Combined Emulsion and Phase Inversion Techniques for the Preparation of Catalytic PVDF Microcapsules

M. G. Buonomenna,* A. Figoli,* I. Spezzano, R. Morelli, and E. Drioli

ITM-CNR c/o University of Calabria, via P.Bucci 87030 Rende (CS), Italy

Received: June 3, 2008; Revised Manuscript Received: June 26, 2008

In this work, polyvinilydene fluoride (PVDF) microcapsules were prepared by using combined emulsion and phase inversion techniques. With this method, microcapsules with different diameters and porosities have been obtained by just controlling the diameter of the membrane used during the preparation. Using a PVDF solution containing the oxidation catalyst ammonium molybdate (20 wt %), catalytic polymeric microcapsules with diameters ranging from 600 to 1200 μm have been obtained. Characterization of catalytic microcapsules by means of SEM, BSE, and EDX analyses showed a uniform ammonium molybdate dispersion in the polymeric matrix. Catalytic microcapsules have been tested in the oxidation of aromatic primary alcohols to corresponding aldehydes. In the range 600−1200 μm, the microcapsule diameter influences the formation of oxidation products: in particular, microcapsule diameters >900 μm slightly diminish the formation of aldehyde due to a beginning diffusion limitation. An interesting structure−reactivity behavior, induced by the interaction between the polymeric membrane and the substituted aromatic alcohol, has been observed.

Introduction

The current trend toward "clean and rapid" synthesis has driven the generation of a number of new strategies for reagent immobilization to enable easy recovery, reuse, and disposal at an acceptable economic cost.[1] Microencapsulation, the process of entrapping material in a polymeric coating, has been demonstrated to be a useful alternative strategy for reagent immobilization.[2,3]

The existing microcapsules have been applied to many fields such as in pharmaceuticals,[4,5] food additives,[6] coatings,[7,8] electronic inks,[9,10] catalysts,[11] dyes,[12,13] etc., because the core materials such as drugs, water, dyes, or oils can be protected by the shell of microcapsules from the damages of the environment or can be released under a controlled condition. In order to develop new, versatile applications of microcapsules, the synthesis and characterization of microcapsules have been researched extensively.[14]

Interfacial phenomena related to physicochemical processes like adsorption/desorption, deposition and mass transport and chemical reactions, e.g., polycondensation, in situ polymerization, and polyaddition, are the major procedures for carrying out microencapsulation.[15]

The methods often used in practice include interfacial polymerization,[16−18] in situ polymerization,[19−32] phase inversion,[34−36] spray drying, solvent extraction, layer-by-layer addition, solvent evaporation, and interfacial polymerization utilizing emulsions and microemulsions.[37] Recently, a novel method for producing epoxy-resin-containing microcapsules via UV-initiated radical copolymerization in an epoxy emulsion was developed.[38]

Using membrane emulsification in a one-stage polymerization process,[39−42] polymer microspheres, hydrophilic and hydrophobic, smooth and rough, solid and hollow, porous and uniform, with different morphologies (spherical, hemispherical, snowman-like, popcorn-like, etc.), with diameters ranging from several micrometers to 100 Am, were successfully produced. In this technique, an oil phase containing a monomer or a mixture of monomers, an initiator, and other potential additives (solvents, diluents, cross-linking agents, etc.) permeates through the membrane into an aqueous solution of emulsifiers and stabilizers to form uniform droplets (O/W emulsion). An inhibitor is dissolved in the aqueous phase to prevent the secondary nucleation of polymer particles in the aqueous phase. The suspension polymerization is then carried out by transferring the emulsion into a reactor and heating it to above the decomposition temperature of the initiator under mild agitation and nitrogen bubbling. This technique has been applied to manufacture polylactide (PLA) and poly(lactide-*co*-glycolide) (PLGA) biodegradable microspheres,[43,44] polystyrene−poly(methyl methacrylate) (PSt−PMMA) composite microspheres,[45,46] and polymer microcapsules containing magnetite (Fe3O4)[47] or TiO2.[48] Also, uniform polyurethaneurea (PUU) particles were prepared by solvent evaporation from PUU−xylene (Xl) droplets after the PU prepolymer underwent a chain-extending reaction at room temperature with a diamine reagent (piperazine (Pz)).[49]

Using the phase inversion method, microcapsule membranes based on cellulose acetate (CA), ethylcellulose (EC),[33,34] polyethersulphone (PES),[35,36] and polysulfone (Psf),[50] characterized by pore microstructure both straight and packed throughout the whole membrane thickness, were prepared. These morphological properties were obtained by using additives in the polymeric solutions responsible for an increase of demixing rate and for a more porous structure.[51] In our early works,[52] microcapsules based on a modified polyetheretherketone (PEEKWC) of different morphology, porosity, and size has been obtained varying the composition of both casting solutions and coagulation bath.

