PRIORITY COMMUNICATION

Polyethylene Formation on a Planar Surface Science Model of a Chromium Oxide Polymerization Catalyst

P. C. Thüne, J. Loos,* P. J. Lemstra,* and J. W. Niemantsverdriet

*Schuit Institute of Catalysis and * Dutch Polymer Institute, Eindhoven University of Technology, 5600 MB Eindhoven, The Netherlands*

A planar $CrO_x/SiO_2/Si(100)$ model for the Phillips ethylene polymerization catalyst has been prepared by spin-coat impregnation from an aqueous solution of CrO_3. In order to test the model catalyst with its extremely low chromium content, a special reactor was designed with a CrO_x/Al_2O_3 filter to effectively remove impurities. The model catalyst polymerizes ethylene in the gas phase at $160°C$ with a constant activity and forms a 350-nm-thick layer of polyethylene in 1 h. Atomic force microscopy reveals the expected spherulite morphology of the polyethylene films in different stages of development. The work opens attractive opportunities for future studies of nascent morphology of catalytically formed polymers. © 1999 Academic Press

INTRODUCTION

Although about one-third of the world supply of linear high-density polyethylene (HDPE) is based on it, our knowledge of the CrO_x/SiO_2 or Phillips catalyst (1–3) is limited in comparison to what is known about the Ziegler–Natta catalyst, which is responsible for the other two-thirds of HDPE production.

Recently, flat surface science model systems, in which the catalytically active phase is applied on a flat, conducting substrate, have attracted interest for spectroscopic and microscopic studies of supported catalysts (4). In order to prove that such systems are realistic, it is essential to demonstrate that a model exhibits representative catalytic turnover. Several activity studies have been described for supported metal particles, but catalytic investigations of nonmetallic model systems are rare. Magni and Somorjai, however, successfully modeled a Ziegler–Natta catalyst in a surface science environment and demonstrated it to be active (5).

Aiming at a quantitative molecular description of polymer formation on CrO_x/SiO_2, we have prepared a model for the Phillips catalyst, based on a silicon single crystal covered with a thin (≈ 90 nm) overlayer of amorphous silica, which was impregnated by spin coating it with an aqueous solution of chromic acid (6). As discussed elsewhere (7, 8), spin-coating impregnation on flat oxide surfaces provides a realistic analog to pore volume impregnation of high surface area supports.

A critical step in the activation of the Phillips catalyst involves calcination in dry air or oxygen up to at least $500°C$, known to partially dehydroxylize the silica surface and to convert all chromium to hexavalent surface chromate, provided that the chromium content is sufficiently low. Upon exposure to ethylene at elevated temperatures (above $100°C$), the catalyst goes through an induction period during which the active site that catalyzes polyethylene formation forms. Increasing the polymerization temperature above $150°C$ diminishes the induction period. Alternatively, prereduction in, e.g., carbon monoxide, also removes the induction period and enables polymer formation at room temperature and even below (9, 10).

The CrO_x/SiO_2 system is extremely sensitive to poisoning by water, acetylene, CO, CO_2, and traces of alkali. Hence, removing impurities is crucial when working with a surface science model exposing 1 cm^2 of active surface only. We describe a reactor with a specially designed filter for the ethylene feed, which has been essential for observing polymer formation on this model system.

The purpose of this communication is to demonstrate that a planar model of the Phillips ethylene polymerization catalysts consisting of CrO_x on a thin film SiO_2 on a silicon (100) substrate displays representative polymerization activity and offers excellent opportunities for visualizing polymers growing on catalysts by atomic force microscopy. The planar model approach will be extended to study the nascent morphology of polyolefins on this and other polymerization catalysts in the future.

EXPERIMENTAL

Preparation of the CrO$_x$/SiO$_2$/Si Model-Catalyst

The CrO$_x$/SiO$_2$/Si model-catalyst was prepared as described in detail before (6). Briefly, Si(100) silicon discs were calcined at 750°C for 24 h to obtain a flat, amorphous silica layer of approximately 90 nm thickness. The silicon wafer is then cleaned in a mixture of concentrated hydrogen peroxide (30 vol%) and ammonia (30%) at 70°C. After further cleaning in boiling water the wafers are covered with the impregnation solution, chromic acid in water, and mounted on the spin-coating device under nitrogen atmosphere. Upon spinning most of the solution is ejected from the wafer, leaving behind a thin evaporation layer. As the thickness of this layer can be calculated for any given rotation speed (2800 rpm), temperature (20°C), and solvent (water), the loading of the model catalyst can be controlled simply by varying the concentration of the (dilute) spin coating solution. The polymerization studies reported here were done with a model containing an initial loading of 2 Cr/nm^2.

