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Oxidation of Cyclohexane Using FePcY-Zeozymes Occluded in Polydimethylsiloxane Membranes

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Cyclohexane is selectively oxidized by tertiary-butyl hydroperoxide at room temperature using a catalyst consisting of iron phthalocyanine in zeolite Y (FePcY) occluded in a polydimethylsiloxane (PDMS) membrane. Different experimental setups are used to study the effect of the membrane incorporation on the catalytic performance. Embedding this catalyst in PDMS results in a new system with considerably higher activity which makes the controlled addition of peroxide redundant. Separating the two immiscible reactant phases, the membrane eliminates the need for a solvent. In addition, it actively controls the concentration of the reactants near the active sites by fine-tuning their respective sorptions. The result is a substrate/oxidant ratio which is beneficial for the reaction. Evidence for this active role is established in the analysis of the composition of the membrane phase after reaction.

INTRODUCTION

When immiscible reactants are involved in a reaction, solvents or phase transfer agents can be added (1). However, phase transfer agents are not generally applicable, and the addition of a solvent inevitably decreases reagent concentrations. Moreover, both ways often complicate the separation of the products from the reaction mixture afterwards. In heterogeneous catalysis, preferential sorption of one of the compounds on the active sites can constitute another problem, inducing low activities (2–4).

These problems can be solved by applying membrane reactors. Until now, one of the greatest problems in membrane catalysis was the incompatibility between the high temperature of catalysis and the limited heat stability of polymeric materials. This restricted membrane catalysis almost exclusively to inorganic membranes (5–7). Even though the catalytic sites were located inside the membrane pores, in most cases the membrane material merely served as a carrier for these sites and did not play an active role in the reactions (8). Nevertheless, it has been shown that for gas–liquid phase reactions the membrane can act as a highly efficient contactor (9, 10). Since the gas–liquid dispersion is pressure controlled, it seems to us that the obligate presence of pores makes this system unsuitable for liquid–liquid phase reactions.

In the past few years, however, the incorporation of fillers in dense membranes has become well developed (11–18) and the possibility to incorporate catalytically active species in such matrices creates interesting new opportunities. The polymer surrounding the catalyst influences the reagent concentrations in the catalyst due to preferential sorption in the membrane matrix. This way, it creates the possibility of fine-tuning in a beneficial way the sorption in the catalyst by choosing the appropriate polymer material. Furthermore, the dense membrane can now be used to keep the two liquid reagent phases separated, eliminating the solvent in the case of immiscible reagents. This new experimental setup, together with the influenced sorption caused by the polymer, can improve catalytic results drastically, as will be shown here for the room temperature oxidation of cyclohexane to cyclohexanone and cyclohexanol (19–24), using tertiary-butyl hydroperoxide as oxygen donor with FePcY (Fe–phthalocyanine–zeolite Y) as catalyst.

The activity of FePcY is restricted by the preferential sorption of polar compounds in the zeolite: peroxide, reaction products, solvent, and water. The high sorption of peroxide in the zeolite induces excessive peroxide decomposition and low efficiencies. To minimize decomposition, a fed-batch setup was applied in which the peroxide is slowly added to the reaction mixture. In this study, it is shown how the sorption and decomposition problems can be overcome by embedding the FePcY "zeozyme" in PDMS (polydimethylsiloxane). This hydrophobic membrane material (26) sorbs cyclohexane preferentially and creates a barrier against polar compounds. Furthermore, this dense polymer is flexible enough to allow high sorptions of the reagents and fast diffusion through the composite membrane, together with a homogeneous and defect-free incorporation of the catalyst particles (11–18). In this way, the resulting composite membrane (Fig. 1) perfectly models the enzyme cytochrome P450, being embedded in a hydrophobic phospholipid layer (25).

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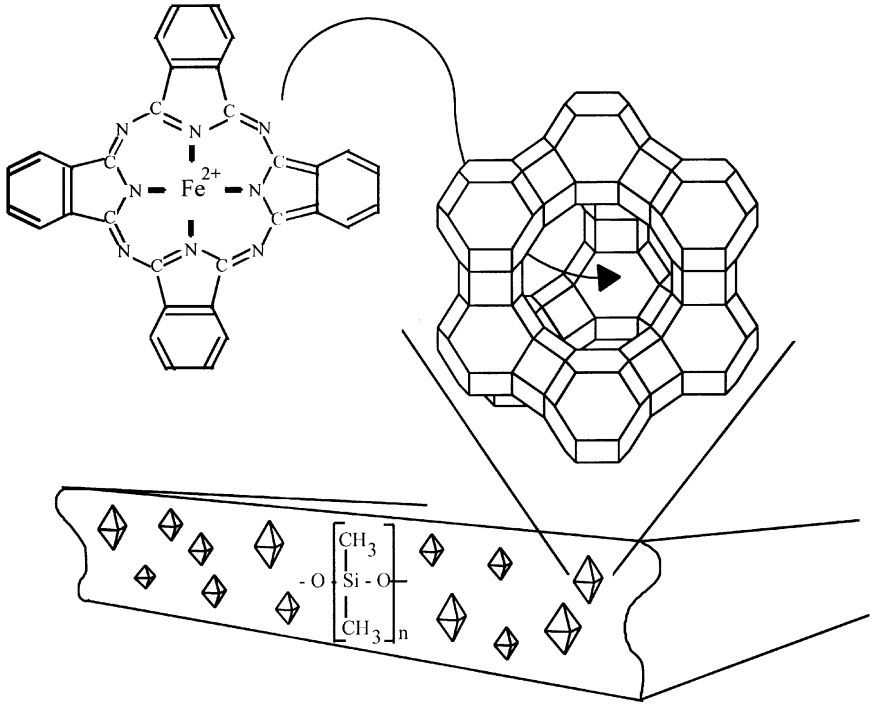

