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Investigation on the polymer particle growth in ethylene polymerization with PS beads supported *rac*-Ph₂Si(Ind)₂ZrCl₂ catalyst

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The mechanism of polyethylene particle growth was investigated using poly(styrene-*co*-divinylbenzene) (PS beads) supported *rac*-Ph₂Si(Ind)₂ZrCl₂ catalyst. From the analysis of the resulting polyethylene particles by SEM (scanning electron microscopy) and EPMA (electron probe microanalysis), it was found that the active species are located on the surface layer of catalyst particles and that the catalytic species are uniformly distributed throughout the polymer particles, whereas the cores of PS beads, which lack a potential active species, were not disintegrated during polymerization. These results suggest that the PS beads supported catalyst also follows the fragmentation and replication process as frequently observed with the MgCl₂ supported Ziegler–Natta catalysts. © 1998 Elsevier Science Ltd. All rights reserved.

Introduction

In the slurry and gas phase olefin polymerizations, the resulting polymer particles often replicate the morphological characteristics of the starting catalyst particles. Buls *et al.* investigated the polypropylene particles obtained with the TiCl₃–(C₂H₅)₂AlCl catalyst system and found that the catalyst undergoes substantial fragmentation[1]. Kakugo *et al.* also observed a similar phenomenon in propylene polymerization over the δ-TiCl₃ catalyst[2,3]. The SiO₂[4] and MgCl₂[5,6] supported catalysts have been also investigated. It is generally accepted that the catalyst particles break up into small fragments after the onset of polymerization and the fragments keep uniformly dispersed in the polymer particles throughout the whole growth process[6]. This process can assure a uniform polymerization rate throughout the particle and finally leads to a perfect shape replication. However, such a fragmentation process might depend upon the properties of the catalyst particles.

We have recently prepared a poly(styrene-*co*-divinylbenzene) (PS beads) supported metallocene catalyst and tested it to ethylene polymerization. The catalyst displayed a very high activity to give polymer particles with a spherical shape replicating the shape of the carrier[7,8], but the mechanism of the polymer particle growth has not yet been clarified.

In this communication, we have investigated a morphological change of the catalyst particles during ethylene polymerization using the electron microscopy techniques.

Experimental

Materials. Poly(styrene-*co*-divinylbenzene) (PS beads, 2% divinylbenzene, commercially obtained from Acros Organics, USA) was washed thoroughly according to the literature[9]. PS beads supported *rac*-Ph₂Si(Ind)₂ZrCl₂ catalyst was prepared according to the procedure reported in our previous literature[7]. *Scheme 1* illustrates the detailed reaction procedures for the synthesis of the catalyst. The content of Zr in the final catalyst was estimated to be 1.26×10^{-2} mmol Zr/g beads. Toluene (extra pure grade; Nacalai Tesque. Inc., Japan) was further purified according to the usual procedures. Ethylene (polymerization grade, donated by Mitsui Petrochemical Co., Japan) was purified with the columns of NaOH (extra pure grade; Nacalai Tesque. Inc., Japan), P₂O₅ (+98.0%; Wako Pure Chemical Industries. Ltd, Japan). Methylaluminoxane (MAO, in toluene solution donated from Tosoh Akzo Co., Japan) was used without further purification.

Polymerization and analytical procedures. Polymerization of ethylene in toluene medium was conducted using a glass or stainless steel reactor. In the case of the glass reactor, a 1 dm³ glass reactor equipped with a mechanical stirrer was repeatedly degassed and filled with nitrogen followed by introduction of the solvent and saturation with a certain pressure of ethylene. The catalyst and MAO were mixed and kept standing at room temperature for 1 h. After the reactor was set to polymerization temperature, the polymerization was initiated by adding the mixed catalyst. A 0.1 dm³ stainless steel reactor was also used for the polymerization at high pressure. After the reactor equipped with a magnetic stirrer was degassed and filled with nitrogen, the solvent was introduced and cooled down to liquid nitrogen temperature. The mixed catalyst was then added, followed by degassing and introduction of 0.31 mol of ethylene. The reactor was quickly warmed up to the polymerization temperature. Polymerization was terminated by acidic methanol. The polymer samples obtained were washed with acidified methanol (5 wt% HCl) and then with fresh methanol for several times. Finally, the samples were dried *in vacuo* at 60°C for 6 h.

