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A Novel Laboratory Slurry Reactor for Ethylene Polymerization Studies

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ABSTRACT: A novel laboratory slurry reactor useful for studies of polymerization of olefins with solid catalysts such as Cr/silica is described. The operation of this reactor, in which gaseous impurities are minimized by purification of incoming gases and by *in situ* activation of the catalyst, has enabled the early stages of the homopolymerization of ethylene to be studied without interference from catalyst deactivation effects. By standardizing the conditions for the experimental runs, the reactor demonstrated its usefulness in isolating and assessing the relative physical roles of different silica supports. Four catalysts supported on different silica supports were compared, and their differences in promoting the polymerization were interpreted in terms of porosity, average particle size, and changes in specific surface area. During early polymerization, the fracturing of catalysts prepared by impregnation of the porous silica support ensures access to these original Cr sites, in the absence of additional concealed sites. At low yields, the polymerization process is clearly affected by the physical character of the silica support; however, at higher yields, the evidence suggests that other causes such as chemical effects are responsible for the continuing acceleration in rate. The porous Cr/silica catalyst tested did not fracture instantaneously; hence, current models of nascent polymer do not describe this process. The "hardcore" model of nascent polymer seems applicable to polymerization on the nonporous Cr/Cab-O-Sil catalyst tested.

1. Introduction

To produce linear polyethylene, three classes of reactors have been employed: gas-phase, solution, and slurry types.[1,2] In many laboratory studies of catalytic olefin polymerization, slurry reactors operated in a semibatch mode have generally been used because of their simpler construction and relative ease of operation (mixing and temperature control).[3] Excellent heat transfer is obtained because of the liquid phase surrounding the catalyst−polymer particles and the good mixing/suspension of the particles in this hydrocarbon liquid medium. In the slurry mode, the polyethylene formed generally does not dissolve or swell. In laboratory-scale slurry reactors, often used to characterize catalyst behavior, operation at lower pressures is more convenient and simpler. One should recognize that the higher pressures and temperatures employed in industrial operations will affect the kinetics of the polymerization, and thus, studies involving simpler/different operating conditions in the laboratory reactor should have clearly defined objectives.

Although slurry reactors have been extensively used in the laboratory, the majority of earlier studies have involved Ziegler−Natta type catalysts.[4−6] Fewer results[7,8] are available concerning slurry reactor studies with Phillips type catalysts (Cr/silica). Too often, these earlier studies fail to present important details concerning the reactor construction, its operation, or the conditions of the measurements being made. This paucity of detail makes it difficult to compare the differing experimental results reported by various workers. This paper will describe a novel slurry reactor and some operating details, *e.g.*, catalyst activation, gas purification, and polymerization procedures, used to compare the performances of different Phillips-type catalysts. This new reactor operates in an open mode (continuous) for ethylene flows but in a closed mode (batch) for polymer−catalyst particles. More commonly, in earlier studies, ethylene was usually injected into the slurry reactor as needed to maintain the preset operating pressure but was not withdrawn unreacted during the course of a run. At high pressures, the closed mode operation probably is not subject to large swings in the ethylene pressure between consecutive ethylene injections. At low pressures, periodic injections of ethylene would likely result in substantial pressure variations.

The use of an open mode for ethylene enables operation at a constant reactor pressure and a constant partial pressure of ethylene over the duration of the polymerization run. Gas phase inerts do not build up in the reactor vessel; however, some of the slurry liquid medium may evaporate into the ethylene gas phase, and the subsequent decline in liquid volume can limit the duration of the run. The kinetics may be interpreted somewhat more simply because the ethylene concentration in the gas phase and, presumably, its corresponding saturation concentration in the liquid phase remain constant even though the reaction rate may be changing with time. The novel reactor was constructed using high-temperature-resistant Vycor glass, which enabled the catalyst to be both pretreated and activated *in situ* within the reactor vessel and to be observed visually throughout the polymerization process.

Careful purification of all gases used in the experiments before their admission to the reactor and contact with the catalyst prevented deactivation and ensured stability of the catalytically active sites throughout the run. Earlier studies[9,10] using this new reactor have shown unique transient rate phenomena to be occurring during the early stages of ethylene polymerization using Cr/silica catalysts. This paper describes this novel slurry reactor and discusses conditions which influence

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Table 1. Physical Properties of Silica Supports

silica	BET surface area (m^2/g)	total pore volume (cm^3/g)
Davison	277	1.57
Crosfield	286	1.56
Ketjen A	666	1.36
Ketjen B	385	1.17
PQCS	359	2.11
Cab-O-Sil	163	nonporous

the early transient phenomena and which are essential to ensure reproducible yield *versus* time measurements (kinetics). Yield curves were obtained for four different silica-based Cr catalysts.

