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Mesoporous nickelsilicate membranes on porous alumina supports
II. Catalytic reactor for oxidation of aromatic hydrocarbons

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Abstract

After successful synthesis and gas permeation study of ordered mesoporous nickelsilicate membranes on porous Al_2O_3 substrates, their catalytic properties have been evaluated in the reaction of styrene and benzene with H_2O_2. Nickelsilicate membranes have active properties for oxidation of styrene and benzene between 297 and 343 K. The effect of permeance of oxidant agent on the catalytic activity of membranes has been studied. Comparative experiments of the membrane reactor and batch reactor with the same catalyst (Ni-MCM-41) in power form revealed quite interesting observation that the oxidation of styrene with membrane reactor conducts to the formation of epoxy ethyl benzene (styrene oxide) while the conventional batch reactor with powdery catalyst gives selectively benzaldehyde. The activity and selectivity of nickelsilicate membrane catalysts have been correlated with their mesoporous structure, permeation properties and characteristics inherent to membrane reactor. It was found that the control of the oxygen peroxide feed and short residence and contact time of reactants and oxidant in membrane reactor result in the selectivity of styrene oxidation to styrene oxide instead of benzaldehyde, a deeper oxidation product, observed in batch reactor. The present paper supplies important information on designing highly efficient and selective catalytic membrane processes.
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1. Introduction

The field of application of membrane technology was significantly extended by the use of inorganic membranes [1–6]. The combination of their selective permeability in a reactor with catalytically active component and mechanic strength can lead to new applications [7] such as waste treatment, biotechnology and biomedical engineering.

The membrane reactor concept is of potential interest for the oxidation reaction in liquid phase with hydrogen peroxide. The membrane can restrict the movement of molecules of reactants across of their structure, control the reactant feeding and improve the contact between the reactants and the catalyst [8,9].

Molecular sieve catalysts are widely studied for selective oxidation reaction with hydrogen peroxide [10–15]. The

control of the hydrogen peroxide feed in oxidation of the hydrocarbon can significantly increase the rate of reaction [13]. The most favorable property of mesoporous molecular sieves, with respect to their potential application in catalysis and separation, explain the great interest in the developing novel inorganic catalytic membranes which are expected to make possible the separation of the products at molecular level and the control of the feed of the reactants [13–19]. Incorporation of the transition metal ions into the lattice can lead to stable isolated and well defined redox active catalytic sites [10–21]. Permeation of the gases through nickelsilicate membranes synthesized on γ-alumina [22] and their selective separation evidenced the influence of synthesis conditions on the porous structure and adsorption properties of the nickelsilicate layer.

The specific adsorption properties of hydrocarbons, reported in the first paper of this research [22] and activation of H_2O_2, significant property of the transitional ions containing mesoporous molecular sieves [13–19], are two important properties for use of the nickelsilicate membranes in catalytic oxidation reaction. On the basis of our previous

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results on the superior catalytic properties of mesoporous nickelsilicate catalysts for selective oxidation of aromatic hydrocarbons with hydrogen peroxide [13–17] and after successful synthesis of nickelsilicate membranes on alumina supports, the present study reports the preliminary data concerning the application of catalytic mesoporous nickelsilicate membranes in the oxidation of styrene and benzene. We try to establish the correlation at molecular level between the catalytic properties, different reactors and the control of oxidant feed.

2. Experimental

The preparation of the nickelsilicate membranes formed on γ-alumina disk (Ø = 28.5 mm and 3 mm in thickness) was described in detail in the first part of our study [22]. The membranes used for oxidation reactions in this study were elaborated by immersion of pretreated γ-alumina disk in nickelsilicate gel [22] and hydrothermally treated 5 days at 373 K. The cleaned alumina supports were pretreated, during 2 h (MS27 and MS28) and 12 h (MS9), with an aqueous solution of TMAOH + H_2O_2 (MS9 and MS28) or TMAOH (MS27), respectively.

