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La_2NiO_4 tubular membrane reactor for conversion of methane to syngas

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Abstract

La_2NiO_4 tubular membranes of relative density over 92% were used to separate oxygen from air and facilitate the partial oxidation of methane to H_2 and CO at 900 °C. When methane was fed into a tube of inner surface area 5.11 cm^2 at a rate of 10.5 ml/min, methane throughput conversion was 89%, CO selectivity 96%, H_2/CO ratio 1.5, and the equivalent oxygen flux was 6.8 ml/min. The surface of the La_2NiO_4 membrane exposed to CH_4 decomposed into La_2O_3 and Ni, while the surface in contact with air remained almost unchanged. It is suggested that the conversion of methane in the membrane reactor involves the reforming of methane by the H_2O and CO_2 catalyzed by nickel.

Keywords: Oxygen-permeable membranes; Membrane reactor; Partial oxidation of methane; Synthesis gas; La_2NiO_4

1. Introduction

Traditionally, syngas, a mixture of hydrogen and carbon monoxide, is produced by reacting methane with steam at high temperatures and pressures. Since the reaction is highly endothermic, steam reforming is very energy- and capital-intensive. An alternative process to produce syngas is the partial oxidation of methane with pure oxygen in the presence of a catalyst [1,2]. A major difficulty with this process lies in the consumption of large quantities of expensive pure oxygen. This difficulty may be overcome by using oxygen-permeable ceramic membranes to integrate the separation of oxygen from air with partial oxidation of methane (POM) [3].

It is reported that La_2NiO_4 possesses appreciable oxygen permeability at elevated temperatures [4]. It is also reported that La_2NiO_4 decomposes into Ni and La_2O_3 [5,6]. The as-formed nickel should be able to catalyze the partial oxidation of methane [7]. Based on these considerations, we envisaged an La_2NiO_4-based catalytic tubular membrane reactor for conversion of methane to syngas.

2. Experimental

2.1. Membrane preparation

Mixture of La_2O_3 (AR) and NiO (CP) in a desired ratio was ball milled for 24 h, and calcined at 1000, 1100 and 1230 °C all for 10 h in air with intermediate ball milling for 24 h. The calcined powder was admixed with some organic additives, and extruded to form tubes. The tubes were sintered at 1250 °C for 20 h. The phase composition of the membrane was analyzed by X-ray diffraction (XRD; D/Max-rA, Japan).

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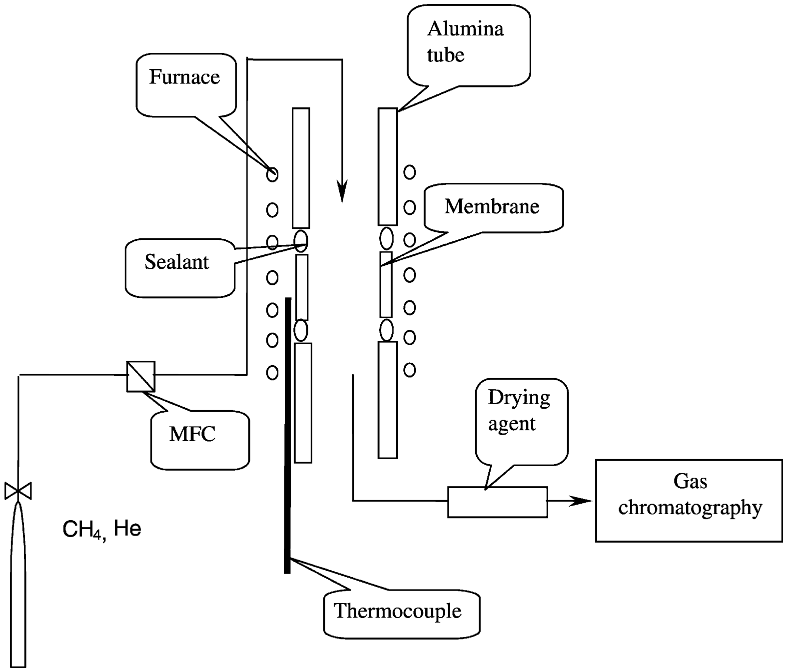

Fig. 1. The schematic diagram of the experimental setup.