Molecular weight (MW) and molar mass distribution (MMD) of the polymers were determined by a high-temperature gel permeation chromatography (Senshu Scientific, 55C7100) at 145°C using *o*-dichlorobenzene as the solvent. Differential scanning calorimetry (DSC) was carried out using Seiko DSC220C at a heating rate of
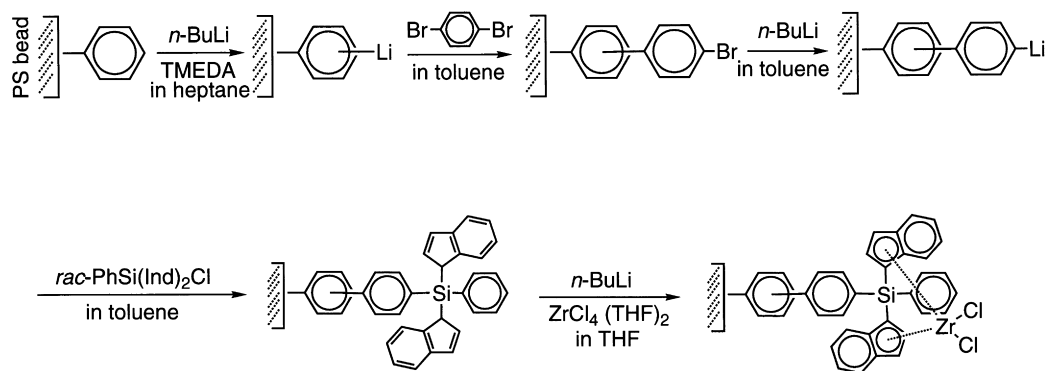
Scheme 1 Reaction procedures for the preparation of the PS beads supported catalyst

Table 1 Properties of polyethylene samples

Run No.	Polym. temp (°C)	Activity in kg PE/(mol Zr·h)	Polymer–catalyst (g/g)	T_m (°C)	X_c^c (%)	M_w ($\times 10^{-4}$)	M_w/M_n
1^a	40	1140	29	136.9	59.2	n.d.	n.d.
2^a	70	2370	60	136.9	59.6	18.8	9.1
3^b	70	15050	192	135.3	58.2	n.d.	n.d.

