Characterization of Sulfonated Poly(styrene–divinylbenzene) and Poly(divinylbenzene) and its Application as Catalysts in Esterification Reaction

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ABSTRACT: Polymeric supports based on divinylbenzene (DVB) were prepared by aqueous suspension polymerization in presence or absence of styrene (S), using toluene and *n*-heptane as diluents of the monomers. Poly(S–DVB) and poly(DVB) were sulfonated with sulfuric acid in presence of 1,2-dichloroethane. The influence of the morphological structure of the supports and as a consequence of the catalyst on the esterification reaction of acetic acid with *n*-butanol was evaluated. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 3616–3627, 2006

Key words: sulfonated poly(styrene–divinylbenzene); sulfonated poly(divinylbenzene); catalyst activity; morphology characterization; sulfonic groups distribution

INTRODUCTION

In many industrial chemical processes homogeneous catalysts are still being used. They are strong mineral acids or Lewis acids, which are highly toxic and corrosive. These acids are dangerous to handle and transport, and corrosive to the storage containers. The final products of the catalyzed reaction need to be separated from the catalyst generating a great volume of waste because frequently those acids are neutralized at the end of the reaction. The use of heterogeneous catalysts offers several practical advantages over the homogeneous ones. The most obvious one being the easy separation of products from the catalyst.[1–3]

The increasing problem with the environment associated with the removal, handling, and disposal of corrosive waste has encouraged a large number of studies aiming the application of heterogeneous catalysts. In this direction, many efforts were dedicated to the search of solid catalysts, more selective, safer, environmentally friendly, recoverable, reusable, and do not need to be eliminated after reaction completion.

The application of cationic-exchange resins as heterogeneous acid catalysts in different reaction systems has been investigated in the last years.[4] Sharma and

Chakrabarti[5] published an extensive review on the applications of cationic-exchange resins as catalysts.

Cationic-exchange resins have been used as heterogeneous catalysts in a variety of organic reactions, such as hydration and etherification of olefins, alkylation of aromatics, dehydration of alcohols, transesterification of esters, and esterification of carboxylic acids. Beyond being easy to separate, the catalyst improves product purity and yield.[6,7] Another important advantage of resins is that they can be used in aqueous and nonaqueous systems.[5,8]

The application of resins as polymeric supports for attaching functional groups has been studied since 1970s.[9,10]

The resins synthesized by aqueous suspension copolymerization of styrene (S) and divinylbenzene (DVB) are among the most used polymeric supports. Those polymeric supports have excellent physical strength, they are not easily degraded by oxidation, hydrolysis, or elevated temperatures. The production of different morphological structures is controlled by the polymerization conditions; mainly by the molar ratio between styrene and DVB, presence or absence of porogen agent, and by the dilution degree of the monomeric mixture. The aromatic rings of those copolymers can react with several reagents mainly the electrophilic ones and at least one active group can be introduced in each aromatic ring, giving rise to resins with high exchange capacities.[11,12]

Polymeric supports based on styrene/DVB are of great interest, especially cation-exchange resins produced by functionalization with sulfonic acid groups,

TABLE I
Physical Characteristics of the Commercial Resins[2,5]

Resins	Cross-linking density (% DVB)	Surface area (m^2/g)	Pore volume (cm^3/g)	Capacity (meq/g)	Temperature stability (°C)
Amberlyst 15	20	45	0.35	4.5	120
Amberlyst 18	a	a	a	4.7	150
Amberlyst 36	a	a	a	5.4	120
Ambertlyst IR-120	a	a	a	4.4	120
Amberlyst XN 1010	100	540	0.47	5.3	120

[a] Data not found.

which also play an important role as heterogeneous acid catalyst.[10,13–15]

The sulfonation of the supports presents no problems if proper precautions are taken. Depending on reaction conditions, the functional groups (sulfonic groups) may be uniformly distributed throughout the resin or, when the modification reaction is diffusion controlled, functionalization can start at the surface of the polymer particle and then move inwards, initially into the pores and finally into the matrix.[16,17]

Butyl acetate is commonly synthesized through esterification of acetic acid with n-butanol in the presence of an acid catalyst. Initially, this reaction was carried out in presence of sulfuric acid as catalyst (homogeneous). Nowadays, solid heterogeneous catalysts are being chosen as catalysts because of their obvious engineering benefits. Many authors investigated the influence of various experimental parameters on the esterification kinetics. Janowskuy et al. have studied the esterification kinetics in presence of a commercial resin (sulfonic) and proposed a pseudohomogeneous kinetic model for that reaction.[18] A study on the kinetic behavior of esterification of acetic acid with amyl alcohol by heterogeneous catalysis was carried out.[19] The authors compared the performance of Dowex 50Wx8–100 with that of Amberlyst 15 (Wu7) for the esterification, and concluded that the Dowex resin is more active than Amberlyst 15 in promoting that reaction. Table I shows the physical characteristics of some commercial resins.

The exchange capacities of those commercial resins are intermediated to those catalysts obtained in this work. The catalysts used in this work are more porous than the commercial ones.

The objective of this work was the synthesis of polymeric supports based on DVB and on S-DVB with varied porosities functionalized with sulfonic groups (SO$_3$H) for use as heterogeneous catalysts. These supports were prepared by aqueous suspension polymerization and subsequent chemical modification of the aromatic rings by reacting the supports with sulfuric acid producing insoluble sulfonic catalysts. The supports and catalysts were characterized by bulk density, surface area, pore volume (by BET and water uptake), optical appearance and surface morphology.

The cationic-exchange capacities of catalysts were determined, and catalytic activity was evaluated by esterification acetic acid with n-butanol.

EXPERIMENTAL

Materials and reagents

Commercial styrene (S) and DVB were donated by Nitriflex Indústria e Comércio (Brazil). Styrene was washed with sodium hydroxide aqueous solution (5%, wt/wt) to remove the inhibitor, followed by several washings with water. DVB was used as-received. The initiator, benzoyl peroxide (BPO, VETEC Química Fina Ltda, Brazil), and the diluents, toluene (Tol, VETEC Química Fina Ltda, Brazil) and n-heptane (Hep, VETEC S.A. Indústria e Comércio, Brazil) all P.A. grade, were used as-received. The components of the aqueous phase, 2-hydroxy-ethyl-cellulose (HEC donated by Union Carbide do Brasil S.A. Indústria e Comércio) and sodium chloride (NaCl, Reagen-Quimibrás Indústrias Químicas S.A., Brazil) all P.A. grades, were used as-received. Aqueous solutions were prepared in deionized water.