The density of the membrane was determined by using the Archimedes' method.

2.2. Oxygen permeation measurements

An La_2NiO_4 tube of relative density 92%, length 2.0 cm, inner diameter 0.73 cm and wall thickness 0.12 cm (inner membrane surface area 4.58 cm^2) was placed between two alumina tubes and sealed with glass rings at 950 °C, as shown in Fig. 1. An oxygen partial pressure difference was applied to the tube by exposing the shell of the tube to air and sweeping the inner wall of the tube with a high purity of helium (36 ml/min) or a mixture of helium (36 ml/min) and methane (32 ml/min). The effluent was analyzed by on-line gas chromatography (Varian 3400), in which H_2, O_2, N_2, CH_4 and CO were separated by 5A molecular sieve column and CO_2 by GDX-502 column, and H_2O was determined using a hydrogen atomic balance. The oxygen permeation flux was calculated from the concentration of the oxygen or the oxygen-containing species and flow rate at the outlet. Besides the permeated oxygen, some oxygen may leak from the air side to the oxygen-lean side. The leaked oxygen was estimated from the nitrogen concentration detected [8]. In all the cases, the leaked oxygen made up less than 1% of the total oxygen flux.

2.3. Partial oxidation of methane

The experimental setup for partial oxidation of methane was similar to that for the oxygen permeation measurement. A tubular membrane of length 2.2 cm, inner diameter 0.74 cm and wall thickness 0.12 cm (inner membrane surface area 5.11 cm^2) was used to construct a reactor with pure methane being fed into the tube at a rate of 5.4–45 ml/min and the shell exposed to air. The CO selectivity was calculated from the total amounts of the products formed. In order to examine the catalytic activity of La_2NiO_4 towards the POM, a fixed-bed reactor experiment was conducted using La_2NiO_4 as a catalyst. Powder of 500 mg with particle size in between 246 and 350 μm was placed at the bottom of the fixed-bed reactor. Methane and oxygen were introduced into the reactor at the same time with methane feeding rate at 33 ml/min, and oxygen at 16.5, 11.3 and 21.7 ml/min.

3. Results

3.1. Oxygen permeation

Fig. 2 shows the Arrhenius plots of the oxygen permeation fluxes in different gradients for a tubular membrane of inner surface area 4.58 cm^2. In the air/helium gradient, the oxygen partial pressure at the oxygen-lean side was ~0.03 bar. The apparent activation energy was calculated to be 43.4 ± 3.3 kJ/mol. As temperature changed from 930 to 840 °C, the oxygen flux decreased from 0.81 to 0.56 cm^3/min (STP), the corresponding oxygen flux densities normalized to the inner surface area of the membrane were 0.18 and 0.12 cm^3/cm^2 min (STP), respectively. In the case that the mixture of CH_4 and He was fed into the tube, a smaller activation energy of 28.9 ± 2.5 kJ/mol and much higher oxygen permeation flux were observed. The oxygen flux was 8.47 cm^3/min (STP) at 930 °C and 6.79 cm^3/min (STP) at 845 °C, and the corresponding flux densities were 1.85 and 1.48 cm^3/cm^2 min (STP), respectively. The cause for the high oxygen flux in the air/helium, CH_4 gradient is obvious. Since CH_4 is available at the oxygen-lean side, the permeation of oxygen is coupled with the (partial) oxidation of methane. This provides a large driving force for the oxygen permeation in terms of thermodynamics. Moreover, the permeated oxide ions need not recombine into oxygen molecules at the oxygen-lean side; instead, they can directly react with the adsorbed methane, which process is favorable in terms of kinetics.

