Catalyst development for steam reforming of methane and model biogas at low temperature

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ABSTRACT

Low temperature steam reforming (400–550 °C) for the production of hydrogen offers significant advantages compared to the conventional process. The milder operating conditions lead to lower operation costs and cost of construction materials. Additionally, no CO shift reactor is required due to favorable temperature for the WGS reaction. In this work, we report the catalytic performance of Ni and Rh catalysts supported on La_2O_3–ZrO_2 and La_2O_3–CeO_2–ZrO_2 for their application in a multifuel membrane reformer operating at low temperature. The performance of the catalysts is assessed in different operating conditions in methane steam reforming (GHSV, temperature, H_2O/CH_4 ratio) as well as in reforming of model biogas. Stability tests were conducted up to 90 h on stream (1 bar and 7 bar) and the tendency toward carbon formation was investigated. All catalysts were active in the reforming reactions at 400–550 °C and the catalysts supported on La_2O_3–CeO_2–ZrO_2 showed superiority in activity and stability probably due to the presence of ceria in the support which contributes to the reforming rate and the resistance to carbonaceous deposits. Ni(10)CeZrLa exhibited remarkably stable performance with minimum amount of carbon formed after 90 h (ca. 0.05 wt%). TPO and TPH analysis of the carbonaceous deposits showed that the dominating type of carbon is highly reactive and can be easily removed by oxidation or hydrogenation at 500 °C. This fact makes the catalyst even more promising for the proposed low temperature process, since the catalyst can be hydrogenated by using part of the H_2 production stream without further heating of the reactor.

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1. Introduction

Hydrogen is a very important raw material in chemical industries and refineries but also an energy carrier. Steam reforming plays a key role in the production of hydrogen using as primary feedstock natural gas or its renewable counterpart; biogas [1,2].

In the conventional process, natural gas reacts with steam at temperatures over 800 °C in the presence of a nickel catalyst [3–5]. The main reaction product is syngas, a mixture of hydrogen and carbon monoxide, which is used as a raw material for the production of other organic chemicals. When hydrogen is the desired product, syngas from the reformer is fed to a water-gas shift reactor where carbon monoxide reacts with steam over a catalyst to produce more hydrogen and carbon dioxide. Finally, the produced gas mixture is sent to a pressure swing absorption unit (PSA) to achieve pure hydrogen. The requirement of elevated temperature due to the endothermic character of the reforming reaction result in low energy efficiency, high operation cost and emissions of greenhouse gases (GHG).

A new process has been recently proposed aiming at the intensification of methane steam reforming [6]. This process is focused on the production of pure hydrogen via steam reforming at the temperature range of 400–550 °C. The milder operating conditions offer significant advantages such as lower operation costs and cost of materials. Furthermore, the temperature conditions applied, favor the water gas shift (WGS) reaction, thus separate CO shift reactor is not required. On the other hand, thermodynamic limitations result in low conversions of methane and consequently in low H_2 yield. In order to shift the obtained conversion, the system is equipped with a hydrogen-selective membrane. As a result, hydrogen is separated with high purity from the product stream in one step, and at the same time the equilibrium of the reforming reaction is shifted

to the product side [7,8]. Experimental and modeling studies in the proposed system have shown that obtained conversion can be shifted to the value of 80–90% [9,10]. However, the use of a Pd-based membrane increases the total cost of the process.

Further reduction of GHG emissions is achieved by using concentrating solar power (CSP) plants as external carbon-free heat supplier. The utilization of molten salts up to 550 °C with a heat storage system can ensure constant-rate solar heat supply even for an energy demanding industrial chemical process like the steam reforming of methane [11]. Moreover, in order to use hydrogen as an energy carrier, a transition period comprising both renewable and fossil sources will exist. Accordingly, the compact small-scale process proposed offers flexibility to use as primary fuel natural gas, biogas or bioethanol according to local availability.

One of the key factors contributing to the success of such an integrated system for hydrogen production is the use of reforming catalysts that show high activity at such low temperatures and suppress coke formation reactions as well. Ni-based catalysts are the most common catalysts for the reforming process due to their high activity and low cost [2,12]. Noble metals are generally more active than Ni in the reforming reaction but their high cost has prevented their establishment in the industrial application [13]. However, it is well known that both the metal type and the support can contribute to the characteristic properties of an ideal reforming catalyst [2]. Some state-of-the-art supports such as alumina, are not so efficient in the dissociation of water in H and OH groups, so they can only be applied in high temperature reforming [14].

In steam reforming of methane, zirconia has been reported as promising support due to the accumulation of water on the surface and the formation of hydroxyl groups at 500 °C [15]. Reducible supports such as CeO_2 and $CeO_2–ZrO_2$ mixed oxides are also good candidates for low temperature MSR due to the active role in the redox mechanism through the mobility of surface oxygen species [16–23]. The oxygen storage capacity of $CeO_2–ZrO_2$ can be improved by the addition of La [24] thus, enhancing the resistance toward carbon formation [25,26] and the thermal stability of the catalyst [27].

