A comparison between alkylgallium and alkylmagnesium reduced vanadium-based Ziegler–Natta catalysts: gallium *versus* magnesium chloride as support for vanadium

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(Received 16 June 1989; revised 1 November 1989; accepted 6 November 1989)

Catalysts have been prepared by the reduction of vanadium(IV) chloride with alkylgalliums and used to polymerize ethene at various temperatures and with various cocatalytic components. By comparison of the results obtained with those obtained from equivalent alkylmagnesium reduced systems, it is clear that the gallium reduced systems show greater activity (up to ~50 kg polymer/g vanadium at 50°C, using triethylaluminium as cocatalyst). These materials are only weakly active for the polymerization of propene.

(Keywords: Ziegler–Natta catalyst; vanadium; support; reduction)

INTRODUCTION

Ever since the original announcement[1] of the action of Ziegler–Natta catalysts, there has been a strong incentive to support the active species on a carrier. This is desirable for at least two reasons: first, the active transition-metal species may be used more efficiently if it is carried upon the surface of a particle, rather than much of it being buried within the bulk of the catalytic material; and secondly, the quantity of undesirable catalyst residues left in the polymer produced may be reduced if the carrier is an essentially inert species such as silica, alumina or a polymer. There are also other possible benefits in that it may be feasible to shape the support particles more easily than would be possible for the actual catalyst species, thus providing better polymer characteristics, and there is the possibility of some favourable interaction with the support to give inherently better catalyst activity or steric control. The use of such a support is, of course, a standard thing in other areas of catalytic practice, and extensive work with essentially inert supports continues to the present day[2].

In this paper we communicate some results directed to exploring the relationship between the active transition-metal species and the support. For this study we concentrate on the catalysts supported upon metal chlorides. These catalytic systems have been studied longer than any other Ziegler–Natta types, since they arose initially from the method of synthesis in first-generation catalysts, wherein titanium tetrachloride was reacted with alkylaluminium to produce an initial metal chloride precipitate, which contained significant quantities of aluminium[3]. Early on it was realized in a number of laboratories, notably in Tornqvist's group[4], that the aluminium had a distinctly beneficial effect upon the catalyst's performance, and a number of publications dealt with methods of introducing the aluminium, and with methods of treating the initially produced solid to optimize its catalytic properties[5].

Later, the use of other metal salts as supports was investigated[6,7], and it was soon established that, at least for the case of ethene polymerization using titanium as transition-metal species, the use of magnesium chloride gave much more active catalysts than did any other species tried at that time. The announcement of active catalysts for propene (also supported on magnesium chloride) followed[8], their main development being contingent upon the use of Lewis-base stereoregulator pairs[9,10] to control the catalytic particle size, to alter the properties of the catalytic sites, and to moderate the reactivities of the cocatalysts used. Since then, the use of magnesium chloride supports for titanium chloride Ziegler–Natta catalysts has become commonplace[11], and the role of the magnesium chloride has been the subject of speculation, albeit the pre-eminence of this particular support has still not been wholly rationalized.

In previous publications[12] we have reported upon our studies of the usefulness of supporting vanadium chloride-based species upon magnesium chloride, whereby reasonably reactive catalysts are obtained, albeit their activities are not as high as those of the corresponding titanium-based preparations. The marked superiority of magnesium chloride over other supports has led us to speculate as to whether the same would be true for other transition metals, i.e. magnesium chloride would be easily the best support, or whether there might be an optimum partnership between support and transition metal, different for each metal.

In pursuit of this idea we have sought to check whether metal chlorides other than magnesium chloride can give the same or better results as does magnesium with vanadium-based species, under conditions as comparable as possible. This latter condition is important, because although it is easily possible to arrange matters such as the cocatalyst and monomer concentrations, and the

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reaction temperature, it is rather more tricky to say with certainty that conditions at the surface of the catalyst particle are equivalent in two preparations.

THEORY AND RESULTS

In this study we have used as working hypothesis the idea that a requirement for good support would be that the ionic radius of the transition metal used should be as close as possible to that of the supporting metal ion. This is of course equivalent to the condition that the metal–chlorine bond lengths be as similar as possible, in order perhaps to facilitate some form of pseudo-epitaxy in the precipitation of the transition-metal species onto the other metal chloride, either as it is formed (coprecipitation) or as the extant entity. This is true of Mg^{2+} and Ti^{4+}, where the radii are very close (*Table 1*), but is far from the truth with other valence states of titanium. This makes the simple alternative hypothesis, that the match of the active species in the reaction with the support geometry is the key feature, difficult to sustain, since few authors suppose that the active state for titanium in the presence of alkylaluminium is Ti^{4+}, although the metal is often introduced into the catalyst in this state.