Sulfuric acid (H$_2$SO$_4$, VETEC S.A. Indústria e Comércio, Brazil), 1,2-dichloroethane (DCE, TEDIA S.A. Indústria e Comércio, Brazil), nitric acid (HNO$_3$, VETEC S.A. Indústria e Comércio, Brazil), sodium hydroxide (NaOH, Quimex, Brazil), hydrochloric acid (HCl, VETEC S.A. Indústria e Comércio, Brazil), acetic acid (HAc, VETEC S.A. Indústria e Comércio, Brazil), n-butanol (n-BuOH, VETEC S.A. Indústria e Comércio, Brazil), and other P.A. reagents were used as-received.

Synthesis of supports beads

Beads of poly(S–DVB) or poly(DVB) were synthesized by aqueous suspension polymerization technique in the presence of mixtures of toluene (Tol) and n-heptane (Hep) as diluents and BPO (1 mol % in relation to the monomers) as polymerization initiator. The polymerizations were carried out in a 1-L round-bottomed flask fitted with a mechanical stirrer, silicon seal, and a reflux condenser. A solution composed of monomers
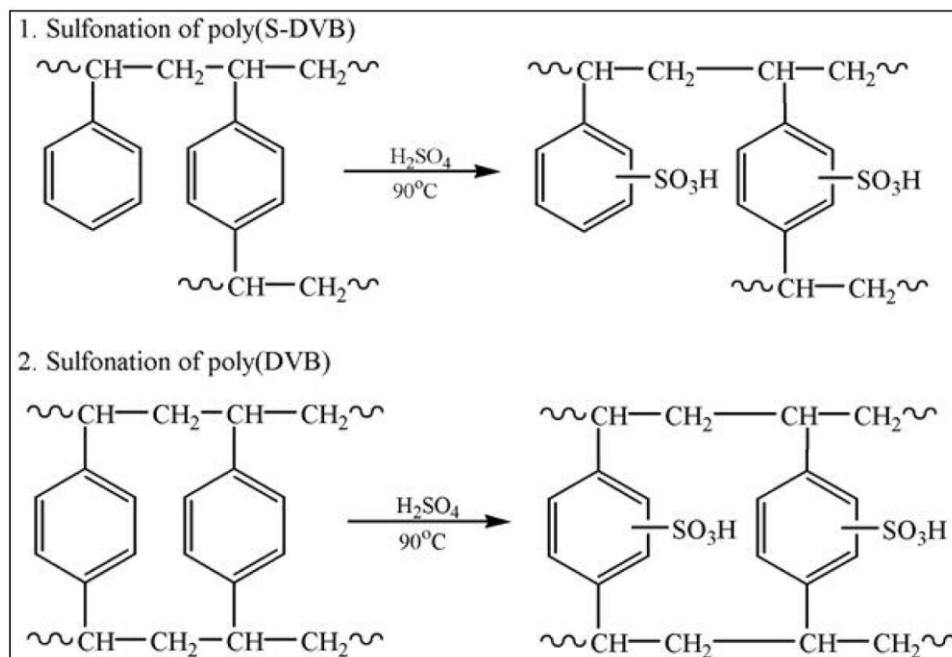
Scheme 1 Schematic representation of poly(S-DVB) and poly(DVB) sulfonation.

(S/DVB or DVB), mixture of diluents (Tol/Hep), and initiator (BPO) was added to the polymerization flask and vigorously mixed by stirring (500 rpm) in the aqueous medium containing 0.2% (wt/v) HEC 0.5% (wt/v) and NaCl for reducing, by salting out effect, the solubility of monomers in water. The volume ratio between aqueous phase and organic phase was 4:1 for all polymerizations. The resultant suspension was heated for 30 h in a thermostatic bath set at 90°C. The polymerization product was filtered, washed with hot deionized water, to remove the stabilizers, and ethanol to remove any traces of monomers and diluents. Before drying, the support beads were sieved to be separated in different size ranges (25, 45, 80, 100, and 200 mesh). The beads with the desired size (45–80 mesh) were collected and finally washed with methanol and dried at 50°C for 48 h.[20-22]

Sulfonation of S-DVB supports beads

Sulfonation was carried out in a 250-mL round-bottomed flask fitted with a mechanical stirrer, silicon seal, and a reflux condenser.

An air-dried sample of poly(S-DVB) or poly(DVB) beads (45–80 mesh) of about 3 g was swollen in DCE (30 mL) for 24 h at room temperature. Sulfuric acid (45 mL) was added and the reaction was carried out for 1 h at 90°C. The sulfonated product was slowly transferred to a 250-mL beaker containing 50-mL of distilled water. The mixture (beads + water) was slowly transferred to a second beaker also containing 50 mL of distilled water. A third dilution was carried out in

1000 mL of distilled water. The successive water dilutions have the objective of reducing H_2SO_4 concentration, which in contact with large quantities of water increase the osmotic pressure of the catalyst beads, causing the beads to break. After the third dilution the catalyst beads were filtered, washed with methanol, and finally dried at 50°C for 48 h. The sulfonation of poly(S-DVB) and poly(DVB) is represented in the Scheme 1.

Characterization methods

Bulk density

The bulk density (d_b) of the supports and polymeric catalysts (sulfonic resins) was determined by the graduated cylinder method, a modification of ASTM D 1895–69 method.[23]

Surface area, pore volume, and pore diameter

The surface area (A), pore volume (Vp_{BJH}), and pore diameter ($\bar{D}$) of the supports and sulfonic catalysts were determined by N_2 adsorption measurements following the BET method (ASAP-2010, Micromeritics).[24-26]

Fixed pore volume

The fixed pore volume V_{pH_2O} of the supports was also determined by water uptake measurements.[27,28]

Swelling percentage

The swelling percentage was determined by measuring in a graduated cylinder the volume change of the support from the dried state until the equilibrium in a given solvent. The swelling percentage was calculated as:

$$\% \ S_w = \frac{\text{Final volume} - \text{Initial volume}}{\text{Initial volume}}$$

To evaluate the supports swelling, toluene and *n*-heptane were used as solvents and deionized water and a mixture of acetic acid and *n*-butanol at mol ratio 2:1 were used to evaluate the catalyst swelling.[29]

Infrared spectra

The supports and catalysts were characterized using infrared spectroscopy in a Perkin–Elmer 1720X FTIR with KBr pellets (1%, wt/wt).[30]

Visual appearance

The appearance of beads was observed using an Olympus optical microscope fitted with a photographic camera (Model SZ10).

