PRODUCTION OF HYDROGEN EMPLOYING Ni-Rh CATALYSTS IN MEMBRANE REACTORS

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Abstract--- Rh, Ni and Rh-Ni catalysts were prepared by wet impregnation of La₂O₃. The Rh content was modified but the Ni loading was kept constant at 2 wt%. The solids were calcined at 823 K in air flow and were reduced at 973 K in flowing hydrogen. The activity, stability, and residue formation during the CO_2 reforming of CH_4 , of all the catalysts were tested in a fixed-bed reactor. Those with low carbon deposition were used in a Pd-Ag membrane reactor. The Rh solids showed the highest activity at 823 K. In order to understand the Rh effect, the catalysts were characterized through XRD and TPR. No evidence of crystalline Ni phase through XRD was observed in either the calcined or used catalysts. On the other hand, both the TPR and XPS results suggest a significant metal-support interaction. The bimetallic solids presented higher carbon deposition. The carbonaceous species formed on stream were characterized through thermal analysis. At least two types of carbons were detected on the catalyst surface with different structural properties which did not affect the catalytic activity. A low carbon deposition was observed on Rh/La₂O₃ which exhibited a stable activity after 100 h on stream. The monometallic Rh solids were tested in the membrane reactor, varying the pressure drop across the Pd-Ag alloy. A significant increase in reactant conversions was obtained when the membrane reactor was used.

Keywords— Hydrogen, CO₂ reforming, Ni-Rh Catalysts, Membrane reactor.

I. INTRODUCTION

The demand for hydrogen is strong and steadily increasing as its use for fuel cells becomes affordable. The production of hydrogen through the methane reforming reaction with carbon dioxide employing a membrane reactor seems to be an interesting approach, since it also combines two gases that produce the greenhouse effect (Prabhu and Oyama, 2000). An active, long-life catalyst at low temperature is a key player in this system.

The carbon dioxide reforming of methane to obtain hydrogen and carbon monoxide has recently captured the attention of a number of researchers (Bradford and Vannice, 1999). Noble metals are selective and active catalysts for this reaction (Bitter *et al.*, 1998, Bitter *et al.*, 1999, Sigl *et al.*, 1999) but, due to their high cost, Ni-based catalysts are often preferred (Kroll *et al.*, 1996). All these solids can reach the equilibrium conversions adequately by adjusting *the* contact time. However, this reaction is accompanied by the undesired formation of different kinds of carbon deposits. In these systems, the deactivation can be fast and the catalysts can become inactive after a short time on stream (Chang *et al.*, 2000, Slagtern *et al.*, 1997).

Noble-metal based catalysts show a better activity and less carbon deposition than non-noble metal systems. Among the former, rhodium has been supported on different oxides. Metal support interaction, dispersion and particle size have been found to be key factors in defining the ability of the solid to catalyze both the desired reaction and the carbon deposition.

No matter how good the catalyst is, this reaction is thermodynamically limited. Therefore, the elimination of H_2 from the reactant stream is a way to increase the conversion to products. To achieve this goal, a membrane reactor appears as an attractive option.

The objective of the present work was to study the activity and stability of Ni-Rh bimetallic catalysts supported on lanthanum oxide, in the CO₂ reforming of methane at low temperature. These catalysts were used in a membrane reactor which cannot operate above 873 K. The catalysts were characterized by XRD, XPS and temperature-programmed reduction while the carbon deposit was quantified through thermal analysis (TGA and DSC).

II. EXPERIMENTAL

A. Catalyst Preparation

Catalysts were prepared by the conventional wet impregnation of La_2O_3 (Anedra 99.99% Sg = 7.5 ml g⁻¹) using Ni(NO₃)₂.6H₂O , and RhCl₃.3H₂O as precursor compounds. The bimetallic solid was prepared by simultaneous impregnation. In all cases, the resulting suspension was then heated at 353 K to evaporate the water, and the solid material was dried in an oven at 383 K overnight. The resulting catalysts were calcined for 6 hours at 823 K.