Research Paper

Active and durable alkaline earth metal substituted perovskite catalysts for dry reforming of methane

Srikanth Dama, Seema R. Ghodke, Richa Bobade, Hanmant R. Gurav, Satyanarayana Chilukuri*

Catalysis Division, CSIR- National Chemical Laboratory, Dr. Homi Bhabha Road, Pune, 411008, India

ARTICLE INFO

## ABSTRACT

Dry reforming of methane is an important process for the utilization of CO_2 and to get valuable synthesis gas. Alkaline earth metal substituted $MZr_{1-x}Ni_xO_{3-\delta}$ perovskites were synthesized by citrate gel method, characterized and evaluated for dry reforming methane. Characterization results show that the type of alkaline earth substituted at the A site of the perovskite oxide plays an important role in terms of structure, basicity, oxygen deficiency and Ni dispersion. Calcium substituted $CaZr_{0.8}Ni_{0.2}O_{3-\delta}$ catalyst shows superior activity in terms of high CH_4 and CO_2 conversion, while maintaining the activity even after 500 h of reaction. Mechanistic investigations were carried out using transient pulse experiments and insitu FTIR-diffuse reflectance spectroscopy. These experiments reveal that redox property and basicity play important role in activation and sustaining the reforming reaction. Insitu FTIR measurements show that surface hydroxyl groups of the support are vital for high activity and durability of $CaZr_{0.8}Ni_{0.2}O_{3-\delta}$ catalyst. XRD and TGA analysis of catalysts after reaction show the structures are retained, but peaks pertaining to coke were observed on $SrZr_{0.8}Ni_{0.2}O_{3-\delta}$ and $BaZr_{0.8}Ni_{0.2}O_{3-\delta}$ catalysts. On the otherhand, $CaZr_{0.8}Ni_{0.2}O_{3-\delta}$ catalyst had only amorphous carbon even after 500 h of reaction. HRTEM studies revealed that $SrZr_{0.8}Ni_{0.2}O_{3-\delta}$ and $BaZr_{0.8}Ni_{0.2}O_{3-\delta}$ catalysts deactivated mostly due to the formation of carbon nanotubes with Ni embedded in them. Raman and XPS analysis helped in identifying types of coke precursors present on the catalysts. The investigation also illustrate that type of carbon formed depends on the basicity of perovskite oxide, metal to support interaction, Ni crystallite size, surface hydroxyl groups and oxygen defects. This study clearly demonstrated that $CaZr_{0.8}Ni_{0.2}O_{3-\delta}$ is an excellent catalyst for dry reforming reaction with long life.

1. Introduction

The world is preparing to overcome the possible effects of global warming attributed to green house gas (GHG) emissions, particularly carbon dioxide emissions, as its level has crossed the 400 ppm level [1]. Hence, numerous initiatives are being taken for the development of CO_2 capture and utilization technologies that can help either to cap or reduce its level in the atmosphere. Similarly, CH_4 being another GHG; its release to the atmosphere is also a cause of concern. In recent times, various research programmes are proposed or initiated to utilize both these green house gases to obtain fuels and chemicals. Dry reforming of methane is one such programme that utilizes both CO_2 and CH_4 to give synthesis gas (syngas). Syngas is an important input for many chemicals and fuels. In dry reforming reaction, H_2/CO ratio of product syngas is low (≈ 1) and hence suitable for production of long chain hydrocarbons through Fischer-Tropsch (FT) synthesis [2,3].

$$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2 \ (\Delta H°_{298K} = +247 \ kJ/mol) \quad (1)$$
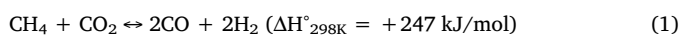
In addition to main dry reforming reaction, reverse water gas shift reaction is also dominant under these conditions;

$$CO_2 + H_2 \leftrightarrow CO + H_2O \ (\Delta H°_{298K} = +40.6 \ kJ/mol) \quad (2)$$
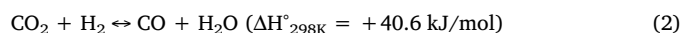
However, to practice dry reforming commercially, the process faces some major challenges. Being highly endothermic reaction, it has to be conducted at high temperatures. As a consequence, catalysts are deactivated due to active metal sintering and coke formation [4]. Numerous investigations attempted to address these twin problems, mostly by using supported precious metal catalysts [5,6]. However, use of supported precious metal catalysts commercially involves high costs. Hence, nickel based catalysts are the best alternative, due to their comparable activity in dry reforming, abundant availability and relatively lower price. But, Ni based catalysts are more prone to deactivation due to carbon deposition and metal sintering. There were many reports on understanding of coke formation on Ni catalysts and how to fortify them to resist coke formation, inorder to get durable catalysts for dry reforming reaction [7].

