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ORIGINAL PAPER

Polymerization of ethylene using a nickel α-diimine complex covalently supported on SiO_2–$MgCl_2$ bisupport

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Abstract Bisupported catalyst for ethylene polymerization was prepared by mixing alcohol solution of $MgCl_2$ with pretreated SiO_2 in heptane, and further treating with bis(4-(4-amine-3,5-diisopropylbenzyl)-2,6-diisopropylphenylimino) acenaphtheneNiBr_2 (abbreviated as NiLBr_2) solution. The bisupported catalyst could be used to polymerize ethylene with high activity using alkylaluminum halides as inexpensive cocatalysts. According to high-temperature GPC, the weight-average molecular weights of the polymers obtained ranged from 2.15×10^5 to 9.27×10^5, with molecular weight distributions of 3.12–4.23. By adjusting the polymerization temperatures, the products with good morphologies could be obtained. The resultant polyethylenes were confirmed by ^{13}C-NMR to contain significant amounts not only of methyl but also of ethyl, propyl, butyl, amyl, and longer side chains (longer than six carbons).

Keywords SiO_2–$MgCl_2$ bisupport · (α-Diimine) nickel complex · Heterogeneous catalysis · Branched polyethylene

Introduction

Branched polyethylenes have become plastic materials of industrial interest in the recent past because the short-chain or long-chain branches in the polyethylene backbone enhance the mechanical strengths of polyethylene products. The branched

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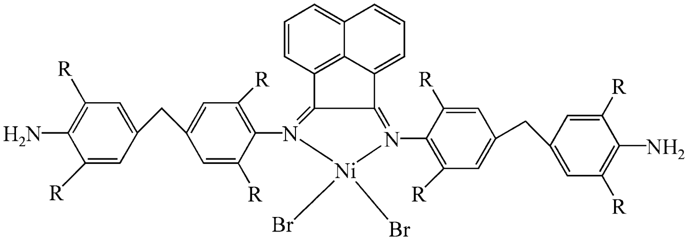
polyethylene is commonly prepared by the copolymerization of ethylene with α-olefin comonomers, such as 1-butene, 1-hexene, and 1-octene using Ziegler–Natta or metallocene catalysts [1]. Moreover, it can also be produced with dual-component or dual-site catalyst system. This technique uses a single feed of ethylene and two catalysts in the same reactor. Ethylene is oligomerized to oligomers with one catalyst, and copolymerized with the obtained oligomers to produce branched polyethylenes with another catalyst [2].

Brookhart has demonstrated that highly branched polyethylenes can be synthesized using homogeneous palladium (II) and nickel (II) catalysts incorporating very bulky chelating diimine ligands [3, 4]. These highly branched polyethylenes are also produced with a single feed of ethylene without the intermediacy of α-olefins. Despite the success of this new approach to the synthesis of branched polyethylenes by homogeneous late transition metal catalysts, the extension of this technique to heterogeneous polymerization catalyst will allow us to implement the late transition metal catalysts in existing industrial processes and to improve the morphology of branched polyethylene. So far, three methods have been developed for the supporting of transition metal supported catalysts. The first method involves direct immobilization of the catalyst on the support surface, which usually significantly suppresses the catalytic activity and changes the catalyst structure and the microstructure of the resultant polymer. The second method is the immobilization of the catalyst on the support pretreated with MAO or alkylaluminium compounds. It is expected that the catalyst and the MAO or alkylaluminium compounds on the support are bound by loose ionic interactions. This fairly weak bond has given rise to the assumption that the catalyst can float on the surface of the support. The third method involves the covalent bonding of the catalyst to the carrier by ligands, which is commonly used in the ethylene polymerization. It is well-known that SiO_2 has been used as catalyst supports due to their high surface area and good morphology [5–9]. $MgCl_2$ is also a good support for preparation of highly efficient late transition metal catalysts [10–15]. In our previous study, the activity and product properties of unsupported, the modified $MgCl_2$ supported, and the modified silica supported bis(4-(4-amine-3,5-diisopropylbenzyl)-2,6-diisopropylphenylimino) acenaphthene-$NiBr_2$ ($NiLBr_2$) for ethylene polymerization has been discussed [16–18]. Up to now, to the best of our knowledge, the polymerization of ethylene using a nickel α-diimine complex covalently supported on SiO_2–$MgCl_2$ bisupport has been few reported. In this study, we report the synthesis of branched polyethylenes by heterogeneous ethylene polymerization using a novel nickel α-diimine complex (Scheme 1, denoted with the formula of $NiLBr_2$) covalently supported on Et_3Al-treated SiO_2–$MgCl_2$ bisupport in a slurry reactor, which is activated by general alkylaluminum compounds. The bisupported Ni catalyst shows excellent activity, and no reactor fouling can be observed during the whole olefin polymerization process. Moreover, the effects of polymerization conditions on catalytic activity and properties of the resultant branched polyethylenes, such as the melting point, the molecular weight, degree of branching, branch type, and morphology were investigated.