Surface morphology

The beads were fractured and fixed, using colloidal carbon, on metallic supports. Then, the samples were coated with a thin layer of gold and the morphology was observed in a scanning electron microscope (SEM) (Digital Scanning Microscope DSM 960 ZEISS and Digital Scanning Microscope JSM 5610 LV JEOL).[31,32]

Determination of the local concentration and distribution of the catalysts sulfonic groups

the local concentration and distribution of the sulfonic groups (SO_3H) was investigated using energy dispersive X-ray analysis (EDX). The beads were fractured and fixed, using colloidal carbon, on metallic supports and coated with a thin layer of carbon. EDX provides a distribution profile of sulfonic groups in the polymer material (SEM, Digital Scanning Microscope JSM 6460 LV JEOL and EDS, Noran System SIX Model 200 Thermo).[33–35]

Ion exchange capacity determination

Approximately 3 g of catalyst were put in 1M HNO_3 (conditioning) for 4 h, and then, it was filtered off and washed with deionized water to remove excess acid. In a glass-stoppered Erlenmeyer flask was placed 1 g of the conditioned catalyst and 100 mL of sodium hydroxide solution (0.1M). The mixture was kept overnight at room temperature. The ion exchange capacity was determined by titrating the supernatant solution with HCl (0.1M). The rest of the conditioned catalyst was put in a glass-stoppered flask and kept at 110°C overnight and finally led to constant weight. The exchange capacity was obtained from the difference between the concentration of NaOH solution firstly added to the catalyst and NaOH concentration in the supernatant solution. The result (exchange capacity) was expressed as $meq_{SO_3H}/g_{catalyst}$.[36]

Catalytic activity

the catalytic activity was evaluated by the esterification reaction of acetic acid with *n*-butanol. The reaction was carried out in a 250-mL round-bottomed flask. The flask was equipped with a condenser, a mechanical stirrer, and silicon seal. The reaction was carried out for 2 h at 90°C using 1 g of catalyst and 2:1 mol ratio of acetic acid to *n*-butanol.[37] The result (catalytic activity) was expressed as g_{ester}/meq_{SO_3H} h.

RESULTS AND DISCUSSION

Two families of supports were prepared in this work, poly(S–DVB) with varied proportions of DVB (10, 20, 40, and 60%, v/v) and poly(DVB) with a dilution degree of 150% in relation to monomer. The organic phase constituted initiator, styrene, DVB, and diluents [toluene (good solvent) and *n*-heptane (bad solvent)]. The diluent mixtures composition was varied (70:30, 50:50, and 30:70 v/v). The diluent composition influenced strongly the support morphology, supports being produced varying from gel-type to macroporous.

This section deals mainly on the on the morphology of the poly(S-DVB) and poly(DVB) supports and their respective sulfonic catalysts. The morphology of supports and catalysts were evaluated in the dry and swollen states.

Influence of the synthesis parameters on the characteristics of the poly(S-DVB) and poly(DVB) supports in the dry state

Table II shows that the morphological characteristics of the supports, such as bulk density (d_b), pore volume (Vp_{BJH}), and surface area (A), change with composition of the diluent mixture and DVB content used in the synthesis. In the case of the supports that did not present measurable value of surface area by N_2 adsorption (BET), it was not possible to determine the pore diameter and pore volume by that technique.

The bulk density determination is a simple and efficient method to evaluate the porosity of spherical

TABLE II
Physical Characteristics in the Dry State of Poly(S–DVB) and Poly(DVB) Supports Synthesized at 150% Dilution Degree and Different Compositions of the Diluent Mixture

Sample	Tol/Hep ratio v/v (%)	d_b (g/cm^3)	A (m^2/g)	$\bar{D}$ (Å)	Vp_{BJH} (cm^3/g)
10 of % DVB					
SUP-13	70:30	0.74	nm	—	—
SUP-21	50:50	0.65	nm	—	—
SUP-17	30:70	0.61	nm	—	—
20 of % DVB					
SUP-14	70:30	0.68	nm	—	—
SUP-22	50:50	0.62	nm	—	—
SUP-18	30:70	0.64	nm	—	—
40 of % DVB					
SUP-15	70:30	0.63	nm	—	—
SUP-23	50:50	0.52	109	73	0.25
SUP-19	30:70	0.50	126	69	0.29
60 of % DVB					
SUP-16	70:30	0.67	0	—	—
SUP-24	50:50	0.56	95	54	0.14
SUP-20	30:70	0.49	141	84	0.35
100 of % DVB					
SUP-25	70:30	0.42	576	66	0.66
SUP-26	50:50	0.36	556	83	0.76
SUP-27	30:70	0.31	575	103	0.96

SUP, support; Tol, toluene; Hep, n-heptane; d_b, bulk density; A, surface area; $\bar{D}$, pore diameter; Vp_{BJH}, fixed pore volume, determined by nitrogen adsorption/desorption; nm, not measurable; —, not determined.

copolymers,[23,38] the decrease in bulk density indicates that there is an increase in the porosity.

For all the poly(S-DVB) supports synthesized with low DVB content (10 and 20%), significant effect on the morphological structure of the supports in the dry state was not observed, i.e., independent of the composition of the diluent mixture, the bulk density, surface area, and pore volume were not affected significantly.

Figure 1 shows the effect of increasing DVB content on optical appearance, and indirectly on the bulk density, of the poly(S-DVB) and poly(DVB) supports synthesized using a diluent mixture 30:70 Tol/Hep.

Generally, as the DVB proportion used in the synthesis of supports increased the bulk density decreased (Table II), making the beads more porous and consequently more opaque (Fig. 1).

