Hydrotalcite-Like Compounds as Catalyst Precursors for Tri-Reforming of Methane Process for Industrial Flue Gas Utilization

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Highlights

- Ni-based catalysts derived from hydrotalcite were evaluated for tri-reforming of methane process.
- Ni-Mg-Al catalysts showed low CH_4 and CO_2 conversions and underwent deactivation.
- Ni-Zn-Mg-Al catalyst displayed excellent activity and remarkable stability.
- Addition of Zn as promoter improved the electronic property of catalyst.

1. Introduction

Tri-reforming of methane (TRM) is a novel methane reforming process for synthesis gas generation. In this process, CO_2, H_2O and O_2 reform methane into synthesis gas in a single reforming reactor. It is a synergetic combination of partial oxidation of methane, steam reforming of methane and dry reforming of methane. The TRM process could be an effective pathway to convert greenhouse gas CO_2 to industrially useful synthesis gas. The presence of O_2 generates heat *insitu* which can make the process mild endothermic/thermo-neutral. The H_2O in feed could provide additional H_2 and hence H_2/CO ratio of synthesis gas can be adjusted. One major source of CO_2 is the flue gases from power plants. The TRM process can be applied to utilize flue gases as it contains all the three compounds CO_2, H_2O and O_2. One important feature of this process is that CO_2 can be utilized as a carbon source without its pre-separation from concentrates sources [1]. However, despite being so advantageous, TRM poses a major challenge in development of highly active and stable catalyst. The reforming catalysts tend to deactivate due to carbon deposition, metal sintering and Ni re-oxidation [2]. In the present study, we explored Ni-based catalysts derived from hydrotalcite-like compounds for tri-reforming of methane process. Moreover, the promotional effect of Cu and Zn was also investigated.

2. Methods

The catalysts were synthesized by co-impregnation method. The nominal loading of Ni was 10 wt.%. This catalyst was designated as Ni-Mg-Al catalyst. Two different batches of catalyst were prepared using memory effect of hydrotalcite compounds. The only difference was the calcination temperature to which the hydrotalcite precursors subjected to prior to incorporating memory effect. These catalysts were denoted as Ni-Mg-Al_me@500 and Ni-Mg-Al_me@900. The catalysts prepared by adding Cu and Zn as promoter are designated as Ni-Cu-Mg-Al and Ni-Zn-Mg-Al catalysts respectively. To study the physical, chemical and electronic properties of catalysts, a detailed characterization was carried out using EDX, XRD, TPR, CO_2 – TPD, NH_3 – TPD, H_2 – pulse chemisorption N_2 – physisorption, XPS, TGA, TPO and TEM techniques. The catalyst performance test was carried out using a fixed-bed reactor at 800ºC, 1 atm, 49,200 mL/g.h. Before catalyst evaluation, the catalyst was reduced insitu in flow of gaseous mixture of H_2 and N_2 at 850ºC temperature for 4 h. The total duration of catalyst performance test was typically 20 h. After the test, each spent catalyst was characterized by XRD, TGA and TEM.

3. Results and discussion

The XRD patterns of catalyst precursors, showed reflections corresponding to (003), (006), (012), (015), (018), (110) and (113) crystal planes of double-layered structure of hydrotalcite; suggesting its successful synthesis [3]. The XRD patterns of calcined catalysts depicted reflections of periclase phase

[Mg(Ni, Al)O, Mg(Ni, Cu, Al)O and Mg(Ni, Zn, Al)O] which formed upon the collapse of hydrotalcite structure during calcination. The TPR profile revealed the reduction behavior of calcined catalysts. The reduction of calcined Ni-Mg-Al did not complete even till 900°C temperature. Incorporation of memory effect did improve reducibility but only at the cost of weak metal-support interaction. On the other hand, catalysts promoted by Cu and Zn displayed a high degree of reducibility (> 90%) and strong metal-support interaction. The XRD patterns of reduced catalyst samples confirmed the formation of Ni-Cu and Ni-Zn alloy in Ni-Cu-Mg-Al and Ni-Zn-Mg-Al catalyst respectively. The XPS spectra revealed the electronic modification of Ni in promoted catalysts; specifically, Ni species in Ni-Zn-Mg-Al catalyst became an electron-rich. TPD profiles of catalysts showed the presence of acidic and basic sites over the surface of reduced catalysts.

Among the catalysts, tested for tri-reforming of methane reaction, the promoted catalysts Ni-Cu-Mg-Al and Ni-Zn-Mg-Al demonstrated better activity and stability than the non-promoted catalysts. It can be attributed to a high degree of reducibility, strong metal-support interaction and alloy formation. As per figure shown below, Ni-Zn-Mg-Al catalyst emerged the best catalyst of this study due to Ni being an electron-rich species. As it can be observed in the figure, Ni-Mg-Al catalyst displayed poor initial CH_4 and CO_2 conversions mainly due to low degree of reducibility. Although Ni-Mg-Al_me@900 catalyst, prepared by adopting memory effect, showed an enhanced initial CH_4 and CO_2 conversions, but, underwent severe deactivation during 20 h run due to metal sintering and coke deposition.
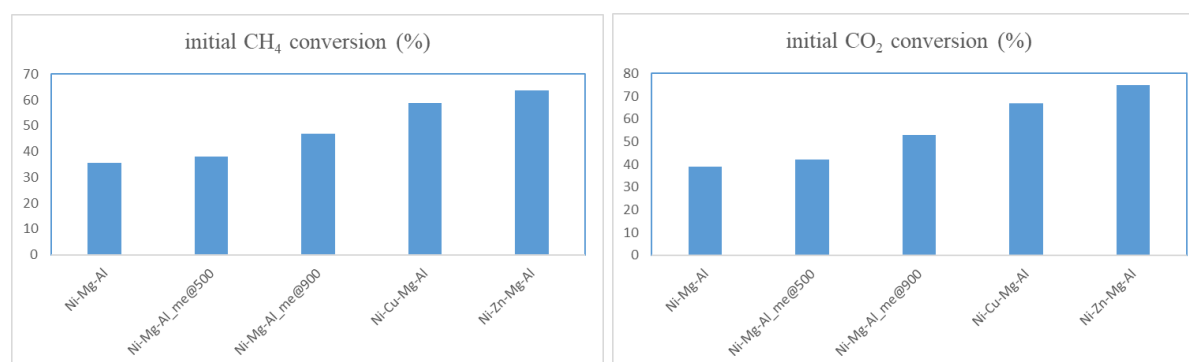

Figure 1. Initial CH_4 conversion and CO_2 conversion

4. Conclusions

Ni-Mg-Al based hydrotalcite-like compounds were successfully synthesized by co-precipitation method and were used as catalyst precursors to form Mg-Al mixed metal oxides supported Ni catalysts. These were tested in tri-reforming of methane reaction at 800°C. The "memory effect" property of hydrotalcite was also adopted to prepare catalyst precursors to investigate its effect on properties and performance of Ni-Mg-Al catalysts. These catalysts did not display satisfactory activity and stability during 20 h experimental run due to either low degree of reducibility or weak metal-support interaction. Catalyst promoted by either Cu or Zn demonstrated excellent resistance against metal sintering and coke formation. Electronic and geometric modifications of Ni species by Zn resulted in superior activity and stability of Ni-Zn-Mg-Al catalyst for tri-reforming of methane process.

References

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