THE INFLUENCE OF $\text{La}_2\text{O}_3$ AND $\text{TiO}_2$ ON NiO/MgO/\(\alpha\)-Al$_2$O$_3$ CATALYST IN CO$_2$-STEAM REFORMING OF METHANE TO SYNGAS

Ali Nakhaei Pour*, Yahya Zamani, Kheirolah Jafari Jozani and Jafar Yeganeh Mehr
Research Institute of Petroleum Industry, National Iranian Oil Company, Gas Research Department, P.O.Box 18745-4163, Tehran, Iran

Received November 27, 2004
In revised form March 23, 2005
Accepted March 29, 2005

Abstract

The effect of $\text{La}_2\text{O}_3$ and $\text{TiO}_2$ on product selectivity, methane conversion and coke formation over NiO/MgO/\(\alpha\)-Al$_2$O$_3$ catalyst were studied in a simultaneous steam and CO$_2$ reforming of methane to syngas. $\text{La}_2\text{O}_3$ and $\text{TiO}_2$ were added to the catalyst via incipient wetness impregnation and bulk precipitation techniques and catalyst activity was tested in a fixed bed quartz reactor. Results reveal that although the addition of these oxides has no effect on the product selectivity and methane conversion, but can reduce coke formation on the surface of the catalysts as it can enhance the mobility of lattice oxygen anions. The results further show that the catalysts prepared by bulk precipitation technique decrease the coke formation more effectively.

Keywords: CO$_2$-steam reforming, Ni catalysts, methane, syngas, $\text{La}_2\text{O}_3$, $\text{TiO}_2$

INTRODUCTION

The catalytic process of carbon dioxide reforming of methane into syngas is becoming increasingly important [1-3]. This process has several advantages over steam reforming or partial oxidation of methane. The syngas produced has a low H$_2$/CO ratio and is more suitable for Fischer-Tropsch synthesis. The process also has important environmental implications as both methane and CO$_2$...
are greenhouse gases [4,5]. Although, carbon deposition is very high in CO₂ reforming of methane, recent studies represented that the carbon deposition is reduced when the steam and CO₂ reforming reactions are carried out simultaneously [6,7]. The development of coke-resistant catalyst has potential significance in commercial utilization of CO₂ and CO₂-steam reforming.

In our earlier studies [7] NiO-MgO catalyst showed a high activity and selectivity in CO₂ reforming of methane to syngas. In this work the effect of La₂O₃ and TiO₂ promoters on the catalyst activity and stability was studied.

EXPERIMENTAL

The catalyst was prepared via bulk impregnation and incipient wetness impregnation techniques. In the first method, alumina gel was prepared by mixing the boehmite with nitric acid followed by addition of aqueous solution of nickel nitrate, magnesium nitrate and titanium oxide or lanthanum nitrate. Then the catalyst precursor was mixed thoroughly, extruded into 5 x 5 mm cylinders, dried at 120°C for 12 h and calcined in air at 950°C for 5 h. Atomic absorption analysis of the final catalysts showed 15 wt.% of NiO, 10 wt.% of MgO and 10 wt.% of TiO₂ for titanium containing catalyst (indicated as AMNTi) and 10 wt.% of La₂O₃ for lantanum containing catalyst (indicated as AMNLa(ex)). In the second method of catalyst preparation, first alumina gel was prepared by mixing the boehmite with nitric acid and lanthanum nitrate solution was added. Then the catalyst precursor was mixed thoroughly, extruded to 5 x 5 mm cylinders, dried at 120°C for 12 h and calcined in air at 950°C for 5 h. Then MgO and NiO were impregnated consequently on this carrier via incipient wetness impregnation of nickel and magnesium nitrate, followed by drying and calcinations according to the first procedure. Atomic adsorption analysis showed 15 wt.% of NiO, 10 wt.% of MgO and 10 wt.% of La₂O₃. This catalyst is indicated as AMNLa(im).

Temperature programmed reduction (TPR) experiments were carried out in a fixed-bed quartz reactor with an inside diameter of 1.2 cm. The samples were heated from room temperature to 950°C at a rate of 10°C/min at 4% H₂/N₂ gas flow with space velocity of 5.35 NL h⁻¹ g-cat⁻¹. Structural characterization of catalysts was performed by powder X-ray diffraction (XRD) technique on a Philips PW 1840 diffractometer using CuKα source at 40 kV and 25 mA.

Catalytic reaction runs were conducted in a fixed-bed quartz reactor (1.2 cm, i.d.) at atmospheric pressure. The feed consisted of carbon dioxide (>99.99%), steam and methane (>99.99%) with a molar ratio of CH₄/(CO₂+H₂O) = 0.87, CH₄/CO₂ = 1 and CO₂/H₂O = 6.4. Gas flow rate was controlled by an electronic mass flowmeter and water was added to the feed using an HPLC pump and a specially designed evaporator. A thermocouple was placed in the catalyst bed to