FIG. 1. Schematic representation of the incorporation of FePc complex in the supercages of zeolite Y and subsequent incorporation of these zeolite crystals in the PDMS-membrane.

The effect of the membrane incorporation is clarified by comparing different experimental setups and by studying the preferential sorption in the membrane material.

EXPERIMENTAL

Materials

Commercial NaY with a silicon-to-aluminum ratio of 2.47 was acquired from Zeocat. Cyclohexane (+99%), cyclohexanol (+99%), cyclohexanone (+99%), toluene (99.9%), secondary butanol (+99.5%), ethanol (p.a.), and acetone (p.a.) were purchased from Janssen Chimica; 1,2-dicyanobenzene (DCB) (+98%), dimethylformamide (99%) (DMF), *t*-BHP (70% in water), and ferrocene (98%) from Aldrich; the PDMS-polymer (RTV 615) from General Electric; and methyl isobutyl ketone (99%) from UCB.

Catalyst Preparation

Iron phthalocyanine Y zeolites (FePcY) were synthesized under nitrogen atmosphere by a solid state adsorption of ferrocene (0.575 g, 1 molecule per supercage) on 5 g NaY (air dried at 523 K). Subsequently, the ferrocene-loaded zeolite was mixed with 3.15 g DCB (excess of 2) and introduced into a Teflon-lined autoclave. The autoclave was heated at 453 K for 24 h. The blue-green solid obtained was successively soxhlet-extracted with acetone, DMF, and again with acetone until a colorless extract was obtained. The extractions remove unreacted reactants and intermediates from the crude catalyst and phthalocyanines from its outer surface. Part of the iron, which is not chelated by the phthalocyanines, is still present as ferrocene and is removed as such during the extractions. The final catalyst was air dried at 343 K. The resultant blue-green catalyst has an X-ray powder diffraction pattern consistent with zeolite Y without any pattern of crystalline phthalocyanines. UV–vis (Varian, CARY 17) and IR (Nicolet 680 Spectral Workstation coupled to a 730 FT-IR-spectrometer) spectra confirm that this catalyst contains a mixture of phthalocyanines with and without iron as central metal ion. UV–vis spectroscopy was used for the determination of the amount of intracrystalline phthalocyanines, after dissolution of the zeolite in concentrated sulfuric acid (0.1 g of catalyst in 100 ml of concentrated sulfuric acid for 4 h). The FePcY catalyst was found to contain about 1.14 FePc complexes and 3.2 Pc molecules per unit cell, indicating that the majority of the phthalocyanines have no iron ion incorporated in the macrocycle. On the other hand, no residual transition metal is left in the zeolite, as confirmed by chemical analysis (atomic absorption spectroscopy of Fe) on dissolved FePcY. Consequently, the catalytic results are not altered by unchelated iron.

Membrane Preparation

FePcY (1.6 g) was vacuum dried at 150°C and then dispersed ultrasonically in methyl isobutylketone (4 g).

The RTV 615B cross-linker (General Electric) (0.33 g) was added to the zeolite suspension and this mixture was stirred for 2 h. After adding the PDMS prepolymer (General Electric, RTV 615A) (3.3 g), mixing was continued for another hour. The mixture was cast on a glass plate as a 0.25-mm film and cured in vacuum at 150°C. The final content of FePcY in the PDMS membrane is 30 wt% and its composition is schematically represented in Fig. 1. The FePcY crystals (1–2 μm) are homogeneously distributed in the membrane (15).

Product Analysis

Identification and quantification of products was made by GC-analysis on a 50-m CP-Sil 5 capillary column (Chrompack), using the appropriate sensitivity factors for a FID detector. For the cyclohexane phase, a 1 wt% solution of toluene in cyclohexane was used as external standard and a 1 wt% solution of secondary butanol in ethanol for the water phase.

