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The Polymerization of Ethylene over $TiCl_4$ Supported on Alumina Aerogels: Low Pressure Results

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High polymerization activities were obtained on catalysts derived from $TiCl_4$ affixed to certain alumina aerogels. Catalysts derived from a modified form of xerogel synthesis were less active. The ability of catalysts to maintain low bulk density and high pore volume appeared to be the key characteristic of active catalysts.

INTRODUCTION

Supported polymerization catalysts find wide application in the multibillion pound per year production of polyolefins, in particular, polyethylene.

Metal oxide-supported ethylene polymerization catalysts fall into two broad classifications based on either chromium or titanium as the active species. Attachment of the catalytically active species to a support is desirable when a broad molecular weight distribution is desired (*1*). The function of the support is generally believed to provide a multiplicity of active sites of inherently different polymerization rates, resulting in a broad distribution of polymer chain lengths. Common supports include MgO, SiO_2, and Al_2O_3.

Conflicting evidence exists in the literature as to the desirable physical properties of a support conducive to high catalytic polymerization activity. Matsuura prescribes an amorphous alumina support having a pore volume less than 0.7 cm^3/g (*2*). On the other hand, use of amorphous alumina supports having high pore volume, preferably between 1.2 and 2.0 cm^3/g, is taught by Ligorati (*3*).

Baulin reported on the ethylene polymerization activity of titanium tetrachloride affixed to various products of alumina manufacture. Although the activities (catalyst weight basis) were modest, they scaled with the porosity and surface areas of the supports (*4*). High surface area was also the key property of the alumina supports used with titanium tetrachloride catalysts in the polymerization of ethylene (*5*), and both high surface area and porosity are prescribed for the alumina supports of Reginato *et al.* (*6*).

Alumina was the support of choice in this study, specifically, aluminas of high pore volume and surface area. In pursuit of these properties, aluminas were synthesized in our laboratory. Two types of preparation were employed. In one case, supports were prepared using the aerogel synthesis (called supports "A" in the text). Aerogels refer to a class of materials (usually metal oxides) that are isolated by removal of the solvent as a supercritical fluid (*7*). Teichner (*8*) has been especially influential in contributing to the use and understanding of this class of materials. To the authors' knowledge, this report is the first published work on aerogel-supported titanium-based olefin polymerization catalysts.

The underlying basis of the aerogel process is the fact that the surface tension of liquids reduces to zero at the critical temperature. Separation of liquid as a supercritical gas from a porous material prevents collapse of the pores that results from surface tension-related capillary forces (*7*).

Besides alumina aerogels, a modified form of xerogel synthesis was explored for

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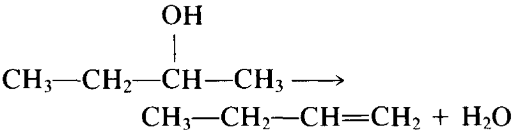
preparing high surface area and pore volume supports (designated "X" in the text) (9). In this case a solution of aluminum butoxide in *s*-butanol was heated to a temperature at which *s*-butanol dehydrates at a convenient rate (around 250°C). The ensuing reaction between the water formed and the aluminum butoxide precipitates aluminum hydroxide, viz.,



$$CH_3{-}CH_2{-}\overset{\overset{\displaystyle OH}{|}}{C}H{-}CH_3 \longrightarrow CH_3{-}CH_2{-}CH{=}CH_2 + H_2O$$

$$3H_2O + Al(OC_4H_9)_3 \longrightarrow Al(OH)_3 + 3C_4H_9OH$$

The amount of water formed could be controlled by manipulation of reaction temperature and holding time (*10*). Instead of isolating the precipitate by supercritical venting of the solvent, the reactor contents were filtered. This modification was employed to facilitate anticipated scaleup of the alumina synthesis. Limitation of the amount of water formed was the principal method of preserving high pore volume and surface area.

