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The effect of temperature on ethylene polymerization over flat Phillips model catalysts

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Abstract

The polymerization properties of a well-defined flat $CrO_x/SiO_2/Si(100)$ catalyst were investigated. To compare this model system with the conventional Phillips catalyst based on porous silica, polymerization reactions were carried out at various temperatures. In contrast to the conventional Phillips catalyst, our model showed constant activity from the start of polymerization. Both the activity and molecular weight were tenfold higher for the flat catalyst. As expected, an increase in polymerization temperature led to an increase in activity; however, the molecular weight distribution was only mildly affected. At a temperature around the melting point of polyethylene, a sudden drop in both activity and molecular weight was observed. Based on our observations, we propose that chromium sites produce polymer chains in short bursts of high activity, followed by a dormant period, and that ethylene polymerization of active chromium sites can result in local ethylene depletions that limit both activity and molecular weight. This can severely affect the polymerization properties in the event of high active site density and reduced mass transfer through the formed polymer layer.

Keywords: Phillips catalyst; Ethylene polymerization; Morphology; Kinetics; Chromium oxide; Silica; Size exclusion chromatography; Long chain branching; Site starvation; Viscometry

1. Introduction

Phillips-type catalyst systems, consisting of chromium oxide dispersed on a porous oxide [1–4], are among the most important catalysts in ethylene polymerization. Due to their high sensitivity toward preparation, such systems give rise to a rich family of catalysts; small changes in the preparation method have a significant effect on the observed activity and the properties of the polymer thus formed. This versatility is responsible for the commercial success of Phillips catalysts, because it allows the possibility of tuning the polymer properties toward different applications. But despite this success, and almost 50 years of academic and industrial research, Phillips catalysts remain poorly understood on the molecular level. The molecular structure of the active site and the mechanism of polymerization remain unresolved. The CrO_x/SiO_2 system has been intensively investigated using a wide variety of spectroscopic techniques and probe molecules [4]. These efforts have increased our understanding of the surface chemistry of supported chromium; unfortunately, however, previous studies have lacked detailed data on the polymerization performance of the model catalyst used. Furthermore, only a small fraction of the total chromium loading in Phillips-type catalysts is believed to be active in ethylene polymerization; values typically do not exceed 10% of the chromium atoms [4]. This property calls into question all far-reaching correlations between spectroscopy and reactivity of the Phillips catalysts. In a recent study, Groppo et al. [5] claimed to have achieved a correlation between infrared characterization of Cr(II) surface sites and microgravimetrical measurement of polymerization activity at room temperature. Although these authors claim to have identified two different classes of active sites, we believe that the extremely low catalytic turnover that they observed precludes a correlation of

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activity with spectroscopy. The total polymer yield in a 10-min polymerization experiment amounted to only one ethylene molecule per Cr atom. Obviously, in these experiments only a tiny fraction of the total chromium formed polymer chains.

The extreme sensitivity toward preparation makes it difficult to compare studies from different groups. To combine the results of various spectroscopic studies, the studies should be applied to a single catalyst batch that should also be characterized in terms of its polymerization properties. In industry, considerable effort has been expended on the empirical mapping of polymerization performance as a function of catalyst preparation (e.g., calcination temperature, type of silica, chromium loading) and polymerization conditions (e.g., temperature, ethylene pressure). But, naturally, this knowledge has rarely been disclosed in detail in the open literature.

In an attempt to correlate catalyst preparation with a detailed molecular-level characterization of the CrO_x/SiO_2 system and a characterization of this system's polymerization properties, we have developed a flat Phillips model catalyst. This model is based on a silicon wafer covered with about 20 nm of thermal silicon oxide. The model support allows wet chemical impregnation of the active phase (e.g., CrO_3 in water) and further treatment similar to its industrial complement. Flat model catalysts are especially well suited for applying surface spectroscopies [e.g., X-ray photoelectron spectroscopy (XPS), Rutherford backscattering spectrometry (RBS), SIMS] and high-resolution microscopic techniques [e.g., scanning electron microscopy (SEM), AFM] [6–10]. The flat nature of the catalyst facilitates study of the morphology of polymer films, because polymer growth occurs only in a direction normal to the catalyst plane. In a previous report [11] we focused on the effect of calcination on this chromium desorption. By applying XPS and RBS, we were able to quantify the chromium coverage after calcination as a function of calcination temperature and initial chromium loading. That study highlighted the importance of chromium desorption and local chromium densities for the activity of the model catalyst.

