Dry reforming of methane over hydrotalcite-derived catalyst: Effect of Ni loading

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1. Introduction

Biogas or landfill gas (LFG) is produced by anaerobic digestion or fermentation of organic matter (such as sewage sludge, municipal sewage water, etc) and contain mainly CH_4 and CO_2. Therefore, the emission of biogas to the atmosphere may contribute significantly to the greenhouse gas effect. However, only a small portion of this biogas is used. In these cases, the LFG is employed for heat or electricity generation through combustion process. The production of hydrogen from LFG for energy generation through fuel cells is a promising technology. In this approach, the LFG is converted to synthesis by the CO_2 reforming of methane process (dry reforming of methane - DRM) followed by H_2 purification steps. One of the main barriers of the dry reforming technology is the catalyst deactivation that occurs due to carbon deposition during the high temperature process [1]. Therefore, the development of a catalyst resistant to carbon deposition during CO_2 reforming of CH_4 is one of the main issues of this technology.

Ni-based catalysts have been extensively studied for the DRM due to its low cost and high activity but this metal is prone to coking. The nickel particle size significantly influences the nucleation rate of carbon. The initiation step for carbon formation is more difficult for smaller particle sizes [2]. Therefore, the control of Ni particle size may inhibit or reduce the carbon formation rate. This can be achieved by the selection of the appropriate catalyst preparation method. Hydrotalcite (HT)-type compounds have been reported as promising precursors for SR catalysts. The calcination of the HT forms a mixed oxide with high thermal stability as well as high specific surface area. The reduction of this mixed oxide produces highly dispersed metallic particles that may improve carbon formation resistance [3]. Therefore, the aim of this work is to study the performance of supported Ni-based catalysts derived from hydrotalcite precursor for the production of hydrogen through DRM.

2. Experimental

HTs precursors were prepared by co-precipitation from an aqueous solution of the metallic cations ($Mg(NO_3)_2 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$) with a $NaHCO_3$ solution and NaOH solution. The solution containing the metallic nitrates and NaOH were added dropwise into the Na_2CO_3 solution kept at 341 K and pH constant (equal to 8) for 90 min. The samples were dried overnight at 383 K. Then, three hydrotalcite-like materials were prepared: NiHT5, NiHT10 and NiHT15, containing 5, 10 and 15 wt % of Ni, respectively. After calcination at 823 K for 2h, three samples were obtained: NiMO5, NiMO10 and NiMO15. The catalysts were characterized by nitrogen adsorption, X-ray diffraction (XRD), temperature programmed desorption of CO_2 (CO_2-TPD). thermogravimetric analysis (TG).

Dry reforming of methane (DRM) was performed in a fixed-bed reactor at 1073 K and atmospheric pressure. Prior to reaction, catalysts were reduced under H_2 at 1023 K for 1 h. The DRM reaction used a CH_4:CO_2 molar ratio of 1.0.

3. Results

The X-ray diffractograms of the hydrotalcite like compounds with different Ni contents are shown in Fig. 1a. All samples exhibited the diffraction lines characteristic of hydrotalcite-like compounds (JCPDS 70-2151) with carbonate anions present in the interlayer spaces [4]. After calcination, XRD patterns exhibit the characteristic lines of the Ni-Mg-Al mixed oxides [4]. Li et al [5] attributed the diffraction lines of NiMgAl mixed oxides to Mg(Ni,Al)O solid solution. However, the line corresponding to hydrotalcite phase at $2\theta = 22.9°$ is still observed for all samples, indicating that the destruction of the layered double hydroxide precursors was not complete. The diffractograms of the reduced samples exhibit the same lines observed on the diffratograms of calcined samples. In addition, it is noticed the presence of the lines characteristic of metallic nickel, indicating that the Mg(Ni,Al)O solid solution was at least partially destroyed. The particle size of Ni^0 was calculated using the Scherrer equation and the line typical of $Ni°$ (200) at $2\theta =$

