

Kinetic Studies on Propylene Polymerization using High-Activity Silica-Supported Ziegler–Natta Catalysts¹

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Abstract—This study concerns the use of silica-supported high-activity Ziegler–Natta catalysts for the polymerization of propylene under slurry conditions. In particular, two types of silica supports are investigated, viz, non-spray-dried and spray-dried materials. The effects of support structure on kinetic behavior are examined in some detail. The distribution of active centers in these silica-supported catalysts is investigated by EDAX and the morphologies of the catalyst particles and the polymer products are recorded by SEM. The results obtained are correlated with the kinetic behavior of the two catalyst systems and appropriate models for polymer particle growth are presented.

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INTRODUCTION

The most successful Ziegler–Natta catalysts developed so far for propylene polymerization are those based on titanium tetrachloride supported on MgCl_2 . The patent disclosures by Montecatini Edison Co. [1] and Mitsui Petrochemicals Ind. [2] of catalysts prepared using TiCl_4 , an activated form of MgCl_2 , and an electron donor, which were capable, when activated by a mixture of trialkylaluminum and an electron donor, of polymerizing propylene with very high activities and stereospecificities, laid the foundations of extensive subsequent commercial applications. Such catalyst systems for propylene polymerization have been the focus for many detailed studies [3–6].

An older and alternative procedure in the ongoing development of Ziegler–Natta catalysts has been the use of calcinated SiO_2 as a support material, often treated with some chemical modifier such as SiCl_4 or SiHCl_3 [7]. Such catalyst systems have been used mainly for ethylene polymerization. Nevertheless, in spite of improvements in catalyst activity by thermal and chemical methods, the activities obtained were still very poor compared to those obtained using MgCl_2 -supported catalysts. However, very significant improvements using TiCl_4 catalysts supported on SiO_2 can be obtained by the incorporation of relatively small amounts of magnesium compounds [8]. The benefits of using SiO_2 as a support material in gas phase and slurry polymerization arise because of the controlled fragmentation properties of this material and also its ability

to replicate its morphology in the final polymer—benefits shared also with MgCl_2 -supported catalyst systems.

Whilst the scientific literature abounds in papers dealing with studies using MgCl_2 -supported catalyst systems for propylene polymerization, there are comparatively fewer papers dealing with the use of SiO_2 -supported Ziegler–Natta catalysts. This paper attempts to provide a study of the use of two specific SiO_2 -supported catalyst systems for propylene polymerization and, in particular, to investigate how support structures can influence the kinetic behavior of polymerization systems.

EXPERIMENTAL

Preparation of catalysts. Two SiO_2 -supported catalysts were prepared as described by workers at BASF [9–11] using non-spray-dried and spray-dried SiO_2 . These catalysts are labeled Catalyst A (angular) and Catalyst S (spherical), respectively. Catalyst S was based on silica prepared by a spray-drying procedure with the aim of producing a catalyst which would fragment in a more controlled manner. The compositions of these catalysts are listed in the table.

Donors. Di-*n*-butylphthalate (DnBP) and di-isobutylphthalate (DIBP) were used as internal donors. Isobutylpropyldimethoxysilane (BUPS) was used as the external donor in all polymerizations together with aluminium triethyl as the cocatalyst.

Polymerization procedure. Polymerizations were carried out in a 500-cm³ Büchi autoclave, equipped with a magnetically driven anchor bladed stirrer capable of stirrer speeds up to 2200 rpm. Dried propylene was supplied on demand and the rate of supply was

¹ The text was submitted by the authors in English.

Compositions of silica supported catalysts

| Catalyst | Silica support | Internal donor | Ti, wt % | Mg, wt % | Cl, wt % | DnBP, wt % |
|------------|------------------------------|----------------|----------|----------|-----------|------------|
| Catalyst A | SG332 Ex-Grace Davison | DnBP | 3.6–4.4 | 7.0–8.0 | 27.0–32.0 | 2.0–4.0 |
| Catalyst B | ES70 Ex-Crossfield | DnBP | 3.6–4.4 | 7.0–8.0 | 27.0–32.0 | 2.0–4.0 |

recorded by means of an automatic print unit. All slurry polymerizations as described in this paper were carried out in purified dried EC180 (pentamethylheptane). The order of addition adopted was first the cocatalyst, then the external donor, and finally the catalyst slurry in EC180 with 2-min intervals between additions.

