

Hydrogen production from steam reforming of renewable feedstocks over Ni supported on mesoporous SiO₂ based supports

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ABSTRACT

Ni based perovskites (LaNiO_3) were successfully embedded into the SBA-15 support by the modified triblock copolymer synthesis procedure. Characterization results indicate that the nickel insertion into SBA-15 support does not affect the mesoporous structure. The addition of cerium along with the lanthanum and nickel also inserted into the SBA-15 support channels successfully. The surface area and pore volume of all the catalysts were remained same, surface area around $400\text{m}^2/\text{g}$ with pore volume $1.34\text{ cm}^3/\text{g}$ and average particle size of 5 nm. These catalysts have to be tested in the steam reforming of renewable feedstocks like glycerol, ethanol and methanol.

1. INTRODUCTION

Increasing global climate change on one hand, depletion of fossil fuels reserves on the other hand necessitated the quest for identification of alternative and renewable energy for the world sustainability. Hydrogen could solve all kinds of energy demands of the present world since it is the highest inherent energy dense molecule [Surendar 2017]. In addition, unlike fossil fuels hydrogen cannot leave any carbon foot prints in the environment during its combustion in the engine so it is an ecofriendly fuel. Hence the production of hydrogen from the renewable feed stocks (glycerol, ethanol and methanol) by steam reforming has been receiving the great attention of researchers. The development of a highly active Ni based catalysts with zero coke formation for the steam reforming has been remained unsolved since from the past last two decades. Ordered mesoporous silica can be synthesized in a variety of pore sizes, pore shapes, pore arrangements, and morphologies. Due to its large surface area, a material with a controllable pore size and a narrow pore size distribution it has immense importance in the catalysis research as a support. In this work we aimed to prepare LaNiO_3 supported on high surface area SiO_2 based materials by the modified triblock copolymer SBA-15 synthesis procedure.

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2. Experimental

2.1 Catalyst Preparation

Ni based perovskites were embedded into SBA-15 support by the modified triblock synthesis method. In brief, firstly 32g of P123 (EO: PO: EO=20:70:20, Avg. molar mass 5800g/mol) was dissolved in 240 mL of distilled water. After formation of the clear homogenous solution required amount of 2M HCl was added into above solution. After 30 minutes stirring the silica source, tetra ethyl ortho silicate (TEOS) was added drop wisely and kept for stirring upto 4h. In the subsequent step pH of the solution was adjusted to 7.5 with ammonia solution and later added $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ precursor solution to the above solution and finally kept for stirring at 40 °C about 24h. The solution was transferred into TFPE bottle and aged for 48h at 100 °C. The solid mass obtained after filtration was dried in oven at 60°C for 12h. Finally, the template free Ni/SBA-15 was obtained after calcination at 550°C for 6h under air flow of 100mL/min. the similar procedure was followed to prepare La, La and Ce promoted Ni/SBA-15 catalysts.

2.2 Characterization

BET Surface area

Nitrogen adsorption–desorption isotherms obtained for Ni/SBA-15 and promoted Ni/SBA-15 catalysts are shown in Fig. 1. According to the IUPAC classification [Sink,1985], these isotherms are of type- IV and are attributed to mesoporous materials. The hysteresis loops are of H1-type (IUPAC) and which indicates the presence of cylindrical pores in mesoporous silica (SBA-15). The type of the isotherms was independent on the catalysts metal oxide composition. However, broadness of the hysteresis loop was decreased with the increasing the total metal oxide (Ni, La and Ce) content from 10 to 20 wt.% suggesting the formation of metal oxide particles inside the SBA-15 mesopores which is in good agreement with previous works [Sietsma 2008, Cheralathan 2008]. As presented in Table 1, BET surface area of the Ni/SBA-15 catalyst was slightly reduced by the addition of La and Ce metal oxides. This is due to the formation of the perovskite unit inside the SBA-15 mesopores.

