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Ethylene Dimerization over Supported Titanium Alkoxides

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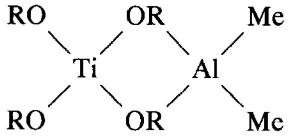
$Ti(OEt)_4$ can be reduced by various metal alkyls to yield an active catalyst for the dimerization of ethylene to 1-butene. Whatever metal alkyl is used for reduction, dimerization occurs only when aluminum alkyl is also present, suggesting that it, too, must be part of the active site. The amount of aluminum added, i.e., the Al/Ti ratio in the reactor, is extremely critical to the activity, and the optimum ratio depends on the particular catalyst preparation. Anchoring the catalyst to a carrier, such as silica, alumina, or aluminophosphate, seems to stabilize the active species as indicated by the relatively constant kinetic response, which produces better overall activity. The effectiveness of each carrier, its calcining temperature, and various preparation methods is discussed.

INTRODUCTION

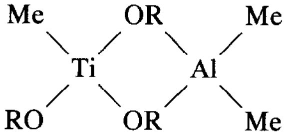
Pioneers of the early olefin polymerization catalysts discovered that one transition-metal-based system, titanium(IV) alkoxide combined with trialkylaluminum, produces butene on contact with ethylene rather than the usual high polymers (*1–5*). Since then, numerous workers have studied the catalyst (*6–16*) and verified that the product can be very selective. 1-Butene is always the main product, but small amounts of 2-butenes and higher olefins can also be formed, depending on the reaction conditions, and the choice of ligands (*16–21*).

Opinions differ concerning the exact nature of the active species, but all agree that the reduction of the titanate is a complicated reaction. A variety of species are formed, depending on the amount of aluminum alkyl used. Numerous trivalent species have been detected by ESR (*6–11*) and various aluminum–titanium bridging structures have been proposed as candidates (*5–12, 15–17*). In some studies, the extent of reduction was believed to be small, leaving mainly Ti(IV) species in solution. In other cases, however, even the divalent state was considered as a likely product. For example, Christenson *et al.* used chemical ionization mass spectrometry in a recent study, and proposed that the following three structures result when titanium isopropoxide is reacted with trimethylaluminum (*17*). The ratio of the two ingredients in solution determines which species predominate.



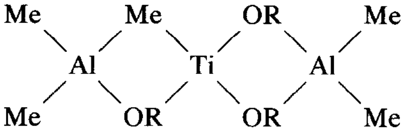
At Al/Ti $\leqslant 1$

I



At Al/Ti = 1

II



At Al/Ti = 10

III

0021-9517/87 $3.00

In addition to ethylene, other monomers can be polymerized by this catalyst system. But again the extent of reduction is critical, and there is evidence that different species are responsible for polymerizing the different monomers. For example, optimum activity for styrene polymerization occurs at an Al/Ti ratio of 1.4 (*9*) whereas butadiene, which exhibits no reaction there, becomes quite active at Al/Ti of 5.8 (*14*). Other monomers prefer other states of reduction: Acetylene 0.75–1.5 Al/Ti (*22*); methylmethacrylate and dienes 5^+ (*13, 14*); ethylene 2.4–3.0 (*5*); styrene 1.5 (*9*). Thus the system seems to be highly complex.

Recently Kissin and Beach (*23, 24*) have utilized this catalyst in a dual dimerization/polymerization system. They report that $Ti(OR)_4$ can function as one component in a system which simultaneously dimerizes and polymerizes ethylene in one reactor. The object is to produce ethylene–butene copolymers from one ethylene feedstock. The 1-butene produced by the dimerization catalyst would then be copolymerized with ethylene by a more conventional $TiCl_4$/$MgCl_2$ polymerization catalyst.

Unfortunately, $Ti(OR)_4$ can also exhibit some undesirable qualities in this application. It has a short, sometimes unpredictable, lifetime. Being a liquid, it can interfere with the solid polymerization catalyst. We have noticed that it often has a tendency to foul a slurry reactor by coating the walls with a polymeric film. In this study, we have tried to address these problems by supporting the catalyst on a high surface area carrier, which to our knowledge, has not been reported previously.

EXPERIMENTAL

The carriers used in this study were all of high porosity, suitable also as polymerization catalyst supports. The silica, Davison Grade 952, has a pore volume of about 1.6 cc/g and a surface area of around 280 m^2/g. The alumina was Ketjen Grade B, having a similar porosity, and the aminophosphate was made by coprecipitation (*25*) of aluminum and phosphate ions in a $P/Al = 0.9$ ratio. It also had a pore volume of about 1.6 cc/g. These supports were calcined by fluidization in dry air at 0.1 ft/s for 3 h. They were then cooled and stored under dry nitrogen.

