INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 41 (2016) 6763–6772

Available online at www.sciencedirect.com

ScienceDirect

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

Effect of support on methane decomposition for hydrogen production over cobalt catalysts

*Rosenir R.C.M. Silva**, *Hugo A. Oliveira, Ana C.P.F. Guarino, Bianca B. Toledo, Mariana B.T. Moura, Bárbara T.M. Oliveira, Fabio B. Passos*

Departamento de Engenharia Química e de Petróleo, Universidade Federal Fluminense (UFF), Rua Passo da Pátria, 156, CEP, 24210-240, Niterói, RJ, Brazil

ARTICLE INFO

Article history:
Received 5 November 2015
Received in revised form
1 February 2016
Accepted 23 February 2016
Available online 2 April 2016

Keywords:
Cobalt supported catalyst
Methane decomposition
Hydrogen production
Support effect

ABSTRACT

Cobalt catalysts were tested in methane decomposition reaction at 450 °C to evaluate their catalytic properties in non-oxidative methane conversion for hydrogen production via accumulation of carbon. Silica, alumina and niobia supported cobalt catalysts were characterized by X-ray diffraction (XRD), temperature-programmed reduction (TPR), X-ray photoelectron spectroscopy (XPS), H_2 chemisorption and BET surface area measurements. The nature of the support strongly influenced this process. The high initial activity of Co/Al_2O_3 catalyst reduced at 500 °C lead to a large formation of carbon deposits and consequent catalysts deactivation. For Co/SiO_2, the activity increased with reaction time due to reduction of cobalt oxide particles that were not reduced during the reduction pretreatment, and this effect was more pronounced for the reduction at 300 °C. Co/SiO_2 reduced at 500 °C was the best catalysts for methane decomposition. For Co/Nb_2O_5, the Nb_2O_X species partially covered cobalt particles even for reduced catalysts at low temperature (300 °C) and this effect completely inhibited the reaction after high-temperature reduction (500 °C).

Introduction

The conversion of natural gas by catalytic reactions may lead to several products, such as hydrogen and synthesis gas, which are very important for various processes. Particularly, hydrogen has been considered one of the most promising energy carriers due to its environmentally friendly characteristics. It may be used in fuel cells to convert chemical energy into electricity and heat without generating greenhouse gas [1–6].

Many processes have been studied to produce hydrogen from natural gas and the most traditional are steam reforming, partial oxidation and auto-thermal reforming of methane (the two previous reactions combined). These processes are characterized by CO_x emissions and by high-energy consumption, usually from burning fossil fuels [4,7]. In this context, the catalytic decomposition of methane has been identified as a promising alternative route, due to the possibility of CO_2-free hydrogen production.

Furthermore, due to the importance of the utilization of natural gas, catalytic decomposition of methane using low

---

* *Corresponding author.*
E-mail address: rosenir@vm.uff.br (R.R.C.M. Silva).

http://dx.doi.org/10.1016/j.ijhydene.2016.02.101

temperature conditions has become an attractive alternative to produce hydrogen. Several researchers have studied the prospect of producing hydrogen on a large scale by this process [2,8]. UOP has operated a pilot plant in the 1960's to produce hydrogen via catalytic decomposition of methane using catalysts based on nickel in moving bed reactors [2]. However, the challenge to turn the hydrogen-based economy viable remains unsurpassed, which would improve the process efficiency, reducing both energy and production costs [9].

From the point of view of kinetics and catalysis, several studies have tried to understand the mechanism of the reaction and develop more active catalysts [5,6,10–14]. Experiments based on Ni, Co and Fe catalysts are commonly reported, although metallic catalysts formed by other metals of Group VIII have also been studied [1,4,5,15–27]. Various supports have been used such as TiO_2, SiO_2, Al_2O_3, ZrO_2, MgO, C and zeolites, being SiO_2 and Al_2O_3 the most studied [1,13,18,19,22–25,28]. Chen et al. [20] found that Ni/Al_2O_3 is the most active, followed by $Co/A1_2O_3$, and finally Fe/Al_2O_3. Ermakova and Ermakov [21] found that Ni/SiO_2 produced more carbon yield than Fe/SiO_2 catalysts and Takenaka et al. [13] found that Ni/SiO_2 was one of the most active catalysts among those reported in the literature. On the order hand, the activity of Co catalysts is lower than of Ni catalysts, but Co catalysts don't require an induction period observed with Ni catalysts, which is necessary to promote an increase of the Ni particle size [17]. Thus, there is much controversy about the influence of metal and support, the resulting effect of metal-support interaction and the participation of the metal particle size in the formation of carbon filaments. Furthermore, Ni catalysts have been studied more than Co and Fe catalysts [22].