Ethylene Polymerization Reactor

Figure 1 shows the reactor used for the activation of the catalyst and the actual polymerization. It consists of two quartz tubes of 4 and 1 cm in diameter, respectively. The larger tube is surrounded by resistive heating cable (10 Ohm) and is closed on one side. The other side allows access to the thin tube and two gas valves, one connecting the reactor to a turbo molecular pump, the other serving as gas exhaust during flow operation. Resting on a Teflon adapter, the thin tube extends into the heated zone. Behind a quartz filter, the tube becomes broader to support up to 6 model catalysts. A cromel/alumel thermocouple, protected by its own thin quartz tube, measures the temperature at this point.

Before the quartz filter, upstream as seen from the model catalysts and within the heating zone, the thin tube is filled with γ-alumina extrudates impregnated with 0.17 wt% chromium (by incipient wetness impregnation from basic chromium(III) acetate solution). The chromium-loaded

FIG. 1. Schematic representation of the polymerization reactor with a catalytic ethylene filter, suitable for performing ethylene polymerization on extremely low surface area catalysts.

γ-alumina serves as a filter for the impurities in the ethylene feed stream. The reactor is sealed against atmosphere using viton o-rings.

Before the reactor is loaded with the model catalyst, it is dried in vacuum to 200°C and subsequently baked out at 750°C in flowing O$_2$/Ar (20% O$_2$, dried with molsieves 4 Å), to remove water and sodium from the reactor walls. Next the model catalyst is inserted. After drying at 200°C in vacuum, the catalyst is calcined in flowing O$_2$/Ar at 550°C for 30 min (heating rate 20 K/min, plateau at 450°C for 15 min). After cooling to 160°C the gas flow is stopped and the O$_2$/Ar is exchanged to argon (purified over (i) Cu–Cat and (ii) molsieves 4 Å) and subsequently to ethylene. The gas exchange takes about 2 min, making the start time for the polymerization reaction uncertain to within at least 1 min. Polymerization takes place in flowing ethylene at 160°C and atmospheric pressure. Pumping away the ethylene and changing to argon atmosphere stops the reaction. The polyethylene formed on the catalyst surface is initially present as a molten film and is allowed to crystallize at 100°C for 2 h before the reactor is cooled to room temperature.

Microscopy

Atomic force microscopy (AFM) images were taken on a Digital Instruments Dimension 3100 scanning microscope under ambient conditions. Measurements, performed in tapping mode (height images only), were recorded by using etched Si$_3$N$_4$ tips (TESP) with a force constant of about 20–100 N/m. Polyethylene layer thickness was determined using the height difference between the Si-substrate and the polyethylene surface after scratching the layer with a scalpel. Reflective light microscopy was carried out using a Zeiss Universal light microscope equipped with crossed polarizers.

RESULTS AND DISCUSSION

Depending on the polymerization time, the CrO$_x$/SiO$_2$/Si model catalyst produces thin films of polyethylene as confirmed by its Raman spectrum (not shown). The films are visible by eye by the Newton colors on the mirror surface of the silicon wafer. Samples polymerized longer than 15 min display the well-known "Maltese Cross" patterns of spherulite structures in the optical polarization microscope, which are typical for polyethylene crystallized from the melt (11). The AFM images in Fig. 2 show the different stages in the formation of polyethylene spherulites during crystallization from the molten state formed in the catalytic reaction at 160°C.

