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Catalysis Today 30 (1996) 41–48

CATALYSIS TODAY

Direct oxidation of methane to methanol at atmospheric pressure in CMR and RSCMR

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Abstract

SiO_2 (I) and Mo–Co–O/SiO_2 (II) microporous membranes supported on porous ceramic substrate were prepared using the sol-gel method. Their structures were characterized using SEM, XRD and pore size measurement techniques. An organic additive is useful for the preparation of (I) and could improve the whole surface of the capping SiO_2 and its pore size distribution. Using the (II) and (I) membranes, the catalytic membrane reactor (CMR) and the reactant-swept catalytic membrane reactor (RSCMR), have been composed to investigate the oxidation of methane to methanol by air at atmospheric pressure and at 500–700°C. When the pressure difference between the two sides of the CMR was equal to 0.5 kPa, a good yield of methanol was obtained. The CMR using (II) microporous membrane supported on (I) of pore radius larger than 4 nm results in poor catalytic activity. Under similar reaction conditions at 1.0% methane conversion, the methanol selectivity is 11.2% in CMR and 4.5% in FBR. For the RSCMR at temperatures below 600°C, the methanol yield is similar to that obtained using CMR. At temperatures above 600°C the methanol yield in RSCMR is higher than that in CMR, e.g. at 700°C the methanol yield is 0.5 g/m^2 h in CMR and 0.9 g/m^2 h in RSCMR.

Keywords: Catalytic membrane reactor (CMR); Reactant-swept catalytic membrane reactor (RSCMR); Oxidation; Methane; Methanol

1. Introduction

The predicted shortage in the supply of crude oil will require full use of natural gas as an alternative source of hydrocarbons for many years. As one important developing process, the selective oxidation of methane to methanol has been studied under a wide range of experimental conditions. These studies considered catalyst, reactor, oxidative reactant, reaction pressure and operating conditions [1–3], in which more progress has been made over the past 10 years. A technology breakthrough is however awaited by means of which both a high methane conversion and methanol selectivity can be achieved at the same time.

In a catalytic membrane reactor, both a catalytic reaction and separation processes are involved and the chemical equilibrium is shifted by removing a product through the membrane. Consequently, the catalytic membrane reactor may have advantages over other reactors [4,5]. In this paper, the preparation of a high-temperature resistant 'catalyst/SiO_2/ceramic' membrane was studied. A catalytic membrane reactor (CMR) and reactant-swept catalytic membrane reactor (RSCMR) were used to investigate the reaction of direct oxidation of methane to methanol at atmospheric pressure. Effects of

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SSDI 0920-5861(95)00333-9

the operating conditions on the properties of CMR and RSCMR and the distinction between them were studied. A higher methanol yield was obtained in CMR and in RSCMR than was obtained in a fixed-bed reactor (FBR).

2. Experimental

2.1. Preparation of an inorganic microporous membrane

The 'SiO_2/ceramic' microporous membrane was prepared using the sol-gel method: silica gel was supported on a porous ceramic substrate (the average pore size is ca. 1–1.5 μm, $\Phi = 12 \times 1.5$ mm) and then dried and calcined in air. The 'catalyst/SiO_2/ceramic' catalytic function membrane was prepared by coating catalyst components onto 'SiO_2/ceramic' membrane by impregnation or smearing. Catalyst loading on the membrane was controlled by repeating the catalyst coating step.

2.2. Catalytic membrane reactor (CMR)

The CMR consists of a inner tube (ceramic membrane, $\Phi = 12 \times 1.5$ mm) and a shell tube (stainless steel, $\Phi = 16 \times 2$ mm). Air or oxygen is passed through the inner tube and methane is passed through the shell layer in the meantime. A sudden-cooler in the CMR system was used especially to prevent the methanol produced from decomposing.