[a] Polymerization conditions; cat: 12 mg, MAO: 0.76 mmol (based on Al, [Al]/[Zr] = 5000), 2 h, constant ethylene pressure (6 kg/cm^3) in 1 dm^3 glass reactor with 0.3 dm^3 of toluene as solvent.
[b] Polymerization conditions; cat: 6 mg, MAO: 0.38 mmol (based on Al, [Al]/[Zr] = 5000), 12 h, constant ethylene feed (0.31 mol) in 0.1 dm^3.
[c] Crystallinity determined from $X_c(\%) = \Delta H_m/\Delta H_m^* \cdot 100$, $\Delta H_m^* = 282.84$ J/g[10]
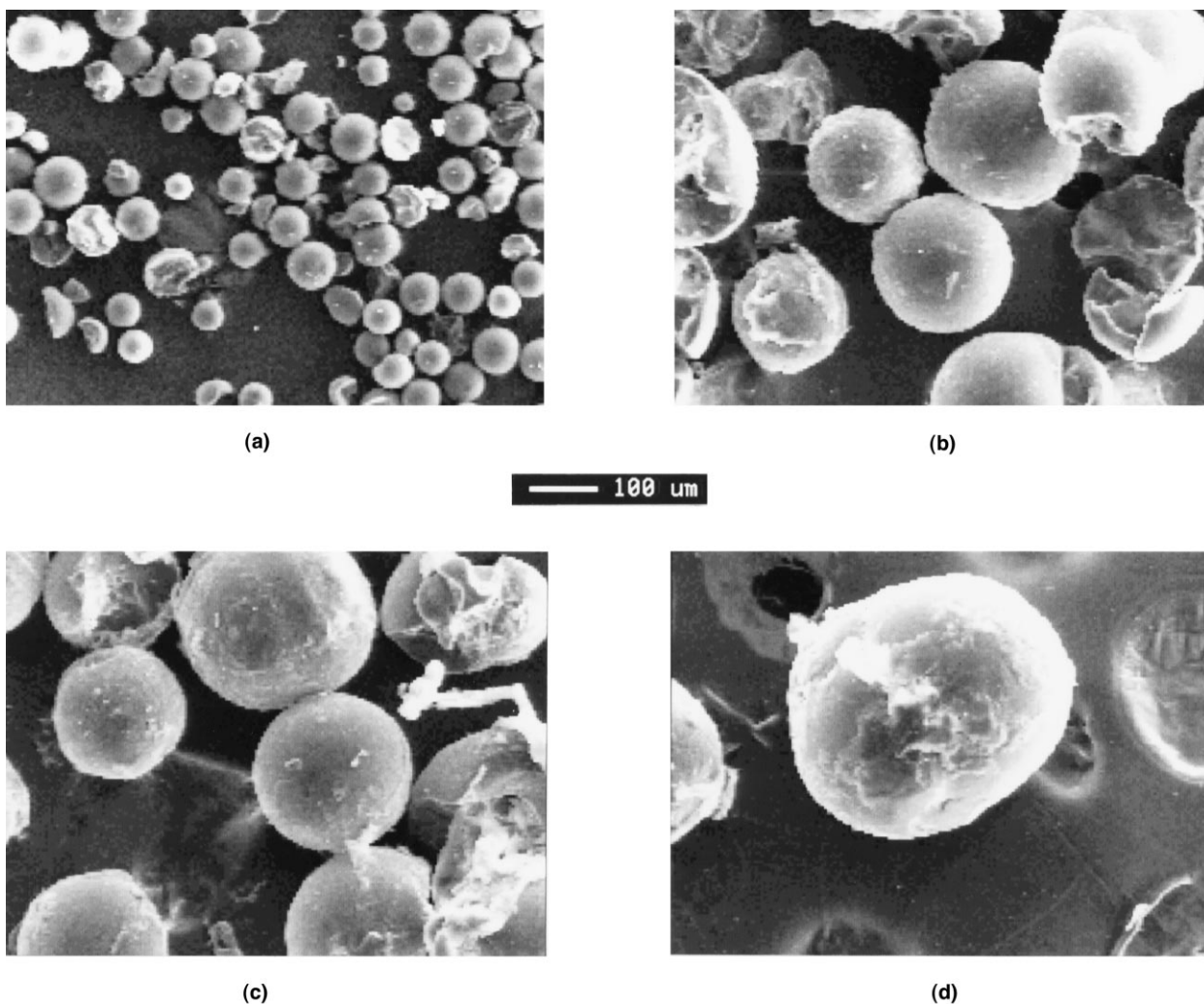