During the initial few minutes of polymerization, when the gas atmosphere changes from inert gas to ethylene, the product layer probably contains some paraffins of relatively low molecular weight (not shown). A polymerization
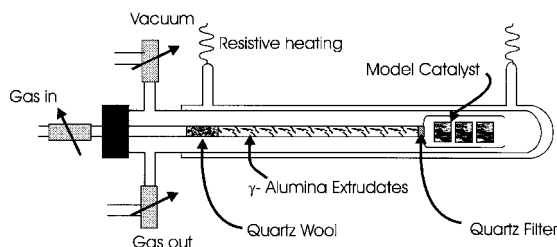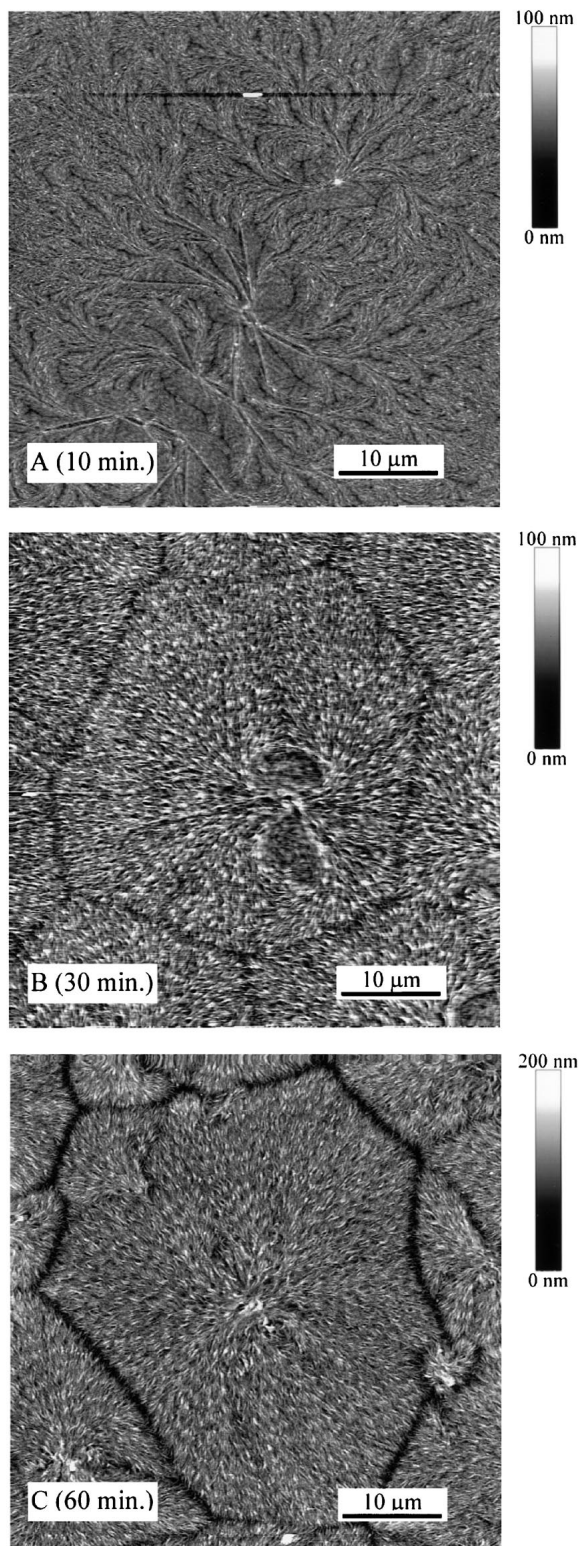
FIG. 2. AFM images of the polyethylene films formed on the CrO$_x$/SiO$_2$/Si model catalyst. The small stripes are stacks of lamellar crystals. They form the well-known spherulite superstructure, when they crystallize from the melt. Depending on the layer thickness, the spherulite growth stops at different stages of development.

time of 10 min results in a closed polymer layer on the Si-substrate (Fig. 2A), with an average thickness of about 80 nm. In this layer, paraffins coexist with polymer, and demixing during crystallization is believed to influence the observed morphology. Besides stacked plate-like parts characteristic of paraffins or edge-on grown Polyethylene lamellae, some lamellar crystal bundles of polyethylene, grown in sheaf-like fashion, are present.

Increasing the polymerization time results in thicker polymer layers and changes in the morphology. After 30 min, the surface contains spherulites of approximately 50 μm in diameter (Fig. 2B). The average film thickness is on the order of 250 nm. Closer examination reveals that all spherulites contain pronounced nucleation centers from which lamellae grow sheaf-like. Adjacent to the center of the spherulites, circular regions appear. These depressed regions show a plate-like morphology as discussed in connection with Fig. 2A.

Fig. 2C shows the AFM image of the polymer layer formed after 60 min of reaction. The average layer thickness is about 420 nm. The nucleation centers, though clearly recognizable, have been covered by a dome-like structure of polyethylene lamellar crystals. The bright contrast of the center and the distinct spherulite boundary are indicative of a three-dimensional spherulite, as is confirmed by optical polarization microscopy.

