An investigation of supported Ziegler–Natta catalysts for the polymerization of butadiene

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The influence of several process variables on the polymerization activity of a supported Ziegler–Natta cobalt catalyst, and on the polymer molecular weight and microstructure, has been studied. Whilst the kinetic order with respect to monomer and catalyst was unity, the addition of water caused a significant decrease in the catalyst activity. The extent of support dehydration was also found to be a critical parameter influencing catalyst activity, exhibiting a maximum activity at a temperature of ~350°C. A comparison with commercial unsupported catalyst systems showed that catalyst activity could be increased 10-fold but with a substantial decrease in molecular weight.

(Keywords: Ziegler–Natta catalyst; polymerization; butadiene; supported catalyst; mechanism)

INTRODUCTION

The polymerization of butadiene by a soluble cobalt–alkyl aluminium catalyst was originally disclosed by Goodrich-Gulf Chemicals Inc. in a patent awarded in 1955[1]. Cobalt chloride with mixtures of mono- and dihalogen substituted alkyl aluminiums were shown to give a high *cis*-1,4 polymer (*cis* content >90%). Horne[2] showed that the active species was a soluble cobalt complex. Utilizing mixtures of mono- and dialkyl aluminium chlorides in conjunction with a soluble cobalt compound enabled highly active and versatile catalysts to be prepared. The polymerization kinetics and polymer properties were also varied by changing the chloride content of the mixed alkyl aluminium cocatalysts. It was shown later that water can act as a cocatalyst modifier in much the same way as the use of mixed alkyl aluminium compounds[3,4].

Despite the rapid development of Ziegler–Natta and related catalysts for the production of polyethylene and mono-α-olefins, which has culminated in the use of supported catalysts of very high activity[5], similar progress has not been made in catalyst development for diene polymerizations. Lasky and coworkers[6] reported achieving a 10-fold increase in activity for isoprene polymerizations using a supported vanadium catalyst such as VCl_3 on TiO_2 or kaolin mixed with $Ti(OR)_4$ and $AlEt_3$. The next year Ueda *et al.*[7] reported that a nickel catalyst supported on SiO_2/Al_2O_3 or active carbon on diatomaceous earth was active for polymerizing butadiene to a high *cis*-1,4 polymer with or without activators.

A comparative study of homogeneous and heterogeneous isoprene and butadiene systems was conducted by Golukbeva *et al.*[8] using macromolecular supports such as polypropylene- and polyethylene-*gr*-poly(4-vinylpyridine). Heterogeneous catalysts were found to give higher yields of polymer with higher molecular weights than those obtained with homogeneous systems. An increase in *cis*-1,4 content of 2–11% for the heterogeneous systems was also reported and catalyst ageing was said to be suppressed. The increased activities were attributed to more of the cobalt atoms being capable of active-centre formation in the heterogeneous systems.

Yermakov *et al.*[9] studied π-allyl–nickel and –chromium compounds for the polymerization of butadiene. Various catalyst supports including SiO_2, TiO_2, MgO and Al_2O_3 were studied, with carrier type influencing the stereospecificity of the catalyst. A change from silica to alumina gave a change in microstructure of the resultant polymer from 96% *cis*-1,4 to 98% *trans*-1,4-polybutadiene. Highly active supported catalysts for the polymerization of butadiene and isoprene have recently been documented by Soga *et al.*[10,11] A range of supports including SiO_2, γ-Al_2O_3, MgO and $MgCl_2$ were evaluated with high-surface-area silica promoting the greatest increase in catalytic activity. Activity increases of 1000% to 2000% were demonstrated compared to conventional catalyst systems. Quite severe reaction conditions were used including monomer concentrations of 70% and temperatures of 65°C, and whilst products had high *cis* content, molecular weights were too low for the polymers to be of commercial use. Other significant aspects of these catalysts were that water was not required as a cocatalyst and the high activities were achieved in hexane solvent.

The purpose of the present studies was to investigate the factors affecting the activity of these supported catalysts particularly with respect to (i) optimizing the catalyst efficiency under experimental conditions similar to those used in homogeneous systems, and (ii) how the catalyst activity is affected by catalyst promoter and cocatalyst, i.e. aluminium alkyl and water levels.

EXPERIMENTAL

All polymerizations were conducted in a 1 litre stainless-steel pressure reactor using procedures as previously

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described[12,13] with the exception that the supported catalyst was prepared *in situ* immediately prior to an experiment.

