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Selective hydrocarbon oxidation using a liquid-phase catalytic membrane reactor

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Abstract

The room-temperature oxidation of cyclohexane and *n*-dodecane was studied in a liquid-phase membrane reactor, in which the organic substrate and aqueous oxidant phase are separated by a catalytic membrane. The influence of the poly(dimethylsiloxane) polymer membrane thickness and the catalyst volume fraction (zeolite-encapsulated iron-phthalocyanine) on the observed reaction rate was investigated. In the *n*-dodecane oxidation in a liquid phase catalytic membrane reactor, the alcohol and ketone products are exclusively recovered in the organic *n*-dodecane phase, demonstrating the possibility of the integrated reaction and separation in one single process unit. ©2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Catalytic oxidation is the most important route to functionalised hydrocarbons [1]. Liquid hydrocarbon feedstocks (alkanes, alkenes and aromatics) are converted into industrial bulk chemicals using molecular oxygen and homogeneous cobalt and manganese catalysts [2]. In the fine chemicals industry, on the other hand, chemist are still using non-catalytic stoichiometric oxidants (chromic acid, potassium permanganate), producing relatively large amounts of inorganic salt-containing by-products. Considering the stringent environmental regulations, it can be expected that such traditional stoichiometric reactions will be gradually replaced by novel selective and cleaner catalytic oxidation processes.

Several novel, selective homogeneous, and heterogeneous, catalysts have been proposed recently [3–5]. Parton, et al. [6] studied the room-temperature cyclohexane oxidation using a zeolite-encapsulated iron–phthalocyanine complex, a mimic of the enzyme cytochrome P-450. As a result of competitive adsorption of solvent acetone, oxidant *t*-butylhydroperoxide and other polar components in the reaction mixture, non-polar reactants are almost completely excluded from the active sites of the catalyst [7]. In an attempt to create a more hydrophobic environment, the zeolite Y was drastically dealuminated. An increase in the Si/Al ratio from 2.5 to 130 resulted in an increase in the observed reaction rate by a factor of three.

Subsequently, the zeolite catalyst was embedded in a hydrophobic poly(dimethylsiloxane) polymer membrane (FePcY-PDMS) [8]. The hydrophobic

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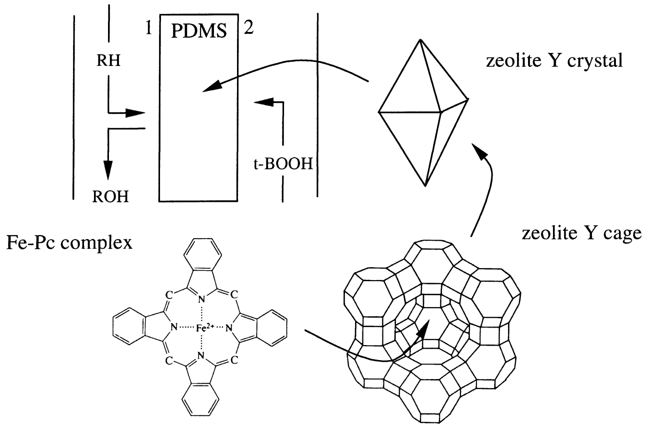

Fig. 1. Supramolecular structure of Fe–Pc–Y membrane catalyst [10].

polymer acts as a barrier between the *t*-butylhydroperoxide and organic cyclohexane phase, hence avoiding the use of a solvent. The influence of poly(dimethylsiloxane) polymer on the catalytic activity of a zeolite-encapsulated iron-phthalocyanine catalyst was already extensively studied by Vankelecom, et al. [9]. In a solvent-free biphase batch reactor configuration, a clearly enhanced reaction rate was observed for the PDMS incorporated FePcY catalyst (2.6 g/g h for the PDMS-FePcY membrane catalyst as compared to 0.9 g/g h for the FePcY zeolite catalyst) [9]. The increased catalyst activity can be explained using the sorption and diffusion properties of the different reactants and products into poly(dimethylsiloxane) polymer [10]. The non-polar cyclohexane substrate is adsorbed approximately three times more strongly than the polar organic peroxide oxidant, and consequently a more favourable substrate/oxidant concentration can be obtained near the transition-metal complex catalyst (Fig. 1).

