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Electron microscopic characterization of Cr/silica catalyst for ethylene polymerization

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Ethylene polymerization was carried out over both porous and non-porous 5 wt% Cr/silica catalysts in a slurry reactor. The polymerization was stopped at selected times to obtain samples for SEM and TEM characterization. Despite the different physical characteristics of the two silica-supported catalysts and their different behavior in the early stages of reaction, high resolution SEM micrographs (taken after runs of longer duration) revealed similar, fibrous and very porous polymer layers on both. This accessibility of the ethylene enables transport of monomer to the active sites at the very high reaction rates.

Keywords: SEM characterization; TEM characterization; Cr/silica catalyst; ethylene polymerization

1. Introduction

The Cr/silica (Phillips-type) catalysts have been used commercially to produce linear polyethylenes (PE) in both slurry and gas reactors. Today Cr/silica accounts for approximately 40% of the world's high density polyethylene (HDPE) production [1]. Despite considerable research examining the behavior of this catalyst system during non-steady polymerization (in its early stages), many questions remain unanswered. For instance, it is not clear how certain physical characteristics of the catalyst structure (i.e. surface area, pore volume, support fragility and particle size) influence its activity. Also, explanations of the mode of monomer transport through the growing polymer layer external to the particle remains speculative [2,3]. It is believed that the morphology of the initial

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catalyst particles and their changes during reaction exert considerable influence on the polymerization process [4,5].

To date, the majority of studies on the morphology of the Cr/SiO_2 PE catalysts have been directed towards catalysts prepared on porous supports and working in gas-phase reactors [3,6]. The work to be described herein presents the results obtained using scanning (SEM) and transmission electron microscopic (TEM) examination of polyethylene formed on both porous and non-porous particles of Cr/silica catalysts during the early stages (0–170 min) of polymerization in a specially designed continuous flow slurry microreactor. To slow the polymerization rate and thus facilitate observation of changes occurring in the physical character of the catalyst–polymer particles, the reaction was carried out at room temperature and low ethylene pressure (1 atm).

2. Experimental

Two 5 wt% catalysts were prepared by impregnating two different silica supports: porous Davison (BET surface area = 277 m/g^2; pore volume 1.57 cm/g^3) and non-porous pyrogenic Cab-O-Sil (BET surface area = 163 m/g^2), with an aqueous solution of chromium(VI) oxide. After evaporation of water, the catalysts were air dried at 105°C for 16 h. Both catalyst activation and polymerization processes were carried out in a 100 cm^3 Vycor glass reactor. For this purpose, about 0.1 g of catalyst was placed in the reactor vessel and treated sequentially: N_2 at 500°C for 16 h, O_2 at 500°C for 1 h, and CO at 350°C for 1 h. Next, the catalyst sample was cooled to 25°C, suspended in high purity *n*-hexane and the polymerization was started in a semi-batch mode by bubbling ethylene at near-atmospheric pressure through the slurry. Additional mixing of reactor contents was achieved by vigorous shaking of the entire reactor vessel by a mechanical agitator. At different polymerization times, the process was interrupted and the yield of PE was determined gravimetrically after evaporation of the hexane.

After each specified polymerization time, the catalyst–polymer sample was deposited on an aluminium holder and coated with a thin electroconductive layer of gold by vacuum evaporation for SEM observations. Specimens were viewed using an ISI-60 SEM at 15 kV accelerating voltage. High resolution micrographs of PE/catalyst particles were taken with a S-2700 Hitachi instrument operating at 25 kV.

Specimens for TEM studies were prepared by deposition of a pentane suspension of catalyst particles onto a 300-mesh copper supporting grid, covered with "holey" carbon film to minimize artifacts. Prior to this preparation procedure, the PE was removed from the catalyst by gentle ashing in oxygen at 400°C. A Philips EM-300 TEM at 80 kV was used for observations.

