

Synthesis of Highly Active Alkene Polymerization Catalysts using MgCl_2 Vapour

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The condensation of MgCl_2 vapours in a frozen matrix produces highly activated, high surface area materials which, when treated with TiCl_4 , yield MgCl_2 -supported, highly active Ziegler–Natta catalysts with controlled catalyst and polymer properties.

A review of the literature^{1,2} indicates that there are two major routes to the generation of MgCl_2 -supported Ziegler–Natta catalysts. Ball milling MgCl_2 in the presence of TiCl_4 and/or electron donors breaks down the bulk material to the appropriate particle size by a combination of mechanical and chemical processes. The reaction of magnesium alkyls with halide donors forms MgCl_2 particles in a thermally activated chemical process. In both cases, it is the formation of high-defect MgCl_2 structures that is essential to catalyst activity.³ Vapour synthesis represents a new, controlled route to these important catalysts.

Magnesium chloride is easily evaporated from a resistively heated crucible, and exists in the gas phase as a monomeric species.⁴ Condensation into a liquid nitrogen-cooled heptane matrix gives MgCl_2 monomers and lower oligomers which associate to form bulk MgCl_2 upon warming slowly to room temperature. X-Ray diffraction indicates that the primary crystallites of this white, free-flowing powder are much smaller than those obtained by ball milling.^{4,5} Measurements indicate that very high surface areas can be achieved. (See Table 1 for synthesis and characterization of the catalysts.) Pore volumes can be varied from a distribution much lower

Table 1. Catalyst preparation, characterization, and activity.

| Catalyst preparation sequence | Titanium content/% | Surface area ^a /m ² g ⁻¹ | Average pore diameter ^b /Å | Activity ^c |
|--|--------------------|---|---------------------------------------|-----------------------|
| MgCl ₂ + TiCl ₄ , ball milled | 2.46 | 45.6 | 109.7 | 26 800 |
| MgCl ₂ into heptane, post-treated with TiCl ₄ | 3.00 | — | — | 11 600 |
| MgCl ₂ into heptane, TiCl ₄ | 4.24 | 72.9 | 191.7 | 20 000 |
| MgCl ₂ into TiCl ₄ | 4.21 | 170.2 | 58.2 | 22 600 |
| MgCl ₂ into toluene, TiCl ₄ | 1.77 | 36.9 | 70.7 | 44 000 |
| MgCl ₂ into (Me ₃ Si) ₂ O, TiCl ₄ | 1.23 | 319.0 | 34.9 | 60 700 |
| MgCl ₂ into <i>m</i> -di-isopropylbenzene, TiCl ₄ ^d | 3.28 | 21.4 | 122.8 | 10 700 |
| MgCl ₂ and ZrCl ₄ into heptane | 20.3 ^e | 39.6 | 119.6 | 240 ^f |

^a Measured by the nitrogen Brunauer–Emmett–Teller method. ^b Measured by N₂ porosimetry. ^c Polymerization at 65 °C, 15 psig ethylene, 2 h. Activity units: (g polyethylene) (g Ti)⁻¹ h⁻¹ bar⁻¹. ^d Solid CO₂-cooled, all others liquid N₂-cooled. ^e % Zr. ^f (g polyethylene) (g Zr)⁻¹ h⁻¹ bar⁻¹.

and narrower than that of ball milled materials to a broad or even bimodal distribution.

The ability to control particle size and surface features is important to the subsequent reaction of these materials with TiCl₄ to give highly active MgCl₂-supported alkene polymerization catalysts. For ethylene polymerization, the catalysts are activated with aluminium alkyls, with or without Lewis base electron donors, using techniques reported elsewhere.⁶ Polymerization activities are comparable to catalysts prepared by standard ball milling techniques when electron donors are not employed, but can be increased substantially by proper choice of preparation conditions.

The cocondensation matrix is not limited to hydrocarbons and liquid nitrogen cooling. An active catalyst is obtained if MgCl₂ is evaporated into a mixture of heptane and TiCl₄, and, eliminating the hydrocarbon completely, MgCl₂ can be evaporated directly into TiCl₄ as a matrix. In the latter case, the dispersion of the primary crystallites was greater, and catalyst activity higher. Catalyst activity is even higher when a toluene matrix is employed. In each of these cases, the MgCl₂ monomer is able to form metastable complexes which then decompose to solid MgCl₂. This is exemplified by the red charge-transfer complex formed between MgCl₂, TiCl₄, and toluene at low temperature which decomposes on warming with precipitation of the solid catalyst. There is little opportunity for the disordered structure to anneal to form larger primary crystals. This effect of stabilization of MgCl₂ is most pronounced when hexamethyldisiloxane is used as the matrix;

activity is improved more than five-fold compared to the use of heptane as a matrix.

To move away from liquid nitrogen cooling, MgCl₂ can be evaporated into a fluid, solid carbon dioxide-cooled matrix of TiCl₄ in *m*-di-isopropylbenzene. Activity is reduced to that expected for a non-co-ordinating alkane matrix. Titanium-free catalysts can be prepared by simultaneously evaporating MgCl₂ and ZrCl₄ into a heptane matrix. Although the activity is low, it is greater than that observed for activated ZrCl₄ without MgCl₂. It was not possible to separate the ZrCl₄ from the ZrCl₄-MgCl₂ mixture and as a result, it was not possible independently to assess the activity of the catalyst supported on MgCl₂.

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