R&D NOTE

A Self-Catalytic Membrane Reactor Based on a Supported Mixed-Conducting Membrane

Xueliang Dong, Chun Zhang, Xianfeng Chang, Wanqin Jin, and Nanping Xu
State Key Laboratory of Materials-Oriented Chemical Engineering, College of Chemistry and Chemical Engineering,
Nanjing University of Technology, Nanjing 210009, P. R. China

DOI 10.1002/aic.11477

Keywords: self-catalytic, membrane reactor, mixed-conducting membrane

Introduction

Methane (CH_4), the main component of natural gas, can be converted to liquid fuels, hydrogen, and other value-added chemicals through a syngas intermediate, a mixture of CO and H_2. Currently, partial oxidation of methane (POM)[1] with pure oxygen in the presence of a catalyst is established to be the most potential process for CH_4 conversion because of its greater selectivity to syngas, its exothermicity, and more desirable CO/H_2 ratio. Recently, an important advance in directly using air as a feedstock for POM process is resulted from the application of a mixed-conducting oxide (with high oxygen ionic and electronic conductivities) membrane reactor, which integrated the oxygen separation and POM processes in a single unit.[2] However, one of the formidable problems for this method is that the performance of the membrane reactor is always restricted by the membrane permeability and catalytic activity. For a dense membrane, the oxygen permeability is controlled by two factors: the rate of oxygen ion diffusion within the bulk and the oxygen surface exchange on both sides of the membrane.[3] Thus, oxygen permeability of the membrane can be improved via decreasing the membrane thickness and/or increasing the surface oxygen exchange rate. The preparation of thin supported membrane is an effective approach to decrease the membrane thickness.[4,5] The application of porous catalytic layers on either side or both sides of the membrane results in the enhancement of surface oxygen exchange rates.[6–9] In addition, the catalytic performance of the membrane reactor can be improved by increasing the dispersity of catalyst.

According to above ideas to improve the performance of the membrane reactor, herein we proposed a novel self-catalytic membrane reactor based on a supported mixed-conducting membrane, as shown in Figure 1. $La_2NiO_{4+\delta}$ (LNO), a mixed ionic-electronic conductor with some catalytic activity for CH_4 reforming,[10] was used not only for the membrane support but also for the catalyst precursor. Considering the match of thermal performances between the membrane and the support, $La_2Ni_{0.9}Co_{0.1}O_{4+\delta}$ (LNCO) mixed-conducting oxide was selected as the membrane. The reduction of oxygen to oxygen ion occurs on the membrane side and the POM takes place simultaneously on the support side (Figure 1a). At the initial of POM reaction, CH_4 was oxidized by the support oxide (LNO) to CO and H_2, and simultaneously parts of LNO on the surface of support were reduced to be zero valent nickel and La_2O_3.[11] This process is expressed as follows:

$$CH_4 + La_2NiO_{4+\delta} \rightarrow CO + 2H_2 + La_2O_3 + Ni^0 \qquad (1)$$

It can be considered as a self-catalytic process because Ni^0 as the catalyst for POM reaction can be produced during the reaction.

Experimental

The LNO and LNCO oxides were prepared via a modified citrate process.[12] A dry-pressing technique[4] was used to prepare the supported dense mixed-conducting membranes (see supporting information, S1). Membrane reactor configuration and experimental procedures for POM reaction are similar to

---

This article contains supplementary material available via the Internet at http://www.interscience.wiley.com/jpages/0001-1541/suppmat

Correspondence concerning this article should be addressed to W. Jin at wqjin@njut.edu.cn.

