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Methanol oxidative dehydrogenation in a catalytic packed-bed membrane reactor

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Abstract

Methanol oxidative dehydrogenation to formaldehyde over a Fe-Mo oxide catalyst was studied experimentally in a packed-bed membrane reactor (PBMR) as well as in a conventional fixed-bed reactor (FBR) under identical overall reaction conditions. Two configurations for PBMR were investigated, using either oxygen (PBMR-O) or methanol (PBMR-M) as permeate, and the other reactant flowing over the catalyst bed. The influence of temperature, reactant residence time, feed concentration and nitrogen diluent split were studied. In the FBR experiments, selectivity to formaldehyde increased for increasing feed concentration of methanol and decreased when oxygen concentration was increased. This behavior indicated that the relative reactor performance should be in the order PBMR-O $>$ FBR $>$ PBMR-M, and this was confirmed experimentally. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Methanol oxidative dehydrogenation; Formaldehyde; Fe-Mo catalyst; Membrane reactor; Fixed-bed reactor; Inorganic membranes

1. Introduction

Owing to the introduction of novel materials and synthesis procedures, recent developments of thermally and structurally stable inorganic membranes have stimulated significant interest in their use for membrane reactors. Several reviews, describing the use and advantages of inorganic membrane reactors have been published recently [3,14,6]. An increasingly important application in this field involves the use of membranes for segregation and controlled addition of one or more reactants, which permeate to the reaction side where the catalyst is located. This can be advantageous in many examples of series, parallel and series–parallel oxidation reactions where a partial oxidation product is frequently desired (cf. [2,10,11,17]).

We have recently investigated ethylene epoxidation in a catalytic packed-bed membrane reactor (PBMR), and demonstrated that significant improvements in ethylene oxide selectivity and yield can be achieved over the conventional fixed-bed reactor (FBR) [9,11]. These works demonstrate the attractiveness of a porous stainless steel (SS) membrane, which includes excellent thermal-mechanical stability and machinability, as compared to other inorganic membrane materials such as ceramics and oxides.

Ethylene epoxidation is an essentially parallel reaction network. For a deeper understanding of the concept of segregation and controlled addition of reactants, in this work we study a consecutive reaction network, viz. oxidative dehydrogenation of methanol on Fe-Mo oxide catalyst. This is a reaction of significant economic value as the desired product, formaldehyde is an important reactant for the production of resins, plastics and coatings [7]. Approximately eight billion pounds of formaldehyde are produced annually

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Nomenclature

F	overall feed volumetric flow rate ($m^3\,s^{-1}$)
L	reactor length (m)
q	membrane feed volumetric flow rate/overall feed volumetric flow rate
Q	volumetric flow rate over catalyst bed as a function of position ($m^3\,s^{-1}$)
s	x/L, dimensionless coordinate along the reactor
t	residence time of the reactants in a FBR (s)
t_0	V/F (s)
t_b	residence time of catalyst bed stream (s)
t_m	residence time over catalytic bed of reactant fed through membrane at position x (s)
V	catalyst bed volume (m^3)
v	Q/F, dimensionless volumetric flow rate (as a function of position)
x	distance from reactor inlet (m)

in the US [8], primarily by the catalytic oxidation of methanol. The reaction is carried out industrially in multi-tube FBR. Earlier catalysts were silver-based, but owing to the high temperatures (∼600–650°C) required, which favor side decomposition reactions, most new formaldehyde installed capacity utilizes the Fe-Mo oxide catalyst [7]. In this case, the operating temperatures are in the range 250–400°C, and the reaction takes place at atmospheric pressure. Under these conditions, side-reactions are insignificant and the reaction network reduces to the consecutive path [5].

$$CH_3OH \xrightarrow[(1)]{+1/2(O_2)} HCHO + H_2O \xrightarrow[(2)]{+1/2(O_2)} CO + H_2O$$

The stoichiometry for the desired reaction (1) is 2:1 methanol to oxygen, however, in order to avoid flammable mixtures, methanol content in air is kept less than 8% for the fixed-bed where the reactants are co-fed [16,19]. For safety considerations, we use the same overall operating conditions in the PBMR.