51.8°. The Ni particle size was 6.8, 6.2 and 5.7 nm, for the samples containing 5, 10 and 15 % of Ni, respectively.
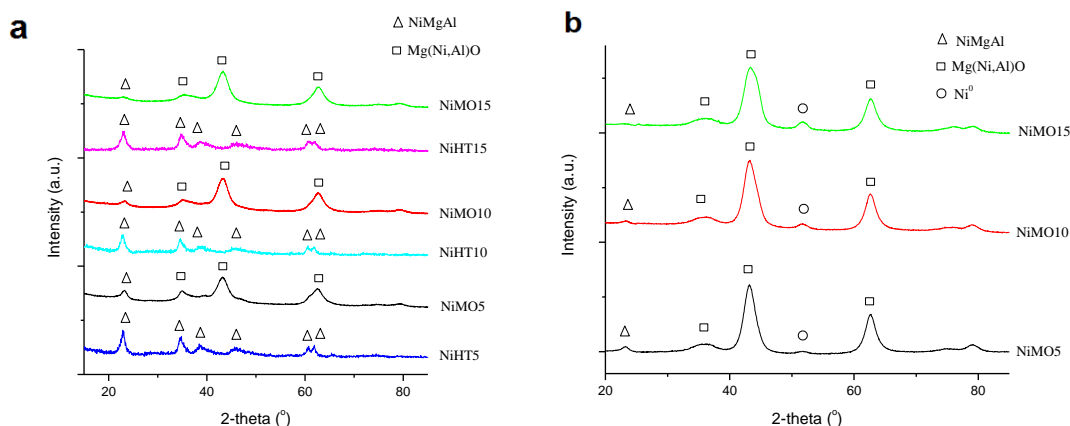

Figure 1: XRD patterns obtained for: (a) the hydrotalcite precursors and the mixed oxides after calcination at 823 K and (b) after reduction treatment.

The initial methane and CO_2 conversion were 67.0 and 76.8% (5%Ni); 67.1 and 76.4% (for 10%Ni); 82.2 and 89.2% (for 15%Ni). Regarding selectivity, H_2 and CO were the only products obtained for all samples. The H_2/CO molar ratio for samples was between 0.67-0.78. The methane and CO_2 conversions and the selectivity to products remained stable during 24 h time on stream (TOS), regardless the Ni content. The amount of carbon deposited over all catalysts after DRM was determined by TG analysis. The lowest amount of carbon was formed on the catalyst with 15%Ni (1.9 mgC.gcat^{-1}.h^{-1}), whereas the other samples exhibited the same amount of carbon deposits (10.2 mgC.gcat^{-1}.h^{-1}).

4. Discussion

The XRD results showed that the increase of the Ni loading from 5.0 to 15 wt% did not affect the metallic Ni crystallite size obtained after reduction. On the other hand, increasing Ni content results in an increase of the density of basic sites, as revealed by CO_2-TPD analysis. This result agrees with those reported by Debek at al [6] for Ni-containing Ce-promoted hydrotalcite derived materials. They also observed that the reduced sample containing the highest Ni content exhibited the highest density of basic sites. This was attributed to the removal of O^{2-} species during the reduction treatment. In addition, this catalyst also showed the lowest carbon formation. According to the literature [6], the use of hydrotalcite as precursor could inhibit carbon deposition by promoting Ni dispersion as well as providing a support with high capacity of CO_2 adsorption, which prevents carbon deposition. In our work, the lower carbon formation observed on the catalyst containing 15% of Ni is likely due to its higher CO_2 adsorption, since all samples presented the same Ni crystallite size.

5. Conclusions

The hydrotalcite-derived catalysts studied in this work were very active and stable during DRM. However, the material with higher Ni content exhibited the lower carbon formation, which could be attributed to its higher capacity of CO_2 adsorption that avoided carbon deposition.

6. References

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