

Rh/La₂O₃ catalysts for hydrogen production using simultaneous CO₂ reforming and partial oxidation of methane in a membrane reactor

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Introduction

In order to produce ultrapure H₂, the dry reforming (DRM) reaction can be carried out in a membrane reactor. This system offers the possibility of overcoming the thermodynamic limitations of the endothermic reaction, allowing the attainment of higher methane conversions at lower temperatures. To decrease the energy consumption, its coupling with the exothermic partial oxidation (POM) has been considered. Recently, several studies [1-3] related to the application of membrane reactors to the dry reforming have achieved higher conversions with respect to a conventional fixed-bed reactor. Moreover, dense Pd/Ag membranes exhibit 100% selectivity towards hydrogen, so that ultra pure H₂ could be produced. In this work, the membrane reactor performance for simultaneous DRM and partial oxidation of methane (POM) reactions is evaluated comparing it to the behavior of a fixed-bed reactor.

Materials and Methods

Catalysts were prepared by conventional wet impregnation of La₂O₃ using RhCl₃·3H₂O as precursor compounds. The double tubular membrane reactor was built using a commercial dense Pd-Ag alloy (inner tube), with one end closed and an inner tube to allow sweep gas flow (REB Research and Consulting). The catalysts were reduced in situ in H₂ flow at 550°C for 2 h. The catalytic measurements were carried out at different W/F and relative concentrations of methane, CO₂, Ar and O₂ in the feed.

Results and Discussion

Rh(0.6%)La₂O₃ has been used as an excellent catalyst for the dry reforming of methane at temperatures below 600°C in a Pd-Ag membrane reactor [3]. For this catalyst, the activity remained unchanged after 150 h on stream. The combination of XRD, TPR, LRS, XPS and DRIFT techniques reveals that the calcined Rh/La₂O₃ solid after reduction is made up of a mixture of La₂O₃ and oxycarbonates on which reduced dispersed rhodium clusters are sitting. The high stability for the dry reforming of methane was attributed to the very strong metal-support interaction.

The catalytic activity in the fixed-bed reactor is shown in Table 1 for both DRM and its combination with POM. The experiments were carried out at 550 °C. This temperature is 50 °C below the maximum value allowed for the Pd-Ag membrane when exposed to a reducing atmosphere. For the DRM reaction, the CO₂ conversion was higher than the CH₄ conversion due to the occurrence of the RWGS reaction in which CO₂ reacted with the H₂ produced in the reforming reaction. It can be observed that the methane conversion increases and the carbon dioxide conversion decreases when oxygen is added to the feed. As a consequence of the POM reaction a higher H₂/CO ratio is obtained [4,5].

Table 1. Catalytic tests in a fixed-bed reactor at 550°C

CH ₄ /CO ₂ /O ₂ /Ar ^a	X _{CH₄}	X _{CO₂}	H ₂ /CO
1 : 1 : 0 : 1 ^b	21.1	32.1	0.82
1 : 1 : 0.20 : 0.8 ^b	25.4	9.2	1.30
1 : 1 : 0.33 : 0.67 ^b	35.5	2.8	1.61
1 : 1 : 0 : 1 ^c	27.8	43.9	0.75
1 : 1 : 0.33 : 0.67 ^c	42.0	11.8	1.65

^aFeed gas composition. ^bW/F= 1.8 10⁻³ g h ml⁻¹. ^cW/F= 4.2 10⁻⁵ g h ml⁻¹.

When oxygen is fed to the membrane reactor, an increase in the methane conversion and the hydrogen /methane ratio was observed at different sweep gas flow rates for the Rh/La₂O₃ catalyst.

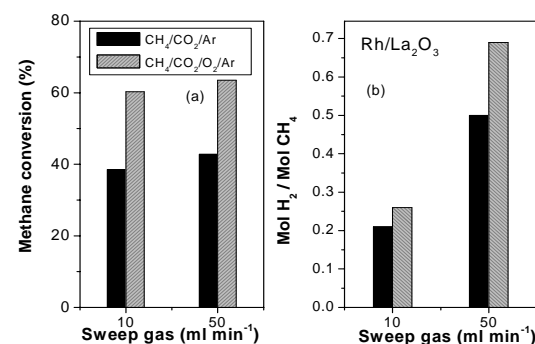


Figure 1. Catalytic tests in a membrane reactor for simultaneous DRM and POM reactions (a) Methane conversion and (b) Permeated H₂/ Fed CH₄ ratio. W/F= 1.5 10⁻³ g h ml⁻¹. T=550 °C. CH₄/CO₂/O₂/Ar=1:1:0.33:0.67

Significance

By coupling the endothermic dry reforming with the exothermic partial oxidation of methane (POM) reaction in a membrane reactor, a higher hydrogen selectivity can be obtained, leading to a more energy-efficient process.

References

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