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Comparison of Ethylene Polymerization in Gas-Phase and Slurry Reactors

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ABSTRACT: This comparative study of ethylene polymerization in gas-phase and slurry reactors, using both a high-activity silica-supported $TiCl_4$ catalyst and a δ-$TiCl_3$ catalyst, showed that catalytic activities and molecular weights of products can be reactor dependent. The high-activity catalyst deactivated much faster in the gas-phase reactor than in the slurry reactor. The difference in the deactivation rates was so large that the rate of polymerization increased with increasing temperature for the slurry reactor whereas it decreased for the gas-phase reactor. Differences in the average molecular weights of the products from the two types of reactors were also observed. Thus, the results of slurry-reactor tests of deactivating catalysts are not necessarily transferrable to gas-phase operation. In contrast, the δ-$TiCl_3$ catalyst had a time-invariant activity. However, the normalized activities were only independent of solvent and reactor type when based on the ethylene concentrations in the solvent for the slurry reactor and in the gas phase for the gas-phase reactor. This illustrates that the proper monomer concentration has to be used when comparing activities from gas-phase and slurry reactors.

Introduction

Slurry reactors, rather than gas-phase reactors, are used in the majority of laboratory studies of catalytic olefin polymerization. The results from slurry reactors are frequently used to predict the activity of catalysts for gas-phase reactors. Gas-phase processes are increasingly being used for commercial production of polyolefins since gas-phase operation has significant advantages over slurry and solution processes.[1,2]

Semibatch slurry reactors are most commonly used in laboratory studies because they are much easier to operate than semibatch gas-phase polymerization reactors. The two main operational problems for gas-phase reactors are proper suspension of the solid particles (stirring) and temperature control. Heat transfer from the catalytically active sites in the "core" of the growing polymer particle is dependent on how effectively the surrounding gas phase, which is a very poor heat-transfer agent, can remove heat to the reactor heat-exchange surfaces.[3] As a result, the temperature of the growing polymer particles can be much higher than that measured by temperature probes in the reactor. These high temperatures can result in rapid catalyst deactivation, possibly by physical encapsulation of the catalyst by "molten" polymer. Reproducible introduction of the catalyst and cocatalyst into gas-phase reactors is another problem. However, these problems can be largely alleviated by proper design of the gas-phase reactor and by using appropriate operating procedures and conditions. In the present study, the overall polymerization activities of two catalysts were determined by using both a slurry reactor with two solvents as well as a gas-phase reactor. The objective of the study was to determine whether catalytic activities obtained with a slurry reactor could be directly related to those encountered in a gas-phase reactor.

Experimental Section

Materials. Titanium tetrachloride (99.9%), silicon tetrachloride (99.999%), neat diethylaluminum chloride (DEAC), and neat triethylaluminum (TEAL) were obtained from Aldrich, and di-*n*-butylmagnesium (in heptane) was obtained from Lithco. Silica, from W. R. Grace, was pretreated at 600 °C under N_2 before use, and from BET measurements, the silica surface area was determined to be 290 m^2/g. Solvents were distilled fresh from CaH_2 and were then stored over sodium wire and sampled under nitrogen. Ethylene (99.9998%) and nitrogen (99.999%) were obtained from Linde, and prior to use, they were passed through individual purification trains for the removal of oxygen, moisture, and carbon dioxide. Complete details of the feed purification, monitoring, and control equipment have been previously described.[4]

Catalysts. Two catalysts were used in the present study. The first catalyst was a commercial δ-$TiCl_3 \cdot {}^1/_3AlCl_3$ Stauffer AA Type 2.1 catalyst (Lot No. 5806), which contained 24.1 wt % Ti. The other catalyst was a silica-supported high-activity catalyst, designated as SMST, prepared in our laboratory by a method similar to that described in the patent literature.[5] The procedure used consisted of the following steps. Ten grams of silica was suspended in 70 cm^3 of *n*-heptane. $Mg(n\text{-}C_4H_9)_2$ (0.01 mol) in heptane was added. The suspension was stirred at room temperature for 3 h, and 50 cm^3 of $SiCl_4$ was added. The mixture was stirred at room temperature for 60 h followed by stirring at 80 °C for 5 h. The solution was then filtered and the solids were washed four times with 100 cm^3 of heptane. The solids were then treated with a large excess of $TiCl_4$ at 80 °C. The excess $TiCl_4$ was removed by washing six times with 100 cm^3 of heptane. Finally, the solids were dried at 60 °C in vacuo. From a colorimetric analysis, the SMST catalyst was found to contain 3.9 wt % Ti.

Reactors. Two semibatch reactors were used in this study. The gas-phase reactor was a 1-L stainless steel vessel that was immersed in an oil bath for temperature control. The solids in the gas-phase reactor were kept in suspension by an AE Magne-Drive stirrer. Complete construction and operating details of the gas-phase reactor system have been previously described.[4] The slurry reactor was a 0.5-L jacketed glass vessel equipped with a variable-speed stirrer.