In this paper we discuss the effect of polymerization temperature on the catalytic performance of the $CrO_x/SiO_2/Si(100)$ model catalyst. For the first time we combined the activity with data on the molecular weight and melting point of polyethylene, which allowed us to compare our catalyst with industrial Phillips catalysts on the basis of polymerization performance.

2. Experimental

2.1. Preparation of the model catalyst and polymerization

The Phillips model catalysts were prepared by immersing a flat silicon wafer in an aqueous CrO_3 solution and spin-coating the polished side (roughness of 5 Å), as described previously [11,12]. After spin-coating, the unpolished backside of the wafer also contained an amount of chromium that remained undefined due to contact with the sample holder. In this study, the chromate loading of the model catalyst was 1 Cr atom/nm^2. The reactor used for catalyst activation and polymerization was a modified version of one described previously [9], comprising a single tube with two spaces separated by a glass filter. The upstream side contained a gas-cleaning catalyst bed (a scavenger material of chromate-loaded γ-alumina extrudates), and the downstream part was loaded with one sample with a surface area of about 5 cm^2.

In the present study, all chromate spin-coated wafers were calcined in a dry O_2/Ar mixture at 650 °C, followed by a reduction treatment in CO at 350 °C for 15 min. After cooling in an argon flow, polymerization was started by introducing ethylene gas at various temperatures between 23 and 160 °C at atmospheric pressure. Polymerizations at 100 °C and above were done for a maximum of 5 h, to prevent the reactor from breaking due to excessive polymer growth of the gas-cleaning catalyst bed. At lower temperatures, at which activities were lower, polymerizations were carried out for 17 h to obtain sufficient material for molecular weight analysis.

2.2. Catalyst activity

Polymerization activity was determined by weighing the catalyst before and after polymerization. Because of the equal calcination, reduction, and polymerization conditions for the polished side and the unpolished back side of the wafer, both sides of the catalyst demonstrated activity. To ensure that activity data were obtained from the polished side only, the polymer formed on the back side was removed.

2.3. Polymer characterization

The morphology of the formed polyethylene films were studied using an environmental scanning electron microscope (XL30 ESEM-FEG, FEI Company, The Netherlands) operated in low-voltage mode. Size exclusion chromatography (SEC) was used to determine the molecular weight of the polymer samples. The required amount of sample (at least 1 mg) was obtained by removing the polymer from the catalyst surface. The measurements were performed at DSM using a PL-GPC220 device with Viscotek 220R viscosimeter, TSK GMHHR-H(S) HT columns, and 1,2,4-trichlorobenzene as an eluent.

Thermal analysis was carried out using differential scanning calorimetry (TA Instruments Q1000). To obtain a polymer melting temperature based solely on polymer properties and not on polymerization temperature induced morphology differences, an initial heating cycle was run to remove the nascent character of the sample. All heating and cooling scans were performed at a rate of 10 K/min.

3. Results

3.1. Catalyst activity and polymer morphology

As outlined in the Experimental section, the active catalysts were treated with ethylene gas at atmospheric pressure at various temperatures between 23 and 160 °C. During polymerization, polyethylene grew in a direction normal to the catalyst plane to form a homogeneous film. Polymer layer thick-

