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Effect of La on the thermal stability of Pd/γ-Al_2O_3 catalytic membranes

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Abstract

Lanthanum-doped Pd/γ-Al_2O_3 and Pd/γ-Al_2O_3 membranes were prepared by sol-gel methods. The thermal stability of the unsupported Pd/γ-Al_2O_3 and La/Pd/γ-Al_2O_3 membranes was investigated with BET (including average pore size, pore volume and BET surface area), XRD, and DTA techniques. The average pore size of the Pd/γ-Al_2O_3 membranes increased sharply after sintering at temperatures higher than 1000°C. Addition of 3 mol% lanthanum can raise the temperature of the γ-Al_2O_3 toα-Al_2O_3 phase transformation significantly. This improves the thermal stability of the Pd/γ-Al_2O_3 catalytic membranes. © 2001 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

1. Introduction

With the development of the petroleum refining industry and the petrochemical industry, the demand for hydrogen has increased rapidly in recent years since hydrogen is a primary chemical feedstock for these two industries [1]. In particular, with the steady depletion of fossil fuel reserves and the greenhouse effect caused by combustion, the demand for hydrogen is expected to accelerate since it is an alternative clean energy source. Production of hydrogen by steam reforming from hydrocarbons has achieved increasing importance in recent years due to the growing need for hydrogen [2].

Ceramic membranes are technically important in separation and filtration as well as in catalytic reactions, because of some unique characteristics in comparison with polymeric membranes, such as chemical stability, long life and good defouling properties. As far as the role of inorganic membranes in catalytic reactors is concerned, separation versus non-separation depends on whether or not membrane permselective is essential in catalytic reactors [3]. The membrane reactor for dehydrogeneration is a good example of a separation application, i.e. hydrogen as one of the reaction products is selectively removed by Pd/γ-Al_2O_3 membranes, resulting in an increase in the percent mass conversion [4].

The dehydrogeneration of hydrocarbons using Pd/γ-Al_2O_3 membranes is commonly operated at high temperatures. However, γ-Al_2O_3 is a metastable phase, and will transform to α-Al_2O_3 at high temperatures (usually about 1000°C) and develop abnormal grain growth (vermicular structure). Above 800°C, the BET surface area of pure alumina membranes start to decrease, and above 1000°C the pore structure which is preferable for membranes application is destroyed, which limits their high temperature applications.

In the limited studies related to the thermal stability ofγ-Al_2O_3 inorganic membranes [5], Burggraaf and Keizer [6,7] and coworkers determined the pore size of top layers of γ-Al_2O_3 membrane for different sintering temperature. Cot and his coworkers [8] has reported a set of data of pore size vs sintering temperature (500–1000°C) for the γ-Al_2O_3 top layers in several publications. These published papers, however, have mainly dealt with synthesis of ceramic membranes and their characterization rather than with their thermal stability. Up to now, there are no reports related to improvements of the Pd/γ-Al_2O_3 catalytic membranes. In this paper, the effect of lanthanum doping on the improvement of the thermal stability of Pd/γ-Al_2O_3 catalytic membranes were reported.

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2. Experimental

The alumina sol was prepared by the Yoldas process [9]. One mol $Al(OPr^i)_3$ was added to 100 mol of distilled water at a temperature higher than 80°C. The sol was vigorously stirred on a magnetic plate for complete alkoxide hydrolysis, and then it was peptized with HNO_3. The molar ratio of H to Al^{3+} is 0.07. This solution was stirred for over 16 h to ensure complete mixing and hydrolysis under reflux condition. A small amount of $PdCl_2$ dissolved in acidic solution was mixed with the pure boehmite sol to form the Pd-doped boehmite sol (weight ratio of $PdCl_2$/AlOOH is 2%). The Pd-doped sol was shaken thoroughly for 5 h to give a homogeneous mixture, and then a small amount of lanthanum nitrate solution (0.3 M) was mixed with the Pd-doped boehmite sol to form the La-Pd-doped boehmite sol (molar ratio of $La(NO_3)_3$ to AlOOH is 0.03).