The sampling of the catalysts for use in either of the reactors was always carried out under nitrogen in a VAC glovebox containing <2 ppm oxygen and <3 ppm water. For the gas-phase reactor, measured amounts of dry catalyst powder were placed in a stainless steel tube that was subsequently sealed at both ends by plug valves. This apparatus was then connected to the reactor vessel, and the vessel was evacuated overnight at 90 °C. Once it was established that the vessel was leak tight, nitrogen was admitted to the reactor to give a background pressure of approximately 0.15 MPa. The cocatalyst (TEAL or DEAC) was then injected via a syringe port into the reactor, and the reactor was allowed to cool to the desired temperature (typically

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1 h was allowed to elapse during the cooling period). Once the reactor temperature was stable, the catalyst was forced into the reactor by first applying a nitrogen pressure upstream of the tube containing the catalyst and then opening and closing the plug valves on either side of the catalyst. This resulted in the nitrogen background pressure in the reactor being approximately 0.25 MPa. The ethylene flow was started immediately following the catalyst injection; typically less than 2 min elapsed between catalyst injection and the start of the ethylene flow. Thus, there was essentially no precontacting of the catalyst and cocatalyst prior to the initiation of the polymerization.

The procedures for the slurry reactor were somewhat different than those used for the gas-phase reactor. Following the addition of freshly distilled solvent to the slurry reactor, the reactor was pretreated at 70 °C for decane, or 50 °C for heptane, using several cycles of a nitrogen sparge followed by vacuum, with solvent reflux from a condenser. The reactor temperature was then adjusted to the desired value, and ethylene was admitted to the reactor with the stirrer operating so as to saturate the solvent with the monomer. Following this, the liquid cocatalyst was injected into the reactor via a syringe port, and at least 5 min was allowed to elapse to allow scavenging of any remaining impurities to occur. At the end of this period, a mixture of the catalyst, suspended in the same solvent that was present in the reactor, was injected into the reactor via the syringe port. The reaction immediately commenced given the presence of ethylene in the reactor. Thus, for the slurry reactor, as with the gas-phase reactor, there was no precontacting of the catalyst with the cocatalyst prior to the start of the polymerization reaction.

The ethylene feed streams to the reactors were controlled by pressure regulators so as to hold the pressure constant in each reactor. The feed stream flow rates were monitored by Matheson mass flow transducers, and the values of the flow rates, temperatures, and reactor pressure were recorded at 10-s intervals by a data acquisition system interfaced with a Hewlett-Packard 1000 minicomputer. The process monitoring and feed purification equipment was common to both reactors (only one reactor could be used at a time).

Molecular Weight Determinations. A Waters 150C gel permeation chromatograph (GPC) with a differential refractive index detector was used to determine the molecular weight distributions (MWDs) of the ethylene homopolymers produced in the two reactors. A series of three packed columns (Waters 10^4-, 10^5-, and 10^6-Å μStyragel columns) was used for all MWD determinations. These columns were operated at 145 °C with 1,2,4-trichlorobenzene (TCB; Fisher HPLC grade) at 1 mL/min used as the solvent. The TCB contained approximately 0.25 g/L of 2,6-di-*tert*-butyl-4-methylphenol as an antioxidant. Sample concentrations were typically between 0.035 and 0.07 wt %, and injection volumes of between 100 and 250 μL were used. Prior to injection, all samples were first heated to 160 °C for 2 h before cooling to 145 °C in order to prevent the formation of supermolecular aggregates.[6] Typically, four repeat injections and MWD determinations were made for each sample, and the average of these repeat analyses was used.

Due to the lack of suitable polyethylene standards in the high molecular weight region, the GPC was calibrated with 13 polystyrene standards ($M_w/M_n \approx 1.01$–1.1) obtained from Waters. These standards spanned the molecular weight range 3000 to 4×10^6. From the universal calibration procedure combined with the use of NBS Standard Reference Materials 1475, 1482, 1483, and 1484, it was estimated that the actual polyethylene molecular weights were approximately 40–50% lower than that determined by using the polystyrene-based calibration curve. Because only relative comparisons were desired, all values of molecular weight reported herein were based on the polystyrene calibration.