Membrane Sorption

Sorption was investigated on 1.5×5-cm membrane strips, pretreated at 150°C under vacuum. The membranes were then immersed in the liquids for at least 1 h. The amounts sorbed were determined by weight. The membrane surface was wiped dry before weighing as quickly as possible, so as to minimize evaporation.

Vacuum Distillation

Two flasks were connected airtight with a glass elbow. Immediately after reaction, the membrane was placed in a flask in an oil bath at 180°C. The other flask was placed in liquid nitrogen before applying vacuum. The distillate was analyzed by GC as described above.

Reaction Systems and Conditions

Before use, all membranes and catalysts were dried at 180°C under vacuum for 45 min. In order to avoid the oxidative destruction of the complex by air, the oven was flushed with nitrogen gas before applying the vacuum. All reactions were performed at room temperature.

A. Fed batch reaction. A 30 wt% zeozyme membrane or pure zeozyme (both containing 0.5 g FePcY) was placed in a mixture of 50 mmol cyclohexane and 30 g acetone to which 100 mmol tertiary-butyl hydroperoxide was added at a rate of 0.6 ml/h.

B. Solvent batch reactor. The reactivity of 0.16 g of zeozyme was compared with that of a 30 wt% zeozyme membrane containing the same amount of FePcY. The reactions were carried out on 0.6 mmol cyclohexane and 60 g of a 7 wt% solution of tertiary-butyl hydroperoxide (0.05 mmol) in water, diluted with acetone to 280 g.

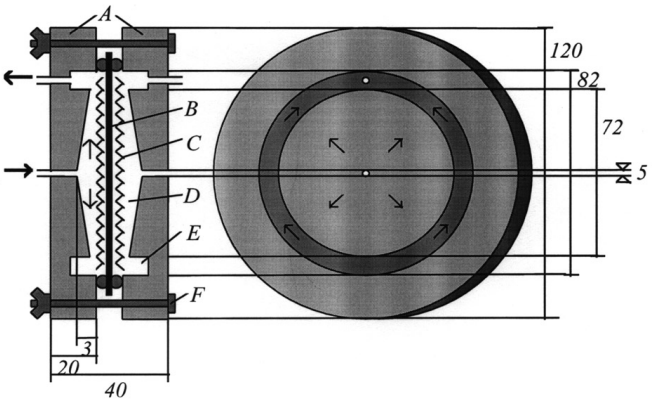

FIG. 2. Schematic representation of the membrane reactor. A, B, C, D, E, and F refer to the codes used in the reactor description given in the Experimental section. The numbers express the dimensions of the system in millimeters.

C. Bi-phase batch reaction. The experiments were made on 0.6 mmol cyclohexane, 60 g of a 7 wt% solution of tertiary-butyl hydroperoxide in water and with 0.16 g zeozyme powder or the same weight cut from a 30 wt% zeozyme membrane.

D. Oxidation of cyclohexane in the membrane reactor. The membrane reactor (Fig. 2) is composed of two Teflon discs (A), each having an inlet and an outlet, a conical cavity (D), and a ring shaped collector (E). Two O-rings are placed between the two discs to hold the membrane. The vessel is closed with six wing nuts and screws. Both compartments are mounted so that the outlets are at the top side of the system, in order to allow the removal of air bubbles or a possibly floating organic phase. Two metal sieves (C) at both sides of the membrane (B) avoid membrane movements under changing pressures caused by the pumping. Chemically inert, flexible tubings connect the membrane reactor, the pump, and the reagent reservoirs (Fig. 3). The reagents are pumped at a flow rate of 240 ml/h. Both reagent reservoirs are sealed with a rubber septum, through which an injection needle is pierced in order to prevent overpressure in the reservoirs. When starting the reaction, the membrane

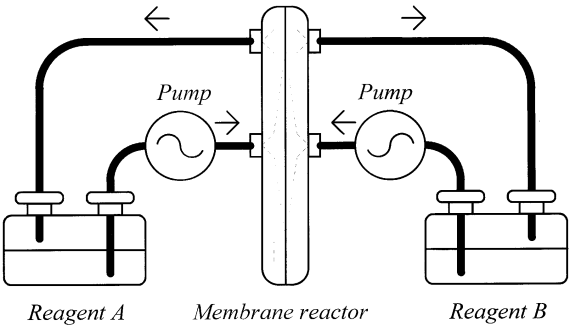

FIG. 3. Schematic representation of the complete reactor system.

is mounted in preswollen condition (using cyclohexane) to prevent the wrinkling of the membrane during the reaction. The cyclohexane circulation is started first, before the water phase is pumped. A PDMS-membrane was used, containing 30 wt% zeozyme, weighing 320 mg, and with a thickness of 65 μm. The reactor reservoirs used for the reaction contained 25 g cyclohexane on one side and 50 g of a 7 wt% solution of tertiary-butyl hydroperoxide in water on the other side of the membrane.