Such images have been obtained from polymers that crystallize slowly or from polyethylene that crystallizes in a matrix of parafin (12–15), but are uncommon for polyethylene, which crystallizes at such low T_c as in our case.

Analyzing scalpel scratches through the polyethylene film on the wafer by AFM profile scans enables us to determine the thickness of the polyethylene films (Fig. 3). Experiments on a blank catalyst were done to check that the steel blade does not damage the silica layer visibly.

Figure 3 (bottom) shows the average thickness of the crystallized polyethylene film as a function of polymerization time. Although the data scatter somewhat, the polymer thickness increases roughly linearly with time, indicating that the polymerization activity of the catalyst is stable for the first 60 min of polymerization.

In order to make a comparison with the activity of a commercial Phillips catalyst, we estimate the amount of polyethylene formed per chromium atom in the catalyst. The model catalyst produces a 420-nm-thick film of polyethylene in 1 hour, corresponding to 42 μg per hour. As the catalyst contains typically 1 Cr/nm^2 after calcination, the activity thus corresponds to about 250 g of polyethylene per mmol of Cr per hour, or to a nominal turnover frequency of 2.5 C$_2$H$_4$ molecules/(Cr atom s). Converted to a high surface area CrO$_x$/SiO$_2$ catalyst from Crossfield (286 m^2/g), the activity corresponds to 120 g of polyethylene per gram of catalyst and per hour at 1 bar total pressure.
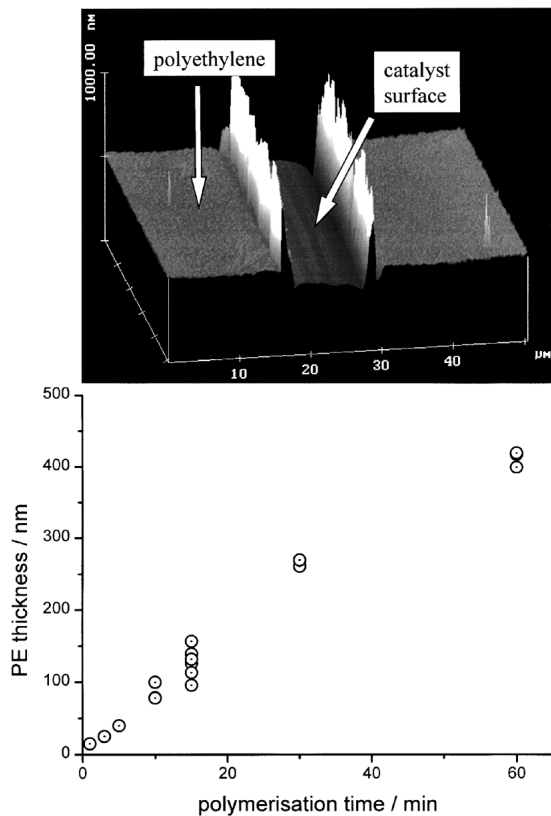
FIG. 3. (Top) AFM Image of a scalpel scratch used to determine the thickness of the polyethylene films grown on the model catalyst. (Bottom) The thickness of the polyethylene film shows a linear correlation with the polymerization time up to 60 min.

An industrial catalyst calcined at $500°C$ produces about 1 kg of polyethylene per gram of catalyst per hour however, in a butene slurry at $105°C$ under a total pressure of about 40 bar and an ethylene partial pressure of about 15 bar (2, 3, 10). Szymura *et al.* (16) report a polymer yield of 25.5 g (PE)/g (catalyst) for a Crossfield silica loaded with 5 wt% Cr, during polymerization at $25°C$ and atmospheric pressure in a hexane slurry, over a CO prereduced catalyst. While the precise values are difficult to compare due to the differences in catalyst preparation and reaction conditions, we conclude that the model catalyst displays a polymerization activity on the same order of magnitude as its industrial counterparts.