Results and Discussion

The overall rates of polyethylene formation are directly related to the feed rate of ethylene to a semibatch reactor operated at constant pressure and temperature. However, to compare the activity of various catalysts, it is necessary to normalize the rates with respect to monomer and catalyst concentrations. This normalization is usually done by means of a simple rate expression that is first order in monomer and catalyst concentrations,[7] i.e.,

$$R_p = k_p[\mathrm{M}][\mathrm{Cat}] \qquad (1)$$

where R_p = rate of polymerization, g_{PE}/(g of catalyst·s); k_p = pseudo-first-order rate constant, g_{PE}/(mol of Ti·s·[mol of C_2H_4/m^3]); [M] = monomer concentration, mol of C_2H_4/m^3; and [Cat] = Ti concentration in catalyst, mol of Ti/g of catalyst. Hence, k_p values are activities that are normalized with respect to monomer and catalyst concentrations, and these k_p values can be used to compare activities for different catalysts or for the same catalyst under different polymerization conditions, i.e., when used at different monomer concentrations or in different reactors. If the intrinsic rate of polymerization is first order with respect to monomer concentration, as assumed in eq 1, and if mass- and energy-transfer effects are negligible, then k_p, for fixed cocatalyst concentration and constant temperature, will be independent of the monomer concentration and reactor type. However, the correct value of the monomer concentration has to be used in the calculation of k_p. The necessity of using the correct monomer concentration is illustrated below for the δ-$TiCl_3$ catalyst.

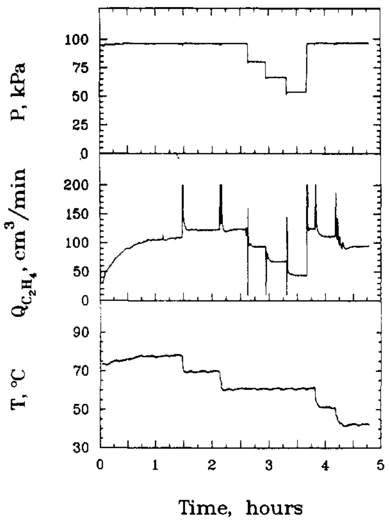

Figure 1. Effect of temperature and pressure on polymerization rate in a slurry reactor (500 cm^3 of heptane, 0.1 g of δ-$TiCl_3$ (AA)/DEAC, Al:Ti = 15.8).

Stauffer δ-$TiCl_3$ (AA)/DEAC Catalyst System. Experiments with the Stauffer catalyst, using DEAC as the cocatalyst, were carried out in which the dependence of the polymerization activity on the concentration and temperature was determined by using the slurry reactor. The results of a typical experiment with the slurry reactor are shown in Figure 1; the results shown are the directly measured data. The top panel in Figure 1 shows the total absolute pressure, *P*, in the reactor as a function of time. The total pressure is set by a pressure regulator and is maintained at the set value by the addition of ethylene. The rate of ethylene addition to the reactor, $Q_{C_2H_4}$ in cm^3 (STP)/min, is shown in the middle panel of Figure 1. The "spikes" in the rate of ethylene addition were due to pressure regulator adjustments. The reactor temperature is shown in the bottom portion of Figure 1.

Examination of Figure 1 shows that steady-state conditions are achieved about 75 min after start-up; i.e., temperature, pressure, and polymerization rate have all become constant. This relatively long stabilization period is due to the lack of precontacting of the catalyst with the cocatalyst prior to initiating the reaction. Similar stabi-

Table I
Typical Data for the Slurry Polymerization Experiment (Experimental Conditions as Shown in Figure 1)

time after start of run, min	reactor T, °C	total pressure, kPa	total rate of polym, cm³ (STP)/min	$[C_2H_4]_V$, mol/m³	$[C_2H_4]_L$, mol/m³
75–87	78	96.0	108.6	14.6	31.6
100–126	70	96.1	122.7	19.6	44.6
140–155	61	96.0	125.5	24.2	59.0
165–174	61	79.9	93.4	18.3	44.7
185–197	61	66.3	67.7	13.4	32.7
210–218	61	53.5	43.5	8.7	21.3
220–227	61	96.0	124.0	24.2	59.0
240–249	51	96.4	111.5	28.6	76.2
270–279	42	96.6	93.6	31.9	91.8

lization periods were also observed when the Stauffer catalyst was used in the gas-phase reactor. New steady states, following subsequent changes in reactor temperature or pressure, were achieved much more rapidly, i.e., after 10–15 min. The observed changes in polymerization rates, $Q_{C_2H_4}$, as a result of changes in reactor temperature were unexpected. For example, a decrease in reactor temperature from 78 to 70 °C at constant total pressure (after 90 min on stream) resulted in a 13% increase in the steady-state ethylene polymerization rate. A further decrease to 61 °C resulted in an additional 2% increase in the polymerization rate. Subsequent decreases in reactor temperature to 51 and 42 °C, at the same total reactor pressure, resulted in the expected decreases in polymerization rates. The steady-state polymerization rates for the experiment shown in Figure 1 are summarized in Table I. The temperature dependence of the polymerization rates is unusual at first glance (apparent negative activation energy at temperatures above 60 °C) because it is normally expected that at constant total pressure a decrease in temperature is accompanied by a decrease in rate. However, in a slurry system, the monomer concentration in the reaction medium is not directly proportional to the total pressure at varying reactor temperatures; hence, a better (correct) measure of the monomer concentration has to be used.

