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Diffusion Control during Synthesis of a Supported Organozirconium Polymerization Catalyst

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The uptake of tetra(neophyl)zirconium by alumina during the synthesis of a highly active olefin polymerization catalyst was measured using infrared spectroscopy. The results are consistent with a model of the synthesis process where diffusion of the organozirconium compound down the pores of the support past the saturated surface is rate controlling. Using measured and estimated values for the parameters of the model, agreement with the data to within an order of magnitude was found. The model explains several observed features of this type of catalyst, including the dependence of catalyst activity on pore structure.

INTRODUCTION

Several groups have described highly active catalysts for the polymerization of ethylene that are synthesized by the reaction of an organozirconium compound with hydroxyls on the surface of a mineral support (*1–5*). The reaction between the hydroxyls and the zirconium compound to form Zr–O bonds is very rapid and irreversible under the conditions of the catalysts synthesis.

Efficient use of the zirconium compound demands that it be dispersed on a support of high surface area. High surface area is usually accompanied by high porosity, either as pores or as voids between agglomerated particles. The process of catalyst synthesis may be controlled by the transport of the organozirconium compound through the pores of the support. There has been extensive discussion of the role of impregnation and diffusion in the synthesis and structure of supported catalysts (*6–10*).

The importance of the pore structure of the supports used in these catalyst systems has been noted. Zakharov *et al.* (*11*) found that the most active catalysts were made using "open-pored" aluminas and silicas. They concluded that silicas with surface areas $\geq$200 m^2/g and pore volumes $\geq$1.5 ml/g and aluminas with 250 m^2/g surface area and pore volumes of 2 ml/g were best (*3*). An average pore radius of $\sim$ 15 nm can be estimated for these optimal supports ($\bar{r} \sim 2$ (pore volume)/(surface area)). The need for disintegration of the catalyst during polymerization was also emphasized.

Candlin and Thomas (*1*) found that the extent of reaction of silica surface hydroxyls with (allyl)$_4$Zr in toluene slurries decreased with increasing slurry concentration. They proposed that diffusion through the larger agglomerates in the more concentrated slurries retarded the reaction.

Setterquist *et al.* (*4*) reported that the activity of tetra(neophyl)zirconium(($C_6H_5C(CH_3)_2CH_2)_4Zr$) reacted with β-alumina doubled as the support pore size was increased from 4.9 to 7.0 nm. They also discovered that fumed aluminas, which are composed of 10- to 20-nm fundamental particles, were superior to aluminas whose surface area was due to internal pores. Steric limitations were proposed to influence the reactivity of hydroxyls inside pores.

An extensive study of silica-supported chromium and titanium/magnesium catalysts with an emphasis on the disintegration of the catalyst during polymerization was

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reported by McDaniel (*12*). A clear dependence of catalyst activity on pore diameter was found in these related catalysts.

With the goal of controlling catalyst synthesis and the properties of polymer made with a supported organozirconium catalyst system, measurements of the rate of uptake of tetra(neophyl)zirconium by an alumina were made using infrared spectroscopy. The vibrational absorptions of the organic ligand are in a convenient region of the infrared spectrum, making quantitative measurements possible.

The catalyst synthesis rate measurements are consistent with a model in which the rate-limiting process is the diffusion of the organozirconium compound down pores past reaction saturated surfaces to an available hydroxyl site. This model explains several features of the catalyst system, including the dependence of activity on pore structure previously noted. In this model catalytic centers are preferentially formed on the outer surfaces of the catalyst, which may minimize mass transfer problems during polymerization.