An induction period was observed when using Catalyst A, whereas no induction period was present in the rate–time profiles obtained using Catalyst S. The highest catalyst activities were obtained at the highest monomer pressure (5 atm in this case), and under these conditions, the average rate of polymerization for Cat-

RESULTS

Kinetic behavior. The effect of monomer pressure in the range 1–5 atm of propylene pressure was investigated using the two catalyst systems and representative rate–time profiles are shown in Fig. 1 for Catalyst A and Catalyst S.

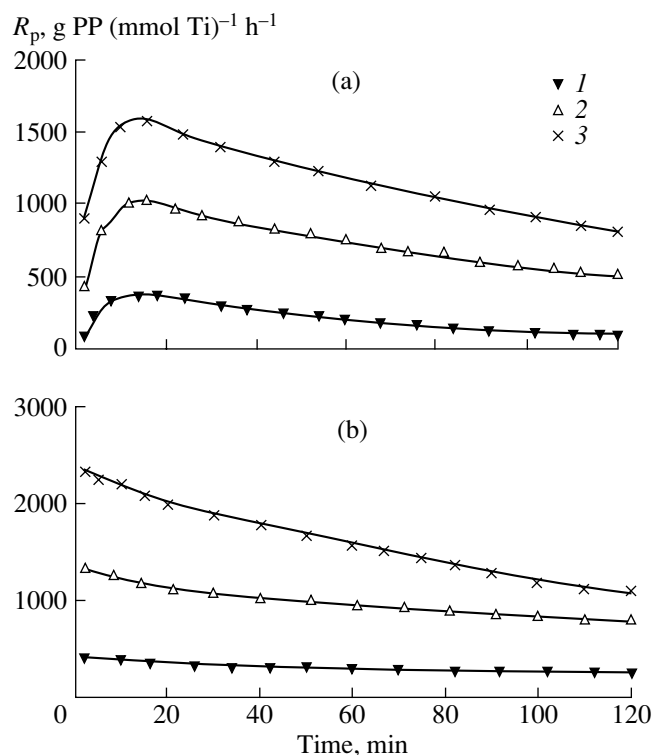


Fig. 1. Influence of monomer pressure on the rate–time profiles for propylene polymerization using Catalyst A (a) and Catalyst S (b). Polymerization conditions: Ti = 0.040 mmol/dm 3 ; TEA = 4.80 mmol/dm 3 ; [BUPS] = 0.40 mmol/dm 3 ; polymerization temperature 80°C; polymerization time 2 h. P = 1 (1), 3 (2), 5 atm (3).

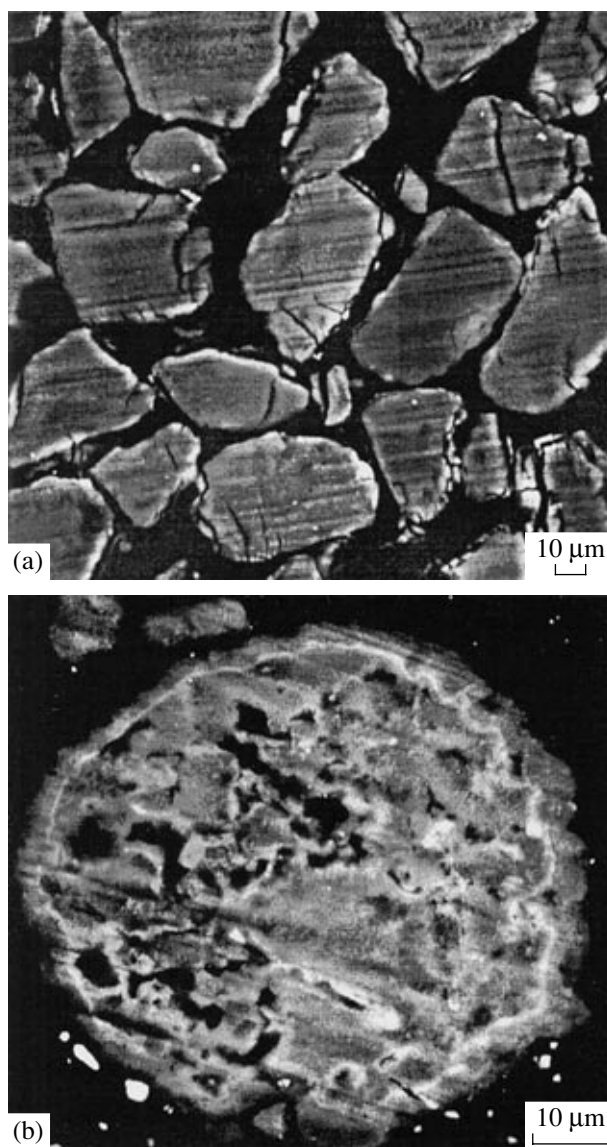


Fig. 2. Internal particle structure of Catalyst A (a) and Catalyst S (b).

