

Research Note

The influence of the permeation regime on the activity of catalytic membranes for methane combustion

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Abstract

The influence of the permeation regime on the performance of catalytic membranes used for methane combustion has been investigated. To this end, membranes with different loadings of the active phase (Fe_2O_3) and different Knudsen contributions to the permeation flux have been prepared and used in combustion. A clear correlation has been found between the proportion of flux in the Knudsen diffusion regime and the light-off temperature for the membranes tested.

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1. Introduction

In recent years extensive efforts have been undertaken to develop combustion catalysts based on transition metals as an alternative to Pt- and Pd-based catalysts. This has included pure metal oxides (Cu, Co, Mn, Cr, Fe) either as bulk or supported catalysts, doped metal oxides, and hexaaluminate and perovskite-type materials. A recent review [1] gives a good summary of these efforts. The main challenge in this field is to obtain highly active catalysts that at the same time are stable at the high temperatures required for the combustion of lower alkanes in general and of methane in particular.

In addition to catalyst development, a parallel, though somewhat less intense, research effort has been aimed at the investigation of more efficient modes of contact between the gas phase molecules and the combustion catalyst. In this area, flowthrough catalytic structures are particularly noteworthy since their use often results in a decreased mass transfer resistance and/or improved heat transfer, leading to a more efficient combustion. Catalytic foam burners (on metal or ceramic foams) [2,3] and fibres [4,5] are examples of alternative reactors that have been investigated for methane combustion on account of their increased heat removal efficiency that leads to lower flame temperatures and reduces

NO_x emissions. In addition, both types of reactors offer the advantages of an immobile catalyst and a short diffusion distance.

An alternative approach in the area of improved gas–solid contact is that of catalytic barriers and filters. These were proposed by Saracco and co-workers [6,7] as dual-function systems for flue gas treatment in which filtration and catalytic conversion were performed simultaneously. The usual arrangement consists of a ceramic filter or a membrane onto which a catalytic material is deposited, and a premixed reactant mixture is forced to permeate through it at the appropriate temperature. A similar type of systems was used in our laboratory [8–10] in the so-called Knudsen-diffusion catalytic membrane reactor. In this case, commercial ceramic membranes were modified not only to introduce catalytic activity but also to reduce their pore size to achieve permeation in the Knudsen diffusion regime. These Knudsen-diffusion catalytic membranes showed high combustion efficiency for different VOCs, such as toluene, hexane, and methylethylketone [9,10], and considerably lower light-off temperatures were observed compared to the case where the same membrane was operated in a monolith-like configuration. These results were explained as a result of operation in the Knudsen-diffusion regime, leading to a more efficient gas–solid contact. However, there could be alternative explanations for the higher efficiency of the Knudsen-diffusion membranes, the main one being the higher probability of bypass in the monolith-like configuration compared to opera-

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tion in the flowthrough mode. Therefore, a more direct proof of the influence of the diffusion regime on membrane performance seems necessary.

In this work we have specifically investigated the influence of the permeation regime on the combustion efficiency of catalytic membranes. To this end, a series of membranes with different degrees of Knudsen contribution has been prepared, and their performance in methane combustion has been compared.

2. Experimental

2.1. Preparation of catalytic membranes

The membranes were prepared on stainless steel (Mott) commercial supports, with a pore size around 5 μm . One end of the permeable zone was welded to a nonporous stainless steel tube, while the other was plugged by soldering a stainless steel cap. The permeation zone was approximately 4 cm long, with 7.5-mm internal diameter, and 9.5-mm external diameter. To provide the necessary catalytic activity, hematite ($\alpha\text{-Fe}_2\text{O}_3$) was deposited inside the membrane pores by impregnation with a saturated aqueous solution of $\text{Fe}(\text{NO}_3)_3$. Impregnation was carried out at 45 $^\circ\text{C}$, in an ultrasound bath, followed by treatment at 180 $^\circ\text{C}$ for 5 h. The impregnation cycle was repeated until the desired weight gain was achieved, and then the membrane was calcined at 600 $^\circ\text{C}$ for 6 h. The Fe_2O_3 content of the membranes was between 2.9 and 6.2%, referred to the total weight of the permeable zone. The only difference between the preparation of the different samples is the number of impregnations carried out and the diverse Knudsen contributions arise from the different load and/or distribution of the Fe_2O_3 deposits. XRD analysis confirmed that the above procedure yielded only $\alpha\text{-Fe}_2\text{O}_3$. The Fe_2O_3 deposits had BET areas around 5 m^2/g .

