THE MECHANISM AND STABILITY OF SUPPORTED ZIEGLER CATALYSIS

R. Spitz, L. Duranel*, and A. Guyot

CNRS - Laboratoire des Materiaux Organiques
BP 24 - 69390 Lyon Vernaison (France)

INTRODUCTION

A family of supported Ziegler catalysts, suited for propene polymerization were studied for more than ten years, beginning in the early 70's. The solid precatalyst used for all the studies can be described by a common formula: MgCl2-E.D.-TiCl4, in which the electron donor (E.D.) is almost always an aromatic ester (A.E.), generally ethylbenzoate (E.B.). The preparation chiefly differs in the way the three components are reacted together by milling or impregnation, the temperatures, the durations and the ratios used.1

Some other additives are described in the patent literature, but do not seem to really change the trends of the system. In all cases, in spite of the progress achieved during recent years, this type of precatalyst used in propene polymerization shows a fast decrease in the polymerization rate with all the common alkylaluminum derivatives used as cocatalysts (mostly: aluminumtriethyl or triisobutyl, mixed in some cases with dialkylaluminum chloride). The decrease is observed at low or high pressure in the usual polymerization temperature range (60-80°C). Some increase in the decay rate is achieved when the catalytic system is made more isospecific by adding an E.D. to the cocatalyst.1,2

Figure 1 shows typical kinetic curves at 4 bar propene pressure emphasizing the effect of Al/E.D. ratio and Figure 2 shows that the kinetics in a propene liquid pool have the same shape. The high performance precatalyst used here is obtained by comilling MgCl2 and E.B. followed by excess TiCl4 impregnation and drying in an improved way.3 Figure 3 shows the kinetic curves of this system using trioctylaluminum and diethylaluminum chloride as cocatalysts.

On the contrary, ethylene polymerization gives rather constant and even sometimes increasing kinetic curves depending on the polymerization temperature. An example is given in Figure 4 with the same catalytic system.

*Present address: ATOChem - SNEA(P)
BP 34 LACQ - 64170 ARTIX (France)
Fig. 1. Propylene Polymerization Kinetic. 4 bars, 63°C, TEA 3 mmol/l Electron
Electron donor: ethylparatoluate (EPT)
 0 Al/EPT = 4 (heptane insoluble fraction HI = 95.2%)
 3 Al/EPT = 3 (HI = 96%)

Fig. 2. Propylene Polymerization Kinetic. Liquid pool 66°C, 26 bars
TEA = 5 mmol/l; Al/EPT = 3 (HI = 96.2%)