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Dependence of Polymerization Activity on Particle and Crystallite Dimensions in Ball Milled $TiCl_3$ and $TiCl_3 \cdot 0.33AlCl_3$ Catalyst Components

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Extensive dry ball milling of layer-lattice type $TiCl_3$ and $TiCl_3 \cdot xAlCl_3$ polymerization catalyst components results in a drastic and surprising increase in catalyst activity. The particle size does not change very much during the milling and influences only the initial buildup of activity in propylene polymerizations. By contrast, the crystallite size, as calculated from the broadening of X-ray diffraction peaks representing directions parallel and transverse to the hexagonal crystal axis, undergoes extensive reduction far beyond what would normally be expected from such a treatment. This size reduction appears to be a function of the particular crystal structure of these materials which makes Cl–M–Cl double layer sliding possible when the intensity of shear is sufficiently high. As a consequence, the crystallite size reduction will always be accompanied by a change in crystal structure from the α- or γ-form to the δ-form which is characterized by disordered stacking of the double layers. For a given catalyst preparation, the activity increases with decreasing crystallite size until a minimum average size has been reached, corresponding to a value of about 50 Å for both directions measured. Further reduction in crystallite size results in a less active catalyst, probably because of a tendency of such small crystallites to change to the less active β-form.

I. INTRODUCTION

Two types of transition metal components, viz, pure or essentially pure, titanium trichloride (*1–3*), usually in the form of α-$TiCl_3$ (*4*), and partially reduced titanium chloride cocrystallized with aluminum chloride, $TiCl_n \cdot xAlCl_3$ ($2.5 < n < 3$, $0 < x < 0.5$) (*5*) have been found particularly useful for making Ziegler-type polypropylene catalysts. Of these, the latter is by far the more active and also exhibits some other properties which are superior to those of pure $TiCl_3$ (*6*). Therefore, it has found widespread use in the industrial manufacture of crystalline polypropylene.

However, as prepared by conventional chemical synthesis methods, neither pure $TiCl_3$ nor the cocrystallized titanium chloride component exhibits sufficient activity when combined with a suitable alkylaluminum compound to make commercial production of polypropylene economically attractive. This situation was remedied when it was found several years ago in our laboratories that the activity of both types of catalyst component can be increased more than tenfold by grinding or otherwise mechanically working the components under inert conditions in the dry state (*7*).

Although it was established that some particle size reduction and hence increase in external surface area takes place during the dry grinding, especially when the original titanium chloride particles are rather coarse, it was found that the great increase in catalyst activity could not be satisfactorily explained on the basis of a corresponding increase in surface area. It was also observed that significant crystallographic changes occur during the grinding as indicated by the X-ray line broadening and the complete or almost complete disappearance of most of the diffraction peaks of the original crystalline material after prolonged grinding (*7*). From our knowledge of the crystalline structures of the starting materials (*8–10*) and the fact that $TiCl_3$ and $AlCl_3$ can be made to cocrystallize by subjecting a mixture of these compounds to intense dry grinding (*11*), we concluded that the primary effect of dry grinding was a sliding of the Cl–Ti–Cl double layers relative to each other in the original materials exhibiting either hexagonal (α-$TiCl_3$) or cubic (γ-$TiCl_3$) closest packing for the chlorine atoms (*12*). This leads to a disorder in the stacking of the double layers which becomes essentially random after prolonged intense dry grinding. The same conclusion was arrived at by Natta, Corradini and Allegra (*4*) on the basis of a more detailed study of the changes in the X-ray diffraction patterns of α- and γ-$TiCl_3$ taking place during prolonged dry grinding. They gave the name δ-$TiCl_3$ to the new crystallographic form exhibiting disordered double layer stacking. However, the crystallographic changes did not seem to offer any explanation for the drastic increase in catalyst activity resulting from the grinding. On the other hand, another observation made by us during our studies of X-ray diffraction patterns of various dry milled catalyst components seemed to offer a clue to the origin of the great activation caused by such treatment. We noticed a considerable line broadening in the patterns of the more intensely dry milled and, hence, activated catalyst components, indicative of a strong reduction in the average size of the diffracting units, which can be considered as small crystals or *crystallites.* For this reason, we undertook a more detailed study to establish if a valid correlation could be found between catalytic activity on one hand and crystallite size, particle size or surface area on the other.

II. EXPERIMENTAL PROCEDURES

A. *Catalyst Preparation and Characterization*

The $TiCl_3 \cdot 0.33AlCl_3$ catalyst components used in these studies were prepared either by direct reduction of $TiCl_4$ with commercial aluminum powder in a steel bomb at about 250°C, which yielded a solid solution type product isomorphous with α-$TiCl_3$ (*5, 6*), or by reduction of $TiCl_4$ with activated aluminum powder (*13, 14*) in a 9/1 mixture of *n*-decane and xylene at about 163°C (*6, 13*) which yielded a product essentially isomorphous with γ-$TiCl_3$. The pure α-$TiCl_3$ was obtained from the Stauffer Chemical Co. and had been prepared by reduction of $TiCl_4$ with hydrogen at a high temperature ($>600°C$).

The activation of the solid catalyst components was carried out by ball milling with steel balls in a nitrogen atmosphere under dry conditions at or slightly above room temperature. For most samples a 1-liter stainless steel jar was used with ⅝ in. diameter chrome alloy steel balls as the grinding medium and a charge of 150 g solid catalyst component. The degree of activation was controlled by the duration of the milling for these cases. However, for more intense milling (and activation) a vibratory mill was used at reduced temperatures. The samples taken for various determinations during the milling were so small, usually 5 g or less, that they had little influence on the grinding efficiency during subsequent periods of milling.

For comparative purposes, wet milling was also carried out in a 1-liter stainless steel jar in which case 200 ml dry *n*-heptane was employed together with a charge of 75 g of α-$TiCl_3$ or α-$TiCl_3 \cdot 0.33AlCl_3$.

Particle size fractions, when required, were obtained with 200 and 400 mesh screen sieves in a nitrogen purged chamber.

Surface area determinations were carried out according to the BET (*15*) method by means of nitrogen adsorption at liquid nitrogen temperature in an Orr (*16*) surface-area pore-volume analyzer, Model 2100, manufactured by Micrometrics Instrument Corp., Norcross, GA. The sample degassing, was usually carried out at 100°C or lower to prevent crystallographic changes during this step.

