Available online at www.sciencedirect.com

Catalysis Today 93–95 (2004) 257–261

www.elsevier.com/locate/cattod

Catalytic partial oxidation of gasoline to syngas in a dense membrane reactor

Wenliang Zhu, Guoxing Xiong*, Wei Han, Wenshen Yang

State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences,
P.O. Box 110, Dalian 116023, PR China

Abstract

In our previous work, it was shown that LiLaNiO/γ-Al_2O_3 was an excellent catalyst for partial oxidation of heptane to syngas in a fixed-bed reactor at high temperature and the selectivity of CO was about 93%. However, pure oxygen was used as the oxidant. We have developed a dense oxygen permeation membrane $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_3$ that can supply pure oxygen for the reaction. In this work, the membrane was combined with the catalyst LiLaNiO/γ-Al_2O_3 in one rector for the partial oxidation of heptane that is typical component of gasoline. A good performance of the membrane reactor has been obtained, with 100% *n*-heptane conversion and >94% hydrogen selectivity at the optimized reaction conditions.

Keywords: Membrane reactor; Partial oxidation; Gasoline; Syngas; Hydrogen

---

1. Introduction

Increasingly stringent legislation requires the emission from internal combustion engines to the point where the development of alternative power sources for vehicle is impelling. One of the attractive alternatives is the electric motor associated with a fuel cell [1]. And the most technically developed fuel cell is proton exchange membranes (PEMFC) using hydrogen as the fuel [1,2]. Hydrogen is a clean fuel; the only product from PEMFC is water. However, there are no available and reliable transportation and storage techniques for hydrogen. The conversion of hydrocarbon to hydrogen for on-board mobile will play an important role in the near future. In recent years, natural gas, methanol, ethanol and hydrocarbons [3,4] have been studied as fuels for hydrogen production. Among them, gasoline and diesel oil have the following advantages: higher heat value, larger hydrogen content and the available infrastructure all over the world [5]. In refineries and petrochemical industry, naphtha is also used as a hydrogen source by steam reforming [6].

Steam reforming is an endothermic reaction and heat required for reaction is supplied from an external source. By contrast, the partial oxidation is exothermic reaction by using air or pure oxygen as the oxidant. If air is used, the syngas contains about 50% N_2, which consumes substantive heat [7]. Though pure oxygen is an ideal oxidant, it is expensive. In GTL conversion, there is increasing interest to develop dense membranes to supply pure oxygen from air directly for the production of syngas from natural gas, because the capital cost could be potentially reduced by 30% with this technology [8]. The dense membrane $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_3$ we developed was found to be highly permeable to oxygen ($11.5\,mL/cm^2\,min$) at POM reaction conditions. At the same time, the POM catalyst LiLaNiO/γ-Al_2O_3 is also an excellent one for the partial oxidation of heptane to syngas in a fixed-bed quartz micro-reactor. This work is to study the hydrogen production in a membrane reactor by combining air separation by this dense membrane with the partial oxidation of heptane, which is a typical component of gasoline.

2. Experimental

Fig. 1 shows the dense ceramic membrane reactor and flow chart. The membrane $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_3$ was pre-

---

[*] Corresponding author. Tel.: +86-411-84379182; fax: +86-411-84694447.
E-mail address: gxxiong@dicp.ac.cn (G. Xiong).