Figure 1 SEM photographs of PS beads and polymer particles: PS beads (a); polymer particles from run no. 1 (b), run no. 2 (c) and run no. 3 (d) ($\times 100$)
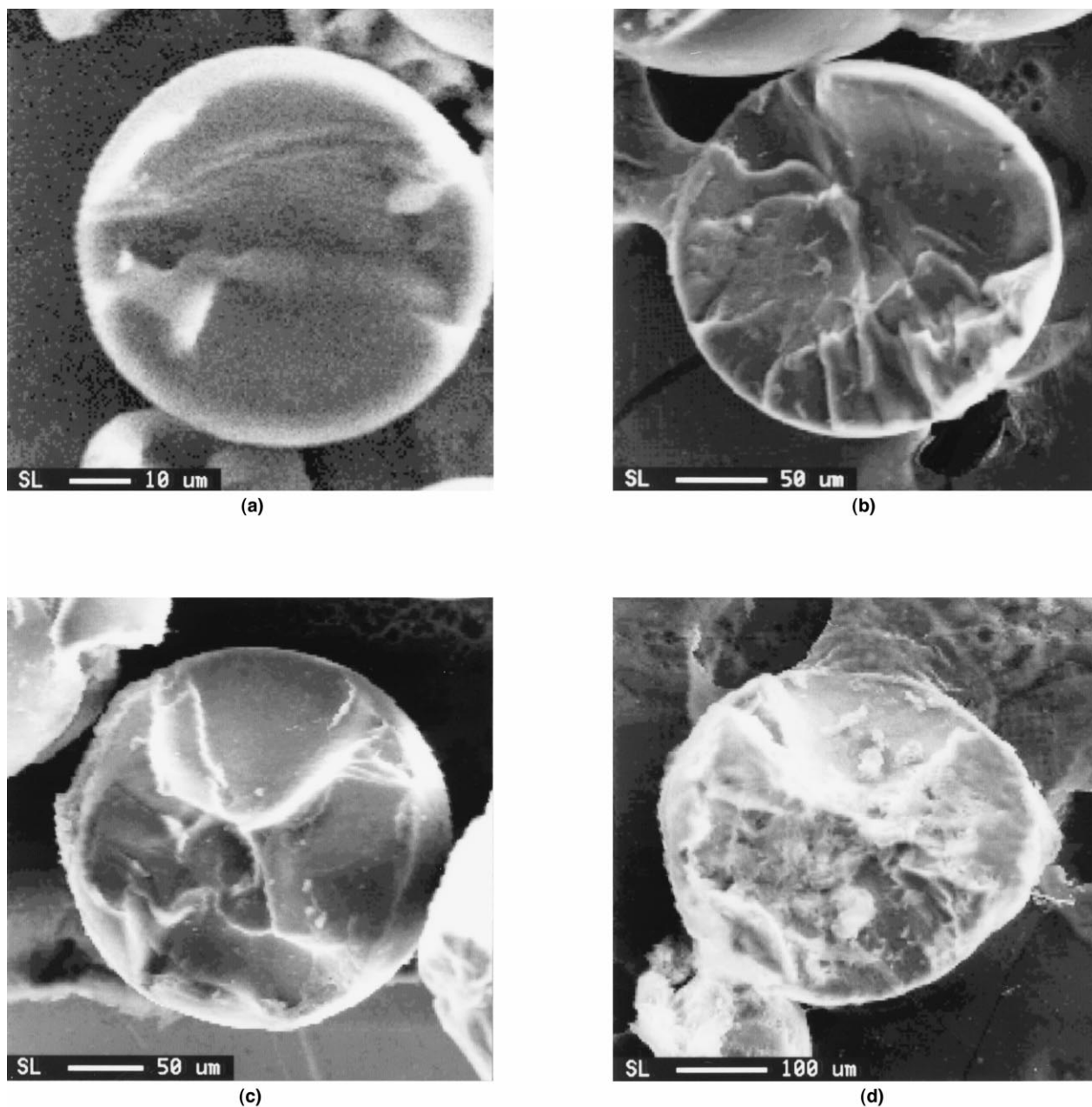
Figure 2 SEM photographs of fractured surface of PS beads and polymer particles: PS beads (a); polymer particles from run no. 1 (b), run no. 2 (c) and run no. 3 (d)

10°C/min to determine the melting temperature (T_m) and crystallinity (X_c) of polymers. Particle shape image and X-ray maps of the catalytic elements were obtained through scanning electron microscopy (SEM) analysis and electron probe microanalysis (EPMA). SEM and EPMA experiments were carried out with a Jeol JXA-8900L WD/ED combined microanalyser. The catalyst and polymer particles were coated with carbon by conventional sputtering techniques.