When poly(S-DVB) supports were synthesized with high DVB content (40 and 60%) and Tol/Hep ratio 50:50 and 30:70, the supports presented lower bulk density and higher surface area. As a consequence, for these diluent mixture compositions, the beads showed an increase in the values of pore volume. In this case, the increase of n-heptane proportion, reducing of solvating power of the diluent mixture, produced more porous polymer structures. In Figure 2 can be observed the increase of porosity with the increase of n-heptane proportion in the diluent mixture for poly(S-DVB) supports synthesized with 60% of DVB content.

Poly(DVB) supports presented the smallest values of bulk density and the highest values of surface area, pore diameter, and pore volume independent of the diluent mixture used. When 100% DVB is used macro-
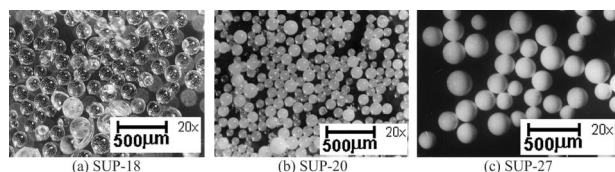

Figure 1 Influence of DVB proportion on the bulk density: (a) SUP-18, 20% of DVB; (b) SUP-20, 40% of DVB; and (c) SUP-27, 100% of DVB.
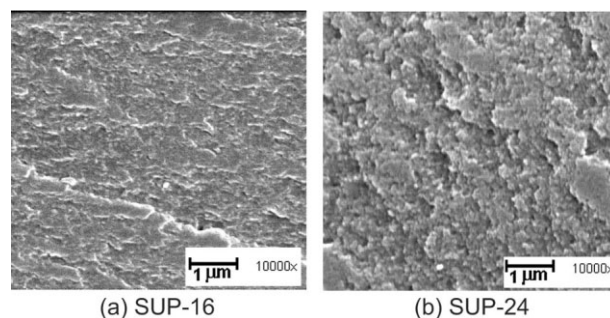

Figure 2 SEM micrographs of internal surfaces of poly(S-DVB) supports synthesized with 60% of DVB: (a) SUP-16, diluent mixture 70:30 Tol/Hep and (b) SUP-24, diluent mixture 30:70 Tol/Hep.
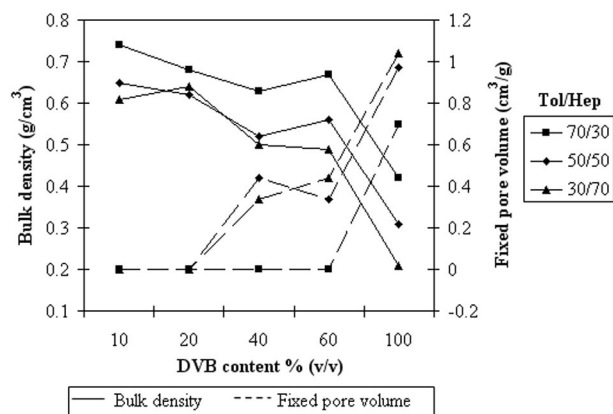
Figure 3 Influence of DVB content and diluent mixture composition on supports bulk density and fixed pore volume.

porous structures are formed, and the porosity increases as the *n*-heptane proportion in the diluent mixture increases.

Figure 3 shows the decrease of bulk density and the increase of fixed pore volume as DVB content and *n*-heptane proportion in the diluent mixture increase.

The reduction of the solvating power of the diluent mixture and the increase of DVB content promote the phase separation (χ-synerese and υ-synerese, respectively) during the synthesis of supports, resulting in the increase in porosity of the polymer beads. Figure 4 presents scanning electron micrographs of the internal surface of the supports synthesized with 40% of DVB and 100% of DVB using 30:70 Tol/Hep as diluent mixture. These micrographs show that the increase of DVB proportion provokes the formation of bigger agglomerates with large holes between them. The porosity consists of wide and narrow spaces between the particles, microspheres, or agglomerates.

Influence of the synthesis parameters on the characteristics of the poly(S-DVB) and poly(DVB) supports in the swelling state

The retention of a good solvent (toluene) by a porous polymer network is considered to be the result of three
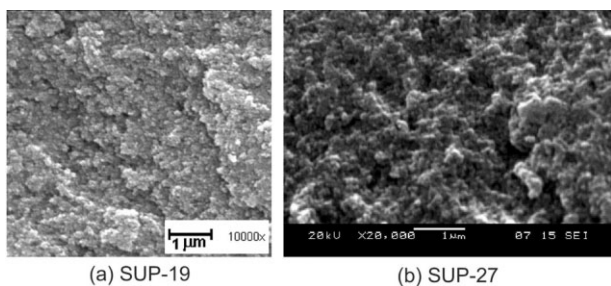

(a) SUP-19   (b) SUP-27

Figure 4 SEM micrographs of internal surface of the supports synthesized using as diluent mixture 30:70 Tol/Hep: (a) SUP-19, poly(S-DVB) with 40% DVB and (b) SUP-27, poly(DVB).

TABLE III
Physical Characteristics in the Swelling State of Poly(S–DVB) and Poly(DVB) Supports Synthesized at 150% Dilution Degree and Different Compositions of the Diluent Mixture

Sample	Tol/Hep ratio v/v (%)	Vp_{H_2O} (cm^3/g)	I_{tol} (%)	I_{Hep} (%)
10 of % DVB				
SUP-13	70:30	0	359	6
SUP-21	50:50	0	286	1
SUP-17	30:70	0	228	3
20 of % DVB				
SUP-14	70:30	0	280	4
SUP-22	50:50	0	163	5
SUP-18	30:70	0	126	15
40 of % DVB				
SUP-15	70:30	0	100	70
SUP-23	50:50	0.44	98	77
SUP-19	30:70	0.34	68	56
60 of % DVB				
SUP-16	70:30	0	93	52
SUP-24	50:50	0.34	57	51
SUP-20	30:70	0.44	80	64
100 of % DVB				
SUP-25	70:30	0.70	47	45
SUP-26	50:50	0.97	45	36
SUP-27	30:70	1.04	23	27

SUP, support; Tol, toluene; Hep, *n*-heptane; Vp_{H_2O}, fixed pore volume, determined by water uptake; I_{tol}, swelling percentage in toluene; I_{hep}, swelling percentage in *n*-heptane.

contributions: filling of fixed pores, expansion of fixed and collapsed pores, and swelling of polymer nuclei. On the other hand, the retention of a bad solvent (*n*-heptane) is resultant of only two contributions: filling of fixed pores and expansion of fixed and collapsed pores.[27,39]

Generally, the supports synthesized with low DVB content in presence of low *n*-heptane (bad solvent) proportion presented gel structures with a large capacity to swell in good solvents. On the other hand, the increase of *n*-heptane proportion in the diluent mixture reduced the swelling capacity of the supports in toluene, due to the increase of the macroporosity, which makes the polymer network more rigid (Table III).

