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Mixed reforming of heptane to syngas in the $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_3$ membrane reactor

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Abstract

Fuel cells are recognized as the most promising new power generation technology, but hydrogen supply is still a problem. In our previous work, we have developed a LiLaNiO/γ-Al_2O_3 catalyst, which is excellent not only for partial oxidation of hydrocarbons, but also for steam reforming and autothermal reforming. However, the reaction needs pure oxygen or air as oxidant. We have developed a dense oxygen permeable membrane $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_3$ which has an oxygen permeation flux around 11.5 ml/cm^2 min at reaction conditions. Therefore, this work is to combine the oxygen permeable membrane with the catalyst LiLaNiO/γ-Al_2O_3 in a membrane reactor for hydrogen production by mixed reforming of heptane. Under optimized reaction conditions, a heptane conversion of 100%, a CO selectivity of 91–93% and a H_2 selectivity of 95–97% have been achieved.

Keywords: Membrane reactor; Mixed reforming; Heptane; Syngas; Hydrogen production

1. Introduction

Because of the high energy conversion efficiency and extremely low emission of pollutants, fuel cells are receiving increasing attention worldwide as the most promising new power generation technology for both stationary power plants (for industrial, commercial, and residential application) and mobile power plants for transportation [1]. Hydrogen is the preferred fuel for present generation fuel cells, due to the higher electrochemical conversion rate compared to fossil fuels [2]; furthermore, hydrogen is one of the environmentally friendly fuels. When oxidized with oxygen, the only product is water which meets the increasingly fastidious environmental standards. However, there is not yet an infrastructure for wide storage and distribution of hydrogen. Therefore, it is believed that the development of fuel processors will have great impact on the successful development of fuel cells [1,3]. Consequently, numerous research groups are actively involved in fuel processing studies for on-site (stationary) or on-board (mobile) production of syngas or hydrogen for fuel cells [4].

Through fuel processing, several common fuels can be used as hydrogen source for fuel cells, such as methanol, natural gas, gasoline, diesel oil, kerosene and so on. Liquid hydrocarbon fuels, such as gasoline, diesel oil and kerosene have a higher energy density and a wider distribution network compared to methanol, and thus are promising fuels for on-board and on-site fuel processing for fuel cells.

Three common methods could be employed for the hydrogen production by fuel processing. They are steam reforming, partial oxidation and autothermal reforming. Steam reforming is an endothermic reaction and the heat required for the reaction is supplied from an external source. In contrast, partial oxidation is a weakly exothermic reaction and autothermal reforming is a thermally neutral reaction using air or pure oxygen as oxidant. However, if air is used the syngas produced contains about 50% N_2, which consumes a substantial amount of heat [5]. Though pure oxygen is an ideal oxidant, it is expensive.

In the primary process of GTL (gas to liquid), there has been an increasing interest in developing oxygen permeable dense membranes to supply pure oxygen from air directly for the syngas production from natural gas, because the capital cost could be potentially reduced by 30% with this technology [6]. The dense oxygen permeation membrane

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$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_3$ developed in our laboratory possesses a high permeability for oxygen (11.5 ml/cm^2 min) at reaction conditions [7,8]. We also have developed a LiLaNiO/γ-Al_2O_3 catalyst that is excellent not only for partial oxidation of hydrocarbons to syngas, but also for steam reforming and autothermal reforming [9–11].

This work is to study the hydrogen production in a membrane reactor by combining air separation using this dense membrane $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_3$ with the mixed reforming of heptane, which is a typical component of gasoline. This provides a new optional way of hydrogen production for both stationary and portable power generation.

2. Experimental

Fig. 1 shows the dense ceramic membrane reactor and the flow chart. The membrane $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_3$ was prepared as described in literature [12], and the catalyst LiLaNiO/γ-Al_2O_3 was prepared via the impregnation method according to report [13]. The membrane reactor was assembled with the membrane, quartz tubes and gold rings, and airproofed at a high temperature of 1070 °C. One side of the membrane was exposed to air while the other side was exposed to the heptane reforming reaction mixture or to helium in case of permeation experiments. The effective area of the membrane disk exposed to the reaction was 1.00 cm^2. Before the reaction, unreduced catalyst particles of LiLaNi/Al_2O_3 (500 mg) were packed above the membrane. The reaction temperature was set to 850 °C.