The controlled addition of reactants to the active site of the catalyst is even more clearly illustrated by Neys, et al. [11]. The oxidation of cyclic alcohols (C_5, C_6 and C_7) in an aqueous solution was studied using a manganese–porphyrin complex catalyst dispersed in a hydrophobic PDMS polymer. The alcohol substrate is preferentially adsorbed from the aqueous solution into the poly(dimethylsiloxane) polymer, which results in high alcohol concentrations near the active transition-metal complex and enhanced reaction rates. As cycloheptanol is preferentially adsorbed over cyclopentanol and cyclohexanol, the increase in oxidation activity was found to be the highest for the C_7 alcohol. In this catalyst system, the turnover number is essentially controlled by the polymer matrix adsorption properties.

The influence of several membrane parameters (polymer thickness and catalyst volume fraction) on the catalytic membrane activity (FePcY-PDMS membrane) will be discussed in this paper. In addition, the feasibility of the combination of reaction and separation in one single catalytic membrane reactor unit will be demonstrated.

2. Experimental

2.1. Materials

Cyclohexane (99.9+%) and chloroform (p.a.) were purchased from Merck. *n*-dodecane (99%) was obtained from Janssen Chimica. *t*-butylhydroperoxide (70 wt.% in water) was acquired from Sigma.

Zeolite encapsulated iron-phthalocyanine catalyst is synthesised by the solid-state adsorption of 0.575 g ferrocene (98% Aldrich) on 5 g NaY (Zeocat, Si/Al 2.47, 1 μm crystals) [6]. The ferrocene-loaded zeolite is then mixed with 3.15 g 1,2-dicyanobenzene (98%, Aldrich) and placed in an autoclave. The Teflon-lined autoclave is heated at 180°C for 17 h. Subsequently, the obtained blue-green solid is Soxhlet extracted with acetone (p.a. Janssen Chimica), dimethylformamide (99% Aldrich) and again acetone to remove unreacted

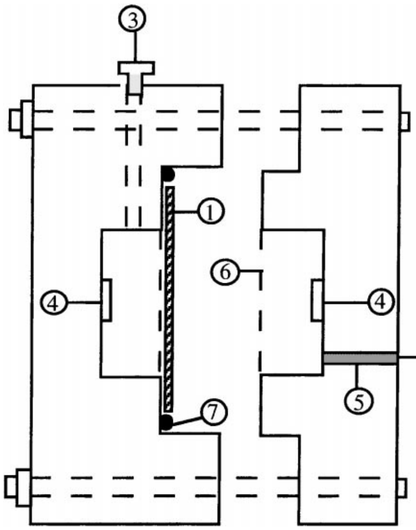

Fig. 2. Schematic representation of the batch catalytic membrane reactor (1, polymer membrane; 2, sample port; 3, sample port; 4, magnetic stirrer; 5, septum; 6, support grid; and 7, O-ring).

reactants and intermediates from the microporous zeolite. The catalyst is finally air-dried at 70°C.

The catalytic membrane was synthesised by preparing an 8 wt.% solution of prepolymer (GE Silicones RTV 615 A) and cross-linker (GE Silicones RTV 615 B) in chloroform solvent [12]. This mixture is stirred at 70°C during 1 h (prepolymer/cross-linker ratio of 10/1). Subsequently, the vacuum treated zeolite catalyst (336 mbar and 150°C during 1 h) is sieved directly into the polymer mixture, which is stirred for another hour at room temperature. The mixture is then cast on a glass plate and the solvent evaporated for 4 h at room temperature. Finally, the poly(dimethylsiloxane) polymer is cured in a vacuum oven (336 mbar and 150°C) for 45 min. Scanning electron microscopy showed a homogeneous dispersion of the catalyst crystals in the polymer membrane [8]. Using this synthesis method, polymer membranes with a thickness ranging from 100 μm to a few millimetres can be prepared. The thickness of the swelled polymer sample was measured using a micrometer (±0.01 mm).

2.2. Catalytic membrane reactor

A schematic representation of the batch catalytic membrane reactor cell is shown in Fig. 2. Two well-mixed chambers (C1 and C2) are separated by the catalytic membrane sample ($S = 7.1 \times 10^{-4}\ \mathrm{m}^2$). Chamber C1 is filled with the hydrocarbon substrate (cyclohexane or *n*-dodecane), while chamber C2 consists of an aqueous *t*-butylhydroperoxide (7 wt.% *t*-BOOH) solution. Small samples (10 μl) are taken at regular intervals from both the chambers and analysed with HP 6890 Hewlett–Packard capillary column chromatograph (HP-1 column and FID detector).

