

Combined steam and CO₂ reforming of methane for syngas production over carbon-resistant boron-promoted Ni/SBA-15 catalysts

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ABSTRACT

The unpromoted and B-promoted 10%Ni/SBA-15 catalysts synthesized via sequential incipient wetness impregnation approach were assessed for combined steam and CO₂ reforming of methane (CSCRM) at various reaction temperatures of 973–1073 K and stoichiometric feed composition. An expected and noteworthy drop in mean NiO crystallite size and BET surface area with boron promotion from 1% to 5%B loading could be due to the agglomeration of B₂O₃ particles and deboration reaction during calcination and hence blocking mesopores of SBA-15 support at elevated B composition. The complete NiO reduction to metallic Ni⁰ form was achieved during H₂ activation and the reduction temperature of NiO phase was shifted towards higher temperature with B-addition owing to enhancing interaction between the acidic B₂O₃ and basic NiO phases. For all reaction temperature employed, 3%B appeared to be the optimal promoter loading in terms of reactant conversions and 3%B-10%Ni/SBA-15 catalyst revealed the greatest H₂ yield (69.4%) at 1073 K. In addition, CH₄ and CO₂ conversions were enhanced about 23.2% and 32.4%, correspondingly with rising reaction temperature from 973 to 1073 K. Ratio of H₂ to CO varied from 1.26 to 2.71 and the desired H₂/CO ratio of about 2 favored for Fischer-Tropsch synthesis was achieved on 3%B-10%Ni/SBA-15 sample at 973 K. Boron promoter suppressed graphitic carbon formation and the amount of carbonaceous deposition was reduced about 4 times. Noticeably, 3%B-10%Ni/SBA-15 was also resilient to metallic Ni⁰ re-oxidation throughout CSCRM.

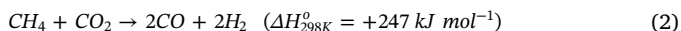
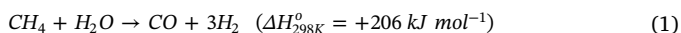
1. Introduction

The growing concerns towards the depleting non-renewable petroleum resources and the excessive release of anthropogenic CO₂ greenhouse gas from the industrial combustion and residential consumption of fossil fuels have led to rising interests in exploring an alternative, sustainable and clean energy as well as diversifying energy sources [1]. In fact, reducing CO₂ emission, replacing petroleum-based energy with less carbon-intensive fossil energy sources and decreasing the currently significant dependency on non-renewable energy are an essential and urgent task. Amongst alternative energies, syngas consisting of H₂ and CO has appeared as a promising and flexible building block for the following downstream production such as synthetic long-chained hydrocarbons via Fischer-Tropsch synthesis (FTS) [2,3] and other

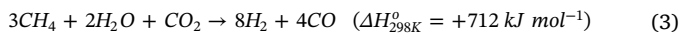
essential chemicals, namely, methyl tert-butyl ether (MTBE), dimethyl ether (DME) and methanol in petrochemical industries [4].

In general, the conventional steam reforming of methane, SRM (cf. Eq. (1)) is currently employed in industry for syngas production. However, this approach yields undesirable ratio of H₂ to CO greater than 3 and substantially releases a large amount of unfavorable CO₂ gaseous by-product [2,3]. Although dry reforming of methane (DRM, see Eq. (2)) could transform unwanted CO₂ greenhouse gas to a value-added syngas, the resulting H₂/CO ratio of less than unity makes this process inappropriate for FTS and methanol production requiring a stoichiometric H₂/CO ratio of 2 [5,6]. Thus, the implementation of this approach could impose auxiliary separation and purification steps in the downstream process for adjusting H₂/CO ratio to around 2 [7] and hence increasing capital cost.