0920-5861/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2004.06.126

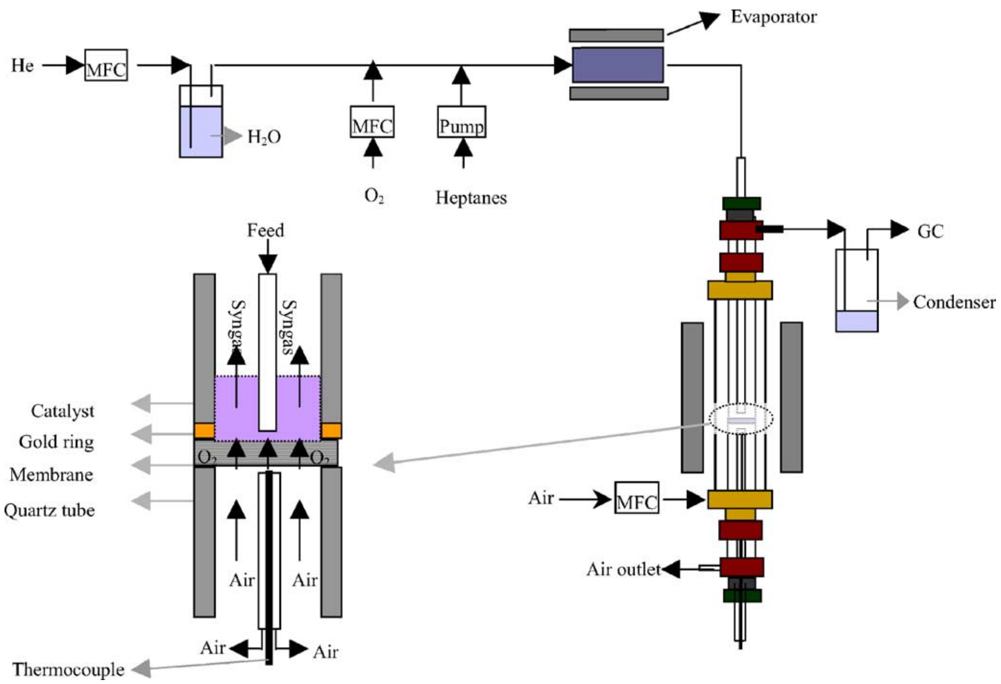

Fig. 1. Reactor configuration and flow chart.

pared as described in the literature [9], and the catalyst LiLaNiO/γ-Al_2O_3 was prepared via the impregnation method according to the report [10], and its performance is shown from the references [11–14]. Heptane was fed by a pump at a constant rate and the steam was brought by He, which was also used to adjust the partial pressure of the reactants. Heptane, water and He were fed into an evaporator. After being vaporized, the gaseous mixture reacted with oxygen, which was supplied by the membrane from the air on the other side. After condensation, the products were analyzed by an on-line HP4890GC with a TCD detector. The purity of heptane was >98.5% and the rest was paraffin with different carbon numbers. A mixture of heptane 40 vol.%, cyclohexane 14 vol.%, toluene 34 vol.% and hexane 12 vol.% simulated the gasoline.

3. Results and discussion

3.1. Blank experiments

Since the membrane reaction is at 800–900 °C, it is necessary to study the homogeneous reaction and carbon deposition of heptane by the thermal cracking. The information can be obtained by blank experiments in a fixed-bed quartz micro-reactor without catalyst at a temperature range of 750–950 °C, and the ratio of W/C (defined as molecular ratio of H_2O/carbon) was 0.42. The results are shown in Fig. 2.

With the increasing of the temperature from 750 to 950 °C, the selectivity of ethene increased from 53 to 72%, and the selectivity of CH_4 increased from 8 to 15%. At the same time, the selectivity of ethane and propylene decreased. The main products are alkenes, which can easily form carbon-deposition. The carbon observed on the reactor wall after the reaction confirmed this.

3.2. The effect of temperature on the membrane reaction

The effect of the temperature on the membrane reaction was investigated, and the results are displayed in Fig. 3(A and B). At the temperature range of 750–950 °C, heptane can be completely converted. Fig 3(A) shows that, with the increasing of the reaction temperature from 750 to 850 °C, the selectivity of CO increased rapidly. However, at a tem-