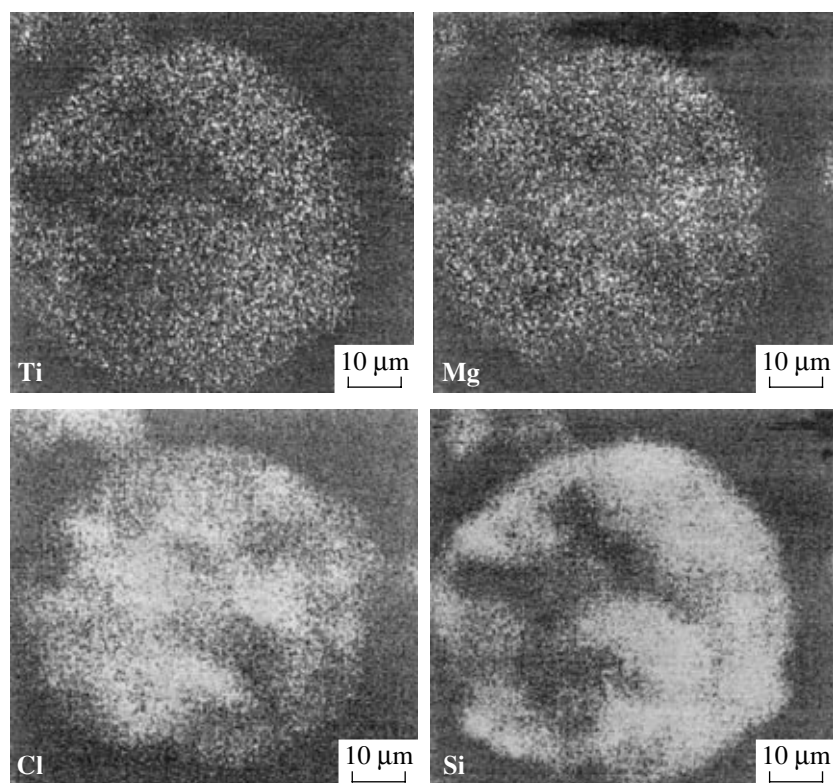


Fig. 3. Elemental distributions within Catalyst A.

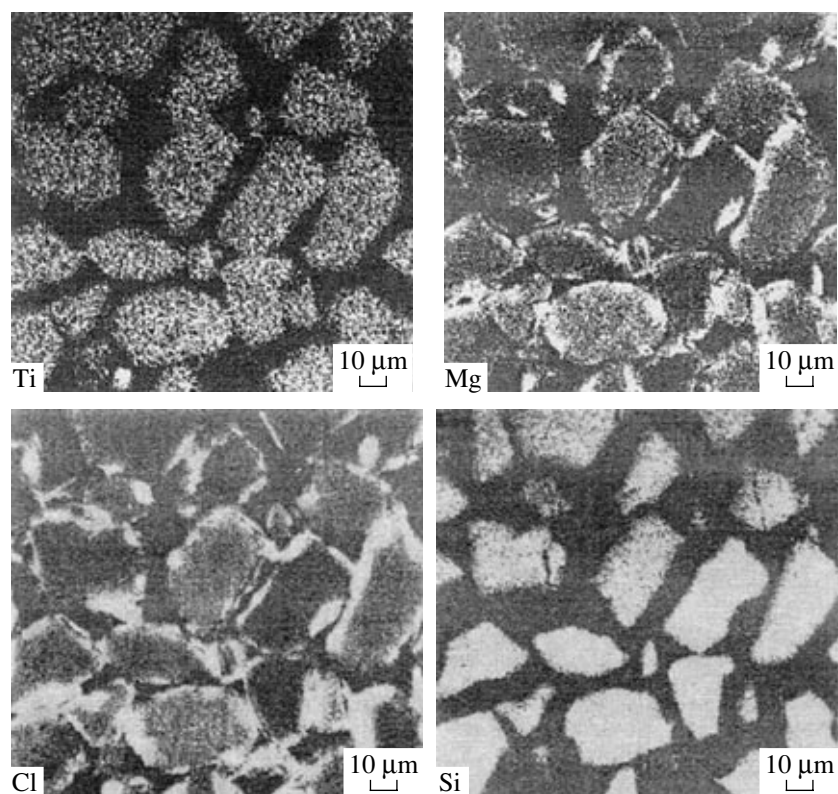


Fig. 4. Elemental distributions within Catalyst S.

