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Research Paper

Coupled reforming of methane to syngas ($2H_2$-CO) over Mg-Al oxide supported Ni catalyst

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ABSTRACT

We report bi-reforming and coupled reforming of methane with carbon dioxide, steam and/or oxygen to produce syngas over Ni supported on Mg-Al mixed oxide. The catalyst has been characterised in terms of specific surface area, TPR, XRD, TGA-DTG, SEM and TPO-MS analysis. Ni/Mg-Al mixed oxide exhibited Ni particle size range (11–30 nm) with a mean of 20.7 nm. Syngas $H_2/CO = 2.0$, suitable for methanol/Fischer-Tropsch fuel synthesis, has been achieved for both reactions ($T = 1048$ K, $P = 1$ atm). The impact of process parameters including temperature, feeding concentration and GHSV on conversion and H_2/CO ratio has been demonstrated. The Ni catalyst suffered temporal activity decline in bi-reforming that can be linked to formation of carbon whiskers encapsulated Ni particles resulting in a loss of active sites. Coupled reforming delivered higher CH_4 conversion and enhanced stability, but lower CO_2 conversion than bi-reforming under similar conditions. The enhanced stability in coupled reforming can be attributed to lower carbon deposition on Ni particles due to combustion of carbon by oxygen.

1. Introduction

Conversion of methane and carbon dioxide, two major greenhouse gases, to valuable chemicals has great significance in terms of global energy security and climate change [1,2]. Reforming of these gases to syngas, a critical intermediate in the manufacture of hydrogen, ammonia, methanol and Fischer-Tropsch products represents a promising route [3]. A variety of reforming reactions including

$$CH_4 + CO_2 \rightarrow 2H_2 + 2CO \tag{1}$$

$$3CH_4 + CO_2 + O_2 \rightarrow 6H_2 + 4CO \tag{2}$$

$$3CH_4 + CO_2 + 2H_2O \rightarrow 8H_2 + 4CO \tag{3}$$

dry reforming (Eq. (1)), oxy-CO_2 reforming (Eq. (2)) and bi-reforming (Eq. (3)) have been studied in the existing literature [4–6]. Bi-reforming to produce syngas offer significant advantages over dry reforming and oxy-CO_2 reforming with respect to (I) flexibility in H_2/CO ratio adjustment for downstream chemical (e.g., methanol, Fischer-Tropsch fuel) synthesis and (II) decreased carbon deposition due to presence of steam [1]. Olah et al. have demonstrated achievement of syngas ($H_2/CO = 2.0$), suitable for methanol synthesis, and stable activity with 320 h on-stream for high pressure (7–42 atm) bi-reforming reaction over Ni/MgO (1103 K, 6.0×10^4 $cm^3\,h^{-1}\,g_{cat}{}^{-1}$) [7,8]. Reaction at atmospheric pressure delivered syngas $H_2/CO = 2.1$ over Ni-based pyrochlore catalyst (1023 K, 9.8×10^4 $cm^3\,h^{-1}\,g_{cat}{}^{-1}$) [9] and $H_2/CO = 2.0$ over (Al_2O_3 [10], MgO-Al_2O_3 [11] and CeO_2 [12]) supported Ni (1023–1073 K, 5.3×10^5 $cm^3\,h^{-1}\,g_{cat}{}^{-1}$). In addition to Ni based catalyst, bimetallic Ru-Ni (supported on MgO) [13] and Ru/$ZnLaAlO_4$ [14] have been examined in bi-reforming reaction to enhance catalyst resistance to carbon deposition.

$$4CH_4 + CO_2 + H_2O + O_2 \rightarrow 9H_2 + 5CO \tag{4}$$

Coupled reforming (Eq. (4)), combined exothermic methane oxidation with bi-reforming, represents an alternative route for syngas production. Relative to bi-reforming, coupled reforming is more energy efficient due to heat release from methane oxidation [1,15]. Use of oxygen provides higher level of oxidant that can address carbon deposition, a critical cause of catalyst deactivation in methane reforming reaction [16]. Coupled reforming of methane to syngas, target at $H_2/CO = 2$ has not been studied to any significant extent. A search through literature found reported studies on coupled reforming of methane over Ni/MgO [17] and tri-reforming over (MgO [18], SiO_2 [19] and CeO_2-ZrO_2 [20]) supported Ni catalysts, producing syngas $H_2/CO = 1.5$-3.0 (973–1123 K).