For the supports synthesized in presence of different diluent compositions (70:30, 50:50, and 30:70 Tol/Hep), the percentage of swelling volume in toluene (I_{tol}) decreased as the DVB content increased (Table III). The polymer chains of macroporous supports are more rigid and entangled than the chains of gel-type polymer networks.[29]

On the other hand, the increase in retention values in *n*-heptane (I_{hep}) is due to the increase of fixed pores. Thus, expansion of fixed and collapsed pores are responsible for the increase of beads volume in presence of that solvent.
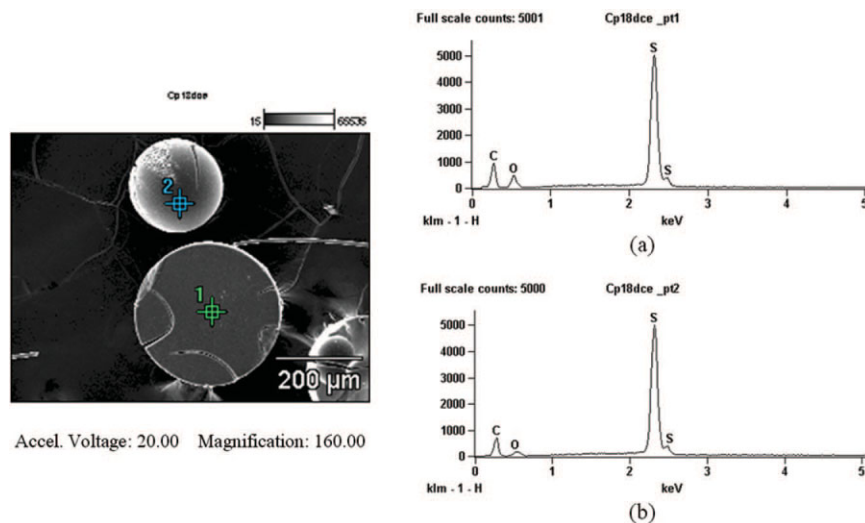
Figure 5 EDX spectra of the sulfur distribution on a bead of poly(S-DVB) catalyst: (a) internal surface and (b) external surface of CAT-18 (20% DVB, diluent mixture, 30:70 Tol/Hep). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

The increase of bad solvent proportion in the diluent mixture, used in the synthesis, produced crosslinked structures more entangled, with a lower capacity to swell in toluene. The macroporous structures are composed of two phases, pore phase and gel phase, the solvent uptake in toluene tends to be higher than that in n-heptane because the gel phase does not swell in n-heptane. The more predominant is the pore phase over the gel phase, closer is the retention values of the good and bad solvents.[40]

Influence of the sulfonation parameters on the characteristics of the polymer catalysts in the dry state

The catalysts were prepared (sulfonation of supports) in presence of DCE, which is a solvent capable of swelling the polymer matrix (supports).[14] As a consequence, the sulfonation occurred in the whole polymer structure. The distribution of sulfonic acid groups was determined using EDX.[33–35] For the catalyst synthesized with 20% DVB in presence of 30:70 Tol/Hep, the homogeneous distribution of the sulfonic groups across the poly(S-DVB) catalyst bead is due to its high swelling capacity in DCE (Fig. 5).

In the case of the poly(DVB), distribution of heterogeneous sulfonic groups was observed. The functionalization of macroporous beads can be affected by diffusion limitation in the gelular microparticle. The EDX spectra of external and internal surfaces of the catalyst bead is shown in Figure 6, in which the decreasing concentration of the sulfonic groups from the shell to the inner region of the bead can be observed.

Table IV shows the physical characteristics in the dry state of the polymer catalysts obtained from poly(S-DVB) and poly(DVB) supports.

For all catalysts, the values of bulk density increased in relation to the precursor supports, due to the introduction of groups containing atoms heavier than carbon (SO_3H). The increase in the bulk density of catalysts was corroborated by the decrease in surface area (Tables II and IV).

The surface area of catalysts decreased, in relation to the supports, because sulfonation occurred inside the fixed pores and in the external surface of the polymer supports. Thus, part of the area became occupied by the sulfonic groups. As expected, the catalysts pore volume also decreased.

The sulfonation reaction modified the morphology of the internal surface of the material (Fig. 7). After sulfonation the produced catalyst became less porous than the precursor support. That effect is corroborated by the values of surface area and pore volume (Tables III and IV). Figure 7b shows that the internal surface of catalyst is less rough than that of the support (Fig. 7a).