Recently, we reported on the preparation of polyvinilydene fluoride (PVDF) catalytic microcapsules by means of the phase inversion technique: a polymeric drop is formed in the air phase by means of a syringe and then passes in the coagulation bath, where it immediately coagulates, forming the microcapsule.[53] The PVDF catalytic microcapsules were prepared without the use of additives in the polymeric solutions to prevent catalyst disactivation: the demixing rate between the polymer solvent

* Corresponding authors. E-mail addresses: mg.buonomenna@itm.cnr.it (M.G. Buonomenna) and a.figoli@itm.cnr.it (A. Figoli).

10.1021/jp804897b CCC: $40.75
Published on Web 08/15/2008

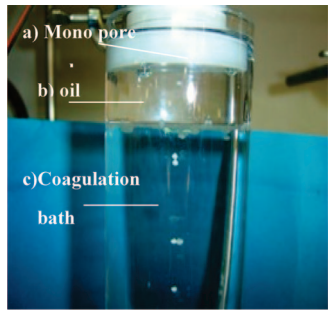

Figure 1. Picture of the system used for catalytic PVDF microcapsule preparation: (a) monopore membrane; (b) oil phase; (c) nonsolvent phase.

and the coagulant affected the final open structure of the microcapsule core.

In the present study, for the first time in literature, preparation of catalytic PVDF microcapsules by using combined emulsion and phase inversion techniques has been described. The preparation of microcapsules by using this technique consists of pressing polymeric solutions through a monopore support of PE: a polymeric drop is formed in the oil phase and passes in the coagulation bath, where it immediately coagulates, forming the microcapsule (Figure 1). PVDF catalytic microcapsules of different pore sizes have been obtained just by varying the size of the monopore film without the need to use different casting solutions, to prevent catalyst deactivation. The effect of addition in the coagulation bath of three surfactants has been studied to increase the porosity of catalytic microcapsules and, thus, to reduce the mass transfer resistance of reactants during the catalytic tests.

The catalyst, ammonium molybdate tetrahydrate, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, added in the casting polymeric solution, was successfully entrapped inside PVDF microcapsules. First, the effect of catalytic microcapsule size on the progress of oxidation of benzyl alcohol to benzaldehyde by using hydrogen peroxide as an oxidant without the need to use organic solvent has been explored. Then, the oxidation of different substituted benzyl alcohols to corresponding benzaldehydes has been carried out to study the effect of the polymeric PVDF matrix on the interaction between active catalytic sites and reaction substrate.

Experimental Section

Chemicals. For the preparation of catalytic microcapsules, PVDF (Solef 6010) was supplied by Solvay, and was used without purification. *N*,*N*-Dimethylformamide (DMF) and dodecane were purchased from Fluka. Water, used for the coagulation bath, was double distilled. Isopropanol from Carlo Erba was added in the coagulation bath as nonsolvent. The surfactants added in the coagulation bath, i.e., Tween 20, Tween 80, and SDS, and acetonitrile were purchased from Sigma-Aldrich.

Ammonium molybdate tetrahydrate, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (MW = 1235.86 g/mol, purity 99.98%), from Sigma-Aldrich was employed as a catalyst.

Benzyl alcohol (MW = 108.14 g/mol, purity 99.99%), 2-chloro benzyl alcohol (MW = 142.58 g/mol, purity 99.99%), and 2-methyl benzyl alcohol (MW = 122.16 g/mol, purity 99.99%) all from Sigma-Aldrich were used as oxidation substrates. Hydrogen peroxide, H_2O_2 (30 wt % solution in water), from Sigma-Aldrich was the oxidant.

Preparation of Catalytic Microcapsules. The system used for the preparation of microcapsules is shown in Figure 1.

A mixture of polymer PVDF (5 g), $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (1 g), was dissolved in 44 g of DMF solvent by stirring. The polymeric solution was pressed in the PE monoporous film until the formed drop in the oil phase (dodecane) precipitated in the coagulation bath, a mixture of water/isopropanol 1:1 (v/v) and 1% (wt/wt) surfactant.

The temperature of the coagulation solution was kept constant using a thermostatic unit. The microcapsules were immersed and washed in the isopropanol bath for 24 h, and then dried in a vacuum oven at 50 °C overnight.

Characterization. The formed microcapsules were characterized by the following methods:

(1) The morphology was evaluated by means of SEM at 20 KV (Cambridge Instruments Stereoscan 360).

(2) The diameter was determined by a digital micrometer (Carl Mahr D 7300 Esslingen A.N.) and by SEM observation of the freeze-fractured cross sections.

(3) The success of entrapment of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and its uniform dispersion in the polymeric microcapsules was evaluated by EDX and BSE techniques. EDX microanalyses were performed using a Philips EDAX analysis system.