The membranes were used in a catalytic reactor for the oxidation of benzene and styrene with hydrogen peroxide (30 wt.%). The experimental set-up used is shown in Fig. 1. The H_2O_2 and the organic reactants and solvent were introduced in the feed via the liquid pumps.

The reaction temperature and time varied from 297 to 343 K and 6 to 12 h, respectively. The molar ratio of hydrocarbon/acetonitrile/hydrogen peroxide was controlled by the permeability of the components through the membranes. Oxidation of styrene was performed in the presence and absence of the solvent (acetonitrile). Permeation measurements of the H_2O_2 were carried out under the reactor conditions. The hydrocarbons and the oxidation products were analyzed by chromatography and the hydrogen peroxide concentration by iodometric titration.

3. Results and discussion

Three ordered mesoporous nickelsilicate membranes synthesized on γ-alumina [22] were utilized in oxidation of benzene and styrene with H_2O_2 in the catalytic reactor. The organic substrate and aqueous oxidant were in contact through the catalytic membrane.

The first interesting observation was that the oxidation of styrene in membrane reactor gave epoxy ethyl benzene (styrene oxide) as final product instead of benzaldehyde, a deeper oxidation product which was formed in batch reactor using same catalyst but in powdery form. In a recent paper [23], we proposed a multisteps reaction mechanism of styrene oxidation with H_2O_2 that styrene oxide as first intermediate was transformed to phenyl ethanediol (styrene glycol) and finally to benzaldehyde. Due to the short residence and contact time of reactants and oxidant in the membrane
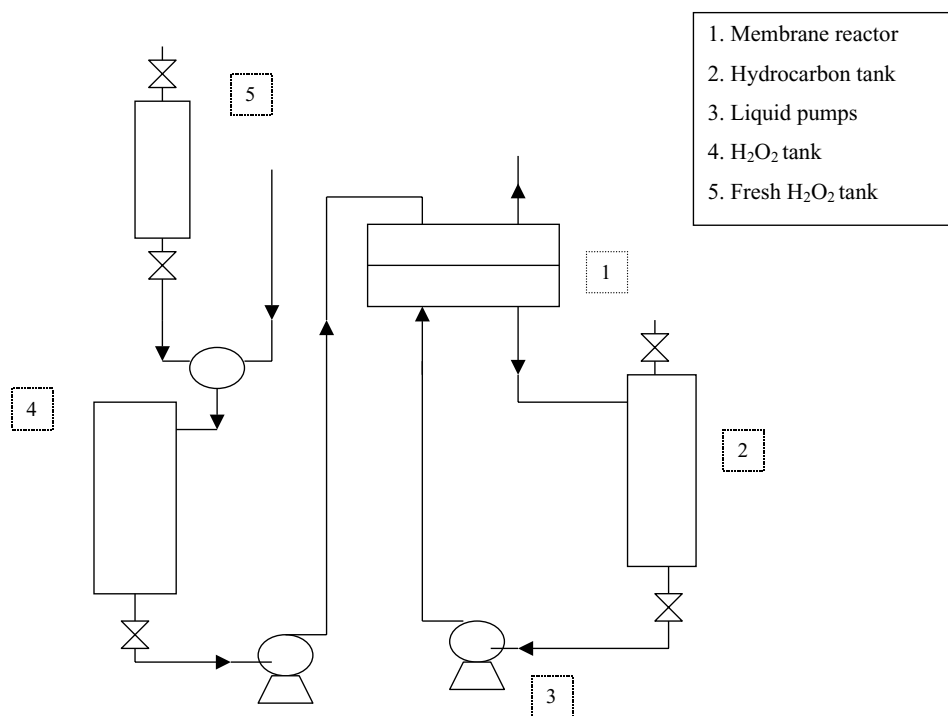

1. Membrane reactor
2. Hydrocarbon tank
3. Liquid pumps
4. H_2O_2 tank
5. Fresh H_2O_2 tank

Fig. 1. Schematic diagram of the experimental set-up.