2.3. Reactant-swept catalytic membrane reactor (RSCMR)

An operation schematic diagram of RSCMR is shown in Fig. 1. The size of reactor is the same as that in the CMR. Mo–Co–O/SiO_2 (Mo/Co = 5 atomic ratio, 20–40 mesh) catalyst was packed in the inner tube, the amount of catalyst packed being similar to that used in the fixed-bed reactor [6]. When the mixture of methane and oxidant gas flows through the annular space as a sweeping gas, the partial oxidation product methanol is swept out at high speed. This permeates through the membrane from the inner tube. After methanol is absorbed in a water-absorber at 0°C and removed, the remaining gas as the feed goes into the inner tube packed a catalyst, in which the topic reaction takes place. Additional partial oxidation products can be recovered from the stream leaving the reactor.

2.4. Reactant analysis and microporous membrane characterization

Inlet and outlet composition was monitored using a Model 102G gas chromatograph. CH_4, CO_2, N_2, O_2 and H_2O were separated by Φ 3 mm × 4 m 5A zeolite and Φ 3 mm × 0.5 m

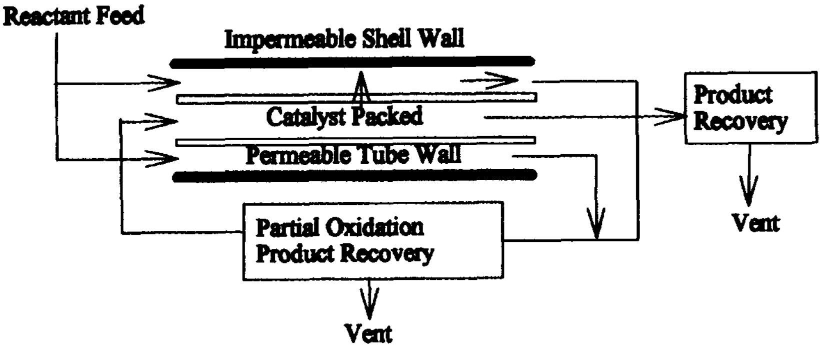


Fig. 1. Operation schematic diagram of a co-current RSCMR.

packed columns and were detected by TCD. For the analysis of CH_3OH, HCHO and a trace amount of formic acid, $HCOOCH_3$ and CH_3OCH_3 absorbed in aqueous solution, the Φ 3 mm × 3 m sorbitol/403 packed column and a FID were used.

The permeation flow of gas through the membrane is defined as: $F_i = F_0 \times C_i$ (F_0 being the flow of sweeping gas; C_i being the concentration of a permeate agent in sweep gas). Permeability (l/min m^2) is: $\rho_i = F_i/S$, (S being the membrane area).

The membrane structure was characterized using SEM (S-250MK II Model, Britain Cambridge), an adsorption porosimeter (ASAP 2400 Model, Micromeritics, USA), XRD (D MAX/RB Model, Japan Rigaku, Cu Kα) and BET surface area analyzer (ST-03 Model, Beijing, China).

3. Results and discussion

3.1. Preparation of 'SiO_2/ceramic' membrane

3.1.1. Effect of organic additive on membrane pore size distribution

An organic additive was found to be useful for the preparation of the 'SiO_2/ceramic' membrane. An appropriate amount of organic additive was added into the silica sol to keep the membrane intact and to enhance its strength and uniformity. If no organic additive is used, the membrane is easy to crack when dried. Pore size distribution data (measured on N_2 adsorbent and He carried gas at 78 K) in Fig. 2A, shows that if the additive is not added into the silica sol, the pore radius of the 'SiO_2/ceramic' membrane prepared is predominantly ca. 5–7 and 10–15 nm. When 5% additive was added to the silica sol, the number of large pores in the membrane decreased and that of small pores increased. After 10% additive was added to the silica sol, its pore radius is predominantly ca. 2.5–4 nm.