RESULTS AND DISCUSSION

A. Membrane Reactor

Reaction rate. Initially, a relatively slow product formation is observed in the membrane reactor (Fig. 4). Indeed, the membrane is saturated with cyclohexane at the start of the reaction while the peroxide diffuses slowly into the membrane and then in the zeolite to the active complex. The reaction rate increases to a maximum around 2 h, after which a small catalyst deactivation can be observed, the nature of which will be made clear in a regeneration experiment.

Regeneration. After a first reaction, the same membrane is used in a second reaction after a 150°C vacuum treatment. No significant difference in catalytic behaviour could be observed between the original and the regenerated membrane. This implies that the deactivation is not due to an oxidative destruction of the FePcY complexes, as might be expected from a zeolite-occluded FePc (2). Therefore, the deactivation of the zeozyme in our membrane system is believed to be due to sorption of hydrophilic compounds formed during reaction. They do not completely desorb from the polar catalyst during reaction, but can be removed after reaction under vacuum at elevated temperature, rendering full activity to the catalyst.

Membrane pretreatment. More evidence for this type of catalyst deactivation is found when investigating to what extent membrane drying, prior to reaction, influences the catalytic activity of the membrane. The last step in the membrane preparation is a complete immersion of the membrane in water, resulting in a water-saturated membrane. Especially the zeolite, being very hydrophilic, will probably sorb large amounts of water. Figure 5 shows that the reaction rate is higher when the membrane is dried before reaction. Drying removes the water molecules from the zeolite so that reagents can reach the active sites more easily. As the reaction proceeds, the rate decreases steadily and both systems end at comparable rates, to be explained by the sorption of hydrophilic reaction products in the zeolite. As this phenomenon occurs irrespective of the membrane pretreatment, the difference in rate between the dried membrane and the nondried membrane diminishes as the reaction continues.

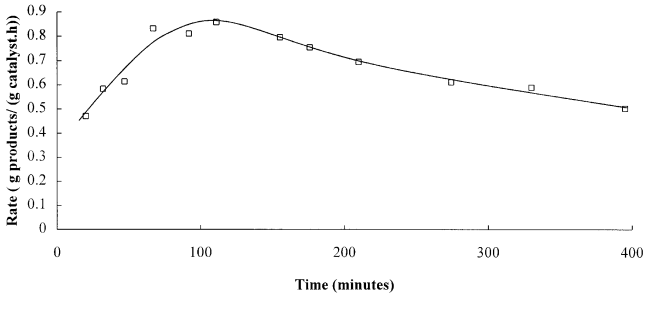

FIG. 4. Rate of cyclohexane oxidation using FePcY-PDMS in the membrane reactor.

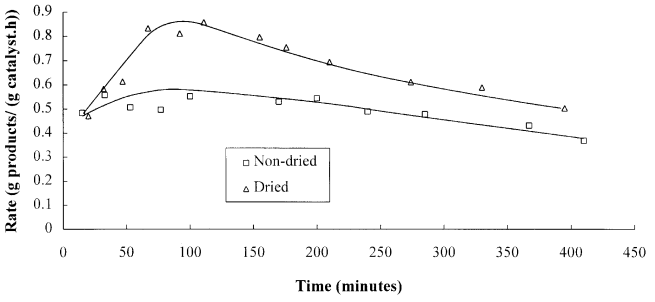

FIG. 5. The influence of predrying on the reaction rate.

Product distribution. In Fig. 6, the yields of both products, cyclohexanol and cyclohexanone, over the two distinct reactor phases are shown. In the beginning, both molecules are preferentially retrieved in the organic phase. As the reaction proceeds, a steady product migration seems to occur from the cyclohexane phase towards the water phase. At the end of the reaction, an enrichment of cyclohexanol in the water phase is even established. It is striking that it takes some time before this enrichment is reached. The evolution in time might be explained, because, as expected from literature and experimentally confirmed below by the sorption measurements, the membrane phase consists of an almost pure cyclohexane phase. This means that both products will diffuse out of the zeozyme into the membrane and subsequently from the membrane into the cyclohexane phase. The dissolution of the products in the water phase is probably a slow process that can proceed only at the organic/water interphase.

Efficiency. The efficiency of the use of tertiary-butyl hydroperoxide by the catalyst in the membrane reactor evolves slowly from 43% at the start of the reaction to 33% after 400 min. This means that two of each three molecules of tertiary-butyl hydroperoxide are decomposed by the catalyst, and that only one-third of the oxidant is effectively used in reaction.