According to the literature, methanol oxidation (reaction 1) over the Fe-Mo oxide catalyst follows a two-step redox mechanism where methanol reacts with lattice oxygen to produce formaldehyde, and then vapor phase oxygen replaces the lattice oxygen [13,15]. Complex mechanistic schemes can be formulated, but simpler models are generally used as they fit the data well. Regarding reaction orders, different authors consider either 0 or 1/2 for oxygen, but with oxygen in large excess even the square root of oxygen partial pressure is essentially constant. For methanol, the best fit order ranges from 1/2 to 1. For reaction (2), very few data are available in the literature Schwedock et al. [15] indicate that a similar redox mechanism to that for reaction (1) is followed.

The objective of this work is an experimental study of methanol oxidative dehydrogenation over a Fe-Mo catalyst, using a PBMR. The results are examined for obtaining the largest formaldehyde selectivity, at a fixed methanol conversion, and the different reactor configurations are compared in this regard. The performance of the membrane reactor (with either oxygen or methanol permeating through the membrane, i.e. PBMR-O or PBMR-M, respectively) was compared with that of a conventional FBR. Various feed reactant concentrations, temperatures, and residence times were analyzed.

2. Experimental

2.1. Catalyst preparation and characterization

The catalyst was prepared based on the procedure outlined by [4]. Ammonia paramolybdate tetrahydrate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, Aldrich Chemical Co.) was used as the molybdenum source, and ferric nitrate non-ahydrate ($Fe(NO_3)_3\cdot 9H_2O$, Aldrich Chemical Co.) was the iron source. Following this procedure, 16.5 g of the molybdenum salt were mixed with 46.7 ml of deionized water in a stirred beaker, and the mixture was cooled to ∼8–10°C using an ice bath. In a separate beaker, 18.9 g of ferric nitrate were mixed with 23.3 ml of water. Using a burette to maintain a flow rate of ∼2 ml/min, the second mixture (at 15–20°C) was added slowly to the first under constant stirring, and a colloidal yellow-sand suspension was obtained. Then, after stopping the cooling, the suspension solidified at 14°C. The mixture was aged at 30°C for 2 h resulting in a dark green homogeneous transparent gel, which was dried in an oven at 70°C for 48 h and converted to a brownish gel. The oven was then heated to 175°C for 24 h, yielding a yellow solid product, that was crushed to powder form. Finally, the catalyst powder was pressed into pellets, crushed and sieved to obtain particles in the range 400–800 μm used for the reaction experiments. These particles possess a BET surface area of 4.8 m^2/g, which is in good agreement with [4].

2.2. Fixed-bed reactor and membrane reactor experiments

The performance of PBMR and FBR for methanol oxidative dehydrogenation was studied in a shell-and-tube configuration, with the membrane or a blank tube located in the center, respectively. The reaction occurred on the catalyst bed located in the annulus.

2.2.1. Apparatus

The experimental apparatus was similar to that used by [11] and a schematic diagram is shown in Fig. 1. The membrane reactor consisted of a shell and tube with two feed inlets and one outlet. The membrane was a 45 mm long porous 316L SS tube (Mott Metallurgical Corporation; 0.20 μm grade; 10 mm o.d.) welded to a non-porous 316L-SS tube. Initially, the flow through the membrane was too high, so it was subjected to a thermal treatment in air to reduce pore size. Then, values of transmembrane pressure drop, for typical flow rates used under reaction conditions, ranged from 0.15 to 0.45 bar, ensuring absence of back-diffusion and bypass into the membrane [1].