For vanadium, if it were accepted that V^{3+} is the predominant catalytically active oxidation level[13], and that this is the dominant interaction, then a search of the ionic radius tables gives no good matches (*Table 1* illustrates) but Ga^{3+} is a remarkably good fit for V^{4+} and we have thus explored the reactivity of catalysts prepared, by coprecipitation, from vanadium(IV) chloride and tributyl gallium. This alkylgallium was chosen for its accessibility from gallium chloride via ligand exchange in a system free from donor solvents:

$$GaCl_3 + 3BuLi \rightarrow Bu_3Ga + 3LiCl\downarrow$$

or

$$2GaCl_3 + 3Bu_2Mg \rightarrow 2Bu_3Ga + 3MgCl_2\downarrow$$

The solutions of alkylgallium thus prepared were reacted directly with freshly prepared vanadium tetrachloride (or vanadium trichloride oxide) in a reaction wholly analogous to our previous work using alkylmagnesium as reductants with both titanium[14] and vanadium[12] chlorides. We assume a change of 1 in oxidation level in this process, in conformity with our and other previous results:

$$Bu_3Ga + 3VCl_4 \rightarrow VCl_3\downarrow + GaCl_3\downarrow + \text{etc.}$$

This mixed precipitate was then employed as procatalyst in the usual way. A similar reaction was also tried, with vanadium trichloride oxide, for comparison with the magnesium reduced catalysts. Some preliminary studies were made to assess the optimum ratio of organogallium to vanadium: as shown in *Figure 1*, the productivity seemed best with high gallium ratios. We have not gone beyond what is shown here since consumption of more organogallium groups seemed unlikely. The best of these procatalysts (or others like it) was used in subsequent work.

Table 1 Some selected crystalline ionic radii[a]

Ion	Radius (pm)	Ion	Radius (pm)
Ti^{4+}	68	Al^{3+}	51
Ti^{3+}	76	Mg^{2+}	66
Ti^{2+}	94	Li^{+}	68
V^{5+}	59	Na^{+}	97
V^{4+}	63	K^{+}	133
V^{3+}	74	Ca^{2+}	99
V^{2+}	88	Ga^{3+}	62
		Zn^{2+}	74

[a] Data abstracted from 'CRC Handbook of Chemistry and Physics', 69th Edn., (Ed. R. Weast), CRC Publishing, Boca Raton, FL, 1988

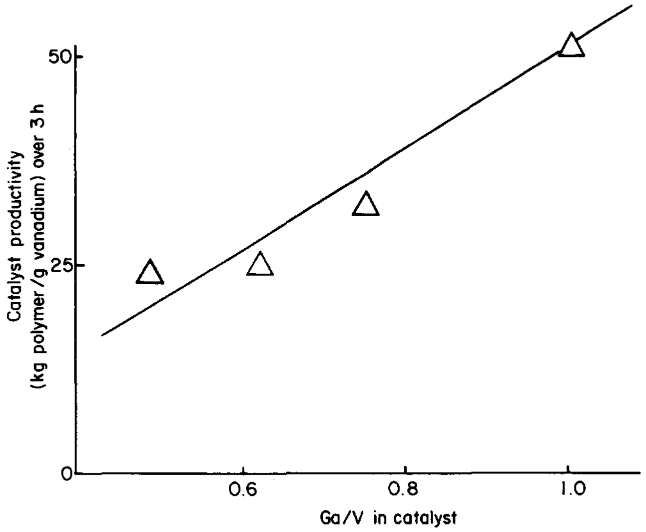

Figure 1 Effect of gallium/vanadium ratio in the reduced precipitate on the activity of the catalyst. Polymerizations at 50°C, 1 atm ethene, [triethylaluminium] = 1.0 mmol dm^{-3}

Table 2 Activities of catalysts prepared by alkylgallium reduction of vanadium tetrachloride and vanadium trichloride oxide

Cocatalyst	Conc. (mmol dm^{-3})	Polymerization temperature (°C)	Yield (kg polymer/ g vanadium)
		From VCl_4	
Et_3Al	1.4	20	21
	1.4	40	41
	1.4	50	51
	1.4	80	18
Et_2ClAl	1.6	30	13
	1.6	50	27
	1.6	80	21
(n-Octyl)$_3$Al	2.2	30	4
	2.2	50	11
	8.8	50	14
	2.2	80	32
		From $VOCl_3$	
Et_3Al	2.0	50	8