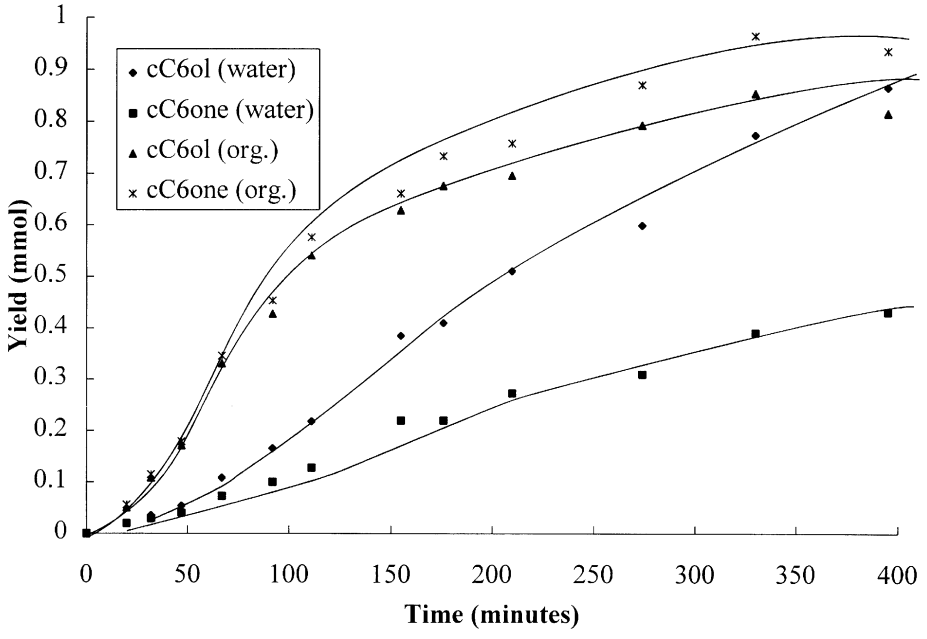

FIG. 6. Yield of cyclohexanol (cC6ol) and cyclohexanone (cC6one) in the cyclohexane (org.) and in the water phase (water).

B. Membrane as "Hydrophobic Reaction Medium"

In the membrane reactor, the membrane is situated between two strongly different phases: on one side there is a hydrophilic 7 wt% solution of tertiary-butyl hydroperoxide in water and on the other side a very hydrophobic cyclohexane phase. The membrane itself is constituted of a highly hydrophobic PDMS-polymer combined with a hydrophilic zeolite Y. These differences in polarity of the different phases make it impossible to predict the composition of the liquid sorbed in the membrane, essential to understanding what actually happens in the membrane phase. As it is impossible to take samples out of the membrane itself, indirect sorption measurements were performed to gain insight into the membrane composition.

Affinity of compounds for the membrane. The affinity of reagents and products for the membrane phase can be determined easily by measuring the sorption of the compounds in the membrane. Figure 7 clearly reflects the hydrophobic nature of the membrane material: cyclohexane is sorbed most by far. Cyclohexanone, the ketone, being more hydrophobic, is sorbed much more than the alcohol. Water sorption is intermediate and mainly to be ascribed to sorption in the zeolite. Sorption of tertiary-butyl hydroperoxide cannot be measured exactly, because this compound is partly decomposed when sorbed in the catalyst. The measurements clearly show that the membrane is predominantly a cyclohexane phase.

Competitive sorption of cyclohexanol and cyclohexanone from a cyclohexane solution. Looking at the operational conditions, the presence of an excess of cyclohexane will probably prevent the sorption of the other, more hydrophilic compounds. This is proved in sorption measurements from cyclohexane/cyclohexanol/cyclohexanone mixtures. The ketone, being 55 wt% of the total alcohol/ketone fraction in the starting solution, is enriched in the membrane to 69 wt%. This clearly demonstrates the strong influence of solvation by cyclohexane on the sorption of both products, since the enrichment is clearly much smaller than expected from the sorption of the pure compounds.

The membrane as organic "solvent phase." In order to have an idea about the *in situ* membrane composition during reaction, vacuum distillation was applied to the membrane directly after reaction. The distilled solution was found to contain 98.9 wt% cyclohexane, while the cyclohexane reservoir and the peroxide reservoir contained 98.4

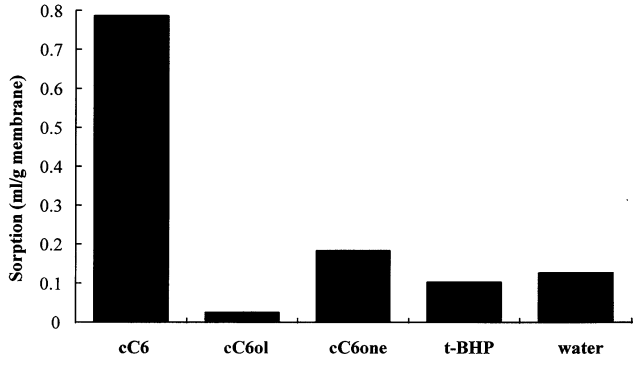

FIG. 7. Sorption of the pure compounds in the FePcY-PDMS membrane.