Materials

Polymerization was conducted with toluene as solvent. After predrying (over calcium hydride) for 24 h the toluene was distilled over calcium hydride, passed through a column packed with molecular sieves (Grace 514) and stored in the calibrated reservoir.

The monomer was supplied by Australian Synthetic Rubber Co. Ltd as 99.5% 1,3-butadiene. Further drying was effected using molecular sieves (Grace 514). Traces of inhibitor were removed with soda asbestos.

Diethyl aluminium chloride (DEAC) was obtained from Shell Chemical as a 12% solution in an aliphatic solvent mixture.

The silica support used was Degussa Aerosil 200 with a BET surface area of $200 \pm 25\ m^2\ g^{-1}$. This was used only after drying at 120°C for 24 h. The moisture content was reported to be less than 1.5% after this procedure[14].

The production of the cobalt complex was adapted from the methods of Reitzenstein[15] and Cox *et al.*[16] In this method 15 g of recrystallized $CoCl_2 . 6H_2O$ and 30 ml pyridine (AR grade) were combined with 300 ml of boiling ethanol for 1 h. On cooling violet crystals of α-$CoCl_2 . 2Py$ were gradually formed. After recrystallization from ethanol the solid catalyst was transferred to a N_2-filled desiccator. The chemical composition was confirmed by solution elemental microanalysis. Owing to the low solubility of this complex in the polymerization solvent toluene, the required solution catalytic concentration was prepared in the solvent reservoir. Complete solvent dissolution was only effected by ultrasonication. Approximately 300 ml of this solution was then added to the reactor to which the silica support (in the form of slurry, also in dry toluene) had previously been added. After stirring at ambient temperature for 30 min total absorption was complete. The Co/Si ratios used in this study were kept below the upper absorption limit as measured by visible spectroscopy.

Molecular weight measurement

The molecular weight was determined on a gel permeation chromatograph (g.p.c.) constructed from individual Waters Associates modules—a 6000 A pump, U6K injector and R-400 differential refractive index detector. Waters μ-Styragel columns with nominal exclusion limits of 500, 10^3, 10^4 and 10^5 Å were used.

The g.p.c. was operated at a flow rate of $1\ ml\ min^{-1}$ with tetrahydrofuran (THF) as solvent. The sample concentration was kept at about 0.1% with a sample volume of $500\ \mu l$. Calibration of the g.p.c. was done according to the universal calibration method[16] by using narrow molecular weight polystyrene standards obtained from Waters Associates. The Mark–Houwink constants used in the calculations were $K = 4.57 \times 10^{-4}$ and $\alpha = 0.693$, respectively.

RESULTS

Our first concern in this study was to establish that the basic polymerization mechanism initiated by these supported cobalt catalysts has not been changed in comparison with their soluble counterparts. *Figures 1a*