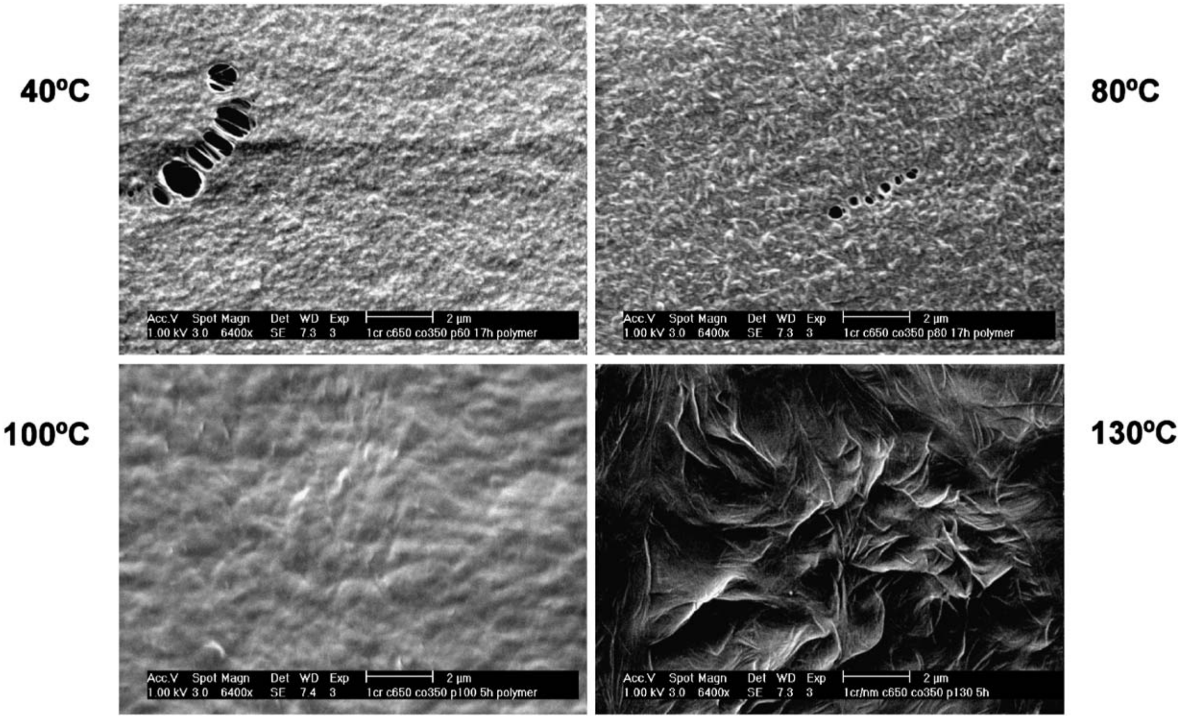

Fig. 1. Scanning electron microscopy images of polyethylene films formed on model catalysts at 40, 80, 100 and 130 °C.

nesses, as determined by SEM imaging, agreed with the activities found by weighing. Fig. 1 shows SEM images of the polymer samples obtained at 40, 80, 100, and 130 °C. The films produced at 40 and 80 °C have a grainy appearance and show cracks with stress fibrils. At 100 °C, larger grains are formed and the surface has a smoother appearance. At 130 °C and above, polymerization proceeds in the polymer melt. On cooling to room temperature, the polymer crystallizes and forms the well-known spherulite morphology [7].

Activities were determined after normalization on the basis of the active surface area and the polymerization time (Table 1). Initially we observed an exponential increase in activity with increasing temperature. At higher temperatures, the rate of increase became smaller; it reached a maximum at 130 °C and then decreased thereafter. The nominal turnover frequencies could be calculated based on surface chromate quantifications as described previously [11]. For the sample loaded with 1 Cr/nm^2, we found no change in chromium loading on calcination at 650 °C. Because only a small fraction of chromium is thought to be active for the Phillips catalyst [2,4,13], the actual turnover frequencies are probably much higher than the values reported here.

3.2. *Molecular weight and viscosity*

Fig. 2 shows the weight average molecular weight distribution results obtained by SEC analyses of six samples, polymerized at 23, 40, 80, 100, 130, and 160 °C. The samples polymerized below 100 °C show similar distributions, with a single maximum at ca. 7×10^5 and a tail on the low molecular weight side. The most striking feature in these molecular weight distributions is the appearance of a second peak in the distribution obtained from the sample polymerized at 130 °C. One of the maxima in this distribution occurred at the high molecular weight side (ca. 8×10^5). The other maximum occurred at a molecular weight of ca. 1×10^4. At 160 °C, the peak at low molecular weight became dominant; however, the high molecular weight compound remained visible. Table 1 gives the number average molecular weight (M_n), the weight average molecular weight (M_w), and the dispersity index (M_w/M_n). Only a small decrease in molecular weight with increasing polymerization temperature can be observed in the range of 23–100 °C, but this decrease became much more significant above 100 °C.

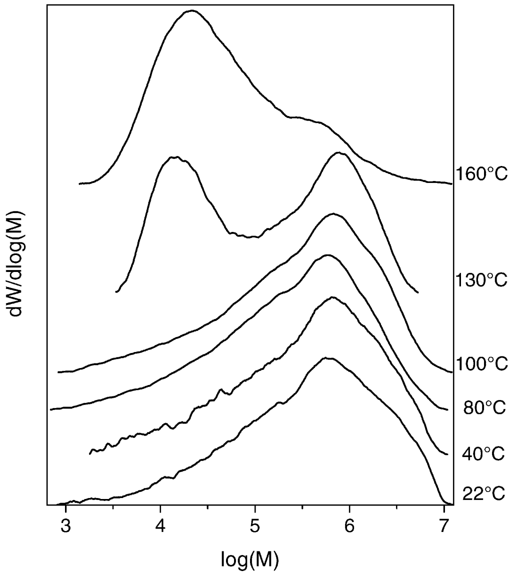

Fig. 2. Molecular weight distribution curves for polyethylene produced over flat model catalysts at the indicated temperatures.