alyst S was some 30% higher than for Catalyst A. The porosity (see morphological section) of the support used to prepare a catalyst evidently controls both the shape of the rate–time profiles and the ultimate catalyst activity.

Morphological studies. The two catalyst systems and the polymers produced were subjected to extensive morphological examinations. The internal catalyst particle structures of Catalyst A and of Catalyst S were investigated by SEM, after slicing the catalyst particles using a microtome, and the resulting pictures are shown in Fig. 2.

These micrographs show clearly the internal structures of both catalysts and reveal that Catalyst S has a higher internal porosity and contains meso pores. Additionally, a number of voids (empty spaces) can be identified. The internal structure of Catalyst A is much more dense and this structure explains the presence of an induction period observed in Fig. 1a and the lower average activity which arises owing to slower and more incomplete fragmentation.

The elemental distributions of titanium, magnesium, chlorine, and silicon atoms were determined by EDAX (energy dispersive analysis by X rays) and the results obtained are shown in Fig. 3 and in Fig. 4 for the two catalyst systems.

In Catalyst A, the titanium atoms are uniformly distributed throughout the catalyst particles. However, magnesium and chlorine atoms are located predominantly in the outer regions of the catalyst particles. In Catalyst S, the titanium, magnesium, and chlorine atoms are all uniformly distributed throughout the catalyst particles. In addition, the silicon distribution in Catalyst S shows dark areas, indicating the presence of porous areas or voids, whereas in Catalyst A there are no such regions. These results are consistent with the SEM results and show that Catalyst S is more porous and contains larger pores than Catalyst A.

Representative samples of polymer produced by both catalyst systems were also subjected to SEM analyses, and the results obtained are shown in Fig. 5.

Replication of catalyst particle shapes takes place in both polymerization systems, but more fines are produced when Catalyst A is used. Also, the polymer produced using Catalyst S shows a more controlled replication of the catalyst particle morphology. It is thus believed that a more uniform and rapid fragmentation occurs when using Catalyst S, which involves the whole of the catalyst particle during a complete polymerization. In the fragmentation process, growing microreactors [12] are produced, leading to excellent catalyst particle replication. The mode of internal fragmentation of Catalyst S allows also retention of porosity, since not all the pores have to be filled with polymer before fragmentation occurs [13, 14].

