

FTIR Spectroscopic Investigation of the Initiation of Ethylene Polymerization on Cr/Silica

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Received July 22, 1994; revised January 20, 1995

The initiation of ethylene polymerization was studied using Cr/SiO₂ catalysts that differed in their Cr content. The interaction between ethylene and the catalyst surface was followed by FTIR transmission spectroscopy after each sequential injection of a small amount of ethylene into the IR cell. The results show that an ethylidene surface species, (CH₃HC=Cr), initiates the polymerization. The polymer chain formed during the early reaction stage has a linear structure with a methyl group on one end and the Cr=CH- group on the other end. The number of active sites on the catalyst surface was estimated after each ethylene injection from the integrated absorbances of the $\nu_{as}(\text{CH}_2)$ band and the number of ethylene molecules added to the IR cell. The maximum concentration of active sites is observed when the total chromium content reaches 1 wt%. The results show that the population of active sites decreases during early reaction to a stable number identical for all catalysts with Cr content ≥ 1 wt%. © 1995 Academic Press, Inc.

INTRODUCTION

The mechanism of ethylene polymerization on Cr/SiO₂ catalysts has been studied and various mechanisms have been proposed. For example, Hogan (1, 2) hypothesized a transfer of a hydride from the β -carbon of the growing polymeric chain to the active site on the catalyst surface. The addition of the hydride to another monomer molecule to form a methyl group provided the means for initiating a new chain and also formed a vinyl group on the terminal end of the polymer chain. This explanation did not show how the initial chain originated nor the origin of its needed hydrogen (3).

Another possibility for the chain initiation arises through the interaction of two adsorbed ethylene molecules on a single Cr site to form an allylic species (4). The chain would then grow at the Cr-allyl bond and the extra

hydrogen would shift to the same Cr atom as a hydride. Such a hydride could also be involved in the initiation of polymerization. These hypotheses are in agreement with the available IR and NMR evidence, according to which each polymer chain contains a vinyl group on one end and a methyl group on the other end (1–4).

Ghiotti *et al.* (5) proposed chain initiation by the formation of metallocyclobutane from two chemisorbed ethylene molecules, followed by propagation via an alkylidene structure. The involvement of the latter species was supported by IR studies (5, 6). They attributed the weak broad absorption band at ca. 2750 cm⁻¹ to the $\nu(\text{CH})$ mode of a carbene group interacting with the adsorption center (5). The carbene was formed by the migration of hydrogen from the CH₂ group to a surface oxygen atom. The catalytic cycle was completed by a shift of a proton from the new hydroxyl group back to its host carbon atom, thereby eliminating hydrogen scrambling. This mechanism concurs with the conclusion of McDaniel and Kantor (3) that no hydrogen shift occurs during the propagation reaction. Al-Mashta *et al.* (7, 8) presented spectral evidence for the formation of an ethylidene species during the early stages of ethylene polymerization on sulfated anatase. They assumed that these species were involved in the initiation and were formed from ethylene itself without the need for an extra hydrogen atom (7).

Since Ghiotti *et al.* (5) did not obtain IR spectral evidence indicating the presence of vinyl or methyl groups in the polymer, they believed that terminal groups were not present in the polymer chains, i.e., the chains formed cyclic structures with both ends attached to the active site(s). The cyclic structure, first proposed by Rebenstorff and Larsson (9), was also supported in our earlier work (10). Our work (10) and that of Vikulov *et al.* (11) showed that polymerization of ethylene was preceded by a rapid initial adsorption of the monomer. Although spectral evidence was lacking, the explanation was offered (10) that carbenes could be formed by dissociation of chemisorbed ethylene molecules on two neighboring Cr sites.

The current evidence is inconclusive regarding any of the above hypotheses, perhaps because of the short life-

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time of the very active species formed during the initiation. Vikulov *et al.* (11) decreased the rate of polymerization of ethylene by injecting sequential small doses of ethylene (5×10^{17} molecules) into their IR cell. By decreasing the reaction rate in this manner, the possibility of observing spectra relevant to the initial step of the polymerization was improved. These authors (11) observed only π -adsorbed ethylene on Cr^{+2} centers at the beginning of the reaction. The FTIR study reported herein employs the sequential injection of even smaller doses of ethylene than those reported by Vikulov *et al.*, enabling the monitoring of the reaction path in even more detail. The transient developments during the reaction initiation were tracked by recording successive spectral scans after each injected dose of ethylene had reacted.