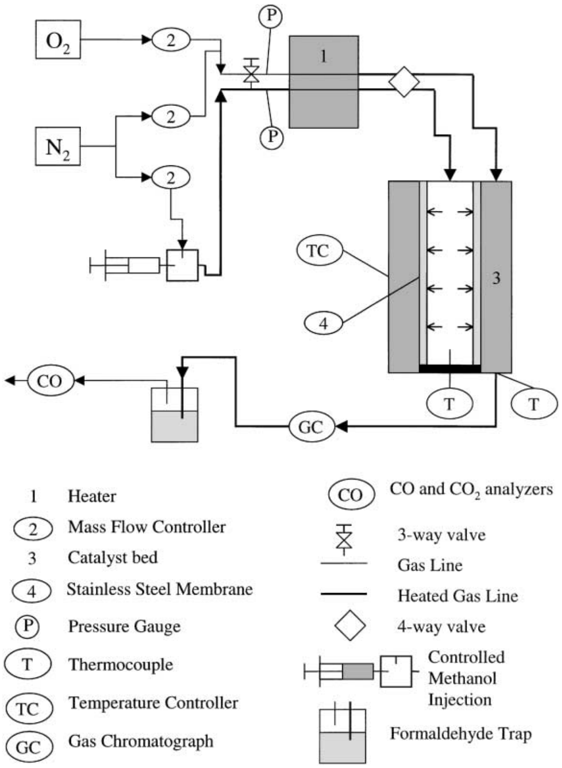

Fig. 1. Schematic diagram of the experimental apparatus.

The membrane feedthrough was inserted into a 19 mm o.d. quartz tube. The volume of catalyst bed was 6.7 cm^3, packed uniformly occupying the 3.5 mm annulus formed by the membrane (10 mm o.d.) and quartz reactor (17 mm i.d.) along the entire membrane length (45 mm). Gases were introduced separately on both membrane and catalyst bed (annulus) sides, and exited together from the reactor.

The gases used in the experiments were oxygen (Linde, zero grade) and nitrogen (Linde, pre-purified). The volumetric flow rates of the individual gases were metered using Unit (models: UFC-1000, UFC-1100 and UFC-8100) mass flow controllers. Liquid methanol at room temperature was injected from a syringe via a thin (0.5 mm i.d.) SS needle into a heated tube at 120°C with inert gas flowing. The feed of liquid methanol was controlled using an automatic syringe pump (KdScientific, model 100). Typical liquid flow values were on the order of 1 ml/h. Special precautions were taken to avoid condensation of methanol and polymerization of formaldehyde. For this, temperature of the flowing gas was maintained at 120°C along the connecting lines up to the exit from the GC.

The temperature control of the reactor was accomplished by two chromel–alumel (type K) thermocouples. One, connected to the controller, was placed at the external wall of the reactor quartz tube (between the tube and the heating tape) while the other was inserted in the center of the membrane tube. In all experiments, the temperature difference between the two thermocouple readings was less than 6°C. The nominal temperature reported in the experiments is the average of both readings. The temperature of reactor effluent gas was also measured, and always found to be within 2°C of the membrane tube. Thus, the reactor is essentially isothermal in the axial direction.

Carbon monoxide and carbon dioxide concentrations in the exit stream were monitored continuously using on-line infrared Beckman 864 and 870 analyzers, respectively. In all experiments, the CO_2

concentration typically remained below 5% of the CO concentration. A Hewlett Packard 5890 II gas chromatograph (TCD detector, Hayesep-DB column; 3.2 mm. o.d., 9.1 m long) and Hewlett–Packard 3396 II integrator were also used to analyze the stream compositions. The carrier gas was helium and the analysis was carried out at 200°C. The concentrations of methanol, formaldehyde, carbon monoxide, carbon dioxide and water in the outlet stream were measured, while the oxygen concentration was calculated using overall mass and oxygen balances over the reactor. The response factors for the different gases were determined using calibration measurements with methanol/nitrogen and formaldehyde/nitrogen mixtures. Carbon balances always closed within ±5%.

2.2.2. Experimental

An initial activation procedure consisting of FBR operation at 275°C with the standard reaction mixture (20% oxygen, 6% methanol, balance nitrogen) flowing at 200 sccm was carried out for 30 h. After this, the catalyst exhibited stable and reproducible activity and selectivity.

Three different reactor configurations were investigated: FBR, PBMR with either methanol (PBMR-M) or oxygen (PBMR-O) as the permeating component. The FBR performance was obtained by simply plugging off the inner membrane inlet, which gave the same results as a blank tube.

The following parameters were varied during the experiments: reactant feed concentrations (CH_3OH and O_2), residence time and temperature. The total flow rate ranged from 50 to 300 sccm. Methanol concentration was kept fixed at 6% in all cases, except when its influence was studied. The molar ratio between the nitrogen introduced with methanol and overall streams was varied from 0.2 to 1. For the membrane reactors, the mean residence times for the catalyst bed and membrane were calculated following the method described below. The data were obtained within the temperature range 210–260°C.

