

Activated carbon supported Ni–Ca: Influence of reaction parameters on activity and stability of catalyst on methane reformation

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Received 21 February 2006; received in revised form 9 May 2006; accepted 13 May 2006
Available online 12 June 2006

Abstract

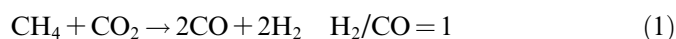
The objective of the present work was to study the influence of some reaction parameters (temperature, chemical nature of pre-treatment gas, mass catalyst) on the yield of methane reforming with carbon dioxide on Ni (5%)–Ca (1%)/AC at atmospheric pressure. The obtained results show that the best system was pre-treated under He flow at 650 °C and then following the reaction at the same temperature. It was also detected that Ca plays a co-support role inhibiting the deactivation of catalyst at long periods of reaction. It can be concluded that it is possible to employ activated carbon as support for methane dry reformation obtaining representative methane conversions up to 40% at mild experimental conditions.

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Keywords: Methane reformation; Ni–Ca catalyst; Activated carbon

1. Introduction

Venezuela has high quantities of natural gas stocks that by 2003 were estimated around 148,000 billions of cubic feet [1] being the first country in Latin-America and the ninth in the world with more natural gas stocks. Therefore, a clear potential in the production and conversion of natural gas in the country is being taken into account for the future years. Particularly, it is important to convert the main component of natural gas methane, in up-grading compounds [2,3] by means, for example, of dry reformation with carbon dioxide to yield syngas as it is indicated in reaction (1):



Different H₂/CO proportions of syngas have been employed in different important industrial processes [4–8] as methanol, dimethyl ether or Fischer–Tropsch synthesis.

Several catalysts have been studied [9–11] for up-grading natural gas. Among them, noble metals as Rh, Pt, Ru and Ir yield high activity and selectivity, but due to the low availability and high price of such metals, nickel has been explored and used as a possible substitute of noble metals [11,12]. However, some studies have shown that Ni has a higher tendency to be deactivated than noble metals by the deposition of carbon [9,10]. Also, studies concerning the dry reformation of methane on supported nickel catalysts [12–15] have shown that support can play an important role on the activity and deactivation by coking. Deactivation of catalysts can be attenuated or even suppressed when the metal is supported on a metal oxide with a strong Lewis basicity [13,16,17] as for example alkaline earth metal oxides, such as MgO, CaO, SrO or BaO which can act as supports [17] or structural promoters [18].

On the other hand, activated carbon (AC) as catalytic support has showed several desirable properties [19,20], e.g., low cost, high surface area, possibility to modify the pore size distribution and surface functionalities, reductive properties, as well as facile recovery of the active metals from the spent catalysts by burning off the support [21].

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In some hydrotreatment reactions, as thiophene hydrodesulfuration [22] and ethylene hydrogenation [19,20], AC has received some attention as it was earlier believed to render higher activities in such reactions than conventional formulations supported on alumina or other common supports [19–22]. However, it is very well known that active carbon has seldom been reported as a catalytic support for methane reforming reactions, principally because it can suffer gasification with carbon dioxide by reverse Boudouard reaction or by steam (Eqs. (2) and (3), respectively), where both



reactions occur spontaneously at temperature around 700 °C or higher. This system has already been studied at a lower temperature such as 55 °C and at atmospheric pressure. It was found [23,24] that carbon supports practically do not suffer an important variation by means of reverse Boudouard reaction. In addition, activated carbon Ni–Ca supported catalysts showed moderate but representative methane conversion values in those mild experimental conditions. Having this in mind, the main objective of the present work was to study the influence of some reaction parameters (temperature, chemical nature of pre-treatment gas, mass catalyst) on the activity and stability of an activated carbon Ni–Ca supported catalyst in methane dry reformation and compared it to the one obtained on other catalytic support as γ -alumina.

2. Experimental

2.1. Catalyst preparation

The catalyst employed in this study Ni (5%)–Ca (1%)/AC was synthesized by incipient wetness impregnation of an activated carbon (AC) of commercial origin [(Merck), Langmuir surface area 907 m² g⁻¹, around 90% of micropore surface, ash content <1 wt%] with nickel and calcium nitrate solutions, heating on a stirring plate at 80 °C to apparent dryness and drying at 120 °C in static air oven for 3 h. The order of impregnation is given by the sequence of elements, i.e., Ni followed of Ca. This catalyst was chosen because it has shown the best activity in previous studies [23,24]. The catalyst was not calcined, but for convenience in the comparison with conventional alumina-supported catalyst the composition is reported as the calculated content of NiO (5%) and CaO (1%) and it was labeled Ni–Ca/AC.

2.2. Catalyst characterization

Homogeneity in the preparation of catalyst was verified from gravimetric analysis of ashes obtained after submitting the catalyst to the pyrolysis of carbonaceous material at 550 °C for 16 h in a ceramic oven (muffle) from Heraeus

following a standard test [23]. Catalyst composition was checked from these ashes by inductively coupled plasma-atomic emission (ICP) in a Perkin–Elmer Optima 3000 apparatus [23,24]. Characterization was performed by X-ray photoelectron spectroscopy (XPS) and by N₂ adsorption isotherms at 77 K. XPS was employed to determine the nature of the chemical species on the surface of samples un-pretreated, pre-treated and after the catalytic test. This was carried out by means of an ESCALAB 220i-XL spectrometer (VG scientific) equipped with a hemispherical electron analyzer and a double anode Mg–Al non-monochromatic X-ray source. The pressure in the analysis chamber was kept below 10⁻⁹ Torr. Pre-treated and post-reaction samples were protected from exposition to the atmosphere by immersion into a hydrocarbon solvent (purified heptanes) while transferring from the reactor to the preparation chamber of the spectrometer. Textural characterization of catalysts was performed by means of N₂ adsorption at 77 K in order to obtain the Langmuir surface areas. The full isotherms in the range of 0.03 up to 630 Torr were measured employing a Micromeritics ASAP-2010 apparatus. Other experimental conditions in textural characterization have already been reported by some of us [19,20,25].

2.3. Catalyst pre-treatments and catalytic test

Samples were submitted to in situ pre-treatments before activity test under helium or hydrogen flow (50 mL/min, 14.5 psi pressure) starting at room temperature up to 550–800 °C with a delta of 50 °C using a heating rate of 10 °C/min. Time of pre-treatment (60 min) was counted from the moment the final temperature was reached. Activity was followed in a continuous flow system (quartz reactor) flowing CH₄ and CO₂ at nearly atmospheric pressure (14.5 psi). Methane was purchased from Matheson (UHP) and CO₂ from BOC (purity higher than 99.9%). Analysis of CH₄ was carried out with gas chromatography (Varian 3700 GC apparatus) with FID detection employing a Porapak R packed column at 50 °C. The reaction conditions employed were: 100–200 g of catalyst sample; 80 mL/min flow of both CH₄ and CO₂, and the reaction temperature was from 550 to 800 °C (similar than that of pre-treatments). In the present conditions CH₄ could only be detected in the reactor gaseous stream off; therefore, catalytic activity is reported as percent methane conversion as a function of time. Some activity tests were done by duplicates or triplicate, the reproducibility of results being better than 5%.

3. Results and discussion

3.1. Characterization of catalyst

Table 1 lists the gravimetric and ICP chemical analysis of catalyst. Ash values obtained from the pyrolysis of three samples indicate a good homogeneity of catalyst prepared.

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