EXPERIMENTAL DETAILS

Catalysts varying in their Cr content were prepared by impregnating a silica support (Davison 955, BET surface area = $277 \text{ m}^2/\text{g}$, pore volume = $1.57 \text{ cm}^3/\text{g}$) with aqueous solutions of CrO_3 (Fisher Scientific). The notations 0.5%D, 1%D, 2%D, and 5%D, are used to designate such catalysts containing 0.5, 1, 2, and 5 wt% of chromium, respectively. Table 1 lists some properties of these catalysts.

Thin catalyst wafers for transmission spectroscopic measurements using a modified Kiselev-type cell (12) were prepared by compressing finely divided dry catalyst powders. The catalyst wafers were activated within the IR cell using procedures previously described (10, 13). The 0.5%D catalyst was reduced with CO (2.66 kPa) at 623 K for 1 h and then evacuated at 523 K for 1 h (10^{-5} Pa). The wafers prepared from the other catalysts were pretreated similarly except that both of the above steps were carried out at 623 K.

Small doses of ethylene (6.5×10^{16} molecules) were admitted to the IR cell through a dosing valve (Vacuum Generators MD6). After each dose had reacted, averaged FTIR scans (900 accumulated) were obtained under steady-state conditions with a Nicolet Model 730 spec-

trometer (spectral resolution of 4.0 cm^{-1}). For measurement of early reaction rates, fast scanning (5 scan/s) and 5-scan averaging were employed using the closed IR cell at room temperature with an initial ethylene charge of 0.133 kPa. The kinetics experiments were of short duration (≈ 150 s) and the amount of polymer formed was negligible, leaving the catalyst pore structure and particle geometry unaffected. Under these conditions, with only ethylene in the gas phase, the initial rates observed were assumed to be free of diffusion effects.

The gases were purchased from Matheson (ethylene and CO of 99.99% research grade; oxygen of UHP grade). Before the introduction of a given gas, the cell manifold was carefully evacuated. Ethylene was stored in a stainless steel bottle which was refilled through a Linde pressure reduction regulator for high purity gases, fitted with a metal diaphragm. The FTIR spectral scan of the gas phase ethylene showed no detectable traces of gaseous impurities.

EXPERIMENTAL RESULTS

IR Band Assignments

Figure 1 contrasts the sequential FTIR spectra obtained after each injection of ethylene contacting 1%D catalyst. In the low-frequency range ($1650\text{--}1350 \text{ cm}^{-1}$), weak absorption appears at 1448 cm^{-1} ; after the fifth dose, a band at 1548 cm^{-1} develops; the intensities of both bands increase continually up to the 28th dose (total of 1.9×10^{18} molecules). After the 36th dose (2.3×10^{18} molecules), a shoulder appears at 1463 cm^{-1} , corresponding to the CH_2 bending mode of polyethylene (5). The weak bands between 1370 and 1350 cm^{-1} , whose intensities also increase with chain-growth, could be assigned to the CH_2 wagging modes of the polymer (5).

In the $3050\text{--}2600 \text{ cm}^{-1}$ region of Fig. 1, an absorption band at 2997 cm^{-1} appeared after the 5th dose. This band and those at 1548 and 1448 cm^{-1} correspond to the $\nu_s(\text{CH}_2)$, $\nu(\text{C}=\text{C})$, and $\delta_{\text{as}}(\text{CH}_2)$ modes, respectively, of ethylene π -adsorbed on Cr^{+2} sites (10, 12, 14, 15). After the 11th and 12th doses, traces of polymer are not yet apparent but a weak band at 3016 cm^{-1} is evident, corresponding to the $\nu(\text{CH})$ mode of the $=\text{CH}-$ group (7, 8, 16–18). In this region, the earliest evidence of polymer appears after the 15th dose (9.9×10^{17} molecules), when two bands at 2927 and 2855 cm^{-1} continue to grow as more ethylene is added. These two bands are clearly attributable to $\nu_{\text{as}}(\text{CH}_2)$ and $\nu(\text{CH}_2)$ of the polymer chain. The band at 3016 cm^{-1} reached its maximum intensity after the 19th dose (1.25×10^{18} molecules). The next few additions of ethylene led to an increase in the bands from CH_2 groups in the polymer chain and to a decrease in the $\nu(\text{CH}=\text{C})$ band. Following the 23rd, 27th, and 31st doses,