3. Results and discussion

Polymer yields for different reaction times and for two catalysts (5 wt% Cr on either Cab-O-Sil or Davison silicas) are shown in table 1. Polymerization over Cab-O-Sil supported catalyst proceeds quite steadily since the yields grow proportionally with time. However, a quite different behavior can be noticed for the Davison support. In this case, after a short initial period of high activity, the reaction role is suppressed (between 4 and 24 min), and then accelerates dramatically. As shown earlier [7], such behavior reflects three sequential processes characteristic for polymerization over porous catalysts: filling the pore network with PE, increase of PE pressure inside the pores, and, finally pore fracturing. The latter phenomenon leads to continued fragmentation of catalyst particles. Because of the absence of pores within the Cab-O-Sil supported catalyst and thus no space limiting factor for the growing PE, the PE forms on the particle exterior without fragmentation of the particles. Up to about 170 min of reaction, polyethylene yields for the Cr/Cab-O-Sil are higher than for Cr/Davison. Despite such behavior, experiments show that this near-constant activity of non-porous catalyst (starting from about 140 min of reaction) is lower than that of the porous catalyst. The final very high activity that porous catalysts can achieve may be related to their expanding surface areas. Increasing areas expose increasing numbers of active sites per gram of catalyst, and excluding the initial reaction time, the rate of polymerization may be independent of the initial pore dimensions and pore volume. These catalyst particles, after fracturing into small fragments, became similar to the non-porous ones, consisting of the separated primary gel globules and/or their small aggregates.

These phenomena are well supported by SEM observations. The set of micrographs in fig. 1 (taken after 0, 4 and 45 min) present changes in the

Table 1
Yields of ethylene polymerization after different times of reaction over 5 wt% Cr catalysts supported on porous Davison and non-porous Cab-O-Sil silicas

Time (min)	Yield (g PE/g cat) for catalysts supported on	
	Davison	Cab-O-Sil
1	0.42	0.25
4	1.12	1.02
9	1.30	2.20
15	–	3.68
24	1.77	–
30	–	7.14
45	2.24	12.07
75	6.39	21.28
105	13.01	31.24
160	39.08	59.72
170	65.64	65.28

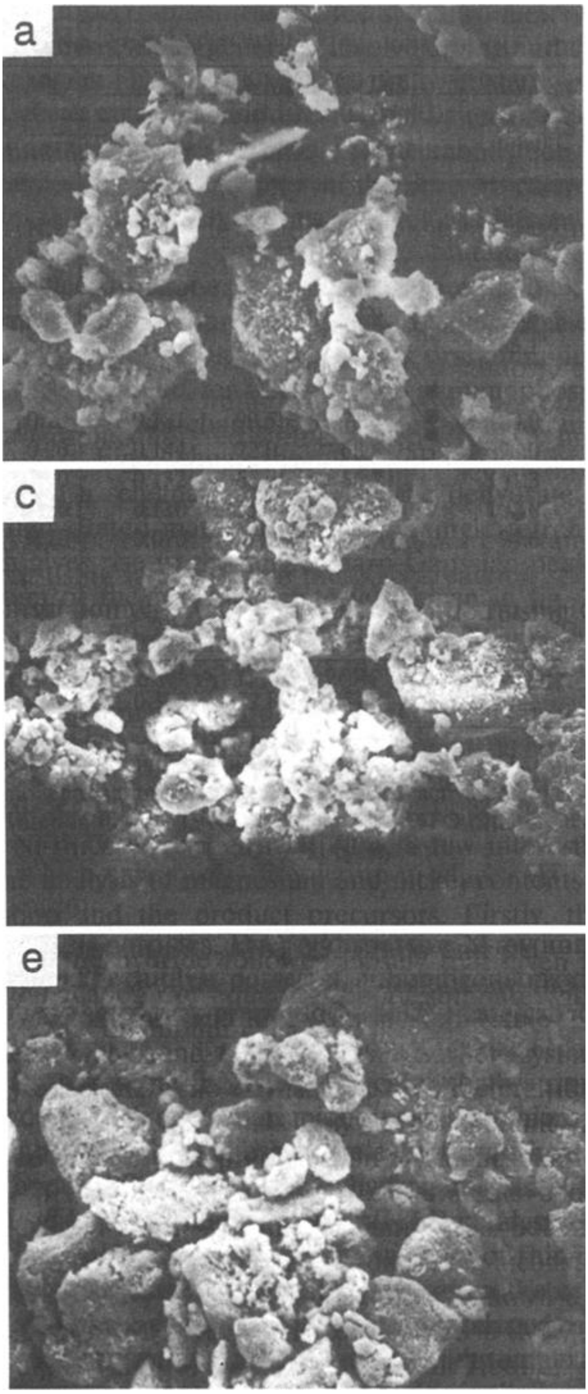

Fig. 1. SEM micrographs of catalyst particles after 0, 4 and 45 min of polymerization over 5 wt% Cr/Cab-O-Sil (a, c, e) and 5 wt% Cr/Davison (b, d, f), respectively.