R=iPr

Scheme 1 Nickel (II) diimine complex

Experimental

Materials

Polymerization-grade ethylene was provided by Shanghai Jinshan Petroleum Co., and was further purified through a DC-IB gas purification instrument before charging into the reactor. Diethylaluminum chloride (DEAC), tri-isobutyl aluminum (TIBA), and triethyl aluminum (TEA) were purchased from Shanghai Petrochemical Co. (China) and used as a solution in *n*-heptane of 400 g/L, respectively. The catalyst complex of $NiLBr_2$ (Scheme 1) was synthesized according to a previously reported procedure [16]. Toluene was purchased from Guangzhou Chemical Co. (China), and dried over sodium under reflux for 24 h. Anhydrous $MgCl_2$ was provided by HuShun aluminum plant. All the other chemicals were purchased commercially, and used without further purification.

Preparation of SiO_2–$MgCl_2$ bisupport

In a typical experiment, 5.5 g of anhydrous $MgCl_2$ and 10 mL of *n*-heptane were introduced into a glass reactor equipped with a magnetic stirrer and then 20 mL of absolute ethanol were added. The mixture was heated to 50 °C and stirred until the $MgCl_2$ was completely dissolved. Calcinated SiO_2 (1.5 g) was then rapidly introduced, so that it was uniformly dispersed in the solution. After stirred at 50 °C for 0.3 h, Et_3Al (20 mL) solution in *n*-heptane was added to the mixture at 0 °C and stirred for 2 h. The modified SiO_2–$MgCl_2$ bisupport was separated by decantation, washing with *n*-heptane, and dried under vacuum at 50 °C for 2 h.

Table 1 shows N_2-BET data of the prepared bisupport. The surface area of the SiO_2–$MgCl_2$ bisupport is slightly less than that of the original SiO_2. Considering the

Table 1 Physical properties of SiO_2–$MgCl_2$ bisupport and SiO_2 support

Support	BET surface area (m^2/g)	Pore volume (mL/g)	Average pore diameter (nm)
SiO_2/TEA	102	0.8	86
SiO_2–$MgCl_2$/TEA	23	0.098	9.6

$$Si\text{-}OH + MgCl_2 \cdot nEtOH \longrightarrow SiO\ MgCl \cdot nEtOH + HCl$$

Scheme 2 The formation mechanism of the SiO_2–$MgCl_2$ bisupport

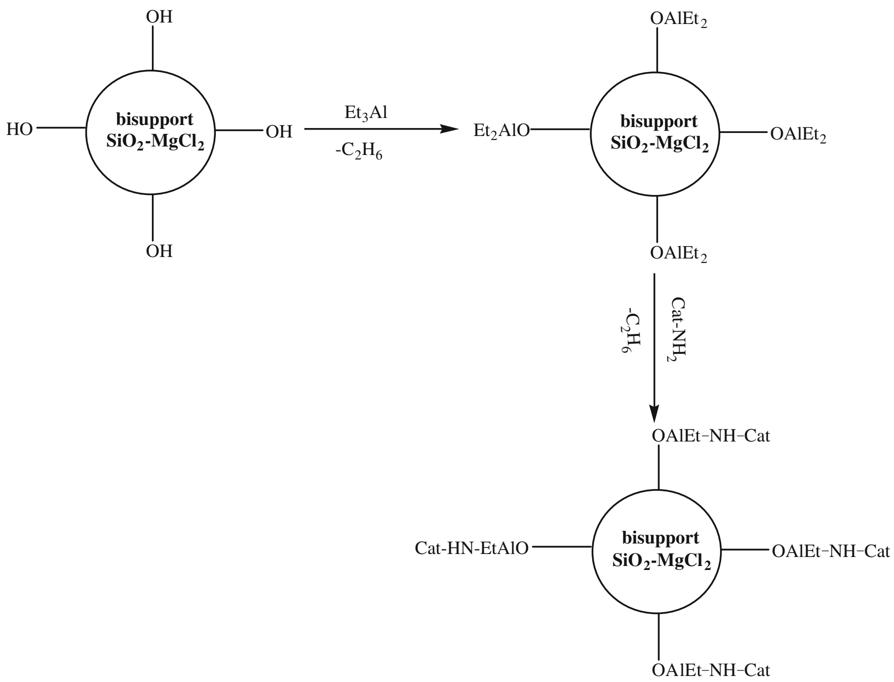
formation mechanism of the bisupport (see Scheme 2), it is possible that $MgCl_2$ could affect the surface area and porosity of the bisupport.