TABLE 1
Physical Properties of Different Cr/Silica Catalysts

Catalyst type	Cr content, (wt%)	BET surface area (m^2/g)	Wafer thickness (g/cm^2)	Number of Cr atoms per gram of wafer
0.5%D	0.5	284	0.019	5.7×10^{19}
1%D	1	284	0.011	1.1×10^{20}
2%D	2	278	0.020	2.2×10^{20}
5%D	5	275	0.014	5.5×10^{20}

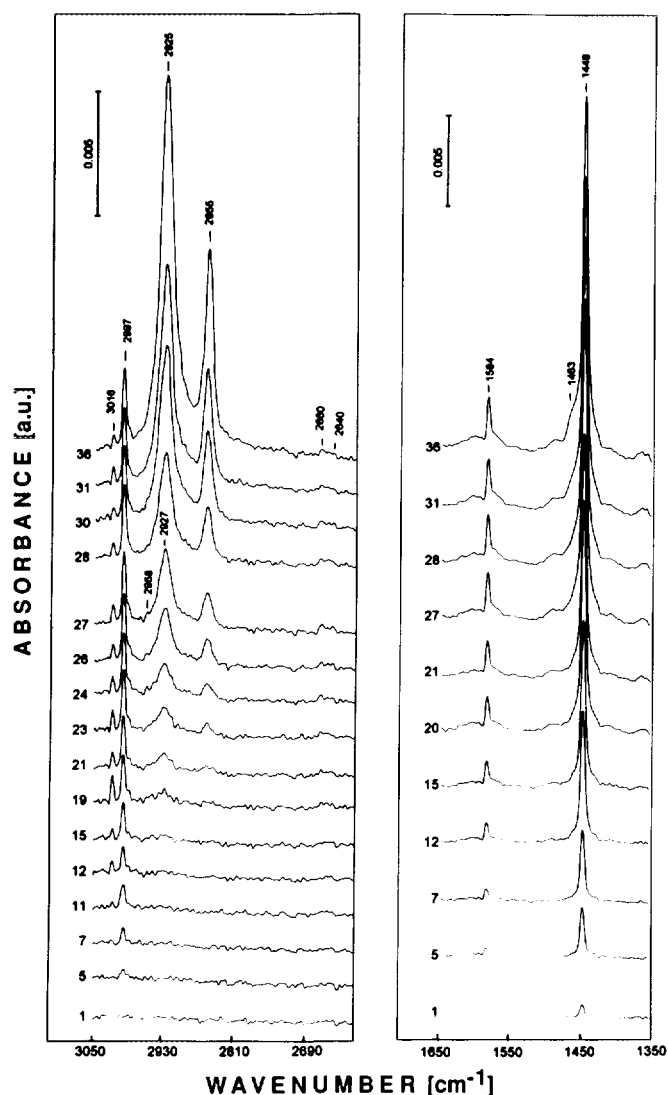


FIG. 1. FTIR spectra recorded after each dose of ethylene injected into the IR cell and allowed to react. The numbers beside each spectral scan correspond to total doses of ethylene added.

increased intensities of the 3016 cm^{-1} band could again be noted, indicative of a continuing involvement of $-\text{CH}=\text{}$ groups in the polymerization, but at an approximately constant surface concentration.

A very weak band between 2960 and 2940 cm^{-1} emerged in the spectra recorded between the 15th and 27th doses. This band appeared as a shoulder at ca. 2960 cm^{-1} , after the 30th injection, and was attributed to the asymmetrical stretching vibration mode of a methyl group connected to the polymer chain. An explanation for the observed low intensity of this band is proposed below.

