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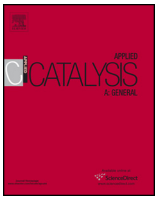

Bi-reforming of methane on Ni-based pyrochlore catalyst

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ABSTRACT

A Ni-based pyrochlore catalyst was synthesized using the modified Pechini method. In this method, 1 wt% Ni was doped into the $La_2Zr_2O_7$ pyrochlore structure. The catalyst was characterized by H_2-TPR, TPO, XRD, and EXAFS, and tested for its methane reforming activity under bi-reforming reaction conditions; i.e., in the presence of CO_2 and steam:

$3CH_4 + CO_2 + 2H_2O \rightleftharpoons 4CO + 8H_2$

Repeated TPR/TPO cycles showed that the two consecutive TPR spectra do not change, showing that the catalyst is stable at high temperatures, and that the nickel oxidation/reduction process is reversible. The catalyst showed constant activity with time at all temperatures in the range of 700–950 °C over a cumulative period of 170 h. After this series of bi-reforming tests, TPO of the spent catalyst was carried out, which showed detectable but unquantifiable carbon deposition. The presence of steam in bi-reforming greatly limits carbon deposition compared to directly related dry-reforming tests on this same catalyst.

1. Introduction

Methane and CO_2 are two major greenhouse gases, and converting them to higher value products is still a major challenge, mainly because these compounds are relatively chemically inactive. Moreover, the production and emission of these gases are predicted to increase in the near future [1], suggesting the importance of reactions of these compounds.

Catalytic conversion of these gases to produce syngas is a viable option [2,3]. Syngas, a mixture of CO and H_2, can be used as an intermediate to produce high value chemicals, such as methanol, higher oxygenates, and Fischer-Tropsch products [4–7]. There are several options to directly convert CH_4 and CO_2 to syngas:

$$\text{Dry} - \text{refor}\min g: \quad CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2 \tag{1}$$

$$\Delta H_{298K} = +247kJ/mol, \Delta G_{298K} = +170kJ/mol$$

$$\text{Oxy} - CO_2\text{reforming}: \quad 3CH_4 + CO_2 + O_2 \rightleftharpoons 4CO + 6H_2 \tag{2}$$

$$\Delta H_{298K} = +58kJ/mol, \Delta G_{298K} = -1kJ/mol$$

$$\text{Bi} - \text{reforming}: \quad 3CH_4 + CO_2 + 2H_2O \rightleftharpoons 4CO + 8H_2 \tag{3}$$

$$\Delta H_{298K} = +220kJ/mol, \Delta G_{298K} = +151kJ/mol$$

Among these reactions, bi-reforming has attracted interest because it has several advantages, e.g. the 2/1 H_2/CO syngas from bi-reforming can be directly converted into products such as methanol and Fischer-Tropsch fuels, eliminating the need to add H_2 from external sources.

There are many challenges in direct conversion of CH_4 and CO_2 to syngas, including the highly endothermic nature of the reaction itself, requiring temperatures of ~800–1000 °C. At these demanding conditions, many catalysts are not stable, resulting in collapse of the support structure or severe sintering of the active metal. Another major problem is due to carbon deposition, which results in inevitable deactivation of the catalyst. Therefore, the reforming catalyst must meet at least three criteria: (a) thermal stability of the support, (b) resistance to sintering of the active metal, and (c) high activity with time-on-stream to reach equilibrium conversions.

Recent work shows the potential for active metals to be doped into thermally stable crystalline oxides for dry reforming [8–11]. Pyrochlores are one example. These are highly crystalline materials with a general formula of $A_2B_2O_7$. They have proven high temperature stability in various applications, such as in gas turbine thermal barrier coatings [12]. The pyrochlore structure, in princi-

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ple, can incorporate active metals such as Ni in the structure at low loadings. This provides a strong interaction between the active metal and the support, which can significantly improve the resistance to carbon deposition [13]. The first report of pyrochlore as catalysts for reforming was by Ashcroft et al. [14], where they tested the structure with several active metals. However, their pyrochlore structure collapsed at dry reforming conditions.

The objective of the present work is to test a Ni-based $La_2Zr_2O_7$ pyrochlore catalyst for bi-reforming of methane. The catalyst was synthesized by modified Pechini method [15,16] and characterized using TPR/TPO, XRD, and EXAFS. The catalyst activity, stability, and selectivity were tested for bi-reforming reaction at temperatures in the range of 700–950 °C, with 24 h time-on-stream at each temperature. Finally, the carbon deposition for the spent catalyst was studied by TPO.

2. Experimental

2.1. Catalyst preparation

The 1% LNZ pyrochlore catalyst was prepared by using a modified Pechini method. The preparation method produces highly uniform pyrochlore crystallites and is explained in detail in the literature [11,15–19]. The precursors used for La, Ni, and Zr were Lanthanum nitrate [$La(NO_3)_3{\cdot}6H_2O$] (GFS Chemicals), Nickel nitrate [$Ni(NO_3)_2{\cdot}6H_2O$], and Zirconium nitrate [$ZrO(NO_3)_2.nH_2O$] (Alfa Aesar) respectively. The nitrate salts were separately dissolved in de-ionized water and then mixed with a citric acid (CA) solution in a molar ratio of CA:metal = 1.2:1. The solution was continuously stirred and heated to 75 °C to ensure complete metal complexation. At 75 °C, a 1:1 molar ratio of ethylene glycol (EG) to CA was added to the solution. The solution was kept stirred on the hot plate until most of the water had evaporated and a transparent, viscous gel was obtained. After this the stirring was stopped and the gel was left on the hot plate to promote the polyesterification reaction between EG and CA to form an organic polymeric network. The nitrate precursors started to decompose at this condition, which was evident from the large plumes of NOx and bubbling in the gel. The resulting mixture foam was placed in an oven at 110 °C to dry overnight. The mixture was then calcined at 1000 °C for 8 h to oxidize the organic precursors to form the pyrochlore catalyst. The bulk density of the catalyst was measured to be 0.77 g/cc.