For gas-phase reactors, the monomer concentration to be used is unambiguous; i.e., it is equal to the gas-phase concentration. For most of the conditions encountered in catalytic gas-phase ethylene polymerization, the gas-phase concentration of ethylene, $[C_2H_4]_G$, is adequately approximated by the ideal gas law; i.e., $[C_2H_4]_G = P_{C_2H_4}/RT$. For slurry reactors, the concentration of monomer in the solvent, $[C_2H_4]_L$, should be used for all activity calculations. This, however, has not been the usual practice in the literature. Usually polymerization rates are normalized with respect to the total pressure (P/RT) or with respect to the monomer partial pressure in the head-space above the liquid in the slurry reactor, $[C_2H_4]_V$. The total pressure can differ significantly from the monomer partial pressure if the solvent vapor pressure is appreciable at the operating temperature (this is the case when heptane is used). Use of the monomer partial pressure is somewhat better since the concentration of monomer in the solvent is directly proportional to the monomer partial pressure in the pressure range where Henry's law is applicable. However, comparisons of activities in slurry reactors based on the partial pressure of the monomer above the solvent are only valid for a single solvent at a single temperature since the solubility of the monomer is a function of both the solvent and the temperature.

The use of the three different approaches for relating the polymerization rate to the monomer concentration for the 61 °C data from Figure 1 is illustrated in Figure 2. The concentrations of ethylene in the vapor phase, $[C_2H_4]_V$, and the liquid phase, $[C_2H_4]_L$, were calculated by using the Peng–Robinson[8] equation of state. The vapor and liquid ethylene concentrations for the run shown in Figure 1 are summarized in Table I. It is seen in Figure 2 that, when the monomer concentration is based on the total pressure of the reactor (dashed line), the polymerization rate varies linearly with the total pressure, but the extrapolation to zero rate produces a non-zero concentration. This value of the concentration intercept (approximately 11 mol/m³) is equivalent to a pressure of 30 kPa at 61 °C, which is approximately equal to the pure component vapor pressure of n-heptane at this temperature. When the concentrations of ethylene in the vapor and the liquid phases are used, straight lines passing through the origin result (first-order dependence on ethylene concentration). From the equation of state calculations, it was found that Henry's law is applicable for these experimental conditions and that the concentration of ethylene in the liquid phase is always a factor of 2.44 times higher than that in the vapor phase (at 61 °C). This is reflected in Figure 2 where the slopes of the two solid lines differ by a constant factor of 2.44. It is worth pointing out that, at a fixed temperature, the specific activity of the Stauffer catalyst is essentially constant and is not altered by variations in reactor conditions (compare the activity for the 140–155-min period to the activity for the 220–227-min period in Table I).

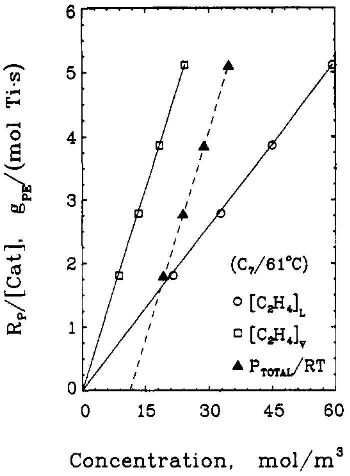

Figure 2. Dependence of rate of reaction on ethylene concentration using different approaches for the calculation of ethylene concentration (61 °C data in Table I).

The data from Table I can also be used to determine the dependence of the rate on the temperature. Because, as just shown, the reaction follows first-order kinetics, then the first-order rate constant at any temperature will be given by $k_p = R_p/([C_2H_4][Cat])$. If Arrhenius-type behavior is followed, then the logarithm of the rate constant should depend linearly on the reciprocal temperature. It is here that the importance of using the "correct" ethylene concentration becomes very evident. Shown in Figure 3 are the results of using the three different approaches for determining the ethylene concentration in the calculation of first-order rate constants at the various reaction temperatures. The experimental results from Table I are the solid symbols in Figure 3; it is seen that only the rate constants based on the ethylene concentration in the slurry liquid (solid circles) fall on a straight line. Basing the first-order rate constants on the ethylene vapor concentration, or on the total pressure, produces strongly curved lines that can even pass through a maximum (solid triangles for rate constants based on total pressure).

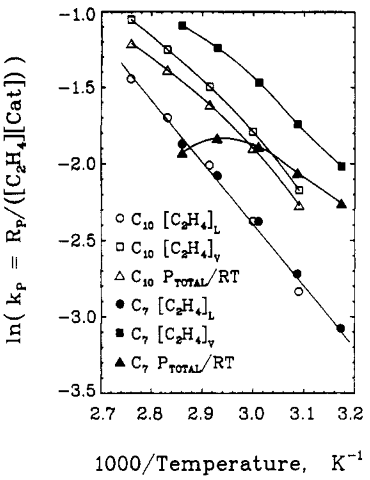

Figure 3. Temperature dependence of the pseudo-first-order rate constants (conditions as in Table I).