Dimerization studies were conducted in a 2-liter stirred autoclave using purified isobutane as the diluent. First the catalyst was charged, usually 0.3–0.9 g of the supported catalysts. Then 1 liter of isobutane liquid was added which also contained triethylaluminum (TEA). Finally, the ethylene was supplied on demand at 550 psig (38.4 atm). The dimerization rate was determined by continuously monitoring the ethylene flow into the reactor. Most runs were stopped after 30 min by flashing off the isobutane. The reactor was then opened and the polymer, if any, recovered. Activities are reported in terms of grams of ethylene consumed per gram of titanium per hour, g/g-Ti/h, as well as moles of ethylene per mole of titanium per second in parentheses (mol/mol-Ti/s).

The reaction temperature was controlled accurately by means of a pressurized jacket. Most runs were made at 95°C, but some were done at other temperatures ranging from 80 to 100°C the vapor pressure of isobutane is near 300 psi (20.4 atm), so the reaction liquid contained about 20 mol% ethylene. In some runs, 50–100 psi (3.4–6.8 atm) of hydrogen was also added to the reactor before ethylene addition. Olefin distributions were determined by sampling the reaction liquid at the end of the run.

Previous workers have reported that the Al/Ti ratio in the reactor is critical for the $Ti(OR)_4$ catalyst. We also found this to be true, and in these experiments tried to hold the TEA concentration within a narrow range, varying the titanium component instead. Usually, 1–3 ml of 15 wt% TEA was added to 1 liter of diluent.

RESULTS AND DISCUSSION

1. *Unsupported Catalysts*

Reduction of titanium alkoxide. When an aluminum alkyl, such as triethylaluminum

(TEA), is added to a hydrocarbon solution of titanium(IV) alkoxide at room temperature, an immediate reaction can be observed. The initially colorless reagents combine to create a dark green or blue-green solution when about one reducing equivalent or less is added to the titanium solution. The reaction is very complex (*5–11*). Many species are thought to be formed, including some reduction to Ti(III). Based on ESR evidence, Takeda *et al.* (*9*) believe that green color comes from an alkylated trivalent titanium alkoxide, TiR $(OR)_2$. Others suggest similar but more elaborate structures involving bridging to one or more aluminum atoms, as shown in **I** (*6–12, 15–17*).

In this study, titanium ethoxide was used as the starting material. In heptane, a blue-green solution forms when TEA is added, followed within an hour by precipitation of a floculent, dark green solid. In toluene, a similar transition takes place but the precipitation occurs over a period of days if at all, depending on the concentration.

We found that other reducing agents can be substituted for the TEA. Adding one reducing equivalent of dialkylmagnesium quickly forms a green precipitate having a slight yellowish appearance. Diethylzinc reacts more slowly with $Ti(OEt)_4$ in toluene, changing from pale yellow at first to green, then to a dark blue solution over about 2 h. Slight precipitation occurs overnight. Butyllithium produced a purple stage before the blue-green color developed. Both the dialkylzinc and alkyllithium reduced material were more soluble than that obtained from dialkylmagnesium. Triethylborane exhibited no apparent reaction.

The blue or green color is no doubt associated with a Ti(III) alkoxide species, but it may also involve a complex with the reducing metal, since the pure trivalent alkoxides are highly insoluble in hydrocarbons (*5, 9*). This would account for the different precipitation rates and the slight color variations. In no case was the white ethoxide of Mg, Li, or Zn observed precipitating out of solution.

If more trialkylaluminum is added, say in a 1 : 1 Al/Ti ratio, a brown or red-brown solution forms, followed sometimes by the slow precipitation over days of a small amount of fine brown solid. Most of the titanium, however, remains in toluene solution. This is thought to be a complex of a Ti(III) or Ti(II) alkoxy species, again possibly alkylated, with bridging to aluminum neighbors (*6–12*), such as in **II** or **III** (*17*). Adding more reducing agent, such as 3 TEA/Ti, yields no further color change. Apparently, the process is reversible because adding $Ti(OEt)_4$ to the brown solution (1 : 1 Al/Ti) converts the color back to green (0.3 : 1 Al/Ti).

Other reducing agents were also found to yield a brown material, similar but not identical to the brown Al complex. Dialkylmagnesium added in a 1 : 1 Mg/Ti ratio yielded heavy red-brown precipitate, and diethylzinc (1 : 1 Zn/Ti) and butyllithium (2 : 1 Li/Ti) formed a brown solution. Adding TEA to a precipitated Mg complex (2Mg/Ti) caused it to dissolve again—evidence for complexation with the TEA.

Ethylene dimerization. All of these compounds were active catalysts for the dimerization of ethylene to 1-butene when placed in a reactor at 80–100°C with additional aluminum alkyl. However, each had a slightly different behavior. In some cases, the dimerization started vigorously and then decayed to zero within 15–20 min. Other catalysts displayed a steady profile. Also, it is known that the Al : Ti ratio in the reactor can be critical (*5*), and here too this was found to be the case, but each compound had its own optimum. These differences are summarized in Table 1.