Preparation of supported catalyst

The modified SiO_2–$MgCl_2$ bisupport (6.8 g) was mixed with a solution of $NiLBr_2$ (0.1 g) in CH_2Cl_2 (40 mL). After 20 h, the solid support was isolated by filtration, washed thrice with CH_2Cl_2, and dried in vacuum at 50 °C to obtain the heterogeneous catalyst. The contents of Ni of this supported catalyst are measured by ICP-OES method. Scheme 3 shows a possible process of fixing $NiLBr_2$ on the bisupport. The content of Ni is ~0.15 wt%.

Polymerization of ethylene

The polymerization of ethylene was carried out in a 250 mL Schlenk flask equipped with a mechanical stirrer. The flask was dried at 80 °C under vacuum for 1 h and swept with dry N_2 for three times. After the flask was dried completely and cooled



Scheme 3 A possible model of fixing $NiLBr_2$ on the bisupport

down to room temperature, the flask was charged with *n*-heptane (50 mL), and the solvent was saturated with ethylene monomer at 0.1 MPa. Alkylaluminum compounds co-catalyst dissolved in *n*-pentane was injected into the reaction solution. The heterogeneous catalyst (0.04 g) was then added, and the reactor was heated to the polymerization temperature within 2 min. After an hour, the polymerization was stopped by the addition of ethanol. The reaction solution was poured into a large amount of 10% HCl–EtOH solution, affording polyethylene as a suspended precipitate. The polymer was filtered and washed with ethanol several times, and dried in vacuum at 40 °C for 20 h.

Characterization

The specific surface area and the pore size distribution of the support were measured by N_2-BET method with CESORPTOMATIC 1990. ^{1}H-NMR spectra were recorded on a Bruker-500 spectrometer. Molecular weights were determined by high-temperature GPC in 1,2,4-trichlorobenzene. The ^{13}C-NMR spectroscopic data for polyethylene were obtained using *o*-dichlorobenzene as the solvent with a Varian INOVA-500 NMR spectrometer at 130 °C. Melting points were determined by differential scanning calorimetry (DSC) with a Perkin-Elmer 7 Series Thermal Analysis System.

Results and discussion

Effects of the cocatalyst

As for $NiLBr_2/SiO_2–MgCl_2$ supported catalyst, the effect of cocatalysts (DEAC, TEA, and TIBA) on ethylene polymerization under the conditions of Al/Ni ratio 800 and temperature 50 °C was investigated. On the basis of our experiment results, we find that the role of cocatalysts in the ethylene polymerization is of great interest. DEAC can effectively initiate ethylene to polymerize, but TEA and TIBA cannot initiate it at all. It has been reported that reaction of halocomplexes with methyl aluminoxanes (MAO) in the presence of ethylene or other olefins is presumed to form catalytical cationic active species [3]. This cationic form of organometallic complexes is helpful in polymerizations. In our reaction system, DEAC is also presumed to react with supported nickel α-diimine complex in the presence of ethylene to form similar catalytical cationic active species, while TEA and TIBA probably make the complex of $NiLBr_2$ reduce excessively and cannot form the cationic species, which is similar to our previous studies [16, 18].

Effects of polymerization conditions

As shown in Table 2, the polymers exhibit high molecular weight and narrow molecular weight distribution (MWD) ranging from 3.12 to 4.23 at Al/Ni ratio of 800.