(4) Swelling experiments have been carried out using samples dried at 60 °C for 24 h. The microcapsules were immersed at 25 °C in solutions 10% (wt/wt) of the oxidation substrates (benzyl alcohol, 2-chloro benzyl alcohol, and 2-methyl benzyl alcohol) in acetonitrile. Membrane swelling was monitored until the microcapsules had reached a constant weight. Samples were withdrawn from the solvent every now and then, and weighed after removal of the surface solvent by light blotting with a filter paper.

Oxidation Reaction. The performance of the PVDF catalytic microcapsules was investigated under batch conditions using comparable total catalyst loading.

A typical procedure for oxidation of benzyl alcohols is reported below. An amount of microcapsules containing 0.185 mmol of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ was kept at 40 °C for 24 h in pure benzyl alcohol or in solutions of benzyl alcohols in acetonitrile 10% (wt/wt).

Then, PVDF catalytic microcapsules were immersed in a 25 mL volumetric flask with 9.26 mmol of alcohol and 9.20 mmol of H_2O_2 (unless otherwise stated). Reaction temperature was maintained constant by immersing the reactor in a constant temperature oil bath. The microcapsules were washed three times before a catalytic run using acetonitrile in which both substrates and products are perfectly soluble. At the end of each run, the weight of the washed microcapsules before and after the catalytic test was unvaried. Obtained results are reported as selectivity to benzaldehyde, benzyl alcohol conversion to benzaldehyde, at a reaction time of 4 h.

The analysis of the organic phase was carried out by GLC using a 6890 network GC system of Agilent on a HP-5 (30 m × 0.320 mm × 0.25 μm) column.

Results and Discussion

Microcapsule Characterization. For the coagulation of polymeric drops at the interface oil phase (dodecane)−nonsolvent phase (isopropanol−water mixture), the presence of a hydrophilic surfactant agent in the coagulation bath was necessary for the microcapsule formation. Three different surfactants have been tested: Tween 20, Tween 80, and SDS. In Figure 2, SEM analysis of PVDF catalytic microcapsules prepared by using the different surfactants is shown. A hollow structure with a porous rough inner surface is clearly visible in Figure 2a,b (right) only for the microcapsules prepared by using SDS as a