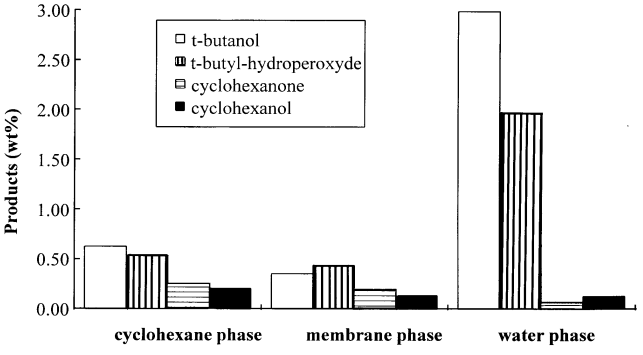

FIG. 8. Distribution of reactants and products over the different phases (cyclohexane, membrane and water phase) in the membrane reactor at a conversion of 2% after 7 h of reaction.

and 0.8 wt% cyclohexane, respectively, at the end of the reaction. This proves that the properties of the membrane solution are very similar to the properties of the cyclohexane phase, reflecting once more the highly hydrophobic nature of the membrane. Analysis of the minor components (Fig. 8) sorbed in the the membrane shows that the membrane phase is not completely identical to the cyclohexane phase: cyclohexanone and tertiary-butanol are enriched in the membrane phase, compared to their more hydrophilic analogues cyclohexanol and tertiary-butyl hydroperoxide. It reflects an even more hydrophobic character for the membrane phase than for the cyclohexane phase. These experiments prove that the composition of both reagent phases change as reaction proceeds. The water phase starts as a 7 wt% hydroperoxide solution in water and changes into a 4.2 wt% hydroperoxide, 2.5 wt% tertiary butanol, 0.15 wt% cyclohexanol, 0.08 wt% cyclohexanone, and 0.035 wt% cyclohexane solution in water. The hydrophobic phase goes from a 100 wt% cyclohexane solution to a 0.35 wt% cyclohexanol, 0.39 wt% cyclohexanone, 0.7 wt% tertiary-butanol, and 0.55 wt% hydroperoxide solution in cyclohexane. Although these changes are rather small, they might also play a part in the partitioning of products over both phases discussed earlier.

C. Comparison with Non-membrane-resident FePcY

The sorption experiments reveal part of the membrane effect already: the catalyst is surrounded by an apolar medium that selectively sorbs cyclohexane at the expense of the peroxide, which is desirable for this system (2). In order to have a full understanding of the membrane role on the level of catalysis, membrane-resident and non-membrane-resident catalyst should be compared under identical conditions. However, this creates a major problem since pure catalyst powder simply cannot be applied in the shape of a membrane between two reagent phases. On the other hand, the fed batch reactor, traditionally used for FePcY, does not allow the evaluation of the full potentials of the membrane-resident system. Indeed, in that system, peroxide is added continuously, which is in complete contrast with the membrane reactor system. A solvent batch reaction type, where both reagents are present in full concentration from the beginning of the reaction, can partly solve this. However, here again the link towards the membrane reactor fails since a solvent is present. Finally, catalysis was carried out in a biphase batch reactor, reflecting the membrane reactor conditions most closely.

Fed batch reactor. This system, being the most favourable setup for non-membrane-resident FePcY in this oxidation reaction, clearly shows no benefits from a membrane incorporation. Similar rates are obtained as a function of time for both catalyst systems (Fig. 9). The slow rate at the beginning of the reaction probably follows from the experimental limitations of the system: as the peroxide-filled syringe is emptied at a very low rate to keep peroxide decomposition limited, it takes a certain time before enough peroxide is present in the reaction mixture to give a reasonable reaction rate. The steady rate decline after the active initial period points towards a deactivation of the catalyst, the nature of which was examined above. In this fed batch system, the role to keep peroxide concentration low is played by the perfusor. Even then, the oxidation rates are low due to the presence of solvent, sorbing competitively in the zeozyme.