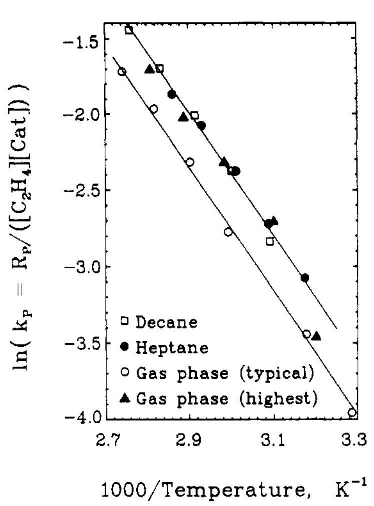

Figure 4. Equivalence of gas-phase and slurry modes of operation (conditions as in Figure 1 for slurry operation). Gas-phase conditions: (○) 0.187 g of δ-$TiCl_3$ (AA)/DEAC, Al:Ti = 33.9; (▲) 0.109 g of δ-$TiCl_3$ (AA)/DEAC, Al:Ti = 14.5.

Table II
Prior Studies Using the δ-$TiCl_3$ (AA)/DEAC System

T, °C	Al:Ti	slurry liq	$[C_2H_4]_L$, mol/m^3	k_p (see eq 1)	k_p(eq 2)/k_p	ref
60	2.0	EC180[a]	62	0.0072	12.6	10
50	10	*n*-heptane	485	0.0097	6.4	11
80	25	kerosene	55	0.061	3.0	12
60	13.4	sinarol[b]	51	0.043	2.1	13
60	1.0	toluene	32	0.021	4.2	9
40	1.0	toluene	54	0.0076	5.4	9
40	0.57	gas phase	20	0.0023	18.0	9

[a] Pentamethylheptane. [b] Saturated aliphatic hydrocarbons.

Figure 3 also contains the results from a slurry-phase experiment with decane, rather than heptane. These results provide further evidence that the rate constants should always be based on the ethylene concentration in the slurry liquid. It is seen that the first-order rate constants for operation in both heptane and decane fall on the same straight line when the rate constants are based on the ethylene concentration in the slurry liquid. If the ethylene concentrations are based either on the vapor phase or on the total pressure, then the rate constants depend on whether decane or heptane was used as the slurry liquid. Thus, if catalytic activities were based on the total pressure or gas-phase ethylene concentration in the reactor, then the incorrect conclusion would be drawn that the catalyst is more "active" in heptane than in decane, while in reality the catalyst activity was the same in both liquids.

From the combined results with decane and heptane, it is determined that the pseudo-first-order rate constant for the Stauffer 2.1 AA/DEAC catalyst system is given by

$$k_p = 17200e^{-4050/T} \quad g_{PE}/(\text{mol of Ti·s·[mol of } C_2H_4/m^3]) \tag{2}$$

The activation energy of 33.7 kJ/mol is in the range 31–36 kJ/mol, which has previously been reported for δ-$TiCl_3$ (AA)/DEAC systems.[9] A comparison of the absolute catalytic activities for δ-$TiCl_3$ (AA) catalysts from earlier studies to that obtained in the present study is presented in Table II. In each case, the value of k_p given in Table II has been based on the estimated concentration of ethylene in the slurry liquid obtained by using the Peng–Robinson equation of state. For the unusual slurry liquids (EC180, sinarol, and kerosene), the pseudocritical properties based on the approximate composition of the liquids were used in the vapor–liquid equilibrium calculations. In Table II, it is seen that the rate constant from eq 2, the activity from the present study, is from 2 to 18 times larger than that found in the prior studies. Thus, version 2.1 of the Stauffer AA catalyst is apparently more active than the earlier δ-$TiCl_3$ (AA) catalysts.

Additional evidence that the ethylene concentration in the slurry liquid should be used for determining the reaction rate constants can be obtained from gas-phase experiments that were carried out in an analogous fashion to that shown in Figure 1. The results from two such experiments are shown in Figure 4 where it is seen that in one case (solid triangles) the values of the pseudo-first-order rate constant cluster about the line for the two slurry-phase experiments, while for the other gas-phase experiment (open circles) the activation energy is approximately the same as that for the slurry experiments but the overall activity is somewhat less. Gas-phase experiments were typically less reproducible than slurry experiments, and the results represented by the open circles in Figure 4 were representative of several gas-phase experiments, whereas the rate constants represented by the solid triangles were obtained from an experiment that displayed the highest specific activity of any of the gas-phase experiments using the Stauffer catalyst. Thus, for a stable catalyst system, a direct comparison of slurry and gas-phase results is possible; i.e., the specific catalytic activity is the same in slurry and gas-phase reactors for catalysts with constant activity.