Earlier views of the nascent polymerization process have been reported by Wagner and Karol,[11] Wagner and Niegisch,[12] and Webb *et al.*,[13] among others. Using our results, we will also attempt to relate to the three catalyst fragmentation mechanisms summarized by Webb *et al.*[13] In a detailed paper, they describe three distributions of catalyst fragments within individual growing polymer particles: (1) a "hard-core" model in which the central catalyst particle remains unfragmented; (2) a "uniform-site" model in which fragmentation creates multiple catalyst particles uniformly distributed within the growing polymer particle; and (3) an "expanding core" model in which the fragments are convected outward within the growing polymer particle.

In a series of papers, Ferrero and Chiovetta[14,15] develop a mathematical description of another model, which may be considered to be a combined "hard-core/uniform-site" model, in which uniform fragments originate from the periphery of the hard core by an exfoliation process.

Since this paper will analyze our results only in terms of these possible model forms, we will not review earlier published evidence concerning the reality of these model forms.

2. Details of Equipment and Supplies

2.1. Catalysts. The earlier results[9,10] suggested that the physical properties of the silica supports were responsible for the early transient behavior. To confirm such views[1,10] and to define clearly the roles of mixing and experimental factors influencing the polymerization results, Cr catalysts were prepared using a number of silica supports differing in their morphological character. Six supports with a broad range of surface areas and total pore volumes, as listed in Table 1, were used. The catalysts were prepared with Cr contents ranging from 0.5 to 5 wt % by impregnating the silica supports with aqueous solutions of chromium(VI) oxide, followed by air drying at 105 °C.

2.2. Novel Reactor. Figure 1 shows a cross-sectional view of the Vycor reactor of volume, 100 cm^3. A second reactor of the same diameter, 4 cm, but of increased length to provide an expanded volume of 150 cm^3 and a larger droplet disengaging volume above the agitated slurry was used to extend the duration of a run and yields of polymer beyond those obtainable in the smaller reactor. The catalyst was pretreated or activated safely in this vessel at temperatures up to 800 °C and at near-atmospheric pressure.

Figure 2 shows a simplified flowsheet of the polymerization laboratory setup. A 100 cm^3 Pyrex storage vessel identical in shape to the reactor enabled purification and storage of the hexane liquid required for the slurry mixture. The storage and reactor vessels were connected to the reaction system through two 4-way valves, 4-2 and 4-1, respectively. A third 4-way valve, 4-3, made it possible to perform "catalyst activation" and "polymerization runs" sequentially, *in situ*. During the activation of the catalyst, the Vycor vessel was heated using a small cylindrical oven (upper limit of 1000 °C), regulated with a CN-2010 Omega controller which had temperature-programming capability. The temperature was monitored with a type K thermocouple inserted in the well shown in Figure 1. During a constant temperature polymerization run, the reactor was immersed in a water bath, usually at 25 °C.

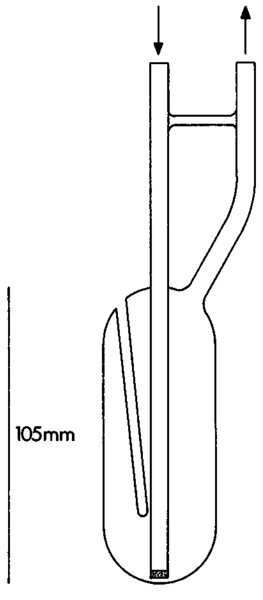

Figure 1. Cross-sectional view of 100 cm^3 Vycor reactor vessel (arrows indicate inlet and outlet ports).

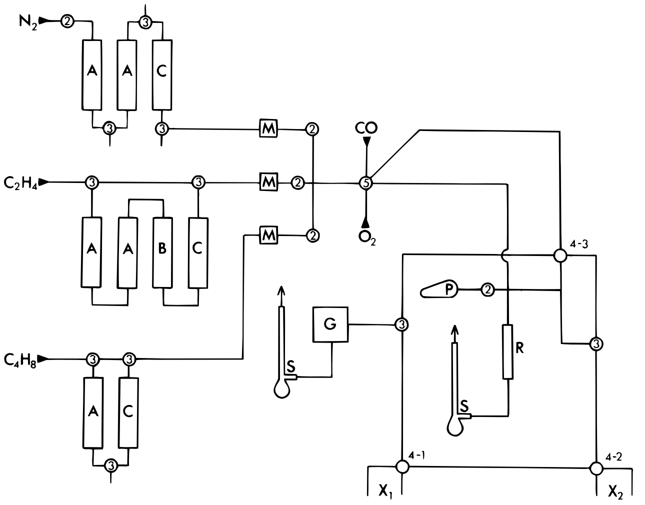

Figure 2. Simple flowsheet of laboratory equipment used for experimental polymerization studies. A: Oxygen trap; B: carbon dioxide trap; C: moisture trap (molecular sieve); G: gas chromatograph; M: mass flowmeter; P: roughing vacuum pump; R: rotameter; S: soap bubble-meter; 2, 3, 4, and 5 denote 2-, 3-, 4-, and 5-way valves, respectively. Slurry reactor connects at X$_1$ and hexane storage vessel at X$_2$.