For methane reforming reactions, catalysts based on noble metals exhibit high catalytic stability and great resistance to coke formation [21]. However, high cost restricts industrial scale application. Inexpensive Ni based catalysts have been used in reforming reaction due

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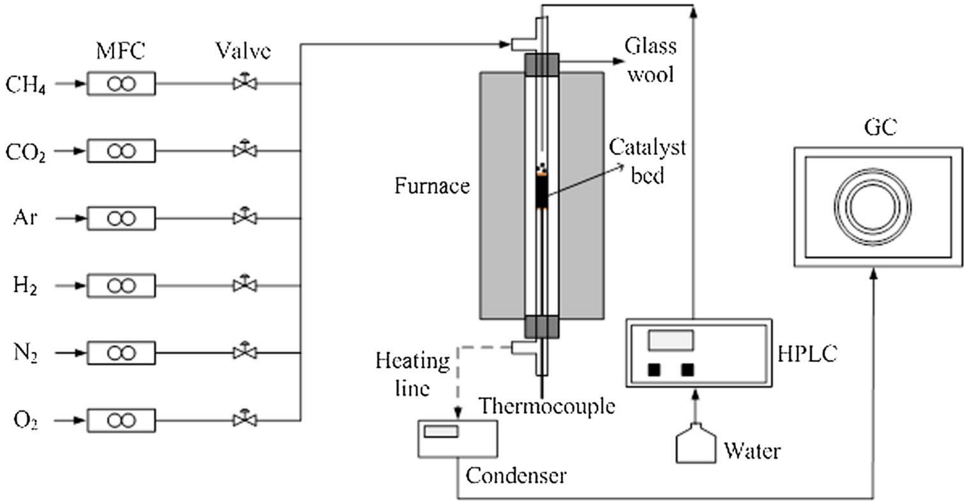

Fig. 1. Schematic diagram of experimental setup.

to high activity comparable to noble metals, but suffered rapid deactivation because of Ni particle agglomeration and carbon deposition [22]. MgO as basic support can enhance CO_2 chemisorption [23]. Inclusion of Al_2O_3 can increase surface area. Moreover, Ni supported on Mg-Al mixed oxide have been shown to bear strong metal-support interaction to suppress Ni sintering and exhibits enhanced catalytic stability in methane reforming reaction [24–26]. In this study, we for the first time examine coupled reforming of methane with steam, carbon dioxide and oxygen to produce syngas $H_2/CO = 2$ at atmospheric pressure over Mg-Al mixed oxide supported Ni catalyst and provide a comparison of catalytic performance to bi-reforming. We also evaluate carbon deposition in both reactions as one critical consideration for catalyst stability.

2. Experimental

2.1. Materials and catalyst preparation

Mg-Al mixed oxide was prepared by co-precipitation of metal nitrates (Sigma Aldrich, > 98%) with aqueous ammonia (10% w/w, Fisher) and ammonium carbonate (VWR Chemicals, 31.4% Assay NH_3) using flow synthesis. Aqueous nitrate salts ($Mg^{2+} = 1.5$ M, Mg/Al = 3/1, 100 cm^3) and a mixture (100 cm^3) of ammonia (5 M) with ammonium carbonate (0.25 M) was delivered separately via teflon line using a peristaltic pump (ISMATEC) at a fixed flow rate (1.5 cm^3 min^{-1}), mixed in a tee (bore = 1.8 mm) and transported continuously to 50 cm^3 water. The suspension was stirred (500 rpm) at 353 K for 2 h. The solid obtained was separated by filtration, washed with distilled water and dried at 393 K overnight. The dried sample was calcined in air at 873 K (10 K min^{-1}) for 4 h. Nickel (15% w/w) on Mg-Al mixed oxide was prepared by deposition-precipitation using aqueous ammonia. An aqueous solution of nickel nitrate (0.25 M, 100 cm^3) and ammonia (0.6 M, 100 cm^3) was added to the support (8 g). The suspension was stirred and heated to 353 K. The solid obtained was separated by filtration, washed with distilled water and dried at 393 K overnight. The catalyst precursor was sieved (ATM fine test sieves) to 60–200 mesh and activated at 10 K min^{-1} to 1073 K in 10 cm^3 min^{-1} H_2 (BOC, 99.99%) for characterisation.