Since the preparation of the supported and non-supported membrane proceeds in a comparable way, the results obtained from the non-supported membrane are expected to be applicable to the supported membrane [10,11]. Hence, in this study, non-supported Pd/γ-alumina membranes were prepared to investigate the effects of La-doping on the microstructure development and thermal stability of the Pd/γ-Al_2O_3 membrane after sintering at different temperatures. Non-supported membranes were prepared by drying mixed sol for overnight in a Petri dish at 45°C and 70% relative humidity. The resulting gels were calcined at a rate of 60°C per hour and kept for 5 h at the pre-set temperature ranging from 450 to 1200°C.

The DTA was carried out in air at a heating rate of 10°C min^{-1} to 1300°C using the Mdsc2910. X-ray powder diffraction (XRD) patterns were obtained using a Rigaku D/Max-RB diffractometer. Pore-size, pore-volume and surface-area measurements of the different samples were determined via the analysis of nitrogen adsorption/desorption isotherms obtained at liquid nitrogen temperature (Micromeritics Tristar 3000 analyzer).

3. Results and discussion

3.1. DTA analysis

The DTA curves for the Pd/γ-Al_2O_3 and La/ Pd/γ-Al_2O_3 are depicted in Fig. 1. In the sample of Pd/γ-Al_2O_3 there are three endothermic and one exothermic peaks, compared with the three endothermic peaks in the sample of La/ Pd/γ-Al_2O_3. The first endothermic peak, centered around 106°C, corresponds to the removal of water present in the pores. The origin of the second endothermic peak, centered around 425°C, may be attributed to the removal of hydroxyl groups (γ-AlOOH$\rightarrow\gamma$-$Al_2O_3 + H_2O$) and of residual nitrates. The nitrates come from the nitric acid, which was used for stabilizing the boehmite sol. The third endothermic peak, centered around 807°C, may indicate crystallization of γ-Al_2O_3 [12]. At temperatures less than 900°C, there is no evident difference in the two DTA curves. A

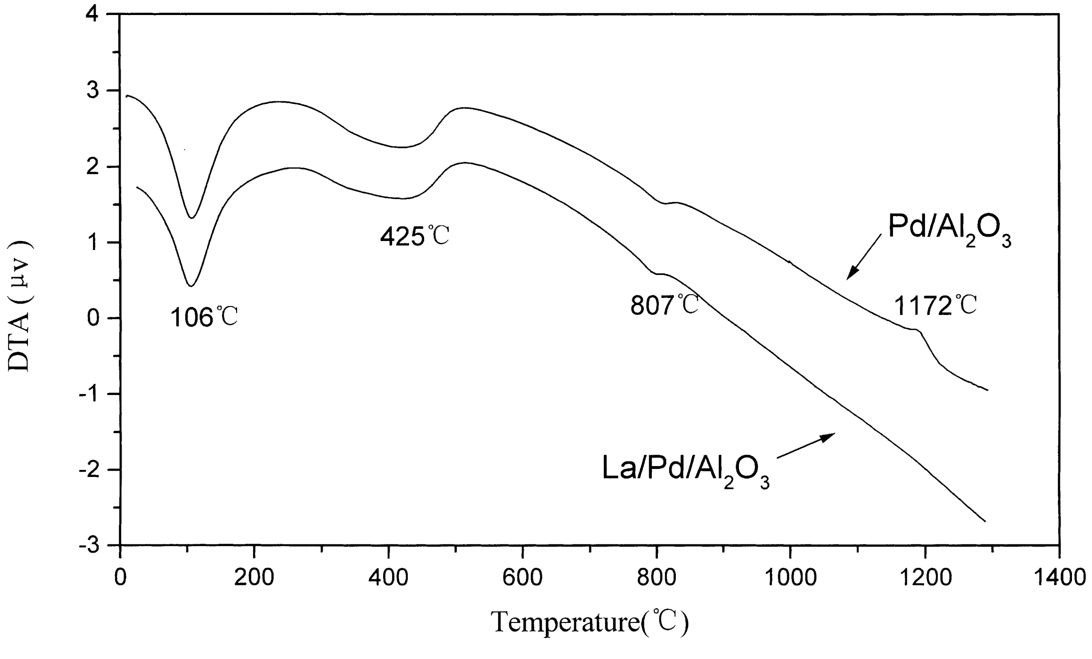

Fig. 1. DTA curves of dried gel (Pd/Al_2O_3 and La/Pd/Al_2O_3) heated at a rate of 10°C/min in nitrogen.