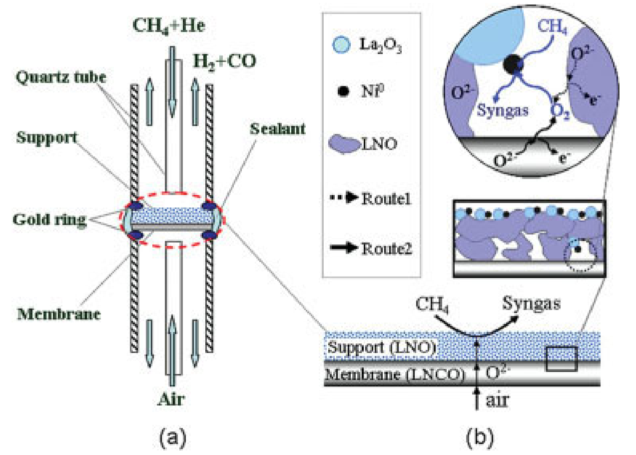

Figure 1. (a) Schematic diagram of the self-catalytic membrane reactor for POM reaction; (b) reaction routes of the self-catalytic membrane reactor for POM reaction.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the previous ones reported by our laboratory (S2).[2] A prepared disk membrane was sealed between two gold rings and mounted on a quartz tube (ID: 6 mm, OD: 12 mm), and the side of the membrane was surrounded with ceramic sealant. The effective area of the membrane for oxygen permeation was about 0.283 cm^2. Air was introduced to the membrane layer surface and CH$_4$ together with He were introduced to the support surface. The flow rates of air, CH$_4$, and He were 80, 2.0, and 18 ml/min (STP), respectively. The effluent streams were analyzed by two online gas chromatographs (Shimadzu Model GC-8A, Japan).

Results and Discussion

The catalytic performance of the self-catalytic membrane reactor at 1123 K was shown in Figure 2. It can be seen that the CO selectivity ($S_{\rm CO}$) is higher than 95%, the conversion of CH$_4$ is kept at about 60%, and the oxygen permeation flux is about 2.3 ml cm^{-2} min^{-1}, which is nearly three times that of the symmetrical LNCO membrane (see supporting information, Figure S3). After 50 h, the $S_{\rm CO}$ decreases slightly with increasing the oxygen flux, which is likely due to the fact that small amount of CO is oxidized by O$_2$ to be CO$_2$. The CO yield of this reactor could be estimated about 4.0 ml cm^{-2} min^{-1}, which is higher than the symmetrical LNCO membrane with a porous Pt/LNCO layer[13] (0.01 ml cm^{-2} min^{-1} at 1123 K) or the symmetrical LNO membrane without additional catalytic layer[14] (about 1.9 ml cm^{-2} min^{-1} even at 1173 K). This indicates that the self-catalytic process is feasible, and the self-catalytic membrane reactor exhibits a high performance for POM reaction.

To further confirm the possibility of the reaction processes that proposed in Eq. 1, the surface chemical composition of the support before (sample a) and after (sample b) POM was analyzed by X-ray photoelectron spectra (XPS). The XPS data were analyzed by the XPS peak fitting program (XPSPeak 4.1) to separate the contribution of La 3d$_{3/2}$ and Ni 2p$_{3/2}$ (see supporting information, Figure S4). For sample a, Ni^0 2p$_{3/2}$ line at 852.3 eV could not be fitted, suggesting the absence of metallic nickel on the support surface before POM reaction. In contrast, for sample b, the Ni^0 2p$_{3/2}$ line can be seen clearly at about 852.3 eV, which suggests the presence of Ni^0 on the surface of the support after POM reaction. This result is also confirmed by the X-ray diffraction (XRD) analysis. From the XRD patterns of the support surface after reaction, Ni^0 peaks can be observed clearly (see supporting information, Figure S5). These results indicate that the reaction process proposed in Eq. 1 is reasonable.

The high performance of the self-catalytic membrane reactor may be attributed to two aspects. First, the oxygen permeability of the membrane reactor is improved by the thin membrane layer and rapid oxygen surface exchange reaction. According to the scanning electron microscope images (see supporting information, Figure S6), the membrane layer thickness is about 130 μm, which decreased the bulk diffusion resistance and improved the oxygen permeability of the membrane. In addition, the porous LNO layer coating on dense LNCO thin membrane performs as a surface modification of dense membrane, which will improve the oxygen surface exchange rate because the effective area for surface oxygen exchange reaction will expand.[6–9] As shown in Figure 1b, there are two routes for the oxidation of oxygen ion to oxygen molecule. In route one, oxygen ion can transfer from membrane to support and then oxidize to oxygen molecule at the surface of the support. In route two, the oxidation of oxygen ion happened at the surface of the membrane. In contrast, the oxidation of oxygen ion only happened in route two for the symmetrical membrane. Therefore, the surface exchange rate of oxygen ion in the proposed membrane reactor was improved. However, from the oxygen permeation flux (about three times that of the symmetrical LNCO membrane at 1123 K), we know that the existence of porous support layer also increases the oxygen diffusion resistance. Therefore, the oxygen permeation flux can be further

