



Reinforcement of Cr/silica catalysts by secondary deposition of silicate oligomers

Max P. McDaniel^{a,*}, Steve L. Kelly^b

^a Chevron Phillips Chemical Co., Bartlesville, OK 74004, United States

^b Chevron Phillips Chemical Co., Kingwood, TX 77339, United States

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ABSTRACT

Ethyl silicate oligomers were impregnated into a generic Phillips Cr/silica catalyst used commercially for ethylene polymerization. After calcination, this treatment results in a secondary deposition of silica into the original silica matrix, which changes the porosity of the catalyst somewhat and strengthens its overall structure. The process can be used as a powerful tool to manipulate polymer properties because the molecular weight of the polymer, the MW distribution, and the amount of long-chain branching (LCB) it contains, were found to be strongly influenced, and with them all aspects of molding behavior. This result provides still more evidence that the physical structure of the Cr/silica catalyst can have major consequences for the polymerization reaction, which shapes the character of the polymer. This method of controlling polymer properties is perhaps more convenient for commercial operations than those described previously.

1. Introduction

In earlier reports [1–9] it was shown that, quite apart from the chemical composition of the Phillips Cr/silica polymerization catalyst, its physical structure plays a major role in determining its activity in ethylene polymerization, and also (less intuitively) the character of the polyethylene it produces. In particular, the molecular weight of the polymer, the degree of long-chain branching (LCB), and the MW distribution are all influenced by the architecture of the silica support. These molecular features of the polymer then go on to direct its molding behavior and the physical properties of the finished part, making control of the silica structure extremely important to industrial operations.

That the activity of Cr/silica should be affected by catalyst architecture is understandable, considering that the growing polymer must fracture the silica support to allow polymer egress. Polymer chains are typically hundreds or thousands of times longer than the diameter of catalyst pores. Although the catalyst may produce thousands of times its weight in polymer during its typical 1-h reaction time, the catalyst pores are filled within the first minute of polymerization. To continue reaction, each silica particle (typically 100 μm) is usually fractured into billions or perhaps trillions of smaller fragments that allow polymer egress. Consequently, anything that weakens the silica structure tends to improve its activity for polymerization. This includes especially the pore volume (PV) of the silica. High PV silicas (> 1.5 mL/g) fragment easily to the point where all of the BET surface can participate in the

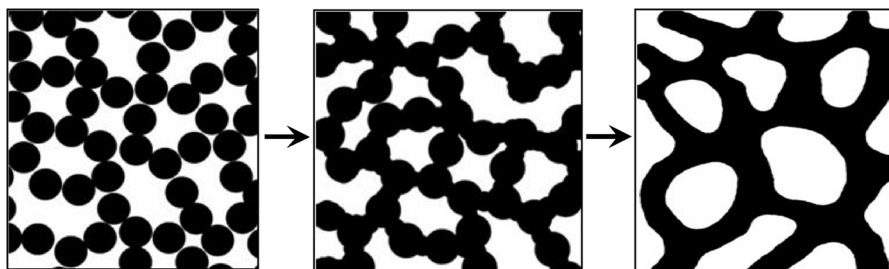
polymerization. This was inferred by comparing the observed activity per square meter of surface to that of non-porous silicas [5,6]. In contrast, silicas of PV less than about 0.8 mL/g usually exhibit little to no polymerization activity. The pores are too strong to permit fragmentation. The dependence of pore strength on PV is explained in terms of the “contact number” of each primary silica particle to its closest neighbors in the sub-structure. Low PV provides a higher number of attached neighbors and thus greater strength.

The “weld-strength”, or degree of fusion between one primary silica particle with its neighbors, also determines the overall strength of the silica matrix. This can be controlled through alkaline aging of the silica hydrogel (Oswald ripening), or by thermal sintering or by hydrothermal treatment (“steaming”). However, while increasing the strength of the silica matrix, such treatments also increase the pore diameter and lower the surface area, because primary particles are fused into a continuous mass resembling Swiss-cheese, as depicted in Scheme 1. Since the more open pores allow easier escape of polymer chains, the net result of such treatments can often be an improvement in activity (per m^2 of surface). Presumably, larger fragments can result from the stronger matrix, but which still permit full egress of polymer [3].

These generalizations describe our experience with silica gels. On the other end of the strength scale, however, are structures in which the sub-particles are not well-connected to each other, such as agglomerations of micro-crystallites, as in some aluminas, or stacks of sheets as

* Corresponding author.

E-mail address: mcdanmp@cpchem.com (M.P. McDaniel).



Scheme 1. Coalescence and fusion of primary particles during sintering or Oswald ripening of silica.

occurs in some clays. Such supports are easily fragmented even at very low pore volume [1,3,10–14].