X-Ray diffractometer traces were obtained on flat powder samples protected by dry nitrogen in a closed aluminum cell equipped with Mylar windows. Crystallite dimensions were determined from the breadth of the diffraction lines at half peak intensity; Sherrer's equation (with the constant 0.89) was used after correction for extraneous broadening had been made according to Warren's (*17*) method. The (003) and (300) planes of the alpha and gamma forms were found convenient for determining an average crystallite dimension in the direction of the crystal *c* axis (hexagonal symmetry axis) and in the directions perpendicular to this axis, respectively. As these planes also occur and reflect in the delta form, a unit cell was selected which would allow the aforementioned plane indices to apply also to the delta form.

B. Polymerization

All polymerizations were carried out in xylene diluent at atmospheric pressure in a baffled 2-liter resin flask equipped with high speed stirrer, propylene inlet tube, ice-cooled condenser and a thermowell containing thermometer and thermocouple. The polymerization procedure was the same as described for ball milled catalyst in a previous paper (*6*) although a temperature of 80 ± 0.5°C rather than 75°C was employed in some experiments as indicated in the text.

In addition to standard polymerizations lasting for 1 hr and giving the average polymerization rate during that period, polymerizations were carried out during which the rate of propylene disappearance was measured about every 2 min to obtain instantaneous kinetic data. In the latter case the inlet rate of propylene was held constant and the exit rate was monitored with a wet test meter. The difference gave the polymerization rate.

Replicate polymerizations with the same catalyst indicated that the polymerization rate for 1 hr could be duplicated with a precision of about 6% (95% confidence limits). The instantaneous rates appeared to be reproducible within about ±0.1 liter/min of propylene absorption, but no statistical limits were measured.

III. Experimental Results

Typical results obtained with the 1-liter mill are first briefly presented to provide a framework and base for the more detailed discussions of the ball milling activation phenomenon.

A. Activity as a Function of Milling Time

The effect of dry and wet milling of the solid catalyst component on catalyst activity is shown in Fig. 1. Note that the rate of activity increase is considerably greater for dry milling than for wet milling. In the case of the α-$TiCl_3 \cdot 0.33AlCl_3$ preparation, the catalyst activity reaches a maximum of only 44 g/g $TiCl_3$/hr after about 4 days of wet milling; by contrast, the activity of the dry milled catalyst is above 200 g/g $TiCl_3$/hr for 3 days of milling and, as previously reported, will eventually reach a maximum upon 6–9 days of milling with the equipment used in this experimental series (*6, 7*). Generally, pure α-$TiCl_3$ will require longer milling than α- or γ-$TiCl_3 \cdot xAlCl_3$ with the same equipment for maximum activity even though this is not clearly indicated by the data in Fig. 1.

B. Effect of Ball Milling on Particle Size, Surface Area and Crystallite Size and their Relationship to Activity

1. Particle size. That a considerable size reduction takes place during the early stages of ball milling is demonstrated by the data presented in Fig. 2. After the initial milling period, only a very modest particle size reduction is observed for dry milled α- and γ-$TiCl_3 \cdot 0.33AlCl_3$, while for the other three preparations, and especially wet milled α-$TiCl_3$ and α-$TiCl_3 \cdot 0.33AlCl_3$, a particle size increase is actually observed. Samples were not taken at sufficiently short intervals during the first day of milling to make it possible to establish the maximum particle size reduction and the time at which this occurred for the different samples. Nevertheless, the data from the wet milling of pure α-$TiCl_3$ indicates that such milling is capable of producing at least as fine particles as dry milling which is, of

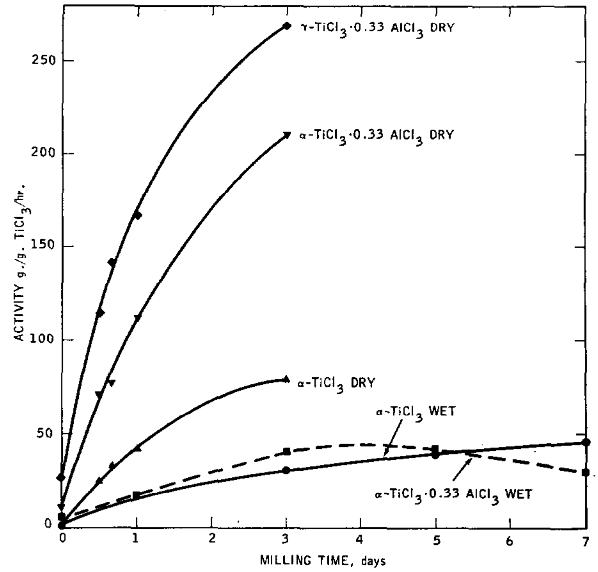


FIG. 1. Effect of milling time and type on catalyst activity.

course, in agreement with past experience in ball milling of solids in general.

A simple experiment was carried out to determine the effect of particle size on activity within a dry milled preparation of α-$TiCl_3 \cdot 0.33AlCl_3$. Two sieve fractions of the milled solid component were used; these fractions are characterized in Table 1. The instantaneous polymerization rate, as shown in Fig. 3, is initially significantly higher for the smaller particles, but after having reached a maximum after a few minutes, the polymerization rate declines more rapidly for the finer particles so that the rates become about the same for the two sieve fractions after about 20 min. As a result, the rate averaged over the first hour becomes only slightly higher for the finer particles.

If sieve fractions of a milled catalyst are

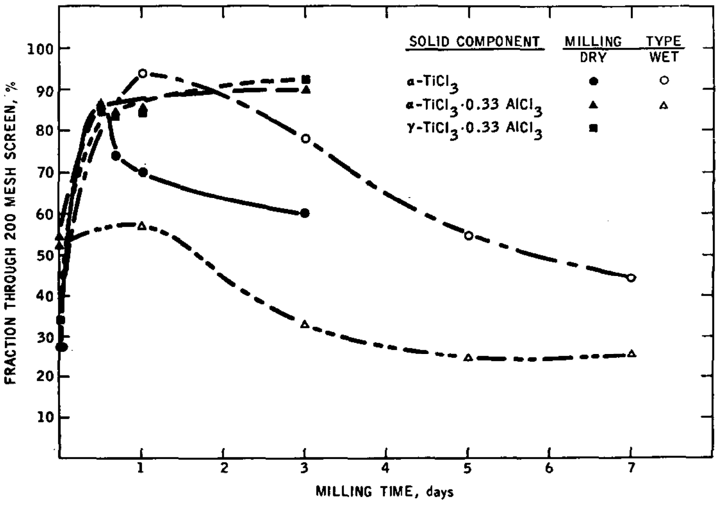


FIG. 2. Effect of milling time and type on particle size.