Figure 8 shows FTIR spectra of poly(S-DVB) support and catalyst prepared with 10% of DVB and composition of the diluent mixture, Tol/Hep 50:50. The resolution of the FTIR spectrum of the catalyst was not good due to the high hygroscopicity of the sulfonic groups in comparison to the material. However, it is possible to observe absorption bands in the range from 1230 to 1120 cm^{-1}, characteristic of sulfonate group. Sulfonic group (SO_3H) reacts quickly with water forming a hydroniun sulfonate ($H_3O^+SO_3^-$), which absorbs in this range of frequency. Sulfonic acids, when anhydrous, absorb at two distinct regions—1350–1342 cm^{-1} and 1165–1150 cm^{-1}.[30]
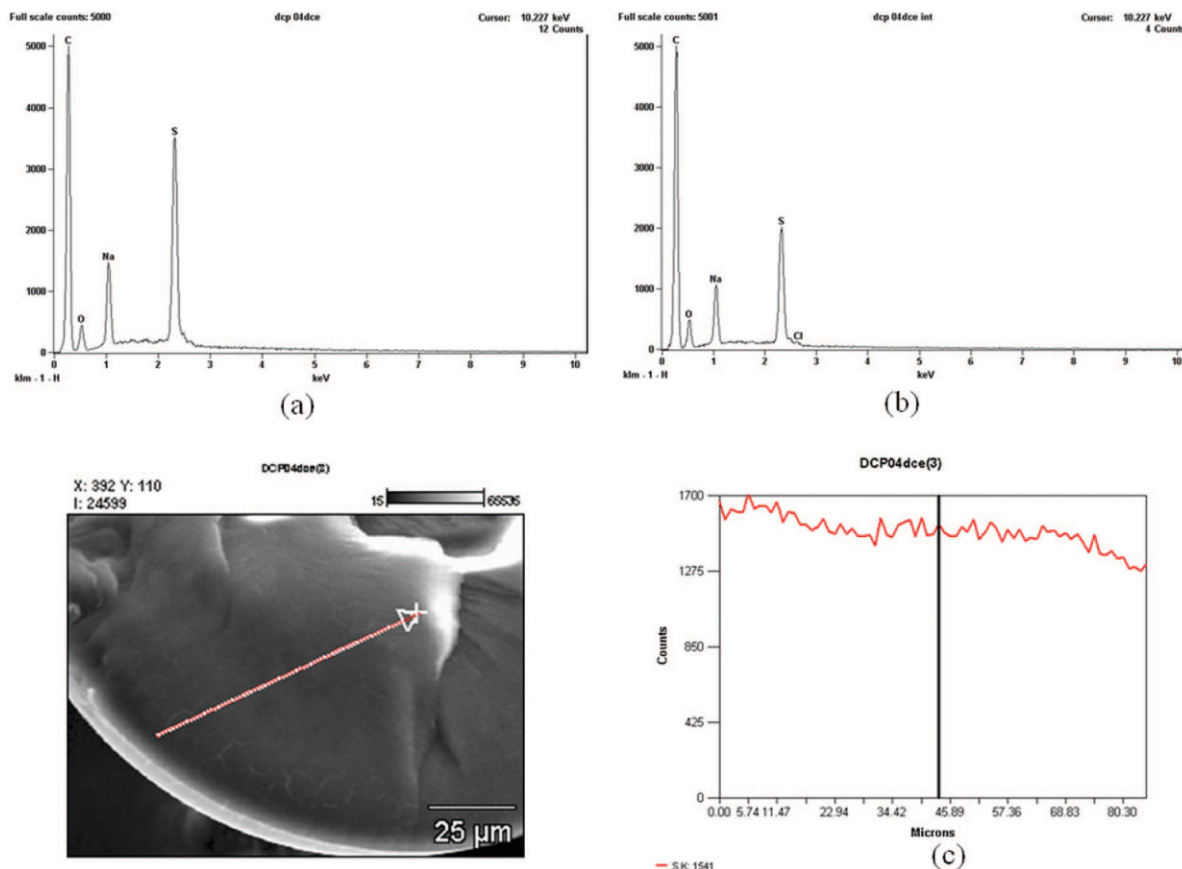
Figure 6 EDX spectra and sulfur distribution over the cross-section of poly(DVB) catalyst: (a) external surface, (b) internal surface of CAT-25 (100% DVB, diluent mixture, 70:30 Tol/Hep) and (c) scan line. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Influence of the sulfonation parameters on the characteristics of the polymer catalysts in the swelling state

The polymer catalysts were not characterized by water uptake measurements $V_{p_{H_2O}}$, because they are highly hydrophilic and in that case the uptake value would be the sum of the volume of water that penetrates in the fixed and collapsed pores and the volume of water that swells the nuclei.

The swelling behavior of the catalysts was evaluated in water I_{H_2O} and in a mixture of acetic acid and n-butanol ($I_{HAc+n\text{-}BuOH}$) at 2:1 mol ratio (Table V). The presence of sulfonic groups in the resin increases its hydrophilic character in relation to the support, which does not have affinity for polar solvents due its nonpolar character.

In general, the values of the percentage of swelling decreased as the DVB content used in the synthesis of the precursor supports increased. The increase of crosslinking degree reduces the polymer chain elasticity, decreasing its swelling capacity.

The poly(S-DVB) catalysts prepared with 10 and 20% of DVB presented the lowest values of the swelling percentage in acetic acid/n-butanol mixture. The

values of the swelling percentage in water were higher due the higher water affinity of sulfonic group.

For the catalysts prepared with the same DVB content, the increase of the proportion of bad solvent in the diluent mixture during its synthesis decreased the swelling capacity of the resultant catalyst. This effect can be attributed to the higher extension of phase separation, during the polymer synthesis, resulting in structures more entangled, with smaller capacity of swelling.

The percentage of swelling in acetic acid/n-butanol mixture followed the same tendency of the swelling in water. As the DVB content in the polymer increased the values of swelling in that mixture decreased. It is important to know the catalyst affinity for the reaction mixture [acetic acid/(n-butanol)] during esterification, if the catalyst presents high capacity to swell in that mixture the active sites of the catalyst will be more accessible.

Evaluation of the cation-exchange capacity and catalyst activity of sulfonated poly(S-DVB) and poly(DVB)

The cation-exchange capacity evaluates the content of sulfonic groups accessible in water medium.[41] The

TABLE IV
Physical Characteristics in the Dry State of Catalysts Obtained from Poly(S–DVB) and Poly(DVB) Supports Synthesized at 150% Dilution Degree and at Different Compositions of the Diluent Mixture

Sample	Tol/Hep ratio v/v (%)	d_b (g/cm^3)	A (m^2/g)	$\bar{D}$ (Å)	Vp_{BJH} (cm^3/g)
10% of DVB					
CAT-13	70/30	0.87	nm	—	—
CAT-21	50/50	0.82	nm	—	—
CAT-17	30/70	0.84	nm	—	—
20% of DVB					
CAT-14	70/30	0.85	nm	—	—
CAT-22	50/50	0.85	nm	—	—
CAT-18	30/70	0.81	nm	—	—
40% of DVB					
CAT-15	70/30	0.83	nm	—	—
CAT-23	50/50	0.73	3	—	—
CAT-19	30/70	0.73	8	88	0.03
60% of DVB					
CAT-16	70/30	0.86	0	—	—
CAT-24	50/50	0.73	19	—	—
CAT-20	30/70	0.74	8	135	0.04
100% of DVB					
CAT-25	70/30	0.51	429	70	0.53
CAT-26	50/50	0.48	432	81	0.64
CAT-27	30/70	0.42	468	104	0.83

CAT, catalyst; Tol, toluene; Hep, n-heptane; d_b, bulk density; A, surface area; $\bar{D}$, pore diameter; Vp_{BJH}, fixed pore volume, determined by nitrogen adsorption/desorption; nm, not measurable; —, not determined.

amount of ion kept by the catalyst depends on the affinity of the ion for catalyst sites and also on the swelling capacity of the catalyst.