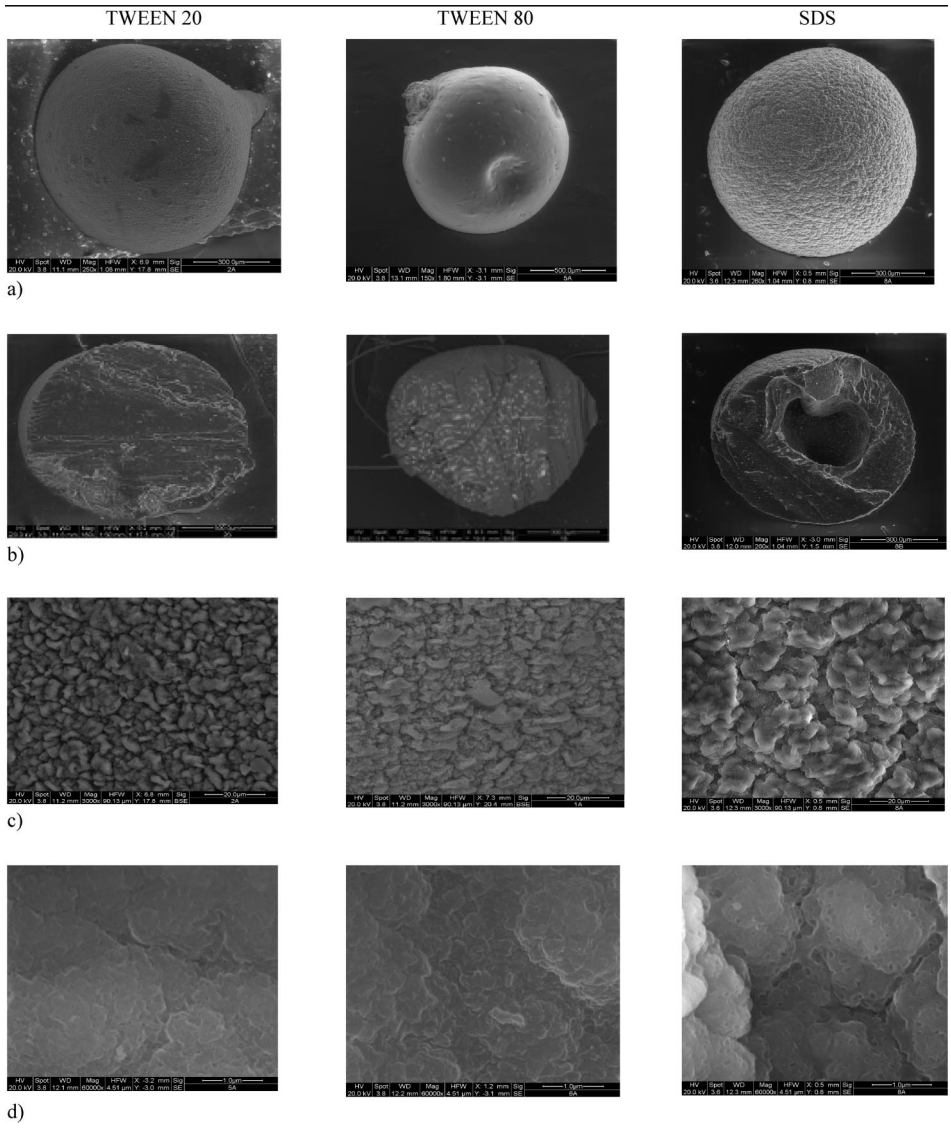

Figure 2. SEM of the catalytic PVDF microcapsule membranes prepared by using Tween 20 (left), Tween 80 (middle), and SDS (right) as surfactants: (a) external surface of the whole microcapsule; (b) cross section; (c) shell surface (×3000); (d) magnification of shell surface (×60 000). Pore size of PE monopore membrane = 600 μm.

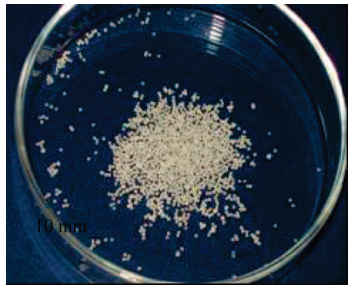

Figure 3. Overview image of catalytic PVDF microcapsules membranes prepared by using SDS and a pore size of PE monopore membrane of 600 μm.

surfactant. It was reasoned that the ideal membrane of the microcapsule entrapping the catalyst should be externally skinned with a spherical wall consisting entirely of narrow bore, closely packed, cavities, radiating inward from just below the skin layer. The microcapsules prepared by using SDS showed a satisfactorily spherical appearance, as shown in Figure 2a (right) and in the overview image of Figure 3.

The size distribution was from 650 to 800 μm, and the median diameter was 720 μm (Figure 4).

By using Tween 20 or Tween 80, neither spherical nor hollow microcapsules have been obtained (Figure 2, left and middle, respectively): a similar nodular surface of the microcapsule shell has been obtained. However, magnification of the shell surface showed a nonporous structure for both microcapsules prepared by using Tween 20 and Tween 80, while diffuse pores are visible on the surface of microcapsules prepared with SDS (Figure 2d).

Using back scattered mode (BSE) analysis, the catalytic particles in PVDF microcapsules prepared with SDS can be visualized as white spots in the dark membrane matrix. A uniform catalyst distribution on the microcapsule surface (Figure 5a) and the inner core (Figure 5b) is clearly visible.

The identification of the white spots (uniformly dispersed) as catalyst was carried out by EDX analyses (Figure 5c).

On the basis of the obtained results, for the preparation of PVDF microcapsules, SDS has been selected as the surfactant to be added in the coagulation phase.

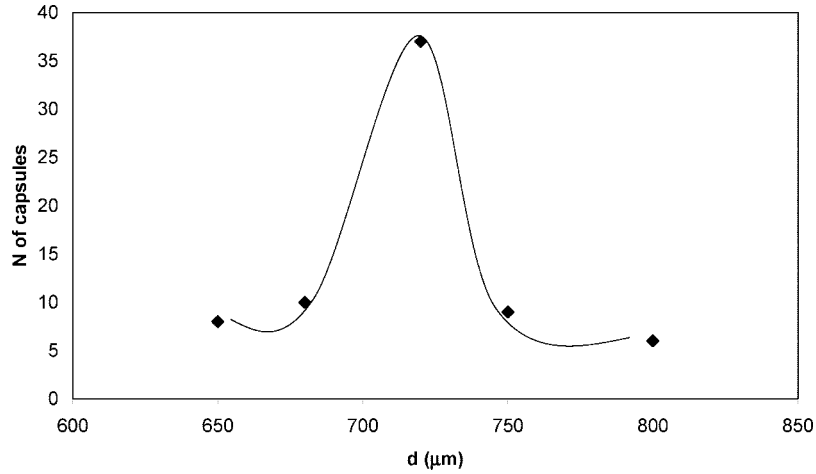

Figure 4. Size distribution of the catalytic PVDF microcapsule membranes prepared by using SDS and a pore size of PE monopore membrane of 600 μm.