METHODS

Synthesis of Supports

The aerogels were prepared in a 300-cm^3 autoclave reactor as described in the literature (*11*). The modified xerogel synthesis has been described previously (*10*). Supports were stored in a glove box after calcination. Surface areas were determined by the BET method (single point) and pore size distributions by mercury porosimetry (Quantachrome Corp., Syosset, NY). A graph of pore size data consists of a mercury intrusion curve, obtained as pressure is increased, and an extrusion curve derived as pressure is decreased to the initial value (1 atm). To determine the bulk density, a weighed portion of catalyst was added to a graduated cylinder and tapped until the material reached constant volume. The procedure was performed in a glove box when analyzing catalysts.

Impregnations

Standard H-reactor and vacuum line techniques were used. The system was capable of 1.3×10^{-4} Pa pressure. Polymerization grade heptane (Phillips Petroleum Co.) was stored over Na/K alloy. $TiCl_4$ stock solutions were prepared by vacuum distillation and protected from light during storage.

Two methods were used for impregnation. In one method $TiCl_4$ was transferred as a vapor from a glass bulb containing neat material into an H-reactor chilled to $-196°C$. The second method involved pipet transfer of liquid $TiCl_4$/heptane solution from a glass bulb attached to the vacuum/gas manifold. The transfer was made while argon was flowing via the manifold through the reactor and the $TiCl_4$/heptane bulb simultaneously. Catalyst properties and polymerization results were independent of the method used.

Polymerization

Catalysts were tested initially in a low pressure (345 kPa) multistation facility. Heavy wall, glass Fisher–Porter bottles served as polymerization reactors. The bottles were connected to a manifold through which vacuum, heptane, ethylene, hydrogen, and argon could be supplied. Each reagent passed through three treaters containing, in succession, activated carbon, BASF Cu catalyst, and molecular sieve 4A or 3A (ethylene) dryer. The reactors were magnetically stirred and housed in a common circulating silicone oil, constant temperature bath. The ethylene flow to each reactor was monitored with a Matheson Model 8160 flow meter and Model 8122 totalizer. One hour was the usual time for a run.

RESULTS

Supports

The lower alcohols, principally methanol, *i*-propanol, and *s*-butanol, were employed as solvents in aerogel preps (supports A), while *s*-butanol was the solvent of choice for supports X.

A variety of X-ray patterns were recorded for the aluminas, including amorphous, boehmite, γ, χ and η. Frequently several phases were observed in a single sample. In aerogels boehmite was only observed when the initial water : aluminum alkoxide ratio was above stoichiometric. High surface area samples invariably contained a major amorphous component, persisting after calcination at 700°C.

Typical bulk densities (tap densities) of supports A were 0.05 and 0.1 g/cm^3 for supports X.

The surface areas of both supports A and X showed parabolic behavior with calcination temperature. Maximum surface area, around 800 m^2/g, was developed in the vicinity of 400°C, decreasing slowly to about 400 m^2/g at 700°C and rapidly at 800°C.

The pore size distribution, typical for both supports A and X, is shown in Fig. 1. These materials exhibit a broad distribution of pores, including a large number of pores having radii smaller than 2 nm.

Catalysts

The catalysts described herein were formed via reaction of $TiCl_4$ with the surface hydroxyl groups on alumina. The impregnations were carried out under rigorous, air-free conditions. The amount of titanium that could be fixed is controlled by the hydroxyl content of the support. Calcination is the general method used to control the hydroxyl concentration.

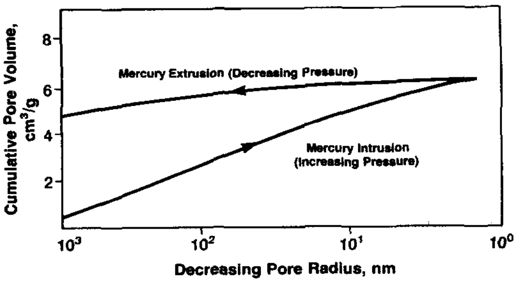


FIG. 1. Typical pore size distribution curve for aluminas prepared in this work.

TABLE 1

Ti/OH Ratio of Calcined Xerogel Aluminas (Supports X)

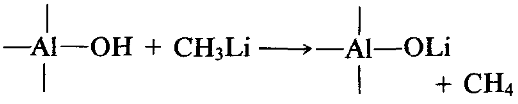
Calcination temperature (°C)	Titanium[b] (wt%)	OH content[a] (mmole/g)	Ti/OH ratio
200	4.15	9.3	0.0932
400	3.41	5.1	0.140
500	4.10[c]	0.83	0.48
600	5.14	0.83	1.29
700	4.56	0.28	3.40

[a] Based on CH_3Li analysis.