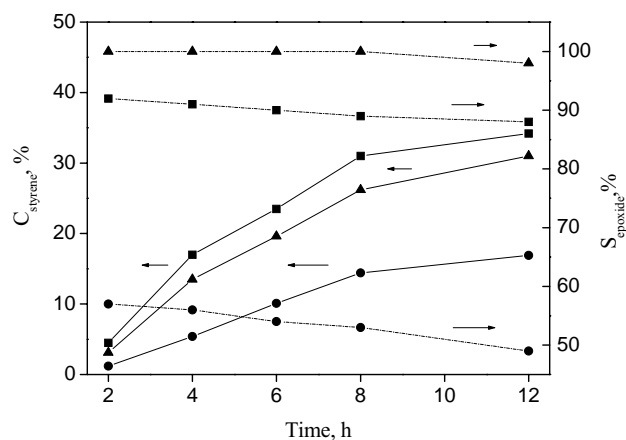Fig. 2. Oxidation of styrene in membrane reactor ($T = 343$ K, molar ratio $C_8H_8/H_2O_2 = 1/3$): (●) MS9, (■) MS27, (▲) MS28.

reactor, the transformation of styrene oxide to deeper oxidation products (styrene glycol or benzaldehyde) was not possible. While in a conventional batch reactor with powdery catalysts, the reactants and intermediates were permanently in contact with oxidant. Styrene oxide and styrene glycol as intermediate products can be continuously transformed to deeper products. That is the typical and important difference between a membrane reactor and a batch reactor.

In Fig. 2, the conversion of styrene and selectivity to epoxide are plotted as a function of the reaction time. The conversion of styrene and rate in the first step of reaction increase and the oxidation of styrene is very selective to epoxide. The highest activity at any reaction time was obtained for the membranes synthesized on the γ-alumina pretreated 2 h with aqueous solution of TMAOH (MS27). In the first part of this work [22], we reported that the permeation of the hydrocarbons through this membrane in gas phase is higher than that of the membranes synthesized on alumina pretreated with aqueous solution of TMAOH + H_2O_2 (MS9 and MS28). The high permeation of hydrocarbons and oxidant molecules through this membrane leads to the high conversion of styrene and selectivity in styrene oxide.

Comparing two other membranes (MS9 and MS28), a higher activity and selectivity to styrene oxide was obtained with MS28 membrane. We revealed that longer wetting with TMAOH + H_2O_2 solution, lower permeation of oxygen molecules and stronger interaction of oxygen molecules with Ni active sites incorporated in the mesoporous framework [22]. It is very possible that during the oxidation reaction, not all the oxidant molecules (H_2O_2) were efficiently used for the oxidation of hydrocarbons (the efficiency of H_2O_2 is very often low [13–17]), part of added H_2O_2 was decomposed to H_2O and O_2. The produced oxygen molecules will interact with Ni ions, inhibiting the further reaction on Ni active sites. That is why a lower conversion is observed on MS9 membrane.

We studied the effect of the H_2O_2 permeance on the conversion of styrene and benzene. Fig. 3 depicts the variation
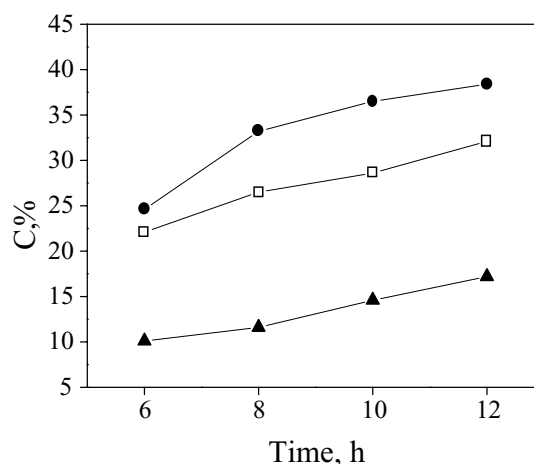

Fig. 3. Variation in time of styrene conversion (MS27 membrane) for various permeance values: (▲) $P = 1.2 \times 10^6$ mol/m^2 s, (□) $P = 5.6 \times 10^6$ mol/m^2 s, (●) $P = 14.2 \times 10^6$ mol/m^2 s.

of the styrene conversion under three H_2O_2 permeance values as a function of reaction time. Under any H_2O_2 permeance value, the styrene conversion increases with increasing reaction time. For a given reaction time, higher H_2O_2 permeation value, higher styrene conversion. This means that higher H_2O_2 content, higher styrene conversion. This is quite in accordance with results previously reported [13–17] that the H_2O_2 efficiency is often low in oxidation reaction and the decomposition of H_2O_2 reduces the amount of oxidant agent in the liquid phase.