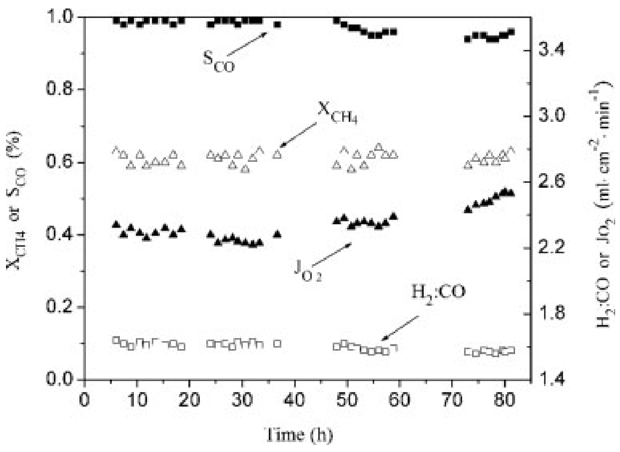

Figure 2. The POM reactivity and the oxygen permeation flux as a function of time in the self-catalytic membrane reactor at 1123 K.

Sweep side: CH$_4$/He = 2.0/18 ml/min^{-1}; air side: air = 80 ml min^{-1}; effective membrane area = 0.283 cm^2.

improved through optimization of the thickness and microstructure of the porous support layer.

Besides the oxygen permeability, the performance of the membrane reactor also depends on the reactor catalytic activity. In this aspect, the self-catalytic membrane reactor has a high-catalytic activity for POM reaction because of the high Ni^0 dispersity. Compared with conventional supported Ni catalyst, the reduced zero valent nickels are dispersed at atomic-scale on the surface of the support. This can be confirmed by the XPS analysis, because the Ni^0 dispersity is always denoted indirectly by the molar fractional content of Ni^0 atom (X_{Ni^0}) on support surface. The result of X_{Ni^0} can be evaluated using the integrated areas of the core-level peaks O 1s, C 1s, La 3d, and Ni 2p. The molar fractional content X_i of one element i (with i = La, Ni, O, C) in an analyzed oxide was calculated with the relation[15]:

$$X_i = \frac{A_i S_i}{\sum_i A_i S_i} \tag{2}$$

where A_i is the area of the peak related to the atom i, and S_i the sensitivity factor of the atom i, which is provided by the XPS apparatus. In this work, X_{Ni^0} is given directly by XPS data to be 0.01, which is lower than the conventional supported Ni catalyst.[16] This demonstrates that metal Ni atom is highly dispersed on the surface of support. Moreover, during the process of POM reaction the Ni^0 was partially oxidized, and NiO was partially reduced. The redox equilibrium was finally attained between the catalyst and the reactant stream.[17] This reversibility of the Ni catalyst avoided the agglomerate and grain growth of Ni^0 during the reaction process. Thus, the membrane reactor shows a self-catalytic property and high efficiency in the partial oxidation of CH_4 to syngas.

Conclusions

In summary, the self-catalytic membrane reactor based on supported mixed-conducting membrane possesses high performance for POM reaction, and the catalytic activity can self-regenerate because of the redox reaction between Ni^0 and NiO during the process of POM reaction. The concept for the novel self-catalytic membrane reactor can also be used for the design and preparation of high efficiency catalytic membrane reactor for conversion of hydrocarbon.

Acknowledgments

This work was supported by the National Basic Research Program of China (No. 2003CB615702), National Natural Science Foundation of China (No.20636020, 20436030), Innovation Foundation for Doctoral Dissertation (No.BSCX200709). The National High Technology Research and Development Program (2006AA030204), and the Natural Science Foundation of Jiangsu Province (BK2006722) of China.