TABLE 1
Particle and Crystal Size of Sieve Fractions

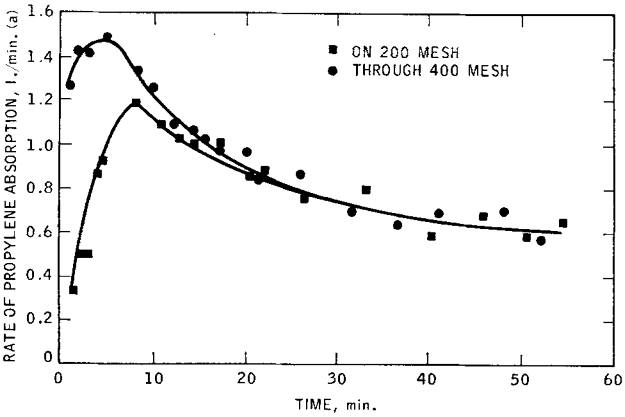
Sieve fraction	Percentage of total	Particle size (μm)	Crystallite size (Å)		Polymerization activity[a] (g/g/hr)
			D_{300}	D_{003}	
On 200 mesh	14	>74	69	89	272
Through 400 mesh	28	<37	70	86	303

[a] Calculated on $TiCl_3$ portion of solid component; polymerization temp, 80°C.

compared with those of the original unmilled catalyst, it becomes apparent that the catalyst activity is not controlled by particle size. This point is brought out clearly by the data in Table 2: coarse (>74 μm) particles of *ball milled* $TiCl_3$ and $TiCl_3 \cdot 0.33AlCl_3$ components are more than one order of magnitude more active than the altogether finer (<74 μm) particles obtained from *unmilled* fractions of the same catalyst preparations.

2. Surface area. The tendency of certain modifications of $TiCl_3$ to undergo crystallographic changes during heating to rather moderate temperatures, i.e., 100–150°C, presents a serious problem when the specific surface area of powders of such modifications is to be determined. That the brown modifications of $TiCl_3$ and $TiCl_3 \cdot xAlCl_3$ can be readily converted to corresponding violet modifications by heating to about 150°C, especially in the presence of a diluent, has been well established (*18*, *19*), but it has also been found that the delta forms of $TiCl_3$ and $TiCl_3 \cdot xAlCl_3$ undergo crystallographic changes, usually toward the formation of the α-$TiCl_3$ structure, when heated to temperatures as low as 100°C and that these changes are associated with an increase in the average crystallite size as measured by X-ray diffraction line broadening (*20*).

Since gases adsorbed on the surface of a sample must be removed before its surface area can be determined by gas adsorption measurement, it is common practice to heat such samples in a high vacuum to temperatures in the order of 200–400°C or even higher. Such heating will, of course, cause significant crystallographic changes in most $TiCl_3$ and $TiCl_3 \cdot xAlCl_3$ samples of the type used in this investigation and render the



(a) 2.5 mmole $TiCl_3 \cdot 0.33\ AlCl_3$, 5 mmole $AlEt_3$, 80°C.

Fig. 3. Rate of propylene absorption vs polymerization time for screened fractions of dry milled α-$TiCl_3 \cdot 0.33AlCl_3$.

TABLE 2
ACTIVITY VS PARTICLE SIZE FOR MILLED AND UNMILLED CATALYST COMPONENTS

Solid catalyst component[a]:	α-$TiCl_3$		α-$TiCl_3 \cdot 0.33AlCl_3$	
Milling time (days):	0	6[b]	0	4[c]
Particle fraction	Through 200 mesh	On 200 mesh	Through 200 mesh	On 200 mesh
Catalyst activity (g/g $TiCl_3$/hr)	4.7	122.0	23.6	251.3

[a] Structure before milling.

[b] 500 g charge in 7.7 liter jar.

[c] 340 g charge in 2.5 liter jar.

surface area measurements meaningless. Surprisingly, all investigators reporting on the surface area of $TiCl_3$ catalyst components, except for Begley (*21*), seem to be unaware of this problem and appear to be using degassing temperatures of 200°C or higher (*22–27*). After having used such high temperatures with at times somewhat erratic results in early investigations (*7*) we lowered the degassing temperature to 80–100°C and carried out this step at a pressure of 0.2 μm Hg for 20 hr or longer. While this may not lead to perfect degassing and hence to somewhat low (by perhaps 10%) values for the surface area, the error should be systematic and not influence the relative values significantly.

The results of surface area measurements on the same titanium chloride preparations as used for the particle size determinations (Fig. 2) are given in Tables 3 and 4. Except for the γ-$TiCl_3 \cdot 0.33AlCl_3$ component, the surface area increases with the time of milling for all preparations and appears to be essentially independent of particle size. In the former case it was noted that the solid contained a small amount of organic matter (less than 1%) which undoubtedly originated from the diluent used for the preparation. This material, which was at least in part volatilized and collected at the neck of the sample flask during the degassing step, probably interfered with the surface area measurement on this highly active catalyst component.

The relationship between the catalyst activity and surface area for dry and wet milled fractions of α-$TiCl_3$ and α-$TiCl_3 \cdot 0.33AlCl_3$, is shown graphically in Fig. 4. A reasonably good linear relationship is indicated for the dry milled catalyst components, especially if the unmilled (initial)

TABLE 3
EFFECT OF BALL MILLING ON MEASURED SURFACE AREA

Milling time (days)		Surface area (m^2/g)				
	Original component:	α-$TiCl_3$		α-$TiCl_3 \cdot 0.33AlCl_3$		γ-$TiCl_3 \cdot 0.33AlCl_3$
	Milling method:	Dry	Wet	Dry	Wet	Dry
0		1.28	1.28	1.13	1.07	5.0 ± 3.9 (3)
½		7.6	—	10.4	—	1.78 ± 0.20 (2)
⅔		12.7	—	11.7	—	4.2 ± 3.4 (2)
1		24.3	5.3	15.5	8.1	2.23 ± 0.99 (3)
3		32.2	13.3 ± 0.5 (2)[a]	30.6	12.2	7.1 ± 2.8 (4)
5		—	15.9		14.5	
7		—	25.5 ± 6.0 (2)		19.4 ± 1.4 (2)	