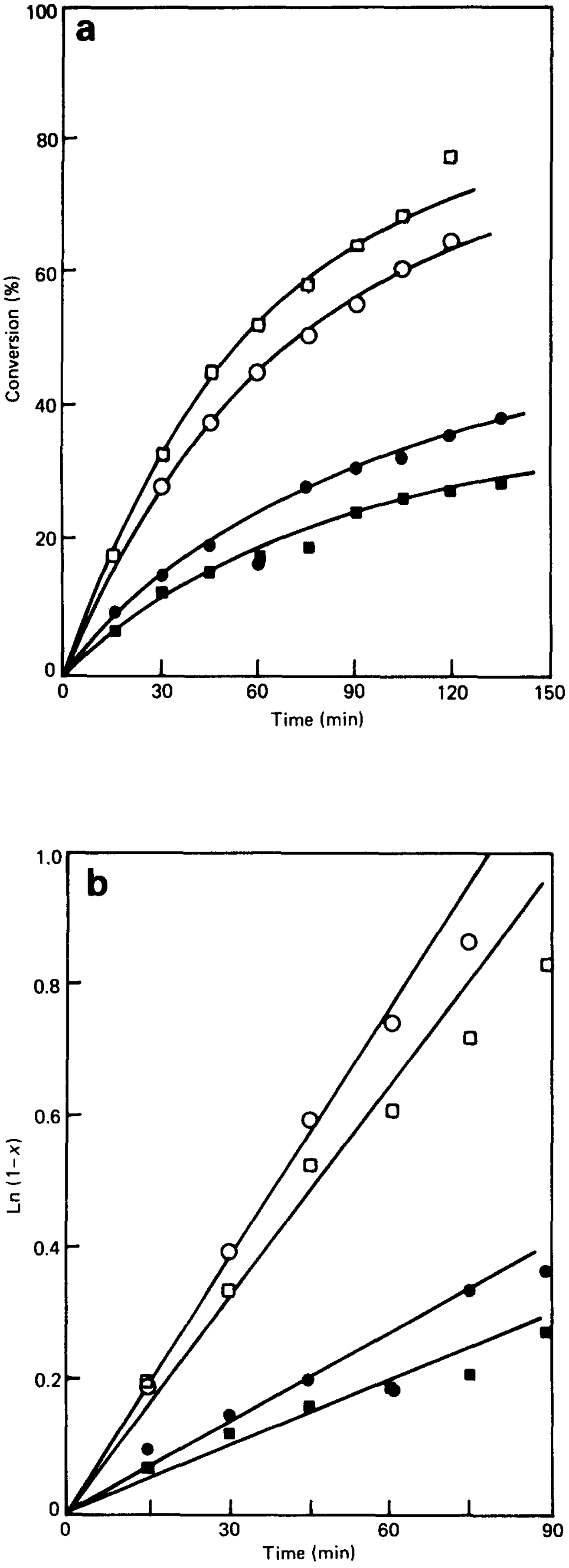

Figure 1 (a) Conversion curves as a function of catalyst concentration: [Co] (10^{-5} M) = 5.63 (□), 3.91 (○), 2.75 (●), 1.95 (■); [monomer] = 1.66 M; [DEAC] = 0.064 M; $T = 20$°C. (b) Integrated first-order plot as a function of catalyst concentration: [Co] (10^{-5} M) = 5.63 (○), 3.91 (□), 2.75 (●), 1.95 (■)

Table 1 Effect of Co/Si ratio on catalyst activity and polymer molecular weight[a]

Co/Si	Catalyst activity (kg polymer (g Co)$^{-1}$ h^{-1})	M_n (10^3) at 30% conv.
1/160	21	60
1/300	20	53
1/470	11	69
1/620	10	55

[a] [Co] = 5.634×10^{-5} M; Al/Co = 1500/1; T = 20°C; [butadiene] = 10 wt%; solvent, toluene

Table 2 Effect of H_2O concentration on catalyst activity and molecular weight[a]

[H_2O] (10^{-3} M)	Catalyst activity (kg polymer (g Co)$^{-1}$ h^{-1})	M_n (10^3) at 50% conv.	M_w (10^3) at 50% conv.	ρ
0	21	56	165	2.9
2	15	95	250	2.6
4	10	160	400	2.5
8	3	260	560	2.2

[a] Conditions are the same as for *Table 1*

and *1b* show that the conversion *versus* time plots were smooth up to high conversions and that the polymerization was first order with respect to monomer up to about 60% conversion. By varying the cobalt concentration at a constant Co/Si ratio of 1/300 we were also able to show that the reaction is approximately first-order in cobalt concentration, thus indicating that the basic reaction steps, i.e. coordination of the monomer with the cobalt complex followed by insertion into the copolymer covalent bond, has not been significantly altered by the supporting of the cobalt complex. However, when the Co/Si ratio was altered, a sharp reduction in the catalyst activity was observed as the ratio was changed from 1/300 to 1/470. The molecular weight remained unchanged. The data are presented in *Table 1*. The catalyst activity has virtually been halved even though the number-average molecular weight (M_n), a sensitive function of the concentration of active sites, remained essentially constant. This indicates therefore that individual site activity has decreased significantly.

Apparently the high Si atom concentration has a negative effect on the cobalt complex activity.

The effect of added water, an important cocatalyst at low concentrations in homogeneous systems of this type, is seen in *Table 2*, where ρ is the ratio of weight-average molecular weight (M_w) to M_n. These results are consistent with the fact that the water in these systems simply acts as a catalyst poison, causing a proportional decrease in the number of active sites. As it could be argued that silica contains bound water, we examined the hypothesis that the catalyst system was being activated by water bound to the silica support. Thus the effect of silica calcination temperature on the catalyst activity, over the temperature range 100–500°C, was examined. Maximum activity was achieved at a calcination temperature of around 300°C, which coincided with the minimum M_n. Thus the maximum catalyst activity coincides approximately with a maximum number of active sites. The decrease in activity and increase in molecular weight at the highest temperature indicate that the active-site concentration has been significantly reduced, which may be related to a change in pore structure of the silica itself. This will be examined by Hg penetration porosimetry and presented in a future publication.