Table 1
Activity and polymer characterization results for model catalysts loaded with 1 Cr/nm^2, calcined at 650 °C and reduced in CO at 350 °C. The active catalyst area is about 5 cm^2

	Polymerization temperature (°C)						
	23	40	60	80	100	130	160
$t_{\text{polymerization}}$ (h)	17	17	17	17	5	5	4.5
Yield (mg cm^{-2})	1.06	1.22	2.36	4.57	2.74	3.95	2.49
Activity per area (mg cm^{-2} h^{-1}atm^{-1})	0.062	0.072	0.139	0.269	0.547	0.790	0.553
(TOF) average (s^{-1})	3.7	4.3	8.3	16.1	32.7	47.2	33.0
Specific activity[a] (g_{PE} $g_{cat}$$^{-1}$ h^{-1} atm^{-1})	1.9×10^2	2.2×10^2	4.2×10^2	8.1×10^2	1.6×10^3	2.4×10^3	1.7×10^3
M_n (g mol^{-1})	57×10^3	62×10^3		43×10^3	49×10^3	32×10^3	20×10^3
M_w (g mol^{-1})	1100×10^3	960×10^3		720×10^3	840×10^3	490×10^3	210×10^3
M_w/M_n –	18.9	15.5		16.9	17.3	15.5	10.2
T_{melt} (°C)	132	131	130	130	129	125	127

[a] For a porous carrier with a surface area of 300 m^2/g.

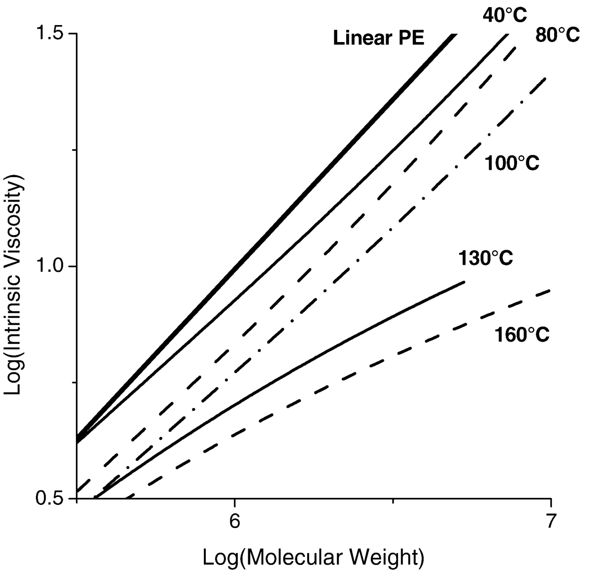

Fig. 3. Mark–Houwink plots of polyethylene produced over flat model catalysts at different temperatures show deviation from linearity pointing to branching.

Fig. 3 displays Mark–Houwink plots for the polyethylene samples polymerized at 40, 80, 100, 130, and 160 °C, together with a straight line representing the theoretical behavior of perfectly linear polyethylene. In a Mark–Houwink plot, the logarithm of the intrinsic viscosity of a polymer in solution is plotted against the logarithm of the molecular weight. At high molecular weight, the slopes clearly began to decrease. This decrease was more pronounced for the samples polymerized at the highest temperatures when polymerization occurred in the polymer melt. Such behavior is generally attributed to long-chain branching.

3.3. Thermal analysis

The melting point of the polyethylene was determined for all polymer samples after a first heating cycle at 160 °C (see Table 1). For the sample polymerized at the lowest temperature (23 °C), the melting point was 132 °C; for samples polymerized at higher temperatures, this decreased to about 125 °C. Both of these melting points are somewhat low considering the normal melting temperature of high molecular weight polymer, 133–135 °C. Most likely these lower melting points originated from a small degree of chain branching. For higher polymerization temperatures, the melting point decreased, suggesting an increase in the degree of chain branching with increasing polymerization temperature, in line with the results found with SEC. The slight increase in melting point on an increase in polymerization temperature from 130 to 160 °C correlates with a significant increase in the low molecular weight peak. This may indicate that this low molecular weight fraction is more linear than the high molecular weight fractions, which demonstrate low viscosity in both cases.

4. Discussion

4.1. Model catalyst in comparison with industrial catalyst

The most important general trends for olefin polymerization over the calcined CrO_x/SiO_2 catalyst system are (1) a monotonous increase in activity and molecular weight with polymerization time, (2) an increase in activity and a mild decrease in molecular weight with increasing polymerization temperature, and (3) an increase in both activity and molecular weight with increasing ethylene pressure. Furthermore, polyethylene produced over CrO_x/SiO_2 catalyst systems is characterized by a broad molecular weight distribution ($M_w/M_n = 10$–40).