Table 2 Effects of polymerization temperature on catalytic activity and properties of PEs

Run	Temperature (°C)	n_{Al}/n_{Ni}^{a}	Activity[b]	Branches/1000 C	M_w ($\times 10^{-5}$)	MWD	T_m (°C)
1	0	800	0.33	16.60	9.27	4.23	124.07
2	20	800	0.95	45.32	7.28	3.12	118.22
3	40	800	1.89	58.60	5.48	3.14	115.29
4	60	800	1.31	100.90	2.15	3.42	–

Polymerization conditions: pressure: 0.1 MPa, polymerization time: 1 h, solvent: heptane, and cocatalyst: $AlEt_2Cl$

[a] n_{Al} = molar number of Al, n_{Ni} = molar number of Ni

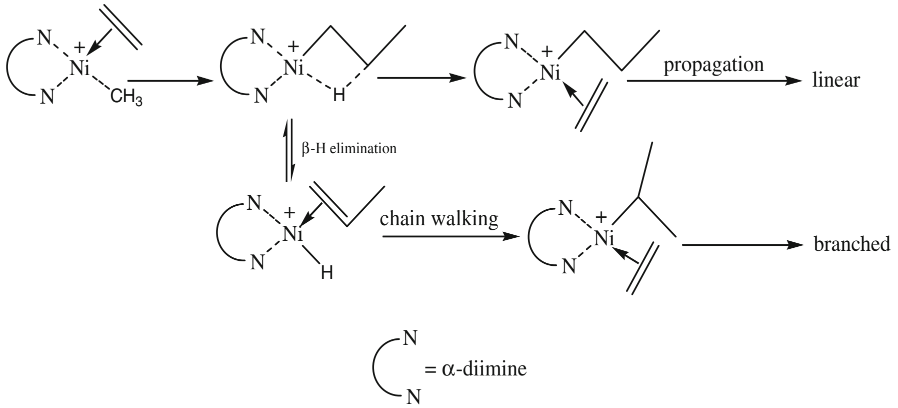
[b] $\times 10^6$ g of PE/mol of Ni h

The molecular weight and polydispersity of the polyethylene obtained from $NiLBr_2$ supported on SiO_2–$MgCl_2$ were found to be slightly lower and narrower, respectively, relative to silica supported $NiLBr_2$ catalysts, but slightly lower and boarder relative to $MgCl_2$ supported $NiLBr_2$ catalysts [14, 15]. A series of experiments were undertaken to determine the effect of temperature on the catalyst performance and properties of resultant polyethylene. Table 2 shows the results of polymerizations performed at four different temperatures (0, 20, 40, and 60 °C). First, the catalysts show the highest activity of 1.89×10^6 g PE/(mol of Ni h) when polymerized at 40 °C, but at higher temperature activity was reduced due to the increase in the catalyst deactivation rate. Second, the molecular weight of polyethylenes decreases with temperature increasing. The M_w of the polymer is 9.27×10^5 as the temperature is at 0 °C, and it decreases to 2.15×10^5 as temperature reaches to 60 °C. Third, the melting temperature (T_m) of polyethylene significantly decreases with the increase of temperature due to the increase of chain-transfer rate. The results are in accordance with those observed by Brookhart et al. [19].

Microstructures of the resulting branched polyethylenes

Different from the conventional Ziegler–Natta catalysts, nickel α-diimine catalyst can produce polyethylene with branch structures without the use of α-olefins comonomers. Branching of polyethylene products is believed to exist according to the mechanism of "chain walking" [3, 20]. Scheme 4 presents a rough outline of the elementary reaction steps involved in α-diimine Ni-catalyzed olefin polymerization.

For the homogenous late transition metal catalyst, the rate of β-elimination will increase faster than the ethylene trapping rate and thus enhance the degree of branching as the polymerization temperature increases. In addition, the ratio of $(diimine)NiR^+/(diimine)Ni(R)(C_2H_4)^+$ will increase with increasing temperature, which will improve the rate of chain walking significantly when compared to chain insertion [21]. According to our results, the support system shows no serious effect on the basic modes of chain growth and branching. Similar to the homogeneous catalysts, the melting points of the polymers catalyzed by the supported systems increase with the decrease of reaction temperature due to the competition of chain



Scheme 4 Mechanism for the preparation of branched PE with nickel α-diimine catalyst

propagation versus chain walking. DSC results indicate that some polyethylene samples exhibit no melting peaks, while the others show broad melting peaks. It is suggested that the polyethylenes obtained in our experiment are branched polyethylenes. The DSC curves of polyethylenes of different branching degrees prepared by the support system are shown in Fig. 1. T_m decreased with an increase of branching degree of polyethylene and then the polymer structure changed from linear semi-crystalline to total amorphism. The polyethylenes prepared at 0, 20, and 40 °C had a T_m value of 124.1 °C (as shown in Fig. 1a), 118.2 °C (as shown in Fig. 1b), and 115.3 °C (as shown in Fig. 1c), respectively. The highly branched polyethylenes prepared at 60 °C showed that no melting peaks (as shown in Fig. 1d). The melting peaks also became broader as the branching degree increased. The melting behavior of polyethylene is mainly related to the short-chain branching density. The high level of branching inhibits polymer chains from crystallization very effectively, resulting in a morphology, i.e., predominantly non-crystalline and has a low melting temperature.