Adding titanium ethoxide directly to the reactor, as has usually been done in previous studies (*5, 15–21*), followed by triethylaluminum in the isobutane diluent, immediately produced a strong dimerization reaction. The activity was short lived, and often the catalyst was inactive after only 20 min, indicating an unstable active species. Figure 1 shows an example. Like previous workers (*5, 23*), we found that the

TABLE 1

Unsupported Catalysts

Starting form	Active range Al/Ti in reactor	Activity g/g-Ti/h	Activity (mol/mol-Ti/s)	Kinetic profile
$Ti(OEt)_4$	3–6	3000–4000	(1.4–1.9)	Vigorous start, rapid decay
Blue-green (0.3 Al/Ti)	1–6	2000–5000	(0.95–2.4)	Vigorous start, then decay
Red-brown (1–3 Al/Ti)	3–5	3000	(1.40)	Steady
Blue-green (0.5 Mg/Al)	0.4–3	2000–4000	(0.95–1.9)	Variable

preferred Al/Ti ratio in the reactor was about 3 to 6. At values below 2, we were unable to obtain activity, and too much reducing agent (Al/Ti = 10) also deactivated the catalyst. Figure 2 plots the activity measurements against Al/Ti ratio in the reactor for this and other catalysts.

The blue-green solution, obtained when TEA is added to $Ti(OEt)_4$ in toluene at a 0.3–0.5 Al/Ti ratio, behaved much the same as a dimerization catalyst except that it required less TEA in the reactor. The reduction to Ti(III) may be more effective in a concentrated toluene solution than in the reactor where the TEA is very dilute and in contact with ethylene. Earlier workers have also noted that mixing conditions and the presence of olefin can be important (*5*, *23*). The activity of the $Ti(OR)_4$ premixed with TEA was similar to, or perhaps slightly better than, adding Ti(IV) directly to the reactor.

The blue-green product made by reduction of $Ti(OEt)_4$ with dialkylmagnesium was inactive in the absence of TEA. However,

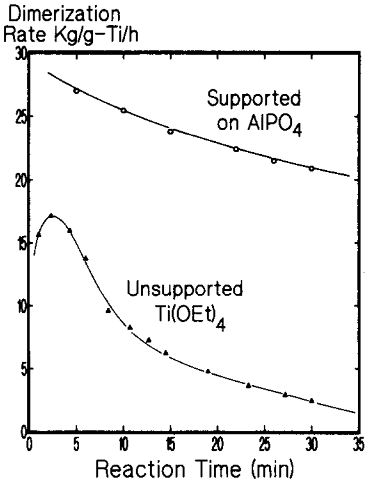


FIG. 1. Dimerization kinetics for two active runs. Unsupported: $Ti(OEt)_4$ was injected into the reactor followed by 6 TEA/Ti, then ethylene. Supported: Porous aluminophosphate was treated with dialkylmagnesium, then $Ti(OEt)_4$, then added to the reactor with 3 TEA/Ti and ethylene. The supported catalysts tended to have a more stable kinetic profile than most of the unsupported ones, and hence better productivity.

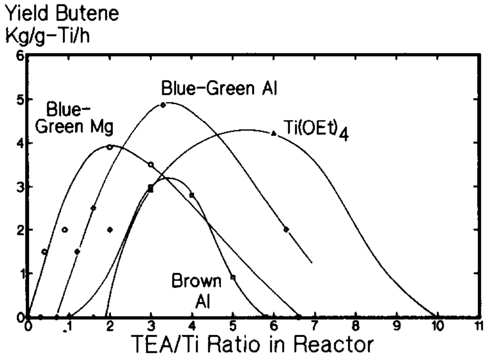


FIG. 2. Dimerization yield of liquid catalysts as a function of TEA/Ti ratio in the reactor. Four solutions of $Ti(OEt)_4$ in toluene were given a reducing treatment before testing. The blue-green solutions were made by adding one reducing equivalent of either $AlEt_3$ or $MgBu_2$. The brown solution also contained $AlEt_3$ but in a 1 : 1 ratio with Ti. The fourth solution of $Ti(OEt)_4$ was given no prereducing treatment. Each was then introduced into the reactor with more dilute TEA, then ethylene.

good runs were obtained with this complex when TEA was used at Al/Ti ratios as low as 0.4. Again, this suggests that the prereduction may have been more efficient than that occurring in the reactor on contact with dilute TEA. Attempts to substitute zinc or lithium alkyl for TEA produced inactive catalysts. This indicates that the TEA is more than just a reducing agent. Apparently, it is a necessary part of the active site.

Finally, although the brown products in Table 1, obtained on premixing TEA and $Ti(OE)_4$ in ratios from 1 : 1 to 3 : 1, were usually less active than the blue-green solutions, obtained when less metal alkyl was used, the activity tended to be more stable. Thus, the overall productivity within an hour was only a little less than the blue-green solutions. This was not true of all the brown solutions, however. The brown Li complex ($2LiBu + Ti(OEt)_4$) and also the Mg complex ($2MgBu_2 + Ti(OEt)_4$) started vigorously and then rapidly decayed.