Unlike previous reports (5–8), we did not detect an absorption in the vicinity of 2750 cm^{-1} . Instead, the weak band near 2660 – 2640 cm^{-1} appeared after the 23rd dose.

The changes in the hydroxyl region (not shown) correspond to the well-known interaction between hydroxyl groups on the silica surface and polymer chains (10).

The surface Cr sites were saturated with adsorbed ethylene beyond the 28th dose (1.9×10^{18} molecules), corresponding to, at most, 40% of the total Cr loading in the 1%D catalyst.

Similar spectra were also observed for the other catalysts after sequential dosing with ethylene. When the ethylene doses aggregated 1.8×10^{18} molecules, equivalent to 50% coverage of all Cr atoms in the 0.5%D catalyst, saturation of the catalyst with π -bonded ethylene was observed. For the 2%D and 5%D catalysts, the saturation point corresponded to injected ethylene totalling 2.3×10^{18} and 2.1×10^{18} molecules, or 16% and 7% of the total Cr loadings, respectively.

Estimation of the Chain Length

Because each dose of ethylene was allowed to react fully, the total number of ethylene molecules polymerizing on the catalyst was available after each dose. By using the relationship between the extinction coefficient for the $\nu_{\text{vas}}(\text{CH}_2)$ band and the number of methylene groups in *n*-paraffinic chains proposed by Jones (19), the average chain length and the cumulative number of active sites involved after each dose of ethylene were estimated. Table 2 shows the results from these calculations for the 1%D catalyst. The calculations assume that the chains are attached to active sites with $\text{Cr}=\text{CH}-$ groups and

TABLE 2

Average Number of Methylene Groups per Polymer Chain and Number of Active Sites on Catalyst 1%D as a Function of Ethylene Doses Added to the IR Cell

Number of ethylene doses	Number of C_2H_4 molecules added ($n \times 10^{-17}$)	Average number of CH_2 groups per polymer chain	Concentration of active sites (sites/g) $\times 10^{-18}$
15	9.9	2	11.2
19	12.5	4	10.0
21	13.8	4	10.9
23	15.1	6	9.0
26	17.3	10	6.8
27	18.0	12	6.1
28	18.6	18	4.4
30	18.9	26	3.4
31	20.6	34	2.7
36	23.2	50	2.2
38	24.5	74	1.5
41	26.9	104	1.2
45	29.3	112	0.9
68	44.3	186	0.9
92	60.0	224	1.0

