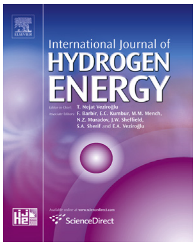
Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/he



# High selectivity to hydrogen on the methane decomposition over Rh/γ-$Al_2O_3$–$Nd_2O_3$ catalysts

M. Caballero [a], G. Del Angel [a,*], A. Bonilla-Sánchez [a], I. Rangel-Vázquez [a], A. Arrieta [a], A. Vázquez-Zavala [a], L. Huerta [b,1], M. Salgado [a]

[a] Universidad Autónoma Metropolitana-Unidad Iztapalapa, Departamento de Química, Área de Catálisis, Av. San Rafael Atlixco No. 186, C.P. 09340, A.P 55-534, México D. F., Mexico

[b] Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Apartado Postal 70-360, México D.F., 04510, Mexico

ARTICLE INFO

*Article history:*
Received 1 June 2016
Received in revised form
1 October 2016
Accepted 2 October 2016
Available online xxx

*Keywords:*
Hydrogen
Methane
Rhodium
Neodymium
Carbon
SEM-EDS

ABSTRACT

Methane decomposition was carried out on Rh/γ-$Al_2O_3$ and Rh/γ-$Al_2O_3$–$Nd_2O_3$ catalysts to produce hydrogen. γ-$Al_2O_3$–$Nd_2O_3$ mixed oxides and Rh/γ-$Al_2O_3$–$Nd_2O_3$ catalysts were prepared by wet impregnation using $Nd(NO_3)_3 \cdot 6H_2O$ and $RhCl_3 \cdot 3H_2O$ as precursors. The concentrations for the catalysts were 1.0 wt% for Rh and 1 and 10 wt% for Nd. The reaction was carried out from 400 to 750 °C. All catalysts showed high activity and selectivity at 700 °C, with conversions around 74–79 vol%. The activity per site (TOF) was higher on Rh crystallites size $\geq$2.1 nm. The Rh catalyst with 10 wt% neodymium concentration was highly selective to hydrogen, 100%. This behavior was explained by the highest interaction between Rh and γ-$Al_2O_3$–$Nd_2O_3$ supports. Rh/γ-$Al_2O_3$ and Rh/γ-$Al_2O_3$–$Nd_2O_3$ with 1 wt% Nd showed selectivities of 89 and 65% at 700 °C respectively and ethane and ethylene products. These products come from the mobility of CHx species on the Rh surface during the reaction. The carbon produced was mainly deposited on the support. Characterization was done by XRD, $N_2$ adsorption isotherms, HRTEM, EDS-SEM, CO-FTIR, $H_2$-TPR, XPS.

## Introduction

Nowadays there is a clear need to find an alternative energy source that will replace, at least partially and progressively, fossil fuels in the near future and hydrogen seems to be one of the most promising energy sources, since it is considered as environmentally benign [1]. The amount of energy produced during the hydrogen combustion is higher than that obtained by any other fuel. The advantages of hydrogen as an energy source is that it represents an abundant raw material and its combustion does not produce $CO_2$, but only water vapor, which makes it an ideal candidate for the reduction of the so-called "greenhouse effect" [2–4].

Nowadays, the main process for producing hydrogen is steam reforming of natural gas [5]. Steam reforming is a multiple stage process. The first stage is conducted at high temperature (800–900 °C). While the second stage is the catalytic water gas shift reaction, occurring in two steps. In addition to steam reforming, partial oxidation is also used to generate hydrogen from fossil fuels [6], but the produced hydrogen is still mixed with CO and $CO_2$, which again needs a

---

* Corresponding author.
E-mail address: gdam@xanum.uam.mx (G. Del Angel).

[1] Fax: +52 55 5622 4715.

http://dx.doi.org/10.1016/j.ijhydene.2016.10.001
0360-3199/© 2016 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

complicated separation process as in the steam reforming case.

The energy required for methane catalytic cracking is nearly one half that required for steam reforming per mole of methane decomposed [7–9]. The energy requirement is 37.4 kJ/mol $H_2$ in methane catalytic cracking compared to 63.3 kJ/mol $H_2$ in the steam reforming process [9]. In addition to the lower energy demand for methane catalytic cracking compared to steam reforming, there is no need for additional energy for steam generation or gas treatment. The heat requirement for catalytic cracking can be covered by burning ~15–20% of the hydrogen produced, which further reduces $CO_2$ emissions [10].

Contrasting the steam reforming process, the catalytic decomposition of methane does not include water gas shift and preferential oxidation of CO, which considerably simplifies the process and may reduce the hydrogen production costs [11].

Steinberg and Cheng [12] compared different methods for hydrogen production at an industrial scale of $10^8$ SCF/D (Standard Cubic Feet per Day) of hydrogen gas at 300–600 psig. They concluded that methane thermal cracking is the most economical method for hydrogen production followed by Hydrocarbon process < steam reforming < Coal gasification with electricity chemical shift (Westinghouse) < Partial oxidation < Steam iron < High temperature steam electrolysis < Texaco gasification < Coal gasification with high temperature electrolysis < K-T gasification < Water electrolysis.