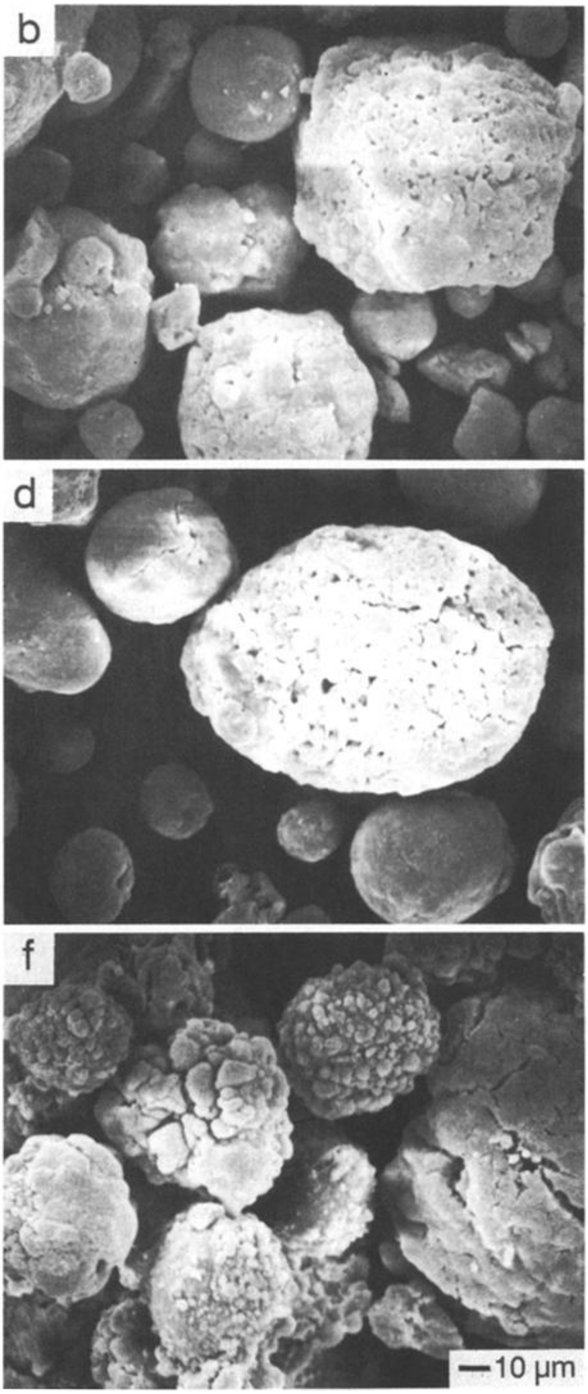

Fig. 1. (continued).

morphology of porous Davison and non-porous Cab-O-Sil catalyst particles as a result of polyethylene growth. In the case of Cab-O-Sil support, the initial highly irregular particles with many kinks and sharp edges grow, forming larger particles with smooth, rounded edges and grouped in larger clusters. This process can be spotted as early as the fourth minute of reaction. However, in the case of Davison-supported catalyst, four minutes of reaction was insufficient to change the particle appearance, since most of the polymer was then produced inside the pores [7]. At this stage, some catalyst particles exhibit a sticking tendency (not shown here), forming grape-like structures [8]. Further reaction caused the particles to grow, along with significant changes in their appearance. One clearly sees typical cauliflower-like structures (fig. 1f) characteristic for the porous support, the result of continued fracturing of catalyst particles. Such structures are not visible for the non-porous catalyst, likely because its different initial polymerization behavior results in uniform and unperturbed PE production.

The effect of repeated fragmentation of the porous particles of Davison-supported catalyst are also visible in TEM micrographs (figs. 2b, 2d). The dense agglomerates of numerous silica globules visible as dark spots before reaction tend to disintegrate during polymerization. Moreover, the sizes of globules seem to decrease with increasing time of polymerization. The non-porous catalyst did not show such changes, since the dimensions of the globules are comparable in samples before and after polymerization (figs. 2a, 2c), both having a rather loose structure.

Fig. 3 shows the PE/porous catalyst particles at a more advanced but still early stage of polymerization (170 min). Under the low magnification (fig. 3a), one can observe the rough surface (unlike that before reaction) of otherwise round particles. A closer look at this surface at high magnification in fig. 3b reveals much more detail of its structure, consisting of small solid areas interconnected with numerous fibrous elements, probably polyethylene. On the surface of the flat areas, one distinguishes small islands likely being tiny fragments of fractured catalyst particles separated by growing polymer. Similar fibrous details (not shown here) were also noticed for non-porous Cab-O-Sil supported catalysts, confirming that the fibres are of PE origin. Fibrous polyethylene became observable at the times corresponding to yields of 2.24 and 3.68 g PE/g cat for porous and non-porous catalysts, 45 and 15 min of reaction, respectively. It seems that the two catalysts, which are so different at the beginning, eventually tend to exhibit similar surface topography in the course of reaction.

