Latin American Applied Research 33:73-78 (2003)

PRODUCTION OF HYDROGEN EMPLOYING Ni-Rh CATALYSTS IN MEMBRANE REACTORS

J. MUNERA[†], S. IRUSTA[†], L. M. CORNAGLIA[†] and E. A. LOMBARDO[†]

[†] *Instituto de Investigaciones en Catálisis y Petroquímica (FIQ, UNL-CONICET)*
Santiago del Estero 2829-3000 Santa Fe-Argentina
nfisico@fiqus.unl.edu.ar

***Abstract*— Rh, Ni and Rh-Ni catalysts were prepared by wet impregnation of La_2O_3. 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/La_2O_3 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, CO_2 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 activiy and stability of Ni-Rh bimetallic catalysts supported on lanthanum oxide, in the CO_2 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 $Ni(NO_3)_2.6H_2O$, and $RhCl_3.3H_2O$ 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.

B. Catalyst Testing

The catalyst (50 mg) was loaded into a tubular quartz reactor (i.d. 5 mm) which was placed in an electric oven. The reaction products were analyzed with TCD gas chromatograph equipped with a Porapak, and a molecular sieve column. The catalysts were heated in He at 973 K and then reduced *in situ* in H_2 at the same temperature for ½ h. After reduction, the reaction temperature (823 K) was reached in flowing He and the feed gas mixture (33% CH_4 v/v, 33% CO_2, 34% He, P=1atm) was then switched to the reactor.

The membrane reactor was built using a commercial dense Pd-Ag alloy with cylindrical geometry (REB Research and Consulting). To prevent damage of the membrane, the manufacturer recommends not to surpass 873 K. 300 mg of catalyst were diluted with quartz chips to achieve a bed height of 3 cm. The catalyst was reduced in situ at the reaction temperature (823 K).

To measure the equilibrium conversions, the reactor was operated with no sweep gas and no pressure difference between the tube and the shell sides. In this case, the conversions were measured after a 30-min stabilization time.

C. Metal dispersion and X-ray diffraction (XRD)

The Rh and Ni dispersion of fresh catalysts, following the H_2 reduction at 973 K for ½ h, was determined by static equilibrium H_2 adsorption at room temperature in a conventional vacuum system, after evacuation at 773 K for 1 h to complete H_2 desorption after reduction. The Ni-containing catalysts were evacuated at 1023 K The XRD patterns of the calcined and used solids were obtained with an XD-D1 Shimadzu instrument, using Cu Kα radiation at 35 kV and 40 mA. The scan rate was 1°/min for values between $2\theta = 10°$ and 80°.

D. Temperature-Programmed Reduction (TPR)

An Ohkura TP-20022S instrument equipped with TCD was used for the TPR experiments. To eliminate the carbonates present, the samples were heated up to 1123 K or 823 K in oxygen flow. This temperature was kept constant for two hours; then, the samples were cooled down in Ar flow. Afterwards, they were reduced in a 5%H_2-Ar stream , with a heating rate of 10 K/min up to the maximum treatment temperature.

E. X-ray photoelectron spectroscopy

The XPS measurements were carried out using an ESCA750 Shimadzu electron spectrometer. Non-monochromatic AlKα X-ray radiation was used. The binding energies (B.E.) were referred to the C 1s signal (284.6 eV). Curve fitting was performed using a Levenberg-Marquardt NLLSCF routine. The background contribution was taken into account by assuming an integral type background. The surface Rh/La and Ni/La atomic ratios were calculated using the areas under the Rh 3d , Ni $2p_{1/2}$ and La $3d_{5/2}$ peaks, the Scotfield photoionization cross-sections, the mean free paths of the electrons and the instrumental function which was given by the ESCA manufacturer.

F. Thermogravimetric analysis

The amount of carbon on the used catalysts was determined by oxidizing the carbon in a Mettler Toledo TGA/SDTA (Model 851) system. The used catalysts (usually 10 mg) were heated at 10 K min^{-1} to 1173 K in a flow of 90 ml min^{-1} air.

Thermal analysis experiments were carried out in a Mettler Toledo DSC 821[e] instrument in order to find out the exothermic or endothermic nature of the changes that take place during the calcination of the used solids.