3.2. Partial oxidation of methane

When pure methane was fed into the tubular membrane of inner surface area 5.11 cm^2 at 900 °C, initially, the effluent stream consisted mainly of CO_2, H_2O, CH_4 and O_2, and a sharp increase in temperature at the reaction zone was observed by about 7 °C. This reveals that at the initial stage, a highly exothermal reaction occurred:

$$CH_4 + 2O_2 = CO_2 + 2H_2O$$

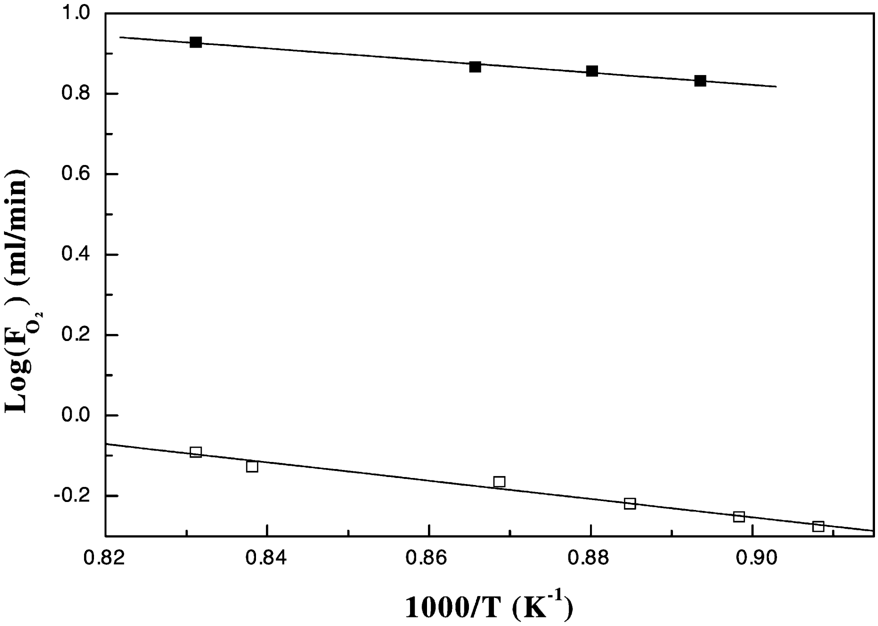

Fig. 2. Temperature dependence of oxygen flux through an La_2NiO_4 tubular membrane in (□) air/helium (36 ml/min) and (■) air/helium (36 ml) + CH_4 (32 ml/min) gradient. Membrane dimension: length 2.0 cm, inner diameter 0.73 cm and wall thickness 0.12 cm (inner membrane surface area 4.58 cm^2).

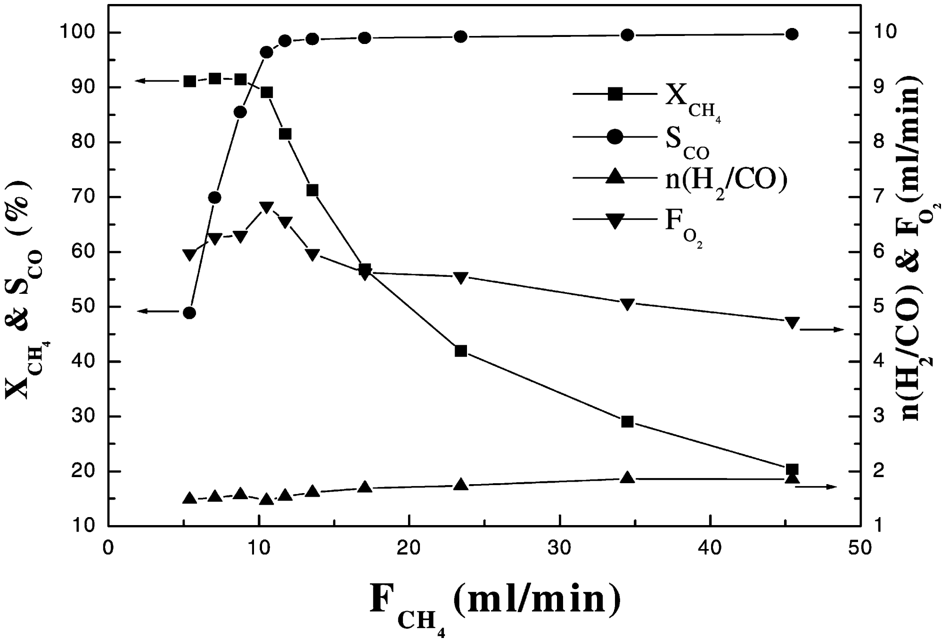

Fig. 3. The performance of an La_2NiO_4 membrane reactor at 900 °C. Membrane dimension: length 2.2 cm, inner diameter 0.74 cm and wall thickness 0.12 cm (inner membrane surface area 5.11 cm^2).