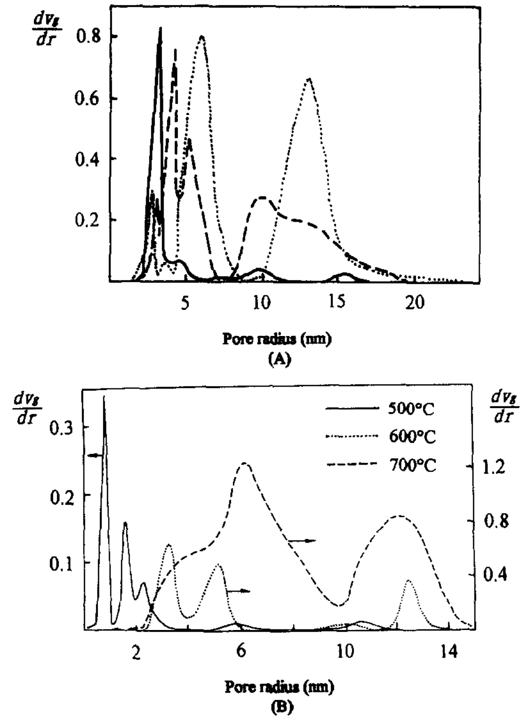


Fig. 2. The pore size distribution of 'SiO_2/ceramic' membrane. (A) Influence of the amount of additive: · · · 0%, – – – 5%, —— 10% and (B) influence of the calcination temperature.

3.1.2. Effect of calcination temperature on the pore size and structure of membranes

XRD study shows that for the 'SiO_2/ceramic' membrane SiO_2 mainly exists in an amorphous phase when calcined at temperatures below 780°C. The crystal phase of SiO_2 was however, observed when calcined at temperatures above 780°C. In this study membranes were calcined at 700°C for 10 h, in order to obtain an amorphous membrane with a higher active surface area.

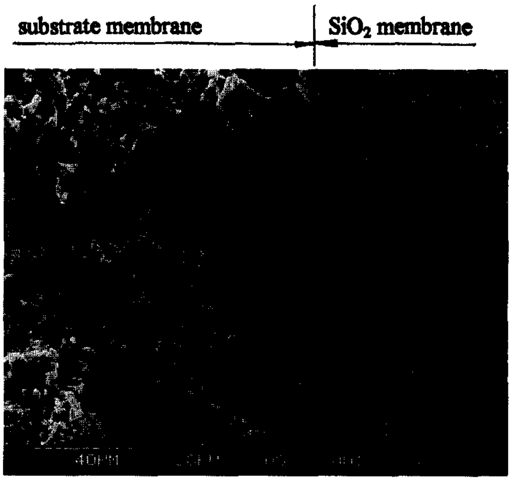
The pore size distribution of the membrane was affected by the calcination temperature. For the 'SiO_2/ceramic' membrane made with ca. 1% additive, its pore size and pore volume increase with increasing calcination temperature. The results shown in Fig. 2B indicate that after calcining at 500°C, the 'SiO_2/ceramic' membrane possesses a large amount of pores which are less than 3 nm in radius. After the membrane was calcined at 600°C and 700°C, pore sizes were mainly distributed between ca. 2–4, 4–6, 12–14, 2–10 and 10–14 nm in radius, respectively. The target reaction, i.e. direct oxidation of methane to methanol, is carried out at 500–700°C, so that this membrane should be calcined at temperatures above 700°C. In this paper, membranes calcined at 700°C are used for the direct oxidation of methane to methanol. The pore radius of the 'SiO_2/ceramic' membrane was controlled between 2–4 nm by adjusting the amount of additive in the silica sol and other preparation parameters.

3.1.3. SEM study

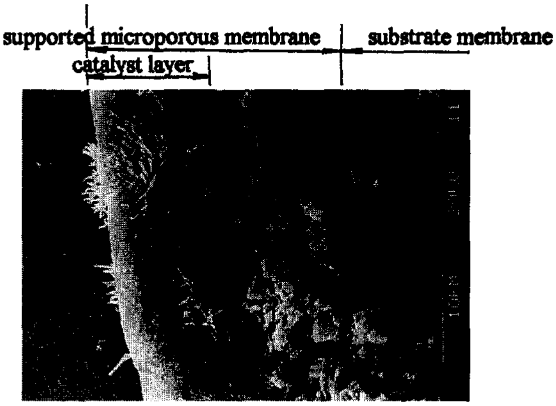
Fig. 3 shows the SEM images of the 'SiO_2/ceramic' and 'Mo–Co–O/SiO_2/ceramic' (Mo/Co = 5 atomic ratio) membranes. The photo clearly indicates a reduction in pore size from base to surface membranes and in its transition between both membranes. The base is loose in comparison with the dense surface layer. It may be concluded that a microporous membrane on a porous supporter can be prepared using the sol-gel method.

