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Correlating catalyst physicochemical properties and activity for tri-reforming of methane process for CO_2 utilization

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Highlights

- Tri-reforming of methane is a synergic combination of dry, steam and oxidative reforming
- Ni/Al_2O_3 displayed superior catalytic activity compared to Ni/MgO and Ni/CeO_2-ZrO_2
- The degree of reducibility of Ni/MgO was low
- Ni/CeO_2-ZrO_2 lacked strong metal-support interaction

1. Introduction

Methane is an important feedstock for fuels and chemicals [1]. Reforming of methane generates synthesis gas, an industrially important precursor for fuels and chemicals. Dry reforming of methane utilizes greenhouse gas CO_2 to reform methane and thereby has environmental implication [2]. However, it requires CO_2 pre-separation from its concentrated source. CO_2 pre-separation from flue gas of electricity power generation plants is highly energy intensive step and it alone reduces plant's net electricity output by as much as 20%. A novel process called "Tri-reforming of methane (TRM)" does away with pre-separation as it employs CO_2, H_2O and O_2 of flue gas to reform methane in a single reforming reactor. TRM offers many advantages over other methane reforming techniques such as production of synthesis gas of desired H_2/CO ratio, in-situ heat generation from partial methane oxidation for occurrence of steam and dry reforming and thereby making whole process mild endothermic. The process avoids hot spot formation and loss of any feed species CO_2, H_2O [3]. However, despite being so advantageous, large scale implementation of TRM has been impeded by lack of highly active and stable catalyst. It remains a challenge to develop a catalyst which is able to adsorb and activate all the reactant species CH_4, CO_2, H_2O and O_2 efficiently. Therefore, the present work aims to study the catalytic behavior of low cost highly active Ni-based catalysts for TRM process. For this purpose, various Ni-based catalysts by employing different metal oxides Al_2O_3, MgO and CeO_2-ZrO_2 as catalyst support were synthesized and tested for TRM reaction at 800^{o}C under atmospheric pressure. A detailed characterization of calcined, reduced and spent forms of each catalyst was carried out and finally correlation between catalyst physicochemical properties and catalyst activity was established.

2. Methods

Ni/Al_2O_3, Ni/MgO and Ni/CeO_2-ZrO_2 catalyst was prepared by wet impregnation method using $Ni(NO_3)_2$ $6H_2O$ as Ni precursor. Each catalyst was characterized by N_2 physisorption, XRD, EDX, TPR, TEM, SEM, TGA CO_2-TPD and NH_3-TPD. The activity of each catalyst was tested in fixed bed reactor at 800^{o}C temperature, 11180 ml/g/h @ STP GHSV under atmospheric pressure.

3. Results and discussion

TEM images (figure 1) reveal Ni dispersion over different support phases of reduced catalysts. The Ni particle size of Ni/Al_2O_3, Ni/MgO and Ni/CeO_2-ZrO_2 determined by TEM was 13, 23 and 55 nm respectively. Figure 2 shows XRD pattern of calcined form of catalysts. NiO/Al_2O_3 displayed a set of diffraction peaks centered at 19.5^o, 31.8^o, 37.2^o, 45.3^o, 60.1^o and 66.2^o which are assignable to $NiAl_2O_4$ cubic spinel-type structure (JCPDS 78-1601). No separate reflection corresponding to either NiO or MgO is observed in XRD pattern of NiO/MgO. It can be attributed to the formation of NiO-MgO solid solution. However, NiO/CeO_2-ZrO_2 showed cubic NiO peaks corresponding to (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2

2) crystal planes centered at 37.2º, 43.3º, 62.8º, 75.4º and 79.2º respectively (JCPDS 78-0643). H_2 – TPR profile presented in figure 3 indicates reduction peak of calcined form of Ni/Al_2O_3, Ni/MgO and Ni/CeO_2-ZrO_2 positioned at 850ºC, 743ºC and 489ºC with 35, 2 and 40 ml/g @ STP hydrogen uptake respectively.