About 20 min after methane was fed into the reactor, appreciable amounts of CO and H_2 appeared. The reaction took ∼100 min to stabilize. At the steady stage, the main products were CO and H_2. Fig. 3 shows the performance of the reactor as a function of the methane feeding rate. It can be seen that with methane rate decreasing from 45 to 5.4 ml/min, both oxygen permeation flux and methane throughput conversion increased, but the CO selectivity and H_2/CO ratio declined slightly. When methane was fed at 10.5 ml/min, the reactor reached an optimal state: methane throughput conversion was 89%, CO selectivity 96%, H_2/CO ratio 1.5 and equivalent oxygen flux was 6.8 ml/min. Note that the H_2/CO ratio is considerably smaller than the stoichiometric number of 2 for the POM reaction. A possible reason for this is that part of the H_2 generated in the fore part of the tubular membrane were consumed by the permeated oxygen at the aft part of the tube.

In order to examine the catalytic activity of La_2NiO_4 towards the POM, a fixed-bed catalytic experiment was conducted at 900 °C, and results were summarized in Fig. 4. It was found that when the CH_4/O_2 ratio was 2, the CO selectivity was as high as 97.8%, methane throughput conversion 97.2%, and H_2/CO ratio 1.6. These results are comparable to those for the tubular membrane reactor operating with the same CH_4/O_2 ratio. When CH_4/O_2 ratio was higher than 2, i.e. the methane was in surplus, and thus conversion was low, but CO selectivity was high. On the contrary, when the CH_4/O_2 ratio was lower than 2, i.e. the oxygen was in surplus, thus part of CO was further oxidized to CO_2, resulting in a lower CO selectivity.

3.3. *Phase composition and stability of La_2NiO_4*

The XRD patterns of the fresh and used membranes are given in Fig. 5. The fresh membrane consists of a single phase that can be indexed based on K_2NiF_4 structure [9]. For the used membrane, at the surface exposed to CH_4, a highly porous layer was formed, and La_2O_3 phase was found, and Ni or NiO should also be present although not detected by XRD, but for the surface exposed to ambient air no change was observed in the phase composition. Examination of La_2NiO_4 powder after the fixed-bed catalytic experiment also reveals the partial decomposition of La_2NiO_4 to La_2O_3 and Ni (or NiO).