The difference between the specific activities for "typical" gas-phase and slurry experiments, accompanied by the constancy of activation energies, implies that the number of active sites is different in the two types of reactors but that the types of sites are the same. There are several factors that can result in a decrease in the effective amount of catalyst during gas-phase operation; these factors include the following: loss of catalyst during injection (a small quantity of catalyst is always retained in the injection valve), entrapment of catalyst in crevices in the reactor (stirrer blades, various entry and exit ports, and "dead" spots in the reactor corners and under the top flange), and encapsulation of some catalyst particles due to agglomeration of catalyst particles on the seed bed particles and reactor walls. All of these factors will result in a decrease in the available amount of catalyst, i.e., a lower rate constant. None of these factors are significant in the slurry reactor. As summarized in Table II, in earlier studies of ethylene polymerization at 40 °C using the Stauffer AA catalyst with DEAC cocatalyst,[9] it was also

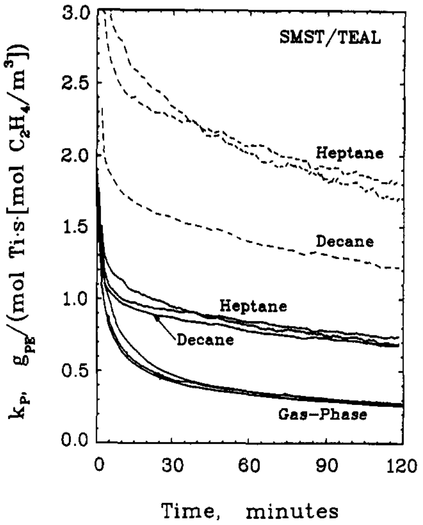

Figure 5. Ethylene polymerization activity in gas-phase and slurry reactors (SMST/TEAL system, 60 °C). Slurry: 0.1 g of catalyst, Al:Ti = 72.6, $P_{C_2H_4}$ = 0.1 MPa. Gas phase: 0.15 g of catalyst, Al:Ti = 92.6, $P_{C_2H_4}$ = 0.5 MPa.

found that the activity for gas-phase polymerization was somewhat less than (approximately 30%) that for slurry (toluene) operation. This is in contrast to that which has typically been found for propylene polymerization when gas-phase operation has usually resulted in higher activities relative to slurry operation.[14]

SMST/TEAL Catalyst System. Comparison of activities in slurry and gas-phase reactors for the laboratory-prepared, high-activity SMST catalyst, in the presence of TEAL as the cocatalyst, is presented in Figure 5. The dashed lines are activities in the slurry reactor based on the concentration of ethylene in the vapor phase, i.e., $[C_2H_4]_V$, while the solid lines adjacent to the solvent designations are based on the ethylene concentrations in the respective solvent, i.e., $[C_2H_4]_L$. The reproducibility of the data is seen in the close agreement between the two replicate slurry experiments using heptane and in the three replicate gas-phase experiments. Four general observations can be made from the results presented in Figure 5; one, all the activities are time dependent; two, the average activity in the gas phase is significantly lower than the activities in either of the solvents; three, activities in the solvents based on $[C_2H_4]_V$ (dashed lines) are solvent dependent; and four, activities for the solvents based on $[C_2H_4]_L$ are essentially solvent independent. The observation that the activities based on $[C_2H_4]_L$ are not dependent on the solvent reinforces the previous conclusion that $[C_2H_4]_L$ rather than $[C_2H_4]_V$ should be used for normalizing activities.

The Al:Ti ratio for the slurry and gas-phase experiments shown in Figure 5 was somewhat different (72.6 compared to 92.6). However, the difference in activities for the slurry and gas-phase experiments is not due to this difference in Al:Ti ratios since separate experiments in which the Al:Ti ratio was varied from 7.0 to 142.5 showed that the polymerization rates were essentially independent of the Al:Ti ratio. The results of these measurements are summarized in Table III for gas-phase and slurry experiments in which the concentration of ethylene in the gas-phase reactor was approximately equal to that in the slurry liquid. The normalized rates for the gas-phase reactor are approximately 30% less than those for the slurry reactor because of both the longer duration of the gas-phase experiments and the more marked deactivation that occurs in the gas-phase reactor in comparison to slurry operation. However, for both types of operation, the average polymerization rate is not affected by the Al:Ti ratio over the range examined in this study.