[a] Numbers in parentheses refer to number of determinations involved in calculating the averages and the *standard deviations.*

TABLE 4
RELATIONSHIP BETWEEN PARTICLE SIZE AND SURFACE AREA FOR VARIOUS TITANIUM CHLORIDE PREPARATIONS

Milling			Surface area (m^2/g)					
		Original component:	α-$TiCl_3$		α-$TiCl_3 \cdot 0.33AlCl_3$		γ-$TiCl_3 \cdot 0.33AlCl_3$	
Time (days)	Type	Sieve fraction:	Total	>200 Mesh	Total	>200 Mesh	Total	>200 Mesh
0			—	—	—	—	4.3	4.9
3	Dry		32.2	29.8	30.6	29.0	7.1	6.7
7	Wet		23.4	20.2	18.9	24.0	—	—

preparations are excluded, whereas in the case of wet milled components, the increase in activity begins to fall behind the increase in surface area for longer periods of milling, and in the case of the $TiCl_3 \cdot 0.33AlCl_3$ preparation, the activity even begins to drop after about 4 days of milling (Fig. 1).

It should be noted further that the $TiCl_3$ samples exhibit almost the same activity for the same surface area independent of the type of milling while, on the same basis, the dry milled $TiCl_3 \cdot 0.33AlCl_3$ fractions are much more active than the wet milled ones.

For reasons given above, no reasonable correlation could be established between surface area and catalyst activity of the dry milled γ-$TiCl_3 \cdot 0.33AlCl_3$ components.

3. Crystallite size. Dry milling causes very drastic crystallographic changes in layer lattice type $TiCl_3$ and $TiCl_3 \cdot 0.33AlCl_3$ preparations as illustrated by the diffraction patterns shown in Figs. 5 and 6. The essentially complete conversion of both the alpha (Fig. 5) and the gamma (Fig. 6) form of $TiCl_3 \cdot 0.33AlCl_3$ into the delta form, which is characterized by disordered chlorine stacking (*4*, *6*, *12*) is easily recognizable after 72 hr of milling. Also it can be noted from the line broadening that a significant crystal size reduction has occurred.

By contrast, intense wet milling of the same preparations produced only minor crystallographic changes. This is illustrated in the diffractograms in Fig. 7 for the alpha

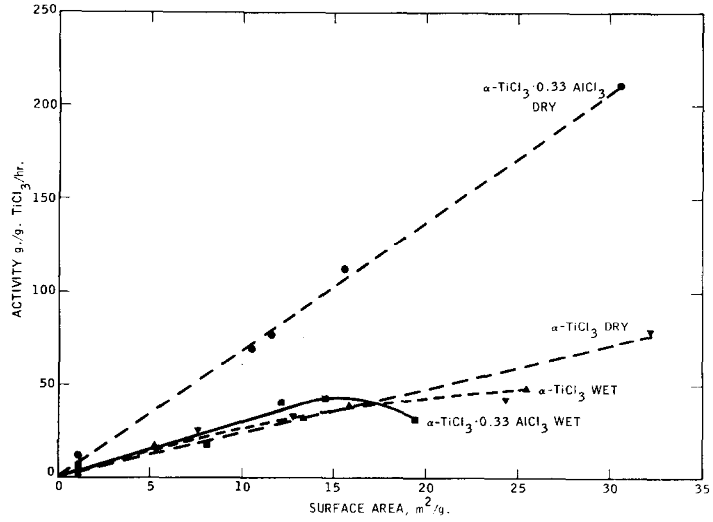


FIG. 4. Relationship between catalyst activity and surface area for various titanium chloride preparations.

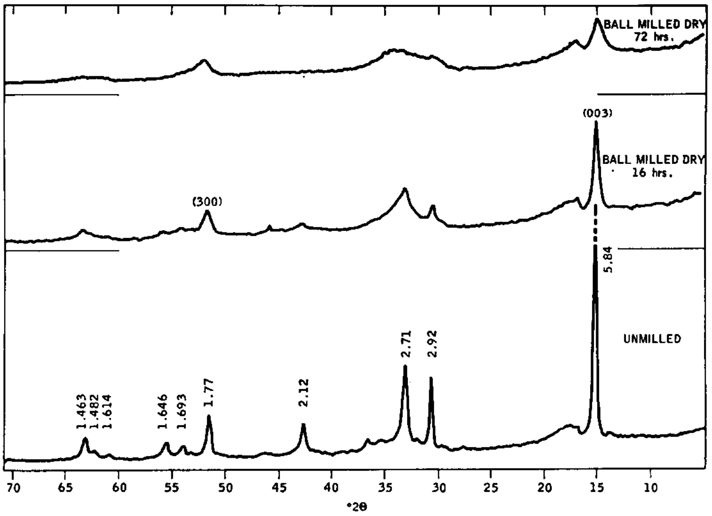


FIG. 5. X-Ray diffraction patterns of unmilled and dry milled α-$TiCl_3 \cdot 0.33AlCl_3$.

form. Even after 7 days of wet milling there is no apparent transformation to the delta form, and the lines are only moderately broadened. Differences in the relative intensity from trace to trace are ascribed to differences in the preferred orientation of crystallites in the respective samples. As these materials tend to crystallize in the form of platelets, the powders are very susceptible to preferred orientation when packed into a sample holder for diffraction analysis.

The greater effectiveness of dry milling in reducing crystal size and increasing activity is demonstrated by the data in Table 5.

A more detailed investigation of the effect of dry grinding on crystallite size and activity was carried out with a separately prepared γ-$TiCl_3 \cdot 0.33AlCl_3$ catalyst component. The experimental data are summarized in Table 6. Note that with increasing milling time the crystallite dimensions D_{300} and D_{003} (measured from the 300 and 003 lines, respectively) decrease progressively. The polymerization rate in-

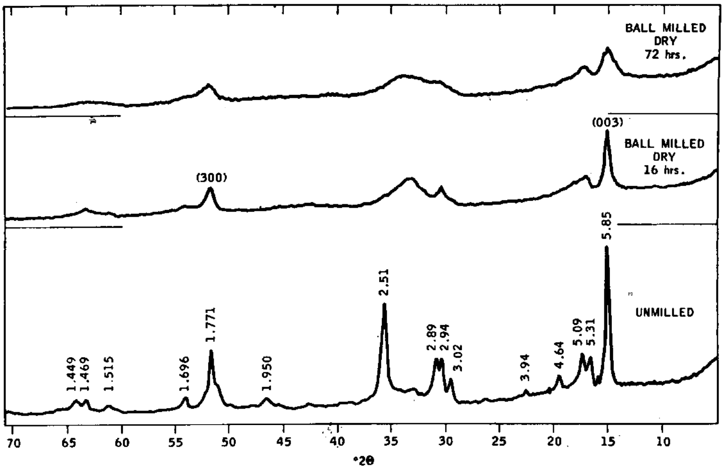


FIG. 6. X-Ray diffraction patterns of unmilled and dry milled γ-$TiCl_3 \cdot 0.33AlCl_3$.