Mixing of the slurry within the reactor was facilitated by the internal bubbling action of the incoming ethylene flow and by vigorous mechanical shaking of the reactor vessel provided by an external rotating eccentric contactor, providing from 150 to 400 lateral displacements per minute (rpm).

The ethylene feed was maintained at the same constant flow and pressure throughout all runs. Because of the good reproducibility of the yields obtained in replicate runs, the liquid hexane in the reactor was assumed to be saturated with dissolved ethylene at the standardized reaction conditions. The total volumetric flow of (unreacted ethylene plus *n*-hexane evaporated) was measured continuously using a rotameter, R, or periodically, with a soap bubble-meter, S. To expel gas impurities or contaminating residual gases from the system, N$_2$ purging could be augmented by evacuation with a roughing vacuum pump, P.

2.3. Feed and Exit Streams. All gases used in this study were purchased from Linde. The possible presence in these gases of impurities such as water vapor or oxygen would deactivate active sites on the catalyst surface. Thus, operating with a continuous feed of ethylene containing such impurities would gradually diminish the catalyst activity and introduce a noncontrolled factor influencing the measured experimental yields. To prevent such decay in activity, the ethylene (minimum purity 99.5% as purchased) was purified by passing sequentially through water vapor, oxygen, and carbon dioxide traps (Alltech), and the nitrogen (minimum purity 99.9995%, containing <1 ppm O_2 and <2 ppm H_2O) through sequential columns for bulk oxygen removal with Cu/alumina and fine oxygen removal with MnO/alumina and water removal with a 13× molecular sieve. UHP oxygen was used to oxidize all Cr states to Cr(VI) as well as any residual organic matter in either the catalyst or the reactor. A 10% mixture of CO in ultra high purity (UHP) helium was used to reduce Cr(VI) in the activation of the catalyst. The latter two gases were used as received. The hexane liquid medium used in the slurry reactor was purchased (Omnisolv) with minimum *n*-hexane content of 85%. Maximum contents of impurities were listed as 0.01% water and 250 ppt sulfur. Prior to placing the hexane in the storage vessel, it was dried by contacting 4 L with 150 g of freshly regenerated 13× molecular sieve.

Flows of the ethylene, nitrogen, and methane (the latter added as an internal standard for GC-FID analysis of the reactor effluent gases) were regulated using Unit CF-100 mass flow controllers. The equipment included capability of sampling and analyzing the exit stream with a Hewlett-Packard 5890 Series II gas chromatograph. (This latter feature was added mainly for subsequent experiments in which the copolymerization of olefins was to be studied, where the composition of the effluent gas mixture was needed.)

3. Operating Procedures and Experimental Results

3.1. Catalyst Activation and Reactor Pretreatment. Catalyst charges ranging from 0.05 to 0.3 g were placed in the reactor vessel prior to connecting it to the equipment manifold. To activate the catalyst, the following sequence was employed:

- pretreatment with 20 cm^3/min flow of N_2 for 16 h at 500 °C.
- calcination (oxidation) using 50 cm^3/min O_2 for 1 h at 500 °C.
- reduction using a 10% CO/He mixture for 1 h at 350 °C.

The reducing CO gas mixture flow (at 50 cm^3/min) was introduced twice (initially and after 10 min, for 1 min duration, each) during the 1 h reduction to avoid over-reduction.

When the initial two steps were carried out at 800 °C, for unknown reasons the resulting catalyst was less active.[16]

Generally, the 100 cm^3 vessel was used, enabling yields of up to 80 g of polymer/g of catalyst, and the 150 cm^3 vessel for yields up to 120 g/g. Under similar reaction conditions, the larger vessel was found to duplicate the yields obtained in the smaller vessel. Thus, different yields measured with either reactor could be plotted on the same yield *versus* reaction time graph to extend over a wider range. Separate runs using *n*-hexane liquid volumes ranging from 30 to 45 cm^3 also showed no effect upon the yields when other operating conditions were kept constant. About 40 cm^3 of liquid *n*-hexane were then used in all of the runs.

During the final 12 h of the pretreatment step, the N_2 flow leaving the reactor was slowly bubbled through the liquid in the hexane reservoir to sweep out any residual oxygen. Experiments indicated that a 50% evaporation of the hexane in the reservoir resulted in a high purity liquid phase for the slurry reactor. Failure to follow this additional O_2 removal invariably resulted in deactivation of the catalyst. The purified hexane was presaturated with ethylene in the reservoir for 30 min at 25 °C before the remaining volume, about 40 cm^3, was displaced into the reactor vessel to contact the catalyst.