The time dependence of the activities seen in Figure 5 is due to catalyst deactivation. The initial activity of the SMST catalyst, in the slurry-reactor experiments, was approximately 20 times higher (on a mole of Ti basis) than the Stauffer 2.1 catalyst; however, after 8 h under reaction conditions, the SMST catalyst was only about 8 times as active as the Stauffer catalyst. It is apparent that deactivation of the SMST/TEAL system proceeds more rapidly in the gas phase than in the solvents. The difference in deactivation rates between gas-phase and slurry operations could result from various causes such as differences in the temperature of catalyst particles due to heat-transfer limitations in the gas phase, differences in inhibition by products of the reduction processes, and differences in the rates and degree of Ti^{4+} reduction caused by differences in temperature and TEAL concentration on the surface of the catalyst. The causes of the differences in deactivation rates were not investigated, but the large differences in deactivation rates for the SMST/TEAL system make direct comparison of rates from the slurry reactor with those from the gas-phase reactor impossible. It should be noted, however, that the normalized initial rates in Figure 5 (solid lines) are approximately equal for slurry (both solvents) as well as for gas-phase operation. Thus, the initial activity is similar for both gas-phase and slurry operation, with the lower average activity for gas-phase operation being due to the differences in the rates of deactivation between gas-phase and slurry operation.

Another aspect of the difference between the rates of deactivation in the gas-phase and slurry reactor is shown in Figure 6 where the results from a number of isothermal experiments are shown. When carried out in the gas phase, the deactivation process was so strongly dependent on the temperature that increases in the reactor temperature led to decreases in the overall rate of polymerization. Similar behavior has recently been reported for the gas-phase polymerization of propylene,[15] and in a modeling study[16] it has been shown that activated catalyst decay provides an explanation of this phenomenon. This unusual type of behavior was not observed when the slurry reactor was used, but instead, increases in the reaction temperature led to increases in the polymerization activity of the catalyst. Obviously, the temperature dependence of the polymerization rate for the SMST/TEAL system determined with a slurry reactor cannot be used for predicting the effect of temperature on the overall polymerization rate under gas-phase conditions.

Molecular Weights of Polymers from Slurry and Gas-Phase Reactors. The above results have dealt with the effects of reactor type and catalyst on the rates of polymerization. In this section, the effects of operating conditions on the molecular weight of the polyethylene produced with the SMST catalyst are discussed. In Table IV are presented molecular weights as a function of operating conditions. For the six experiments in which the effect of the Al:Ti ratio was examined, the reaction was carried out for a total period of 1 h at the constant reactor conditions given in Table IV. Following this period, the reaction was stopped and the molecular weight distribution determined for the product. The same procedure was carried out for the other experiments summarized in Table IV with the exception that in each case the polymerization was allowed to proceed for 2 h.

The molecular weights of all the products produced in this study are high (the weight-average molecular weights

Table III
Effect of Aluminum-to-Titanium Ratio (SMST/TEAL System at 60 °C)

	1-h Duration Slurry-Reactor Experiments with Decane					
Al:Ti ratio	7.0	18.5	35.2	53.1	73.2	141.7
rate, g_{PE}/(h·g catal.)	76.3	86.1	83.5	83.1	77.7	78.2
	2-h Duration Gas-Phase Reactor Experiments					
Al:Ti ratio	14.0	43.8	80.6	109.0	142.5	
rate, g_{PE}/(h·g catal.)	51.3	57.4	48.5	54.3	54.8	

Table IV
Effect of Operating Conditions on Average Molecular Weights (SMST/TEAL System)

T, °C	[C_2H_4], mol/m^3	Al:Ti	reactor type	M_w	M_n	polydispersity, M_w/M_n
			Effect of Aluminum-to-Titanium Ratio			
60	59.5	7.0	slurry (decane)	1.73×10^6	6.72×10^5	2.57
60	59.5	18.5	slurry (decane)	1.97×10^6	6.36×10^5	3.10
60	59.5	35.2	slurry (decane)	1.97×10^6	6.47×10^5	3.04
60	59.5	53.1	slurry (decane)	1.85×10^6	6.98×10^5	2.65
60	59.5	73.2	slurry (decane)	2.18×10^6	7.99×10^5	2.73
60	59.5	141.7	slurry (decane)	1.60×10^6	4.96×10^5	3.22
			Effect of Ethylene Concentration			
60	61.2	73.2	slurry (decane)	1.96×10^6	7.62×10^5	2.57
60	59.7	72.6	slurry (heptane)	1.92×10^6	5.39×10^5	3.57
60	54.8	89.6	gas phase	2.17×10^6	4.14×10^5	5.23
60	119.5	89.0	gas phase	2.29×10^6	6.34×10^5	3.61
60	184.2	92.6	gas phase	2.38×10^6	7.22×10^5	3.30
60	239.0	88.4	gas phase	2.51×10^6	8.77×10^5	2.86
60	306.2	86.7	gas phase	2.48×10^6	6.69×10^5	3.70
			Effect of Temperature: Gas-Phase Operation			
40	190.7	91.4	gas phase	3.15×10^6	1.27×10^6	2.47
50	187.3	88.4	gas phase	2.87×10^6	1.01×10^6	2.83
60	184.2	92.6	gas phase	2.38×10^6	7.22×10^5	3.30
70	174.0	88.4	gas phase	1.96×10^6	3.35×10^5	5.84
80	171.4	87.8	gas phase	1.78×10^6	2.76×10^5	6.46
			Effect of Temperature: Slurry Operation			
40	94.0	72.6	slurry (heptane)	2.30×10^6	9.80×10^5	2.35
55	68.0	72.6	slurry (heptane)	2.25×10^6	5.24×10^5	4.30
60	59.7	72.6	slurry (heptane)	1.92×10^6	5.39×10^5	3.57
65	51.7	72.6	slurry (heptane)	1.54×10^6	3.74×10^5	4.13
70	41.3	72.6	slurry (heptane)	1.56×10^6	5.34×10^5	2.93