In the FBR, residence time is the same for both reactants and is given by the expression

$$t = t_0 \int_0^1 \frac{\mathrm{d}s}{v(s)} \tag{1}$$

where t_0 is the residence time based on overall feed volumetric flow rate.

In the membrane reactor, the segregation of reactants affects the residence time for both reactants differently. For the reactant entering the catalyst bed, t_b is affected by the variation of flow rate, $v(s)$, due to the feed permeating through the membrane. For the reactant entering the membrane, in addition to the effect mentioned above, there is a distribution of residence times, $t_m(s)$ along the catalyst bed, hence, an average value, $\langle t_m \rangle$ is calculated.

The expressions for residence times used in this work are somewhat different from those employed by [18]. To develop these, let us consider a schematic of the flow diagram as shown in Fig. 2. If there is no change in number of moles with reaction, for a uniform membrane we have

$$v(s) = 1 + (s-1)q \tag{2}$$

where q ranges from 0 to 1. Similar to Eq. (1), the local residence time is defined as

$$t_m(s) = t_0 \int_s^1 \frac{\mathrm{d}s'}{v(s')} \tag{3}$$

and its average value gives the residence time for the reactant fed through the membrane.

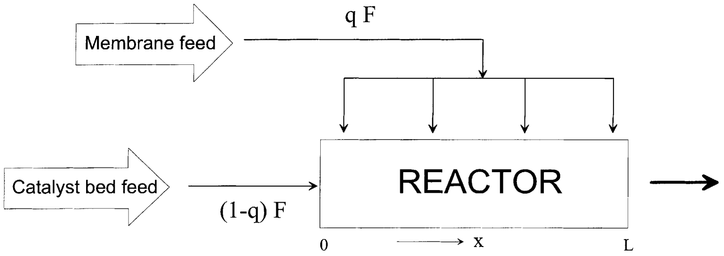

Fig. 2. Schematic flow diagram in the membrane reactor.

$$\langle t_{\mathrm{m}}(s) \rangle \geq \int_0^1 t_{\mathrm{m}}(s)\,\mathrm{d}s = \frac{t_0}{q}\left[1+\left(\frac{1}{q}-1\right)\ln(1-q)\right] \tag{4}$$

Meanwhile, the residence time for the reactant fed directly to the catalyst bed is given by substituting Eq. (2) in Eq. (1):

$$t_{\mathrm{b}} = -\frac{\ln(1-q)}{q}t_0 \tag{5}$$

The formulas reported by Tonkovich et al. [18] are as follows:

$$\langle t_{\mathrm{m}}(s)\rangle = \frac{2t_0}{q} - \left[1+\frac{2\ln\{1-(q/2)\}}{q}\right] \tag{6}$$

$$t_{\mathrm{b}} = \frac{t_0}{1-(q/2)} \tag{7}$$

A comparison between the two sets of expressions is shown in Fig. 3. It can be seen that for $q < 0.5$, the difference between them is insignificant. For q values approaching unity, it is clear that $\langle t_{\mathrm{m}}(s)\rangle / t_0$ must be close to 1, while t_{b}/t_0 must become infinite. Eqs. (4) and (5) satisfy the correct limits, while Eqs. (6) and (7) exhibit deviations for values of q near unity.

3. Results and discussion

We now consider and compare the performance of FBR and PBMRs. The comparisons are made for identical temperatures, overall flow rates and feed compositions, and catalyst mass.

The first group of experiments was designed to investigate the influence of temperature on reactor performance. It was conducted using the FBR at constant feed conditions (300 sccm, 6% methanol, 20% oxygen, balance nitrogen) and at different temperatures ranging from 210 to 225°C (in 5°C increments).

The second group of experiments showed the influence of overall residence time on reactor performance, the remaining parameters being unchanged. For this, the standard feed composition and a fixed temperature (250°C) were used in the FBR. The residence time was adjusted, in this case, by varying overall flow rate through the reactor.

