Morphological investigation of Ziegler-Natta catalyst supports

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Introduction

The ZieglerNatta catalysts, discovered in 1954 by Karl Ziegler and Giulio Natta - awared the Nobel Prize in Chemistry 1963 for their discoveries in the field of the chemistry and technology of high polymers - are the basis for the industrial production of polyolefins.

Starting from the earlier titanium trichloride based catalysts, the discovery of magnesium chloride as the election support for titanium tetrachloride and of the routes to obtain a control of particle morphology represented the most important breakthrough for the development of modern catalysts. Now, the complete control of morphology from the support to the catalyst and, finally to the growing polymer particles represent a key point in leading industrial polymerization processes. [1]

In this study a morphological investigation based on an interdisciplinary approach involving different microscopy techniques was used, made possible by the setup of a new sample preparation procedure. The combination of the complementary information brought about a deepen awareness of the observed morphology.

Materials and Methods

Catalyst supports

The materials used for this study are supports produced in our industrial plants that differ for the residual final composition in term of Ethanol content, in association with the catalyst derived from one of the selected supports. All materials were investigated as for surface and section morphology knowledge. The sample preparation procedure requires all steps performed under inert atmosphere, with an improved analytical method for the section investigation, based on sample embedding in proper low viscosity resin plus cutting with Ultracryomicrotome apparatus.

Equipment

Scanning Electron Microscope

Samples were examined on ESEM Quanta 200 FEG (FEI) using the low vacuum mode and the solid state detector, imaging the backscattered electrons originated by the interaction between the sample and the primary beam. EDS analysis was also performed by Bruker XFlash® 5030 (SDD detector) as in semi quantitative mode and in map one.

Atomic Force Microscopy

The same specimen samples investigated by ESEM have been further analyzed by Nanoscope V (Bruker) under inert atmosphere, collecting amplitude and phase data by using Bruker silicon tapping probe RTESP model.

Transmission Electron Microscopy

A Tecnai 10 (FEI) apparatus was used to image the sample after a manual milling in a crucible and suspension in anhydrous hexane.

Results and Conclusions

The ESEM analyses performed on the selected samples prepared under inert atmosphere have confirmed the presence of a network type inner morphology with presence of porosity channels. By the use of EDS maps the channels have been uniquely identified allowing further Image Analyses interpolation for quantitative measurements of their mean diameters.

The same sample sections identified by ESEM were investigated by AFM in tapping mode at high magnification. Interesting differences between support and catalyst intrinsic morphology have been revealed, showing a granular structure with differences in dimension and shape as reported in Figures 1 and 2.

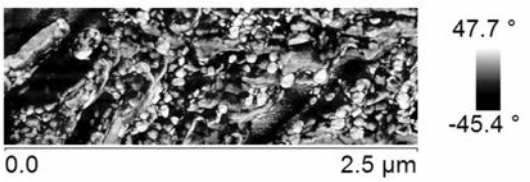

Figure 1. AFM phase image of support.

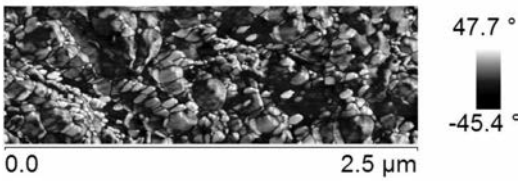

Figure 2. AFM phase image of derived catalyst.

The granular structure morphology has been confirmed also by TEM analyses

The present study has showed that an interdisciplinary approach with different microscopy techniques applied on the same prepared specimen is able to catch the catalyst supports primitive morphology directly on real spherical samples from plant productions. The obtained results of porosity network by ESEM and granular structure by AFM and TEM are in line with data literature on lab scale samples [2].

In particular the AFM technique thanks to its atomic resolution has evidenced the intrinsic granular structure of catalyst supports allowing further studies of correlation between plant process conditions and obtained morphologies.

References

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2. A. Andoni, et al. J Catalysis. 2007;247:129.