The exchange process between an ion in solution and a mobile ion of the polymer network (resin) involves the following steps[42–44]:

- transfer of the ion through the aqueous solution to the surface of the resin;
- transfer of the ion from the resin surface resin to the exchange site;
- ion exchange reaction;
- transfer of the exchanged ion from exchange site to the resin surface;
- transfer of the exchanged ion from the resin surface to the aqueous solution.
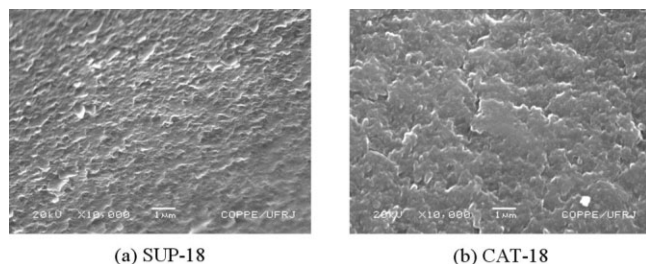
The exchange capacity is directly proportional to the swelling of the gel phase of the supports, i.e., the larger is the difference between the swelling in a good solvent (toluene) and in a bad solvent (*n*-heptane) (Table III) higher is the exchange capacity (Table VI). That difference is a measure of the elasticity of the polymer network.

Table VI shows the swelling percentages, cation-exchange capacity and catalytic activity of the polymer catalysts obtained from poly(S-DVB) and poly-(DVB) supports by sulfonation.

The values of cation-exchange capacity of all the poly(S-DVB) catalysts fell in the range between 5.78
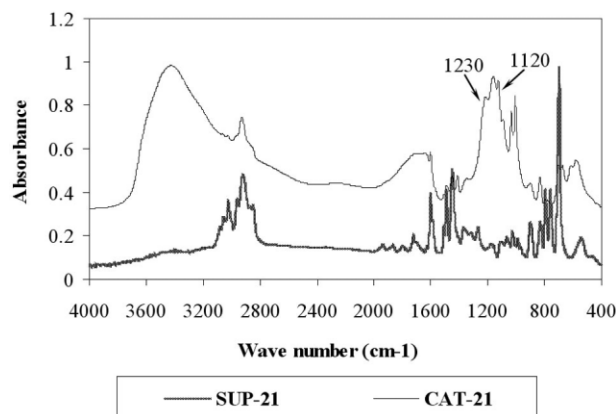

(a) SUP-18   (b) CAT-18

Figure 7 SEM micrographs of internal surface of support and catalyst: (a) SUP-18 and (b) CAT-18 (20% DVB, Tol/Hep 30:70).

Figure 8 FTIR spectra of support and catalyst: SUP-21 and CAT-21 (10% DVB, Tol/Hep 50:50).

TABLE V
Physical Characteristics in the Swelling State of Catalysts Obtained from Poly(S–DVB) and Poly(DVB) Supports Synthesized at 150% Dilution Degree and at Different Compositions of the Diluent Mixture

Sample	Tol/Hep ratio v/v (%)	I_{H_2O} (%)	$I_{(HAc+n\text{-}BuOH)}$ (%)
10% of DVB			
CAT-13	70:30	337	89
CAT-21	50:50	267	83
CAT-17	30:70	154	60
20% of DVB			
CAT-14	70:30	304	84
CAT-22	50:50	190	115
CAT-18	30:70	93	77
40% of DVB			
CAT-15	70:30	124	78
CAT-23	50:50	84	110
CAT-19	30:70	42	82
60% of DVB			
CAT-16	70:30	115	84
CAT-24	50:50	26	41
CAT-20	30:70	39	69
100% of DVB			
CAT-25	70:30	23	27
CAT-26	50:50	8	12
CAT-27	30:70	9	19

CAT, catalyst; Tol, toluene; Hep, n-heptane; I_{H_2O}, swelling percentage in water; $I_{(HAc+n\text{-}BuOH)}$, swelling percentage in the mixture acetic acid/n-butanol.

and 3.76 meq/g (Table VI). Generally, the highest values were attributed to the catalysts that presented the highest values of swelling in water. This behavior can be attributed to the easier access of sulfonic groups by the water solution, located inside the gel phase of the polymer structure.

In the case of catalysts synthesized with 100% DVB [poly(DVB)], the low values can be attributed to the more crosslinked structures (more rigid) that hindered the access of the water solution to the sulfonic groups, and consequently to the occurrence of ion-exchange reaction resulting in the lowest values of exchange capacity.

Figure 9 represents the effect of DVB content and composition of diluent mixture on the catalysts cation-exchange capacity.

Figure 10 shows scanning electron micrographs of two catalysts synthesized in presence of diluent mixture 30:70 Tol/Hep. The catalyst prepared with 20% of DVB (CAT-18) presents smooth external surface and internal surface with small agglomerations of microspheres with narrow spaces between them. The catalyst produced with 60% DVB (CAT-20) shows rough external surface with small channels and several holes. Large agglomerations of microspheres and large spaces between them can be observed in the internal surface.