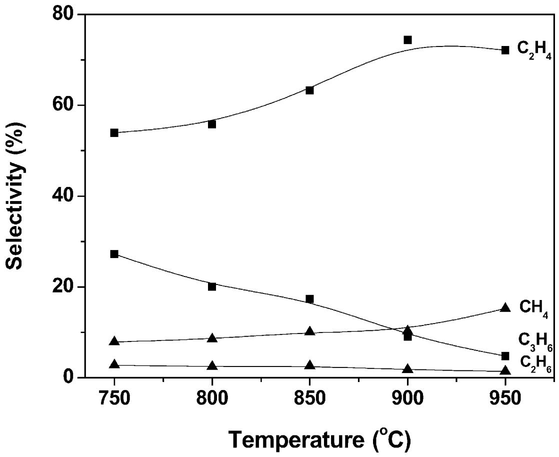

Fig. 2. The effect of the reaction temperature on the selectivity of the products in a blank reaction. Reaction conditions: $T = 850\,°C$, $V_{He} = 35$ mL/min, W/C = 0.42, $V_{air} = 200$ mL/min.

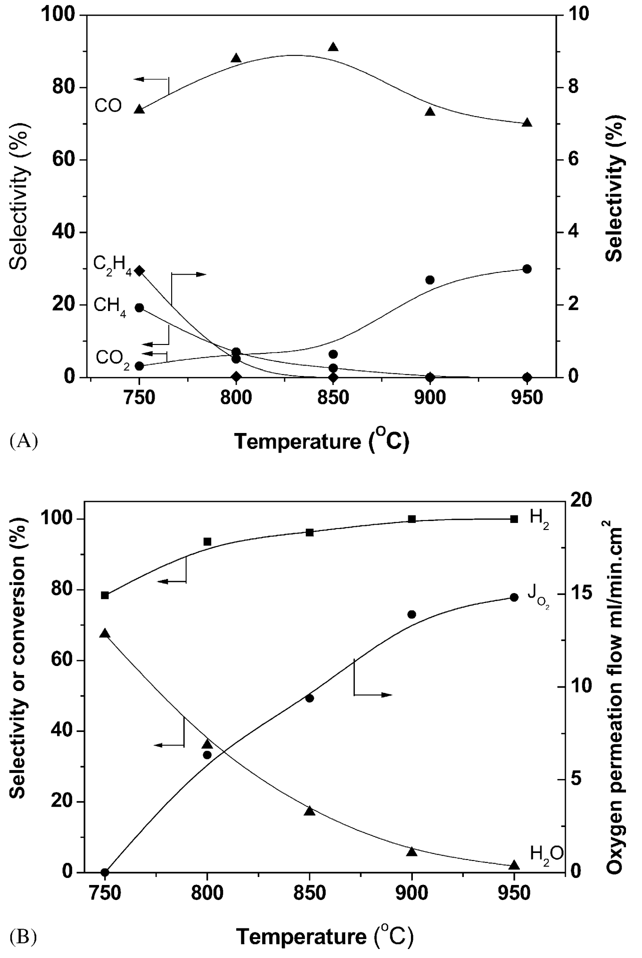

Fig. 3. (A and B) The effect of reaction temperature on the selectivity of the products in the membrane reactor. Reaction conditions: $V_{He} = 35$ mL/min, $V_{air} = 200$ mL/min, $V_{H_2O} = 8.9$ mL/min.

perature >850 °C, the selectivity of CO began to decline, and the highest value was 91%. The selectivity of CH_4, C_2H_4 and C_2H_6 decreased rapidly in the whole range of the temperature (C_2H_6 was not shown in the Fig. 3). At the temperature of 850 °C, no C_2H_4 and C_2H_6 were observed in the products. The selectivity of CO_2 increased with the temperature. The observed phenomenon is due to the increased oxygen supplied by the oxygen membrane, which is a function of the temperature. Fig. 3(B) shows that the oxygen flux gradually increased from 0.0 to 14.8 mL/cm^2 min with the increasing of reaction temperature from 750 to 950 °C. At a lower temperature (<850 °C), the oxygen supplied by the membrane is not sufficient to completely convert all C_2H_6 and C_2H_4 into CO, H_2. Therefore, we observed C_2H_6 and C_2H_4 in the products. As the flux of oxygen grew, the C_2 in the products became less and disappeared at last. Simultaneously, the selectivity of CO reached its highest value. At a temperature >850 °C, the oxygen permeating through the membrane is more than the amount needed for the reaction which converted not only all of the C_2 to CO and H_2, but also produced some CO_2. Thus, the selectivity of CO began to decrease. Fig. 3(B) also shows that the selectivity of H_2 was 100% at 900 °C. The conversion of water decreased with the rising of the temperature. At 950 °C, it was 0%.