Solvent batch reactor. For the non-membrane-resident FePcY, product concentrations are so low in the initial phase of this reaction that no measurements with sufficient accuracy could be obtained (Fig. 10) as the detection limit of the GC was not yet exceeded. Therefore, the real rate curve (as might reasonably be assumed) should start somewhere around 0.1 g/g · h and then decline slowly. For the membrane-resident system, the GC-detection limit is clearly passed much faster, so that, in spite of the error on the initial rate values, an enhanced reaction rate is found when the catalyst is polymer embedded. Preferential PDMS-sorptions can explain this. The acetone, being present in high quantities, and the peroxide sorb easily in the polar zeozyme. This undesired sorption is predominant

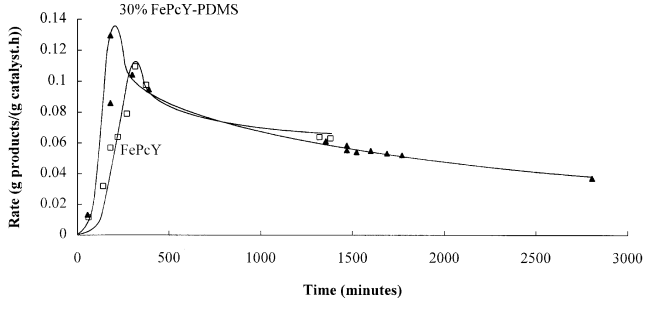

FIG. 9. Rate of cyclohexane oxidation using FePcY and FePcY-PDMS in the fed batch reactor.

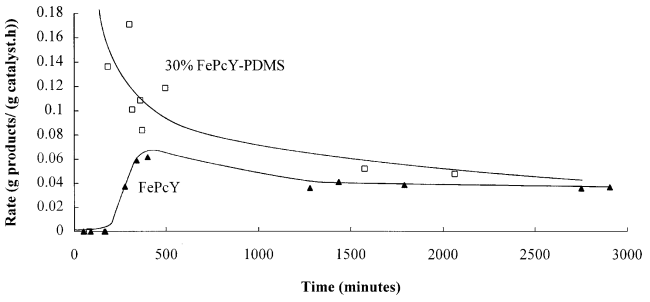

FIG. 10. Rate of cyclohexane oxidation using FePcY and FePcY-PDMS in the solvent batch reactor.

in the FePcY-system, leading to a lowered catalyst activity. On the other hand, the presence of the polymer around the catalyst enriches cyclohexane in the catalyst and severely reduces the competitive sorption of the solvent.

Bi-phase reactor. It is rather surprising to see that the elimination of solvent in the bi-phase reactor leads to increased rates for both catalytic systems as compared to the reaction modes mentioned above (Fig. 11). Looking at the membrane effect, the initial rate is increased upon incorporation in PDMS (2.6 g/g · h compared with only 0.9 g/g · h for the nonresident zeozyme powder). Here again, PDMS enriches cyclohexane in the catalyst and makes reagent concentrations in the zeozyme more favourable for reaction. The high reaction rate is maintained over a longer time in the membrane system. The hydrophobic polymer creates a barrier against water, preventing its sorption in the zeozyme and, consequently, the deactivation of the catalyst. It is remarkable that both the zeolite and the pieces of composite membrane are present at the interphase of both reagent phases. By heavily stirring, they are forced to swap between both phases from time to time, enabling the reaction to take place.

When comparing the rate of the bi-phase batch reactor mode with that of the membrane reactor, highest activities are obtained in the former system. In the membrane reactor, a small reaction front is probably formed where peroxide is able to reach the catalyst in the cyclohexane

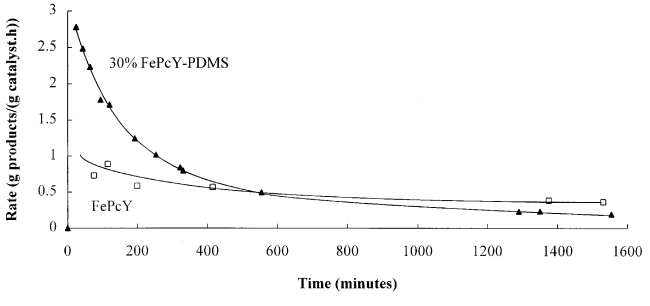

FIG. 11. Rate of cyclohexane oxidation using FePcY and FePcY-PDMS in the bi-phase reactor.

saturated membrane. In the bi-phase system, continuously vigorous stirring forces the membrane into the peroxide phase and into the cyclohexane phase by turns. The peroxide supply is then much easier. It should be emphasized that it is not generally true that both the catalyst and the membrane-resident catalyst will be present at the interphase in a bi-phase batch mode. This is directly dependent on the densities of the different phases. Consequently, this bi-phase reaction mode is surely not generally applicable. In the membrane reactor on the other hand, the membrane, and thus the catalyst, inherently constitutes the interphase, allowing sorption of both reagents from the respective contacting sides. When thinking about large scale feasibility, the membrane reactor can easily be optimized for high area to volume ratios while applying a tangent reagent stream at both membrane sides. The bi-phase reactor mode, on the other hand, is far less practical. Another advantage is that the membrane reactor is the only setup ending with an intact membrane, not damaged by stirring.