METHODS

The alumina used was Degussa C fumed alumina, made by flame hydrolysis of aluminum chloride. Tetra(neophyl)zirconium (TNZ) was prepared by the reaction of neophyl magnesium chloride with $ZrCl_4$ (*4*). The alumina was pressed into wafers of 14 mm diameter weighing 51 ± 6 mg before drying for 4 hr at 670 K under dry N_2 (the error value given for sample weight is one standard deviation). The wafers were pressed in a steel mold at 10^4 kPa. Surface areas and pore volumes of both pressed and unpressed aluminas were measured by nitrogen adsorption and desorption. Measured physical properties of the alumina are 80–100 m^2/g surface area, 0.5 ml/g pore volume, and 16–27 nm average pore diameter. Properties of alumina pressed into wafers and dried at 670 K for these experiments fall in the same range as the properties of powders.

Dried wafers were immersed in *n*-hexane solutions of TNZ for measured lengths of time with occasional stirring. Upon removal from the TNZ solution, the wafers were rinsed five times with hexane. After evaporation of the hexane, the wafers were mounted into a Pyrex infrared cell with CaF_2 windows sealed by Viton O-rings. The cells were evacuated, and the ir spectra were recorded using a Perkin-Elmer 599 grating spectrophotometer.

The dried alumina is very hygroscopic, and both the TNZ and the supported complex are extremely air and moisture sensitive. All manipulations were done in a Vacuum Atmospheres Dri-Lab glovebox under a nitrogen atmosphere continuously purified of oxygen and water.

RESULTS

Figure 1 shows the mid-ir spectrum of the supported Zr catalyst. Vibrations of unreacted hydroxyl groups of the support cause the absorption at 3800–3300 cm^{-1}, and vibrations of the neophyl groups account for all other bands above the alumina low-frequency cutoff. Control experiments in which dried alumina wafers were immersed in hexane and *tert*-butylbenzene (the hydrolysis product of TNZ) and treated as the catalyst samples showed that all vibrational absorptions seen are due to neophyl groups bound to Zr, and none are due to adsorbed hydrocarbons.

The peak absorbance of the $-CH_3$ asymmetric stretching mode at 2960 cm^{-1}, corrected for a linearly interpolated baseline, was taken as a measure of the amount of Zr compound taken up by the alumina. The 2960 cm^{-1} absorbance after reaction for various times with three different concentrations of TNZ solution is given in Table 1 and plotted in Fig. 2. Each measurement was made on a different alumina wafer, and the precision of the data is largely determined by the reproducibility of sample weights and treatments. No changes in the shapes of any of the neophyl group absorb-

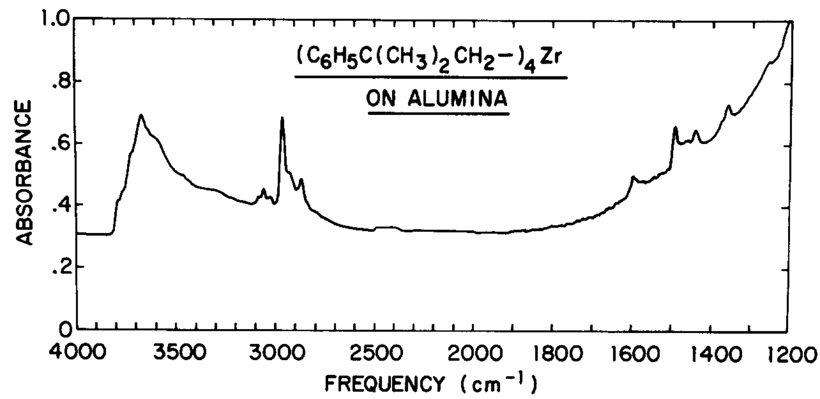

FIG. 1. Mid-infrared spectrum of polymerization catalyst produced by reaction of tetra(neophyl) zirconium with alumina dried at 670 K.

ances were observed during these experiments.

The corresponding changes in the hydroxyl stretching region of the ir spectrum are shown in Fig. 3.