Although presumably highly reduced already, the Li complex (2Li/Ti) still required a fairly high level of TEA in the reactor for the development of dimerization activity. It was inactive at 0.5 and 1 TEA/Ti, but became active at 3 TEA/Ti. Apparently, the TEA is more than just a reducing agent, and must complex with the Ti, in this case perhaps competing with the Li, to form the active species. The use of more lithium alkyl (5Li/Ti) produced an inactive catalyst even at 3 TEA/Ti, implying perhaps that too much of any reducing agent, not just TEA, will cause deactivation.

The brown Mg complex (2Mg/Ti) displayed the same low TEA requirements as its blue-green counterpart. It was inactive at 3 TEA/Ti, but exhibited activity at 0.5 TEA/Ti.

Many compounds, although inactive in solution, become active polymerization catalysts when anchored to a support, which is thought to prevent the active sites from reacting with each other (*26, 27*). We wondered whether a similar mechanism might be responsible for the decay of dimerization activity here. However, no correlation was apparent between kinetic profile and the solid/liquid state. Some solutions displayed relatively constant activity while other precipitated catalysts had steadily decaying activity. However, this is inconclusive because a question has been raised as to whether these apparent solutions are not actually colloidal (*13*), and we have already seen that precipitated catalysts can redissolve in the reactor on contact with TEA.

Aging experiments also gave no correlation. For example the blue-green solution of $Ti(OR)_4$ + TEA lost little or no activity on standing for 4 days, even though considerable precipitation occurred during the interval. The $Ti(OR)_4 + MgR_2$ complex was at least partially precipitated when it was tested immediately after preparation. Twelve days later it was tested again, now being completely precipitated, but performed exactly as before. The age stability of these catalysts contrasts with their instability in the reactor, and suggests that the active species becomes unstable only after contact with additional TEA or with ethylene.

2. *Supported Catalysts*

$Ti(OR)_4 + MR_x$ on carrier. Solid Ti(IV) alkoxides have been reported to be inactive for dimerization of ethylene (*23*). Thinking that this may simply reflect the low surface area of a bulk material, we determined to see if the active species could be supported on an oxide carrier with a high surface area. Several methods of attachment were investigated.

As a first approach, the blue-green solution of $Ti(OR)_4$ and a metal alkyl was reacted with a carrier. In one experiment, Ketjen Grade B alumina, calcined at 600°C, was exposed to a blue Ti–Mg toluene solution. It quickly adsorbed the first increment when the slurry was warmed. The alumina turned blue and the solution became colorless. A second increment was added, but this time only partial adsorption occurred, giving a maximum of only about 0.17 wt% Ti adsorbed. The catalyst was then washed four times in heptane; no fading of the color was seen. Then it was dried under nitrogen at 100°C, giving it a light blue-gray color. With so little titanium retained this material was obviously not very active for dimerization of ethylene.

The experiment was repeated with an aluminophosphate (P/Al = 0.9) as the carrier, which was also calcined at 600°C. Again, the solution clarified at first, and the carrier turned blue. However, in the end, the adsorption totaled only about 0.1 wt% Ti on the catalyst. After being dried at 100°C, the catalyst had a light green color. Again, little or no dimerization activity was noticed when the catalyst was introduced into the reactor with TEA.

The failure of the blue $Ti(OR)_4 + MgR_2$ solution to adsorb onto either carrier in any quantity is difficult to understand. One possible explanation is that the blue-green complex, although appearing to be in solution, is actually somewhat polymeric or even colloidal. This would limit its access into the pore structure of these supports.

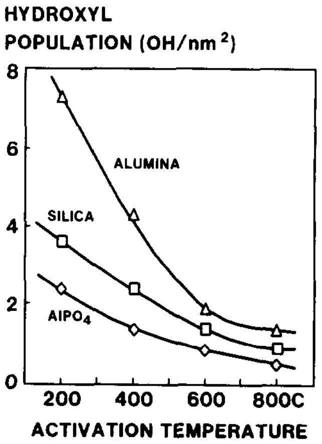
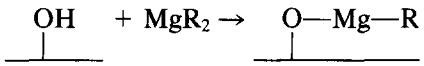


FIG. 3. Hydroxyl populations as measured by reaction with methylmagnesium iodide on the three carriers used in this study.