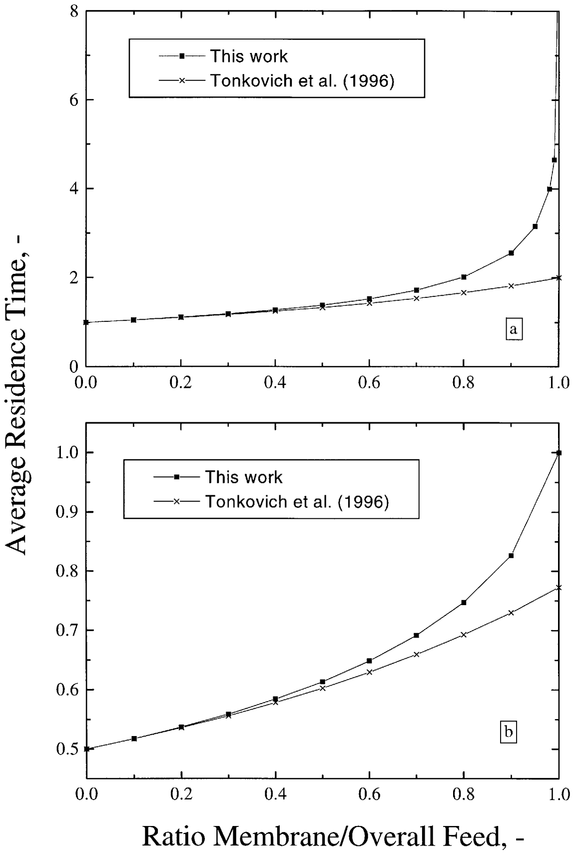

Fig. 3. Variation of the residence time in a PBMR as a function of the fraction of overall flow permeated through the membrane: (a) reactant fed over the catalyst bed; (b) reactant fed through membrane tube.

In the third group, the effect of feed reactant concentrations was studied. Data for a methanol range (1–6%) were obtained for a constant 20% oxygen in the feed. Also, experiments for a constant 6% methanol and varying oxygen levels (3–20%) were carried out.

The fourth group of experiments compares the performance of PBMRs with that of FBR for the same overall feed conditions. The standard feed concentrations and temperature of 250°C were used, but the reactant residence times were varied. This was accomplished, in this case, by changing the split of inert gas (nitrogen) between permeate and catalytic bed feed streams.

The fifth set of data also shows a comparison between the different reactor configurations, when the

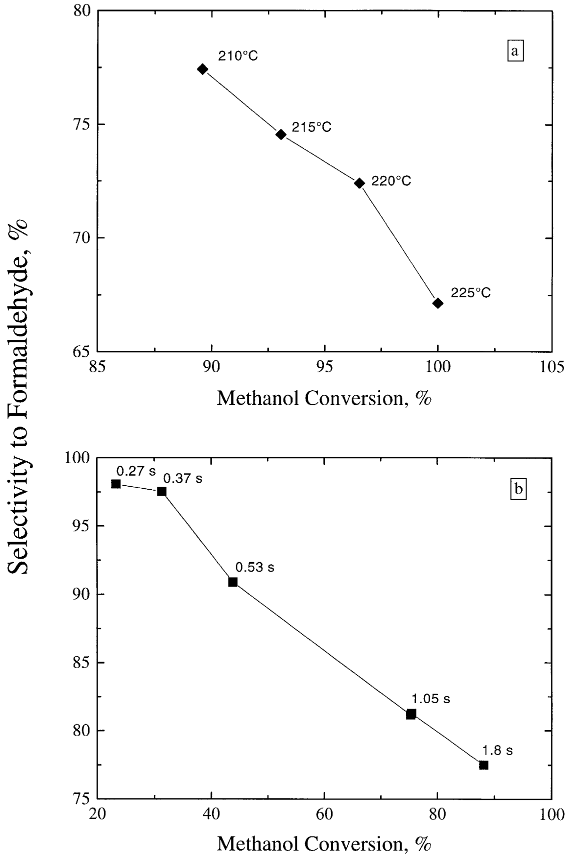

Fig. 4. Methanol oxidative dehydrogenation in a fixed-bed reactor (FBR): selectivity to formaldehyde vs. methanol conversion for 6% methanol and 20% oxygen in feed. Influence of varying (a) temperature at overall residence time 1.8 s and (b) overall residence time at 210°C.

temperature was varied in the range of 210–235°C using the standard feed conditions. In this experiments, nitrogen fed with the methanol stream was fixed as 60% of the overall nitrogen flow.