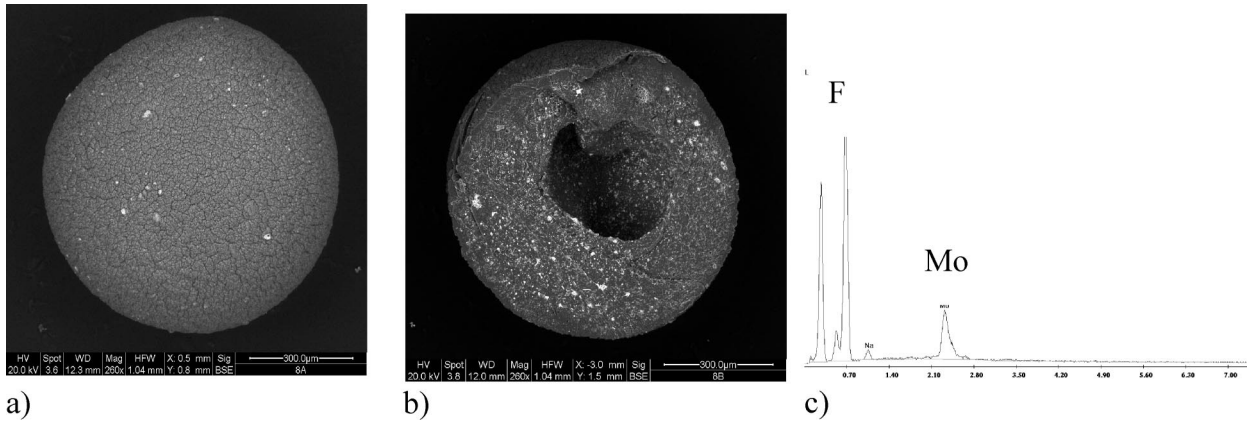

Figure 5. BSE analysis of PVDF catalytic microcapsules: shell (a) and inner (b). (c) EDX analysis of white spots.

TABLE 1: Diameter of Catalytic Microcapsules (d_{cps}) Obtained by Varying the Pore Size of the PE Monopore Membrane (p_m); T = 20 °C; Oil Phase, *n*-Dodecane; Coagulation Bath, Isopropanol/Water = 1:1 (v/v)

entry no.	p_m (μm)	d_{cps} (μm)
1	350	600
2	450	700
3	600	720
4	1000	1000
5		1200[a]

[a] From ref 53.

Varying the pore size of the PE monopore membrane in the system for their fabrication (Figure 1), catalytic microcapsules with different diameters have been obtained (Table 1).

In particular, on the basis of results obtained, it is evident how the catalytic microcapsule diameter increased as the membrane pore size was raised. In our previous work,[53] using air instead of the oil phase, without the membrane module, catalytic microcapsules of 1200 μm (entry 5) were obtained. It is important to emphasize that, for the application of the produced microcapsules in catalysis, a hollow structure with a small diameter has to be preferred to reduce the mass transfer of reactants during the reaction. Therefore, this fabrication technique constitutes an easy way to decrease the catalytic microcapsule diameter and to obtain a hollow structure (Figure 2b, right) without the use of additives in the polymeric solutions to prevent catalyst deactivation.

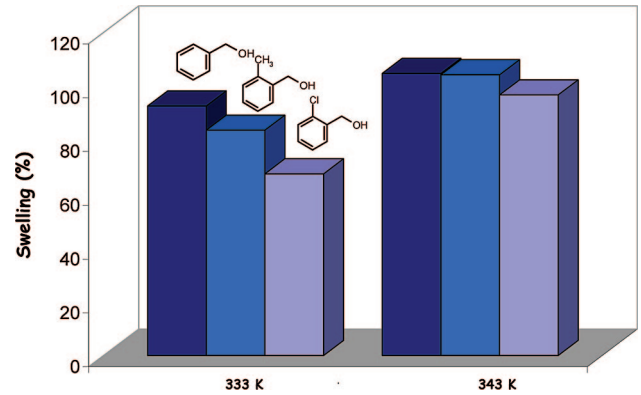

Figure 6. Swelling data of PVDF catalytic microcapsules in mixtures of benzyl alcohols/acetonitrile (10 wt %) at two different temperatures: 60 and 70 °C.

In Figure 6, swelling results at 333 and 343 K of PVDF catalytic microcapsules in pure acetonitrile and mixtures of substituted benzyl alcohols have been reported.

At 333 K, the lowest swelling value was obtained using a mixture of 2-chloro benzyl alcohol (67.5%), while higher values were observed with mixtures of 2-methyl benzyl alcohol (83.69%) and of benzyl alcohol (92.7%). These results reflected preferential interactions between PVDF microcapsules and the substituted alcohols in the order: H > CH_3 > Cl. At 343 K, swelling for all three benzyl alcohols increased without a strong difference among them, as observed at 333 K. In fact, for all

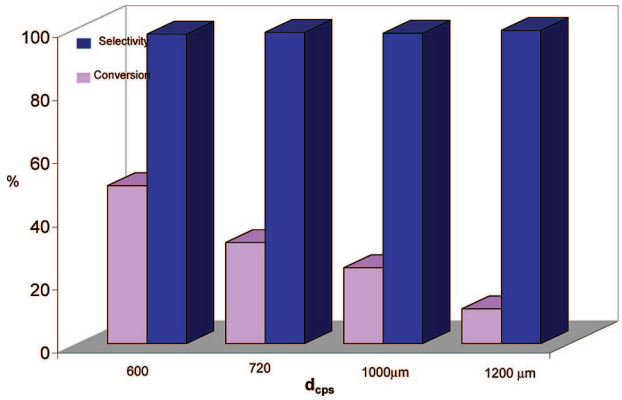

Figure 7. Selectivity, benzyl alcohol **1** conversion using PVDF catalytic microcapsules with different diameters (d_{cps}) (reaction time = 4 h; T = 343 K).