A pump fed liquid heptane at a constant rate and steam was brought into the reactor by helium, which was used to adjust the partial pressure of the reactants. The amount of steam was controlled by the helium flow rate and the temperature of water in the tin. An oxygen flow (0.5 ml/min) supplied by a mass flow controller (MFC) was added to keep thermal cracking of heptane within limits. Heptane, steam, oxygen and helium were fed into an evaporator. After being vaporized and mixed homogeneously, the mixture reacted with oxygen, which was supplied by the oxygen permeation membrane from the air side. The products were first condensed and then analyzed by an on-line HP4890 GC with a TCD detector. After the reaction, the temperature of the reactor was rapidly decreased to room temperature. X-ray diffraction and SEM were used to characterize the catalyst and the membrane.

3. Results and discussion

3.1. Effect of temperature on the oxygen permeation flux

Fig. 2 shows the oxygen permeation flux through a $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_3$ membrane at different temperatures with helium as sweep gas. The air flow rate was 200 ml/min and the oxygen partial pressure on the air side was maintained at 0.21 atm. It can be seen from Fig. 2 that the oxygen permeation flux obviously increases with a rise of temperature, which is due to the increase of the diffusion rate of oxygen ions and oxygen vacancies through the membrane. At

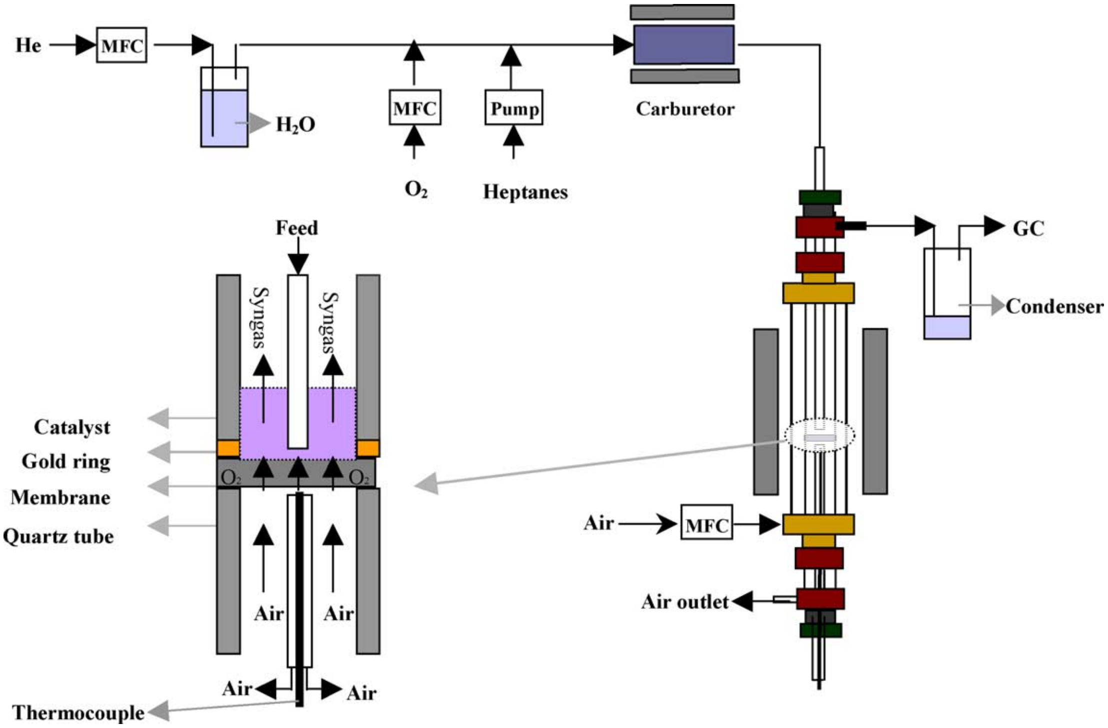

Fig. 1. Reactor configuration and flow chart.