III. RESULTS

The reaction rates obtained at 823 K for all the catalysts are reported in Table 1. Note that the increase of the Rh content from 0.2% to 0.6% only slightly improves the performance.

The H/metal ratios obtained by H_2 chemisorption are shown in Table 1. With this dispersion, the TOF (Table 1) was calculated as proposed by Mark and Maier, 1996.

Conversion values were used to evaluate catalyst stabilities. As clearly shown in Table 1, over a testing period of 100 hours at 823 K there is practically no loss of activity of the catalysts assayed.

Table 1. Catalytic behavior of Ni-Rh solids

Catalysts	R_{CH4}[a]	R_{CO2}[a]	H/M	TOF (s^{-1})		θ = 2h[b]		θ = 100h[b]		TGA (mg g_{cat}^{-1})		
	(mol h^{-1} g^{-1})			CH_4	CO_2	X_{CH4}	X_{CO2}	X_{CH4}	X_{CO2}	640 K	900 K	1100 K
Rh(0.2%)/La_2O_3	0.20	0.42	0.64	4.4	9.1	5.4	13.2	4.8	14.0	61	0	33
Ni(2%)/La_2O_3	0.12	0.21	0.06	1.7	2.5	6.4[c]	14.5[c]	6.7[c]	14.4	0	147	64
Ni(2%)Rh(0.2%)/La_2O_3	0.24	0.42	0	-	-	5.9	13.0	5.2	11.7	0	332	54
Rh(0.6%)/La_2O_3	0.26	0.51	0.14	13.8	16.7	-	-	-	-	-	-	-

[a] Initial reaction rates. [b] Time on stream (T= 823 K, W/F= 4.5 10^{-6} g h ml^{-1}, 33% CH_4 v/v, 33% CO_2, 34% He, P= 1atm). Conversions in %.

[c] W/F = 1.1 10^{-5} g h ml^{-1}

The TPR profile of the Ni(2%) solid shows two peaks at 618 and 760 K (Fig. 1A) after treatment at 1123 K. The NiO TPR profile exhibits a single peak at 693 K (Brown *et al.*,1982). The Ni/SiO$_2$ profile presents only one peak at 629 K (Fig. 1B), indicating that there is no significant metal-support interaction. In view of these results, the low temperature peak may be assigned to well-dispersed nickel oxide in the support while the high-temperature peak suggests that the reducibility of some of the nickel ions decreases by strong interactions with the support, possibly by formation of a nickel spinel or perovskite. However, no crystalline phases containing Ni or Rh are observed on any of the samples using XRD. Note that Ni catalysts are almost totally reduced at temperatures lower than 873 K.

The TPR profiles of the Ni samples treated at 823 K (Fig. 1B) present a low temperature peak (590 K) with higher hydrogen consumption, indicating that in these cases the proportion of well-dispersed Ni is higher than those recorded on solids treated at 1123 K. The highest-temperature peak (not shown) presents a broadening due to the presence of carbonates in the sample. The Rh (0.2%) and Rh (0.6%) (not shown) catalyst shows two peaks at 481 and 545 K. The Rh/SiO$_2$ system exhibits a single reduction peak at 395 K. The appearance of the highest temperature TPR peak in the Rh/La$_2$O$_3$ catalysts as compared to the SiO$_2$ solid indicates that there is a significant interaction between rhodium oxide and the La$_2$O$_3$ support. The same effect was reported by Wang and Ruckeinstein, 2000.

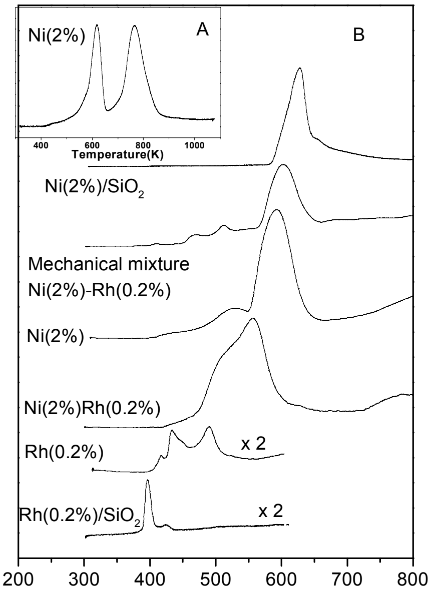

Figure 1. TPR profiles of calcined Ni-Rh catalysts A) pretreated in O$_2$ at 1123 K, B) pretreated in O$_2$ at 823 K. Conditions: 5%H$_2$-Ar, flow rate 30 ml min^{-1} and 10 K min^{-1}.