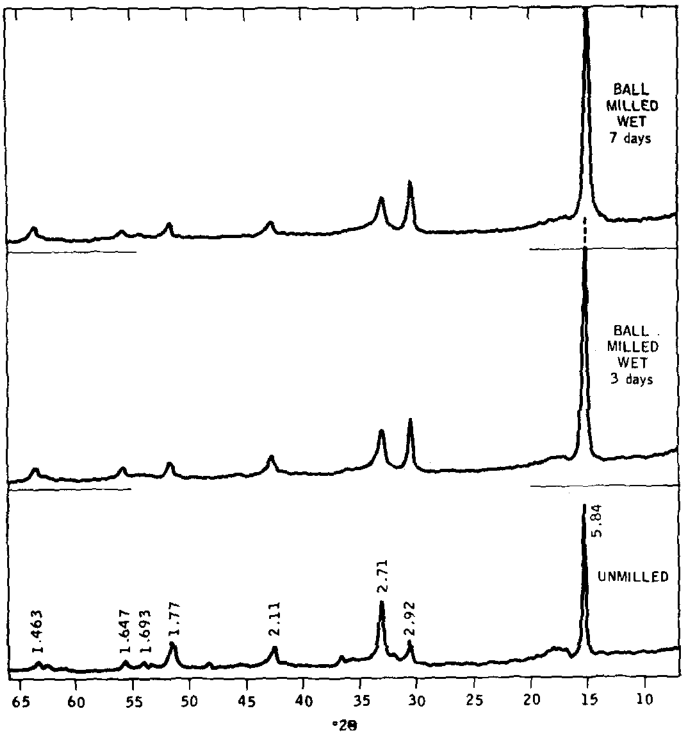


FIG. 7. X-Ray diffraction patterns of unmilled and wet milled α-$TiCl_3 \cdot 0.33AlCl_3$.

creases with decreasing crystallite size down to about 50 Å. Further reduction of the crystallite size, either by longer milling time or by milling at low temperature, leads to an anomalous decrease in activity; and the catalyst is referred to as being in an "overmilled" condition.

For the "normally" milled catalyst components, plots of the activity as a function of $1/D_{300}$ and $1/D_{003}$, respectively, indicate

TABLE 5
COMPARISON OF THE EFFECT OF WET AND DRY MILLING ON THE CRYSTALLITE SIZE AND POLYMERIZATION ACTIVITY OF TITANIUM CHLORIDE COMPONENTS

Titanium chloride[a]	Milling conditions: Type	Milling conditions: Time (days)	Crystallite size (Å): D_{300}	Crystallite size (Å): D_{003}	Polymerization rate[b] (g/g/hr)
α-$TiCl_3$	—	0	>1000	690	1.35
	Dry	3	138	182	78.8
	Wet	7	1000	527	46.9
α-$TiCl_3 \cdot 0.33AlCl_3$	—	0	358	660	10.4
	Dry	3	87	84.5	210.9
α-$TiCl_3 \cdot 0.33AlCl_3$	—	0	274	>1000	5.2
	Wet	7	276	527	30.8

[a] Structure refers to starting material.

[b] Calculated on $TiCl_3$ portion of solid component.

TABLE 6

EFFECT OF DRY GRINDING ON CRYSTALLITE SIZE AND POLYMERIZATION ACTIVITY OF $TiCl_3 \cdot 0.33AlCl_3$ COMPONENT

	Milling time (hr)		Crystallite size (Å)		Polymerization rate[a] (g/g/hr)
	Tumble mill	Vibrator mill	D_{300}	D_{003}	
A. Normal Milling					
a. Initial material	—	—	820	318	—
b.	2	—	206	275	93.5
c.	4	—	180	280	113.0
d.	6	—	120	207	131.1
e.	8	—	119	167	148.4
f.	12	—	93	148	174.9
g.	16	—	84.5	130	211.7
h.	24	—	74	78.5	264.2
i.	48	—	55	56	375.6
j.	96	—	47	55	414.5
B. Overmilling					
k.	159	—	46	46	334.2
l.	96	0.5 (−40°C)	45	33	312.7
m.	—	0.5 (−70°C)	43	23	175.1

[a] Calculated on $TiCl_3$ portion in solid component.

reasonably close linear correlations as shown in Fig. 8. A marked departure from each correlation line is apparent for the overmilled cases.

IV. DISCUSSION

The data presented in the preceding sections demonstrates clearly that drastic and surprising milling effects are obtained only when the solid titanium chloride preparations are ground under *dry* conditions. The only unexpected results of wet milling are the increase in particle size which occurs after about one day of milling for both preparations (Fig. 2) and the fall off in activity which is observed for the $TiCl_3 \cdot 0.33AlCl_3$ component after 4–5 days of grinding. However, these effects appear to be caused by tarry material formed via diluent degradation during the milling. The

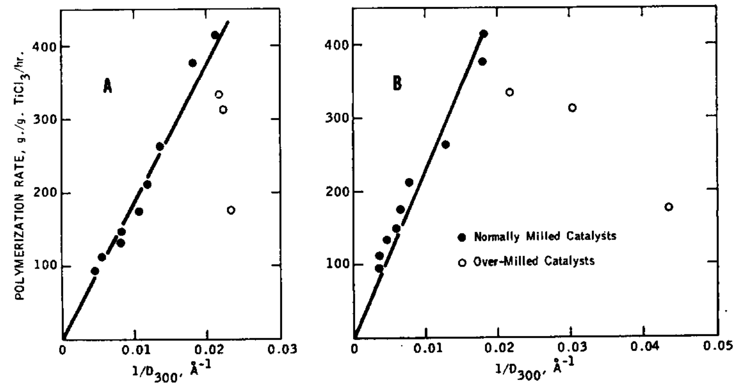


FIG. 8. Correlations between polymerization rate and crystallite dimensions. Lines are least squares fit through the origin. Standard deviations of polymerization rate from correlation lines are 15 and 20 g/g/hr for the $1/D_{300}$ and $1/D_{003}$ plots, respectively.

strong Lewis acid character of the $TiCl_3$ preparations, and especially those containing cocrystallized $AlCl_3$, is unquestionably responsible for this phenomenon which will not be discussed further, since it has no direct bearing on the inherent properties of the catalysts under discussion.