DISCUSSION

The TNZ uptake by alumina plotted in Fig. 2 shows several interesting features. No saturation of the alumina surface with TNZ has been found over 2 hr. There is a strong dependence of uptake on concentration of the TNZ solution. If the reaction of TNZ with alumina hydroxyls is indeed rapid and irreversible, then transport and not the rate of reaction is determining the uptake. The three uptake curves can be reasonably fit by functions of the form $(\text{time})^{1/2}$ and are consistent with diffusion control of the catalyst synthesis.

While fumed alumina is nonporous in the sense that the primary 10- to 20-nm particles are not porous, the voids between the agglomerated particles behave as pores, and their volume and size distribution can be measured. During catalyst synthesis, the outer surfaces of the alumina would be expected to saturate with the Zr compound most quickly. Subsequent uptake could occur only at the rate that TNZ molecules could diffuse past the saturated surfaces into the pores.

Analysis appropriate to the present case of rapid adsorption from dilute solution onto small support particles is the treat-

TABLE 1

TNZ Uptake by Alumina
Absorbance of 2960 cm^{-1} CH_3 Mode

Time (sec)	TNZ solution concentration (mmol/liter)		
	0.18	0.59	1.5
5	0.02, 0.025	0.01	0.05
30	0.02	0.03	0.08
180	0.045	0.06	0.12
900	0.045	0.15, 0.17	0.31
7.2×10^3	0.09	0.32, 0.44	0.88
7.2×10^4	—	0.79	—

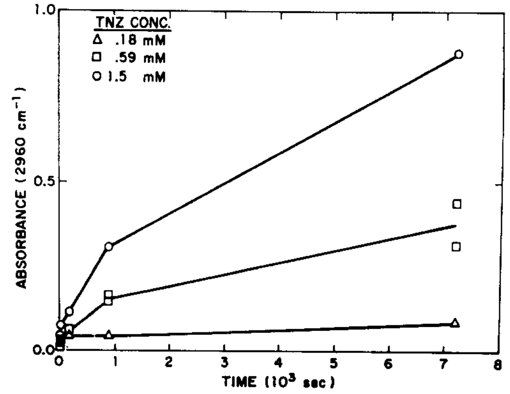

FIG. 2. Growth of neophyl group absorbance of catalyst with time of reaction with tetra(neophyl)zirconium solutions of three concentrations.

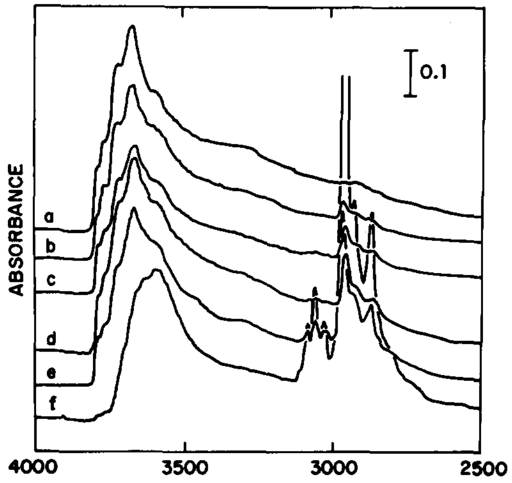

FIG. 3. Hydroxyl and C–H stretching vibrations of alumina reacted with 1.5 mmol/liter tetra(neophyl)zirconium solution for various amounts of time: (a) 0 sec, (b) 5 sec, (c) 30 sec, (d) 3 min, (e) 15 min, (f) 2 hr.

ment of Weisz (*6*) which has been expanded by others (*7–10*). Weisz discussed diffusional effects during impregnation for the case of constant solution concentration (*6*). General criteria for determining diffusion behavior were given by Ott and Rys (*7*). Herriott (*8*) presented results for the case of depletion of the impregnating solution during adsorption. Recently calculations and comparison to experiment were reported by Melo *et al.* (*9, 10*), who analyzed the dependence of total uptake and distribution profile on adsorption site density and diffusion, mass transfer, and adsorption equilibrium constants.