They detected the presence of LaRhO$_3$ over the 10 wt.% Rh/La$_2$O$_3$ sample through XRD analysis. Note that the bimetallic Ni-Rh solid shows a lower reduction temperature (559 K) compared to the Ni catalyst, thus suggesting a possible interaction between the well-dispersed metals. The TPR profile of the mechanical mixture supports this analysis, because it shows separate reduction peaks similar to those observed for the monometallic ones (Fig. 1B).

For the rhodium supported samples the XPS Rh/La signal intensity ratio increased from 0.067 to 0.15 with the increasing rhodium content, from 0.2 to 0.6 wt% (Table 2). The Rh 3d$_{5/2}$ binding energies were obtained for the calcined catalysts. The C1s peak at 289.0 eV was attributed to carbonate carbon (Milt *et al.*, 1996). The binding energies were referenced to C 1s = 284.6 eV, which resulted in a binding energy for La 3d$_{5/2}$ = 834.6 eV in the monometallic rhodium solid. For these solids the B.E.s of Rh 3d$_{5/2}$ were between 308.0 and 309.1 eV (Table 2). According to the literature, these high energy values indicate the presence of Rh^{+n} species. Values in the range (308.4-309.3eV) for Rh^{+2} compounds have been reported by Gysling *et al*, 1987.

In the Ni(2%) solid, no Ni signal was detected; however, in the bimetallic solid the Ni /La surface ratio was equal to 0.026. The Ni 2p$_{1/2}$ peak was employed to calculate the surface ratio due to the overlapping of the Ni 2p$_{3/2}$ and La 3d$_{3/2}$ signals. In the bimetallic solid the Rh 3d peak shows a significant broadening (FWHM =2.6 eV) and the Rh/La ratio presents the same value as in the monometallic one (Table 2).

Table 2 . Surface features of Ni-Rh catalysts.

Catalyst	La 3d$_{5/2}$^{a}	Rh 3d$_{5/2}$^{a}	C$_{CO3}$/La)$_s$^{b,c}	Ni/La)$_s$^{c}	Rh/La)$_s$^{c}	O/La)$_s$^{c}
Rh(0.2%)	834.6 (3.0)	307.9 (2.3)	0.8	-	0.067	4.9
Rh(0.6%)	834.6 (3.2)	309.1 (2.1)	1.9	-	0.15	4.0
Ni(2%) Rh(0.2%)	835.1 (3.6)	309.1 (2.6)	0.9	0.026	0.067	6.9
Ni(2%)	835.0 (3.4)	-	0.7	0	-	11.5

[a] Binding energies (FWHM).

[b] C 1s)$_{CO3}$ B.E. were between 289.0 and 289.5 eV. Contamination carbon was taken as reference at 284.6 eV.

[c] Surface atomic ratios.

The FWHM of the Rh 3d$_{5/2}$ peak mainly reflects the particle size (Zafeiratos, 1984). The increased FWHM for small particles, where the B.E. is also sensitively size-dependent, originates from the particle size distribution. The low loading catalyst exhibits larger FWHM than Rh (0.6%) and the B.E. for Rh(0.6%) is 1 eV higher than Rh(0.2%). This indicates smaller average particle size and broader size distribution in the former solid.