3. Results and discussion

The room-temperature oxidation of cyclohexane into cyclohexanol and cyclohexanone was studied in a liquid-phase catalytic membrane reactor. The membrane consist of poly(dimethylsiloxane) polymer in which a zeolite-encapsulated iron-phthalocyanine catalyst (FePcY) is incorporated. The organic substrate and aqueous oxidant, contacted through the catalytic membrane, sorb into the PDMS polymer and diffuse towards the FePcY catalyst crystals, where the oxidation reaction takes place.

In a first step, the influence of the polymer membrane thickness (100, 200, 300, 800 and 1500 μm) was investigated. Fig. 3 shows the results of a typical reactor experiment, where cyclohexanol and cyclohexanone oxidation products are recovered in both, the aqueous and organic phases. Catalyst deactivation was observed at longer reaction time, presumably a result of oxidation product pore blocking. However, a vacuum treatment (150°C, 336 mbar) could restore the

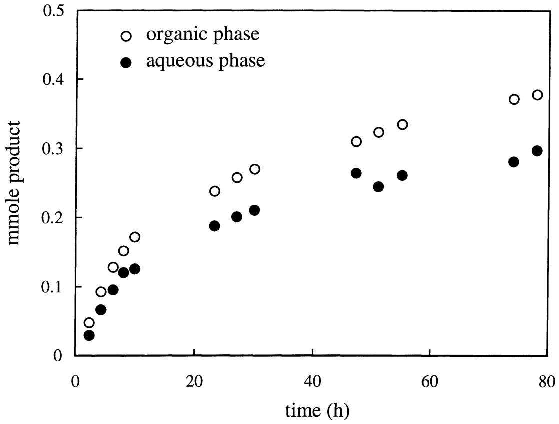

Fig. 3. Cyclohexane oxidation products in the aqueous and organic phase as a function of time (200 μm thickness, 24 vol.% FePcY).

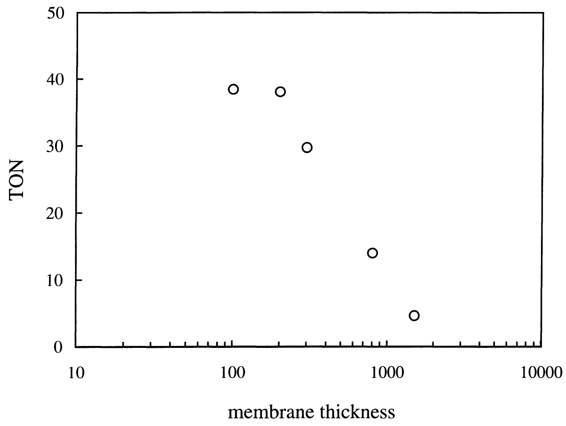

Fig. 4. Influence of the membrane thickness (μm) on the catalyst activity (24 vol.% FePcY catalyst, TON after 4 h of reaction).

initial activity, which implies that no leaching occurs and the membrane catalyst system is truly heterogeneous [9].

High turnover numbers (mol product (mol FePc)$^{-1}$ after 4 h of reaction) were obtained for a polymer thickness of up to 200 μm. In these catalytic membranes, uniform reactant concentrations are obtained over the membrane and each catalyst particle is efficiently used. Hence, the observed turnover number is kinetically controlled ($<$200 μm). The reactant concentrations are then uniform over the membrane and each catalyst particle is efficiently used. However, using thicker membranes, the observed reaction rates decreased rapidly with increasing membrane thickness (Fig. 4). The supply of reactants towards the zeolite-encapsulated iron-phthalocyanine catalyst decreases with increasing polymer thickness, and low substrate or organic peroxide concentrations are obtained at the membrane boundaries (low cyclohexane concentrations are obtained at the polymer–water interface, low *t*-BOOH concentrations at the polymer–organic interface). Consequently, the zeolite catalyst is not effectively used and the observed reaction rates become mass-transfer limited ($>$200 μm).