Biogas reforming is an attractive feedstock for the utilization of biogas and the production of hydrogen, especially due to its renewable nature. The most commonly studied process for the reforming of biogas is dry reforming, in which the main components (CH_4 and CO_2) contribute to the production of syngas [28,29]. Steam reforming of biogas has also been investigated [30,31], but there are only few experimental data in the low temperature range [32].

In this work, we report the catalytic performance of Ni and Rh catalysts supported on $La_2O_3–ZrO_2$ and $La_2O_3–CeO_2–ZrO_2$ in view of their application in a multifuel membrane reformer operating at low temperature. Both the activity and stability of the catalysts are assessed at different operating conditions, as well as their tendency toward the formation of carbonaceous deposits.

2. Experimental

2.1. Catalyst preparation

The catalysts investigated in this work were prepared via the wet impregnation method. As precursors of the active metals, $Ni(NO_3)_2·6H_2O$ (Merck) and $RhCl_3·3H_2O$ (Pressure Chemical) were used to obtain metal loading of 10 wt% in the case of Ni-based catalysts and 1 wt% in the case of Rh-based catalysts. Lanthanum doped cerium–zirconium oxide (78 wt% ZrO_2, 17 wt% CeO_2, 5 wt% La_2O_3, Mel Chemicals) and lanthanum doped zirconium hydroxide (oxide-based composition: 90 wt% ZrO_2, 10 wt% La_2O_3, Mel Chemicals) were used as catalyst supports, while the latter was precalcined under air flow at 800 °C for 4 h in order for the oxide to

be formed. The supports were either sieved or pelletized and then crushed and sieved, in order to obtain a particle size of 250–355 μm. The aqueous solution of the metal precursor was mixed with the support particles and stirred for 1 h at 70 °C. The solvent was removed via evaporation under mild vacuum conditions followed by drying overnight at 120 °C. The catalytic materials supported on $La_2O_3–CeO_2–ZrO_2$ were calcined in air flow at 800 °C for 5 h while those supported on $La_2O_3–ZrO_2$ were calcined at lower temperature (600 °C) due to precalcination of the support. In the following text, the catalysts are referred to as M(x)CeZrLa for those supported on $La_2O_3–CeO_2–ZrO_2$ and to M(x)ZrLa for those supported on $La_2O_3–ZrO_2$, where M is the active metal and x the metal loading %wt.

2.2. Catalyst characterization

The surface area of the prepared materials was measured by N_2 adsorption at 77 K, using the multipoint BET analysis method with an Autosorb-1 Quantachrome flow apparatus. The samples were dehydrated in vacuum at 250 °C overnight, before surface area measurements. X-ray diffraction (XRD) patterns were obtained using a Siemens D500 diffractometer, with Cu Kα radiation, in order to identify the crystalline phases apparent. The crystallite size was calculated using XRD data by the Scherrer equation.

Temperature Programmed Reduction (TPR) experiments were performed in a gas flow system using a U-tube reactor connected online with a quadrupole mass analyzer (Omnistar). The catalyst sample (100 mg) was placed in the reactor and pretreated for 0.5 h at 250 °C followed by cooling at room temperature in He flow. The temperature was then raised from ambient to 800 °C at a rate of 10 °C/min in a 10% H_2/He flow (50 mL/min). The mass numbers (m/z) 2 and 18 were used for H_2 and H_2O monitoring, respectively.

The metal dispersion was measured through H_2 temperature-programed desorption (TPD-H_2). Using the same flow system as mentioned above, the catalysts (200 mg) were reduced in 20% H_2/He for 1 h at 550 °C to simulate the reduction treatment prior to the catalytic tests. After reduction, the sample was heated at 600 °C in He flow to desorb any H_2 that might have been spilled over the support and then was cooled to ambient temperature. The chemisorption step took place under a flow of 10% H_2/He for 1 h at 25 ± 2 °C. The temperature of adsorption was selected in order to minimize the effect of hydrogen spillover in $La_2O_3–CeO_2–ZrO_2$ support. The minimization of the latter effect has been thoroughly investigated in literature over noble metal catalysts supported on ceria-related materials and the main conclusions are that the adsorption temperature of −78 °C is required to suppress hydrogen spillover [33] and that when the reduction temperature is as high as 500 °C the spillover effect is significantly slowed down without suppression of the chemisorption on Rh due to SMSI [34]. It has also been shown for Rh/CeO_2 catalysts that after reduction at 500 °C, the metal remains chemically active and hydrogen adsorption would only take place on the metal both at adsorption temperature of −82 °C (191 K) and 25 °C (298 K) [35]. In this work, the reduction temperature is higher than 500 °C (550 °C), but it was selected so as to simulate the reduction process prior to each catalytic test. Especially for noble metal catalysts, the spillover effect is expected to be higher, but on the other hand, the use of $RhCl_3$ as precursor strongly inhibits this [35,36]. However, even though there are several publications reporting the measurement of Ni dispersion at adsorption temperature below 50 °C [19,37,38], the effect on hydrogen spillover has not been discussed. The TPD analysis was carried out in a heating rate of 10 °C/min until the temperature of 850 °C. In order to determine the amount of H_2 desorbed, the peak area was compared to that obtained when known amount of H_2 was pulsed. For the calculation of the moles of metal on the surface, the atomic ratio H:M of 1:1 was used. The specific surface area of metal