Aside from the very great increase in catalyst activity, the most striking effect of dry grinding are the crystallographic changes which take place during such treatment. The nature of these changes is by now well understood, and they can be explained as a direct consequence of the layer lattice structure of these materials. Apparently, only dry grinding produces sufficiently strong shear forces to cause sliding at the metal-free interfaces of the Cl–M–Cl double layers. However, the resulting crystallographic changes do not in any way offer an explanation for the drastic activating effect of dry grinding.

On the other hand, the rather good linear correlations established between catalyst activity and both measured surface area and crystallite size, suggests that either or both of the latter parameters are of primary importance for the activity. As we are dealing with heterogeneous catalysis, it may seem logical to assume that the increased activity derives directly from the increase in surface area. However, aside from the fact that a direct relationship between surface area and catalyst activity could not be derived for the ball milled fractions of γ-$TiCl_3 \cdot 0.33AlCl_3$, which were the most active ones for any given time of milling, there are certain factors that speak strongly against such a notion.

On the basis of the particle size analyses and the surface area measurements, it can be concluded that most of the surface area of the various ball milled fractions must be internal and that the ratio between the internal and external surface areas increases with the degree of milling. Since the specific surface area appears to be independent of particle size within each given sample (Table 4), one may also conclude that the degree of porosity is essentially independent of particle size.

If the reactants and reaction products were small gaseous or at least hydrocarbon soluble molecules, it would indeed be reasonable to expect the activity to be proportional to the available surface area. However, polypropylene is insoluble in the reaction medium and cannot escape from the particles, especially when formed in a cavity or "pore." Since the bulk density of the extensively dry milled components is about 1.0–1.3 g/ml and the X-ray density of α-$TiCl_3$ is 2.68 g/ml (*8*) and somewhat less for α-$TiCl_3 \cdot 0.33AlCl_3$, the maximum volume fraction of pores *and* void space between particles in a bulk sample is 60%, corresponding to 0.6 ml/g. As the efficiency of the more active catalysts reaches values in the order of 300–400 g polymer/g $TiCl_3$/hr and the density of polypropylene is about 0.9 g/ml, this volume can only accommodate the amount of polymer formed during 5–10 sec at the average polymerization rate observed in 1 hr polymerizations. After the pores have been filled with polymer the particles will either have to disintegrate with the formation of much new surface area or the polymerization on the internal surfaces will have to cease. In neither case will the measured surface area be meaningful for the determination of specific activity.

Since the catalyst activity does not decline but rather continues to increase until it reaches a maximum after about 5 min (Fig. 3), it is obvious that a dispersion phenomenon must occur shortly after the polymerization has started. Actually, it was noticed early in our studies that catalyst dispersion is of critical importance to good catalyst activity (*5*), and the same observation was subsequently made and reported by several workers (*28–31*).

When examining a sample of hydrogen reduced violet $TiCl_3$ under a microscope, Natta, Pasquon, and Giachetti (*29*) found that the individual particles were largely made up of aggregates of more or less well developed hexagonal crystals. The relatively slow buildup in activity to a constant value, within about 2–7 hr, in propylene polymerizations was attributed to a breakup of the crystalline aggregates and a cleavage of imperfect crystals under the influence of the growing polymer. In order to prove that a slow catalyst dispersion was, indeed, responsible for the long induction period, Natta subjected the $TiCl_3$ sample to wet grinding, either in pure *n*-heptane or in *n*-heptane containing some $AlEt_3$, in the belief that such treatment would cause good dispersion of the catalyst prior to the polymerization. When the wet milled $TiCl_3$ preparations were tested without intermediate drying, it was found that the induction period had indeed been shortened very drastically.

From the evidence presented for the dry milled catalyst components, it may be concluded that they, too, consist of particles which are agglomerates or at least have the character of agglomerates of much smaller units which are separated from each other during the polymerization. On the basis of the rather close linear correlations found between activity and both $1/D_{300}$ and I/D_{003} (Fig. 8), it seems reasonable also to conclude that the smaller units in the agglomerates are crystallites having the average dimensions corresponding to D_{300} and D_{003}. However, the question that has to be answered is what these small units look like and why they are formed only during dry and not during wet milling.

As observed by Natta, Pasquon and Giachetti (*29*) for α-$TiCl_3$ and Bailey (*28*) for a variety of layer–lattice type $TiCl_3$ and $TiCl_3 \cdot xAlCl_3$ preparations, these materials, as originally prepared, largely consist of more or less well-developed thin hexagonal crystals which have a great tendency to agglomerate into large particles in the dry state. The average diameter of the crystals is in the range of 0.1–1 μm and the ratio between their breadth and their height is usually in the range of 25–100. In the agglomerates the crystals are primarily stacked on top of each other in the manner indicated in Fig. 9. The forces that hold together the Cl–M–Cl double layers within the crystals will, of course, also act between the corresponding basal (001) faces of two separate crystals if they are brought into proper contact. Since little particle size reduction occurs, it is clear that dry grinding does not result in any extensive breakup of the agglomerates. However, such treatment, if sufficiently intense, does cause extensive sliding between the Cl–M–Cl double layers within the individual crystals