Despite the fact that all the catalysts tested did not change their activities with time on stream, TGA and DSC experiments proved the presence of carbon deposits on all the solids. The weight change profile for the oxidation of Rh(0.2%) catalysts used for 100 h is shown in Fig 2. Three peaks are observed, the first one at 600 K being the largest one. The same peak was observed during the TGA of the calcined catalysts that showed the presence of hydroxide through XRD. Besides, the DSC experiments (Fig. 2) show that this weight loss is endothermic so it could be attributed to the $La(OH)_3$ decomposition. This peak is assigned to the dehydration of the hydroxide that could have been produced by water originated from the reverse water gas shift reaction. On the Ni catalyst the carbonaceous species is oxidized between 800 and 900 K. In the bimetallic catalyst the largest peak appears between 700 and 950 K while there is a small weight loss at higher temperatures. On the other hand, the DSC curve of this solid (Fig. 2) shows a small exothermic peak at 610 K. This could be due to the oxidation of a reactive carbonaceous deposit that is not detected by TGA. This curve also shows that the weight loss between 750 and 900 K is an exothermic process. The same TGA experiment was carried out on lanthanum oxide showing only one peak at 1100 K, which could be due to oxycarbonate decomposition (Turcotte *et al.*, 1969). This compound was detected by XRD analysis in all the solids and was also previously reported on lanthanum oxide supported catalysts (Milt *et al.*, 1996).

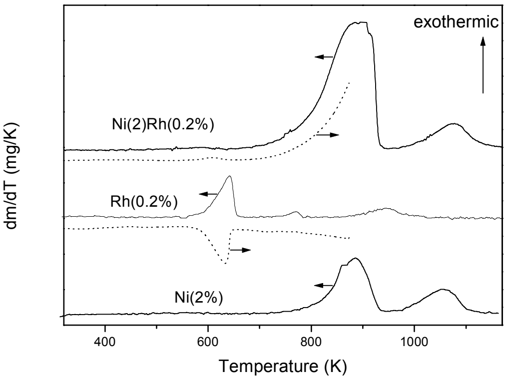

Figure 2. DTGA and DSC profiles of solids used 100 h at 823 K, W/F=$2.67x10^{-5}$ g h ml^{-1}. Air flow 90 ml min^{-1}, heating rate 10 K min^{-1}.

The best candidates for use in the membrane reactor were the monometallic Rh catalysts because they were stable and produced non-measurable carbonaceous residues. Fig. 3a shows that for Rh (0.6%) the CH_4 conversion increases 35% while the CO_2 conversion increases 20% compared to those obtained with no sweep gas flow and no pressure difference. The effect of a pressure difference between both sides of the membrane is also illustrated in Fig. 3a. As expected, the conversion decreases when the pressure increases but there is also an increase in H_2 permeation (Fig. 3b) through the membrane. Similar results were obtained with the Rh (0.2%) catalyst. For this solid, a 67 % higher W/F was needed to reach the equilibrium conditions.

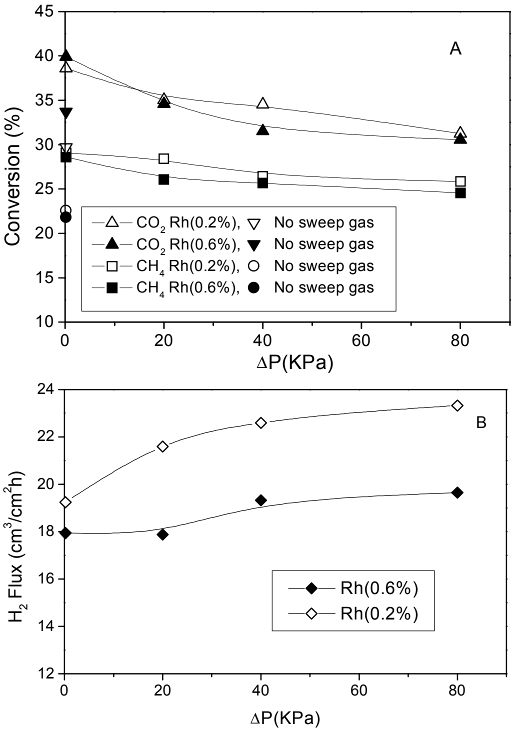

Figure 3. A) Catalytic behavior of Rh solids in a membrane reactor at 823 K vs pressure drop across the membrane. W/F= $1.8x10^{-5}$ g h ml^{-1} for Rh(0.2%) and W/F = $1.1x10^{-5}$ g h ml^{-1} for Rh(0.6%). Sweep gas: 10 ml min^{-1} He. B) Hydrogen flux.

IV. DISCUSSION

The catalytic behavior of the Ni-Rh based catalysts depends on the supported metal. In the monometallic Rh catalysts, the activity slightly increases with Rh loading while the TOF is significantly affected (Table 1).