3.3. *The effect of the space velocity on the membrane reaction*

Fig. 4(A and B) shows the results of the partial oxidation of heptane (POH) reaction at different space velocities in the membrane reactor. It can be seen that the space velocity affected the membrane reaction drastically.

The space velocity is an important factor on the selectivity of products and the activity of the catalyst. The catalyst LiLaNiO/γ-Al_2O_3 has been shown an outstanding catalyst for the partial oxidation of methane, ethane, and heptane in a fixed-bed reactor. At a high space velocity (2.7×10^5 L/(kg h)) of methane, the selectivity of CO and the conversion of CH_4 still kept at >97 and 95%, respectively. However, the catalytic conversion of heptane in the membrane reactor is expected to be different from the one in the fixed-reactor.

From the Fig 4(A), it can be seen that the selectivity of CO first increased rapidly as the space velocity increased from

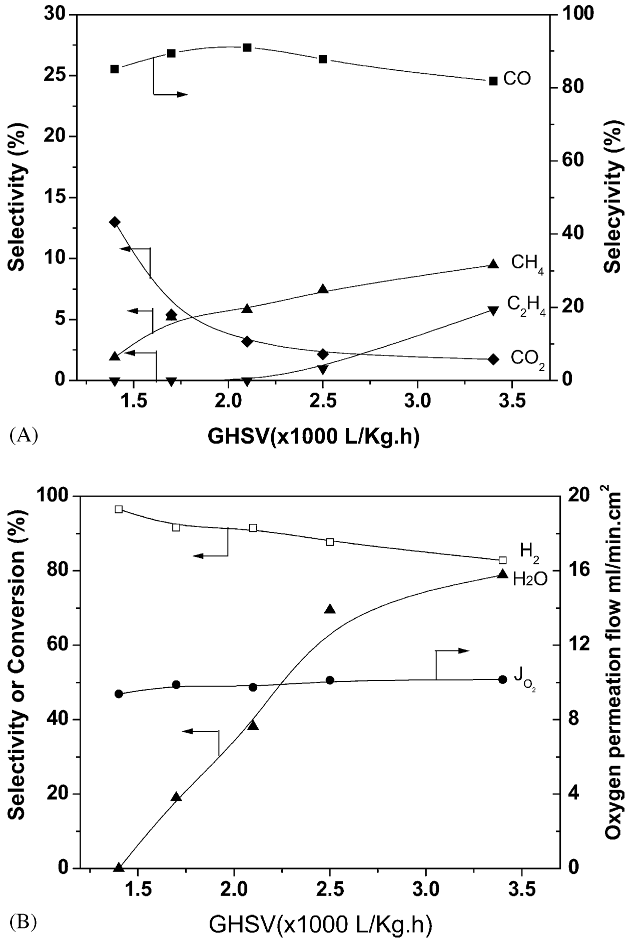

Fig. 4. (A and B) The effect of the space velocity on the selectivity of the products in the membrane reactor. Reaction conditions: $T = 850$ °C, $V_{air} = 200$ mL/min, W/C = 0.42, $V_{He} = 35$ mL/min.

1.4×10^3 to 2.1×10^3 L/(kg h). After reaching a maximum (selectivity: CO 96%, H_2 98%) at the space velocity of 2.1×10^3 L/(kg h), the selectivity of CO began to decline rapidly. Simultaneously, C_2H_4 was observed in the products and the selectivity to this product increased with the space velocity. Fig. 4(B) shows that, in the whole examined range of the space velocity, the oxygen flux almost kept constant around 10 mL/cm^2 min, since the permeation of oxygen is only a function of the temperature at a certain driving force. At a low space velocity, the oxygen permeated from the membrane was sufficient to react with heptane. Higher space velocity means the higher feed rate of heptane, which makes oxygen deficient for the reaction. A space velocity higher than 2.1×10^3 L/(kg h) resulted in undesired product of C_2.