Table 2. Experimental Results from Ethylene Polymerization Runs Using Cr/Davison Silica Catalyst: 25 °C, 94 kPa, 100 cm^3/min Ethylene Feed, 100 cm^3 Reactor Volume, and 300 rpm Shaking[a]

run no.	Cr content (wt %)	reaction time (min)	initial wt of catalyst (g)	polymer yield (g of PE/g of catalyst)
1	0.5	60	0.200	3.00
2	1	60	0.198	3.16
3	5	60	0.200	3.94
4	5	90	0.200	7.05
5	5	90	0.200	8.32
6	5	180	0.200	25.43
7	5	180	0.200	55.76
8	5	120	0.267	18.87
9	5	120	0.200	18.35
10	5	120	0.150	18.57
11	5	120	0.138	17.93
12	5	120	0.100	17.62
13	5	120	0.090	16.24
14	5	120	0.080	14.84
15	5	120	0.070	12.62

[a] Yields in runs 4 and 6 obtained without mechanical agitation.

Before the hexane was introduced, the strongly adsorbed CO remaining after the reduction step was removed by purging the reactor using a 70 cm^3/min flow of nitrogen for 15 min at 350 °C, followed by cooling to room temperature. The reactor vessel was then immersed in a water bath at 25 °C for the duration of the run. Polymerization was started by reversing the ethylene flow, thereby displacing the about 40 cm^3 of ethylene-saturated hexane from the reservoir into the reactor. The ethylene flow then contacted the catalyst by bubbling through the resulting slurry.

3.2. Determination of Polymer Yield. The run was stopped after the desired reaction time by admitting air into the reactor, which deactivated the catalyst, effectively terminating further polymerization. The amount of polyethylene (PE) formed during the run was determined gravimetrically by subtracting the initial weight of [Vycor vessel plus catalyst] from that of [vessel plus polymer−catalyst mass (after evaporation of the liquid hexane)]. The yield in g of polymer/g of catalyst could then be easily calculated. This approach provided a very reproducible direct measurement in contrast to other methods such as measurement of monomer consumption[17,18] or determining the ultimate carbon content.[19]

3.3. Evaluation of a Standard Experimental Run. A number of factors which influenced the rate of polymerization (at the constant temperature of 25 °C and constant pressure of 94 kPa) were examined: Cr loading on silica support, degree of agitation of reactor vessel, volume of hexane used, and mass of catalyst charge. The results from 15 preliminary runs using Cr/Davison silica catalysts are summarized in Table 2.

Runs 1−3 examine the role of Cr content on yield of polyethylene, other conditions being fixed. In the experiments at the specified temperature and pressure, the reaction conditions lead to somewhat slower rates than those likely to be encountered in industrial slurry reactors, enabling runs to be completed even for very short reaction times. The 5 wt % Cr content gave the fastest rate of the three Cr loadings tested, and it was selected to be the standard Cr content for the balance of the runs. The rate of polymerization catalyzed by this Cr loading enabled reliable observation of the transient rate phenomena throughout the early polymerization period. The large Cr content also provided a larger "buffer" of active sites, relatively insensitive to slow deactivation by trace impurity gases which might be present. However, such deactivation effects, cumulative over several hours of continuous operation, were subsequently found to be insignificant because of the careful purification of the gases in the equipment.

Runs 4−7 tested the influence of varying the degree of agitation of the slurry during a run by comparing yields obtained without mechanical agitation and with mechanical agitation at 300 "shakes" per minute. Preliminary experiments had shown that the latter degree of mixing was sufficient to ensure reproducible results. Run 4 (without agitation) shows a smaller yield after 90 min than from run 5 (with agitation); however, after 180 min the yield from run 6 is more than doubled in run 7 (with agitation). Since the bubbling action of the ethylene feed alone did not provide sufficient mixing to prevent mass transfer limitations, the 300 rpm mixing level was employed in all experimental runs.

The remaining runs, 8−15, examine the influence of mass of catalyst charged to the reactor. As shown earlier,[7,20] ethylene polymerization in the slurry reactor using Phillips-type catalysts proceeds only if the initial mass dispersed in the liquid medium exceeds a certain threshold value. The magnitude of this threshold value relates to the poisoning of the active Cr sites by the level of gaseous impurities (mainly O_2 and H_2O) which may be present in the reaction system. According to Yermakov and Ivonov,[7] the least amount of catalyst (effective mass) which should be used to ensure reproducible yields is an amount several times that of the threshold value. For the conditions employed in this work, runs 8−15 suggest an effective mass near 0.1 g for the 5 wt % Cr/Davison silica. Expressing this effective mass relative to volume of hexane liquid in the reactor at startup gives 2.5 g of catalyst/L of hexane. The above authors[7] report a threshold value of 0.5 g/L for ethylene polymerization over 2.5 wt % Cr/silica−alumina in cyclohexane slurry at 50 °C and 202 kPa. This suggests that the 2.5 g/L value employed in the runs at the lower temperature of 25 °C and ethylene partial pressure of 94 kPa is reasonable.

The mild reaction conditions used in these experiments slowed the chemical and physical rate phenomena sufficiently that the different polymerization behavior of catalysts differing only in their silica support could be observed.