MgR_2 on carrier. In another approach the reducing agent was first supported on the carrier, which was then reacted with $Ti(OEt)_4$. Aluminophosphate (P/Al = 0.9) calcinced at 600°C was slurried in heptane, to which dialkylmagnesium was added, and the mixture refluxed for about 10 min. A reaction occurs with the hydroxyl groups on the surface of the support, probably giving a surface bound reducing species.



$$\underline{\overset{\displaystyle OH}{|}} + MgR_2 \rightarrow \underline{\overset{\displaystyle O—Mg—R}{|}}$$

The amount of magnesium added was 5.0 wt% based on the support, which is in great excess of the hydroxyl population, as can be seen in Fig. 3. The support was then washed several times in heptane to remove unadsorbed magnesium, and exposed to a large excess of $Ti(OEt)_4$. It turned blue immediately. After another 10 min of refluxing, the support was again washed with heptane which removed some of the blue compound. At this point, the catalyst had a blue-purple color, but this changed to green during drying under nitrogen at 100°C.

This approach proved successful. These catalysts contained 3–4 wt% Ti on analysis, and were very active for ethylene dimerization. Like the solution catalysts, these supported catalysts were not active unless a small amount of TEA was also added to the reactor. Generally, 80–350 ppm TEA was added to the diluent, and best activity was obtained at a TEA/Ti ratio of 3. This can be seen in Fig. 4.

The kinetics of dimerization were different on the supported catalysts. An example is shown in Fig. 1. Instead of a rapid evolution and decay of activity, which was characteristic of most of the liquid catalysts, these supported catalysts exhibited more of a constant kinetic profile. The dimerization rate was high and much more stable with time, suggesting that the active site is stabilized by being anchored to the support. Actually, the reaction rates on the supported catalysts were often higher than the peak rates seen briefly from the unsupported cat-

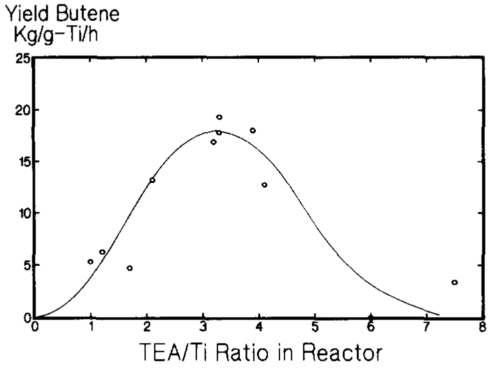


FIG. 4. Dimerization activity of supported catalyst as a function of TEA/Ti ratio in the reactor. Aluminophosphate carrier was treated with dialkylmagnesium, then $Ti(OEt)_4$, then introduced into the reactor with TEA.

alysts, which suggests a better utilization of the titanium on the support. As a result, the supported catalysts were considerably more productive over a 1-h period. (Note the differences in scale between Figs. 2 and 4.)

Chromatographic analysis of the product indicated mainly 1-butene. In one experiment in which the TEA concentration was 3 TEA/Ti, the product was 98.9% 1-butene, 0.5% *trans*-2-butene, 0.2% *cis*-2-butene, and 0.4% hexenes. Hydrogen could be added to the reactor with no harm to activity or noticeable change in the product distribution. Reactor temperature and contact time may also influence the product distribution, but these were not studied in detail.

Like the unsupported catalysts, these supported catalysts produced a small amount of polymer in addition to the butene, usually 1–5% of the product. However, much of this polymer was recovered as tiny beads on the catalyst instead of deposited on the reactor walls as with the unsupported catalysts. The formation of polymer on the reactor walls and catalyst particles indicates that a small amount of the blue complex was extracted from the catalyst by the TEA cocatalyst. Thus, lowering the TEA levels in the reactor seemed to decrease the amount of polymer formed.

In contrast, addition of chloride to the catalyst favored polymer formation. One catalyst was treated with $TiCl_4$ as an additional final step, and this completely destroyed the dimerization activity. Instead only polymer was formed, in rather high yield. Chloride containing cocatalysts, such as diethylaluminum chloride had the same effect.

Several carriers were tested. Table 2 lists the results of three experiments in which all conditions remained the same except the support, which varied between silica, alumina, and aluminophosphate, each calcined at 600°C. The porosity of these three were very similar. Again, enough dialkylmagnesium was added to saturate the surface (3.5%), and the excess was then rinsed off. In each case a blue color resulted when $Ti(OEt)_4$ was added, but the final catalyst color varied a little. The alumina catalyst was blue, and barely active for ethylene dimerization; the silica catalyst was green and highly active; aluminophosphate was blue-green, and also very active.

Just why alumina performs so poorly as a carrier is not obvious. Unlike the other two supports, it prefers octahedral coordination. Also, it is clear in Fig. 3 that alumina has a much higher density of hydroxyl groups on its surface than the other supports, which could affect the formation of active sites. Varying the temperature at which the support has been calcined also affects the density and spacing between hydroxyls (*26–29, 33*). Low calcining temper-

TABLE 2

Carrier

Carrier[a]	Color of catalyst	Activity	
		g/g-Ti/h	(mol/mol-Ti/s)
Silica	Green	14,900	(7.06)
$AlPO_4$	Blue-green	13,200	(6.26)
Alumina	Blue	1,140	(0.54)
Solution	Blue-green Mg	3,800	(1.8)

[a] Each carrier (600°C) treated with 3.5% Mg, washed, treated with excess $Ti(OEt)_4$, washed, dried, tested at 85°C with TEA/Al = 2–3.