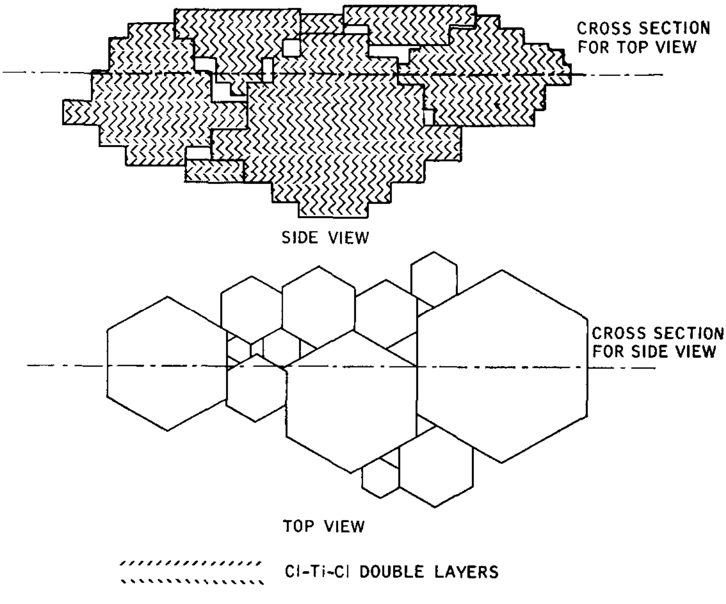


FIG. 9. Schematic representation of part of $TiCl_3$ particle consisting of several agglomerated crystals.

as indicated by the observed crystallographic changes. The distance of the slide at the interface between two double layers will undoubtedly vary from case to case depending upon the size of the crystal and the intensity of the shear causing the slide. Complete cleavage will probably occur occasionally with the formation of two thinner and hence more easily fragmented crystals, but in most cases the slide will undoubtedly amount to only a fraction of the width of the crystal. This results in the formation of an imperfect crystal which has two thinner portions protruding in opposite directions from the center which has the thickness of the original crystal. The protruding sections will obviously be broken off very readily, yielding much smaller crystalline fragments or crystallites. This process will continue until an equilibrium has been reached between the rates of crystal breakdown and crystal buildup, which must also be taking place. The average crystallite size at this equilibrium will undoubtedly depend upon the grinding conditions, and, under certain conditions, the reduction in size may be so great that other crystallographic phenomena begin to enter into the picture as discussed below.

The small fragmented crystals or crystallites in the particles should be responsible for the X-ray line broadening and thus correspond in average size to the calculated D_{300} and D_{003} values. As shown in Table 6, the particles in the more intensely milled "normal" samples have D_{300}/D_{003} ratios close to unity. Hence, they can no longer consist of thin leaf-like hexagonal crystals as in the original preparations. In consequence the tendency toward ordered stacking of the type indicated in Fig. 9 may be considerably lower than in the original unmilled preparation. While the total surface area of the individual crystallites should eventually become exposed to $AlEt_3$ and monomer as a consequence of the dispersion caused by the growing polymer, only the outer surfaces of the agglomerated particles will be immediately available for active site formation and polymer growth. Hence, it is only natural that finer particles—which should also disperse faster—should exhibit significantly higher initial polymerization rates than coarser ones as shown in Fig. 3. That considerable polymer formation does, indeed, take place on the outside of the agglomerates before any significant dispersion has taken place is also demonstrated by the fact that a very close size relationship exists between the original catalyst particles and the resulting polymer particles (*31–33*). The polymer envelope formed around the original catalyst particles at the beginning of the polymerization will be stretched very considerably as the catalyst disperses and more polymer is formed, but it will continue to contain the crystallites within the same particle.

The rather close linear relationship between the reciprocal of either catalyst dimension and the average catalyst activity over 1 hr (Fig. 8) may seem surprising in view of the fact that the catalyst dispersion does require some time to reach completion. However, the time required for this process is much shorter than 1 hr in all cases (cf. Fig. 3) so that the amount of polymer produced in 1 hr is large compared to that formed during the catalyst dispersion. In addition, the more intensely milled catalysts, which are subject to the greater activity increase during the dispersion period, seem to disperse more readily than the less intensely milled components, a behavior that is not unexpected since the forces that hold together the crystallites in the particles should get weaker as the crystallites decrease in size and regularity.

As the parameters $1/D_{300}$ and $1/D_{003}$ have simple geometric interpretations, $1/D_{300}$ being proportional to the specific lateral surface area and $1/D_{003}$ to the specific basal surface area, if prismatic crystallites are considered, a statistical analysis of the correlations in Fig. 8 could possibly be used for determining the location of the active sites on the primary catalyst particles (crystallites). Both the basal (001) and the lateral (*hk*0) faces have been suggested as the preferred location of these sites. However, it is now fairly well agreed that the active sites are normally formed and located on the lateral faces (*34*). The particular structural features exhibited by the edges of a Cl–

Ti–Cl double layer were initially used as a very strong argument in favor of active site formation on these faces (*6*, *35*). The correctness of this notion was confirmed by Rodriguez and Van Looy (*36*) who published electron micrographs of α-$TiCl_3$ showing polypropylene being formed on the lateral faces. On the basis of this fact one would expect the polymerization rate to be proportional to $1/D_{300}$ as is shown to be the case in Fig. 8A. However, statistical evaluation reveals that this correlation is not significantly better than the one obtained when activity is plotted against the $1/D_{003}$ dimension (Fig. 8B). A significant difference can occur only if the two crystallite dimensions change in a nonproportional manner. Although the relative decrease in these dimensions was not proportional, it did not differ much for many milling intervals, especially if one disregards the original unmilled material for which the polymerization activity was not determined. Consequently, the correlations of Figure 8 cannot be used with any reasonable degree of confidence in assigning the location of the active sites. To be consistent with other experimental evidence, we prefer the correlation of Fig. 8A which implies that the active sites are on the lateral faces of the crystallites. Even though the interpretation cannot presently be refined to a greater degree, this correlation method appears universally useful for layer lattice type $TiCl_3$ and $TiCl_3 \cdot xAlCl_3$ preparations, and, unlike the surface area–activity correlation, it will be useful also when substances that interfere with surface area measurements are present.

Our final comments concern the anomalous effect referred to as overmilling. The overmilled solid component is characterized by a very small crystallite size, especially for the D_{003} dimension. If such materials are carefully heated so that the crystallite size increases (e.g., to circa 200 Å), their catalytic activity falls on the correlation line for normal milled components (*37*). From this, one could infer that the abnormally low activity of overmilled catalyst is somehow associated with the small size of the crystallites rather than with possible poisoning effects during the intensive milling.