Superficial inspection of the data from polymerization over the $CrO_x/SiO_2/Si(100)$ model catalyst reveals expected trends for activity and molecular weight. Increases in polymerization temperature increased the overall activity and termination rate/propagation rate ratio, the latter of which led to shorter polyethylene chains. A popular explanation for this trend is that of McDaniel [1], who posited a destabilizing effect on the chromium-chain bond at higher temperatures.

However, several features of the model catalyst are quite remarkable in the light of the established view of olefin polymerization over CrO_x/SiO_2 systems. First, the activity of our model catalyst (Table 1) appears to be rather high compared with high-surface area Phillips catalysts with similar pretreatment. Detailed results on the activity of the Phillips catalyst together with data on catalyst pretreatment and polymerization conditions are

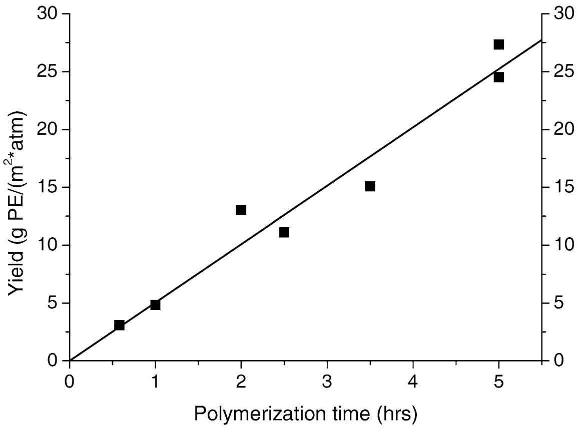

Fig. 4. Polyethylene yield vs. polymerization time at 100 °C for polymerization over flat model catalysts. The catalysts were loaded with 1 Cr/nm^2, calcined at 650 °C and reduced in CO at 350 °C.

rare in the literature. McDaniel and Merryfield [1,14] reported activity reaching a maximum of about 2.9 $kg_{PE}/(h\,g_{cat})$ in a slurry polymerization in isobutane at 105 °C and an ethylene pressure of ca. 19 bar. Their catalyst was calcined at a temperature of 595 °C and reduced in CO at 350 °C. Assuming a first-order ethylene pressure relation [1], the activity was estimated as 0.15 $kg_{PE}/(h\,g_{cat}\,atm)$. Comparison between slurry and gas-phase polymerizations is not straightforward [15–17]; however, slurry processes usually demonstrate higher productivity, partly due to the higher ethylene concentration in the slurry solvent compared with the gas phase [18].

Fang et al. [19] used a chromium content of 1.0 wt% and a calcination temperature of 600 °C. After a reduction step in CO at 350 °C the catalyst was allowed to polymerize ethylene at a pressure of 1.3 bar in heptane solvent. Triethyl aluminium was used as a co-catalyst, and the temperature was kept at 60 °C. Based on measurements of ethylene consumption, the activity was estimated as 6.5 $g_{PE}/(h\,g_{cat}\,atm)$. In comparison, our model catalyst exhibited at least a tenfold-higher turnover frequency than the conventional catalysts on high-surface area supports.

The second significant difference that sets our model apart from conventional Phillips catalysts relates to the development of activity over time. The Phillips catalyst in the McDaniel study [1] showed an increase in activity in the first hours of polymerization; in contrast, our model catalyst polymerized ethylene with constant activity over a period of several hours. Individual polymerization runs deviated from this linear trend by only about 12%, as shown in Fig. 4 for a series of polymerizations at 100 °C.

Third, the molecular weight produced over the flat model catalyst was surprisingly high. At a much higher ethylene pressure, McDaniel obtained an M_w of almost 2×10^5 g/mol. Because the industrial catalyst and our model system have the same preparation chemistry [9,11,14], an explanation involving a change in the reactivity or number of active sites is unsatisfactory. Considering the spatial differences between the two catalysts, a mass transfer limitation is more plausible. An 1-cm^2 area of our model catalyst contains about the same amount of active sites as a 100-μm^3 volume of industrial catalyst. Obviously, in the latter, a much higher flux of monomer is needed to feed all of the active sites, making the likelihood of diffusion limitation much higher in this three-dimensional system than in the two-dimensional model catalyst. During polymerization, as the particles break up and the metal volume concentration decreases, the activity increases. In what follows we further develop the mass transfer proposition to explain the reactivity of the $CrO_x/SiO_2/Si(100)$ model system.