Finally, it is worth noticing that this fibrous structure of PE enables relatively easy penetration of monomer through the PE layers toward the active chromium sites located on the surface of the catalyst fragments. The Cr/SiO_2 particles are distributed throughout the polymer either by simple separation of globules from the larger aggregates in non-porous silica or by fracturing of the pore network of

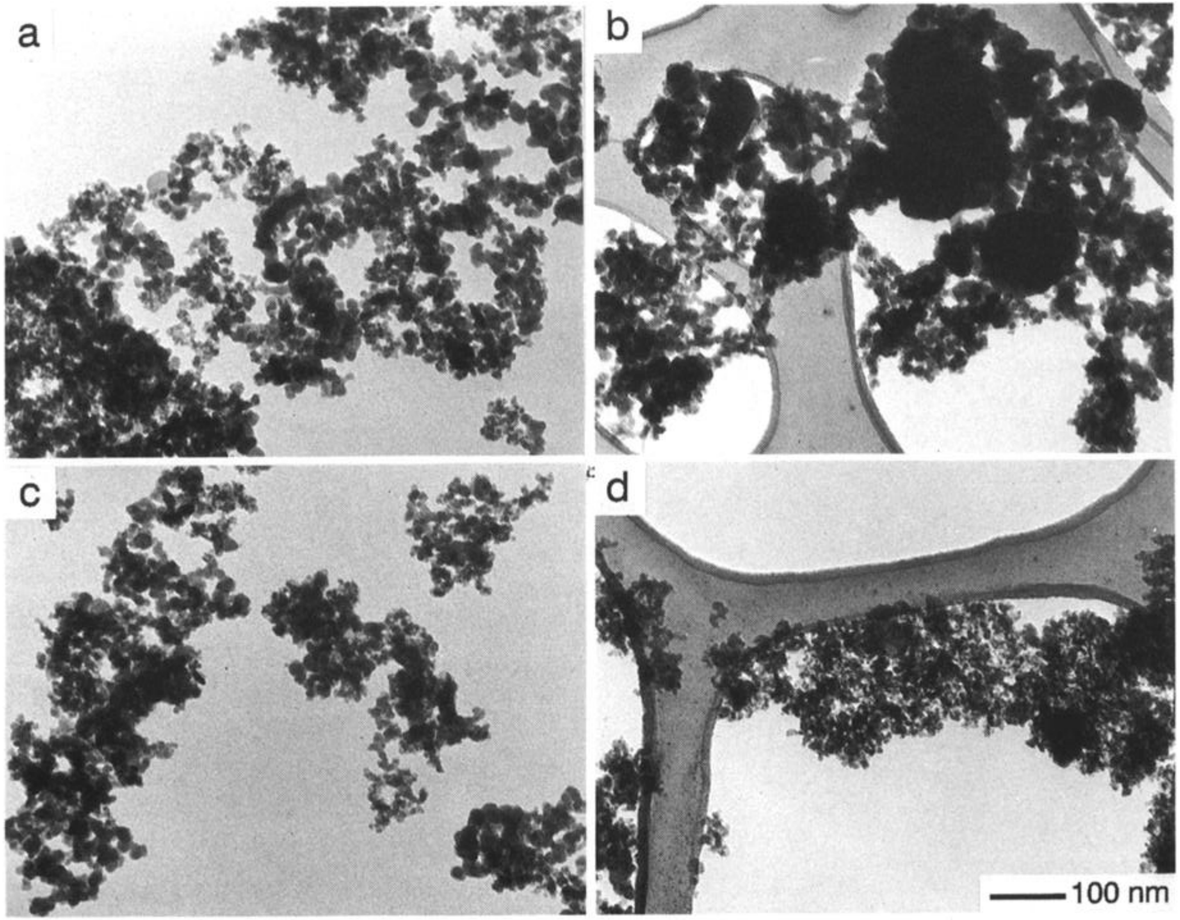

Fig. 2. TEM micrographs of particles of both 5 wt% Cr/Cab-O-Sil (a, c) and 5 wt% Cr/Davison (b, d) after 0 (a, b) and 75 min (c, d) of ethylene polymerization.