Results and discussion

Ethylene polymerization was performed over the supported catalyst combined with MAO as cocatalyst. Three nascent polyethylene particles with different polymer/catalyst ratios were prepared, the analytical data of which are shown in *Table 1*.

To obtain the morphological information, both the catalyst and polyethylene particles were observed by SEM. The SEM pictures are illustrated in *Figure 1*, clearly indicating that the shape of the polymer particles replicate that of the original catalyst morphology. The polymer particles became much bigger with increasing polymer–catalyst ratio and maintained a spherical shape even up to the polymer–catalyst ratio of 192.

Since the content of divinylbenzene in PS beads was very low (2%), the mechanical strength of catalyst particles was not so high. As a result, some polymer and catalyst particles were fractured during the sample preparation for SEM analysis, as can be seen in *Figure 1*, which gave us a nice sectioned surface. The SEM pictures of the fractured surfaces are shown in *Figure 2*.

As shown in *Scheme 1*, the final catalytic species is composed of three major heavy elements: Zr, Si, and Cl.
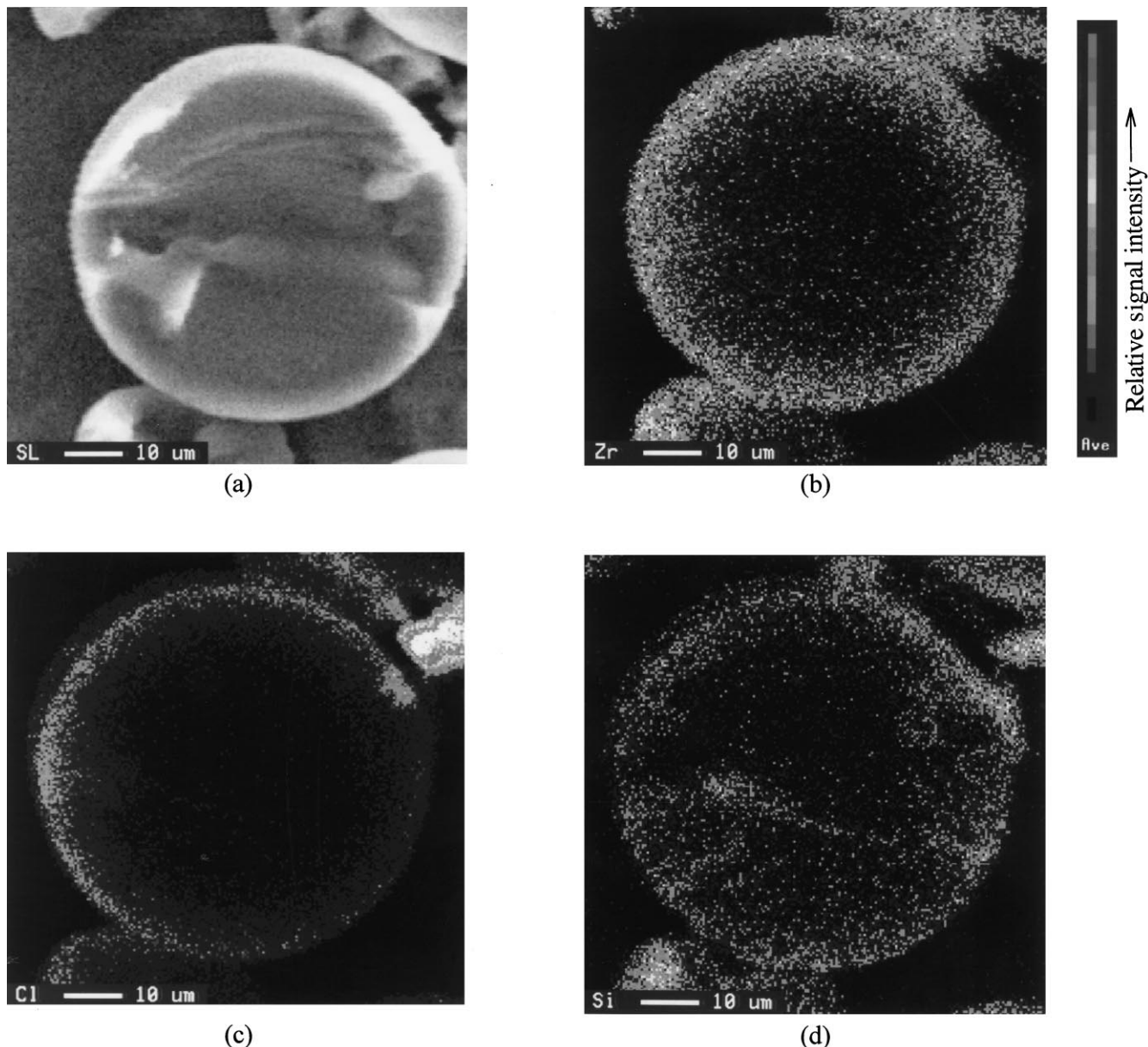
Figure 3 SEM photographs and element distribution map of fractured surface of PS beads: SEM image (a); Zr (b), Cl (c) and Si (d) distribution map (×1000)