2.2. Temperature programmed reduction (TPR)

Temperature programmed reduction (TPR) profiles of the calcined catalyst were recorded using an Altamira AMI 200 unit equipped with a thermal conductivity detector (TCD). 50 mg of catalyst sample was first oxidized in a fixed-bed micro-reactor system under flowing 5% O_2/He at 950 °C. It was then cooled to 25 °C under helium flow. TPR was performed using a 10% H_2/Ar mixture at a flow rate of 50 cm^3/min while the temperature was linearly ramped from 25 °C to 950 °C at 10 °C/min. The catalyst was then cooled to 25 °C under helium flow and then again oxidized under 5% O_2/He at 950 °C. The catalyst was again cooled to back 25 °C under helium flow. A second TPR was carried out under the same conditions as those of the first TPR mentioned above. The hydrogen consumptions under different peaks were calculated by deconvoluting the TPR profile and calculating the areas under the individual peaks, which directly correspond to hydrogen consumption. The thermal conductivity detector was calibrated with a standard silver oxide sample, where area under the peak was correlated to the H_2 consumption.

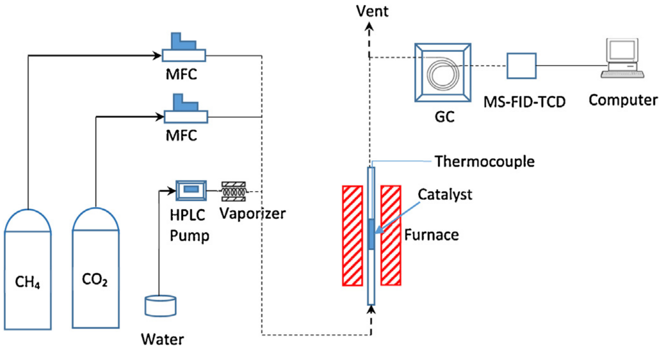

Fig. 1. Schematic diagram of experimental setup for bi-reforming reaction. The dotted lines are heat traced to avoid condensation of steam.

2.3. X-ray characterizations

X-ray absorption (XAS) spectra were measured at the electron storage ring of the Center for Advanced Microstructures and Devices (CAMD), Louisiana State University, USA. This synchrotron light source operates the storage ring at 1.3 GeV with a ring current between 50 and 150 mA. The measurements were made at the High Energy X-Ray Absorption Spectroscopy Beamline located on an 11-pole, 7.5 T multi-pole wiggler. The edge was calibrated to 8333 eV with a nickel foil. XAS spectra were collected for the Ni K-edge in fluorescence mode from −200 eV to 14 k relative to the Ni K-edge energy. The steps were 5 eV from −200 eV to −30 eV, 0.3 eV from −30 eV to 30 eV around the edge, and 0.05 k up to 14 k. Fluorescence spectra were obtained with an 80 mm^2 Ketek silicon drift detector by averaging at least four to five scans. XAS spectra were also collected for reagent grade NiO (Alfa Aesar) and nickel foil in transmission. Spectra were analyzed with Athena [20] in Demeter and WinXAS [21]. In extended X-ray absorption fine structure (EXAFS) analysis the amplitude reduction factor ($S_0{}^2$) was obtained from standards and kept fixed for the catalyst spectra.

X-ray diffraction (XRD) experiments were carried out using Empyrean x-ray diffractometer (PANalytical) using Cu Kα radiation (λ = 1.5406 Å). The scan angle was varied from 0° to 90° with a step size of 0.017°. Data analysis was done using the software X'Pert HighScorePlus (v3.0).

2.4. Catalyst activity test

Catalytic activity tests were carried out in a ¼" size flow reactor made of quartz, which can withstand up to 1200 °C under 1 atm. The pretreatment of the catalyst involved oxidation under 10% O_2/He flow at a temperature of 800 °C before cooling down to room temperature under pure helium. The catalyst was then reduced under 10% H_2/He flow at 800 °C. After the reduction, the catalyst was cooled to the reaction temperature under helium flow.

The schematic of the reactor and gas analysis system is presented in Fig. 1. The reactor system consists of various mass flow controllers for metered flow of gases. The water was fed to the reactor using a HPLC pump. The water flows through a vaporizer where steam is formed, which is later mixed with other gases before flowing through the catalyst bed. The dotted lines in Fig. 1 represent heat-traced lines, which were typically kept at 200 °C to avoid any condensation of steam. The reactor is equipped with a thermocouple that is inserted directly into the catalyst bed to measure the actual temperature of the catalyst. Both ends of the catalyst bed were plugged with quartz wool to avoid entrainment of any catalyst particles with the gas stream. Outlet gases were analyzed using an inline gas chromatograph (GC) equipped with a flame ionization detector (FID). The GC uses a Restek^{TM} RT-Q Bond column (25 m), where helium is used as a carrier gas. Part of the gases coming out