4.2. Polymerization kinetics and mechanistic implications

Both the activity of our model catalyst and the molecular weight of the polymer produced showed remarkable changes in trend when going from low polymerization temperatures to polymerization temperatures of 130 °C and above. The sudden drop in activity and molecular weight was accompanied by a dramatic change in the molecular weight distribution curves at 130 and 160 °C and coincided with the change from polymerization in the solid to polymerization in the melt. This temperature regime is inaccessible for gas-phase polymerization with conventional catalysts, because of reactor fouling. To the best of our knowledge, there are no reports in the literature on Phillips catalyst molecular weights covering polymerization temperatures extending from as low as room temperature to as high as above the melting point of polyethylene. Publications that deal with molecular weights of polyethylene obtained with Phillips-type catalysts usually do not present the entire distribution curve and give only number- and weight-averaged molecular weights.

At least two possible explanations can be given for the sudden drop in activity and molecular weight. These are based either on heterogeneity of active chromium centers dominating polymerization at different temperatures or on the abrupt change in the local polymerization conditions of the chromium centers. As mentioned earlier, both activity and molecular weight are known to decrease with a decrease in ethylene concentration. McDaniel [1] claimed that the propagation step was highly dependent on the ethylene concentration. He found a nearly first-order increase in activity, with increasing molecular weight for higher ethylene pressures. This means that the rate of termination was less affected than the rate of propagation by a change in ethylene concentration.

The inset of Fig. 5a shows the temperature dependence of the polymerization activity between 25 and 100 °C. From this Arrhenius plot, we estimate an activation energy of 27 ± 3 kJ/mol. This value is close to those found by Clark (30 kJ/mol) [20] for the Phillips catalyst and by Scott et al. (30.2 ± 0.9 kJ/mol) [21] for tetra-alkylchromium fragments on silica.

Fig. 5b shows the rate of polymer chain formation per chromium atom, obtained by dividing the normal activity by the number-averaged molecular weight. This represents the rate of chain initiation. At higher temperatures, no dramatic drop in chain formation rate is observed, in contrast to the overall polymerization activity. The inset of Fig. 5b shows the temperature dependence of the chain formation rate as an Arrhenius plot. In this case, the full range of experiments (23–160 °C) is fitted, obtaining an energy of activation of chain initiation of

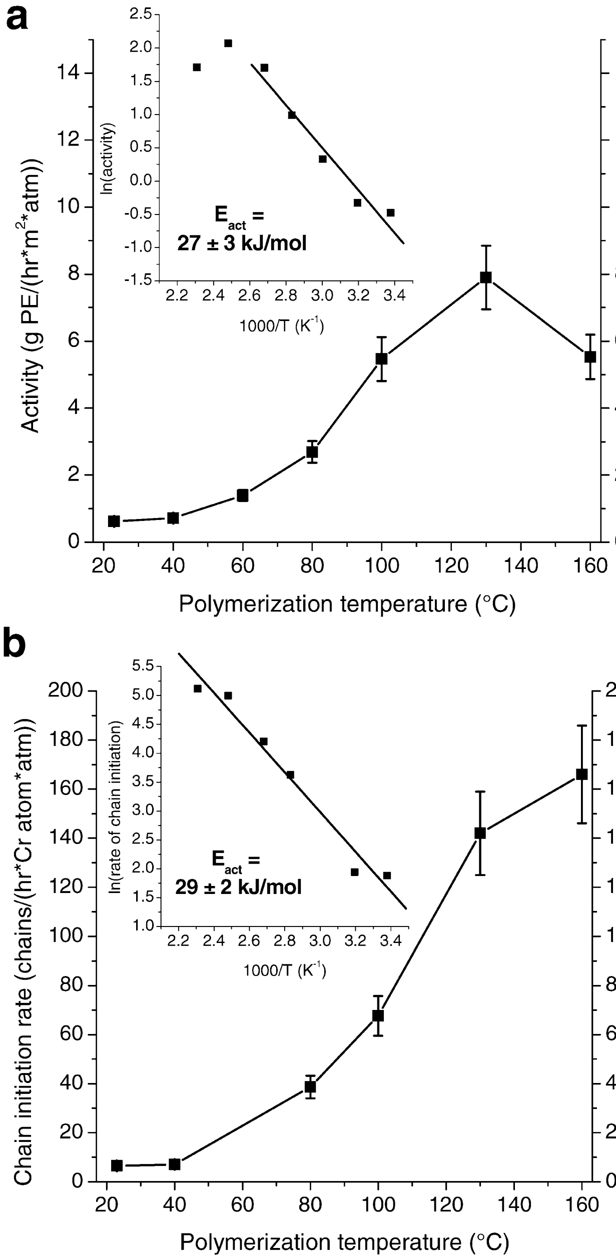

Fig. 5. (a) Polymerization activity plotted vs. polymerization temperature for a flat model catalyst loaded with 1 Cr/nm^2, calcined at 650 °C and reduced in CO at 350 °C. The active catalyst area is about 5 cm^2. Errors of 12% based on Fig. 4 are included. (Inset) Arrhenius plot of the activity in the interval from 23 to 160 °C. (b) The rate of chain formation plotted against polymerization temperature for the same type of catalyst. (Inset) Arrhenius plot of the rate of chain formation.