The influence of reaction temperature is represented in Fig. 4a in a selectivity to formaldehyde versus methanol conversion plot. As expected, there is a continuous decrease in formaldehyde selectivity and increase in methanol conversion as temperature increases. The overall residence time effect, for the FBR configuration, is given in Fig. 4b. It shows a significant decrease in selectivity to the intermediate formaldehyde product with residence time increase, as is typical for consecutive reactions.

The key issue in determining the relative performance of FBR and PBMRs is how the selectivity to formaldehyde depends on reactant concentrations. For this, results of experiments conducted in the FBR are presented in Fig. 5. For a fixed methanol conversion (90%) the formaldehyde selectivity decreases with increasing feed oxygen concentration (Fig. 5a), while it increases with increasing methanol concentration (Fig. 5b). These results clearly imply that the optimal reactor configuration should be PBMR-O, where oxygen is fed through the membrane tube and methanol directly over the catalyst. In this mode, the reactor operates at higher methanol and lower oxygen local concentrations, both factors improving reactor performance.

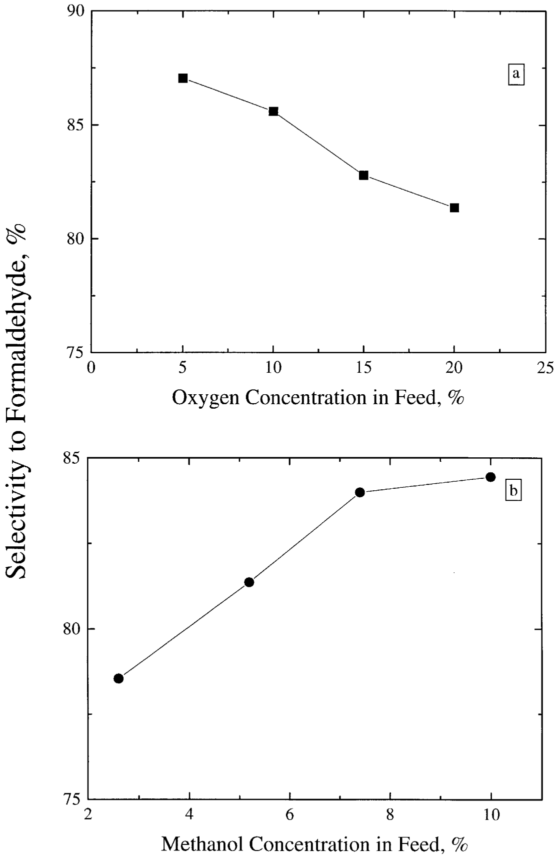

Fig. 5. Methanol oxidative dehydrogenation in a fixed-bed reactor (FBR): selectivity to formaldehyde at 90% methanol conversion and 0.45 s overall residence time as a function of (a) oxygen feed concentration (for 5.2% methanol in feed) and (b) methanol feed concentration (for 20% oxygen in feed).

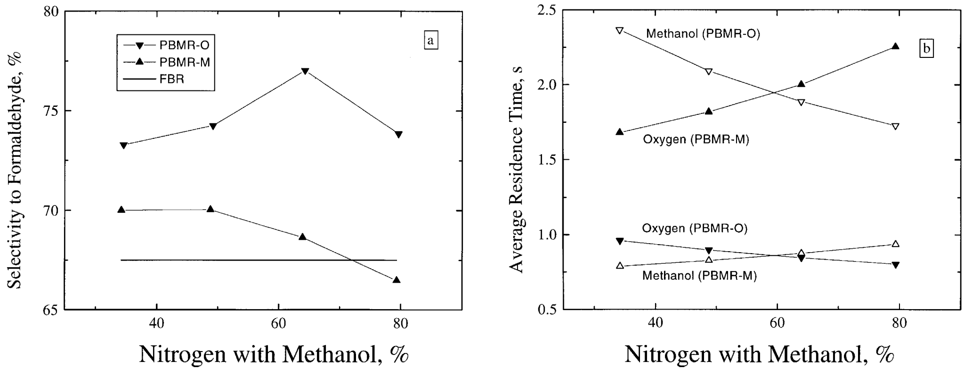

Fig. 6. (a) Selectivity to formaldehyde as a function of percent nitrogen fed with the methanol stream for different reactor configurations, at a temperature of 240°C and 6% methanol, 20% oxygen in feed. (b) Variations of the average residence times, according to Eqs. (4) and (5), for reactants as functions of percent nitrogen fed with methanol stream. Overall residence time is kept constant at 0.72 s.