CONCLUSIONS

Compared with non-membrane-resident catalysts, the newly developed membrane reactor system shows major benefits in the fact that the membrane forms a physical barrier between two immiscible phases, rendering a solvent redundant. It makes the membrane reactor superior to conventional catalytic systems, in which the solvent causes dilution of the reagents and fast catalyst deactivation. The membrane polymer, acting as an "apolar solvent phase," influences the sorption of reagents in the zeozyme: it acts as a reservoir for the lipophilic reagent and forms a barrier against water, retarding the catalyst deactivation and increasing reaction rates substantially. In the regeneration experiment, it was proved that this catalyst deactivation is caused by the sorption of polar compounds in the zeozyme, such as the formed polar compounds, water, or solvent (if present). Membrane drying, prior to reaction, improved activity in the membrane reactor drastically, especially in the initial stage of the reaction.

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REFERENCES

1. Starks, C. M., "Phase-Transfer Catalysis: New Chemistry, Catalysts, and Applications." ACS Symposium Series 326.
2. Parton, R. F., Peere, G. J., Neys, P. E., Claessens, R., Baron, G. V., and Jacobs, P. A., Submitted for publication.
3. Venuto, P. B., and Landis, P. S., *Adv. Catal.* **18**, 259 (1968).
4. Venuto, P. B., *Adv. Chem. Ser.* **102**, 260 (1971).

5. Armor, J. N., *Appl. Catal.* **49**, 1 (1989).
6. Armor, J. N., *Chemtech* 557 (1992).
7. Shu, J., Grandjean, B. P. A., Van Neste, A., and Kaliaguine, S., *Can. J. Chem. Eng.* **69**, 1036 (1991).
8. Hsiue, H. H., Liu, C. H., and Wang, C. C., *Chem. Techn. Appl.* **4**, 219 (1992).
9. Cini, P., and Harold, M. P., *AIChE J.* **37**, 997 (1991).
10. Peureux, J., Torres, M., Mozzanega, H., Giroir-Fendler, A., and Dalmon, J.-A., *Catal. Today* **25**, 409 (1995).
11. te Hennepe, H. J. C., Bargeman, D., Mulder, M. H. V., and Smolders, C. A., *J. Mem. Sci.* **35**, 39 (1987).
12. Bartels-Caspers, C., Tusel-Langer, E., and Lichtenthaler, R. N., *J. Mem. Sci.* **70**, 75 (1992).
13. Duval, J.-M., Folkers, B., Mulder, M. H. V., Desgrandchamps, G., and Smolders, C. A., *J. Mem. Sci.* **80**, 189 (1993).
14. Vankelecom, I. F. J., Depré, D., De Beukelaer, S., and Uytterhoeven, J. B., *J. Phys. Chem.* **99**, 13193 (1995).
15. Jia, M.-D., Peinemann, K.-V., and Behling, R.-D., *J. Mem. Sci.* **73**, 119 (1992).
16. Vankelecom, I. F. J., Scheppers, E., Heus, R., and Uytterhoeven, J. B., *J. Phys. Chem.* **98**, 12390 (1994).
17. Parton, R. F., Vankelecom, I. F. J., Casselman, M. J. A., Bezoukhanova, C. P., Uytterhoeven, J. B., and Jacobs, P. A., *Nature* **370**, 541 (1994).
18. Vankelecom, I. F. J., Merckx, E., Luts, M., and Uytterhoeven, J. B., *J. Phys. Chem.* **99**, 13187 (1995).
19. Parton, R. F., De Vos, D. E., and Jacobs, P. A., *in* "Zeolite Microporous Solids: Synthesis, Structure and Reactivity" (Derouane, E. G., Lemos, F., Naccache, C., and Ribeiro, F. R., Eds.), p. 552, NATO ASI Ser. C352. Kluwer Academic, 1992.
20. Huybrechts, D. R. C., Parton, R. F., and Jacobs, P. A., *Stud. Surf. Sci. Catal.* **60**, 225 (1991).
21. De Vos, D. E., Thibault-Starzyk, F., Knops-Gerrits, P. P., Parton, R. F., and Jacobs, P. A., *Macromol. Symp.* **80**, 157 (1994).
22. Parton, R. F., Huybrechts, D. R. C., Buskens, Ph., and Jacobs, P. A., *Stud. Surf. Sci. Catal.* **65**, 47 (1991).
23. Herron, N., Stucky, G. D., and Tolman, C. A., *J. Chem. Soc. Chem. Commun.* 1521 (1986).
24. Tolman, C. A., and Herron, N., *Catal. Today* **3**, 235 (1988).
25. Ingelman-Sundberg, M., *in* "Cytochrome P-450" (Oritz de Montellano, P. R., Ed.), p. 119. Plenum, New York, 1986.
26. Mulder, M., *in* "Pervaporation Membrane Processes" (R. Y. M. Huang, Ed.), Chap. 3, p. 225. Elsevier, Amsterdam, 1991.