29 ± 2 kJ/mol. The rates at the high polymerization temperatures of 130 and 160 °C agree well with the linear fit, suggesting that, unlike the overall activity, the initiation rate is not significantly affected in this temperature range.

The change in molecular weight at 23–100 °C is small compared with the change in activity. Hence the apparent activation energies found for chain initiation and polymerization are almost identical in this temperature range. We conclude that the activity increase can be ascribed mainly to the increasing rate of chain initiation, making it the rate-determining step in ethylene polymerization. This would imply that the activation energy of polymerization over a CrO_x/SiO_2 catalyst is not that of propagation, as is often assumed. The activation energy of the latter is probably much lower than the value shown in Fig. 5a. A direct consequence of this proposition is that an active Cr site does not continuously polymerize, but rather stays dormant after chain termination until another initiation reaction occurs.

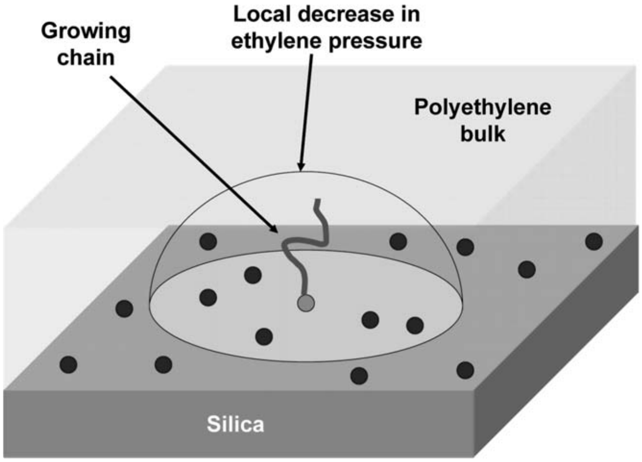

Fig. 6. Schematic representation of an ethylene depletion zone caused by short bursts of high propagation rates. The local low ethylene pressure affects the propagation of the active site and its neighbors, leading to reduced activity and shorter chains.

Based on this, we claim that the active sites of the Phillips catalysts exhibit short bursts of very fast propagation, followed by relatively long periods of inactivity. The availability of ethylene monomer at the active sites determines the molecular weight of the growing chain and thus also the overall polymerization activity. Rapid ethylene consumption resulting from extremely fast propagation rates will result in a volume of decreased ethylene pressure in the vicinity of the polymerizing sites, as illustrated in Fig. 6. Polymerizing sites situated in this volume will compete for the monomer present. Activity and average molecular weight will drop, because propagation speed is hindered by low ethylene concentrations but termination is not. This proposition qualitatively explains the discrepancies between the polymerization behavior of the flat model catalyst and the industrial Phillips catalyst from the McDaniel study. For the latter, active site densities are much larger because of the three-dimensional spacing of chromate.

Above 100 °C, the initiation reaction still exhibits Arrhenius behavior, which means that the drop in activity is attributed to the strong decrease in molecular weight during polymerization in molten polyethylene. The fact that the rate of chain initiation demonstrates Arrhenius behavior suggests that no change occurs in the amount and/or nature of active sites when the polymerization temperature is increased beyond the melting temperature. Therefore, it is unlikely that the decrease in molecular weight can be explained by the existence of two types of sites that dominate polymerization at different temperatures. Site starvation, as shown in Fig. 6, can explain this observation.

Along with the decreased activity and molecular weight, melting point and viscometry analyses point to an increase in long-chain branching. At high temperatures, in increased number of side reactions can be expected. Moreover, as the concentration of ethylene near the catalyst surface decreases, the chain/ethylene ratio increases. This favors long-chain branching in polyethylene samples formed at high polymerization temperatures.