2.2. Reaction tests

To carry out the combustion experiments, the catalytic membrane was set in a stainless steel module that was placed in an electrical furnace. A mass-flow-controlled mixture containing 3 vol% methane in air was passed over the catalyst with a weight-hourly space velocity (referred to the weight of Fe_2O_3 deposited on the membrane) of 42 h^{-1} . Online gas chromatography was used to analyse the product stream for unreacted methane, CO, and CO_2 . The sensitivity of the analysis was increased by using a methanator coupled to the FID detector in the gas chromatograph. Carbon mass balance closures were always within 4% and usually within 2% for the experiments reported in this work. The light-off temperatures quoted below were determined by fitting the conversion-temperature data to a Boltzman function and then reading the value corresponding to 50% conversion.

2.3. Permeation measurements

To characterize the permeation regime, the membranes were placed in a permeation unit where the permeation flux (pure N_2 at room temperature) and the pressure drop across the membrane were measured simultaneously. The permeation data were fitted to the following equation [11],

$$F = 1.06 \times 10^{-5} \frac{\varepsilon r}{L \tau \sqrt{MRT}} + 0.125 \frac{\varepsilon r^2}{L \tau \mu RT} P_{\text{av}} \\ = \alpha + \beta P_{\text{av}}, \quad (1)$$

where F is the permeation flux normalised per unit of time, area, and pressure difference ($\text{mol}/(\text{m}^2 \text{s Pa})$), P_{av} is the average pressure across the membrane (Pa), M is the molecular weight of the permeating species, and L , ε , τ , and r are the membrane thickness, porosity, tortuosity, and pore radius, respectively. α and β indicate the Knudsen and laminar contributions to the permeation flux. The percentage of Knudsen contribution of each membrane has been defined as $100\alpha/(\alpha + \beta)$.

3. Results and discussion

Fig. 1 shows the permeation flux versus average pressure plot (Eq. 1) for the membranes used in this work. A good linear fit of F vs P_{av} was obtained in all cases, and a considerable variation is apparent from the slope of the different lines, indicating that the laminar and Knudsen contributions present a significant change among the different membranes. The data of Fig. 1 covered a wide interval of Knudsen contributions (evaluated at room temperature and $P_{\text{av}} = 1 \text{ atm}$), from 28 to 90%.

The light-off curves corresponding to these membranes are shown in Fig. 2. Under the conditions used, only CO_2 was detected as a product up to the maximum temperature tested (600 $^\circ\text{C}$). These light-off curves were obtained with

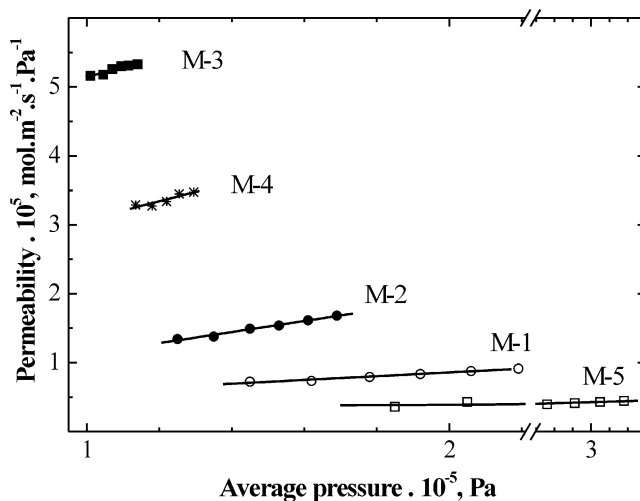


Fig. 1. Permeation flux versus average pressure (Eq. (1)) for the different membranes used in this work.