The microstructures of the branched polyethylenes obtained by the supported (α-diimine) nickel catalyst are analyzed by the high-temperature ^{13}C-NMR spectroscopy. The analysis indicates that some polyethylenes are extensively branching, and the branched structures are mainly consisted of methyl branches. Representative ^{13}C-NMR spectra of polyethylene prepared by the support catalyst at different temperatures are shown in Fig. 2. Based on chemical shift calculations performed by the method of Linderman and Adams [22], each resonance peak was assigned. Branches are named by $x\mathrm{B}_n$, where B designates a branch chain, n is the length of the branch, x is the carbon number starting with the methyl group of the branch chain, and the end methyl noted as $n = 1$ [23]. The corresponding branch resonance peaks can be found in our polymer spectra. The characteristic chemical shifts at 19.73 ($1\mathrm{B}_1$), 32.98 (brB_1), 10.96($1\mathrm{B}_2$), 39.42 (brB_2), 14.37 ($1\mathrm{B}_3$), 23.15 ($2\mathrm{B}_4$), 37.95 (brB_4), 22.64 ($2\mathrm{B}_5$), 31.94 ($3\mathrm{B}_n$), and 29.35 ($4\mathrm{B}_n$) for the supported catalyst. However, for a linear semi-crystalline polyethylene prepared at 0 °C, only the signals of methyl branches (Fig. 2a) in the ^{13}C-NMR spectrum is observed.

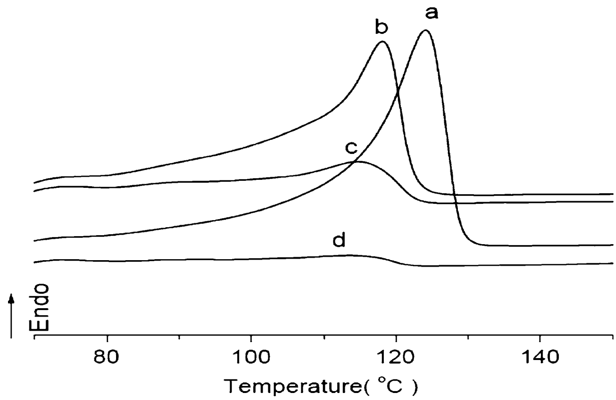


Fig. 1 DSC heating curves thermograms for polyethylenes produced with supported nickel diimine catalyst at reaction temperature 0 °C (*a*), 20 °C (*b*), 40 °C (*c*), and 60 °C (*d*), Al/Ni = 800

Some small resonances attributed to ethyl, propyl, butyl, and pentyl branches can be observed in Fig. 2b and c for branched polyethylene polymerized at 20 and 60 °C, respectively. It is surprising that long branches (longer than six carbons) are confirmed by the presence of the $3B_n$ and $4B_n$ carbon resonances at 31.94 and 29.35 ppm, and a pair of resonances attributable to a branch terminated with a *sec*-butyl group are also found in Fig. 2c. This is possibly due to the smallest branch-on-branch in an ethylene polymerization.

Table 3 shows the effect of temperatures on degree of branching and branching distribution of polyethylenes. The degree of branching at 0 °C is low, and almost all the methyl branches are incorporated into the polyethylene backbone, and the incorporation of long branches cannot be observed in the ^{13}C-NMR spectrum. As the temperature increases, the content of methyl branching decreases, and the long