3.4. Influence of Various Silica Supports upon Catalytic Activity. To illustrate the sensitivity of ethylene polymerization in the novel reactor to the physical character of the silica support used to prepare a "standard" 5 wt % Cr/silica catalyst, the following conditions were kept constant during runs in which only the catalyst support was varied:

- ethylene feed flow at 100 cm^3/min
- mass of catalyst of 0.1 g
- near atmospheric pressure, ≈94 kPa
- reaction temperature of 25 °C
- Cr loading of 5 wt % on each supported catalyst
- duration of reaction, 60 min

Table 3. Comparison between Polymerization Performances of Six Silica Supports under Standardized Reaction Conditions: 25 °C, 94 kPa, 100 cm^3/min Ethylene Feed, 300 rpm Shaking, Catalyst Charge of 0.1 g, and Polymerization Time of 60 min

run no.	type of silica support used	yield (g of PE/g of catalyst)
1	Davison	3.80
2	Ketjen A	0.62
3	Ketjen B	0.53
4	Crosfield	25.46
5	PQCS	1.37
6	Cab-O-Sil	16.81

Table 3 shows the relative yields measured for six different commercial silicas at the standardized polymerization conditions. The results indicate significant differences in catalytic activity clearly attributable to the different physical characteristics of the various silicas. These differences are listed in Table 1. Longer runs, such as for several hours, would have emphasized even more the differences in behavior of the various supports. Yields over 100 g/g were possible in the 150 cm^3 reactor vessel for the Davison, Crosfield, and Cab-O-Sil supports, but above 150 g/g the experimental results became unreliable because of the extremely large polymerization rates encountered. Because of the inability of the equipment to provide the flows of ethylene feed needed at these very large polymerization rates, the evaporation of the hexane liquid medium, and the inadequate mixing which developed within the increasingly thickening slurry, the reaction conditions could no longer be controlled at the higher yields.

As an incidental observation, some tests to measure the IR transmission spectra of polymer films as well as differential scanning calorimetric curves for bulk polymers showed that the various homopolymers obtained with these catalysts were essentially identical. Both methods indicated that chain-branching was not present. Gel permeation chromatography provided an average molecular weight of about 500 000. This suggests that the polymers formed are linear high density polyethylenes.

3.5. Polymerization Yields as a Function of Reaction Time. The type of silica support used for catalyst preparation has been reported to influence strongly the kinetics of polymerization.[1,19] The various yield curves shown in Figure 3 for Cr/silica catalysts prepared using four of the six silicas listed in Table 1 confirm that each silica exhibits a significantly different kinetics behavior. In fact, the ethylene consumption with the Crosfield catalyst was so rapid that after 60 min the ethylene flow had to be increased to 150 cm^3/min. Since the slopes of the yield curves at any time are proportional to the rate of polymerization of ethylene at that instant, it is evident that the early polymerization process is essentially transient in rate over the range of these plots.

Additional evidence helping to show the physical changes ongoing during the early polymerization stages was obtained by the measurement of BET surface areas from N_2 adsorption on polymer−catalyst products collected after each of a series of sequential runs varying in polymerization time. Figure 4 shows both the yields and the corresponding product surface areas plotted *versus* reaction times up to 200 min for the polymerization of ethylene using the 5 wt % Cr/Davison silica catalyst. With this reactor, reliable runs of duration as short as 0.33 min were possible.

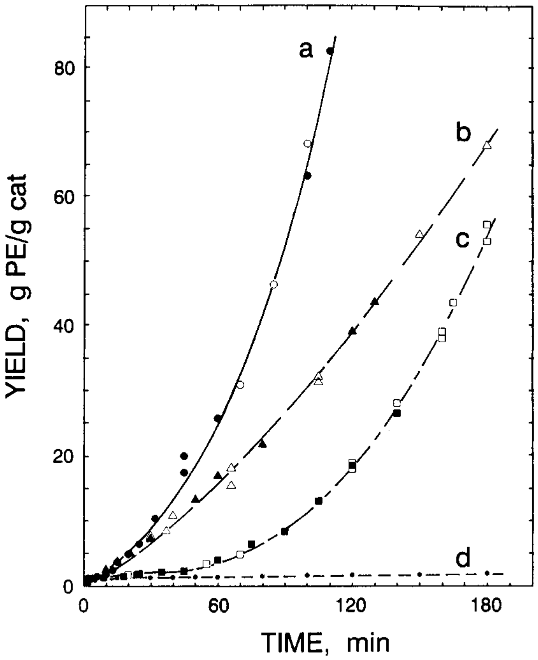

Figure 3. Polyethylene production experiments: yield (g of polymer/g of catalyst) *versus* reaction time (min) obtained at 25 °C and 94 kPa. Full symbols denote use of 100 cm^3 Vycor vessel; open symbols denote use of 150 cm^3 vessel. Catalysts: 5 wt % Cr, supported on silicas: a = Crosfield; b = Cab-O-Sil; c = Davison; d = PQCS.