3.4. The effect of W/C on the membrane reaction

Fig 5(A and B) shows the effect of W/C (defined as molecular ratio of H_2O/carbon) at a range of 0.0 to 1.51 on the reaction of heptane in the membrane reactor. Fig 5(A) displays that, When W/C was 0, namely there was no water, a large mount of CH_4, C_2H_4, and C_2H_6 were detected in the products. The selectivity of CO was only 20% and selectivity of CO_2 and H_2 were 0%. At the same time, the pressure was observed to increase and carbon deposited on the catalyst. At this time, the oxygen flux was only 4.8 mL/cm^2 min accordingly (Fig. 5(B)). When water was added to the reactant, the selectivity of CO, CO_2 and H_2 began to increase rapidly. However, the selectivity of methane and ethane decreased. At a W/C ratio of 0.52, the selectivity of CO as high as 98% was obtained, and no C_2H_4 and C_2H_6 were detected. However, further increase of the W/C ratio resulted in a decreased selectivity of CO, and continuous increasing selectivity of H_2.

3.5. The long-term test of the partial oxidation of heptane in the membrane reactor

Fig. 6(A and B) shows the stability of partial oxidation of heptane in the membrane reactor. The reaction was very stable. The heptane converted completely at the reaction

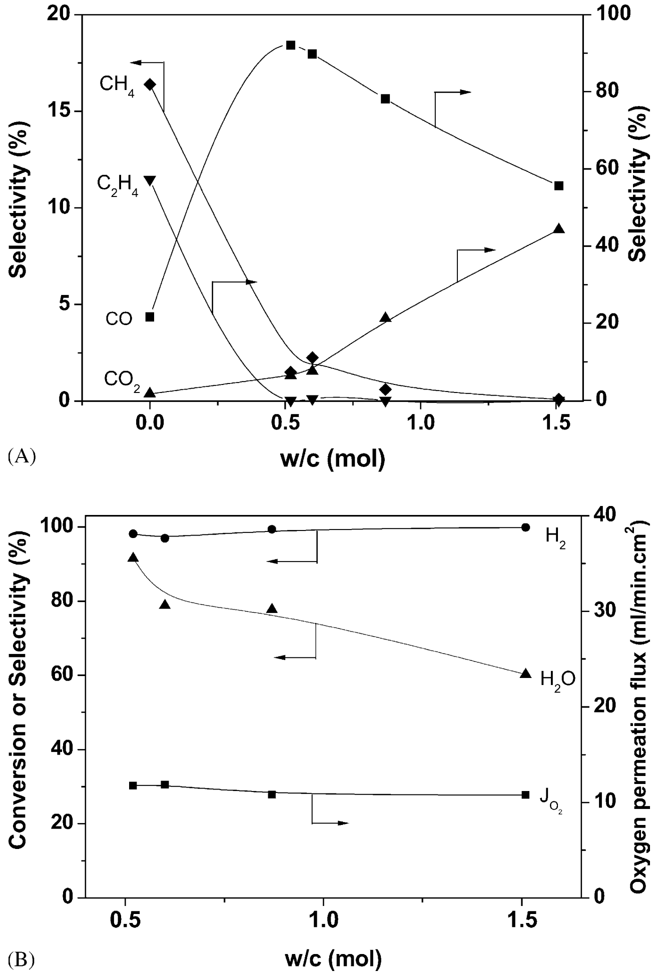

Fig. 5. (A and B) The effect of W/C on the selectivity of the POH products in the membrane reactor. Reaction conditions: $T = 850\,°C$, $V_{He} = 35$ mL/min, $V_{air} = 200$ mL/min.