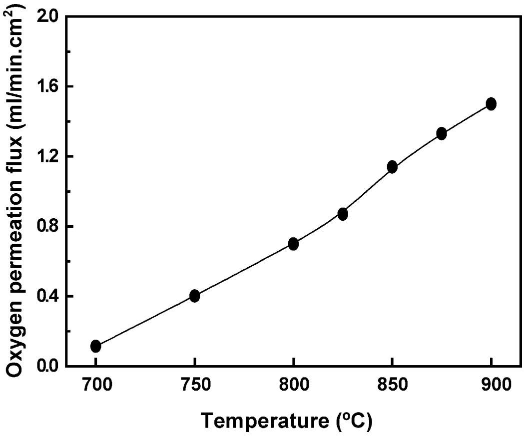

Fig. 2. Effect of temperature on the oxygen permeation flux through the membrane. Reaction conditions: membrane thickness, 1.4 mm; air flow rate, 200 ml/min; helium flow rate, 30 ml/min.

900 °C, the oxygen permeation flux through the membrane reached 1.6 ml/cm^2 min, higher than for any other mixed ion conducting dense ceramic membrane reported.

3.2. Effect of temperature on the membrane reaction

Fig. 3 shows the results of the mixed reforming of heptane with oxygen and water in the membrane reactor at different temperatures. It shows that temperature influences the membrane reaction drastically. In the temperature range of 750 to 950 °C, heptane was completely converted. Fig. 3(A) shows that the CO selectivity reaches a peak at 850 °C with a maximum value of 91%. At temperatures below 850 °C the selectivity to CO increased with increasing temperature whereas above 850 °C it began to decline. In the whole range of temperature, the selectivity to CH_4, C_2H_4 and C_2H_6 decreased rapidly with temperature (C_2H_6 is omitted in Fig. 3) and when the temperature reached 850 °C there was no C_2H_4 and C_2H_6 observed in the products. Fig. 3(B) shows the oxygen flux which gradually increased from 0.0 to 14.8 ml/cm^2 min with an increase of the reaction temperature from 750 to 950 °C. At lower temperature (<850 °C) the oxygen supplied by the membrane is not sufficient to completely convert all C_2H_6 and C_2H_4 to CO and H_2. Therefore, we observed C_2H_6 and C_2H_4 in the products. With the increase of temperature and, consequently, the oxygen flux, the C_2 fraction in the products became less and disappeared at 850 °C; simultaneously, the selectivity of CO reached its maximum value. When the temperature was above 850 °C, the quantity of oxygen transported through the membrane was more than the reaction needed, which resulted in the production of CO and H_2 as well as CO_2. Thus, the selectivity to CO began to decrease. Fig. 3(A) also shows that the selectivity to CO_2 and H_2 increased with temperature and the selectivity to H_2 was 100% at 900 °C. The conversion of water decreased with increasing temperature. At 950 °C, it was 0%.

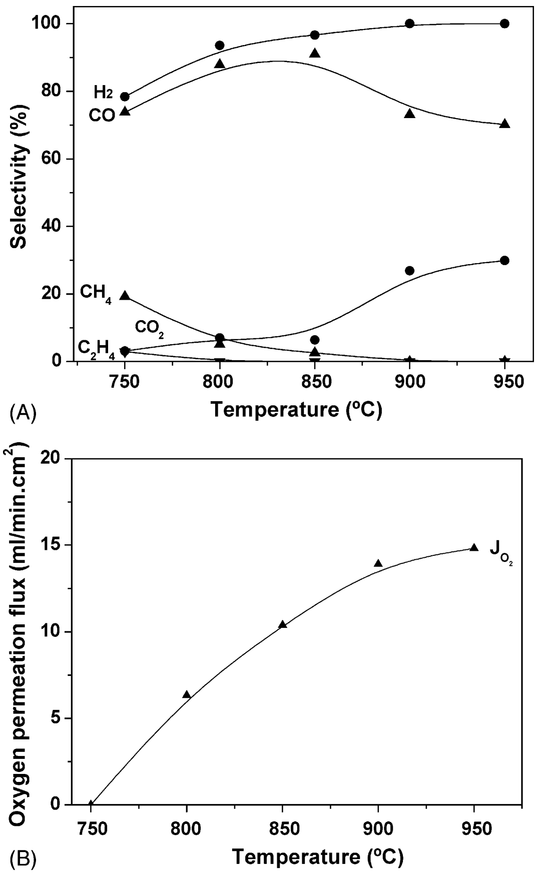

Fig. 3. Effect of temperature on the selectivity of the membrane reaction (A) and the oxygen permeation flux (B) through the membrane. Reaction conditions: membrane thickness, 1.4 mm; air flow rate, 200 ml/min; W/C, 0.42.