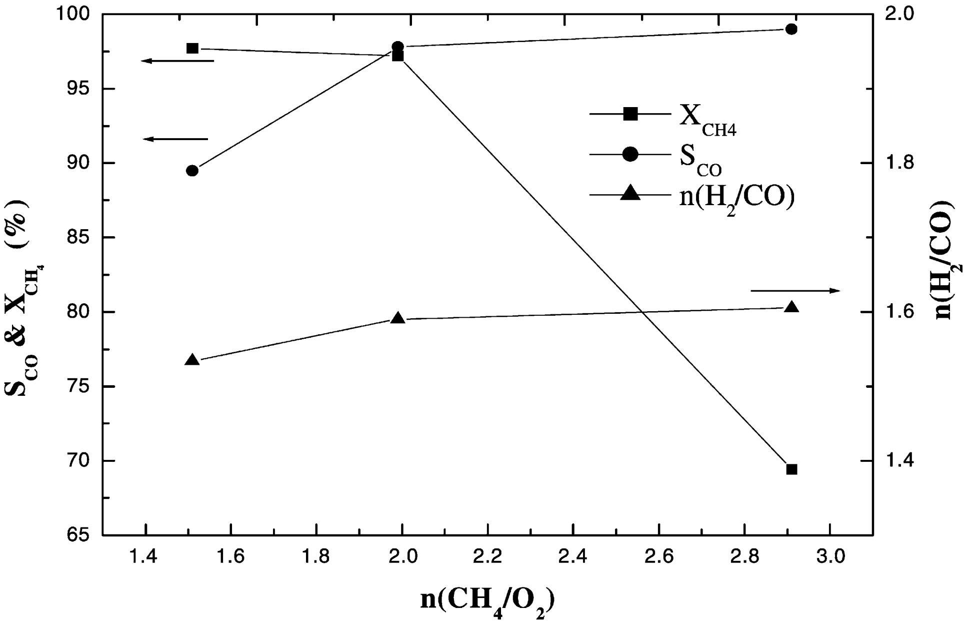

Fig. 4. The performance of the fixed-bed reactor at 900 °C. Catalyst: La_2NiO_4 powder of 500 mg and particle size in between 246 and 350 μm.

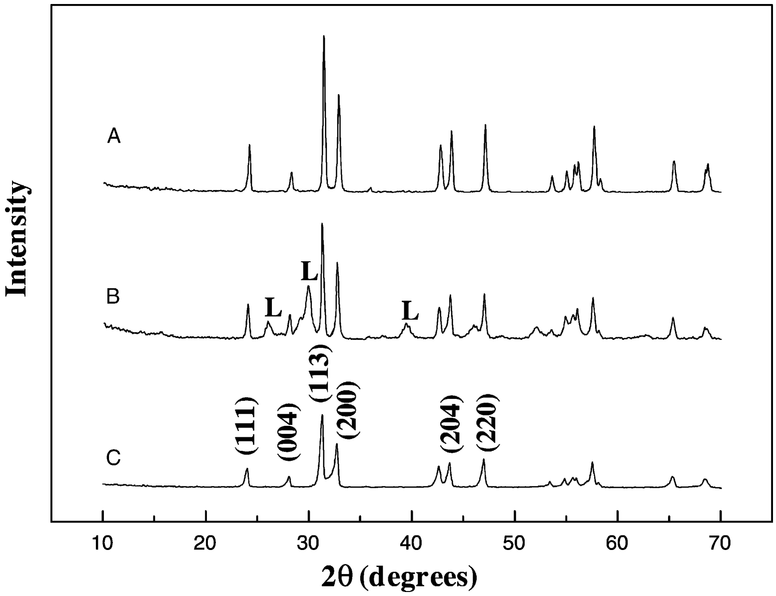

Fig. 5. XRD patterns of La_2NiO_4 membranes taken from (A) the surface exposed to air, (B) the surface exposed to methane and (C) the surface of as-prepared sample. L denotes La_2O_3. The peaks for La_2NiO_4 of K_2NiF_4 structure are indexed.

4. Discussion

Production of syngas from methane in an oxygen membrane reactor has been conducted by a number of groups [3,10–13], but the mechanism remains unclear. The work on the mechanism of the POM in the methane and oxygen co-fed reactor may provide some clue to understanding the reaction mechanism in the membrane reactor. It has been shown by Dissanayake et al. that the conversion of methane to syngas follows oxidation-reforming mechanism in the Ni/Al_2O_3 catalyst bed reactor [7]. In that reactor, at the fore part of the catalyst bed, part of methane react with oxygen, and the resultant H_2O and CO_2 are transferred to the aft part of the bed reactor where the remaining methane are reformed to H_2 and CO. There are evidences that the oxygen-permeable membrane reactor follows the similar reaction mechanism. In disk-shaped perovskite oxide membrane reactors [10,11] and in the present case, the reforming agents H_2O and CO_2 arising from the oxidation of methane with the permeated oxygen are observed in the effluent stream at the initial stage at which the reforming catalyst has not been activated. It has also been revealed recently in the authors' laboratory that as long as the reforming process commences, the reforming agents H_2O and CO_2 are also available through the reactions of the H_2 and CO with the permeated oxygen [14].

5. Conclusions

The oxygen-permeable La_2NiO_4 membrane-based reactor can integrate the processes of separation of oxygen from air with the partial oxidation of methane. The reactor exhibits desirable performance in terms of CO selectivity and CH_4 throughput conversion when the CH_4/O_2 ratio is around 2. The catalytic activity of La_2NiO_4 towards the partial oxidation of methane can be attributed to the presence of nickel metal generated through the partial decomposition of La_2NiO_4.

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