3.1.4. Measurement of O_2 permeability

In the measurement of O_2 permeability through a 'SiO_2/ceramic' membrane, air is used as a permeable agent and CO_2 as a sweep gas. The results in Fig. 4 show that the ceramic base membrane is more permeable to oxygen, and that its permeability increases with increasing permeation pressure. When a SiO_2 membrane is coated on the base membrane, O_2 permeability (OP) is significantly reduced and that it increases less significantly with increasing permeation pressure, in comparison with OP through the original base membrane. By comparison with membrane (I) prepared using one coat of silica gel, it can be observed that the OP through membrane (II) which is coated using a double coat of with silica gel, is further reduced. The difference in OP between membranes (I) and (II) is significantly less than the difference existing between membrane (I) and the ceramic base



(A) "SiO_2/ceramic" membrane



(B) "Mo-Co-O/SiO_2/ceramic" membrane

Fig. 3. SEM image of the membrane section.

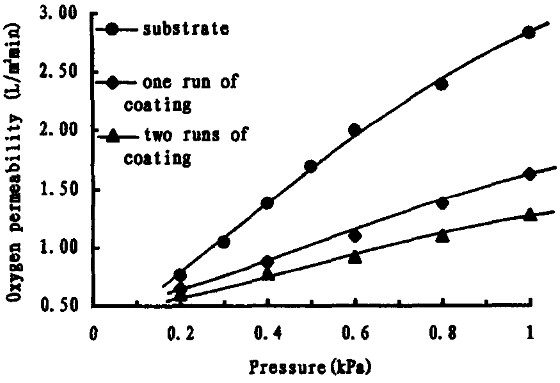


Fig. 4. Influence of the capping microporous membrane on oxygen diffusion.

membrane. It is clear that the multiple coating of SiO_2 on the ceramic membrane could increase the thickness of capping microporous membrane and slightly affect its pore structure and size distribution.

In similar experiments to those investigating O_2 permeability, permeability of N_2 and CH_4 were investigated with similar results being obtained. It is observed that working temperature is a factor which affects the permeabilities of N_2, O_2 and CH_4 through the membrane. At temperatures below 200°C, the permeabilities increase proportionally with increasing temperature and can be ranked in the order of $CH_4 > N_2 > O_2$. At temperatures above 200°C, increasing temperature has very little effect on their permeabilities.

3.2. Oxidation of methane to methanol in CMR

A CMR with 'Co–Mo–O/SiO_2/ceramic' (Mo/Co = 5 atomic ratio) membrane has been used in the oxidation of methane to methanol at atmospheric pressure. For this catalytic reaction process in the CMR, it is observed that influence exercised by the permeability of the oxidation agent through the membrane on catalytic activity is different from that in a fixed-bed reactor (FBR) system.

3.2.1. Influence of the oxidant (air) pressure and reaction temperature

Data in Fig. 5 indicate that CH_4 conversion increases with increasing air pressure. This is attributed to high air pressure leading to a high permeability of O_2 which in turn enhances the concentration of active oxygen in the reaction zone. It has however been observed that only a trace amount of methanol can be detected at 0.15 or 1.0 kPa air pressure. Only when the reaction was carried out at 0.5 kPa was a good yield of methanol obtained Fig. 6.

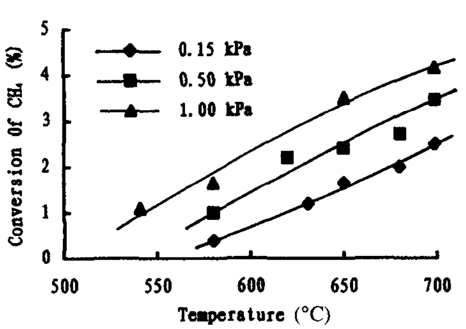


Fig. 5. Conversion of CH_4 as a function of air pressure.