The literature offers conflicting views about the role of the support and particle size effects for Rh-based formulations. Bitter *et al.*, 1998, have reported TOFs of CO_2 at 875 K for Rh catalysts supported on ZrO_2 , γ-Al_2O_3 and SiO_2 . Through deactivation studies, they concluded that the activity of their catalysts was mainly determined by the availability of Rh and was less influenced by the support. For Pt catalysts, these authors (Bitter *et al.*, 2000) found a strong metal-support interaction. The metal is decorated by partially reduced support as suggested for Rh/ZrO_2 (Morterra *et al.*, 1990) and Ni/ZrO_2 (He *et al.*, 1989). The activity of these catalysts is related to Pt atoms located on the Pt-ZrO_2 perimeter. Mark and Maier, 1996, have calculated the CH_4 TOFs at the same temperature, employing similar supports. They found that the reaction rates per unit surface area showed no trend and concluded that the reaction is independent of the metal dispersion and the nature of the support. However , Zhang *et al.*, 1996, contend that the initial values of TOF obtained over their supported Rh catalysts exhibit a dependence on particle size, but this dependence might be related to metal-support interactions.

Crisafulli *et al.* (1999) reported the catalytic activity of Ni/SO_2 catalysts at 873K They obtained results similar to ours but their solids deactivated at an average rate of 2.8% h^{-1}. Even though there are many publications concerning Ni catalysts, only a few of them reported TOF values. This could be due to the difficulties in measuring Ni dispersion (Bartholomew, 1990).

In our catalysts, addition of Rh to Ni solids caused an improvement in the reaction rates of methane and carbon dioxide measured at 823 K. On the other hand, the stability of the solids was not modified by the presence of the noble metal. However, the carbon deposition on the bimetallic sample is remarkably higher than that of both Rh and Ni monometallic catalysts. On the basis of the characterization data, these behaviors could be related to the different metal-support interactions. Using TPR a fraction of well-dispersed metal was observed while the second (high temperature) peak suggests the presence of a metal support interaction. In the case of the bimetallic solid, the temperature decrease of the first TPR peak could be due to either an interaction between the dispersed metals or to the presence of metallic Rh which could increase the reducibility of Ni oxide species, or to both effects. Studying the Ni-Ru and $Ni-Pd/SiO_2$ catalysts (Crisafulli *et al.*, 1999) or the $Pt-Ge/Al_2O_3$ solids (Garetto *et al.*, 1996) all these authors have found a significant decrease in the hydrogen chemisorption. In all cases, this behavior was a consequence of a strong metal-metal interaction. In our catalysts, the simultaneous presence of both metals inhibited the hydrogen chemisorption, even though no alloyed particles were detected.

The XPS Ni/La surface ratio is measurable only in the Ni(2%) Rh(0.2%) catalyst (Table 2). This is also symptomatic of some sort of interaction between the two metals. As a matter of fact, these two elements form alloys in all proportion (Moffett, 1978). So, these arguments lend more weight to the hypothesis that Ni/Rh alloy formation is the cause of impaired hydrogen chemisorption in the bimetallic catalysts.

Catalyst deactivation and coke formation are very important factors in methane reforming with carbon dioxide. The formation of carbon deposits is a key factor when the catalyst is to be used in a membrane reactor. In our case, the catalyst activity has not been influenced by the carbon deposition after 100 h on stream. This behavior could be related to the carbon deposition sites and/or the ability of carbon to play a role as a reaction intermediate (Zhang *et al.*, 1996).

The carbon formation at different reaction temperatures has been widely studied on supported catalysts containing either Ni or Rh . Kroll *et al.*, 1996, have shown that the carbon filaments do not deactivate the catalyst directly, except after a massive carbon accumulation. In Ni/La_2O_3 catalysts, an unusual catalytic stability was reported by Slagtern, *et al.* 1997. The tight coating of the nickel particles by layers of lanthanum carbonate could hinder the formation of deactivating coke, possibly by limiting the carbon migration through the nickel particles and its recombination as an encapsulating veil around the particle. Taking into account the high C 1s B.E. obtained for our samples, it can be concluded that the C 1s peak at 289.2 eV is due to the presence of surface carbonate species in the oxides, in agreement with the bulk XRD results.