For convenience of discussion and clarity, a simple model for diffusion control of the catalyst synthesis is derived in the Appendix. Assumptions of the model are: (i) cylindrical pores, (ii) irreversible, rapid adsorption of TNZ, (iii) no radial diffusion limitations (justified because pore length $\gg$ pore radius), (iv) no concentration gradients or mass transfer limitations in the solution outside the pores, and (v) quasi-steady-state concentration gradient in pores (justified because the amount of TNZ in the pore volume is much less than the adsorption capacity (*6*)).

The model results in a TNZ uptake of the form:

$$\eta + \ln(1 - \eta) = -\tau$$

where

$\eta = N/N_0$
$\tau = At/N_0$
N = moles Zr taken up
N_0 = initial moles Zr in solution
t = time
A = constant (see Appendix)

For small η, the equation reduces to $\eta \sim \tau^{1/2}$ (Eq. (A-3)). If this model is appropriate, then the data at each concentration should fall on one curve if plotted as Abs/N_0 vs time/N_0. Such a plot is shown in Fig. 4. There is good agreement with the form of the uptake given by the model.

Using various estimated and measured values for the parameters of the model, a quantitative comparison can be made with the data. Such a comparison is presented in Fig. 4 where the data and model are plotted on the same scales. (See the Appendix for numerical values used.) The calculated curves lie an order of magnitude from the data, which may be viewed as satisfactory agreement in the face of the number and

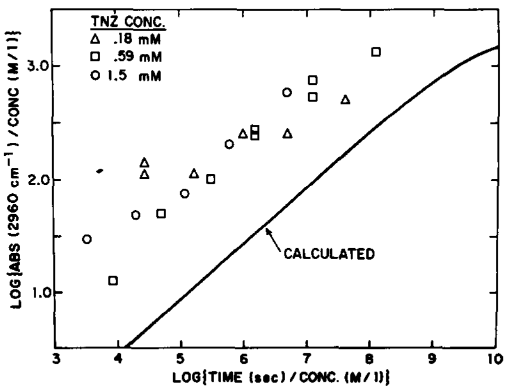

FIG. 4. Log–log plot of neophyl group absorbance divided by tetra(neophyl)zirconium solution concentration vs. reaction time divided by solution concentration. Symbols, data of Fig. 2. Line, result of diffusion model (see text).

uncertainties in the values of the parameters used.

The evolution of the OH stretching region of the infrared spectrum of the catalyst with time is also consistent with diffusion control of the Zr uptake. There are two classes of hydroxyl on the alumina surface distinguishable by ir. Sharp bands at 3800–3650 cm^{-1} are assigned to several kinds of free hydroxyls, while a broad absorption with a maximum near 3600 cm^{-1} and tailing to much lower frequency is due to hydrogen bonded hydroxyls (*13*). Mainly, the free OH groups react with TNZ, as has been found in similar studies with other Zr alkyls (*14, 15*).

It can be seen in Fig. 3 that the four free OH bands at 3790, 3770, 3730, and 3680 cm^{-1} decrease in intensity together as TNZ uptake proceeds. Diffusion control of the reaction between the hydroxyls and TNZ would mask differences in the reactivity of the individual hydroxyl types (*13*) and yield the observed behavior. The TNZ binding reaction proceeds to saturation over the outer surfaces, leaving all hydroxyls on inner pore surfaces intact. From the near total attenuation of the free hydroxyl absorptions in Fig. 3f, it appears that after 2 hr in the highest concentration TNZ solution nearly all of the alumina surface is saturated.

The uptake of TNZ by alumina wafers is fit well by a model where diffusion down pores past Zr saturated surfaces is rate controlling. The similarity of measured surface areas, pore volumes, and average pore diameters between the pressed wafers and loose powder implies that diffusion controls the reaction of TNZ with powders also, and with adjustment of the pore length value to reflect powder agglomerate size, the model should describe the process.