clearly visible exothermic peak at approximately 1172°C can be identified in the DTA curves of Pd/γ-Al_2O_3, which correspond to the formation of α- Al_2O_3. In contrast, no such exothermic peak is visible in the DTA curves of La/ Pd/γ-Al_2O_3. It should be noted from the XRD results that γ-Al_2O_3 in Pd/γ-Al_2O_3 heated at 1100°C (with a heating rate of 1°C min^{-1}) for 5 h has considerably converted to well-defined α-Al_2O_3. This is because of the slow heating rate and long soaking time. It is also important to note that the transformation to α-Al_2O_3 is a metastable-to-stable transformation. Unlike equilibrium transformations, these are not reversible and there is no real equilibrium transformation temperature. The transformation temperature, or the extent of transformation, is dependent on the factors such as heating rate and soaking time.

3.2. XRD analysis

Fig. 2 compares the XRD spectra of Pd/γ-Al_2O_3 and La/ Pd/γ-Al_2O_3 after sintering at different temperatures ranging from 450 to 1200°C. When the sintering temperature is below 800°C, the Pd/γ-Al_2O_3 and La/ Pd/γ-Al_2O_3 have similar XRD spectra and the influence of lanthanum doping was almost undetectable. There is a trace of θ-Al_2O_3 in the sample of Pd/γ-Al_2O_3 after sintering at 1000°C. The phase transitions of alumina, which have been studied for decades, always follow the same sequences:

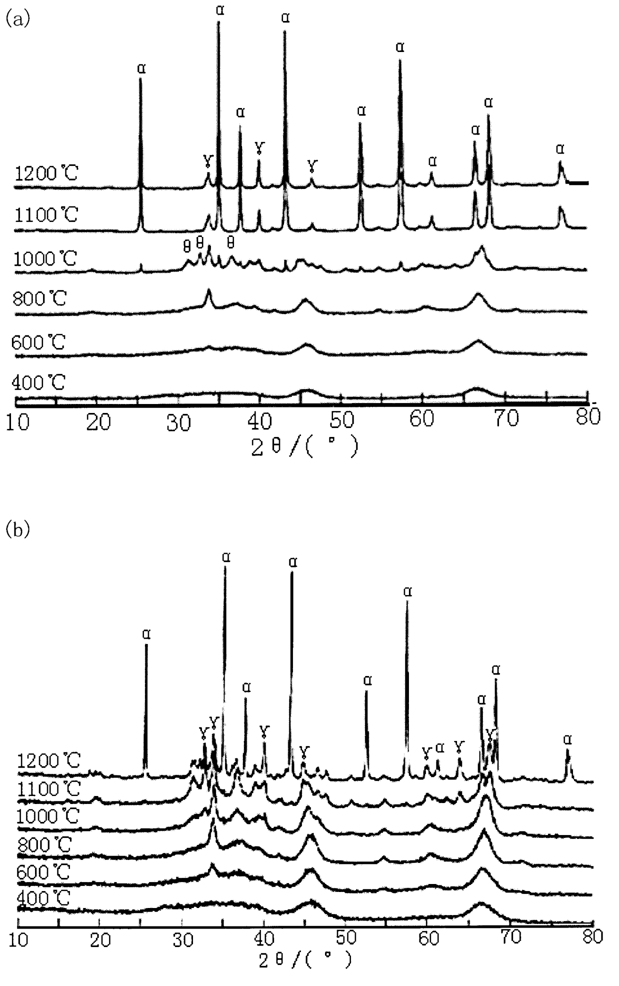

Fig. 2. XRD patterns for the samples of (a) Pd/Al_2O_3 and (b) $La/Pd/Al_2O_3$ after sintering at different temperatures for 5 h (α: α-Al_2O_3; γ: γ-Al_2O_3; θ :mixture of θ- and δ-Al_2O_3).