TABLE 3

Calcining Temperature

Support[a]	Color	Ti adsorbed (%)	Activity	
			g/g-Ti/h	(mol/mol-Ti/s)
600°C-silica	Dark blue-green	3.7	10,800	(5.11)
400°C-silica	Blue	4.0	12,900	(6.12)
200°C-silica	Light blue-gray	4.2	375	(0.18)
600°C-$AlPO_4$	Blue	2.7	16,900	(7.99)
400°C-$AlPO_4$	Gray	2.7	13,800	(6.54)
400°C-Silica[b]	Blue	3.1	13,400	(6.37)

[a] Samples impregnated with 1.5% Mg, washed, treated in excess $Ti(OEt)_4$ (3Ti/Mg) washed, dried, tested with 2 TEA/Ti at 85°C.

[b] $Ti(OEt)_4$ not added in excess (1.2 Ti/Mg).

atures leave closely spaced hydroxyls on silica which can react in pairs with $SiCl_4$, BCl_3, and other reagents. However, by about 600°C, only "single" hydroxyls remain, which are more widely spaced, and therefore react with these same reagents in a one to one ratio only.

Table 3 shows the results of some experiments in which silica was calcined at 200, 400, and 600°C. In this recipe, the amount of dialkylmagnesium was decreased to 1.5 wt% Mg, which equals one Mg per OH on the 600°C silica, but is less than saturation at 400 and 200°C. Therefore, each sample should have adsorbed the same amount, leaving some hydroxyls unreacted. Notice that the amount of titanium adsorbed by each catalyst was approximately the same, but the blue color became less intense at the lower calcining temperatures. This suggests that the reducing power of the dialkylmagnesium may have been wasted in a bifunctional reaction with closely spaced hydroxyl pairs.

$$2\equiv\text{Si—OH} + \text{MgR}_2 \rightarrow \equiv\text{Si—O—Mg—O—Si}\equiv$$

Notice also that activity of the 200°C sample was much less than the others, suggesting that the spacing of hydroxyls may indeed be important.

The amount of $Ti(OEt)_4$ picked up by the support actually increased at the lower calcining temperatures. Apparently, two types of adsorption take place, one by reactions with magnesium alkyl to yield the blue-green species, and another by reaction with leftover hydroxyls to yield a colorless Ti(IV) surface ester. In the last run the catalyst was treated with a minimum of titanium. Instead of the usual threefold excess, barely enough $Ti(OEt)_4$ was added to react with the dialkylmagnesium in a 1 : 1 ratio, leaving none to react with leftover hydroxyls. Almost all of this titanium was adsorbed, giving a catalyst with less titanium and less overall activity (or the same activity based on Ti content). This suggests that the Ti(VI) species may also contribute, being reduced later in the reactor by the TEA (see following section)

The amount of magnesium alkyl added was also varied, and these results are shown in Table 4. Although the 600°C supports should have been saturated at 1.5% Mg, adding more dialkylmagnesium deepened the color and increased Ti adsorption. This suggests that, in addition to reacting with hydroxyls, some excess magnesium may also react with oxide species, or even adsorb onto the surface and not be removed by rinsing. This extra adsorption improved the overall activity, giving essentially the same activity based on Ti content.

Only a brief survey of other aluminum alkyls was undertaken. Diethylaluminum chloride and ethylaluminum dichloride completely removed the dimerization activity. Triisobutylaluminum was inactive at Al/Ti = 1.0, as was diethylaluminum ethoxide at 1.6 Al/Ti. Trimethylaluminum, however, was highly active yielding 15,000 g/g-Ti/h (7.11 mol/mol-Ti/s) at 1.8 Al/Ti with less polymer formation. Since the reducing and alkylating power of each alkyl is different, each may require its own optimum concentration.

$Ti(OEt)_4$ on carrier. A third way of supporting the catalyst is to treat the carrier with $Ti(OEt)_4$, then reduce it. This is somewhat different from previous preparations

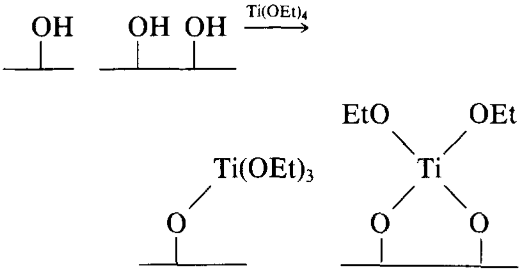
TABLE 4

Loading

Support[a]	Mg added (%)	Ti adsorbed (%)	Color	Activity	
				g/g-Ti/h	(mol/mol-Ti/s)
$AlPO_4$ 600°C	1.5	2.7	Light blue	16,900	(7.99)
	3.5	3.0	Dark blue-green	13,200	(6.25)
	5.0	3.2	Dark green	15,400	(7.30)
Silica 600°C	1.5	3.7	Dark blue-green	10,800	(5.11)
	3.5	4.0	Green	14,700	(6.95)

[a] Samples run with 2–3 TEA/Ti at 85°C.

because we no longer reduce the tetraalkoxide species. Instead, it involves a surface bound species with Ti—O—Si bonds as well as Ti—O—Et. Therefore the formation of a reduced Ti alkoxide colloid could be more difficult.