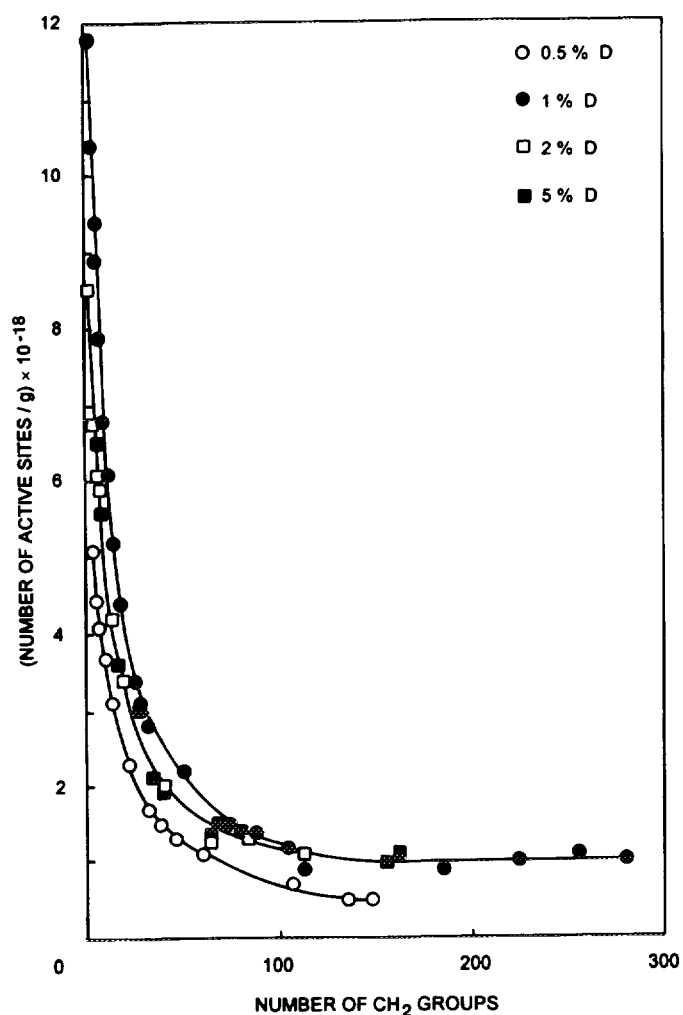


FIG. 2. Relationship between the number of active sites on the catalyst surface and the average chain length observed for various Cr loadings on silica.

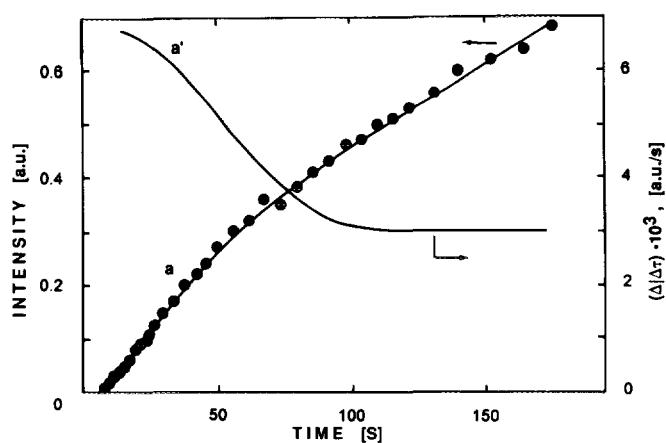


FIG. 3. Polymerization rates versus time for 1%D catalyst at ambient temperature. Initial pressure of ethylene added to the IR cell = 0.133 kPa.

that they are linear with a methyl group at the free end of each chain (see justification below). Figure 2 shows the number of active sites per gram of catalyst as a function of the chain length (number of methylene groups) calculated after each dose of ethylene.

Polymerization Rates

The growth of the polymer chains on the 1%D catalyst (expressed in terms of the intensities of the 2920 cm^{-1} band) and the slopes of this curve (the rates of consumption of ethylene) are plotted against reaction time in Fig. 3. The initial pressure of ethylene charged to the IR cell was 0.133 kPa.

DISCUSSION

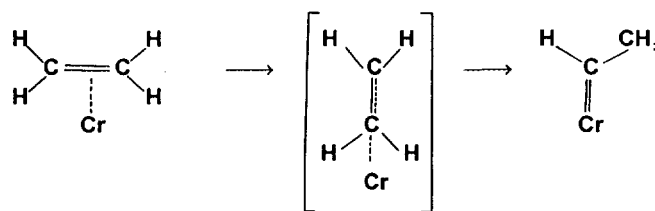
Chain Initiation

The IR spectral evidence suggests that the initiation of ethylene polymerization on the 1%D catalyst involves at least two steps: (i) adsorption of ethylene on the Cr centers by π -complexation; and (ii) formation of $-\text{CH}=\text{}$ groups attached to the Cr sites. The appearance of the surface species containing $-\text{CH}=\text{}$ groups precedes the formation of polymer chains and consequently, they may be considered to be a precursor adsorbed state.