$$\gamma - \mathrm{AlOOH} \rightarrow \gamma - \mathrm{Al_2O_3} \rightarrow \delta - \mathrm{Al_2O_3}$$
$$\rightarrow \theta - \mathrm{Al_2O_3} \rightarrow \alpha - \mathrm{Al_2O_3}$$

It is difficult to distinguish the δ-Al_2O_3 and θ-Al_2O_3 phase in the XRD spectra, so θ-Al_2O_3 stands for both δ-Al_2O_3 and θ-Al_2O_3. When the sintering temperature is higher than 1100°C, γ-Al_2O_3 transformed to well-defined α- Al_2O_3, and with a trace of γ-Al_2O_3 remained in the samples of Pd/γ-Al_2O_3. In contrast, there is nearly no detectable α-Al_2O_3 in the XRD spectra of La/ Pd/γ-Al_2O_3 sintered at 1100°C. Quite a few γ-Al_2O_3 reflections remained even after sintering the latter at 1200°C. This indicates that the lanthanum doping retarded formation of α-Al_2O_3 from γ-Al_2O_3 in the samples of the La-doped Pd/γ-Al_2O_3.

3.3. BET surface area and pore characterizations

The specific surface area depends on the sample composition and heat treatment condition as shown in Fig. 3. When the sintering temperature is below 700°C, the lanthanum dopant slightly decreases the BET surface area of the La/ Pd/γ-Al_2O_3 membranes, compared with the BET surface area of Pd/γ-Al_2O_3 membranes. This may be partially due to deposition of dopant oxides, formed by the decomposition of the nitrates, into the smaller pores of the doped samples. Up to about 1000°C the BET surface area reduction is gradual in both Pd/γ-Al_2O_3 membranes and La/ Pd/γ-Al_2O_3 membranes. Thereafter, the rate of decrease in Pd/γ-Al_2O_3 is higher, up to 1100°C, than in La/Pd/γ-Al_2O_3. From the XRD spectra it can be found that the major phase is still one of the transition aluminas (a mixture of γ-, δ- and θ- Al_2O_3) up to 800°C, but by 1100°C it converts to well-defined α- Al_2O_3; all the major peaks correspond to those of α- Al_2O_3. The above results indicates that the BET surface area reduction process is enhanced by the γ-α transformation). The BET surface area of the samples of Pd/γ-Al_2O_3 and La/ Pd/γ-Al_2O_3, sintered at 1100°C for 5 h, is 51.6 and 4.46 m^2/g, respectively. The high BET surface area undoubtedly favors the catalytic ability.

The average pore diameter and pore volume for Pd/γ-Al_2O_3 and La/ Pd/γ-Al_2O_3 membranes are plotted

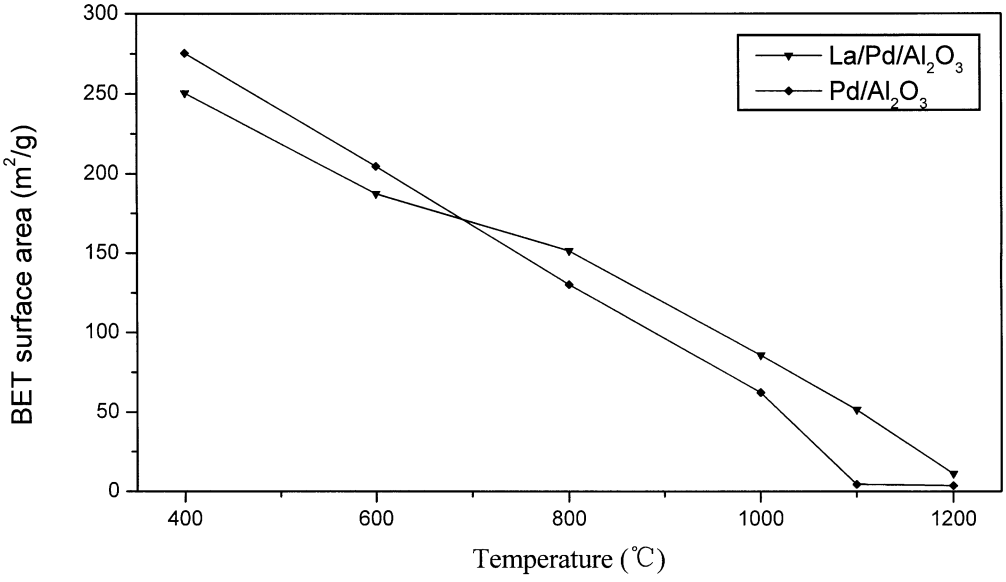

Fig. 3. The effects of La-dopant on the BET of samples sintered at different temperatures for 5 h.