3.3. Effect of the air flow rate on the membrane reaction

Fig. 4 shows the influence of the air flow rate on H_2 and CO selectivity and on the oxygen permeation flux at 850 °C. In Fig. 4(B), when the air flow rate increased from 50 to 200 ml/min, the oxygen permeation flux increased from 6 to 11.5 ml/cm^2 min; however, when the air flow rate was higher than 200 ml/min, its influence on the membrane reaction became negligible (Fig. 4(A)) and the oxygen permeation flux remained constant at 11.5 ml/min cm^2. This shows that, when the air flow rate was above 200 ml/min at 850 °C, the exchange of oxygen on the air side of the membrane was not the rate controlling step of oxygen permeation. So, at a reaction temperature of 850 °C, the air flow rate was fixed to 200 ml/min. It was also found that the oxygen permeation flux under reaction conditions was ten times higher than the flux under non-reactive air/He conditions at 850 °C. This is due to the oxygen partial pressure gradient across the membrane, which determines the oxygen permeation flux through the membrane at a certain temperature. Under reaction conditions, the reactants consume the oxygen and the oxygen partial pressure near the membrane surface on the reaction side becomes very low. On the contrary, under

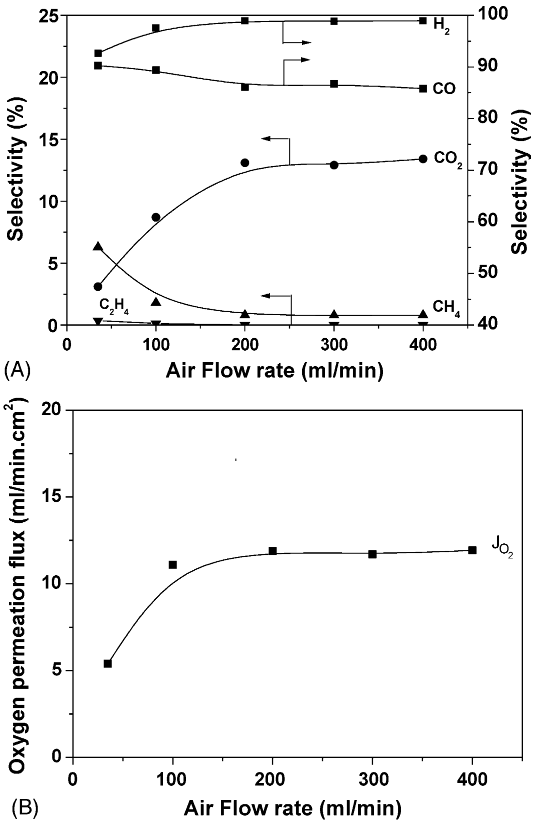

Fig. 4. The effect of the air flow rate on the selectivity of the membrane reaction (A) and the oxygen permeation flux (B) through the membrane. Reaction conditions: membrane thickness, 1.4 mm; temperature, 850 °C; W/C, 0.42.

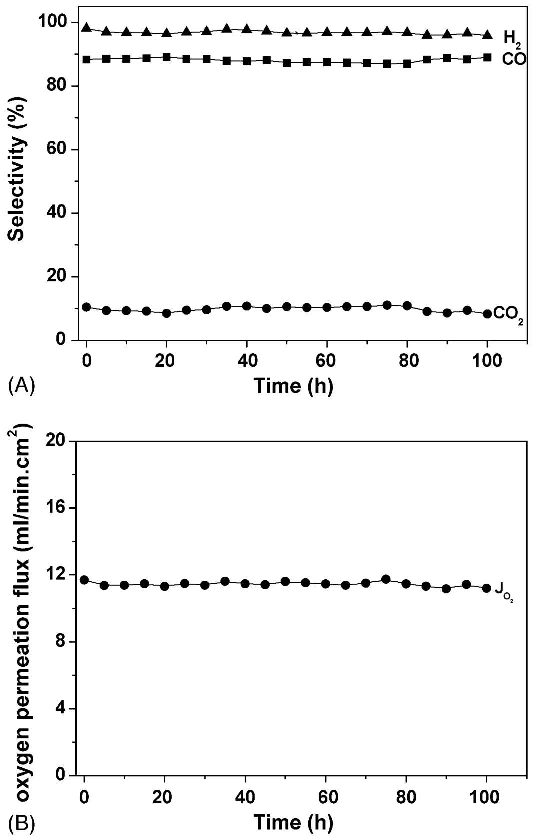

Fig. 5. Selectivity (A) and O_2 permeation flux (B) within a 100 h long-term test under heptane reforming conditions: membrane thickness, 1.4 mm; temperature, 850 °C; W/C, 0.42.

non-reactive air/He conditions, molecular oxygen reaches to the helium side and results in a relatively high oxygen partial pressure. Therefore, the oxygen permeation flux is lower compared to the situation under reaction conditions.