Recent investigations have focused on improving the process of hydrogen production by decomposition of methane to form hydrogen and elemental carbon as an attractive alternative to the steam reforming [10], using metal or carbon catalysts for a higher conversion of methane and stability long-term catalyst [13–15]. In recent years different metal based catalysts mono and bimetallic have been studied in the hydrogen production as Fe [16], Ni–Cu–Fe/$Al_2O_3$ [17].

For simultaneous production of hydrogen and nanocarbon particles, nickel-based catalysts have been used. However, the major drawback in the case of the decomposition on metal catalysts (Ni, Co or Fe), is that the catalyst is quickly deactivated because of deposits of carbon [18,19]. In general, the noble metals show better catalytic activity and resistance to the deactivation, but the use of the catalysts based Ni is due to its lower cost [20].

In recent years, the investigation of the behavior of the addition of lanthanides elements to noble metal catalyst has begun [21,22]. Manoj et al. [23] concluded that yield of hydrogen and carbon increased significantly with increasing the reaction temperature from 600 °C to 700 °C. A maximum initial hydrogen yield of 62%, 61% and 58% and a final carbon yield of 1360 wt%, 1159 wt% and 1576 wt% was achieved over ceria, zirconia and lanthana supported catalysts respectively, at 700 °C.

Ahmed et al. [24] studied Catalytic methane decomposition in a fixed bed reactor. The effect of promoting Fe with Ce and Co and reduction temperature is investigated. The results reveal that Ce addition has shown a negative impact on $H_2$ yield while a positive effect on $H_2$ yield and catalyst stability are observed with Co addition. In terms of number of moles of hydrogen produced per active sites, Fe/$Al_2O_3$ has shown a higher number of moles of hydrogen compared to bimetallic catalysts.

Tang et al. [25] employed Fe/$CeO_2$ for methane decomposition using a fixed bed reactor at 750 °C. The optimum activity was observed with a catalyst composed of 60 wt. % $Fe_2O_3$ and 40 wt. % $CeO_2$. CO was detected due to carbon oxidation by high mobility lattice oxygen from Ceria. Comparing Fe and Ceria and Fe–Ce bimetallic catalysts, Ce monometallic catalyst showed very small $CH_4$ conversion activity. Fe catalyst showed 60% $CH_4$ conversion after 25 min, then the catalyst was completely deactivated after 50 min.

As example it has been assumed that the component of cerium has a crucial role in the maintenance of the catalytic activity of noble metals, at the same time, the oxide of cerium shows a good stability in presence of precious metals, such as Ru, Rh, Pd, Pt, and can lead to decrease the carbon deposit during the decomposition of methane. The purpose of the present study was to investigate the influence of rare-earth as Neodymium on the Rh/$\gamma Al_2O_3$–$Nd_2O_3$ catalysts in the activity, selectivity and stability of Rh for the $CH_4$ decomposition. Two concentrations of Nd (1 and 10 wt%) in the Rh catalysts where evaluated in the decomposition of $CH_4$ to produce hydrogen. The $\gamma$-$Al_2O_3$ was selected because of its high specific surface area and also it has reported good activity on Rh supported on alumina for $CH_4$ reforming. Neodymium was selected to give stability to the alumina and because it is not widely used in this type of reaction.

The characterization was done by $N_2$ adsorption-desorption, X-ray diffraction, $H_2$-TPR, FTIR of CO adsorption, XPS, HRTEM, SEM-EDS.

## Experimental

### *Supports and catalysts preparation*

$\gamma$-$Al_2O_3$ support was prepared from Bohemita Catapal B. Firstly the Boehmite was dried to 120 °C for 12 h, then the solid was calcined in air flow of 60 mL/min for 24 h using a ramp of temperature from 25 °C to 650 °C. The $\gamma$-$Al_2O_3$–$Nd_2O_3$ (loaded with 1 and 10 wt% Nd) mixed oxides, were prepared by wet impregnation of the Boehmite with the necessary quantity of $Nd(NO_3)_3 \cdot 6H_2O$ (Strem Chemicals, 99.99%) aqueous solutions to obtain 1 and 10 wt% of Nd on the support, the mixture was maintained in stirring for 3 h. Then, the solids were dried in an oven to 120 °C for 12 h, after that, samples were calcined at 650 °C in airflow of 60 mL/min for 24 h.

Rh catalysts were prepared by wet impregnation of the $\gamma$-$Al_2O_3$–$Nd_2O_3$ supports with $RhCl_3 \cdot 3H_2O$ (Strem Chemicals, 99.99%) aqueous solution. The solids were left in stirring for 3 h, and then, the water is evaporated using a vacuum evaporator bath at 60 °C and vacuum of 72 millibars. Subsequently the solids were dried in an oven at 120 °C, for 12 h. The catalysts were calcined in air at 500 °C under airflow of 60 mL/min for 5 h and finally reduced in $H_2$ flow of 60 mL/min at 500 °C for 5 h. The Rh percentage on the catalysts was obtained by atomic absorption technique. Catalysts were labeled as: RhANdX, where: Rhodium, as Rh, alumina as A, neodymium as Nd, and X is the concentration of Neodymium in wt%.

Please cite this article in press as: Caballero M, et al., High selectivity to hydrogen on the methane decomposition over Rh/$\gamma$-$Al_2O_3$–$Nd_2O_3$ catalysts, International Journal of Hydrogen Energy (2016), http://dx.doi.org/10.1016/j.ijhydene.2016.10.001