The dry reforming reaction proceeds through CH_4 decomposition followed by oxidation of the carbon species. This mechanism requires bi-functional metal supported catalysts that can effectively catalyze CH_4 cracking and simultaneous removal of carbon species. In order to meet these requirements, high metal dispersion and resistance to metal sintering are essential, while redox property of the support helps to oxidize the carbon formed during the reforming process. Structured oxides like perovskites and hydrotalcites have been investigated for this reaction [8]. It is also reported that the metal catalysts can be promoted by using supports that consist of basic oxides/redox oxides [9,10]. Bimetallic systems were also explored for improved activity and long term durability [11]. Addition of basic oxides to the support is expected to enhance the CO_2 activation and also helps in gasification of deposited carbon on the active sites [12]. In general, ZrO_2 is considered as a good support, because of its higher thermal stability and unique chemical properties like redox and acid-base functionality [13]. There were several reports dealing with Ni supported on ZrO_2, but most of them deactivated due to coke formation and sintering. Addition of promoters like CaO, MgO and CeO_2 is reported to help improve the catalyst stability [14].

Perovskite type oxides have a well defined structure and they can facilitate high metal dispersion, even on subjecting to severe oxidation-reduction processes at high temperatures [15]. Hence, efforts were made to synthesize catalysts that have active metals (transition metals like Ni or precious metals) incorporated in to the perovskite lattice and use them for DRM. In addition, substitution of Ca, Sr and Ba in the A site of perovskite lattice is expected to improve and help stabilize dry reforming activity of the catalyst. In this report, Ni is substituted in $MZrO_3$ (M = Ca, Sr and Ba) family of perovskite type oxides and their activity and durability was investigated for dry reforming ($CH_4 + CO_2$) reaction to obtain syngas. The perovskite oxides were synthesized using citrate gel method and characterized using XRD, Raman spectroscopy, BET surface area, CO chemisorption, CO_2-temperature programmed desorption (CO_2-TPD), O_2 −temperature programmed desorption (O_2-TPD), temperature programmed reduction (TPR), transient pulse technique and in-situ FTIR. Among the catalysts studied, Ca substituted perovskites were found to be more active in terms of CH_4 and CO_2 conversions and the activity was extraordinarily stable even after long hours (500 h) on stream. The carbon formed on these catalysts was investigated by XRD, TEM, TGA, XPS and Raman spectroscopy.

2. Experimental techniques

2.1. Preparation of the catalysts

The $MZr_{1-x}Ni_xO_{3-\delta}$ (M = Ca, Sr and Ba; x = 0 and 0.2) perovskite type oxides were prepared by conventional citrate gel method. Stoichiometric quantities of the corresponding metal nitrates were dissolved in minimum required water and added drop wise to the citric acid solution under constant stirring at 353 K. Following complexation, the solution was evaporated and dried at 453 K for 12 h to obtain spongy amorphous citrate gel. This fluffy material was crushed and calcined at 1023 K for 6 h in air flow to get the corresponding $MZr_{1-x}Ni_xO_{3-\delta}$ (M = Ca, Sr and Ba; x = 0 and 0.2) perovskite type oxides.

2.2. Characterization techniques

Powder X-ray diffraction (XRD) pattern of the $MZrO_3$ and Ni substituted $MZr_{1-x}Ni_xO_{3-\delta}$ perovskites were collected using PANalytical X'pert Pro dual goniometer diffractometer equipped with an X'celerator solid-state detector. Nickel filtered Cu Kα (1.5418 Å) radiation was used for the data collection using a flat holder in Bragg-Brentano geometry with 1° slit at the source side. The data were recorded in 2θ range (10–90°) in step size of 0.008°. Rietveld refinements of powder XRD pattern were carried out with the GSAS EXPGUI programme. Profile refinements utilized the pseudo-Voigt function. Initially, background

and scale factors were refined by cell parameters and positional parameters. The mean crystallite sizes of the oxides were calculated using Debye–Scherrer equation.