against sintering temperature in Fig. 4. The pore size for both membranes increases slightly from 450 to 1000°C. When the sintering temperature is higher than 1000°C, a substantial increase in the pore size for the Pd/γ-Al_2O_3 membrane was found, in contrast to the approximately unchanged pore size in the lanthanum-doped Pd/γ-Al_2O_3 membranes. It was found that the substantial pore growth for the pure alumina membrane occurs in the temperature range of the phase transformation temperature of γ- to α-Al_2O_3. The addition of 3 mol% lanthanum to the Pd/γ-AlOOH sol can stabilize the membrane with a pore diameter smaller than 7.2 nm even at temperatures as high as 1100°C, much smaller than the value of 35.1 nm for Pd/γ-Al_2O_3 membranes at the same temperature. The patterns of change for the pore volumes of the Pd/γ-Al_2O_3 membranes and La/ Pd/γ-Al_2O_3 membranes is consistent with the BET surface area curves. At 1100°C, the pore volume of the Pd/ γ-Al_2O_3 membrane is only 0.051 cm^3/g as compared to 0.138 cm^3/g of the La/ Pd/γ-Al_2O_3 membrane, indicating that the pore structure of the Pd/γ-Al_2O_3 membrane is almost collapsed.

The pore size dispersions (PSD) of Pd/γ-Al_2O_3 and La/ Pd/γ-Al_2O_3 membranes after calcination and sintering at different temperatures are shown in Fig. 5. The PSD of both Pd/γ-Al_2O_3 and La/ Pd/γ-Al_2O_3 membranes after calcination at 800°C is rather narrow, and the influence of lanthanum doping was almost unde-

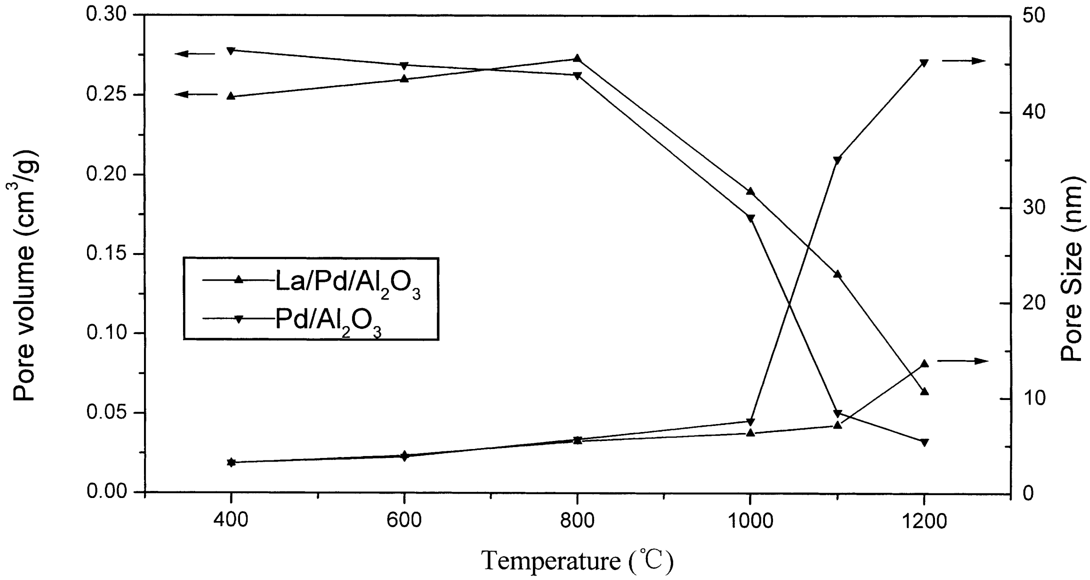

Fig. 4. The effects of La-dopant on the pore volume and pore size of samples sintered at different temperatures for 5 h.