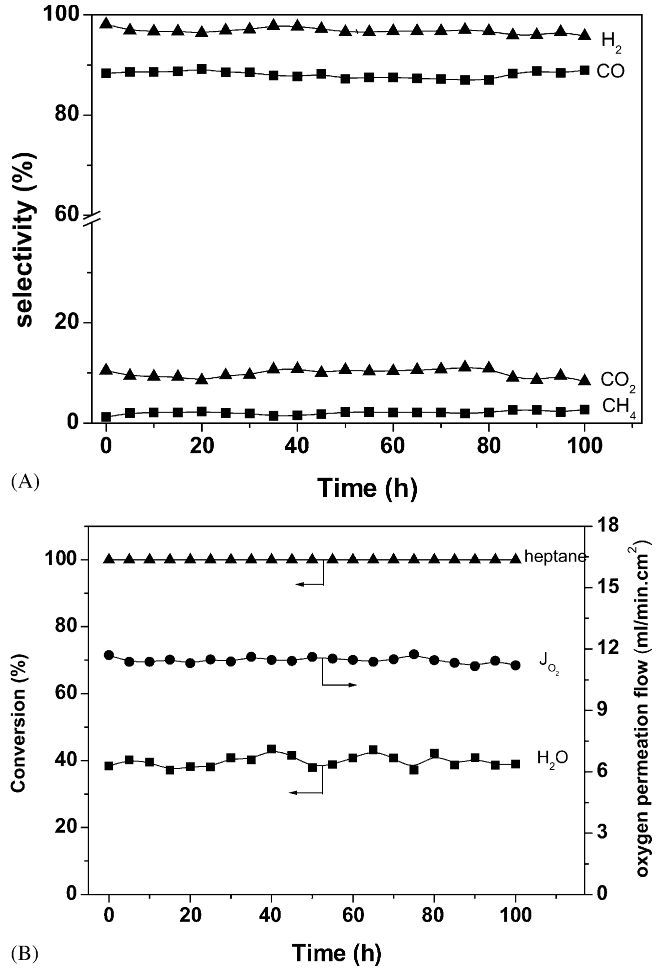

Fig. 6. (A and B) The stability of the partial oxidation reaction of heptane in the membrane reactor. Reaction conditions: $T = 850\,°C$, $V_{He} = 35$ mL/min, $V_{air} = 200$ mL/min, W/C = 0.36.

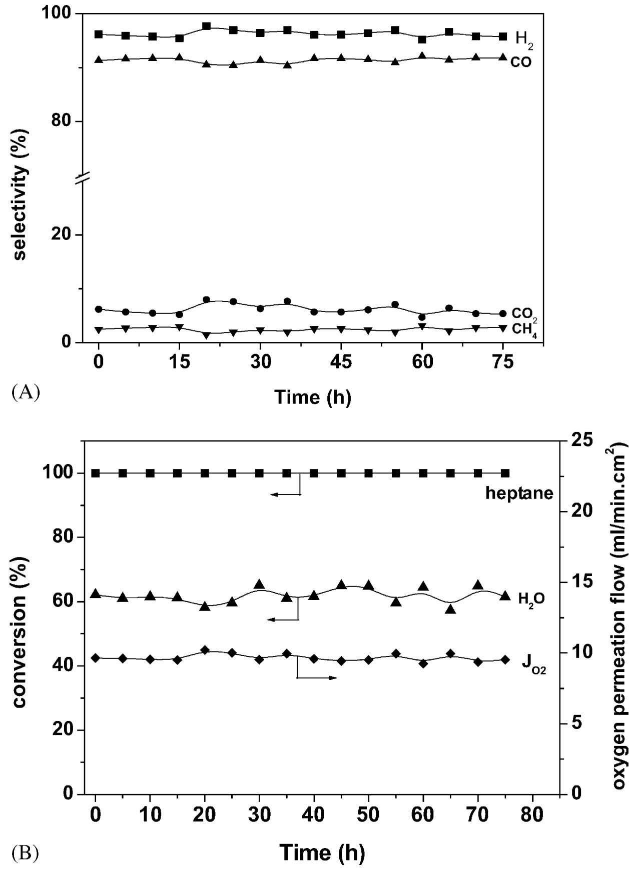

Fig. 7. (A and B) The stability of the partial oxidation reaction of gasoline in the membrane reactor. Reaction conditions: $T = 850\,^{\circ}C$, $V_{He} = 35$ mL/min, $V_{air} = 200$ mL/min, W/C = 0.46.