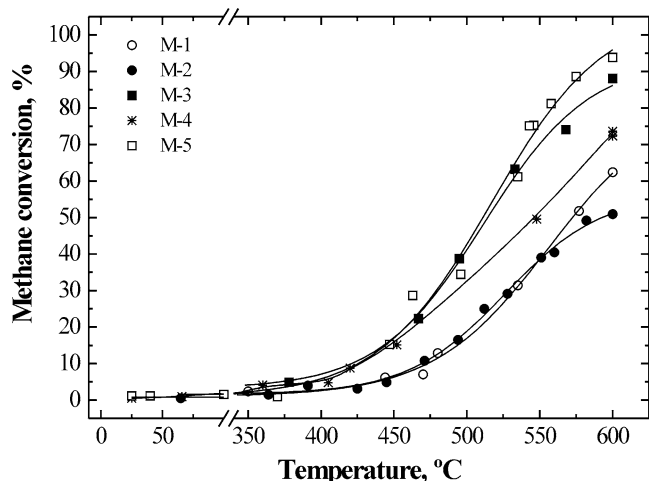


Fig. 2. Light-off curves for the membranes used in this work. Reaction conditions given in the text.

the recently prepared (after calcination) membranes. It is known that unsupported iron oxide undergoes sinterization at high temperatures [12] and therefore some displacement of the light-off curves is expected with time on stream. In this case, however, the maximum temperature was limited to 600 °C, and sinterization was moderate. After the light-off experiments of Fig. 2 were repeated three times, only a small displacement was observed; e.g., the light-off temperature increased from 511 to 525 °C for membrane M-5 and from 592 to 600 °C for membrane M-2.

The light-off temperatures are plotted in Fig. 3 as a function of the percentage of Knudsen contribution found in the permeation experiments. It is clear that a correlation exists: while all the data points in the figure are obtained under the same conditions of temperature and space velocity, the light-off temperature drops markedly as the Knudsen contribution increases (over 80 °C of decrease in the light-off temperature as the Knudsen percentage increased from 28 to 90%). This seems to be a direct consequence of the

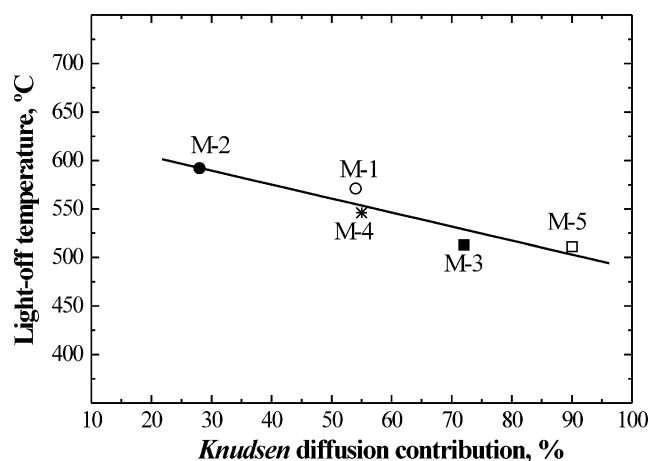


Fig. 3. Light-off temperature as a function of the percentage of Knudsen contribution.

higher contact efficiency achieved in the Knudsen regime: under Knudsen-controlled permeation, the collisions occur mainly between molecules in the fluid phase and the wall of the pores, rather than among the molecules themselves. Since it is precisely on the internal pore surface where the catalyst is located, this scenario implies a reduction of the gas phase diffusion resistance and a higher turnover rate. For reacting systems with slow kinetics, operating in the Knudsen regime would make no difference. However, for fast intrinsic kinetics, as in most combustion reactions, this mode of operation is clearly advantageous, as shown by the results in Fig. 3.

4. Conclusions

The diffusion regime has a direct effect on the gas–solid contact efficiency of catalytic membranes, and therefore on their performance as catalytic reactors. A clear relationship has been established between the percentage of Knudsen contribution in forced permeation through catalytic membranes and the apparent activity of the catalytic material (measured by the decrease in the light-off temperature for methane combustion). While an increase in the percentage of Knudsen contribution is always obtained at the expense of a larger pressure drop, the decrease of reaction temperature is substantial, and this may justify Knudsen-flux combustors, especially for small-scale applications requiring a high combustion efficiency, such as the incineration of hazardous compounds.

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