Unlike catalyst activity, the dependence of polymer character on the catalyst's physical structure is less intuitive, and is still not fully understood. It was shown in earlier work that the PE molecular weight seems to be influenced by the catalyst pore diameter [3,5,15] and that the degree of long-chain branching (LCB) is related to the strength of the silica matrix [3,4,6]. The MW distribution was also shown to vary with catalyst structure. Two peaks were visible, indicating that polymer was formed under two different physical environments. It was proposed that these two peaks represent: 1) polymer made on the exterior of fragments, and 2) polymer “extruded” under pressure through pores from the interior of fragments. Weckhysen et al. [16] has published a particularly interesting micrograph of polymer being “extruded” from the pores of MCM-41. This latter component is much higher in MW and contains significantly more LCB. Its size, relative to the more prominent peak 1, can be varied widely by manipulation of the catalyst architecture, from an almost invisible high-MW tail, to a second equally-sized peak in a bimodal MW distribution.

Just why formation and extrusion of polymer from crowded pores would produce higher MW and more LCB is still unclear. It might be related to the difficulty of assuming the necessary precursor position. For example, chain termination by beta-hydride elimination requires that it first assume the “pucker position” to allow agostic beta-H coordination as depicted in Scheme 2 below. This position may be more difficult in a tightly-packed pore. Likewise, the incorporation of macromer to produce LCB requires either retention by coordination [17], or the ability to capture a neighboring chain, which may be easier inside a crowded pore. One could also argue that ethylene concentration is lower inside crowded pores. However, this explanation is not entirely satisfactory because although it would favor LCB formation (which is observed), it would also favor chain termination (which is opposite to observation). One would have to assume that inside crowded pores steric inhibition of chain termination is greater than the effect of low ethylene concentration on MW, which is conceivable.

In this paper, we have explored another way to probe the effect of catalyst strength on activity and polymer character. Sintering, steaming or alkaline aging was not used, because these lead to a coalescence of the fine structure, enlargement of pores and loss of surface area. Instead, in the present study the silica matrix was reinforced by a secondary deposition of silica into an existing silica pores. A typical polymerization grade silica was impregnated with various amounts of ethyl silicate oligomers to buttress the network with a secondary

coating of silica. Catalysts were then made from these silicas and the resultant activity and polymer behavior was examined.

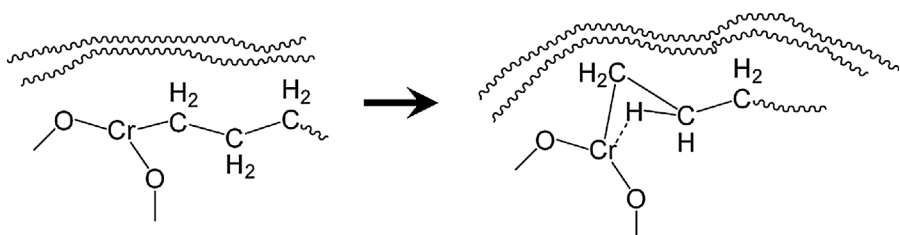
Finally, it is perhaps useful to put this study into a larger general context. Although the present study presents a new way of buttressing the catalyst matrix, it will be shown that its results are nevertheless consistent with these earlier observations from other methods of reinforcement [1–3,5–7,9,16]. A secondary deposition of silica onto the pore walls strengthened the overall catalyst matrix. Polymers made from such catalysts were found to have high MW and LCB content, the result of adding a second, high-MW shoulder to the MW distribution. The results of this form of reinforcement were comparable to, or perhaps more potent than, reinforcement by sintering, “steaming” or alkaline aging. However, this method of buttressing the silica structure is more adaptable to commercial practice, given that PE manufacturers start with pre-formed generic silicas, and cannot fine-tune LCB during plant operation by using aging, sintering or steaming treatments.

2. Experimental

2.1. Catalysts

The silica used in this study was manufactured by Philadelphia Quartz Co. under the trade name of MS3050. The oligomers of ethyl silicate were obtained from Evonik Corp. under the trade name Silbond 40 condensed tetraethyl orthosilicate, described as having a molecular weight of around 800. Methanol solutions were made to contain the desired amount of silicate, and enough dissolved basic chromium acetate to equal 1 wt% of the final catalyst. The volume of each solution was set to reach incipient wetness when added to the silica (i.e. about 3.5 mL/g). After impregnation, the silica samples were dried in a vacuum oven at 100 °C overnight. The added silica content was described as silica added as Silbond 40, divided by the total amount of silica from both sources.

To activate the final catalyst, approximately 10 g of the dried silica was added to 2-inch diameter quartz tube containing a coarse sintered glass frit (gas distribution plate) at the bottom. An air stream, dried through 13X molecular sieve, was added at the bottom of the tube so that it passed up through the frit and fluidized the catalyst. The air flow was initially set at 0.05 ft/s at 25 °C, and remained constant thereafter. The tube was placed in a furnace and the temperature raised over 1.5 h to 800 °C where it was held for three hours. Afterward the catalyst was flushed with dry nitrogen at 25 °C for 15 min and then captured in a sealed flask.



Scheme 2. Coordination of agostic β -H (the “pucker position”), which is necessary for chain termination, and possible interference in pores crowded with other polymer chains.

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