The catalytic activity of these materials, used with a number of cocatalysts, is shown in *Table 2*. Each of these results was obtained from a 3 h reaction period, and may be used to judge the activity in comparison with the magnesium reduced materials. Before this comparison is made, it is interesting to note that the activity obtained using diethylaluminium chloride as cocatalyst is comparable with that from triethylaluminium: this is similar to the results for magnesium reduced vanadium catalysts, but quite different from the usual results[15] for magnesium-supported titanium species. It is, of course, comparable with results obtained for aluminium containing titanium procatalysts.

The effects of polymerization temperature are also shown in *Table 2;* these are not unexpected, with the highest productivity for triethylaluminium and diethylaluminium chloride coming at 50°C, while that for tri(n-octyl)aluminium occurs at 80°C. Presumably this latter system might give better activities at even higher temperatures, but this was not possible with our experimental set-up. These temperature profiles are again similar to those found for the magnesium reduced vanadium species, and presumably represent a combination of the effects of different reducing powers of the alkyls, different activating powers of the alkyls (assumed to be essentially steric in origin), and the reduction in monomer solubility with increasing temperature.

The importance of over-reduction by the cocatalyst in heterogeneous Ziegler–Natta systems generally is, of course, well documented[16,17] and the relevance here is reinforced by the rate–time profiles at two temperatures shown in *Figure 2*, which shows clearly that the constant rate found at 30°C converts to a decaying curve at 50°C for otherwise identical reactions, and by the effects of varying the concentration of triethylaluminium on catalyst productivity at 50°C (*Figure 3*). Increasing the concentration of tri(n-octyl)aluminium at 50°C, however, actually increased the productivity (*Table 2*). We include in *Figure 2* also a rate–time profile of an alkylmagnesium reduced catalyst at 30°C, to illustrate that this behaviour is common to both types of procatalyst. Parenthetically, we have extended the constant rate out to 5 h reactions at 30°C, and find it to vary little over this time. With tri(n-octyl)aluminium, the rate fall-off is much less pronounced at higher temperatures than is the case with triethylaluminium, but at low temperatures the rates with this cocatalyst become too low for reliable measurement in our experimental set-up.

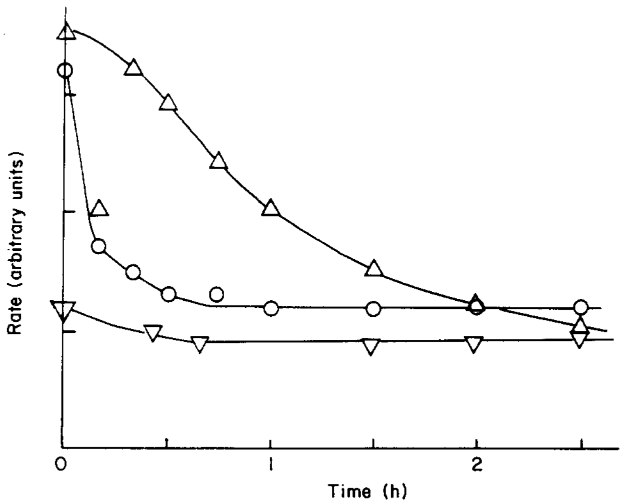

Figure 2 Typical rate–time profiles for various catalysts: (○) gallium reduced catalyst at 30°C; (△) gallium reduced catalyst at 50°C; (▽) magnesium reduced catalyst at 30°C

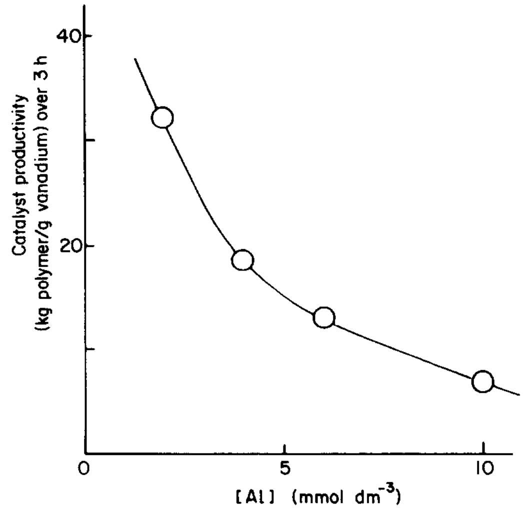

Figure 3 Effect of triethylaluminium concentration on the productivity of the gallium reduced catalyst. Polymerizations at 50°C, 1 atm ethene, [V] = 0.04 mmol dm^{-3}