These elements should emit their characteristic X-ray in EPMA analysis, which gives us the information on the spatial distribution of elements. The resulting element distribution maps in the catalyst particles are shown in *Figure 3*.

The Zr element, which may represent the active species, was distributed only on the surface layer of the PS beads. In the previous studies highly porous catalysts were employed[1-6], where the active species are distributed uniformly throughout the catalyst particles. In such cases, the whole catalyst particle breaks up into primary particles, which are dispersed uniformly in the polymer mass.

On the contrary, the PS beads used in the present study can be justified as microporous PS beads. Good solvents may create micropores, but removal of solvent or non-solvent should collapse the pores[11]. The solvent used in the first step to functionalize the PS beads in this experiment was heptane, a non-solvent, and thus there might be no pores inside the beads. Therefore, only the surface part of PS beads may undergo further reactions to form the active species. As seen in *Figure 3*, Cl and Si elements were also

observed only on the surface layer of the catalyst. These results clearly indicate that the potential metallocene catalysts are located only on the surface layer of the carrier.

Ethylene polymerization was then performed over the catalyst. The distributions of Cl element in the resulting polymer particles are shown in *Figure 4*.

The spatial distribution of Cl seems to be fairly uniform throughout the polymer particle, which clearly suggests that such an organic carrier as PS beads also follows the fragmentation and replication process observed with various inorganic carriers. However, the polymer particles exhibited the isolated cores without containing Cl element. A similar result was also obtained in the Zr distribution map of the polymer particles. There is little doubt, therefore, that the inner part of PS beads, which is free from the active species, is not disintegrated and remains in the core part of the polymer particle. In other words, the development of hydraulic forces by the growing polymer chain and thus fragmentation of carriers can only occur on the region where the active species are in existence. These results provide more direct and clearer evidence to the fragmentation and
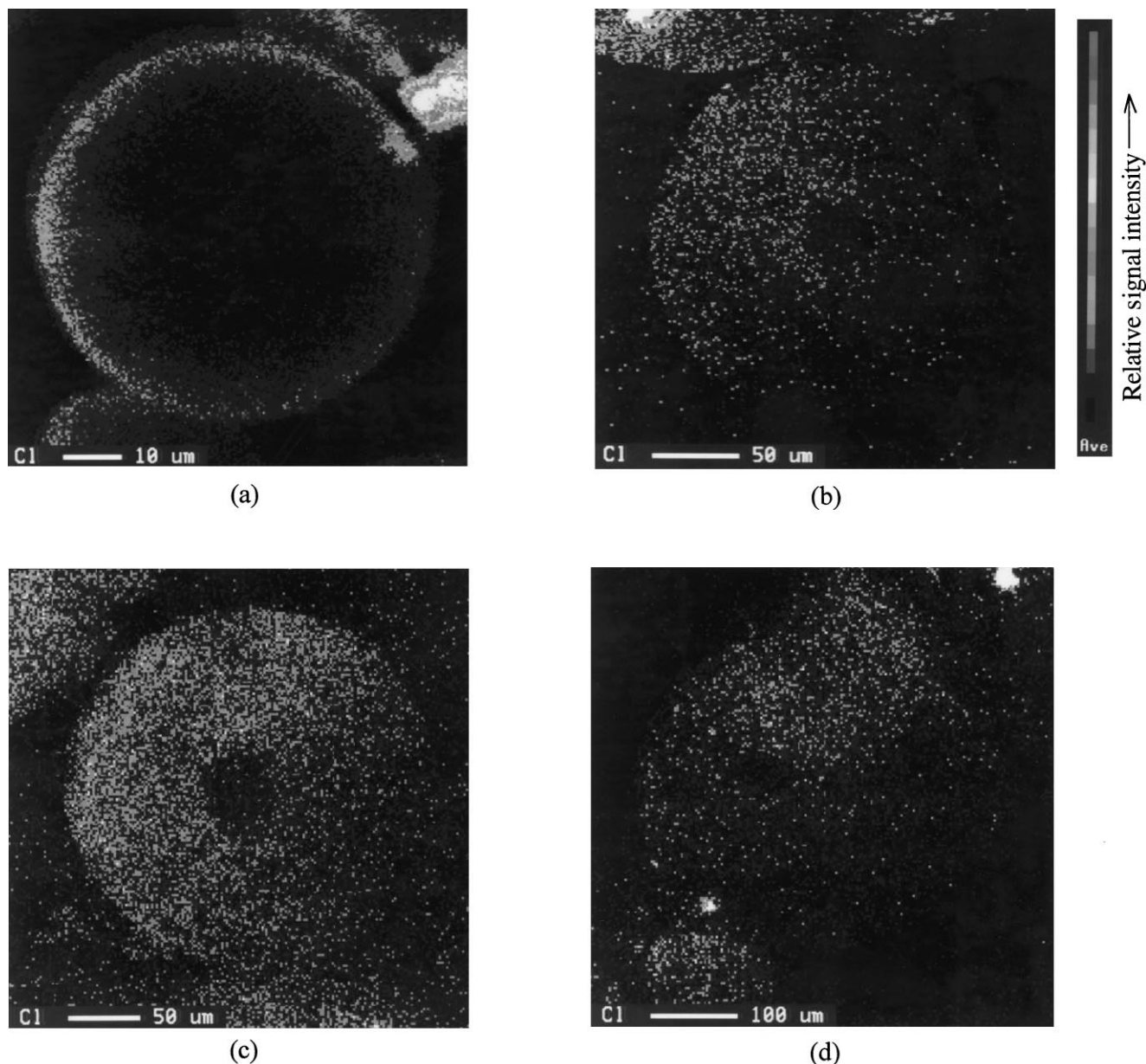
(a)

(b)

(c)

(d)

Figure 4 Chlorine distribution map of fractured surface of PS beads and polymer particles: PS beads (a); polymer particles from run no. 1 (b), run no. 2 (c) and run no. 3 (d)

replication process suggested by the previous literature[1–6]. At a higher conversion above 100 g of polymer per g of catalyst, it is difficult to distinguish the remaining island of PS beads due to excessive dilution in the polymer particles.

Conclusion

In conclusion, it was found that the potential active species in the present PS beads supported catalyst are located only on the surface layer of catalyst particles, and that such an organic carrier like PS beads also follows the same fragmentation and replication process frequently observed with inorganic carriers.

A further study using the macroreticular PS beads as a carrier is now in progress, the results of which will be reported elsewhere.

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