There is evidence for diffusional control of synthesis in these catalysts. The specific rate constant for the reaction of TNZ with alumina powder decreases during catalyst synthesis (*4*), indicating control of the reaction by an additional factor such as diffusion. Also slow uptake of TNZ continues beyond usual synthesis times (*4*) showing saturation of the alumina surface occurs slowly.

Clear evidence for diffusional limitations during synthesis was presented by Murray (*16*). An electron microprobe scan across a microtomed particle of a tetra(benzyl)zirconium reacted with alumina catalyst showed high Zr/Al ratio in the outer 20 μm of the particle and very low levels of Zr in the center. This distribution of Zr was attributed to the method of impregnation.

The above observations are in accord with the diffusion model and show that diffusional effects can occur in practical catalysts. A dependence of polymerization rate constants or polymer properties on Zr loading or alumina pore structure must be interpreted in terms of two mass transfer effects, first diffusion control of catalyst structure during synthesis as discussed here, and second the effects of monomer transport into and polymer transport out of pores during polymerization. Mass transfer effects during polymerizations over heterogeneous catalysts have been discussed previously (*17–20*). The two simultaneous dependencies on support pore structure hinder discussion of pore structure effects on the details of polymer yield or properties, but such effects have been observed.

Diffusion control of catalyst synthesis can explain the apparent dependence of catalyst activity on pore size (*1, 3, 4, 11*). For alumina of a given surface area, the total Zr uptake in a period of time is roughly proportional to the square root of the pore radius. Small pore aluminas would take up less Zr and would have reduced activity. Large pore aluminas would be able to saturate their surfaces with Zr but would have decreased total surface area. Therefore, Zr uptake and thus activity should show a maximum with pore diameter.

The greatly increased activity of mineral-supported Zr compounds over solutions of the compounds is postulated to be due to the prevention of association of the active

Zr species (*2*). Interactions between Zr centers are prevented when the Zr is dispersed on a support. This would imply a Zr loading dependence of the catalyst and the polymer produced since residual interactions between Zr centers would depend on the distance between Zr sites on the alumina surface. No such dependence of the catalyst properties on loading was observed in the ir and uv-visible spectra of heat treated or hydrogenated catalysts, except that the magnitude of spectral features scaled with total Zr uptake (*21*).

In the diffusion model there would be no variation of Zr surface density and no variation of local structure around the Zr centers with Zr loading. There will only be saturated and empty surfaces. Attempts to modify catalyst site properties by separating the sites on the surface must be made under conditions where the transport of the organometallic catalyst precursor is not rate limiting or where other factors such as the bulk of the ligands (*4*) controls Zr distribution on the support.

When (allyl)$_3$Cr was reacted with silica in the presence of ethylene, very rapid polymerization occurred, much faster than the rate observed with preformed catalyst (*22*). After reaching a maximum, the rate fell off steadily, approaching the rates measured with preformed catalyst. The diffusion model of catalyst synthesis can explain this result. The first catalytic sites to form would be on the exterior surfaces of the silica, the sites most accessible for monomer approach and polymer expulsion. These sites should have high polymerization efficiency. With time, these sites would deactivate and less accessible sites in the pore would carry on the reaction. Eventually, rates comparable to those of preformed catalyst would be reached as the distribution of catalyst sites in the pores become comparable.

The Zr-deficient centers of catalyst particles which would result from diffusion-controlled synthesis can lead to polymer particles containing voids. Murray observed such polymer particles with electron microscopy (*16*). He warned that the voids could lead to bubbles in extruded polymer and to inferior mechanical properties of the polymer.

SUMMARY

Infrared spectroscopy was used to measure the uptake of an organozirconium compound by alumina to form an olefin polymerization catalyst. The time dependence of the uptake was found to agree well with a model of the catalyst synthesis process in which diffusion of the organozirconium compound down pores past saturated surfaces was rate controlling. The model explains several properties of this type of catalyst including the dependence of catalyst activity on support pore structure and the constancy of the spectral features of the catalyst with Zr loading. Mass transfer effects during polymerization are also important. To properly understand the effect of pore structure on the performance of supported organometallic polymerization catalysts transport effects during both synthesis and polymerization must be considered.