[b] Supports impregnated with excess $TiCl_4$.

[c] Impregnated using $TiCl_4$ to match the CH_3Li hydroxyl content.

Titration of the surface hydroxyl groups on supports X with methyl lithium was attempted in an effort to correlate hydroxyl concentration with the titanium concentration ultimately fixed. The titration is based on the reaction



$$-\overset{|}{\underset{|}{Al}}-OH + CH_3Li \longrightarrow -\overset{|}{\underset{|}{Al}}-OLi + CH_4$$

The methane evolved is therefore representative of the surface hydroxyl concentration (*12*).

Results obtained from the CH_3Li titration on supports X are given in Table 1. Column 4 indicates that at calcination temperatures at or above 600°C more Ti could be attached than predicted by the titration. Our interpretation of this result is that the methyl lithium assumes more highly associated multinuclear species in the hydrocarbon solvent employed (heptane) and therefore cannot penetrate pores below a size that remains accessible to $TiCl_4$. As pointed out above, presence of pores below the lower limit of detection by mercury porosimetry (about 2 nm in size) is typical for these supports.

The fixed Cl : Ti atomic ratio is revealing as to the variety of processes that can occur at the surface. This ratio is given in Table 2 for several catalysts used in this work. Stoichiometric reaction between $TiCl_4$ and

TABLE 2

Activities and Physical Properties of Various $TiCl_4$–Alumina Catalysts

Support type[a]	Elemental (wt%)		Cl : Ti atomic ratio	Activity per g cat.[b]	Bulk density[c] (g/cm^3) impregnation		Pore volume[c] (cm^3/g) impregnation		Surface area[c] (m^2/g) impregnation	
	Ti	Cl			Before	After	Before	After	Before	After
B–M	4.0	7.0	2.4	236	0.050	0.073	5.38	6.69	498	501
B–M–F[e]	3.2	6.6	2.8	161	0.038	0.10	4.06	4.54	335	335
B–B	3.2	6.1	2.6	84.8	0.040	0.14	3.59	3.12	289	287
B–B	2.6	6.9	3.6	34.3	0.17	0.25	2.34	2.67	222	228
Hybrid[d]	2.3	—	—	15.5	0.15	0.32	2.95	—	282	—
M–M–F[f]	1.8	3.5	2.6	13.8	0.26	0.69	—	1.73	—	171
B–B	—	—	—	8.69	0.13	0.39	1.25	1.83	370	277
Fumed	1.4	3.1	3.0	1.40	0.061	0.40	3.94	3.23	96	103

[a] Abbreviations: all supports are aerogels except for the commercial fumed alumina. B, *s*-butanol; M, methanol; F, fluoride. The sequence given refers to hydrolysis solvent-venting solvent-fluoride, if present.

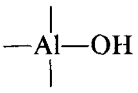
[b] g(PE)/h/atm(C_2H_4). (1 atm = 101.3 kPa.)

[c] Before values are for supports calcined at 700°C.

[d] Hybrid indicates that the alumina was prepared in water and vented in methanol.

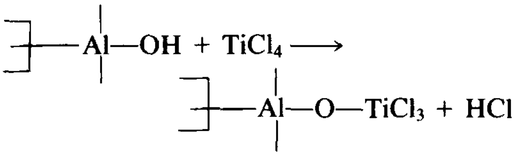
[e] 2.7 wt% F.

[f] 3.2 wt% F.