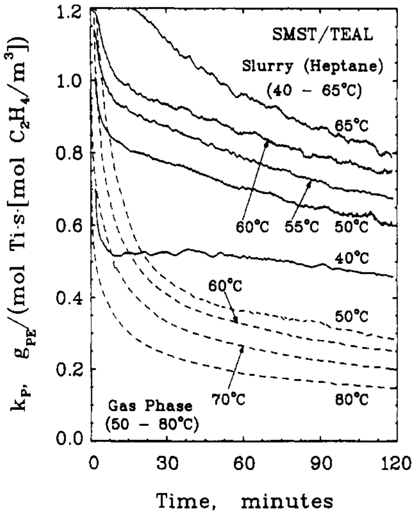

Figure 6. Differences in deactivation behavior in gas-phase and slurry reactors (temperature varied, other conditions as in Figure 5).

range from 1.54×10^6 to 3.15×10^6), but certain trends in average molecular weights and polydispersity as a function of operating conditions are apparent. The high molecular weights were expected since chain-transfer agents such as hydrogen were not added to the reactor. In the absence of hydrogen, the termination of the growing chains can occur spontaneously via a β-hydrogen shift or via transfer reactions with cocatalyst or monomer. It is readily shown that both the weight- and number-average molecular weights should be directly proportional to the monomer concentration if termination occurs via a β-hydrogen shift or via transfer to the co-catalyst. In the latter case, the average molecular weights should also be inversely proportional to the cocatalyst concentration. However, if termination occurs via transfer with the monomer, then the average molecular weights should be independent of both the monomer and cocatalyst concentrations. This last situation is seen to be the case in Table IV, and thus, it can be concluded that chain termination occurs primarily by transfer to monomer for the SMST/TEAL catalyst system at 60 °C.

From Table IV, it is seen that increases in temperature during gas-phase operation cause decreases in the average molecular weights. This will occur if the activation energy of the termination process is greater than that of the propagation step, as has been shown to be the case for $TiCl_3$ catalysts.[17] The effect of temperature on the polydispersity is somewhat more difficult to understand as it has usually been found that increasing temperatures tend to narrow the molecular weight distribution,[18] which is opposite to that seen for the gas-phase results in Table IV. If the deactivation of the catalyst results in an increase in the nonuniformity of the activity of the catalytic sites, then a broadening of the molecular weight distribution will occur as has been shown from examinations of multisite models of Ziegler–Natta catalysts.[19] As seen in Table IV, an unequivocal broadening of the MWD with increasing temperature was not found to occur when the slurry reactor was used. This further supports the conjecture that the

MWD broadening is linked to the catalyst deactivation because, as shown in Figure 6, the catalyst deactivation during slurry operation is not as pronounced as that experienced under gas-phase conditions.

Conclusions

It has been shown that the concentrations of ethylene in the solvent ($[C_2H_4]_L$), and not the partial pressure or concentration of ethylene above the solvent ($[C_2H_4]_V$), should be used when slurry-phase activities are compared for different solvents or with activities determined in a gas-phase reactor. It has also been shown that high-activity catalysts of the type used in this study, when used in conjunction with TEAL, deactivate much more rapidly in gas-phase reactors than in slurry reactors.

Direct comparison of normalized activities was possible for gas-phase and slurry reactors for the δ-$TiCl_3$ catalyst since the activity of this catalyst was essentially constant. However, the differences in activation and deactivation rates observed for the high-activity catalyst in gas-phase and slurry reactors makes direct comparisons of activities obtained with these two types of reactors impossible. Quantitative understanding of the differences in activation and deactivation processes in the two types of reactors, or the development of operational procedures that eliminate these differences, is required before direct comparison of rate data obtained from slurry and gas-phase reactors is possible.

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Registry No. DEAC, 96-10-6; TEAL, 97-93-8; $Mg(n\text{-}C_4H_9)_2$, 1191-47-5; $SiCl_4$, 10026-04-7; $TiCl_4$, 7550-45-0; δ-$TiCl_3$, 7705-07-9; (C_2H_4) (homopolymer), 9002-88-4.