**Study on mesoporous-supported catalysts for simultaneous CO2 and steam reforming of biogas**

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**1.Introduction**

Conversion of methane and carbon dioxide, which are two of the most abundant carbon-containing materials, into useful products is an important area of the actual catalytic research. The methane-CO2 reforming (dry reforming) to produce syngas

CH4 + CO2 🡪 2 CO + 2 H2 ∆H = 260,5 kJ/mol

is a very attractive route to produce energy and valuable compounds. This reaction offers advantages over methane steam reforming to produce a H2/CO ratio of about 2, adequate for processes such as the production of higher hydrocarbons and derivatives [1,2].

The process is inevitably accompanied by deactivation due to carbon deposition. In order to reduce the carbon deposition, CO2 reforming of methane with a feed gas containing steam has been suggested. Moreover, in the presence of steam, methane steam-reforming occurs simultaneously and thereby higher selectivity for both CO and H2 can be achieved, and also the H2/CO ratio of the product gas can be controlled [3,4].

Recently, the most widely used catalysts for CO2 steam reforming reaction are based on Ni. However, many of these catalysts undergo severe deactivation due to carbon deposition. Noble metals have also been studied and are typically found to be much more resistant to carbon deposition than Ni catalysts but are generally more expensive [5,6].

Moreover, the silica SBA-15, which possesses larger pores and higher thermal stability, may be used as a promising catalyst support [7,8].

In the present study, 10%Ni/SBA-15 and 0.5%Rh/SBA-15 catalysts were prepared, and their performances over the reaction of combined carbon dioxide and steam reforming of methane were investigated.

**2. Methods**

Ordered mesoporous silica SBA-15 was synthesized in a spherical shape, according to the procedures reported by Hussain et al. [9] and used as catalyst carrier.

The supported Rh and Ni catalysts were prepared with the Incipient Wetness Impregnation (IWI) method by using Rh(NO3)3 and Ni(NO3)2·6H2O as precursor, respectively. The catalyst powders, after grinding in an agate mortar, were calcined in air for 1 h to remove the nitrate ions.

The phase structures of the samples were characterized by X-ray powder diffraction (XRD). CO2 temperature programmed desorption (CO2-TPD) analysis was performed using an analyzer equipped with a TCD detector. Multi-point BET surface area and pore volume of catalysts were measured via N2 physisorption at 77 K. Morphology was observed by a Field Emission Scanning Electron Microscope (FESEM). In order to verify real amount of deposed metal, ICP-MS apparatus was used.

The activity of the prepared catalysts was analyzed feeding a gas mixture, composed by CO2, CH4 and steam (CO2/CH4 > 0.75 ÷ 1.5, H2O/CH4 ≅ 1.5), to a catalytic fixed-bed micro reactor. The gas hourly space velocity (GHSV) through the catalytic bed was varied.

**3. Results and discussion**

The first tests were carried out on both Ni and Rh supported catalysts at GHSV = 26000 h-1 and with CO2/CH4 ratio equal to 0.85. Results in terms of CH4 conversion, H2 yield and H2/CO ratio are shown in Fig. 1. The two catalysts reached similar methane conversion and H2 amount produced was about comparable. Otherwise, H2/CO ratio doubled with Rh based catalyst, meaning higher selectivity toward H2 production. In particular, with 0.5%Rh/SBA15 catalyst H2/CO ratio was equal to 2.



**Figure 1.** Comparison between Rh/SBA15 and Ni/SBA15 at GHSV=26000 h-1 and CO2/CH4=0.85.

Deeper studies were performed on Rh/SBA15 catalyst by varying space velocity. Activity test at GHSV equal to 44000 and 15000 h-1 were carried out and performances were compared with those obtained at GHSV = 26000 h-1. As expected, CH4 conversion and H2 yield decreased by increasing space velocity, but H2/CO ratio was maintained about 2.

**4. Conclusions**

Two SBA15 supported catalysts (Rh 0.5 wt% and Ni 10 wt%) were tested for CO2 and steam reforming reaction. SBA15 supported Ni showed high CH4 conversion but poor H2 yield and low H2/CO ratio, that reached very promising value using Rh supported catalyst. By increasing GHSV on Rh/SBA15 catalyst, CH4 conversion and H2 yield was decreased but the H2/CO ratio was maintained. In conclusion, SBA15 supported 0.5 wt% Rh was proved to be a promising catalyst over the reaction of combined carbon dioxide and steam reforming of methane.

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