The catalytic activity was evaluated by the esterification reaction of acetic acid with n-butanol. The catalytic activity of the different sulfonic resins varied as

TABLE VI
Swelling Percentages, Cation-Exchange Capacity, and Catalytic Activity of the Sulfonic Catalysts

Sample	Tol/Hep ratio v/v (%)	I_{H_2O} (%)	Cation-exchange capacity (meq$_{SO_3H}$/g$_{cat}$)	$I_{(HAc+n\text{-}BuOH)}$ (%)	Catalytic activity (g$_{ester}$/meq$_{SO_3H}$ h)
10% of DVB					
CAT-13	70:30	337	5.49	89	4.18
CAT-21	50:50	267	5.78	83	3.96
CAT-17	30:70	154	5.63	60	3.86
20% of DVB					
CAT-14	70:30	304	4.56	84	4.61
CAT-22	50:50	190	4.92	115	4.52
CAT-18	30:70	93	5.12	77	5.05
40% of DVB					
CAT-15	70:30	124	4.26	78	4.05
CAT-23	50:50	84	4.41	110	4.84
CAT-19	30:70	42	4.26	82	4.49
60% of DVB					
CAT-16	70:30	115	4.69	84	5.42
CAT-24	50:50	26	3.76	41	5.69
CAT-20	30:70	39	4.35	69	4.97
100% of DVB					
CAT-25	70:30	23	2.78	27	5.53
CAT-26	50:50	8	2.67	12	7.21
CAT-27	30:70	9	2.76	19	7.33

CAT, catalyst; Tol, toluene; Hep, n-heptane; I_{H_2O}, percent swelling in water; $I_{(HAc+n\text{-}BuOH)}$, swelling percentage in acetic acid and n-butanol mixture.
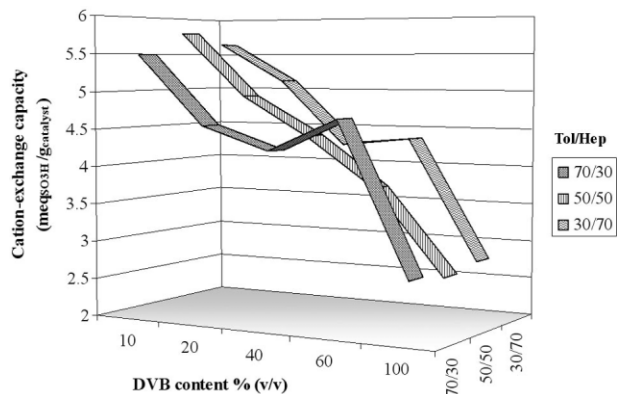
Figure 9 Influence of support synthesis parameter (DVB content and Tol/Hep composition) on cation-exchange capacity.

a function of their morphology. The most porous catalysts (60 and 100% DVB) presented the highest values of catalyst activity. The access to the active sites is not through the swelling of the network but through the porous structure.

Thus, the catalytic activity cannot be directly related with cation-exchange capacity, where polymer networks with larger swelling elasticity possess the active groups more easily accessible, resulting in high exchange capacities.

In general, the values of the catalytic activity increased as the DVB content, used in the synthesis of the supports, increased. The catalysts with the highest proportion of DVB permit an easier access of the re-
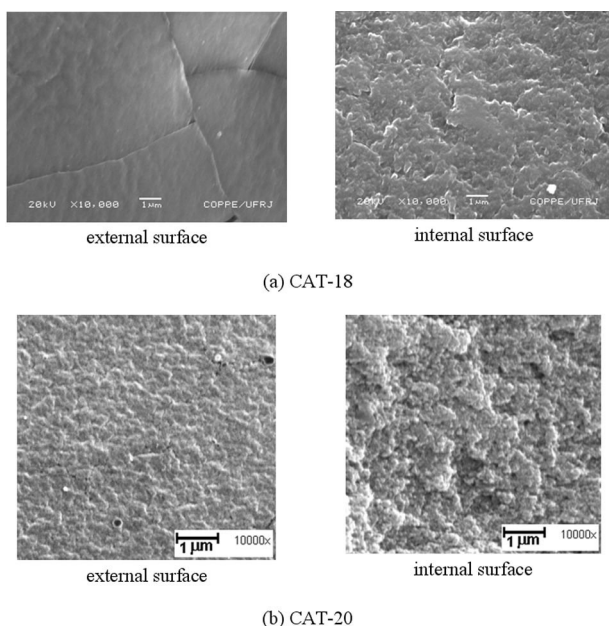
action mixture to the active sites (SO_3H groups) because of their macroporosity. These catalysts possess a more accentuated macroporous character, i.e., present higher degree of a permanent porosity, making the active groups more easily accessible (Table VI).

For catalysts with the same DVB content, the increase of bad solvent proportion (*n*-heptane) used in the synthesis of supports also favored an increase in the values of catalytic activity, as this variation also resulted in the porosity increase.

The catalyst synthesized with 100% of DVB presented the lowest values of cation exchange capacity, but the highest values of the catalytic activity. The structure of those catalysts is macroporous and therefore they do not need to swell for the active sites accessing.

Figure 11 shows the effect of DVB content and diluent mixture composition on the catalytic activity. At the same composition of diluent mixture the increase of DVB content provoked an increase on the values of catalyst activity.

CONCLUSIONS

- For the supports synthesized with 40, 60, and 100% of DVB the increase of the *n*-heptane proportion in the composition of the diluent mixture produced more porous structures.
- Poly(S-DVB) catalyst presented homogeneous distribution of the sulfonic groups across the bead, due its high capacity of swelling in DCE. However, the catalyst obtained with poly(DVB) presented heterogeneous sulfonic groups distribution.
- All catalysts were active in the acetic acid esterification with *n*-butanol. The highest values of catalytic activity were presented by the most macroporous catalysts.
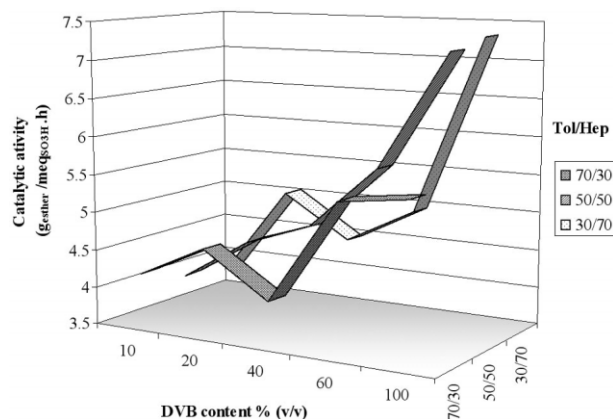

external surface   internal surface

(a) CAT-18

external surface   internal surface

(b) CAT-20

Figure 10 SEM micrographs of external and internal surfaces of the poly(S-DVB) catalysts: Diluent mixture, 30:70 Tol/Hep: (a) CAT-18, 20% DVB and (b) CAT-20, 60% DVB.

Figure 11 Influence of the supports synthesis parameter (DVB content and Tol/Hep composition) on catalyst activity.

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