The conversion of benzene is lower than that of styrene under any H_2O_2 permeance (Fig. 4). This was previously observed with same catalyst, but in powdery form. It is also observed that higher H_2O_2 permeance, higher benzene conversion. However, when the H_2O_2 permeance reaches a value of 8.6×10^{-6} mol/m^2 s, no effect of H_2O_2 permeance on the conversion of benzene and styrene can be noted, indicating that the amount of H_2O_2 introduced is high enough to ensure the reaction although part of them will be decomposed.

The conversion of styrene with membrane reactor has been compared with that realized in a conventional batch
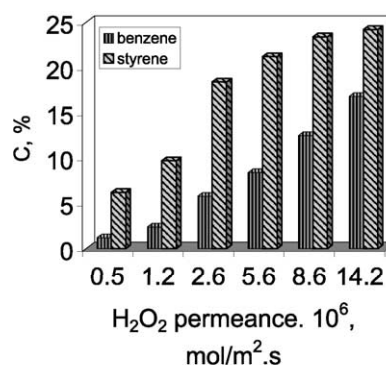

Fig. 4. Conversion of styrene and benzene as a function of H_2O_2 permeance (MS28, reaction time: 6 h).
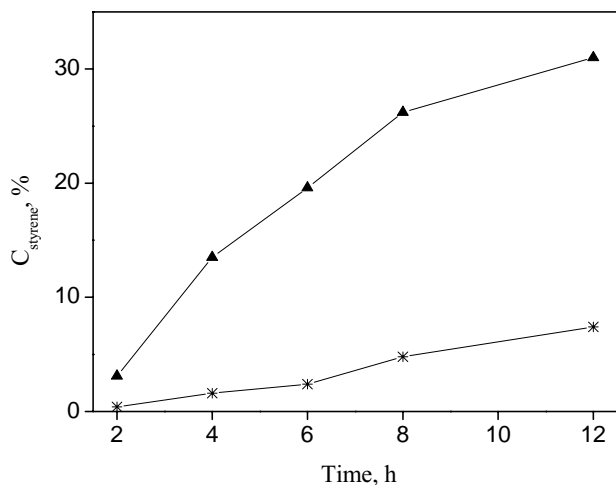
Fig. 5. Oxidation of styrene to epoxide in membrane reactor and to benzaldehyde in a batch reactor ($T = 343$ K, molar ratio $C_8H_8/H_2O_2 = 1/3$): (▲) MS28, (✳) Ni-MCM-41 powder.

reactor with powdery catalyst (Fig. 5). To make a good comparison, the amount of powdery catalyst used is similar to that in membrane attached on γ-Al_2O_3 support. The amount of catalyst in membrane can be approximately calculated on the basis of thickness and diameter of membrane. The conversion with membrane reactor is always higher than that realized in batch reactor. This can be explained by the fact that in a membrane reactor, only one reaction, the oxidation of styrene to styrene oxide, occurs while in a batch reactor, the oxidation of styrene to styrene oxide and the oxidation of styrene oxide to styrene glycol and to benzaldehyde (three reactions) simultaneously take place for the same amount of catalyst. For membrane reactor, styrene oxide is the only product while in batch reactor, other than benzaldehyde, some condensed products were formed [13–17].

4. Conclusions

Mesoporous nickelsilicate membrane can be used as efficient catalyst in selective oxidation of styrene to epoxy ethyl benzene and benzene to phenol. The membrane offers a very good possibility to control the hydrogen peroxide feed and the selectivity in oxidation of styrene to styrene oxide and to increase of the reaction rate.

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