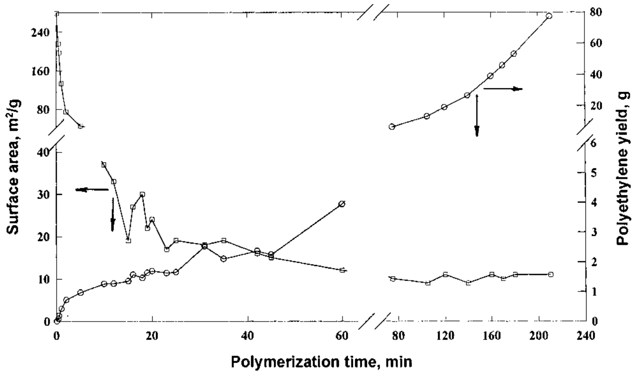

Figure 4. Role of specific surface area of polymer–catalyst particles during ethylene polymerization on 5 wt % Cr/Davison catalyst at 25 °C and 94 kPa.

Discussion

Much of the transient character of the early polymerization rates may be related to fracturing and fragmentation resulting from the internal stresses generated within the support pores by the growing polymer. Examining Figure 3 shows that active Cr catalysts such as those supported by porous Crosfield or Davison silicas (curves a and c in Figure 3) are characterized by three sequential stages during the observed transient period:

1. A rapid initial polymerization from the outset of reaction which then declines after a few minutes;
2. A period of declining rates which may approach a constant value;
3. A final period in which the rate of polymerization accelerates continuously.

The first stage, <10 min, coincides with the filling of the support pores with polymer. N_2 adsorption–desorption measurements confirm that only about 1% of the support pore volume remained. The points for stage 1 plotted in Figure 3 are rather crowded and do not show this stage clearly (a more clear view of this first stage may be seen in ref 10).

The second stage involves the buildup of pressures within the pores while they are filling and becoming plugged with polymer. Eventually, if the physical structure of the support is susceptible to fracturing from the internal pressures generated by the polymer growth, the pores are reopened through fissures and additional surface area may be exposed. Repeated fracturing and/or fragmentation, first investigated by McDaniel,[21] has been suggested as a cause of the second stage accelerating rate.

The final continuing acceleration conforms to the third stage, during which fracturing greatly diminishes and the residual form of the disintegrated original catalyst particle is encapsulated by massive polymer formation.[9,22,23]

Table 4 summarizes rates [mol of C_2H_4/(g of catalyst·s)] and polymer volume multiples [(vol of polymer)/(vol of initial pores)] estimated at several times on the yield curves, at $t = 0$, 10, 30, and 180 min, corresponding to the initial rate, the declining rate, the rate-stabilization period, and the final accelerating rate, respectively. Rates are shown for both the Davison and the Cab-O-Sil supports and the volume multiples only for the Davison support, Cab-O-Sil being nonporous. Rates were not expressed in terms of individual Cr atoms because the use of 5 wt % Cr in our catalysts precludes comparisons with most catalysts containing about 1 wt % Cr.

In the case of porous active catalysts, monitoring the early stages of the polymerization process using scanning-electron microscopy (SEM) photographs of the Davison catalyst–polymer particles provided additional direct evidence of particle fracturing. The polymer covering the original individual catalyst particles or binding the fragments into the polymer mass appears as a "cauliflower"-like growth at lower magnifications (500–1000×), and as a "cobweb" structure at higher magnifications (~5000×) after 120 min of polymerization time with a yield of 17.6 g of PE/g of catalyst. The microphotograph in Figure 5 shows this "cobweb" growing about the expanded/separated fragments of catalyst (one large fragment is visible centrally within the photograph). The fissures between the "cobwebs", apparently from fracturing, suggest separate polymer growth about each fragment of catalyst. These external features, as shown in Figure 5, were photographed at 120 min, well into the stage 3 involving the final acceleration in rate shown by the Davison catalyst, curve c in Figure 3.

Extrapolation of the yield curve beyond the observed 180 min suggests continuing acceleration of the rate for porous silica supports, but the extent of this continuing acceleration could not be measured using the novel reactor. Assuming that fragmentation of particles has a physical limit, *e.g.*, residual pore sizes are too small to facilitate additional fracturing, the catalyst particles should become increasingly more distributed within the growing polymer mass. However, it was not possible within the range of yields obtained here to discern whether a second period of declining rates from possible mass transfer limitations follows the growth of very large polymer particles.

From many experiments using porous silica supports, the relative durations of these three stages could change because of variations in the procedures for catalyst preparation, the character of the silica support, the

Table 4. Rates of Reaction and Polymer Volume (Expressed as Multiples of Pore Volume) Obtained at Polymerization Times of 0, 10, 30, and 180 min and 25 °C, 94 kPa, 100 cm^3/min Ethylene Feed, 300 rpm Shaking, and 0.1 g of Davison or Cab-O-Sil Supported 5 wt % Cr Catalysts

polymerization stage	time (min)	yield (g of PE/g of catalyst)	(volume of polymer)/(volume of initial pores)[a]	rate × 10^4 (mol of C_2H_4/g·s)
initial rate (est'd)	0	0 [0][b]	0	0.26 [0.86][b]
declining rate (pores filling)	10	1.2 [3]	0.7	0.2 [0.89]
constant rate (fracturing)	30	4 [13]	2.4	0.17 [1.6]
final rate (accelerating)	180	53 [69]	32	4.5 [2.9]

[a] Basis: bulk density (PE) = 0.96 cm^3/g; pore volume = 1.57 cm^3/g of catalyst. [b] Values in brackets for Cab-O-Sil support.