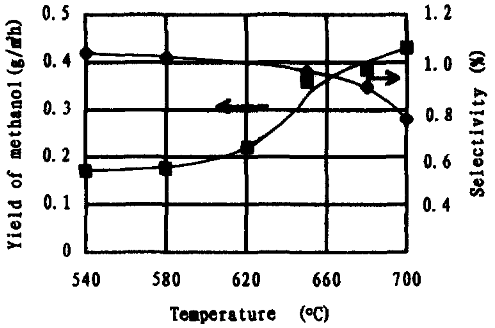


Fig. 6. Yield and selectivity of methanol as a function of temperature (P_{air} = 0.5 kPa, CH_4 = 130 ml/min).

Increasing reaction temperature is effective in terms of enhancing methane conversion Fig. 5 however not in terms of enhancing selectivity with respect to methanol. The effect of temperature on the selectivity of methanol is less significant than it is on the conversion of methane, and a high reaction temperature in the range of 500–700°C is favored to enhance methanol yield Fig. 6.

3.2.2. Influence of the base membrane pore size

Two catalytic membranes made with different base membranes, i.e., 'ceramic' (pore size,

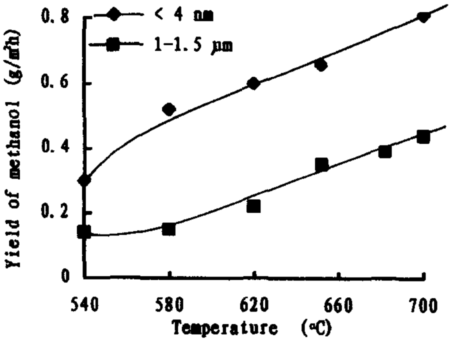


Fig. 7. Influence of the pore size of substrate membrane on the yield of methanol (P_{air} = 0.5 kPa, CH_4 = 130 ml/min).

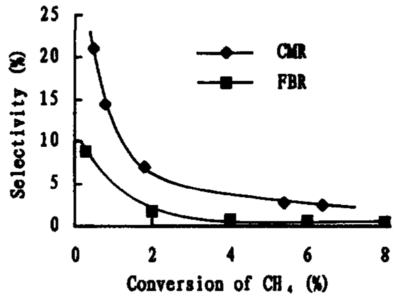


Fig. 8. Comparison of the performance between CMR and FBR.

1–1.5 m) and 'SiO_2/ceramic' (pore radius, < 4 nm), were used in the CMR and the results are shown in Fig. 7. The methanol yield in the CMR using 'SiO_2/ceramic' base membrane is higher than that in the CMR using a ceramic base membrane. This is similar to the results reported by Huang et al. [7]. In this study, the reduction of membrane pore size was limited by the preparation technique used. Membrane pore size should be suitable for O_2 to permeate easily through the catalytic membrane so as to become activated and to react with methane.

3.2.3. A comparison between CMR and FBR

Using the same catalyst composition (Mo–Co–O/SiO_2, Mo/Co = 5) and under similar reaction conditions, performances of CMR and FBR have been compared. The results are shown in Fig. 8. At a methane conversion of 1.0%, the selectivity of methanol is 11.2% in CMR and 4.5% in FBR. At a methane conversion of higher than 3% the selectivity of methanol is higher than 3% in CMR and nearly 0% in FBR.

3.3. Oxidation of methane to methanol in RSCMR

The reactant-swept catalytic membrane reactor (RSCMR) has many similarities to an inert-swept catalytic membrane reactor (ISCMR). The difference between them is that the RSCMR does not require a membrane permselective to methanol, while the ISCMR requires one [8,9]. As can be seen in Fig. 1, the reactant gas in the inner reactor does not permeate through the tube wall because there is no driving force to enable it to do so. The partial oxidation products can permeate through the wall from the inner (reactor) tube and be recovered to avoid further reaction. There are two important factors affecting the behavior of RSCMR. One is its inherent properties as indicated in the Damkohler number (*Da*) and the Peclet number (*Pe*) of the membrane. *Da* can be varied by changing the reactor length and diameter, the molar flow rate of methane on the shell (annular), etc. *Pe* can be varied by changing the reactor diameter, membrane thickness, diffusion coefficient of methane in the membrane, the molar flow rate of methane, etc. *DaPe* is a dimensionless number. At both very high and very low values of this dimensionless number, the reactor will behave just like a plug flow reactor. This means that the RSCMR can always be expected to perform as well as, or better than a plug flow reactor [9]. Another factor affecting the behaviour of the reactor are the conditions under which it operates, e.g. temperature, flow of feed gas, etc., which affect not only the operation of the catalyst bed, but also the flow of the sweep gas and diffusivity of the product methanol. Based on the specific properties of the RSCMR and similarity in the dimensions of the base membrane, the effects of the operating conditions on the properties of RSCMR have been studied to define optimum conditions in terms of utilizing methane.