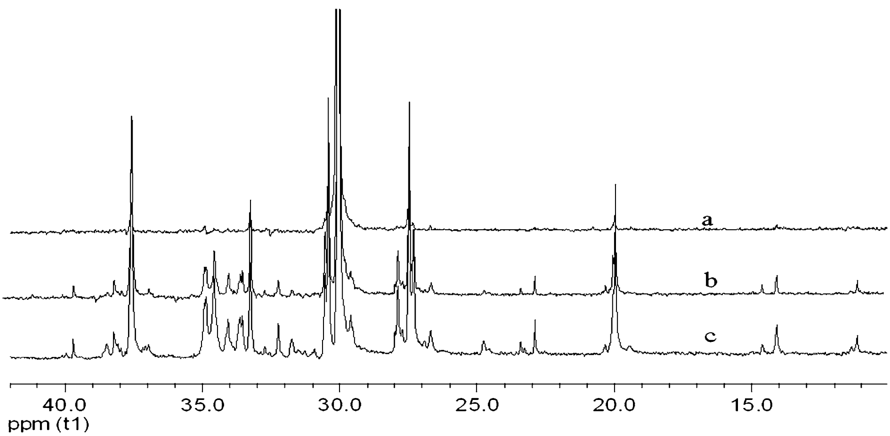


Fig. 2 The high-temperature ^{13}C-NMR spectroscopy of polyethylene produced with supported catalyst at the following polymerization conditions: 0 °C (*a*), 20 °C (*b*), and 60 °C (*c*), Al/Ni = 800

Table 3 Effects of different temperatures on branches distribution of polyethylenes

Temperature (°C)	Branches[a] (1000 C)	Branches distribution (%)					
		Methyl	Ethyl	Propyl	Butyl	Pentyl	Long($n \geq 6$)
0	16.60	100	–	–	–	–	–
20	45.32	82.43	7.33	0.27	0.45	2.99	6.53
40	58.60	78.50	6.95	2.14	0.72	2.99	8.70
60	100.90	72.41	7.45	2.69	2.04	8.24	7.17

[a] Determined by high-temperature ^{13}C-NMR measurement as branches/1000 carbons

branches and degree of branching increases. At 60 °C, the methyl branches of 72.41% and long branches of 7.17% are incorporated into the polyethylene backbone. It can also be noted that the chain walking mechanism appear to be pronounced in the supported catalyst system. An increase of polymerization temperature improves the rate of chain walking and results in the formation of more branched polyethylene. The ^{13}C-NMR (Table 3) results of the polyethylene produced by these catalytic systems are consistent with the results reported by Brookhart and his co-workers [3].

Scanning electron microscope (SEM) was also used to examine the morphology of PE particles produced by supported catalysts. The SEM photograph in Fig. 3 showed that particles of the supported catalyst were irregular in shape with roof surface and filled with pores, which were useful for the dispersion of the active species. The results of BET surface area, pore volume, and average pore diameter of the bisupport were shown in Table 1. The surface morphology and internal porous structure of the supported catalysts will influence the catalyst performance for ethylene polymerization and the structure of resultant polymers. The polymer particles revealed in Fig. 3 showed that retention and replication of the spherical morphology of the original support during catalyst immobilization and polymerization. Replication of

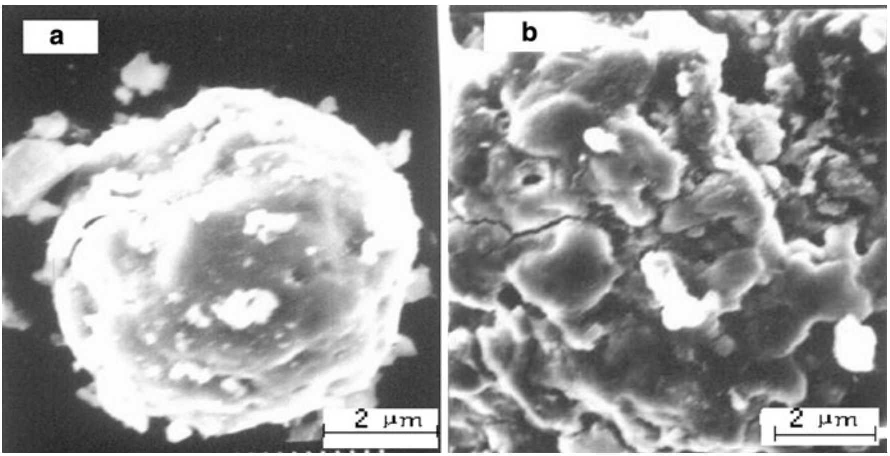


Fig. 3 SEM images of supported catalyst (**a**) and PE particles produced by supported catalyst (**b**)

the support morphology for the polymers indicated that the supported catalyst had a uniform distribution of active sites and high porosity. The received polymers were free-flowing powders and show no evidence of reactor fouling.

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