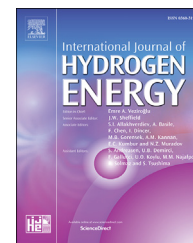


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Selective substitution of Ni by Ti in LaNiO₃ perovskites: A parameter governing the oxy-carbon dioxide reforming of methane

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ABSTRACT

A series of LaNi_{1-x}Ti_xO₃ perovskite catalysts varying titanium ($x = 0.0, 0.2, 0.4, 0.5, 0.6$ and 1.0) are synthesized and investigated using BET, XRD, TPR, TEM, FT-IR and XPS. The catalysts were evaluated for oxy-carbon dioxide reforming of methane at 800 °C under atmospheric pressure maintaining CO₂/CH₄/O₂ ratio 0.8/1.0/0.2. LaNi_{0.5}Ti_{0.5}O₃ is showing typical stability with gradual H₂ consumption in TPR. The stability of these catalysts is supported by O 1s binding energies wherein it is clearly evident that incorporation of Ti stabilized LaNiO₃ generating suitable catalysts in the range of $x = 0.4-0.6$ with high performance.

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Introduction

The growing concern over the global warming led new technologies to emerge in the area of reforming of green house gases especially for methane and carbon dioxide. The catalytic carbon dioxide reforming of methane to syngas is an established technology that has been investigated over decades by modifying the catalytic systems in order to improve its stability and coke resistance [1,2]. The coking, metal sintering, reaction endothermicity are always subjects for R & D. In order to overcome these problems, it is recommended to combine dry reforming with partial oxidation of methane for syngas production. The heat produced in the exothermic reaction of partial oxidation of methane is used to compensate the endothermicity of dry reforming, resulting in mutual benefits

like making the process more efficient, avoiding hot spot formation, preventing deactivation of the catalyst, overcome reaction runaway conditions and making safe operation [3,4]. The syngas generated by the reforming process has a high CO content which is favourable for the synthesis of the value-added chemicals. On the other hand, by changing the feed composition, the syngas ratio and the selectivity for the various Fischer-Tropsch synthesis products can be tailored to the customer's need [5,6]. The use of noble metals especially Pt, Pd, Rh, Ir as catalysts has also been explored in many earlier reports [7] due to their interesting intrinsic properties like better resistance to coke and sulfur poisoning but they are expensive and have limited availability [8]. On the contrary, much attention has been focused on the development of catalysts with nickel as the active element based on its

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technical and economic viability in commercial reforming applications [9]. However, Ni catalysts display a moderate to rapid deactivation due to the carbon formation and sintering effects [10], which occur at higher temperatures. In order to overcome these obstacles, the Ni species must be modified or inserted in a definite chemical structure, such that the active component is stabilized under the operating conditions. Structures, such as perovskites of (ABO₃) type, in which A and B are compatible elements, have been found to be efficient and are extensively studied.

As the A-site cation is considered to be responsible for thermal stability, lanthanum is chosen to be an excellent element in perovskite catalysts than the other rare earth species [11]. The B-site cation accounts for the catalytic activity. In order to improve the structural stability and to initiate structural and electronic defects in perovskite, partial substitution of B-site cation with a different cation B' is suggested, where the valence of B' is different from that of B cation. Titanium is found to be suitable as a B' cation due to its high oxygen storage capacity, stabilization of (B-site) metal dispersion and favourable electronic and ionic conductivity to enhance the catalytic performance [12]. As the trimetallic perovskites can be completely or partially reduced to active metallic species at a temperature close to the reforming temperature, it is possible to create strong metal-support interaction through an appropriate activation. Oxy carbon dioxide reforming studies over LaNiO₃ [13], Ce-promoted Ni/SiO₂ [14], Gd₂O₃-modified Ni/SiO₂ [6], Co-Ni bimetallics [15], PdO-NiO supported systems [16], Ni/ α -Al₂O₃ [17], noble metal catalysts (Rh, Ru, Pt, Pd, Ir) supported on alumina-stabilized magnesia [7], Ni/SrO-SiO₂ [18] and Ni-La/SiO₂ [19] are reported in the literature. Hassan et al. claimed 100% methane conversion over La_{1-x}Sm_xNiO_{3- δ} catalyst at 700 °C [20]. Furthermore, the activity studies carried out over LaFe_{1-x}Co_xO₃ [21], achieved a maximum conversion with optimum 0.4–0.6 Fe/Co ratio. Yttrium strontium titanate perovskite with substitution of Ti by Ni, Co and Ru are investigated for autothermal reforming of dodecane. The excellent activity and stability of YSTRu catalysts is highlighted due to high resistance to carbon formation [22]. Development of Ni-doped Sr_{0.92}Y_{0.08}TiO₃, based catalyst for H₂ production by reforming of biogas has been studied. The authors claimed that small amount of Ni doped in the Ti lattice and N₂ pretreatment greatly improved the catalytic activity [23]. Ni impregnated BaTiO₃ is studied for dry reforming of methane. As this catalyst is more prone to coking, the incorporation of Al₂O₃ in the system showed better resistance towards coking. BaTiO₃ perovskite phase on the surface of γ -Al₂O₃ inhibits formation