Although our studies concern polyethylene grown in the melt which crystallizes upon cooling, the work clearly opens the way for studying nascent morphology of polyolefins (polyethylenes and polypropylenes) growing on the surface of a heterogeneous catalyst, or on "single site" (metallocene) catalysts deposited on a planar substrate. This is a very important topic. The development of the nascent state morphology of polyolefins in a reactor is reasonably well understood on the micrometer level (17, 18), but not

on the scale of (macro) molecules, however. As an example we mention that nascent ultra-high molecular weight polyethylene powder produced in a reactor exhibits an unusually high melting temperature, which is attributed to the formation of extended chain crystals during polymerization (19), more or less similar to the formation of cellulose fibrils in nature. Other authors claim that the high melting temperature is related to the formation of highly metastable folded chain polymer crystals during polymerization, which reorganize prior to melting (20, 21). The study of nascent polymer morphology is hampered by the fact that supported catalysts fragment during polymerization. We believe that a systematic investigation using planar models to monitor the early stages of polymer growth on catalyst surfaces will contribute significantly to a better insight in these questions.

CONCLUSIONS

A $CrO_x/SiO_2/Si(100)$ system prepared by spin-coat impregnation from an aqueous solution of CrO_3 shows considerable activity for ethylene polymerization and performs as a realistic surface science model for the Phillips catalyst. It polymerizes ethylene in the gas phase at $160°C$ with a constant high activity to form polyethylene. Atomic force microscopy not only reveals the expected spherulite morphology of thick polyethylene films but also enables the visualization of intermediate stages of spherulite formation. We conclude that the flat model catalyst approach offers new important opportunities to study the morphology of freshly formed or even nascent polymers on catalytic surfaces. Work to characterize the structure and morphology of nascent polyethylene on chromium catalysts that have been prereduced to enable polymerization at low temperature is currently in progress to monitor the effect of simultaneous polymerization and crystallization.

ACKNOWLEDGMENTS

REFERENCES

1. Hogan, J. P., and Banks, L., U.S. Patent 2,835,721 (1958).
2. McDaniel, M. P., *Adv. Catal.* **33**, 47 (1985).
3. Choi, K.-T., and Ray, W. H., *J. Macromol. Sci. Rev. Macromol. Chem. Phys.* **C25**, 1 (1985).
4. Gunter, P. L. J., Niemantsverdriet, J. W., Ribeiro, F. H., and Somorjai, G. A., *Catal. Rev.* **38**, 77 (1997).
5. Magni, E., and Somorjai, G. A., *Surf. Sci.* **345**, 1 (1996).
6. Thüne, P. C., Verhagen, C. P. J., van den Boer, M. J. G., and Niemantsverdriet, J. W., *J. Phys. Chem.* **101**, 8559 (1997).
7. Kuipers, E. W., Laszlo, C., and Wieldraaijer, W., *Catal. Lett.* **17**, 71 (1993).

8. van Hardeveld, R. M., Gunter, P. L. J., van IJzendoorn, L. J., Wieldraaijer, W., Kuipers, E. W., and Niemantsverdriet, J. W., *Appl. Surf. Sci.* **84**, 339 (1995).

9. Krauss, H. L., and Stach, H., *Inorg. Nucl. Chem. Lett.* **4**, 393 (1968).

10. Merryfield, R., McDaniel, M. P., and Parks, G., *J. Catal.* **77**, 348 (1982).

11. Billmeyer, F. W., "Textbook of Polymer Science," 3rd ed. Wiley Interscience, New York, 1984.

12. Basset, B. C., and Vaughan, A. S., *Polymer* **26**, 717 (1985).

13. Rensch, G. J., Phillips, P. J., Vatansever, N., and Gonzales, A., *J. Polym. Sci. Polym. Phys.* **24**, 1943 (1986).

14. Lacroix, F. v., Loos, J., and Schulte, K., *Polymer* **40**, 843 (1998).

15. Norton, D., and Keller, A., *J. Mater. Sci.* **19**, 447 (1984).

16. Szymura, J. A., Dalla Lana, I. G., Fiedorow, R., and Zielinski, P. A., *Macromolecules* **29**, 3103 (1996).

17. Morre, E. P., "The Rebirth of Polypropylene." Hanser, München, 1998.

18. Philips, R. A., *J. Polymer Sci. B* **36**, 495 (1998).

19. Chanzy, H., and Marchessault, R. H., *Polymer* **8**, 567 (1967).

20. Engelen, Y. M. T., and Lemstra, P. J., *Polymer Commun.* **32**, 343 (1991).

21. Rastogi, S., Kurelec, L., and Lemstra, P. J., *Macromolecules* **31**, 5022 (1998).