The high temperature peak (1100K) observed in our TGA experiments might be the contribution of oxycarbonate decomposition from the support and the combustion of a very stable carbon species. In our Ni monometallic catalysts, the carbonaceous deposits formed after 100 h on stream are made up of a reactive species that burnt out at 900K. These species could be the graphitic filaments observed by Irusta *et al.*, 2001. The presence of this non-deactivating coke explains the stability of our catalysts containing Ni, despite the large amount of carbonaceous deposits. In the case of our bimetallic catalyst, this could be the most abundant species. In a separate study, we have thoroughly characterized the carbonaceous deposits through Laser Raman Spectroscopy and SEM (Irusta *et al.*, 2001).

There is no general agreement about the role played by the support in the case of rhodium (Bitter *et al.*, 1998, Wang and Ruckeinstein, 2000). In our case, the strong interaction between Rh and La oxide is probably responsible for the high stability of these solids. Even though $LaRhO_3$ formation has not been detected in our catalysts, our TPR and XPS data suggest that the stability of Rh(0.2%) is due to the strong metal/support interaction.

The reaction equilibrium is shifted using a Pd membrane reactor in which the hydrogen partial pressure is lower at the reaction zone due to continuous removal of hydrogen through the membrane. By increasing the pressure difference between the shell and the tube side, the magnitude of the equilibrium shift decreases because the equilibrium conversion decreases when the pressure increases. The hydrogen flux permeated through the membrane increases due to the higher driving force for permeation. At low values of W/F, the methane conversion was not restricted by equilibrium since the methane conversion was lower than the theoretical equilibrium value. So, for the less active solid (Rh(0.2%)) higher values of W/F were used to reach the equilibrium conditions.

The 100% selectivity towards H_2 separation by the commercial Pd membrane prevents reactant dilution during reaction (Prabhu, 2000), providing conversions higher than the values obtained with no sweep gas. This demonstrates the so-called “drain-off effect” of the Pd membrane reactor on this endothermic reactor. The same effect has been reported in the literature (Prabhu and Oyama, 2000; Liu *et al.*, 1998, Kikuchi, 2000) for other endothermic systems.

V. CONCLUSIONS

In our Ni-Rh catalysts, the formation of carbon species does not affect the activity after 100 hours on stream at 823 K (Fig. 2). The Rh catalysts are stable and present the lowest carbon deposition at 823 K. A significant metal-support interaction, hinted by TPR and XPS, seems to be responsible for the high activity and stability of these catalysts. The use of a membrane reactor allows a 35% increase of the CH_4 conversion.

Acknowledgements

The authors wish to acknowledge the financial support received from UNL, CONICET and ANPCyT. Thanks are given to the Japan International Cooperation Agency (JICA) for the donation of the major instruments, to Elsa Grimaldi for the edition of the English manuscript, to Fabricio Charles and Carolina Mosimann for their technical assistance, and to Prof. María Alicia Ulla for her helpful discussions.

REFERENCES

Bartholomew, C. H., “Hydrogen adsorption on supported cobalt, iron, and nickel”, *Catal. Letters,* **17**, 27 (1990).

Bitter, J.H., K. Seshan and J.A. Lercher, “Mono and bifunctional pathways of CO_2/CH_4 reforming over Pt and Rh based catalysts”, *J. Catal.*, **176**, 93 (1998).

Bitter, J.H., K. Seshan and J.A. Lercher, “Deactivation an coke accumulation during CO_2/CH_4 reforming over Pt catalysts”, *J. Catal.*, **183**, 336 (1999).

Bitter, J.H., K. Seshan and J.A. Lercher, “On the contribution of X-ray absorption spectroscopy to explore structure and activity relations of Pt/ZrO_2 catalysts for CO_2/CH_4 reforming”, *Topics in Catalysis*, **10**, 295 (2000).

Bradford, M. and A. Vannice, “ CO_2 reforming of CH_4”, *Catal. Rev. Sci. Eng*., **41(1)**, 1 (1999).

Brown, R., M. Cooper and D. Whan, “Temperature programmed reduction of alumina-supported iron, cobalt and nickel bimetallic catalysts”, *Appl. Catal.*, **3**, 177 (1982).