This expectation was confirmed experimentally. In Fig. 6a, the dependencies of formaldehyde selectivity on inert split between the membrane tube and catalytic bed feeds, are given for both PBMR-O and PBMR-M configurations. The horizontal line on the graph represents formaldehyde selectivity level for the FBR. The corresponding average reactant residence times for both PBMR configurations, computed using Eqs. (4) and (5), are given in Fig. 6b. For each configuration, both reactants follow the same trend: as the fractional nitrogen fed with methanol increases, the residence time for both reactants increases (decreases) for the PBMR-M (PBMR-O).

In Fig. 6a, it may be seen that for increasing N_2 fraction fed with methanol, selectivity to formaldehyde increases for PBMR-O and decreases for PBMR-M. This feature is related to the variation of reactant residence times presented in Fig. 6b, since increasing

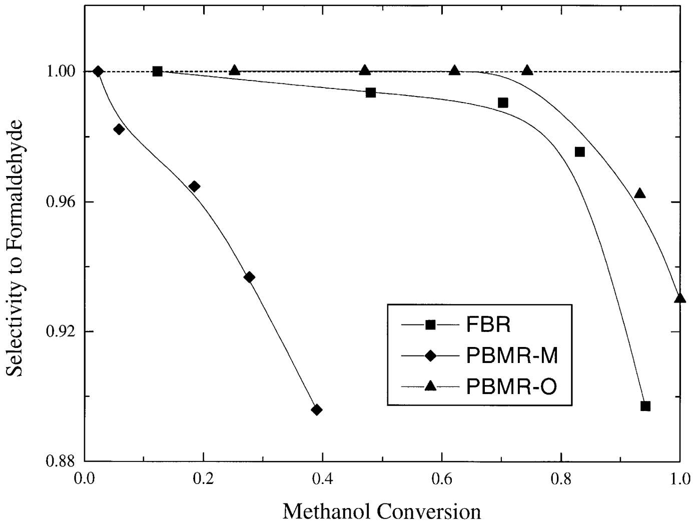

Fig. 7. Comparison between different reactor configurations: selectivity to formaldehyde vs. methanol conversion for 6% methanol and 20% oxygen in feed, with 60% of nitrogen fed with methanol.

residence time leads to decreasing selectivity (see also Fig. 4b). For the case of PBMR-O, the data for the highest nitrogen fraction fed with methanol shows anomalous behavior in Fig. 6a; this feature can be attributed to insufficient radial mixing of oxygen over the catalyst bed, as the stream entering the catalyst bed from the membrane is small and oxygen-rich. Note that the data in Fig. 6a were obtained for essentially complete methanol conversions, so that methanol exhausted somewhere within the reactor and subsequent portion of the catalyst bed degraded the produced formaldehyde. Thus, in the left part of Fig. 6a, the higher values of formaldehyde selectivity for the PBMR-M over the FBR occur because the favorable decrease in methanol residence time for the PBMR-M (see Fig. 6b) overcomes the unfavorable local concentration effect.

The trends outlined in Fig. 6a were also verified for other experimental conditions, where the methanol conversion is limited so that the local reactant concentrations dominate issues related to formaldehyde selectivity. The results shown in Fig. 7 clearly demonstrate that the relative reactor performance is in the order PBMR-O > FBR > PBMR-M. The PBMR-M performance is clearly inferior to the other two reactors. Further, formaldehyde selectivity is higher for the PBMR-O as compared to the FBR, especially at higher methanol conversions which are the most relevant for industrial practice.

4. Conclusion

This work demonstrates that significant improvements in formaldehyde selectivity can be achieved by use of a PBMR as compared to a conventional FBR. This result is similar to that reported by us previously for the ethylene epoxidation reaction [9,11]. However, the optimal configurations for the two reaction networks are different. Specifically, the PBMR with ethylene flowing through the membrane and oxygen over the catalyst exhibits the best performance for ethylene epoxidation, while oxygen through the membrane and methanol over the catalyst is best for methanol oxidative dehydrogenation. The basic principle in both cases is that the reactant flowing through the membrane is the one whose lower concentrations improve desired product selectivity. This issue has been recognized in [12], and these reaction networks may be considered as examples of the general principle.

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