This approach was also successful, despite the different starting species. Silica was refluxed for about 10 min in a large excess of $Ti(OEt)_4$, then rinsed several times in heptane. Next dialkylmagnesium was added. The catalyst turned blue with the first increments of metal alkyl, then green as more was added, and finally brown with an excess of MgR_2, which is the same pattern observed with the unsupported catalyst. After being washed in heptane, these catalysts were tested for dimerization activity. The brown catalyst exhibited none, but the green catalyst, which had adsorbed 2.7 wt% Ti, did yield a respectable 6010 g/g-Ti/h (2.85 mol/mol-Ti/s) at TEA/Ti = 2.4.

As a simplification of this approach, the treatment with dialkylmagnesium was omitted, and instead the TEA in the reactor was used to reduce the titanium *in situ*. Again, this approach worked. The kinetics of dimerization were constant, and the activity was quite good compared to the solution catalysts. Unlike previous preparations, however, these catalysts developed the best activity at fairly low levels of TEA in the reactor, generally around 1.4 TEA/Ti as shown in Fig. 5. Reducing the catalyst with butyllithium (0.7 Li/Ti) did not further decrease the amount of TEA required for best activity. In fact, reduction with butyllithium or dialkylmagnesium did not help the activity.

Again, the amount of polymeric film deposited on the reactor was greatly diminished compared to the solution catalysts. A thin film did form on the walls, probably due to titanium leached from the catalyst by complexation with TEA in the reactor. In studies with surface bound $TiCl_4$, the Si—O—Ti bond has been found to be susceptible to attack by $AlEt_2Cl$, and more slowly by TEA as well (*30, 32*). We too found that some titanium could be extracted from these catalysts by a hot TEA solution. This may explain why the kinetics of dimerization on the supported catalysts (Fig. 1) are not completely constant but show some gradual decline with time.

Figure 5 also shows how the calcining temperature of the carrier affects the activity. In some experiments the silica was calcined at 600–700°C, in others 400 and 200°C. Each was then refluxed with an ex-

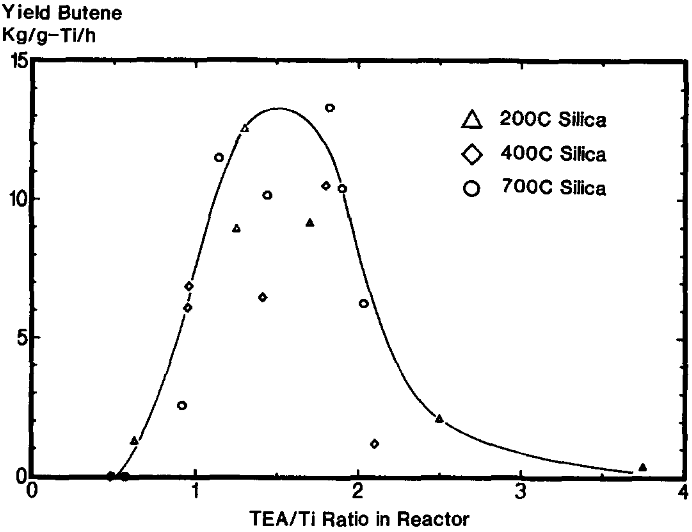


FIG. 5. Dimerization activity of supported catalyst as a function of TEA/Ti ratio in the reactor. Silica, calcined at 200, 400, or 700°C, was treated with $Ti(OEt)_4$, then introduced into the reactor with TEA.

cess of $Ti(OEt)_4$ so that the surface was saturated, then unreacted titanium was removed by several heptane washes. The 600°C sample adsorbed about 2.7 wt% Ti, which is very close to the 2.9 wt% expected from a 1 : 1 reaction with its hydroxyls, which are isolated and single. Thus $\equiv Si—O—Ti(OEt)_3$ should be the only species present, and it apparently gives high dimerization activity.

In contrast, the 200 and 400°C silicas have more closely spaced hydroxyls, and $Ti(OEt)_4$ could react bifunctionally with a good part of them to yield the diadsorbed species $(\equiv Si—O—)_2Ti(OEt)_2$ (*28, 29*). In theory, about 6.0 wt% Ti could adsorb on the 200°C sample, consisting of about half mono- and half diadsorbed species. Instead, only 4.5 wt% was actually measured, suggesting that adsorption may be limited by steric crowding. The 400°C sample adsorbed a similar amount (4.6 wt% Ti), which is higher than the 3.8 wt% expected. Thus, even the paired hydroxyls seem to react as singles to give the monoadsorbed species, and this explains why in Fig. 5 the dimerization activity is independent of calcining temperature. We cannot say from these data whether the diadsorbed species can also be active.