The molecular weight as a function of conversion for a typical polymerization is shown in *Figure 2*. Both M_n and M_w increase rapidly in the initial stages of the reaction and then remain relatively constant. At high conversions, a slight yet significant and reproducible decrease in both molecular weight averages is also observed. This is caused by monomer depletion at these high conversions. This trend is in direct contrast to that obtained with the soluble cobalt–octoate system as reported by Honig *et al.*[12]

Molecular weight averages also vary as expected with cobalt concentration, as shown in *Table 3*.

Significantly, polydispersity steadily decreases with decreasing catalyst concentration (and hence polymerization rate), a result that is also seen in *Table 2*. These trends were consistent despite significant errors arising from molecular weight determination inherent in size exclusion chromatography procedures. Presented also in *Table 3* are microstructure details typical of this system,

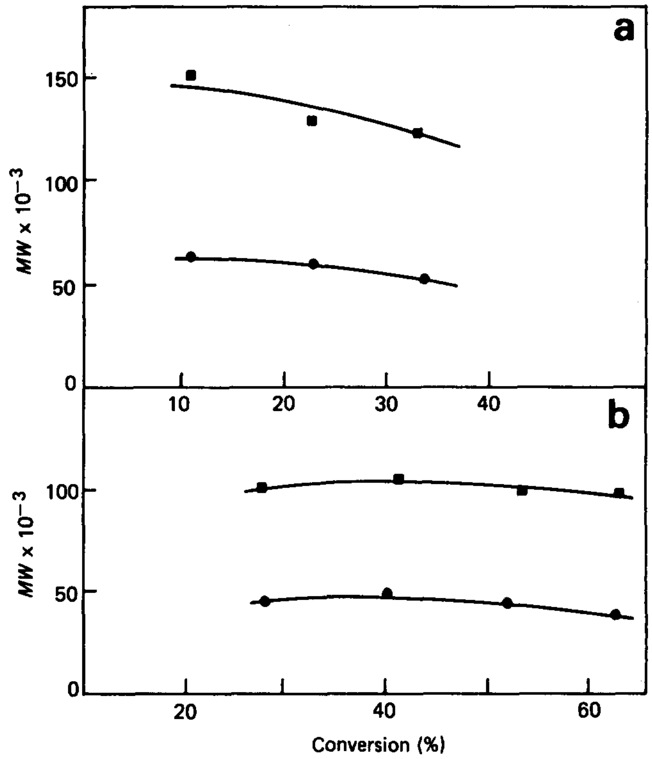

Figure 2 Molecular weight trends as a function of conversion and catalyst concentration for: (a) [Co] = 2.75×10^{-5} M, (b) [Co] = 3.91×10^{-5} M; [monomer] = 1.66 M; [DEAC] = 0.064 M; T = 20°C

Table 3 Effect of cobalt concentration on molecular weight and microstructure

[Co] (10^{-5} M)	M_n (10^3)	M_w (10^3)	ρ	*cis*-1,4 (%)	*trans*-1,4 (%)
1.93	69	148	2.1	94.2	2.0
2.75	54	132	2.4	95.0	3.8
3.91	41	127	3.1	93.8	1.7
5.63	32	101	3.2	93.3	2.5

