and C_2H_4 on the same center so that AB of ethylene were slightly disturbed and appeared at about 3006 and 1445 cm^{-1}. Following these results it is possible to propose that the 3000 and 1448 cm^{-1} AB were due to an ethylene molecule forming a 1 : 1 complex with some type of Cr ions (probably Cr_A^{2+} as it is the most reactive in the notation used in ref. [4]). Assuming that the saturation of these bands upon ethylene dosing corresponded to the full coverage of such centers, it is possible to estimate their concentration to be about 50% of the total number of Cr atoms in the sample.

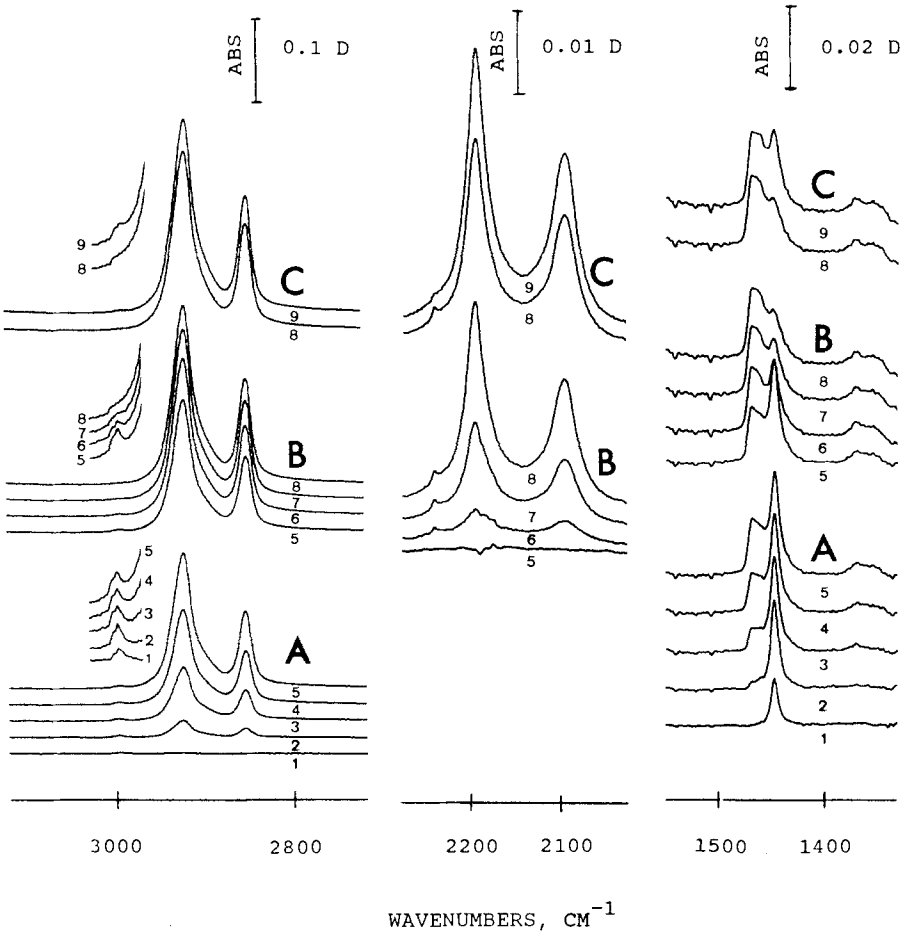

Fig. 2. FTIR spectra of successive (A) five doses of C_2H_4 (7.8×10^{17} molecules each); (B) subsequent four doses of C_2D_4 (6.6×10^{17} molecules each) and (C) subsequent one dose of C_2H_4 (7.2×10^{17} molecules) on the surface of reduced 0.5% Cr/SiO_2 (3.2×10^{18} Cr atoms in the sample). Background of reduced sample was subtracted, spectra 2–9 were shifted. The region about 3000 cm^{-1} is shown being expanded ten times.

Further information about the properties of coordinated ethylene was obtained when subsequent small doses of C_2D_4 were chemisorbed on the catalyst. Fig. 2 shows that upon such treatment AB at 3000 and 1448 cm^{-1} tended to disappear while $(CH_2)_n$-polymer bands increased a little. At the same time new AB at 2243 ± 2, 2197 ± 2 and 2096 ± 2 cm^{-1} appeared in the spectrum. The behavior of the 2243 cm^{-1} AB seems to be similar to that of the 3000 cm^{-1} AB as it was formed at the initial doses of C_2D_4 and tended not to increase its intensity upon further chemisorption of ethylene-d_4. Thus it is possible to assume that this AB corresponds to the same stretching mode of coordinated C_2D_4 as 3000 cm^{-1} AB of coordinated C_2H_4.

AB at about 2197 and 2096 cm^{-1} appearing after ethylene-d_4 dosing may be assigned to stretching modes of $(CD_2)_n$-polymer. The small increase of the normal polyethylene AB in fig. 2 might be due to polymerization of residual C_2H_4 chemisorbed on Cr ions and substituted by C_2D_4. Bending modes of deuterated polyethylene could not be observed as they were at lower wavenumbers than 1100 cm^{-1} [3] where silica was not transparent enough.

The reversible character of 2197 and 2096 cm^{-1} AB was proved by introducing a small dose of C_2H_4 on the sample. Curves 8 and 9 of fig. 2 show that coordinated C_2D_4 was substituted by normal ethylene so that the original set of bands at about 3000 and 1448 cm^{-1} was restored.

Performing these experiments we tried to distinguish between polyethylene and initially formed short hydrocarbon chains by depressing artificially the speed of polymerization. However, we faced with some problems. We observed no AB of terminal groups of growing chains in the CH stretching region (which might be methylic or vinylic group vibrations at wavenumbers higher than 2950 cm^{-1}) but only slight changes of the polymer AB, such as the above mentioned initial asymmetry of 2927 cm^{-1} AB and relative changes of 1469 and 1461 cm^{-1} AB intensity.

On the one hand this may be interpreted in terms of short chains of a polymer. Probably CH_2 units close to the center of polymerization exhibit a slightly different IR spectrum than those in the middle of the growing chain. Should this be so, AB at 1469 cm^{-1} might be due to the internal CH_2 group scissoring mode and AB at 1461 cm^{-1} to that of CH_2 unit close to Cr cation. Upon polymerization the intensity ratio between these two AB must increase because the amount of internal CH_2 groups is growing whereas the number of "end" groups is limited by the number of active sites.

On the other hand, the group of bands observed in the 1500–1300 cm^{-1} region may be due not only to short hydrocarbon chains but also to a highly conformationally "defective" structure of a long polyethylene molecule [3] interacting with the surface. Considering the fact that the spectrum of the polymer observed after introducing the very first doses of ethylene in our experiments and that of polymer formed on the same catalyst at much higher initial pressure of ethylene [1] are quite similar, it might be assumed that the number of active sites on the surface was very low and that was the reason why no indications of any initialization step were observed.

In conclusion, our results show that the surface of reduced chromia–silica catalyst contains a relatively large amount of reduced Cr centers capable to coordinate ethylene molecules (their population being up to 50% of Cr atoms) but only a small number of active sites responsible of polymerization.

References

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