3.4. Long-term test of the mixed reforming in the membrane reactor

For an ideal dense oxygen permeation membrane, it is not enough to have a high oxygen permeation. Above all, the membrane should possess excellent stability in long-term operation under a highly reducing atmosphere. Fig. 5 shows the long-term stability of the membrane reactor at 850 °C with an air flow rate of 200 ml/min. A heptane conversion of 100%, CO selectivity of 91–93%, and H_2 selectivity of 95–97% were achieved (Fig. 5(A)). Over the whole duration of 100 h, the oxygen permeation flux was stable at values around 11.5 ml/cm^2 min (cf. Fig. 5(B)), which demonstrates the excellent performance of the $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_3$ membrane reactor.

Shown in Fig. 6, results of XRD measurements indicate that the bulk of the BSCFO membrane retained its perovskite structure after 100 h under reaction conditions at 850 °C, which proves the high stability for oxygen permeation and the excellent phase stability of the BSCFO membrane under the highly reducing atmosphere. Fig. 7 shows SEM micrographs from a top view (Fig. 7(A)) and a cross-sectional view (Fig. 7(B)) of the used membrane after 100 h. The boundary of the grains in the membrane was still clear, which also demonstrates the excellent stability of the BSCFO membrane.

Furthermore, it should be pointed out that the stability of the catalyst is another determining factor for the stable

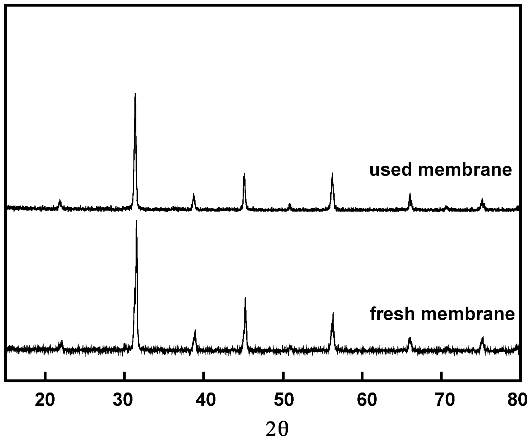

Fig. 6. XRD patterns of fresh and used membranes after 100 h under heptane reforming conditions.

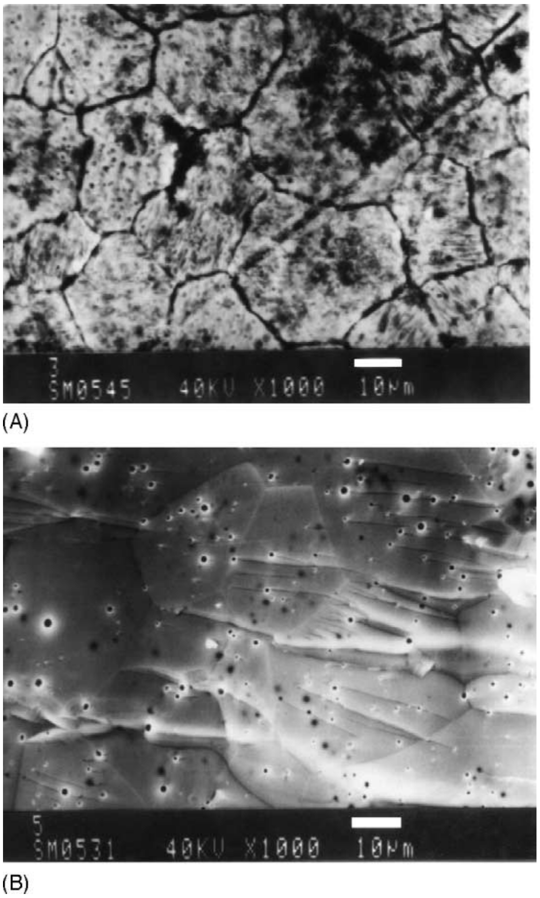

Fig. 7. SEM micrographs of a top view (A) and a cross-sectional view (B) of the used membrane after 100 h under heptane reforming conditions.