Table1. Textural properties of the Ni supported on SBA-15 catalysts

Catalyst	BET Surface area (m^2/g)	Pore volume (cm^3/g)	Pore diameter (nm)
10Ni/SBA-15	403.4	1.340	16.4
10Ni- 5La/SBA-15	388.6	1.301	15.3
10Ni-5La-5Ce/SBA-15	394.7	1.310	15.0

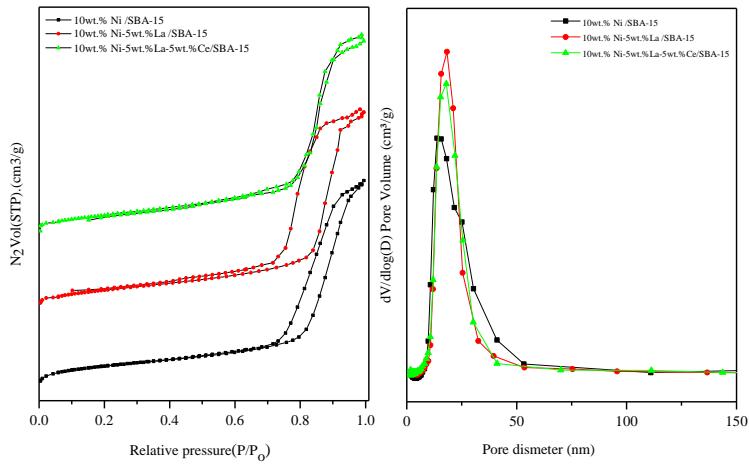


Fig. 1. N_2 adsorption-desorption isotherms and particle size distribution

X-ray diffraction

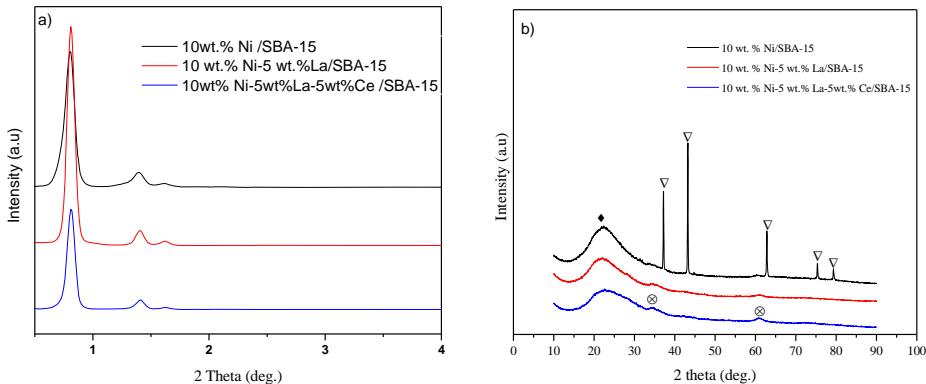


Fig. 2. a) Lower angle XRD and b) Broad angle XRD of the Ni/SBA-15 catalysts

The XRD patterns of the Ni based catalysts supported on SBA-15 were presented in Fig. 2. From the low angle XRD (Fig. 2a), the XRD diffractions obtained at 0.81, 1.4 and 1.6 ° confirms the hexagonal arrangement mesopores inside the SBA-15[Tao 2017]. It is clear that the SBA-15 structure was not disturbed by the pH adjustment with ammonia addition (pH=7.5). Furthermore mesoporous structure was confirmed with presence of the broad peak in all the catalysts at Ca. 20° related to the mesoporous SiO_2 . The diffraction patterns of 10wt. % Ni/SBA-15 is very sharp while the La, La and Ce promoted Ni/SBA-15 catalysts were very broad. The broadness in the XRD peaks obtained for promoted Ni/SBA-15 catalysts is strongly suggesting the formation either small or poor crystals by the addition of La and Ce. As shown in the Fig. 2b the sharp diffractions at 37.1, 43.1, 62.8, 75.4 and 79.3° of 2θ values are suggesting the presence of NiO [Calles, 2009]. The diffraction patterns of La, La and Ce promoted Ni/SBA-15 were completely different from the Ni supported SBA-15. Although the broad

diffraction obtained at 34.0° and 60.9° is seems to be higher than the LaNiO₃ perovskite. It is possible that the perovskite insertion into the SiO₂ frame work might lead to shift in the perovskite related peaks to higher 2theta values. In addition, these peaks are not related to not relate any other metal oxides (NiO/La₂O₃/CeO₂/mesoporous SiO₂). Hence it could be reasonable to assign for the LaNiO₃. The broadness of the peaks is strongly suggesting the poor crystallinity to the perovskite LaNiO₃.

3. CONCLUSIONS

Ni supported on SBA-15 catalysts was prepared in the single step by the modified triblock copolymer synthesis method. The addition of La, La and Ce to Ni/SBA-15 causes the formation of perovskite with poor crystallinity. During the reduction process these LaNiO₃ perovskite embedded SBA-15 catalysts would produces the tiny nickel particles uniformly dispersed over SBA-15 support and its channels might offer the excellent results in the steam reforming of renewable feed stocks such as glycerol, ethanol and methanol.

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