of NiAl₂O₄ and enhances Ni dispersion [24]. Mesoporous Ni(Co)Gd_{0.1}Ti_{0.1}Zr_{0.1}Ce_{0.7}O₂ synthesized by co- and precipitation is shown to demonstrate high activity and selectivity in CH₄-O₂ partial oxidation CH₄-CO₂ reforming. It is revealed that Co and Ni-Co systems are more active in partial oxidation than Ni alone [25]. The LaNi_xAl_{1-x}O₃ perovskite catalysts prepared by sol-gel and hydrothermal methods are tested for dry reforming of methane. The formation of tri metallic perovskite phase in both methods has been achieved and this phase plays a vital role in enhancing the dispersion of Ni [26]. LaNi_xFe_{1-x}O₃ perovskite catalysts also showed the tri metallic perovskite phase which is confirmed by the 2 θ shifting from LaFeO₃ (32.3) to LaNiO₃ (32.8). The doping of Ni improved the stability of perovskite and the catalytic activity [27]. To our knowledge, no studies are reported over LaNi_{1-x}Ti_xO₃ perovskites for the oxy-carbon dioxide reforming of methane and in the present work, it is proposed to synthesize the LaNi_{1-x}Ti_xO₃ perovskites, characterize and evaluate for oxy carbon dioxide reforming. The objective of this work is to determine the optimum composition of Ti in LaNi_{1-x}Ti_xO₃ perovskite that offers the best activity and H₂/CO ratio, apart from its stability in the reaction with time-on-stream.

Experimental

The catalyst preparation, characterization, catalyst activity evaluation and Fig. S1–S7 are given in supplementary section.

Results and discussion

Surface area & X-ray diffraction studies

The surface area, pore volume, pore diameter and crystal size (110 plane) for the catalyst systems are summarized in Table 1. The XRD pattern of LaNi_{1-x}Ti_xO₃ (x = 0.0, 0.2, 0.4, 0.5, 0.6 and 1.0) calcined at 850 °C are shown in Fig. 1. The peaks at 23.6, 32.9, 47.3 and 58.9° (2 θ) are in agreement with the characteristic lines of the rhombohedral phase of LaNiO₃ (JCPDF 34-1028) with high intensity. Furthermore, the catalysts with x = 0.2, 0.4, 0.5 and 0.6 showed similar characteristic 2 θ peaks as that of LaNiO₃, however, with shift towards lower 2 θ angle. The lattice parameters for the prepared catalysts are calculated and tabulated (Table 1). The partial substitution of the Ti for Ni influenced the lattice parameters, resulting in expansion of both a- and c-axes. The partial substitution of Ni by Ti in La NiO₃ is known to influences the lattice parameters, expanding

Table 1 – Surface area, pore volume, pore diameter and particle size of the LaNi_{1-x}Ti_xO₃ systems.

S.No.	Catalyst	SSA (m ² /g)	Pore Volume (cc/g)	Pore Diameter (nm)	Particle size (nm) (110 plane)	a (Å)	b (Å)	c (Å)	Vol (Å ³)
1	LaNiO ₃	1.4	0.003	4.6	21.1	5.457	5.457	6.603	158.84
2	LaNi _{0.8} Ti _{0.2} O ₃	3.4	0.007	3.6	34.1	5.565	5.565	6.791	182.18
3	LaNi _{0.6} Ti _{0.4} O ₃	4.4	0.011	4.7	27.1	5.549	5.549	6.781	180.90
4	LaNi _{0.5} Ti _{0.5} O ₃	3.8	0.007	4.2	26.8	5.555	5.555	6.789	181.45
5	LaNi _{0.4} Ti _{0.6} O ₃	9.1	0.021	3.6	16.6	5.544	5.544	6.767	180.18
6	La ₂ Ti ₂ O ₇	4.1	0.008	3.6	–	8.102	5.577	13.499	582.53

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