Alumina performed differently when treated with $Ti(OEt)_4$ and tested as a dimerization catalyst. Some results are shown in Table 5. Alumina calcined at 200°C was almost inactive, but the 500°C sample exhibited some activity, and by 800°C the alumina catalyst performed quite well. This suggests that the spacing of hydroxyls is

TABLE 5

$Ti(OEt)_4$ on Alumina

Support	Ti adsorbed (%)	TEA/Ti in reactor	Activity	
			g/g-Ti/h	(mol/mol-Ti/s)
200°C-alumina	5.1	0.8	0	(0)
		1.2	180	(0.085)
		1.7	380	(0.180)
		2.0	0	(0)
500°C-alumina	3.4	0.6	0	(0)
		1.2	4,700	(2.23)
		1.8	3,800	(1.80)
		2.5	1,600	(0.76)
800°C-alumina	2.4	0.8	0	(0)
		1.7	14,300	(6.78)
		2.5	6,500	(3.08)

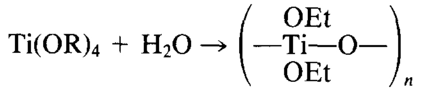
indeed important, and perhaps the diadsorbed species is not very active. Just why alumina displayed this trend and not silica is unclear, but the higher density of hydroxyls on alumina at 200°C may especially favor a bifunctional reaction with hydroxyls pairs.

Other approaches. In one experiment a silica–titania cogel containing 8 wt% Ti and having a high surface area (400 m^2/g) was heated in methanol vapor at 300°C to esterify the surface.

$$\equiv Ti\text{—}OH + MeOH \rightarrow \equiv Ti\text{—}O\text{—}Me + H_2O\uparrow$$

This sample had minimal dimerization activity. Reducing the catalyst in CO at 300°C or 500°C made no improvement. Neither did using isopropanol instead of methanol. This probably produces the mono- or at most the dialkoxide species, which are apparently not very active.

A viscous titanate polymer can be made by adding about 1 mole of water per mole of titanium, resulting primarily in long chains of a dialkoxy species.



$$Ti(OR)_4 + H_2O \rightarrow \left(\begin{array}{c} OEt \\ \text{—}Ti\text{—}O\text{—} \\ OEt \end{array}\right)_n$$

When reduced by TEA this polymer did not go through the green stage. Instead, a brown color was obtained with the first addition of TEA. It produced 2800 g of butene/g-Ti/h (0.66 mol butene/mol-Ti/s) at 0.5 TEA/Ti optimum, with a constant kinetic profile despite being a liquid. Thus, it was better than those made by esterification of TiO_2, but not equivalent to the supported catalysts above. This suggests that the trialkoxy species is most active, followed by the dialkoxide, and the monoalkoxide is poorest.

CONCLUSIONS

The reduction of $Ti(OEt)_4$ is a complicated reaction yielding Ti(III) or Ti(II) complexed with the reducing metal, which can vary in solubility. It appears that aluminum must be part of the active site because, while other metal alkyls can reduce the titanium, activity develops only when aluminum alkyl (TEA) is added to the reactor. Aluminum may even replace the initial reducing agent in the complex to yield the active species. Thus, the amount of TEA needed to produce optimum activity, and the activity profile itself, depends somewhat on the particular catalyst preparation.

This same catalyst system can be supported on a porous carrier and still retain activity for ethylene dimerization. In fact, the active sites seem to be stabilized by being anchored to the support, giving an improvement in overall productivity. This suggests that in solution the activity may be destroyed by a reaction between active sites, as has also been proposed for some polymerization catalysts (*27*). In addition to improved productivity, supporting the catalyst also minimizes the reactor fouling associated with the liquid systems, and there is less tendency to poison polymerization catalysts when used in dual dimerization/polymerization systems.

Silica and aluminophosphate served well as carriers but alumina, unless highly dehydrated, did not. One possible explanation, although by no means certain, is that only the monoadsorbed species is very active, whereas alumina, with its greater hydroxyl density, may favor the diadsorbed species. Silica calcined at only 200°C, which is also capable of supporting a diadsorbed species, performed with mixed results.

It is possible that all of these catalysts, supported and unsupported, produce a similar active species after contact with TEA in the reactor. Apparently, the attachments to the carrier can indeed be broken by the TEA (*30–32*). However, the relatively small amount of polymeric film deposited by the supported catalysts, and the more constant kinetics, suggests that this leaching is slow and limited under conditions used here. This is reasonable considering the dilute concentration of TEA in the reactor.

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