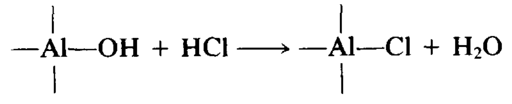
$$-\underset{|}{\overset{|}{Al}}-OH$$

might be expected to lead to a Cl : Ti ratio of 3:



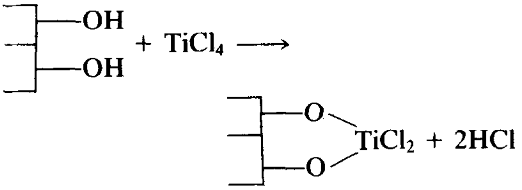
$$]-\underset{|}{\overset{|}{Al}}-OH + TiCl_4 \longrightarrow\ ]-\underset{|}{\overset{|}{Al}}-O-TiCl_3 + HCl$$

However, readsorption of all or part of the HCl can lead to ratios up to 4. Readsorption may occur by



$$-\underset{|}{\overset{|}{Al}}-OH + HCl \longrightarrow -\underset{|}{\overset{|}{Al}}-Cl + H_2O$$

Reaction of $TiCl_4$ with two hydroxyls has also been postulated (*12*):



$$]\begin{matrix}-OH\\-OH\end{matrix} + TiCl_4 \longrightarrow\ ]\begin{matrix}-O\\-O\end{matrix}\!\!>TiCl_2 + 2HCl$$

Combinations of the above processes can therefore lead to Cl : Ti ratios ranging from 2 : 1 to 4 : 1.

In certain cases the impregnation step brought about a change in physical properties, e.g., tap density and pore volume. Indeed, the ability of a catalyst to survive the impregnation step unchanged was frequently a decisive factor in determining its polymerization activity.

The activities and important physical properties of the $TiCl_4$-impregnated catalysts are collected in Table 2. Numerous variations were employed in preparing the catalysts. Details of the aerogel preparation procedure were important in determining activity. The most active catalysts were derived from supports in which hydrolysis was done in *s*-butanol and the butanol exchanged for methanol before venting. Much less active catalysts were obtained when *s*-butanol was used as the venting solvent.

To obtain active catalysts from the xerogel-type supports X, excess $TiCl_4$ was required for impregnation. The activities of catalysts as a function of calcination temperature of the supports are shown in Fig. 2

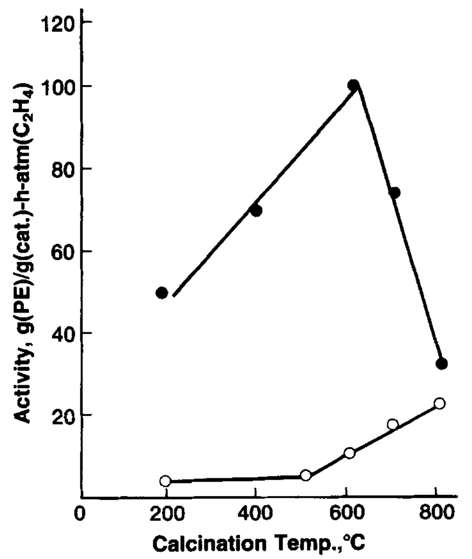


FIG. 2. Catalyst activity (weight basis) of modified alumina xerogels. ○, limited impregnation; ● excess impregnation, (see text).

for two impregnation levels, excess and limited. Limited impregnation means that the quantity of $TiCl_4$ used matched the hydroxyl content (according to the methyl lithium titration). The most active catalysts were obtained from supports calcined at 600–700°C and impregnated using excess $TiCl_4$.

For supports X, fluoride caused a reduction in the amount of titanium that could be fixed and a marked increase in specific activity (Ti basis) with no improvement in overall activity based on catalyst weight. A catalyst containing 2.1 wt% fluoride had a specific activity of 5192 g(PE)/g(Ti)-h-atm(C_2H_4) and overall activity of 65.4 g(PE) per gram of catalyst.

A comparison of the best catalyst from this work with other Ziegler catalysts reveals that its activity is in the range of early MgO-supported $TiCl_4$ catalysts, i.e., greater than that of traditional, unsupported $TiCl_4$/alkyl$_3$Al, but less than the activity of modern high efficiency $MgCl_2$/$TiCl_4$ compositions (*4*, *13*). The characteristic feature of the $TiCl_4/Al_2O_3$ catalysts, however, is in the preparation of high-molecular-weight polyethylene having broad molecular weight distribution and low melt index.

DISCUSSION

Correlation of Activity with Catalyst Physical Properties

As a class of materials, supports A led to more active catalysts than supports X. As a result the following discussion is limited to supports A only.