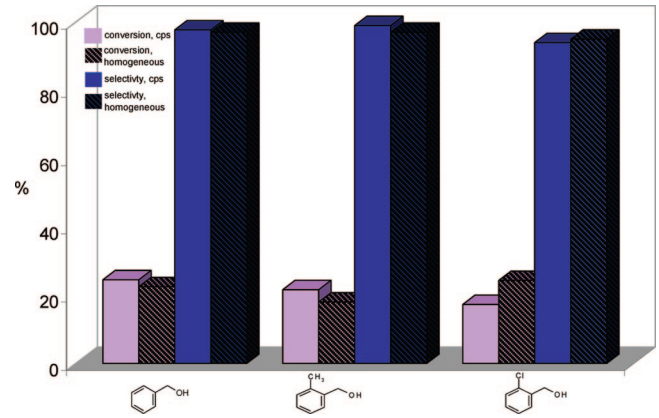

Figure 8. Benzyl alcohol conversion, selectivity using PVDF catalytic microcapsules (cps) and homogeneous $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (homogeneous) (reaction time = 4 h; T = 333 K; d_{cps} = 1000 μm).

three alcohols, diffusion through the capsule polymeric walls increases as the temperature is raised, minimizing the difference due to alcohol size.

During swelling experiments, no leaching of the ammonium molybdate was observed. This is due to two facts: ammonium molybdate is soluble neither in benzyl alcohols nor in acetonitrile; the interactions between the catalyst and the polymer PVDF are enough to avoid leaching.

Oxidation Reactions. The benzyl alcohol oxidation to corresponding benzaldehydes happens by the following reaction:

$$RC_6H_4CH_2OH + H_2O_2 \rightarrow RC_6H_4CHO + 2H_2O$$

where **1**, R = H; **2**, R = Cl; **3**, R = Me.

First, the oxidation reaction of benzyl alcohol **1** was carried out under solvent free conditions and microcapsules with different diameters have been used to study the effect of this variable on the mass transfer of reactants to active catalytic sites and thus on the reaction progress. Then, the reaction was performed using a mixture of benzyl alcohols/acetonitrile 10% (wt/wt), to study the effect of the interactions between different substrates and polymers on the conversion of benzyl alcohols to the corresponding benzaldehydes.

The effect of microcapsule diameter (d_{cps}) on the progress of oxidation of benzyl alcohol was studied using catalytic microcapsules with d_{cps} ranging from 600 to 1200 μm. The experimental results are reported in Figure 7.

It is observed in these experiments that conversion of **1** to the corresponding benzaldehyde increased as d_{cps} decreased, without a substantial loss of reaction selectivity (>98%).

In fact, conversion of **1** from 11% using microcapsules with a d_{cps} value of 1200 μm increased up to 50%, reducing d_{cp} up to 600 μm. That means that the oxidation reaction is limited by diffusion. These results confirmed data of our early work[53] about the strong effect of reaction temperature on the conversion of **1** by using catalytic microcapsules.

To evaluate if the different swelling of polymeric microcapsules observed for benzyl alcohols **1**−**3** (Figure 6) effected the conversion to corresponding benzaldehydes, the oxidation reactions were carried out at 333 K using a mixture of benzyl alcohols/acetonitrile 10% (wt/wt), containing the same amount of benzyl alcohol used to study the reaction under neat conditions.

In Figure 8, conversion and selectivity data for the oxidation of substituted alcohols by using catalytic PVDF microcapsules and homogeneous $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, as a reference, are reported.

Inspection of the results shows an interesting structure−reactivity behavior, that is indeed induced by the interaction between the PVDF of microcapsules and the substrate. In particular, by using PVDF catalytic microcapsules, the observed conversion is in the order benzyl alcohol (24.5%) > 2-methyl benzyl alcohol (21.6%) > 2-chloro benzyl alcohol (17.3%), which reflects the order observed for swelling tests (Figure 6).

It is worth noting that with the homogeneous catalyst a preferential reactivity toward 2-chloro benzyl alcohol is registered, resulting in a different order from that registered for PVDF microcapsules, i.e., 2-chloro benzyl alcohol (24.3%) > benzyl alcohol (22.5%) > 2-methyl benzyl alcohol (18%).