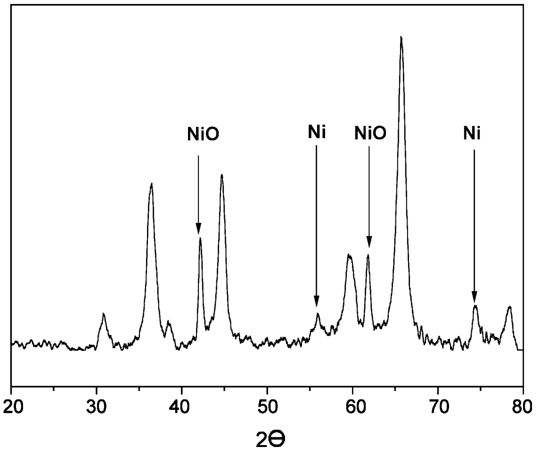

Fig. 8. XRD patterns of the LiLaNiO/γ-Al_2O_3 catalyst after 100 h under heptane reforming conditions.

performance of the membrane reactor besides membrane stability. In Fig. 8, results of XRD measurements are shown which were performed to determine the crystalline phases of the LiLaNiO/γ-Al_2O_3 catalyst after 100 h of reaction. Only peaks of γ-Al_2O_3, Ni and NiO appeared, while those of $NiAl_2O_4$ and α-Al_2O_3 did not appear; namely, the γ-Al_2O_3 support did not undergo crystalline transformation into α-Al_2O_3. Metallic nickel obviously did not aggregate after 100 h, even by treatment at 1050 °C before the reaction in the membrane reactor. It can be concluded that the crystalline phase structure of LiLaNiO/γ-Al_2O_3 is stable during the high temperature reaction.

4. Conclusion

At 850 °C under the gradient of air/He, the BSCFO membrane showed very high oxygen fluxes around 1.1 ml/cm^2 min. In the membrane reaction, the air flow rate was shown to influence the oxygen permeation flux when it was relatively low. At optimized reaction conditions in presence of the reforming catalyst LiLaNiO/γ-Al_2O_3, the membrane reactor was successfully operated for 100 h with a stable oxygen permeation flux of 11.5 ml/min cm^2 in highly reducing atmosphere. The conversion of heptane was 100% and the selectivity to CO and H_2 was 90–92 and 95–97%, respectively. The catalyst LiLaNiO/γ-Al_2O_3 exhibited a good activity and a favorable stability during the 100 h run; simultaneously, XRD measurement showed that the bulk structure of the membrane was still of the perovskite-type after 100 h of operation. The membrane possesses excellent phase stability.

References

[1] C.S. Song, Catal. Today 77 (2002) 17.
[2] S. Katikaneni, C. Yuh, S. Abens, Catal. Today 77 (2002) 99.
[3] D.J. Moon, K. Sreeksumar, S.D. Lee, Appl. Catal. A 215 (2001) 1.
[4] C. Song, Am. Chem. Soc. Div. Fuel Chem. Prep. 46 (1) (2001) 8.
[5] J.P. Lange, Ind. Eng. Chem. Res. 36 (1997) 4282.
[6] C.M. Chen, P.N. Dyer, K.F. Gerdes, Stud. Surf. Sci. Catal. (2002).
[7] H. Dong, Z.P. Shao, G.X. Xiong, et al. Catal. Today 67 (1–3) (2001) 3.
[8] Z.P. Shao, H. Dong, G.X. Xiong, et al. J. Membr. Sci. 183 (2001) 181.
[9] S.L. Liu, G.X. Xiong, Catal. Lett. 63 (1999) 167.
[10] S.L. Liu, G.L. Xiong, S.S. Sheng, Appl. Catal. A 198 (2000) 261.
[11] R. Ran, G.X. Xiong, S.S. Sheng, Catal. Lett. 88 (1–2) (2003) 55.
[12] Z.P. Shao, G.X. Xiong, et al. J. Membr. Sci. 172 (2000) 177.
[13] S.L. Liu, G.X. Xiong, et al. Prog. Nat. Sci. 9 (1999) 198.