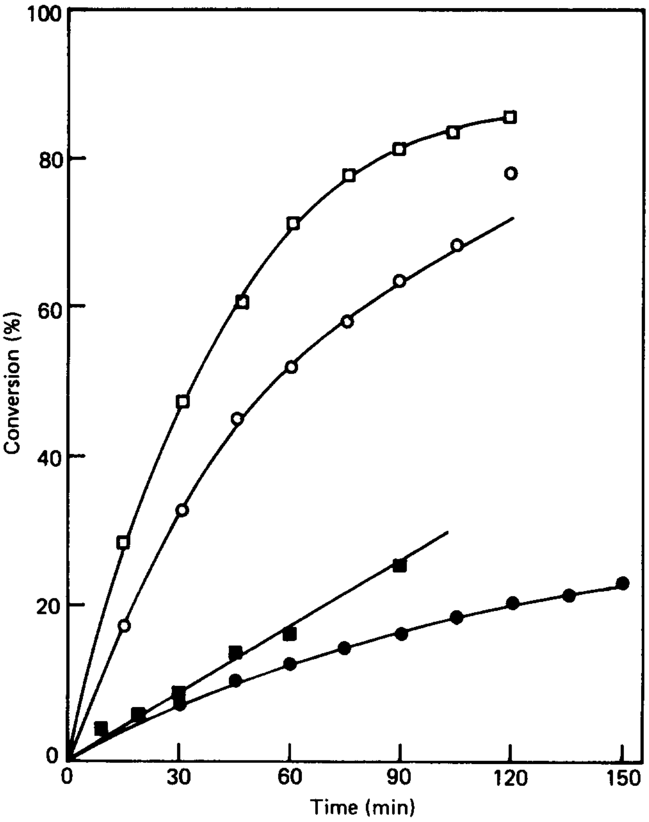

Figure 3 Conversion curves as a function of catalyst system. Heterogeneous: (□) Co(octoate)$_2$.SiO$_2$; (○) CoCl$_2$.2Py–SiO$_2$; Co/Si = 1/300. Homogeneous: (■) Co(octoate)$_2$; (●) CoCl$_2$.2Py. $[H_2O] = 7 \times 10^{-3}$ M; $[Co] \approx 5 \times 10^{-5}$ M; $[\text{monomer}]_0 = 1.66$ M; [DEAC] = 0.064 M; $T = 20°C$

which are slightly lower than average *cis*-1,4 levels reported for homogeneous systems.

The maximum activity obtained by this supported catalyst system was 28 kg polymer per gram of cobalt per hour, which is significantly below that reported by Soga *et al.*[10] for their catalyst system. More importantly, the catalyst activity is only slightly greater than achieved in conventional homogeneous systems employing cobalt–octoate catalysts[17]. We thus examined the activity of a supported cobalt–octoate catalyst. Even though cobalt–octoate has a high solubility in toluene it was irreversibly absorbed onto the silica, at least at Co/Si ratios of 1/300 or less. The results of these experiments and a comparison with the CoCl$_2$.2Py system are shown in *Figure 3* and *Table 4*. The supported cobalt–octoate catalyst showed a considerable increase in catalyst activity compared with the CoCl$_2$.2Py system and the homogeneous systems. Thus the ligand initially attached to the cobalt has a direct influence on the catalyst activity.

DISCUSSION

It is apparent from these results that the basic mechanism of polymerization remains essentially unchanged from the homogeneous system. This is seen from the kinetic data showing the reaction to be first-order in both catalyst and monomer concentrations. However, the factors that affect the active-site concentration on the supported catalyst are clearly different. The activity increase in this system appears to be due entirely to an increase in the active-site concentration, as shown by the lower molecular weights obtained.

A method that has been used previously to gain an insight into the mechanism of the polymerization process has been the calculation of the ratio of moles of polymer produced per mole of cobalt[12]. Thus in the corresponding homogeneous polymerization system this ratio was found to be close to and often slightly greater than unity. The basic problem with this calculation is, however, that it can never take into account the actual concentration of cobalt atoms that are active. The corresponding ratio for this heterogeneous system is around 10, which reflects the substantially lower molecular weights obtained in this system. This greater ratio could be caused by two factors: (i) the presence of chain transfer in this system presumably with the aluminium alkyl, as has been reported in other Ziegler–Natta systems[19] but not for the homogeneous Ziegler–Natta polymerization of butadiene[12], or (ii) a substantially increased number of active cobalt atoms, i.e. those cobalt atoms that actually are involved at any instant in time in the production of a polymer molecule. Although some estimation of the active-centre concentration can be made from molecular weight data as a function of conversion, the method proved to be too inaccurate, with M_n rapidly reaching a limiting value as seen in *Figure 2*. A less ambiguous technique involves radiolabelling using either quench methods with labelled methanol, or radiotagging. The method is well established for propylene polymerization[20] but for butadiene conflicting data have been presented[21,22]. Recently, Pan *et al.*[23] have used ethanol quenching for determining the active-centre concentration in the polymerization of butadiene catalysed by rare-earth salts, with some success. Between 4 and 8% metal atoms were found to be active in the polymerization process. Further development of these two techniques will obviously be of considerable use for the detailed understanding of the mechanism of both the homogeneous and the supported catalyst polymerization of butadiene.