These results point to a specific substrate recognition exerted by the heterogeneous matrix; the preferential interaction with the polymeric membrane, leading to an enrichment of the substrate concentration on the catalytic surface, close to the catalytic sites, promotes the oxidation. This fact is also consistent with the increased selectivities for 2-methyl benzyl alcohol (99%) and benzyl alcohol (97.7%) by using PVDF microcapsules compared to homogeneous references (97% for both alcohols).

Conclusion

In this work, for the first time, PVDF microcapsules containing $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ catalyst were prepared by combined emulsion and phase inversion techniques. The presence of SDS in the coagulation phase, at the interface with the oil phase, was necessary to obtain spherical, regular, catalytic microcapsules with a uniform catalyst distribution, as shown by BSE and EDX analyses. Varying the pore size of the PE monopore membrane in the system for the fabrication, catalytic microcapsules with different diameters (from 600 to 1200 μm) have been obtained without the need to use additives in the casting solution. It is observed that conversion of benzyl alcohol **1** to corresponding benzaldehyde increased as d_{cps} decreased, without a substantial loss of reaction selectivity (>98%): conversion from 11% using microcapsules with a d_{cps} value of 1200 μm increased up to 50%, reducing d_{cp} up to 600 μm. That means that the oxidation reaction is limited by diffusion.

Primary benzyl alcohols can be oxidized selectively to corresponding benzaldehydes. In particular, an interesting structure−reactivity behavior, that is indeed induced by the interaction between the PVDF of microcapsules and the substrate, has been found. In fact, on the basis of different conversions obtained with catalytic microcapsules compared to homogeneous references, a specific substrate recognition exerted

by the heterogeneous matrix, leading to an enrichment of the substrate concentration on the catalytic surface, has been observed.

References and Notes

(1) Kirschning, A.; Monenschein, H.; Wittenberg, R. *Angew. Chem., Int. Ed.* **2001**, *40*, 650.

(2) Ramarao, C. S.; Ley, V.; Smith, S. C.; Shirley, I. M.; DeAlmeida, N. *Chem. Commun.* **2002**, 1132.

(3) Akiyama, R.; Kobayashi, S. *Angew. Chem., Int. Ed.* **2002**, *41*, 2602.

(4) Biju, S. S.; Saisivam, S.; Maria, N. S.; Rajan, G.; Mishra, P. R. *Eur. J. Pharm. Biopharm.* **2004**, *58* (1), 61.

(5) Yutaka, U; Kenichi, H; Kageyosi, S.; Kazunori, A.; Yoshikazu, T.; Mutsuo, S. *Surgery* **2001**, *130* (3), 513.

(6) Yúfera, M.; Fernández-Dı´az, C.; Pascual, E. *Aquaculture* **2005**, *248*, 1.

(7) Giraud, S.; Bourbigot, S.; Rochery, M.; Vroman, I.; Tighzert, L.; Delobel, R. *Polym. Degrad. Stab.* **2002**, *77* (2), 285.

(8) Krishnan, S.; Bhosale, R.; Singhal, R. S. *Carbohydr. Polym.* **2005**, *61*, 95.

(9) Kim, C. A.; Joung, M. J.; Ahn, S. D.; Kim, G. H.; Kang, S. Y.; You, I. K. *Synth. Met.* **2005**, *151* (3), 181.

(10) Guo, H. L.; Zhao, X. P. *Opt. Mater.* **2004**, *26* (3), 297.

(11) Ji, H. B.; Kuang, J. G.; Qian, Y. *Catal. Today* **2005**, *105*, 605.

(12) Sawada, K; Urakawa, H. *Dyes Pigm.* **2005**, *65* (1), 45.

(13) Yamamoto, T.; Dobashi, T.; Kimura, M.; Chang, C. P. *Colloids Surf., B* **2002**, *25* (4), 305.

(14) Yuan, L.; Liang, G.; Xie, J. Q.; Li, L.; Guo, J. *Polymer* **2006**, *47*, 5338.

(15) Deasy, P. B. *Microencapsulation and related drug processes*; Marcel Dekker: New York, 1984; pp 119, 219.

(16) Scher, H. B. U.S. Patent 4,285,720, 1980.

(17) Ley, S. V.; Ramarao, C.; Gordon, R. S.; Holmes, A. B.; Morrison, A. J.; McConvey, I. F.; Shirley, I. M.; Smith, S. C.; Smith, M. D. *Chem. Commun.* **2002**, 1134.

(18) Brenmeyer, N.; Ley, S. V.; Ramarao, C.; Shirley, I. M.; Smith, S. C. *Synlett* **2002**, 1843.

(19) Benita, S. *Microencapsulation: Methods and Industrial Applications*; Marcel Dekker: New York, 1996.

(20) Kondo, A. *Microcapsule Processing and Technology*; Marcel Dekker: New York, 1979.

(21) Chang, T. M. S. *Science* **1964**, *146*, 524.