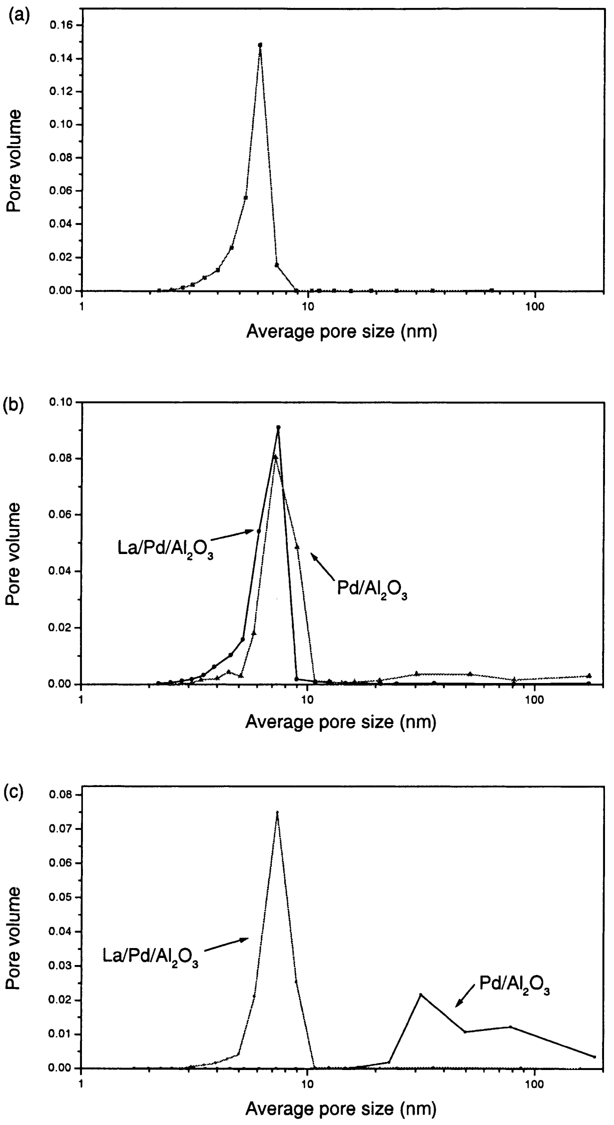

Fig. 5. Pore size distributions of La/Pd/Al_2O_3 and Pd/Al_2O_3 after sintering at different temperatures for 5 h; (a) 800°C; (b) 1000°C; (c) 1100°C.

tectable. These results agree with the results from the DTA and XRD. After heat treatment at higher temperature, the pore size dispersion spreads out and the pore size increases. After the two samples were sintered at 1000°C, the pore size dispersion of the Pd/γ-Al_2O_3 membranes is slightly broader than that of the La/ Pd/γ-Al_2O_3 membranes, and the pore size of Pd/γ-Al_2O_3 membranes is a little larger than that of the La/ Pd/γ-Al_2O_3 membranes. After sintering at 1100°C, The pore size of Pd/γ-Al_2O_3 membranes obviously has a double peak dispersion, compared with only one peak of the La/ Pd/γ-Al_2O_3 membranes.

4. Conclusions

Pd/γ-Al_2O_3 and La/ Pd/γ-Al_2O_3 membranes were prepared by sol-gel methods. Lanthanum doping improves the pore characteristics including average pore diameter, pore volume and BET area of Pd/γ-Al_2O_3 catalytic membranes. After sintering at 1100°C for 5 h, the average pore diameter, pore volume and BET area of the Pd/γ-Al_2O_3 membranes were 35.1 nm, 0.051 cm^3/g and 4.46 m^2/g, respectively, as a contrast, for the La/ Pd/γ-Al_2O_3 membranes, these parameters were 7.2 nm, 0.138 cm^3/g and 51.6 m^2/g, respectively. The higher thermal stability of La-doped Pd/γ-Al_2O_3 membranes is related to the retarded phase transformation from γ-Al_2O_3 to α-Al_2O_3 in the La-doped Pd/γ-Al_2O_3 membranes.

Acknowledgements

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