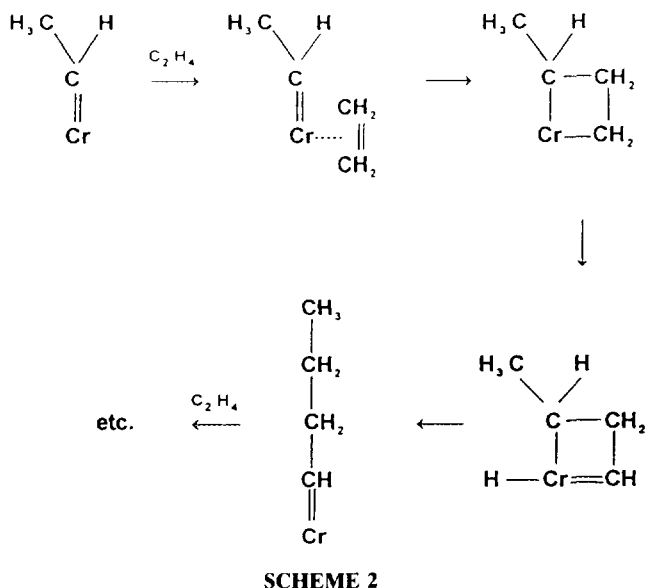
Based on the analysis of the spectral features of ethylene adsorbed on Pt(III), Skinner *et al.* (17) concluded that absorption associated with the 3015 cm^{-1} band is evidence for the formation of an adsorbed ethylidene species (with the $-\text{CH}=\text{}$ structure). Al-Mashta *et al.* (7, 8) studied ethylene polymerization on sulfated anatase and observed surface species characterized by bands at 3010 cm^{-1} ($\nu(\text{CH}=\text{})$) and 2965 cm^{-1} ($\nu_{\text{as}}(\text{CH}_3)$) assigned to ethylidene groups. These studies support our view that the surface species on Cr/silica, characterized by absorption at 3016 cm^{-1} ($\nu(\text{CH}=\text{})$), could also represent an ethylidene species. Scheme 1 summarizes these steps.

To be involved in chain propagation during ethylene polymerization, the ethylidene species participates as shown in Scheme 2, as proposed earlier by Al-Mashta *et al.* (7).

According to Scheme 2, the insertion of additional ethylene molecules occurs at the $\text{Cr}=\text{C}$ bond and is accompanied by the formation of a metallocyclic compound.



SCHEME 1

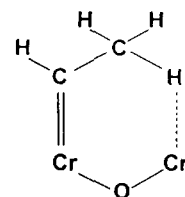


After ethylene insertion, the Cr=C bond is restored. In our experiments this was suggested by an observed irregular oscillation of the 3016 cm^{-1} band intensity. This behavior was observed successively from the 19th to the 36th ethylene doses.

The NMR measurements of McDaniel and Kantor (3) do not support the above mechanism because they ruled out the possibility of hydrogen scrambling during chain propagation. Additional experiments using deuterium-tagged ethylene might clarify this point. Formation of the resulting polyethylene with different isotopic contents could be monitored directly using the FTIR technique.

The terminal methyl group (see Scheme 2) was observed as a very weak $\nu(CH_3)$ band after dose 15, the onset of polymerization, and persisted until the average chain length reached 26 methylene groups (see Fig. 1 and Table 2). Jones (19) earlier reported a similar behavior with *n*-paraffins. Analysis of the IR bands of these *n*-paraffinic compounds shows that the intensity of the asymmetrical vibration, $\nu_{as}(CH_3)$, decreases and becomes less than that of $\nu_{as}(CH_2)$ with increasing chain length. The $\nu_{as}(CH_3)$ band could not be resolved when the number of methylene groups reached 34 (19). When the number of methylene groups in *n*-paraffins exceeded 16, the $\nu_{as}(CH_3)$ band appears as a shoulder of the methylene band. The polymer chains growing on the catalyst surface contain only half the number of methyl groups present in the corresponding *n*-paraffins. With increasing chain length, the methylene bands intensify and overlap the methyl stretching bands so that the latter become increasingly less visible.