Literature Cited

1. Hickman DA, Schmidt LD. Production of syngas by direct catalytic oxidation of methane. *Science*. 1993;259:343–346.
2. Jin WQ, Li SG, Huang P, Xu NP, Shi J, Lin YS. Tubular lanthanum cobaltite perovskite-type membrane reactors for partial oxidation of methane to syngas. *J Membr Sci*. 2000;166:13–22.
3. Bouwmeester HJM, Burggraaf AJ. Dense ceramic membranes for oxygen separation. In: Burggraaf AJ, Cot L, editors. *Fundamentals of Inorganic Membrane Science and Technology*. Amsterdam: Elsevier,1996:435–528.
4. Chang XF, Zhang C, Jin WQ, Xu NP. Match of thermal performances between the membrane and the support for supported dense mixed-conducting membranes. *J Membr Sci*. 2006;285:232–238.
5. Kovalevsky AV, Kharton VV, Maxim F, Shaula AL, Frade JR. Processing and characterization of $La_{0.5}Sr_{0.5}FeO_3$-supported $Sr_{1-x}Fe(Al)O_3$-$SrAl_2O_4$ composite membranes. *J Membr Sci*. 2006;278:162–172.
6. Deng HM, Zhou MY, Abeles BJ. Diffusion-reaction in mixed ionic-electronic solid oxide membranes with porous electrodes. *Solid State Ionics*. 1994;74:75–84.
7. Lee TH, Yang YL, Jacobson AJ, Abeles B, Milner S. Oxygen permeation in $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ membranes with porous electrodes. *Solid State Ionics*. 1997;100:87–94.
8. Kharton VV, Kovalevsky AV, Yaremchenko AA, Figueiredo FM, Naumovich EN, Shaulo AL, Marques FMB. Surface modification of $La_{0.3}Sr_{0.7}CoO_{3-\delta}$ ceramic membrane. *J Membr Sci*. 2002;195:277–287.
9. Teraoka Y, Honbe Y, Ishii J, Furukawa H, Moriguchi I. Catalytic effects in oxygen permeation through mixed-conductive LSCF perovskite membranes. *Solid State Ionics*. 2002;152–153:681–687.
10. Liu BS, Au CT. Sol-gel-generated $La_2NiO_{4+\delta}$ for CH_4/CO_2 reforming. *Catal Lett*. 2003;85:165–170.
11. Batiot-Dupeyrat C, Valderrama G, Meneses A, Martinez F, Barrault J, Tatibouët JM. Plus study of CO_2 reforming of methane over $LaNiO_3$. *Appl Catal A: Gen*. 2003;248:143–151.
12. Wu ZT, Zhou W, Jin WQ, Xu NP. Effect of pH on synthesis and properties of perovskite oxide via a citrate process. *AIChE J*. 2006;52:769–776.
13. Kharton VV, Yaremchenko AA, Tsipis EV, Valente AA, Patrakeev MV, Shaula AL, Frade JR, Rocha J. Characterization of mixed-conducting $La_2Ni_{0.9}Co_{0.1}O_{4+\delta}$ membranes for dry methane oxidation. *Appl Catal A: Gen*. 2004;261:25–35.
14. Zhu DC, Xu XY, Feng SJ, Liu W, Chen CS. La_2NiO_4 tubular membrane reactor for conversion of methane to syngas. *Catal Today*. 2003;82:151–156.
15. Glorieux B, Berjoan R, Matecki M, Kammouni A, Perarnau D. XPS analyses of lanthanides phosphates. *Appl Surf Sci*. 2007;253:3349–3359.
16. Zhu TL, Stephanopoulos MF. Catalytic partial oxidation of methane to synthesis gas over Ni-CeO_2. *Appl Catal A: Gen*. 2001;208:403–417.
17. Hu YH, Ruckenstein E. Catalytic conversion of methane to synthesis gas by partial oxidation and CO_2 reforming. *Adv Catal*. 2004;48:297–345.

Manuscript received Oct. 9, 2007, and revision received Jan. 29, 2008.