Subsequently, reaction experiments were performed using FePcY-PDMS membranes with different catalyst loading (16, 24 and 32% FePcY). A linear increase of the observed yield (mole cyclohexanol and cyclohexanone products after 24 h of reaction) with increasing catalyst volume fraction was obtained (Table 1), which means that the amount of oxidation products produced per mole FePc complexes was found to be identical for the different membranes (16, 24 and 32% FePcY). Although, as a result of an increased tortuosity factor, the effective membrane diffusion coefficient slightly decreases with increasing catalyst loading [10], the above described observation suggests that the influence of the catalyst volume fraction on the activity (TON) of 200 μm catalytic membranes is rather insignificant. Obviously, the influence of the membrane thickness on the observed catalytic activity is stronger as compared to the catalyst loading.

Table 1
Influence of volume fraction of catalyst (200 μm thickness, TON after 24 h of reaction)

Volume fraction catalyst (%)	TON	Products (mmol)
16	103	0.28
24	104	0.43
32	104	0.57

Finally, the recovery of alcohol and ketone oxidation products into the aqueous and organic phase was studied for the oxidation of cyclohexane and *n*-dodecane (Table 2). In the cyclohexane oxidation, cyclohexanol and cyclohexanone are found in both the reactor chambers (Fig. 3). Higher product concentrations are obtained in the organic cyclohexane substrate phase, which is in good agreement with the partitioning of cyclohexanol and cyclohexanone into a biphasic water/cyclohexane mixture.

On the other hand, dodecanol and dodecanone oxidation products are not soluble in water, and consequently, cannot permeate through the membrane–water interface. As a result, alcohol and ketone products can only desorb into the organic phase, which is confirmed by the experimental observations (Fig. 5).

Table 2
Cyclohexane and *n*-dodecane oxidation in a catalytic membrane reactor (200 μm thickness, 24 vol.% FePcY catalyst, TON after 24 h of reaction)

Substrate	Products (mmol)	α[a]
Cyclohexane	0.43	0.79
n-Dodecane	0.07	0

[a] Mol product in aqueous phase/mol product in organic phase.

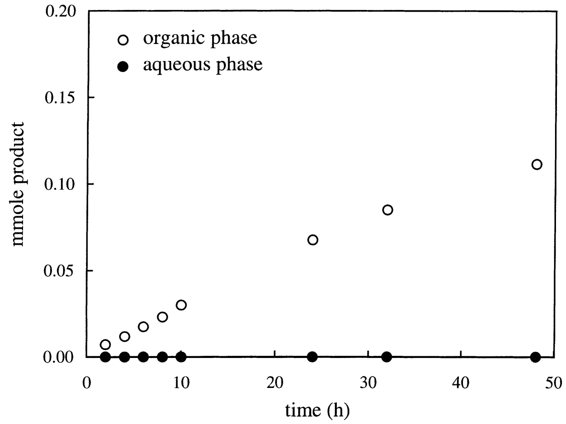

Fig. 5. *n*-Dodecane oxidation products in the aqueous and organic phases as a function of time (200 μm thickness, 24 vol.% FePcY).

Hence, in a liquid phase catalytic membrane reactor, *n*-dodecane oxidation products are exclusively recovered from the organic substrate phase.

4. Conclusion

The selective liquid-phase hydrocarbon oxidation was studied in a catalytic membrane reactor. In this reactor configuration, the organic substrate and aqueous oxidant phases are contacted through a catalytic membrane and, consequently, the necessity for a solvent is completely eliminated. Moreover, high reaction rates are obtained as a result of the optimised substrate/oxidant ratio achieved near the active sites of the catalyst.

In order to obtain a high productivity over reactor volume ratio, thin polymer membranes (≈200 μm) with a high catalyst volume fraction have to be applied.

Alcohol and ketone oxidation products are recovered from the aqueous and organic phases, depending on the solubility of the reaction products in both phases. In the *n*-dodecane oxidation, dodecanol and dodecanone are completely recovered in the organic phase and, hence, the combination of reaction and separation in one single process unit is demonstrated.

Future research should focus on the synthesis of novel catalytic polymer membranes, in which the active transition-metal complex is incorporated into the backbone structure of the polymer. In this way, a high stability against leaching is achieved and the optimal substrate/oxidant concentration ratio can be obtained by simply adjusting the polymer adsorption properties.

Moreover, the recovery of oxidation products into the aqueous or organic phases could possibly be controlled using a composite catalytic membrane (a catalytic membrane coated with a selective polymer barrier — low product and high reactant permeability).

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