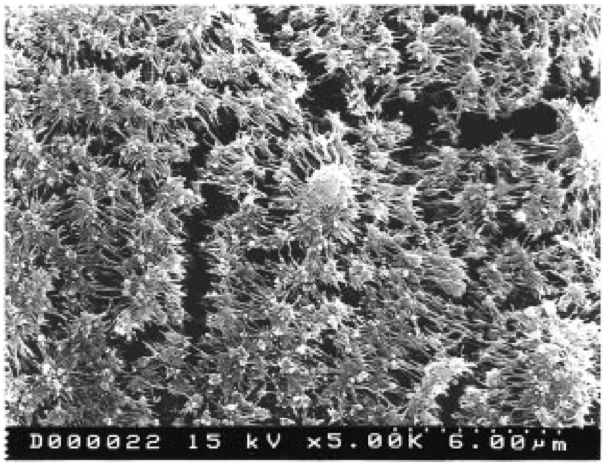

Figure 5. Scanning electron microphotograph [5000× (original magnification; reduced 50% for publication)] of polymer–catalyst product at 120 min (see curve c in Figure 3).

amount of Cr loading, or the purity of the ethylene. Nonetheless, the shape of these three-zone curves was representative of ethylene polymerization over Cr catalysts supported on porous "friable" silicas. It is interesting to note that other reports[19,24] show nonaccelerating or even decaying behavior in their yield–time plots, effects which seem incompatible with the concept of maintaining or enhancing the rate from fracturing of the silica support. From the experience obtained in this work, if a decaying rate behavior is observed with the nascent polymer, this decay likely results from ongoing deactivation of the active sites on the catalyst by impurities introduced continuously with the ethylene feed, or by incomplete elimination of impurity gases originally within the reaction equipment. Aside from the initial decline in rate during the filling of pores, our evidence suggests that no decline in rate occurs up to our maximum measured yield of 120 g/g if the active sites are not poisoned or otherwise deactivated.

Returning to Figure 3, curve d suggests that the porous support PQCS is active only until the pores are filled with polymer. Apparently, this support fails to fracture in the novel slurry reactor because the pressure stresses developed within the pores are insufficient (the temperature and pressure are lower than those used in industrial slurry reactors). The resulting particles with plugged pores may have active sites available only on the external surface of the particles, but these are insufficient in number to provide good catalytic polymerization rates. In contrast to this behavior, curve b, obtained using an essentially nonporous silica support, Cab-O-Sil, exhibits a nearly linear apparently good rate of polymerization throughout the 180 min test. The slight initial curvature (mild acceleration in rate) may be attributed to a slight increase in accessible active sites resulting from the separation of very fine primary particles, many of which are present in Cab-O-Sil in the form of physically agglomerated clumps of particles. The Cab-O-Sil particles are sufficiently small that their initial specific surface area exposes a population of active sites adequate to ensure a good initial rate of polymerization. In contrast to Cab-O-Sil, the particle sizes of the support, PQCS, were much larger. After the pores of PQCS become plugged with polymer, the remaining population of active sites on its external area are inadequate to provide a good rate of polymerization.

The preceding discussion links the early transient rate behavior of ethylene polymerization in the slurry reactor to "physical" changes in the catalyst particles. This approach, also recognized earlier,[18] is in apparent conflict with the views of others who favor a "chemical" rather than "physical" explanation. Figure 4 is helpful in resolving this conflict in views because the rate behavior can be contrasted directly with ongoing changes in the specific surface area of the polymer–catalyst particles.

In interpreting Figure 4, the area of the original catalyst measured 277 m^2/g and that of polyethylene[25] alone may be considered to be less than 1 m^2/g. After sufficient polymerization has occurred, the area of the products stabilizes to 10 m^2/g. This difference in area between the polymer and the polymer–catalyst particles at reaction times exceeding 80 min may be attributed to accessible catalyst surface (likely silica) which has not been covered or affected by polymer growth, even though the reaction rate continues to increase at larger reaction times. This inert silica surface likely represents either initial silica surface not promoted with Cr or new unpromoted silica surface exposed after fracturing of the particles during polymerization.