A further interesting aspect of this catalyst system is the effect of the Co/Si ratio on the catalyst activity and M_n, as seen in *Table 1*. It is apparent that the active-site concentration has not changed as the cobalt dispersion increased but the activity has been significantly retarded. This result suggests either that a steric effect is hindering the growth rate of the polymer chain, which appears unlikely in these high-surface-area supports, or that the active centre involves a significant cluster of cobalt atoms and aluminium alkyl to achieve a certain activity. This latter explanation could also explain the low

Table 4 Comparison of heterogeneous and homogeneous systems' *MW* and initial activity data[a]. Conditions as for *Figure 4*

Catalyst	M_n (10^3)	M_w (10^3)	Initial activity (kg polymer (g Co)$^{-1}$ h^{-1})	*cis*-1,4 (%)
CoCl$_2$.2Py–SiO$_2$	34	136	22	93
CoCl$_2$.2Py[b]	198	436	2.5	96
Co(octoate)$_2$–SiO$_2$	47	140	34	97
Co(octoate)$_2$[c]	250	470	4	97

[a] *MW* averages at 50% conversion
[b] Data from Nemeth[18]
[c] Data from Honig *et al.*[12]

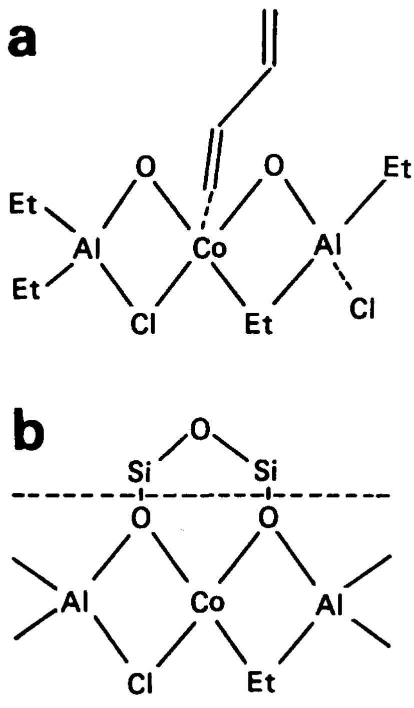

Figure 4 Proposed active-site structure: (a) alumoxane coordinated cobalt; (b) silica coordinated cobalt

concentration of active cobalt atoms that occurs in these systems.

The role of water in both the homogeneous and heterogeneous systems outlines the difficulties confronting the researcher in defining the active-site structure. Whilst Howell *et al.*[24] were able to provide a detailed structure of the active site in a soluble cobalt catalyst system, no indication of the role of water or of why only 10% of the cobalt atoms are active could be deduced from their data. That the addition of water increases the activity by the formation of alumoxanes, which are involved in the formation of the active site, has been well established in recent publications[25–27]. What is not apparent, however, is why a critical ratio of alkyl to water is observed in these systems, since increasing the water concentration should also increase the alumoxane concentration as the alkyl is always in excess. A solution to this problem may be gained by looking at the effect of water concentration on M_n in both homogeneous and heterogeneous systems. In homogeneous systems, whilst water influences the catalyst activity, M_n is virtually unchanged[3,12,28]. The active-site structure must contain a critical ratio of free alkyl and alumoxane concentration, with the alumoxanes directly involved in the cobalt–oxygen bond formation as shown in *Figure 4*. This critical ratio is defined by the ratio of alkyl to water concentration. Excess water above this ratio decreases the catalyst activity, probably by a reduction in the free alkyl concentration. A further point to notice is that the alumoxane concentration is much greater than the total cobalt concentration, with a 40-fold excess being typical in many systems, which must require some rethinking of the traditional structure of the active site.

In the heterogeneous system, however, water must react directly with the active site, causing a significant decrease in its concentration as indicated by the results in *Table 2*. A possible structure for an 'active' cobalt site is analogous to that proposed for the homogeneous system and is also shown in *Figure 4*. It should be indicated, however, that further exploratory work will be necessary before the structure of the active site can be adequately defined and the polymerization mechanism elucidated. In particular, the excess aluminium alkyl concentration and the low ($\sim$10%) concentration of active cobalt atoms must be explained. However, this active-site concentration is greater than that for the homogeneous system, and reasons for this will be investigated.

It may well be that the study of these supported catalyst systems will enable the many vexing questions as to the active-site structure in the polymerization of butadiene to be successfully answered.

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