A weak band in the $2660\text{--}2640\text{ cm}^{-1}$ region, more visible after larger numbers of ethylene doses, suggests an unusual interaction between CH groups in the polymer chain



SCHEME 3

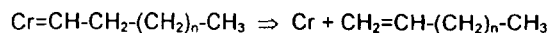
and cationic surface sites, as proposed earlier (8). We assigned this band to the methyl group in the ethylidene species, which is involved in an agostic interaction with chromium centers. See Scheme 3. The lower frequency of this band compared to the value 2750 cm^{-1} reported earlier (5–8) may be due to the increased length of the C–H bonds. This explanation would account for the absence of the stretching and bending modes of the methyl group, which should be observed (18) when the ethylidene groups alone are present. In this case, the expected C_{3v} symmetry of a normal methyl group is distorted with the result that the $\nu(CH)$ band is shifted to lower frequencies. This view is supported by NMR and IR spectral data for different agostic alkyl systems (21, 22). If the M–C–H bond angle approaches 90° , the intensity of the $\nu(CH)$ band of the agostic bond will be small (8, 22). It is evident that the detection of this band will be difficult at low surface concentrations of the ethylidene species.

Finally, the absorption at 3016 cm^{-1} due to the $\nu(=CH)$ stretching mode suggests that the carbene hydrogen is not involved in an agostic interaction, contrary to the view proposed by Ghiotti *et al.* (5).

Hogan proposed (1, 2) that the termination of the growing chain may be caused by desorption of the polymer from a β -hydrogen transfer and formation of a vinyl group, as shown in Scheme 4. We do not have evidence in support of Scheme 4.

Participation of Surface Sites

Figure 2 shows that the 1%D catalyst contains the largest number of active sites among the samples with different Cr content examined in this work. A significant number of the sites initially involved are responsible for the production of shorter chains. Only 1% of the total Cr content in the 1%D catalyst appears to remain effective during polymerization. This number of active sites remains the same for the catalysts with higher Cr loadings, indicating the maximum concentration of active sites on the silica support is achieved with a 1 wt% Cr content. The number of sites presumably active in the polymerization comprise about $\frac{1}{40}$ of the number of chromium ions to which ethylene is π -adsorbed. It is worth noting that the



SCHEME 4

number of active sites on the 1%D catalyst estimated at the start of ethylene polymerization (1.2×10^{19} sites/g) corresponds approximately to the number reported by Hogan (1), 2.5×10^{-5} mole active Cr sites/g.

The average concentration of coordinatively unsaturated titanium cations on sulfated anatase is reported (23) as $5 \text{ Ti}^{4+}/\text{nm}^2$, i.e., about two orders of magnitude larger than the maximum concentration of active sites on the 1%D catalyst (ca. 4×10^{-2} sites/ nm^2). This smaller number of active sites on the 1%D catalyst would correspond to the much lower intensities of the bands attributed to the terminal methyl groups on Cr/silica compared to those on sulfated anatase (7, 8).

Finally, Fig. 3 shows that reaction rates decrease during reaction initiation, in agreement with the observed decrease in the number of active sites (see Fig. 2), and that the rate reached a constant value early in the propagation stage. The latter constant rate would correspond to the constant number of active sites which had developed.

The experimental gas-phase conditions for polymerization employed in this study are different from those employed during typical industrial polymerization on Cr/silica catalysts. Nonetheless, the molecular events occurring during the slow reaction initiation and chain growth in the IR cell probably relate to both. Our measured rates do not, however, relate to events observed at more advanced stages of ethylene polymerization, such as when fragmentation of catalyst particles is occurring. A description is available of the subsequent changes in rate behavior resulting from physical changes in a porous Cr/silica catalyst from reaction initiation to more advanced polymerization stages (24).

CONCLUSIONS

The technique of sequentially contacting very small increments of ethylene with the Cr/silica catalyst and then using FTIR spectroscopy to monitor the polymerization process events was successful in generating additional novel evidence concerning the initiation and propagation mechanisms. The important observations include:

1. IR spectral evidence indicates that ethylidene species are formed directly from π -adsorbed ethylene molecules without need for a hydrogen donor.
2. During the early stages of ethylene polymerization, the polymer chains have a linear structure with a methyl group and a Cr=CH- group at opposite ends.
3. The maximum concentration of active sites on the silica support occurs at a total Cr content near 1 wt%. By calculating the number of active sites as a function of the average number of methylene groups per chain, approximately 1% of the total number of Cr atoms appear to be active sites when the early polymerization rate becomes constant.