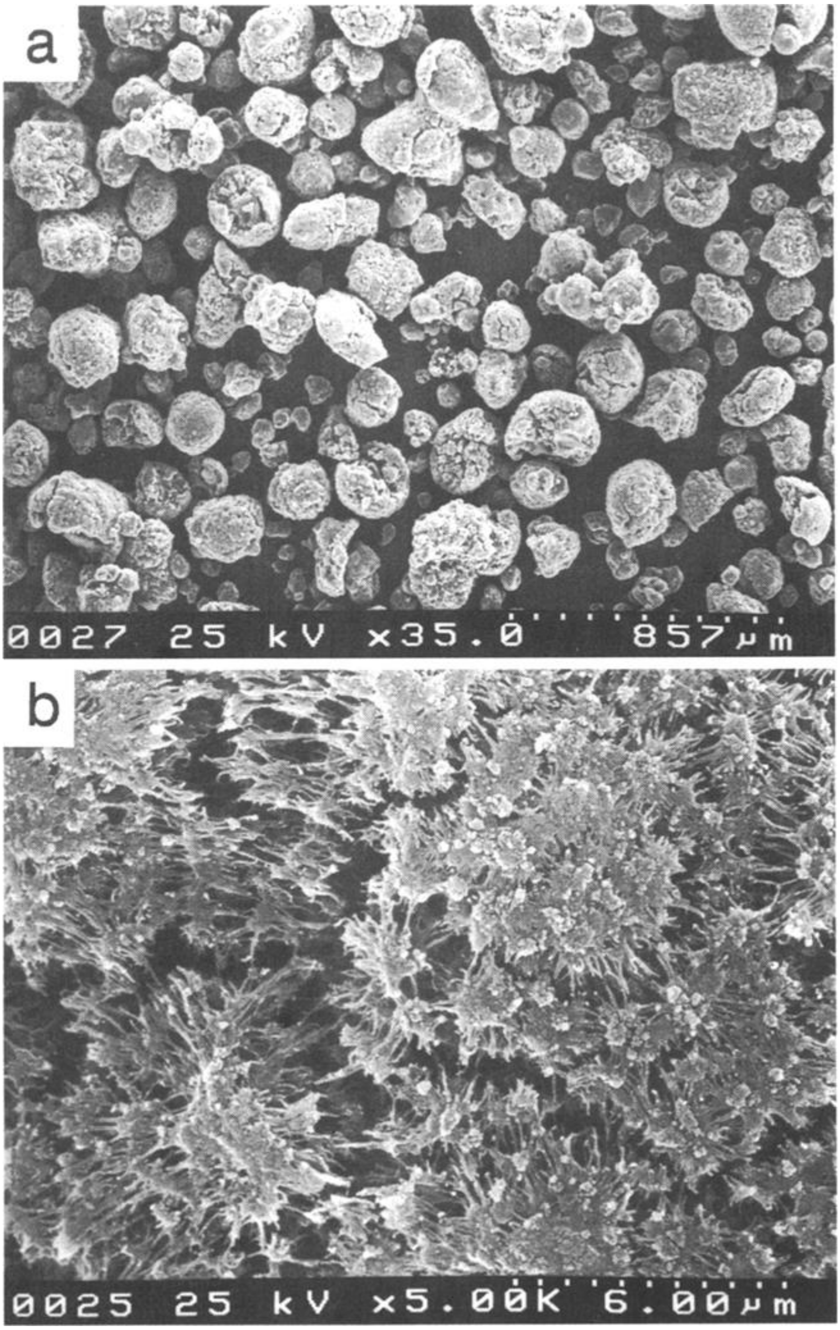

Fig. 3. SEM micrographs of 5 wt% Cr/Davison catalyst after 170 min of ethylene polymerization: (a) general view of particles, (b) enlargement showing micro-topography of particle surface.

porous silica. The separation of fragments is responsible for the extensive acceleration in rate for the initially porous catalyst and for the high continuous rate for the non-porous catalyst (see table 1).

4. Conclusions

Fracturing of the porous catalyst particles was clearly observed whereas it was not seen for the non-porous catalyst. The early polymerization on porous catalyst proceeds mainly within the pores and therefore is invisible in SEM since the particles do not fracture. Further disintegration of particles with reaction causes the appearance of cauliflower-like structures, not observed for non-porous catalyst with its uniform and undisturbed PE production.

Despite the quite different initial morphologies of the two supports used in this study, SEM shows that the resulting PE/catalyst microstructure at the particle surface has a fibrous character for both supports. This open structure enables continuation of reaction without retardation of the rate by monomer diffusion effects.

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