3.3.1. Influence of operating conditions

Influence of air flow: When the flow of methane was fixed at 150 ml/min, methanol yield was varied by changing the flow of air, as shown in Fig. 9. These results indicate that at temperatures above 620°C, methanol yield increases with increasing air flow; at temperatures below 600°C, an air flow of 200 ml/min resulted in the highest methanol yield, and a higher or lower air flow results in a lower yield. In fact, the change in air flow lead to variation in the reactant gas flow and the respective oxygen and methane concentrations.

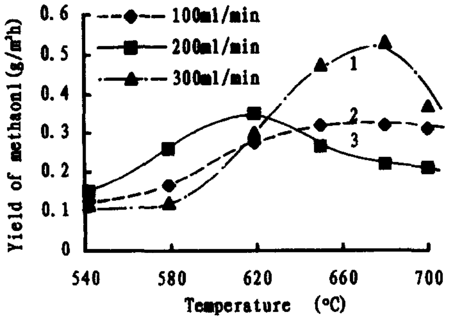


Fig. 9. The yield of methanol as a result of the flow of air (the flow of methane, 150 ml/min). (1) 300 ml/min (O_2 14%, CH_4 33%), (2) 100 ml/min (O_2 8.4%, CH_4 60%) and (3) 200 ml/min (O_2 12%, CH_4 43%).

Influence of oxidant concentration: In FBR, O_2 as an oxidant is better than air for the direct oxidation of methane to methanol at atmospheric pressure [6]. An analogous result was obtained in RSCMR (shown in Fig. 10), which shows that the operational nature of the RSCMR is similar to that of the FBR. As shown in Fig. 10, methanol yield can be enhanced by using a higher concentration of oxygen.

Influence of methane flow: Fig. 11 shows the effect of methane flow on the yield of methanol. It is clear that the increase in methane flow is related to higher methanol yield in both cases in which oxygen or air was used as the oxidant. A higher flow of methane plays a role in increasing the concentration of methane and the flow of a sweep gas.

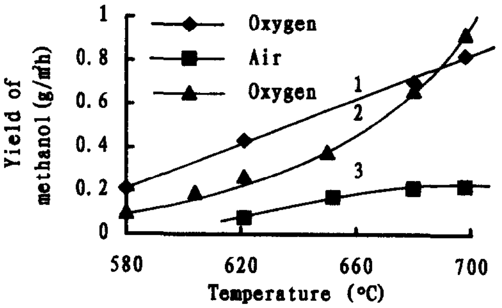


Fig. 10. The yield of methanol as a result of the flow of the oxidant (the flow of methane, 130 ml/min). (1) O_2 200 ml/min (O_2 61%, CH_4 39%), (2) O_2 100 ml/min (O_2 43%, CH_4 57%) and (3) air 200 ml/min (O_2 13%, CH_4 39%).

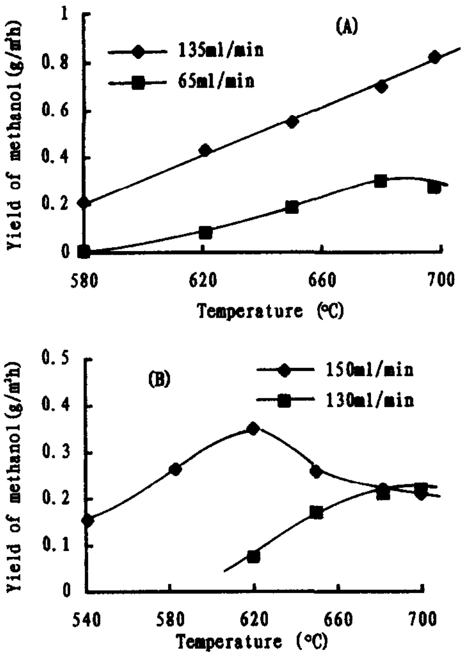


Fig. 11. The yield of methanol as a result of the flow of methane (the flow of an oxidant, 200 ml/min). The oxidant: (A) O_2 and (B) air.