Chang, J., S. Park, J. Yoo and J. Park, “Catalytic behavior of supported KNiCo catalyst and mechanistic consideration for carbon dioxide reforming of methane”, *J. Catal.*, **195**, 1 (2000).

Crisafulli, C., S. Sciré, R. Maggiore, S. Minicò and S. Galvagno, “CO_2 reforming of methane over Ni-Ru and Ni-Pd bimetallic catalysts”, *Catal. Letters*, **59**, 21 (1999)

Garetto, T., A. Borgna and C. Apesteguía,”High-thiotolerant Pt-Ge/Al_2O_3 naphtha reforming catalyts by in-situ alloying”, *Studies in Surf. Sci. Catal.*, **101**, 1155 (1996).

Gysling, H., J. Monnier and G. Apai, “Synthesis, characterization and catalytic activity of $LaRhO_3$”, *J. Catal.*, **103**, 407 (1987).

He, M. and J. Ekerdt, “Temperature-programmed studies of the adsorption of synthesis gas on zirconium dioxide”, *J. Catal.,* **87**, 238 (1984).

Irusta, S., L. Cornaglia and Lombardo, E., “Hydrogen production using Ni-Rh on La_2O_3 as potential low temperature catalysts for membrane reactors”, *J. Catal.,* **210,** 7*(2002).*

Kikuchi, E., “Membrane reactor application to hydrogen production”, *Catal. Today*, **56**, 97 (2000).

Kroll, V., H. Swaam and C. Mirodatos, “Methane reforming reaction with carbon dioxide over Ni/SiO_2 catalysts. I. Deactivation studies”, *J. Catal.*, **161**, 409 (1996).

Lin, Y., G. Lee and M. Rei, “An integrated purification and production of hydrogen with a palladium membrane-catalytic reactor”, *Catal. Today*, **44**, 343 (1998).

Mark, M. and W. Maier, “CO_2 reforming of methane on supported Rh and Ir Catalysts”, *J. Catal*, **164**, 122 (1996).

Milt, V., R. Spretz, M. Ulla, E. Lombardo and J. García Fierro, “The nature of active sites for the oxidation of methane on La-based perovskites”, *Catal. Letters*, **42**, 57 (1996)

Moffett, W., *The Handbook of Binary Phase Diagrams*, **4**, General Electric Co (1978).

Morterrra, C., E. Gianello, L. Orio and M. Volante, “Formation and reactivity of Zr^{3+} centers at the surface of vacuum-activated monoclinic zirconia”, *J. Phys. Chem.,* **94**, 3111 (1990).

Prabhu, A. and T. Oyama, “Modeling of the methane reforming reaction in hydrogen selective membrane reactors”, *J. Membrane Sci.*, **176**, 233 (2000).

Sigl, M., M. Bradford, M., H. Knözinger and M. Vannice, “CO_2 reforming of methane over vanadia-promoted Rh/SiO_2 catalysts”, *Topics in Catal.*, **8**, 211 (1999).

Slagtern, A., Y. Schuurman, L. Leclercg, X. Verykios and C. Mirodatos, “Specific features concerning the mechanism of methane reforming by carbon dioxide over Ni/La_2O_3 catalysts”, *J. Catal.*, **172**, 118 (1997).

Turcotte, R.P., J.O. Sawyer and L. Eyring,”On the rare earth dioxymonocarbonates and their decomposition”, *Inorganic Chem*. 8(2) 238 (1969)

Wang, H. and E. Ruckeinstein, “Carbon dioxide reforming of methane to synthesis gas over supported rhodium catalysts: the effect of support”, *Appl. Catal. A: General*, **204**, 143 (2000).

Zafeiratos, S., V. Nehasil and S. Ladas, “X-ray photoelectron spectroscopy study of rhodium particle growth on different alumina surfaces”, *Surface Science,* **433-435**, 612 (1999).

Zhang, Z., V. Tsipouriari, A. Efstathiou and X. Verykios, “Reforming of methane with carbon dioxide to synthesis gas over supported rhodium catalysts”, *J. Catal.*, **158**, 51 (1996).

Received: September 16, 2001.
Accepted for publication: September 05, 2002.
Recommended by Guest Editors J. Cerdá, S. Díaz, and A. Bandoni.