condition, and the conversion of water was only 40%. The selectivity of CO and H_2 was 91 and 96%, respectively during 100 h (Fig. 6(A)). The oxygen permeation flux kept constant 11 mL/cm^2 min (Fig. 6(B)).

3.6. The long-term test of the partial oxidation of gasoline in the membrane reactor

Fig. 7(A and B) shows the stability of partial oxidation of gasoline in the membrane reactor. A mixture of heptane 40 vol.%, cyclohexane 14 vol.%, toluene 34 vol.% and hexane 12 vol.% simulated the gasoline. During 75 h, the reaction is stable. The selectivity of CO and H_2 were about 91 and 96%, respectively. The conversion of water was about 60% and the oxygen flux was about 10 mL/cm^2 min.

4. Conclusion

At optimized conditions, the conversion of heptanes was 100% and selectivity of CO was 90–92% at a temperature of 850 °C, W/C ratio of 0.51, and a space velocity of 2.1×10^3 L/(kg h). At these conditions, we investigated the long-term performance of the partial oxidation of gasoline in the dense membrane reactor. The catalyst LiLaNiO/γ-Al_2O_3 exhibited a good activity and a favorable stability during 75 h running; simultaneously there was no obviously change in the membrane.

References

[1] T.R. Ralph, G.A. Hards, Chem. Ind. 9 (1998) 337.
[2] W. Vielstich, T. Iwasita, Handbook of Heterogeneous Catalysis, 1997, pp. 20–90.
[3] S. Chalk, S.R. Venkateswaran, Fuel Cell Program, 1996, 258 pp.
[4] M. Krumpelt, S. Ahmed, in: Proceedings of the Annual National Laboratory R&D Meeting of the DOE Fuel Cells for Transportation, Los Alamos, NM, 1998.
[5] Y.H. Wang, D.Y. Wu, Int. J. Hydrogen Energy 26 (2001) 795.
[6] S.R. Hao, Int. J. Hydrogen Energy 23 (1998) 315.
[7] J.P. Lange, Ind. Eng. Chem. Res. 36 (1997) 4282.
[8] C.M. Chen, P.N. Dyer, K.F. Gerdes, C.M. Lowe, S.R. Akhave, D.R. Rowley, K.I. Asen, E.H. Eriksen, Stud. Surf. Sci. Catal. 136 (2002) 45.
[9] Z.P. Shao, G.X. Xiong, Y. Cong, H. Dong, J.H. Tong, W.S. Yang, J. Membr. Sci. 172 (2000) 177.
[10] S.L. Liu, G.X. Xiong, S.S. Sheng, M. Qing, W.S. Yang, Y.H. Zhang, Z.P. Shao, Prog. Nat. Sci. 9 (1999) 198.
[11] S.L. Liu, G.X. Xiong, S.S. Sheng, W.S. Yang, Appl. Catal. A 198 (1/2) (2000) 261.
[12] S.L. Liu, L.Y. Xu, S.J. Xie, Q.X. Wang, G.X. Xiong, Appl. Catal. A 211 (2) (2001) 145.
[13] Z.P. Shao, H. Dong, G.X. Xiong, J.H. Tong, W.S. Yang, J. Membr. Sci. 183 (2001) 181.
[14] H. Dong, Z.P. Shao, G.X. Xiong, J.H. Tong, S.S. Sheng, W.S. Yang, Catal. Today 67 (2001) 3.