Table 3 Results for magnesium reduced catalysts for comparison with those from gallium reduced species[a]

Cocatalyst	Polymerization temperature (°C)	Yield (kg polymer/ g vanadium) (2 h run)
	From VCl_4	
Et_3Al	50	20.1
	75	13.3
Et_2AlCl	50	20.6
$(i\text{-Butyl})_3Al$	50	13.9
$(n\text{-Octyl})_3Al$	50	14.7
	From $VOCl_3$	
Et_3Al	50[b]	11.1
	50	9.3
	50	2.7

[a] All polymerizations at 1.0 atm ethene pressure in 'Isopar C'. Yields calculated by weighing dry polymer and analysis of catalysts for V

[b] Varying yield due to different Mg/V ratios in the catalysts (see text)

We now come to the main point of these experiments, viz. is the magnesium reduced family of vanadium-based catalysts better, worse, or about as productive as the gallium reduced ones? Here the evidence is unequivocal for the vanadium chloride-derived materials: the use of alkylgallium gives a significantly more active preparation than does alkylmagnesium. Thus, at 50°C, with triethylaluminium as cocatalyst, the activity recorded in the present study is 51 kg polymer/g vanadium, whereas the corresponding figure (over 2 h) for the magnesium reduced system is 20.1 kg. Similar improvements are seen with other cocatalysts (*Table 3*). It might be argued that the superiority of the gallium reduced materials is less marked than is shown here, since the 2 h result for the magnesium reduced species ought to be multiplied by 1.5; this is not wholly so, however, since the fall-off in rate with time is quite significant at 50°C, so that the significant advantage of the gallium reduced material is still evident.

The polymerization of propene with these materials, by contrast, is not very successful. Although a single series of experiments is probably not conclusive, it remains true that the best activity we obtained was 0.4 kg polymer/g vanadium (40°C; triethylaluminium 2.8 mmol dm^{-3}, 1.9 atm pressure, 3 h reaction). It is thus improbable that good propene catalysts will be available via this route.

With vanadium trichloride oxide as starting material, the results are less self-evidently favourable: the highest productivity obtained for such a catalyst in the present study was 8 kg/g, which compares unfavourably with the results of our study[18] using equivalent magnesium reduced species, where activities of up to 11 kg/g were recorded under similar conditions. These results are,

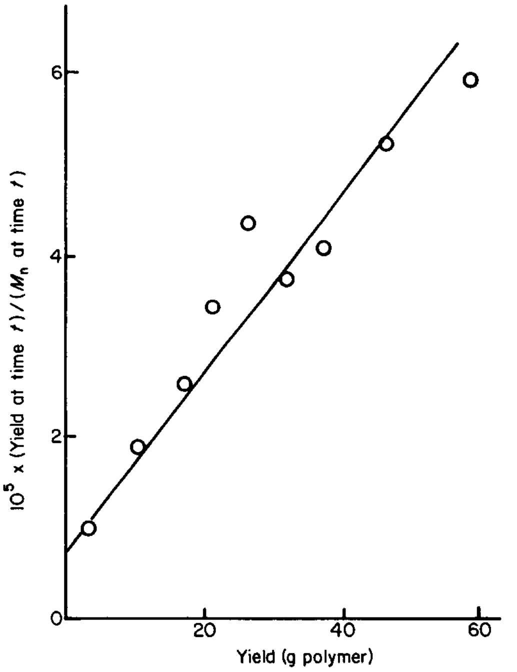

Figure 4 Kinetic plot for the estimation of C^* for a gallium reduced catalyst. Method explained in ref. 14

however, complicated by the fact that the best results were recorded for preparations with very high ratios of magnesium to vanadium; the results under conditions comparable to the methods used here are close to 2 kg/g, so that the superiority of alkylgallium over alkylmagnesium reduction is also seen for this case.