The area oscillations in the region 10–40 min are believed to be significant since their magnitudes exceed the scatter in the data clearly seen at times larger than 80 min. Moreover, during the period 10–40 min, the polymerization rate (slope of the yield–time curve) appears to be nearly constant even though significant fracturing of the catalyst particles occurs concurrently. Evidently, the fracturing or fragmentation of the silica support does not expose additional Cr sites—this is likely because the catalysts were prepared by adding Cr with an impregnation technique. Essentially, the polymerization process only involves the surface Cr sites initially accessible and fragmentation enables polymer growth to continue on these existing active sites. As a consequence, the acceleration in the polymerization rate, evident beyond 70 min, originates elsewhere because the population of Cr sites available from impregnation procedures has not increased. The view that chemical and not physical effects are responsible for the acceleration in rate in this region seems justified. In industrial polymerization using Cr-impregnated catalysts, where much larger yields are obtained than measured in our laboratory reactor, these "chemical" effects of cause unknown likely are important in attaining the ultimate very large catalytic activities.

On the basis of the evidence presented above, the rate behavior in stage 1 of the yield−time curve (<5 min) for porous friable catalyst particles is relatively short and the initial decline in rate relates to the filling of pores with polymer and the inability of ethylene to access these internal active sites.

Fracturing and fragmentation of the catalyst particles influences the near-steady rate of polymerization in helping to maintain this rate while pores are being "plugged". This describes stage 2 (5−40 min). Beyond 40 min, the continuing acceleration in rate is clearly not attributable to surface area effects. This stage 3 (>40 min) involves acceleration in rate for reasons not clearly known. The explanation, if "chemical" in nature, may involve increasing activity from higher temperatures increasing the reaction rate within the polymer−catalyst particle interior when the particle size exceeds a critical value and heat transfer to the liquid medium becomes less effective or, somehow, the number of active sites increases (activation of previously inactive Cr sites by reduction with ethylene?). Additional studies are required to explain the "chemical" causes of this acceleration in rate.

Contrasting our experimental results with the various physical models postulated for the nascent polymer may be useful in verifying or extending these concepts. The evidence shows the porous Davison silica-supported catalyst is repeatedly fractured, creating fissures which facilitate transport of ethylene to the original active Cr sites on the interior surface of the impregnated catalyst. The polymer growth expands the volume occupied by the original catalyst particle and/or its fragments. If the fragmentation was instantaneous, one would expect the catalyst fragments to remain uniformly distributed within the growing polymer particle, *i.e.*, the "uniform-site" model would be applicable. Figure 4 shows that the fragmentation is not instantaneous. In this case, one may anticipate that the fragments formed early in the process would be separated by "dikes" of polymer thicker than those covering the interior space of particles just fragmented. Fragmentation appears to be an ongoing process in which consecutively smaller particles are likely formed. Model 2, the "uniform-site" model, at best, only approximates this behavior. Perhaps, the uniform-site model should be regarded as a special case of a more general time-dependent catalyst fragmentation pattern.

The nonporous Cab-O-Sil supported catalyst, with its yield curve near-linear from the origin, does not suggest fracturing. Because of the expense involved, a complete specific surface area−time−yield analysis was not completed. SEM photographs clearly show the support to contain agglomerates of very fine particles, and N_2 adsorption/desorption measurements show negligible porosity. Extending the physical separation of the individual particles in the agglomerates maintains the exposure of Cr sites deposited on their external surfaces and, perhaps, may improve access to sites in the interstices of the agglomerated particles, which may account for the slight curvature of the yield curve. The "hard-core" model provides the most apt description of this nascent polymer behavior.

4. Conclusions

The novel laboratory slurry reactor described herein has been demonstrated to provide quantitative information about the transient rates of polymerization of ethylene during the early stages, *i.e.*, up to yields of about 80 g of polymer/g of catalyst. The improvements included *in situ* pretreatment and activation of the catalyst, removal of impurities such as O_2 and water vapor from the gases used in substantial amounts (ethylene and N_2), direct gravimetric measurement of the polymer yield, operation at constant pressure with continuous input of ethylene, visual monitoring within the transparent Vycor vessel, and careful mixing of the slurry to prevent mass transport limitations.

The studies of homopolymerization of ethylene over Cr/silica catalysts were carefully controlled to isolate the influences of porosity and size of particle of the silica supports. The experiments with different porous silica supports which were susceptible to fragmentation all show three sequential stages during the early polymerization, culminating in continuously rising yield curves with time. At the corresponding maximum rates observed, near yields of 60−80 g/g, the porous friable catalysts tested, Crosfield or Davison, suggest that acceleration in the polymerization rate continues beyond our experimental yield limits. The polymerization behavior during stages 1 and 2 may be explained in terms of physical effects (porosity and particle sizes); however, the behavior during stage 3 clearly is not attributable to these physical effects. The latter acceleration in rate, if present, does not appear so clearly when a nonporous silica support is used. After the initial 5 min, the reaction rates were never observed to decline with time, negating the likelihood of ongoing deactivation of the catalyst.

The models available for describing the nascent polymer catalyst fragmentation phenomena inadequately describe the sustained fragmentation pattern which our experiments suggest. A limited time-dependent fragmentation pattern would appear to be more appropriate for describing the distribution of catalyst particles within the large polymer particles formed in the laboratory slurry reactor. On the other hand, the "hard-core" model may be appropriate for polymerization involving nonporous catalyst particles such as Cab-O-Sil.

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