3.3.2. *A performance comparison between RSCMR and CMR*

A comparison of performance between RSCMR and CMR under the same operating condition has been done and results are shown in Fig. 12. This study shows that at temperatures below 600°C, the catalytic reaction system of RSCMR is little different from that of CMR; at temperatures above 600°C the yield of

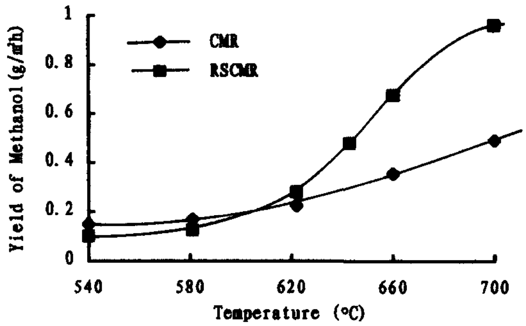


Fig. 12. The yield of methanol as a result of the reaction temperature (CH_4: 130 ml/min, O_2: 200 ml/min).

methanol in RSCMR is significantly higher (about 100%) than that in CMR, for example, the yield of methanol at 700°C is 0.5 g/m^2 h in CMR and 0.9 g/m^2 h in RSCMR, respectively. It is clear that the removal of the product from the reaction zone in time is an important way to enhance methanol yield, particularly at higher reaction temperatures since this prevents the methanol from secondary reaction or decomposition. Under the reaction conditions tested in this study, the RSCMR has more advantages when compared to the CMR and the FBR.

3.4. Decomposition of methanol in membrane reactors

Based on characteristics of the RSCMR, the CMR and operating limits, we selected 115 ml/min N_2 instead of methane gas for in the CMR, and 400 ml/min air instead of the reactant gas for in the RSCMR in order to investigate methanol decomposition. Methanol decomposition curves as shown in Fig. 13, indicate that the decomposition of methanol in the RSCMR is slower than it is in the CMR. T_s (at this temperature 50% methanol has decomposed) in the CMR and RSCMR is ca. 340 respectively, 430°C. Methane and the oxidant flow separately along two sides of membrane in the CMR, which differs from the RSCMR system. The flow of a sweep gas air in the CMR is less than the flow of the mixture of methane and air as a sweep gas in the RSCMR. A high flow of a sweep gas in the RSCMR can ensure that the product methanol is removed rapidly from the reaction zone so that decomposition thereof is prevented. At temperatures above 600°C the decomposition of methanol is still very fast, which results in a decrease in the yield of the product in the RSCMR system. The conclusion can be drawn that the main reason for low methanol yield in the topic reaction is that the product methanol decomposes too rapidly at high reaction temperatures for the product to leave the reactor. We look forward to the development of a highly active catalyst for this topic reaction, which would enable this reaction to take place at lower reaction temperatures.

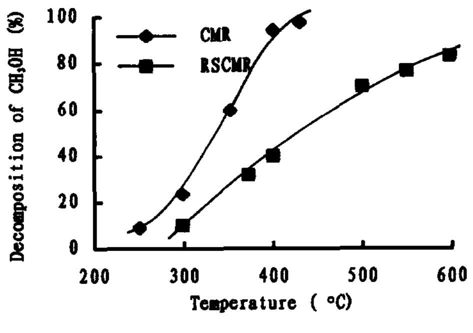


Fig. 13. The curves of methanol decomposition in CMR and RSCMR (Carrier gas: CMR, N_2 115 ml/min, RSCMR, air 400 ml/min).

Acknowledgements

This project was supported by the Academic Foundation of Shanghai Municipal Higher Education Bureau for Young Teachers.

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