The question of why this superiority should occur is still an open one. We have attempted to measure the numbers of active centres in the gallium reduced catalysts at 50°C, using a kinetic method which we and others[19] have employed before. The results of this study (*Figure 4*) give a reasonable straight line, and this leads to a figure of 33% of the transition-metal ions being active. In a previous study a figure of 23% was arrived at for the concentration of active sites in a similar magnesium reduced preparation at 40°C; given the errors in the determination and the temperature difference, this difference seems not to be significant, particularly since the method always gives very high values for C^*, the fraction of transition-metal atoms active. ^{14}C studies on the magnesium reduced species suggest[12] a figure nearer 6% active transition-metal species, which is much more in line with the bulk of other determinations. It is clear that the kinetic method has more attendant difficulties than the radio-tagging methods, but it may presumably still be used to provide a merit order for different catalysts.

We thus conclude that, at least, magnesium chloride is not a uniquely good support for vanadium-based catalysts, as it seemingly is for titanium-based species, and that it is therefore likely that other active species may benefit from the use of optimized supports. This is clearly the case for the vanadium-based catalysts, where the use of alkylgallium as reductant gives catalysts of significantly higher activities than does alkylmagnesium reduction. Although our evidence is not strong, the present study offers support for the hypothesis that the radius of the supporting metal ion, and thus the crystalline lattice spacing of the support, is important.

EXPERIMENTAL

Materials

Gases were supplied by BOC Ltd; all were dried and purified as previously described[12]. Liquid diluents were purified by refluxing under N_2 overnight (at least) over either Na/K alloy or $LiAlH_4$. The main diluent used was Isopar C (Esso), an aromatic-and-olefin-free hydrocarbon mixture boiling between 98 and 100°C. CCl_4 was dried over molecular sieves before use, and vanadium tetrachloride[20] was freshly prepared as required from vanadium metal and chlorine. The solution of (n+s)-butylmagnesium in Isopar E (Texas Alkyls) was a gift from ICI, and the alkylaluminium used were either gifts from ICI or supplied by Schering AG.

Catalyst preparations

Gallium trichloride. This was prepared from gallium metal by direct reaction between the elements in a slow stream of Cl_2, and the product swept out of the reaction tube in a stream of N_2. This material was then converted to tri(n-butyl)gallium by reaction with n-butyllithium as follows. In a typical experiment, $GaCl_3$ (5.3 g, 0.0301 mol) was dissolved in dry n-heptane (100 cm^3) in a three-necked 250 cm^3 flask fitted with magnetic stirrer, N_2 inlet and outlet, a thermometer and a dropping funnel, which was charged with dry n-heptane and n-butyllithium (55.3 cm^3 of a 1.6 molar solution in hexanes; 0.09 mol). This mixture was added dropwise with stirring to the $GaCl_3$ solution over 1 h. After completion of the addition the mixture was refluxed for a further 12 h, then cooled and allowed to settle overnight before decantation of the clear supernatant liquor, which was analysed by ethylenediaminetetraacetic acid (EDTA) titration[21] and shown to have a gallium content of 10.0 ± 0.1 mg cm^{-3}. An essentially similar reaction using di-((n+s)-butyl)-magnesium as alkylating agent gave a similar result. In both cases these preparations were carried out under N_2.

Gallium reduced vanadium chloride catalysts. The preparations were carried out under N_2 in vessels having internal provision for washing and filtering the precipitated material. Catalysts were made by rapid addition via syringe of the tributylgallium solution to a vessel containing a stirred solution of freshly prepared VCl_4; this was followed by washing (×3) with n-heptane. The final, purple, solid precipitate was reslurried in n-heptane and transferred by syringe to an N_2-filled storage vessel.

All the final catalyst slurries were analysed for V by a photometric method[22] before use.

Polymerizations

These were carried out as described before[12] in a 2.0 dm^3 mechanically stirred glass pressure vessel, which could be run at up to approximately 8 atm pressure. Gas consumption was measured with an inlet rotameter. Cocatalyst and procatalysts were added by syringe to the diluent; the diluent was saturated with ethene before addition of procatalyst. Polymers were isolated and weighed to give the recorded yields.

Viscometry. This was carried out in Ubbelohde suspended-level viscometers, at 135 ± 0.05°C, in decalin solution. Values for M_n were estimated using the relationship of Elliot[23], whereby a one-point determination of the relative viscosity was used to generate the intrinsic viscosity via tables, and the equation of De la Guesta and Billmeyer[24]:

$$[\eta] = 2.3 \times 10^{-4} (\bar{M}_n)^{0.82}$$

to estimate $\bar{M}_n$.

ACKNOWLEDGEMENTS

One of us (MA-H) thanks the Government of the Republic of Iraq for a Scholarship. The generous gift of materials by ICI Plastics Division is also warmly acknowledged.

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