A possible clue to the low activity is the observed change in color from bright purple-violet for the normally milled catalyst component to brownish purple for the overmilled. As the color of the β-modification of $TiCl_3$ is brown, while that of all the other modifications, including the δ-form, is purple to violet, it is definitely suggested that a change from δ- to β-structure was taking place. Such a change appears quite reasonable in view of the high percentage of incompletely coordinated Ti atoms that must be present in crystallites of the size indicated for the overmilled preparations if they retain their layer lattice structure (Table 7).

Unquestionably, the pentacoordinated Ti atoms at the surface will have a great tendency to increase their coordination number to six either by complexing with some other available compound or by a structural rearrangement. Since no other compound is present, except for other crystallites which could get involved through an annealing effect at higher temperatures, only the latter alternative is available for solving the coordination problem, at least at lower temperatures.

One possible rearrangement which will decrease the number of incompletely coordinated Ti atoms for very small crystallite sizes involves a change to the so-called β-modification, which is catalytically much less active than the α-, γ- or δ-forms. As first described by Natta *et al.* (*9*) β-$TiCl_3$ has the chlorine atoms in a close packed hexagonal layer arrangement as in α-$TiCl_3$, but the titanium atoms are arranged in columns parallel to the *c* axis so that a

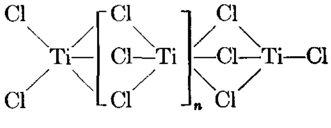
TABLE 7

FRACTION OF INCOMPLETELY COORDINATED TITANIUM ATOMS IN A HEXAGONAL DOUBLE LAYER OF A GIVEN WIDTH

Width D_{300} (Å)	Percentage incompletely coordinated Ti atoms	
	(110) Face[a]	(100) Face[a]
46	26.7	23.0
45	27.3	23.6
43	28.6	24.7

[a] As defined by the system of hexagonal axes employed by Klemm and Krose (*8*).

fiber-like rather than a layer-lattice type structure is obtained. Electroneutrality as well as the correct composition is obtained by putting titanium atoms on each side of three closest-packed chlorine atoms and by making each fiber a self-contained unit. Therefore, independent of its length each fiber unit will contain only two exposed and hence incompletely coordinated Ti atoms as shown below:



Actually, in the case of $TiCl_3 \cdot xAlCl_3$, the tetracoordinated metal atom may be aluminum, in which case one would have only one incompletely coordinated Ti atom per fiber unit. By comparison, a single Cl–M–Cl double layer will have a minimum of 6 incompletely coordinated Ti atoms as shown in Fig. 10. The species shown in Fig. 10a represents the extreme case in which all the Ti atoms are pentacoordinated. If ever obtainable, this particular species would certainly be expected to rearrange to a more stable structure, e.g., the β-form. The average D_{300} dimensions for the overmilled catalysts, 43–46 Å, are, of course, much greater than that of the species in Fig. 10a which corresponds to about 9.7 Å; but although the exact size distribution for the crystallites in the milled samples is not known, some crystallites will undoubtedly be considerably smaller than the average, e.g., of the size shown in Fig. 10b. Although there may be some tendency for the transformation to the β phase to occur in the larger crystallites, the tendency will be stronger in the smaller ones, especially, when the D_{003} dimension is also small and the reinforcing effect of several layers is diminished. Although this mechanism seems reasonable, it is presently regarded as a tentative explanation of overmilling, pending further confirmation.

V. CONCLUSIONS

The unique and surprising activating effect resulting from extensive dry ball milling of layer lattice type $TiCl_3$ and $TiCl_3 \cdot xAlCl_3$ components has been shown to be a direct consequence of the capability of these materials to undergo extensive crystallite size reduction far beyond what would normally be expected from such a treatment. This crystallite size reduction, which increases with the severity of milling up to a certain level, appears in turn to be a function of the particular crystal structure of these ma-

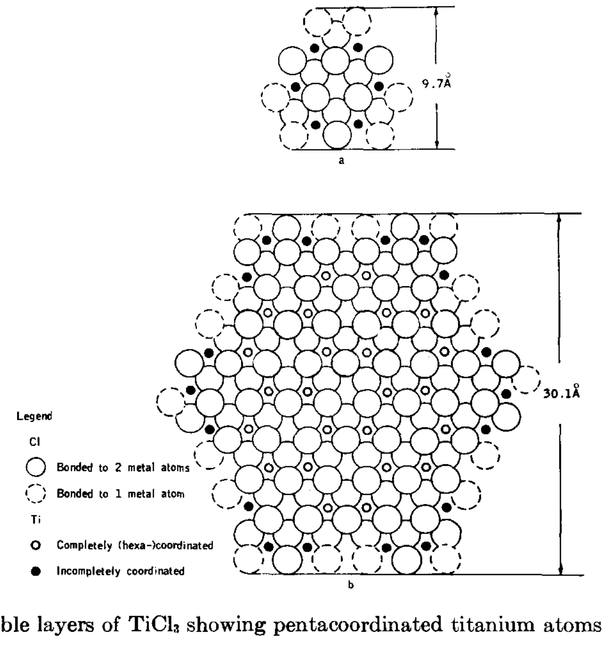


FIG. 10. Double layers of $TiCl_3$ showing pentacoordinated titanium atoms at the edges.

terials, which makes double layer sliding possible when the intensity of shear is sufficiently high. As a consequence, the crystallite size reduction will always be accompanied by a change in the basic crystal structure from the α- or the γ-form to the less ordered and hence in a sense less "crystalline" δ-form. Complete conversion to the latter form will normally occur before maximum crystallite size reduction has occurred, hence, a properly activated catalyst component will normally exhibit the X-ray diffraction pattern of the δ-form.

Another factor, closely associated with the crystal structure, which tends to make the unusually severe crystallite size reduction possible, is the tendency of the crystallites to agglomerate into rather firm but porous particles of almost constant size independent of the crystallite size itself, thus allowing the shear forces acting on the crystallites to be much more severe than they would have been had the crystallites existed as individual species or in small agglomerates.

Stresses produced, first at the surface and later within the particles, as a result of polymer growth leads to deagglomeration of the particles and exposure of fresh active surface which eventually, for more active catalysts within 5–10 sec, approximates in size the surface area of the individual crystallites. When this has happened, the catalyst activity becomes dependent upon the crystallite size.

For a given catalyst preparation, the activity increases with decreasing crystallite size until a minimum average size has been reached, corresponding to a value of about 50 Å for both the D_{300} and D_{003} dimension. Further reduction in crystallite size results in a less active catalyst, probably because of the tendency of very small crystallites to change their crystal structure to the less active β-form.

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