High resolution transmission electron microscopy (HRTEM) investigations were conducted using a FEI Technai TF-30 instrument operating at 300 keV. Samples were prepared by dispersing them in isopropyl alcohol; a portion of this suspension was transferred onto carbon coated copper grids and allowed for natural drying at room temperature.

The Brunauer-Emmett-Teller (BET) surface areas of the samples were measured by nitrogen sorption at liquid nitrogen temperature (77 K) using a Quantachrome Autosorb iQ equipment. Prior to N_2 adsorption, the samples were degassed at 573 K for 3 h to remove any residual moisture and other volatiles.

Nickel dispersion was determined through CO chemisorptions of H_2 using Quantachrome Autosorb-iQ instrument. Prior to sorption, samples were reduced in-situ in H_2 stream at 773 K for 2 h. Following this, the samples were evacuated for 2 h at the same temperature and subsequently cooled to 313 K under evacuation to record CO adsorption isotherm. The isotherms include both physisorption and chemisorption portions. Chemisorbed CO uptakes were determined by extrapolating the linear portion of the isotherm to zero pressure. The dispersion of nickel was calculated under the assumption that the stoichiometry of CO/Ni (surface) is equal to 2.

Temperature programmed reduction (TPR) profiles were obtained using a Micromeritics Autochem 2920 catalyst characterization system, equipped with TCD detector. Freshly calcined samples were treated in 5% O_2-He gas mixture (30 ml min^{-1}) by ramping the temperature to 673 K at a heating rate of 5 K min^{-1}. Following this heat treatment for 1 h, the sample was cooled to 323 K in argon (purity 99.995%) flow. Subsequently, the gas was changed to 30 ml/min of 5% H_2 in Ar flow and the catalyst was heated to 1273 K at a heating rate of 5 K min^{-1}. The change in H_2 concentration at the outlet was monitored by TCD and plotted against temperature to yield TPR profiles. Water produced during the reduction process was condensed and collected in a cold trap.

Temperature programmed desorption of CO_2 (TPD- CO_2) was carried out to study the nature of basicity of the support using a Micromeritics Autochem 2920 equipped with a TCD detector. The samples were first degassed at 573 K in 40 ml min^{-1} of He flow for 60 min. Then the sample was cooled to 323 K in He, and the gas was switched to 30 ml min^{-1} of 10%CO_2 in He for 30 min. Following this, the sample was purged with He for 30 min by ramping the temperature to 373 K at 5 K/min in order to remove the physisorbed CO_2. Subsequently, the sample was heated at 10 K/min to 1273 K under He flow (40 ml/min) while monitoring the TCD signal for desorbed CO_2.

Temperature programmed desorption of O_2 (TPD- O_2) was carried out to study the defective sites in substituted perovskites using a Micromeritics Autochem 2920. Approximately 50 mg of the sample was filled in a U shape quartz tube and calcined in 5% O_2/Ar (30/min) at 773 K for 30 min. Following this, the sample was cooled to 373 K and gas was switched to 10% H_2 and heated to 773K to carry out reduction. Later, the sample was cooled to 313 K under He (30 ml/min) flow and exposed to 5% O_2/Ar for 30 min. Afterwards, the sample was purged in He (40 ml/min) for the removal of weakly adsorbed oxygen and TPD of O_2 was carried out by heating up to 1273 K at a ramping rate of 10 K/min.

In situ FTIR of the perovskite samples was carried out using Bruker Tensor 27 spectrometer in diffuse reflectance mode (DRIFT) equipped with MCT detector. Before the analysis, the sample was heated inside the diffuse reflectance cell in N_2 at 673 K to clean the surface. Following this, the sample was reduced in H_2/N_2 (1/4) mixture for 2 h and later the cell chamber was purged with N_2 at 673 K for 20 min while cooling the sample to room temperature. The dry reforming reaction was carried out by passing $CH_4 + CO_2$ mixture (30 ml/min) in 1:1 ratio through the sample in a DRIFT cell. The spectra were recorded at