The activities of the catalysts appearing in Table 2 are correlated with bulk density, pore volume, and surface area in Fig. 3. A

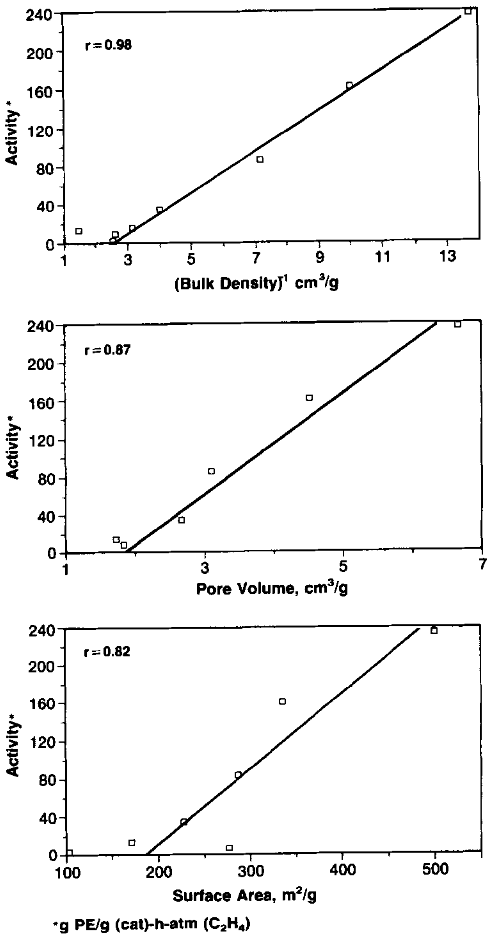


FIG. 3. Correlation of catalyst activity with physical properties.

great variety of supports is represented in Table 2, including aerogels made according to different procedures as well as a commercial fumed alumina. Figure 3 is composed of three plots relating activity on a catalyst weight basis to the reciprocal of bulk density, pore volume, and surface area, respectively. Physical property values obtained after impregnation were used in these plots. The least squares regression lines are drawn in the plots, and the correlation coefficient, r, calculated in each case is given. Activity correlates best with the reciprocal of bulk density followed by pore volume and weakly with surface area.

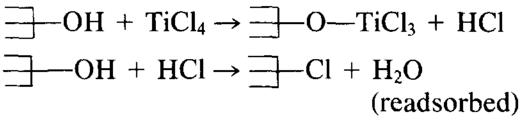
The key feature of active catalysts is their low bulk density after impregnation. Reference to Table 2 reveals marked differences in the resistance of the various supports to undergo compaction upon impregnation. The most active catalysts were derived from supports whose bulk densities were initially low and remained low after impregnation with $TiCl_4$. In contrast to the effect on pore volume and surface area, all of the supports appearing in Table 2 suffered some loss in bulk density as a result of the impregnation process. The degree of compaction was decisive in determining the ultimate activity as the graphical analysis shows.

Intuitively, one would expect a connection between bulk density and pore volume. Bulk density, however, is a macroscopic property whereas pore volume is microscopic in nature. The data reported here suggest that macroscopic features of a polymerization catalyst have important bearing on activity, most likely having to do with the accessibility of the active site to monomer.

The striking inactivity of fumed alumina is understandable on the basis of the bulk density correlation. Fumed alumina is superficially similar to alumina aerogels with its low bulk density and broad pore size distribution. $TiCl_4$-impregnated fumed alumina was found to be quite inactive as a polymerization catalyst support in this study, however. In spite of its low initial bulk density, it suffered severe compaction as a result of the impregnation procedure employed.

Susceptibility of a support to impregnation may be related to the secondary reactions following the primary $TiCl_4$/OH reaction. Shrinkage of aerogels in water can be quite remarkable. The bulk density of one alumina aerogel in this study changed from 0.05 to 0.85 g/cm^3 after contact with liquid water at room temperature. The shrinkage was accompanied by almost total elimination of pore volume (5.42 to 0.20 cm^3/g) but less than a twofold decrease in surface area (640 to 353 m^2/g).

The compaction of certain aluminas during impregnation may be related to the H_2O and/or HCl formed in the presumed surface reaction:



At the current level of understanding, however, the authors are unable to offer an explanation as to why certain aerogel supports were less susceptible to the impregnation process than others.

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