APPENDIX

Here, the equation for rapid and irreversible uptake or adsorption onto a solid with cylindrical pores from a solution with a finite amount of adsorbate is derived. Radial diffusion and mass transfer in the solution outside the support pores are ignored. The analysis is similar to that of Weisz (*6*) and to that describing pore mouth poisoning in catalysts (*23, 24*). The starting point is Fick's first law (see Table 2 for definitions of symbols). For one pore

$$\frac{1}{\pi r^2}\frac{dn}{dt} = D\frac{dC}{dX}. \qquad \text{(A1)}$$

The concentration gradient down the pore depends on the uptake because of both depletion of adsorbate in the solution outside the pore and the increasing length down the pore that the adsorbate must diffuse. Assuming a quasi-steady-state concentration

TABLE 2

Definition of Symbols and Values for Model Parameters

r	Pore radius (10 nm, measured)
n	Uptake per pore
t	Time
D	Diffusion constant for adsorbate (10^{-6} cm^2/sec, estimated)
C	Concentration of adsorbate
X	Dimension down pore
N	Uptake
V	Volume of adsorbate solution (20 cm^3, measured)
C_0	Initial adsorbate concentration
ρ	Area density of adsorbate sites on adsorbent (10^{14} cm^{-2}, estimated)
PV	Adsorbent pore volume (0.6 ml/g, measured)
SA	Adsorbent surface area (100 m^2/g, measured)
b	Number of pores per wt. of adsorbent (3×10^{12}/g, estimated)
L	Pore length
w	Weight of adsorbent (45 mg, measured)
Abs	Infrared absorbance
ϵ	Extinction coefficient (2×10^{-19} cm^2/neophyl, estimated)
S	ir sample area (1.5 cm^2, measured)

gradient down the pore, that is the motion of the reaction front is slow compared to the diffusion of molecules down the pores (*6*).

$$\frac{dC}{dX} = \frac{\Delta C}{\Delta X}$$

$$\Delta C = C_0 - N/V$$

$$\Delta X = \frac{n}{2\pi r \rho}.$$

The total uptake N is related to the uptake per pore n by the number of pores, b, estimated in two equivalent ways:

$$b = \frac{PV}{\pi r^2 L} \quad \text{or} \quad b = \frac{SA}{2\pi r L}.$$

Taking these relations together, the differential equation for the total uptake becomes

$$\frac{dN}{dt} = A\left(\frac{C_0 - N/V}{N}\right) \qquad \text{(A2)}$$

$$A = 2(\pi b w)^2 r^3 \rho D.$$

For the case of a great excess of adsorbate or at short times $C_0 \gg N/V$ and Eq. (A2) reduces to

$$\frac{dN}{dt} = \frac{AC_0}{N}$$

which has the solution

$$N = (2AC_0t)^{1/2}. \qquad \text{(A3)}$$

The solution for boundary condition $N = 0$ at $t = 0$ is

$$\eta + \ln(1 - \eta) = -\tau \qquad \text{(A4)}$$

$$\eta = \frac{N}{VC_0}$$

$$\tau = \frac{A}{V^2C_0}t.$$

To make a quantitative comparison to the data, the conversion from infrared absorbance to uptake is needed. Beer's law is used.

$$\text{Abs} = \frac{N\epsilon}{S}.$$

The value for ϵ is taken as twice the value given by Rice (*25*) for the CH_2 symmetric stretch. Surface stoichiometry of one neophyl per Zr and two methyls per neophyl is used (*4*).

The value for the diffusion constant of TNZ in hexane can be estimated to be 10^{-6} cm^2/sec following Satterfield (*26*). Other values taken for the comparison are given in Table 2.

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