This paper reports a comparative study about the methane decomposition reaction to hydrogen production over cobalt catalysts supported on conventional oxides as SiO_2 and Al_2O_3 and one less usual, Nb_2O_5 [29,30]. Li et al. [31] found that Nb_2O_5 is an effective support for Ni catalysts for methane decomposition to hydrogen production. However, when Co/Nb_2O_5 catalysts are reduced at high temperature, partially reduced species of support can cover the cobalt surface [32]. Oliveira et al. [33] didn't observed methane chemical vapor deposition on Co/Nb_2O_5 catalyst after reduction at 500 °C. This way, the catalysts were reduced at two different temperatures (300 and 500 °C) before methane decomposition reaction in order to evaluate the influence of reduced niobium species.

Two types of experiments were performed: methane decomposition conducted in a standard unit coupled to gas chromatograph, for the period of approximately 3 h, and temperature programmed surface reactions of methane (TPSR), in order to identify the reactions involved in the early stages of reaction, followed by temperature programmed hydrogenation (TPH) of the carbonaceous species generated to determine their reactivity.

Therefore, this paper aims to evaluate the effect of interactions between the metal and the support on the reaction activity. Although, some of these catalysts have been reported in the literature for this reaction, there still a lack of a fundamental view of the support effects on this reaction. Complementary characterization of the catalysts by BET, hydrogen chemisorption, XPS, DRX and TPR was also carried out.

Experimental

Catalysts preparation

The used supports were SiO_2 (Davicat SP 550-10022), γ-Al_2O_3 obtained from boehmite (Catapal) and Nb_2O_5 obtained from niobic acid (HY 340 CBMM). All of these materials were calcined at 550 °C in air for 2 h.

Cobalt supported catalysts were prepared by incipient wetness impregnation using $Co(NO_3)_2\cdot 6H_2O$ as a precursor. After impregnation, the samples were dried overnight at 120 °C and calcined in air at 400 °C for 2 h. The prepared catalysts contained 10% wt. of Co supported on SiO_2, Al_2O_3 and Nb_2O_5. Since 10%Co/SiO_2 catalyst has showed better results on hydrogen production, two additional Co/SiO_2 catalysts were prepared with 5 and 20% wt. of Co for further investigation.

Catalyst characterizations

Catalyst surface areas were measured by N_2 adsorption–desorption using a Micromeritics ASAP 2010 device. The samples were pretreated at 120 °C overnight and then degassed at 150 °C for 2 h prior to measurements. The test was conducted at a cryogenic temperature using liquid nitrogen at 1 atm.

X-ray diffraction (XRD) analysis of the supports and fresh catalysts were performed in a RIGAKU Miniflex diffractometer with a CuKα ($\lambda = 1540$ Å) radiation source. The XRD patterns were obtained between $2\theta = 2°–90°$, using a 0.05° step size and 1s/step. Co_3O_4 powder was used as a reference sample in the same analysis conditions.

H_2 chemisorption uptakes were measured using a Micromeritics ASAP 2010C assuming an adsorption stoichiometry of one hydrogen atom per surface Co atom. Samples were firstly dried overnight at 120 °C, under flowing He, reduced under flowing H_2 at 300 °C for 3 h or 500 °C for 2 h and then outgassed under vacuum at reduction temperature for 1 h. Total and reversible hydrogen adsorption was carried out at 150 °C, because of activated chemisorption on Co [28]. The isotherms were plotted up to pressures of 300 mmHg. From H_2 chemisorption, metal dispersion and average diameter of the metal particle were calculated.

Temperature programmed reduction (TPR) experiments were performed in a multipurpose unit coupled to a Balzers Omnistar quadrupole mass spectrometer. The samples were previously dried at 150 °C for 30 min under He flow (30 mL/min), followed by reduction under 5% H_2/Ar flow (30 mL/min) at a heating rate of 10 °C/min to 800 °C.

XPS experiments were performed with an ESCALAB 250Xi Thermo Scientific with monochromatic Al Kα X-rays with a spot size of 650 μm. The base pressure inside the analysis chamber was 1×10^{-9} mbar or better. For the survey spectra an energy step size of 1.0 eV and pass energy of 100 eV were used. For the individual element spectra, Co2p, O1s and Al2p energy step size of 0.05 eV and pass energy of 25.0 eV were used. The number of scans ranged from 10 to 15 in function of