2.2. Catalyst characterisation

Nitrogen physisorption was performed on the Micromeritics ASAP 2020 system and total specific surface area (SSA) was calculated using the standard BET method with pore volume obtained from BJH desorption. Prior to analysis, samples were vacuumed and outgassed at 573 K for 1 h. Nickel content was measured by inductive coupled plasma optical emission spectroscopy (ICP-OES, PerkinElmer 5300DV) from the diluted extract in HNO_3. Temperature programmed reduction (TPR) was conducted in a quartz tube cell. The sample was heated in 84 cm^3 min^{-1} 5% v/v H_2/Ar at 6 K min^{-1} to 1073 K and held for 1 h. Hydrogen consumption was monitored by a thermal conductivity detector (TCD). X-ray diffractograms (XRD) were recorded on a Bruker D5005 X-ray diffractometer using Cu Kα radiation. Samples were scanned at 0.02° $step^{-1}$ over the range $30° \leq 2\theta \leq 80°$ at ambient temperature and the diffractograms identified against the JCPDS-ICDD reference standards, *i.e.* Ni (04-0850), MgO (89-7746), γ-Al_2O_3 (10-0425) and $MgAl_2O_4$ (77-1193). Nickel particle morphology (size and shape) and carbon deposition was examined by Zeiss Supra 55VP field emission scanning electron microscopy (SEM). Mean metal size (*d*) was based on a count of up to 500 particles. Thermogravimetric-derivative thermogravimetric analysis (TGA-DTG) of the samples post-reaction was performed on a simultaneous thermal analyser (NETZSCH STA449) by monitoring temporal mass with temperature. The samples (*ca.* 30 mg) were heated in 50 cm^3 min^{-1} air to 1073 K (at 10 K min^{-1}). TPO-MS analysis of the spent catalysts was conducted in a quartz tube by recording CO_2 signal with time and temperature on a Pfeiffer OMNIStar mass spectrometer. The samples (*ca.* 15 mg) were heated in 20 cm^3 min^{-1} 10% O_2/Ar to 1073 K (at 5 K min^{-1}).

2.3. Catalytic procedures

Catalyst testing was conducted at atmospheric pressure (973–1073 K), *in situ* after activation, in a continuous flow fixed bed (alumina) tubular reactor (i.d. = 8 mm). The schematic diagram of the reactor and gas analysis system is shown in Fig. 1. The catalyst (5–30 mg) was mixed with ground quartz (60–200 mesh) and sandwiched between quartz wool. A layer of quartz particles was placed on the top of quartz wool before the catalyst bed. Reaction temperature was monitored by a thermocouple inserted in the catalyst bed. Water was delivered to the reactor using a Shimadzu HPLC (LC-20AD) pump and vaporized to steam in the upper part of the reactor. Reactant gases (CH_4, CO_2 and/or O_2, BOC, 99.99%), N_2 (BOC, 99.99%) as internal standard and Ar (BOC, 99.99%) as balance gas were introduced to reactor by Brooks mass flow controller (SLA5800 series) at (reactant) gas hourly space velocity (GHSV) = 2×10^4–2×10^5 h^{-1}. For all reactions, the flow rate of methane was fixed at 9 cm^3 min^{-1}. The reactor effluent was condensed in a gas sample cooler (Bühler) for subsequent analysis using online gas chromatography (Shimadzu 2014) equipped with a 0.5 cm^3 sampling loop, thermal conductive detector (TCD) and flame ionization detector (FID), employing serial Hayesep Q (3.0 m × 2.1 mm i.d.) and Molecular Sieve 5A packed columns (2.0 m × 2.1 mm i.d.). Data acquisition and manipulation were

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