4. The population of active sites decreases during the early chain propagation stage, eventually stabilizing at a constant number. This is in accord with the constant polymerization rate observed after about 2 min of reaction.

5. The polymer chain grows by insertion of ethylene molecules into the Cr=C bond, accompanied by the formation of a metallocyclic compound. After the ethylene insertion, the Cr=C bond is restored and additional insertion occurs.

ACKNOWLEDGMENTS

Financial support for this work was provided by the Natural Sciences and Engineering Research Council of Canada and by Novacor Chemicals Ltd.

REFERENCES

1. Hogan, J. P., *J. Polym. Sci. A-1* **8**, 2637 (1970).
2. Hogan, J. P., in "Applied Industrial Catalysis," Vol. 1, Chap. 6. Academic Press, New York, 1983.
3. McDaniel, M. P., and Kantor, D. M., *J. Polym. Sci. Polym. Chem. Ed.* **21**, 1217 (1983).
4. McDaniel, M. P., *Adv. Catal.* **33**, 47 (1985).
5. Ghiotti, G., Garrone, E., and Zecchina, A. J., *J. Mol. Catal.* **46**, 61 (1988).
6. Ghiotti, G., Garrone, E., Coluccia, S., Morterra, C., and Zecchina, A. J., *J. Chem. Soc. Chem. Commun.*, 1032 (1979).
7. Al-Mashta, F., Sheppard, N., and Davanzo, C. U., *Mater. Chem. Phys.* **13**, 315 (1985).
8. Al-Mashta, F., Davanzo, C. U., and Sheppard, N., *J. Chem. Soc. Chem. Commun.*, 1258 (1983).
9. Rebensdorff, B., and Larsson, R. J., *J. Mol. Catal.* **11**, 247 (1981).
10. Zielinski, P., and Dalla Lana, I. G., *J. Catal.* **137**, 368 (1992).
11. Vikulov, K., Spoto, G., Coluccia, S., and Zecchina, A., *Catal. Lett.* **16**, 117 (1992).
12. Karge, H. G., *Z. Phys. Chem.* **122**, 1033 (1980).
13. Zielinski, P., Szymura, J. A., and Dalla Lana, I. G., *Catal. Lett.* **13**, 331 (1992).
14. Davydov, A. A., *Mater. Chem. Phys.* **13**, 243 (1985).
15. Busca, G., Lorencelli, V., Ramis, G., Sausey, J., and Lavaley, J. C., *J. Mol. Struct.* **267**, 315 (1992).
16. Bellamy, L. J., in "The Infra-red Spectra of Complex Molecules." Chapman & Hall, London, 1975.
17. Skinner, Ph., Howard, M. W., Oxton, I. A., Kettle, S. F. A., Powell, D. B., and Sheppard, N. J., *J. Chem. Soc. Faraday Trans. 2* **77**, 1203 (1981).
18. Anson, C. E., Sheppard, N., Powell, D. B., Norton, J. R., Fischer, W., Keiter, R. L., Johnson, B. F. G., Lewis, J., Bhattacharyya, A. K., Knox, S. A. R., and Turner, M. L., *J. Am. Chem. Soc.* **116**, 3058 (1994).
19. Jones, R. N., *Spectrochim. Acta* **9**, 235 (1957).
20. Ibach, H., and Lehwald, S. J., *J. Vac. Sci. Technol.* **15**, 407 (1978).
21. Brookhart, M., and Green, M. L. H., *J. Organomet. Chem.* **250**, 395 (1983).
22. Schultz, A. J., Williams, J. M., Schrock, R. R., Rupprecht, G. A., and Fellmann, J. D., *J. Am. Chem. Soc.* **101**, 1593 (1979).
23. Hadjiivanov, K. and Davydov, A., *Kinet. Katal.* **29**, 398 (1988).
24. Dalla Lana, I. G., Szymura, J. A., and Zielinski, P., in "Proceedings, 10th International Congress on Catalysis, Budapest, 1992" (L. Guzzi, F. Solymosi, and P. Tetenyi, Eds.), p. 2329. Akadémia: Kiadó, Budapest, 1993.