(22) Chu, L.-Y.; Park, S.-H.; Yamaguchi, T.; Nakao, S. *Langmuir* **2002**, *18*, 1856.

(23) Chu, L.-Y.; Yamaguchi, T; Nakao, S. *Adv. Mater.* **2002**, *14*, 386.

(24) Chu, L.-Y.; Liang, Y.-J.; Chen, W.-M.; Ju, X.-J.; Wang, H.-D. *Colloids Surf., B* **2004**, *37*, 9.

(25) Hong, K.; Nakayama, K.; Park, S. *Eur. Polym. J.* **2002**, *38*, 305.

(26) Yan, N.; Zhang, M.; Ni, P. *J. Membr. Sci.* **1992**, *72*, 163.

(27) Hwang, J. R.; Sefton, M. V. *J. Membr. Sci.* **1995**, *108*, 257.

(28) Lingaiah, N.; Mohan Reddy, K.; Seshu Babu, N.; Narasimha Rao, K.; Suryanarayana, I.; Sai Prasad, P. S. *Catal. Commun.* **2006**, *7*, 245.

(29) Kiyoyama, S.; Yonemura, S.; Yoshida, M.; Shiomori, K.; Yoshizawa, H.; Kawano, Y.; Hatate, Y. *React. Funct. Polym.* **2007**, *67*, 522.

(30) Yuan, L.; Liang, G. Z.; Xie, J. Q.; Li, L.; Guo, J. *J. Mater. Sci.* **2007**, *42*, 4390.

(31) Yuan, L.; Liang, G. Z.; Xie, J. Q.; Li, L; Guo, J. *Polymer* **2006**, *47*, 5338.

(32) Ichiura, H.; Morikawa, M.; Fujiwara, K. *J. Mater. Sci.* **2005**, *40*, 1987.

(33) Wang, C. Y.; Ho, H. O.; Lin, L. H.; Lin, Y. K.; Sheu, M. T. *Int. J. Pharm.* **2005**, *297*, 89.

(34) Thombrea, A. G.; Cardinal, J. R.; De Noto, A. R.; Herbig, S. M.; Smith, K. L. *J. Controlled Release* **1999**, *57*, 55.

(35) Wang, G. J.; Chu, L. Y.; Zhou, M. Y.; Chen, W. M. *J. Membr. Sci.* **2006**, *284*, 301.

(36) Wang, G. J.; Chu, L. Y.; Chen, W. M.; Zhou, M. Y. *J. Membr. Sci.* **2005**, *252*, 279.

(37) Chang, T. M. S. *Biotechnol. Annu. Rev.* **1995**, *1*, 267.

(38) Xiao, D. S.; Rong, M. Z. *Polymer* **2007**, *48*, 4765.

(39) Omi, S.; Ma, G. H.; Nagai, M. *Macromol. Symp.* **2000**, *151*, 319.

(40) Omi, S. *Colloids Surf., A* **1996**, *109*, 97.

(41) Ma, G. *China Particuology* **2003**, *1*, 105.

(42) Kubota, J.; Hirabayashi, N.; Kato, A.; Yoshizawa, H. *Colloids Surf., A* **2007**, *302*, 320.

(43) GH, Ma; Nagai, M; Omi, S. *Colloids Surf., A* **1999**, *153*, 383.

(44) Shiga, K.; Muramatsu, N.; Kondo, T. *J. Pharm. Pharmacol.* **1996**, *48*, 891.

(45) Ma, G. H.; Nagai, M.; Omi, S. *J. Colloid Interface Sci.* **1999**, *214*, 264.

(46) Ma, G. H.; Naga, i M.; Omi, S *J. Colloid Interface Sci.* **1999**, *219*, 110.

(47) Omi, S.; Kanetaka, A.; Shimamori, Y.; Supsakulchai, A.; Nagai, M.; Ma, G. H. *J Microencapsulation* **2001**, *19*, 749.

(48) Supsakulchai, A.; Ma, G. H.; Nagai, M.; Omi, S. *J. Microencapsulation* **2002**, *19*, 425.

(49) Yuyama, H.; Yamamoto, K.; Shirafuji, K.; Nagai, M.; Ma, G. H. *J. Appl. Polym. Sci.* **2000**, *77*, 2237.

(50) Torras, C.; Gezahegn, D.; Pitol-Filho, L; Garcia-Valls, R. *Desalination* **2006**, *200*, 12.

(51) Mulder, M. *Basic Principles of Membrane Technology*; Kluwer: Dordrecht, The Netherlands, 1991.

(52) Figoli, A.; De Luca, G.; Longavita, E.; Drioli, E. *Sep. Sci. Technol.* **2007**, *42*, 2809.

(53) Buonomenna, M. G.; Figoli, A.; Spezzano, I.; Davoli, M.; Drioli, E. *Appl. Catal., B* **2008**, *80*, 185.

JP804897B