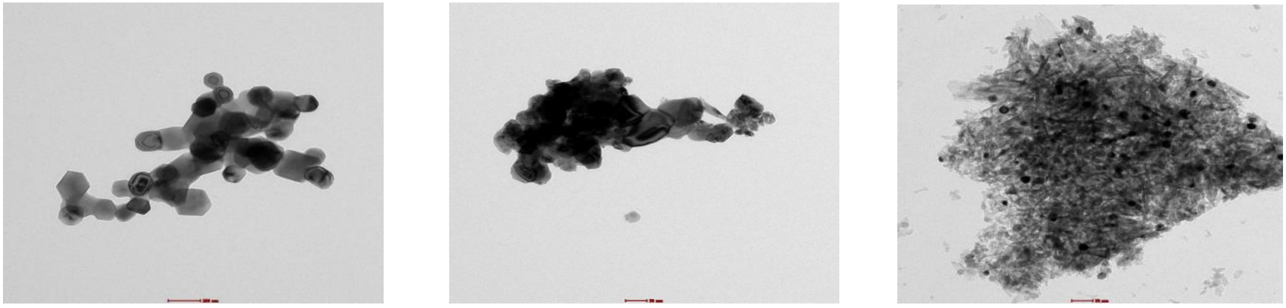

Figure 1. TEM image of Ni/MgO, Ni/CeO_2-ZrO_2 and Ni/Al_2O_3 (from left to right)

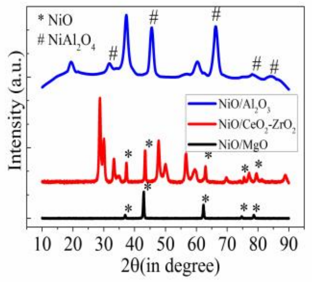

Figure 2. XRD pattern

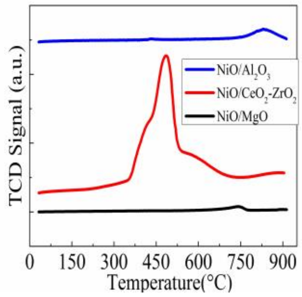

Figure 3. TPR profile

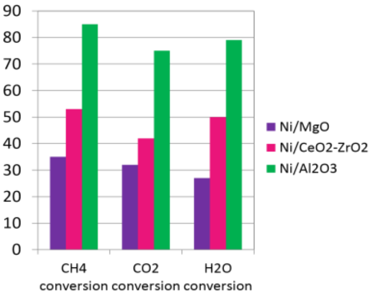

Figure 4. Catalyst activity

The performance of these catalysts for tri-reforming reaction has been compared at identical condition of 800ºC temperature, 1 atm pressure and 11180 ml/g/h @ STP GHSV and their activity results are shown in figure 4. Ni/Al_2O_3 had higher activity with 85%, 75% and 79% CH_4, CO_2 and H_2O conversion respectively. The combination of strong metal-support interaction and high degree of reducibility of this catalyst governed its performance. The high activity can also be attributed to basic sites, as verified by CO_2 - TPD (not shown here) and smaller Ni particle size. The low degree of reducibility of Ni/MgO catalyst, evident from its TPR profile, suggests that Ni was not be present in metallic phase over MgO support during reaction. The absence of active Ni phase resulted in relatively low activity of this catalyst. On the other hand, Ni/CeO_2-ZrO_2 must had large population of metallic Ni species. However, due to its large particle size Ni metal dispersion over CeO_2-ZrO_2 was poor, which eventually led to average catalytic activity.

4. Conclusions

Ni/Al_2O_3 derived from spinel $NiAl_2O_4$ displayed superior activity than Ni/MgO and Ni/CeO_2-ZrO_2. Detailed catalyst characterization reveals that both strong metal-support interaction and high degree of reducibility is essential for high catalyst's activity. In addition, the performance of the catalyst strongly affected by basicity and Ni particle size for the tri-reforming of methane reaction.

References

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Keywords
“CO_2 conversion”, “methane tri-reforming”, “synthesis gas”, “Ni-based catalyst”