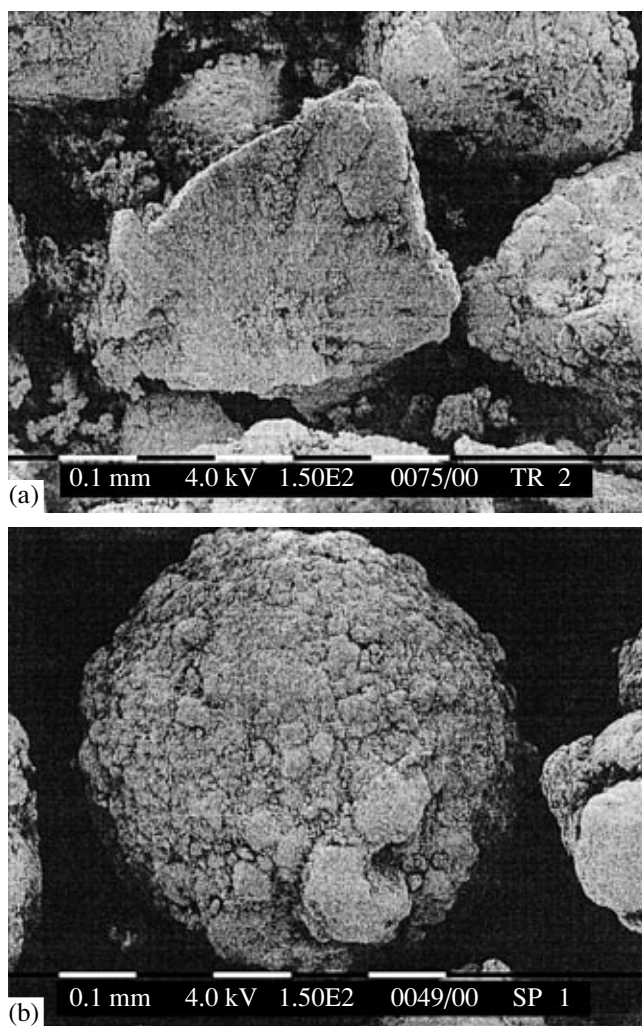


Fig. 5. SEM of polymer produced by Catalyst A (a) and Catalyst S (b).

We propose the mechanism shown in Fig. 6 for polymer growth when using SiO_2 -supported catalysts. A polymer layer formed around Catalyst A particles is envisaged which takes place upon the onset of polymerization. Diffusional effects of reactants through this polymer layer will govern the shapes of the resulting rate–time profiles. It is believed that the actual process of polymer growth in the case of Catalyst S takes place within microreactors and that the growth process can be described by the multigrain model proposed by Ray et al. [15]. The onion-skin type of model advanced for MgCl_2 -supported catalysts [12] has not yet been validated for SiO_2 -supported catalysts, although it is certainly the case that Ti atoms in the outer surface layers will be the first to become activated as polymerization centers.

In conclusion, these results show very clearly how in the use of supported high-activity Ziegler–Natta catalysts the observed kinetic behavior can be related to

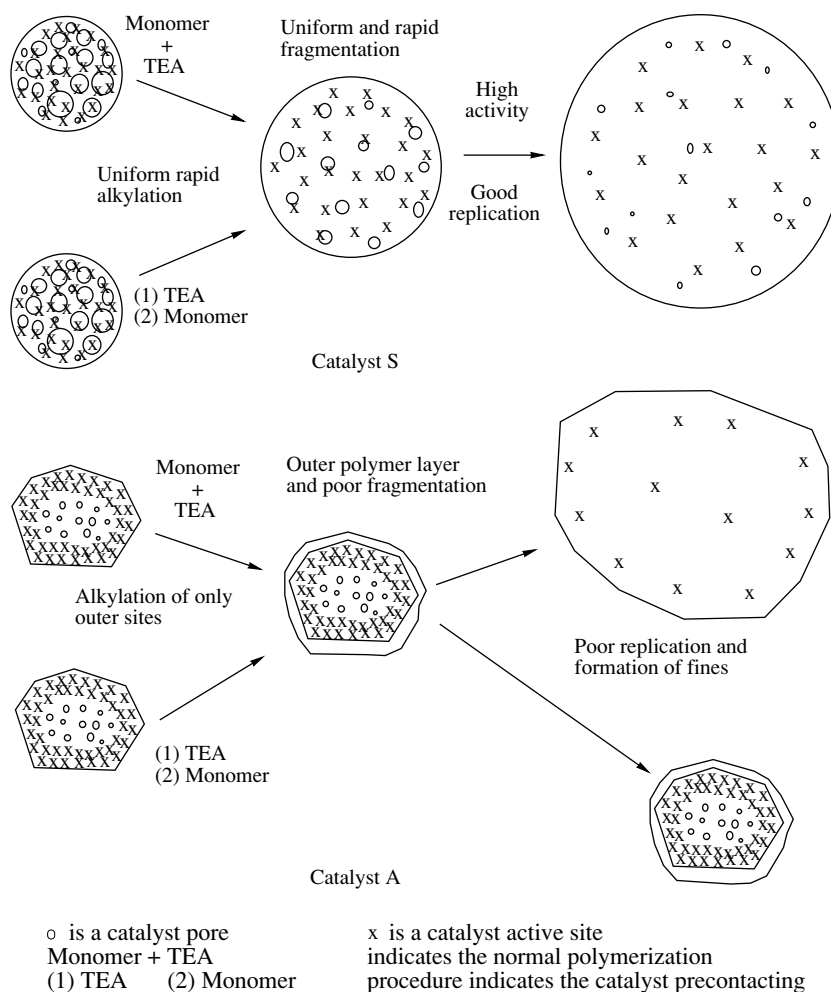


Fig. 6. Models for polymer particle growth.

the external and internal structures of the supporting matrixes.

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