The low ethylene pressure near the catalyst surface at 130 °C and above could originate from decreased ethylene solubility in the polymer matrix. The solubility of ethylene in polyethylene is known to drop with increasing temperature at not overly high pressure [22–26]. For solid polyethylene in polymerizations below the melting point, the ethylene concentration inside the polymer depends on both crystallinity and temperature [24]. High crystallinity results in decreased solubility. Whether a continuous decrease in ethylene solubility with temperature can account for the sharp changes in activity and molecular weight observed is a matter of debate. This is true especially in cases in which solubility changes are minor compared with direct temperature effects. The fact that the activity and molecular weight decreases occur suddenly around the melting point obviously suggests a role for morphological changes. This possibility is bolstered by the SEM images in Fig. 1. The surface of the polymer formed at low temperature is clearly under stress, as indicated by the cracks and holes in the film. Thus, the polymer could exhibit higher porosity. Supplying ethylene to the active catalyst surface may be much easier through a porous medium than through a bulk of polymer, in which solution and diffusion in the polymer melt is the only method of transport.

5. Conclusion

In this study, we evaluated the flat $CrO_x/SiO_2/Si(100)$ catalyst for activity and selectivity on polymerization at temperatures ranging from 23 to 160 °C. Our model catalyst differs from the conventional Phillips catalyst in that it does not demonstrate increased activity with polymerization time, but immediately develops a constant activity. Both the activity and average molecular weight of the resulting polymer are about 10 times higher than those of the Phillips catalyst on porous support. On increasing polymerization temperature, the $CrO_x/SiO_2/Si(100)$ catalyst exhibited increased activity and mildly decreased molecular weight. At around 130 °C, a sharp drop in both activity and molecular weight was observed, with an increase in long-chain branching.

Based on the Arrhenius plots of the model catalyst activity and chain initiation, we propose that active chromium sites produce polymer chains in short bursts of high activity rather than through a continuous and constant propagation. Local ethylene depletion zones can develop as a result of this temporary high monomer consumption. Active sites situated in this zone have to compete for the available monomer, affecting both activity and molecular weight. This simple model, shown in Fig. 6, can qualitatively explain all of the observed trends in polymerization reactivity of the model catalysts and also may be an important factor in the differing polymerization performance with respect to high-surface area Phillips catalysts. These differences originate from the high metal concentration at the beginning of polymerization for the conventional Phillips catalyst. The catalyst's three-dimensional structure offers higher active site densities than the two-dimensional structure of the model catalyst. As polymerization proceeds, the active sites in the conventional catalyst are diluted, and the activity and molecular weight increase. We attribute the decreased activity at polymerization temperatures of 130 °C and above to the decreased mass transfer of ethylene through the polyethylene layer when it is in the melt. The porous nature of the nascent polymer film below the melting temperature makes the active sites more accessible for fresh monomer.

6. Implications for real Phillips catalysts and other Cr-based polymerization catalysts

A link between mass transfer limitations and the kinetic profile of Phillips catalysts has been discussed previously [1,4,27] but has never been fully accepted. Choi and Tang [28] ascribed the increase in activity over time for conventional Phillips catalysts to active site poisoning. Reaction products (aldehydes) formed during the reduction of hexavalent to divalent chromium by ethylene act as a catalyst poison. Over time, the concentration of poisoned sites will decrease as the reaction products diffuse out of the pores. However, for CO-prereduced catalysts, the carbon monoxide poison will have had ample time to diffuse away from the active sites before the start of polymerization. Still, McDaniel [1] reported a rise in activity for his CO-reduced Phillips catalysts.

According to McDaniel [1], the rise in activity often can be eliminated by adding alkylmetal-reducing agents. In addition, Ziegler catalysts – which have an overall activity at least as high as that of Phillips catalysts – do not exhibit as strong an increase in activity, even though the active site concentrations are thought to be much higher. However, the polymerization mechanisms over Ziegler catalysts or over alkylated chromium catalysts do not need to resemble those of the bare Phillips catalyst, which lacks a preformed metal carbon bond. Scott et al. [21] grafted organochromium fragments on amorphous nonporous silica with a chromium loading comparable to that of our flat model catalysts. They reported truly impressive activity of $5.9 \times 10^6\ g_{PE}/(h\ mol_{Cr}\ atm)$ at 80 °C, about three times that of the flat Phillips model catalyst in the present study. Our proposed polymerization scheme does not seem to apply to these highly active catalyst derived from organochromium precursors.

Despite these complications, we believe that the proposed combination of chain initiation-controlled polymerization with short bursts of ethylene consumption and mass transfer-limited chain growth at the active site provides a valid alternative to describe the reactivity of (CO-reduced) Phillips catalysts. This scheme can at least complement the more prominent proposals based on chemical heterogeneity of active chromium sites.

Acknowledgments

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