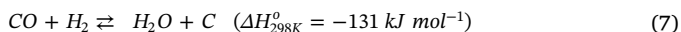
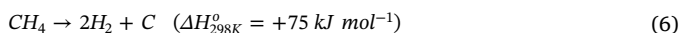
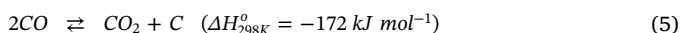
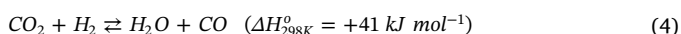
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From the above reasons, the combined steam and CO₂ reforming of methane, abbreviated as CSCRM (see Eq. (3)), also known as bi-reforming of methane, has recently appeared as a promising technique since it is capable of generating a green and sustainable energy source from biogas, a non-fossil fuel resource mainly consisting of methane, carbon dioxide and water [8]. In fact, CSCRM is reportedly a prospective substitution of other common reforming processes owing to its high catalytic stability in the coexistence of CO₂ and H₂O oxidizing reactants and flexible adjustment of H₂/CO ratios by the manipulation of feedstock composition [9,10].



Nevertheless, the bibliographic knowledge about CSCRM reaction is still little-known as reported in literature due to the complexity of this reaction involving multiple main reactions, namely, SRM (see Eq. (1)) and DRM (see Eq. (2)) as well as several parallel reactions including non-coke (*viz.* reverse water-gas shift reaction given in Eq. (4)) and coke forming reactions (see Eqs. (5)–(7)).



In general, from an industrial standpoint, Ni-based catalyst is recognized as one of the most attractive candidates for the large-scale industrial application of reforming processes since this catalyst type is cost-effective, abundant availability and relatively high catalytic activity comparable to precious metals [2,3,10]. However, Ni-based catalysts could encounter challenging barriers of coke formation and Ni metal sintering resulting in rapid catalyst deactivation at high reaction temperature. In the research of CSCRM reaction over Ni-Ce/Al₂O₃ catalyst, Koo et al. [11] reported that high CH₄ and CO₂ conversions of about 90.9% and 69.2%, respectively were achieved at 1023 K with the feed composition, CH₄:CO₂:H₂O:N₂ of 1.0:0.4:0.8:1.0. However, graphitic carbon formation was still evident even with the utilization of redox CeO₂ promoter widely reported as carbon removal agent [2,3]. The same behavior was also observed by Park et al. for spent La-Ni/MgAl₂O₄ catalyst after CSCRM reaction at 1173 K and 5 atm with CH₄/H₂O/CO₂/N₂ of 1/1.2/0.4/0.3 [12]. Thus, exploring a new catalyst system resistant to carbon deposition by the implementation of suitable combination of support and promoter is crucial in CSCRM.

In recent years, mesoporous siliceous SBA-15 support has drawn significant attention from both academics and industry for wide-ranging heterogeneous catalytic reactions, namely, methane steam reforming [13,14], methane dry reforming [15,16] and methane cracking [17] due to its substantially large specific surface area, thick framework walls with ordered mesoporous structure and high thermal stability [18]. The confinement effect of highly ordered two-dimensional hexagonal SBA-15 support could anchor metal nanoparticles inside the mesoporous silica channels, inhibit metal sintering and hence resistance to carbon deposition [7,19].

Apart from utilizing rare-earth metal oxides as redox promoters for elimination of carbonaceous species [2,3], by using first principles density functional theory (DFT) computations, Saeys' group found that boron promoter may bind to the octahedral sites of the first Ni (1 1 1) subsurface layer preferred for carbon adsorption and thus suppressing surface carbon diffusion for forming graphene islands [20–22]. However, after meticulously exploring published literature, there were no reportedly preceding experimental studies regarding synergetic influence of boron promoter and SBA-15 support on CSCRM. Therefore, the

goal of this project was to scrutinize the influence of B-promoter on the physicochemical properties of 10%Ni/SBA-15 catalyst and examine impact of reaction temperature on CSCRM performance.

2. Experimental

2.1. Synthesis of catalyst

Hydrothermal preparation technique was used for the synthesis of siliceous SBA-15 support. An accurately measured quantity of Pluronic P-123 triblock copolymer (EO₂₀PO₇₀EO₂₀, triblock-poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) supplied by Sigma-Aldrich Chemicals) was mixed with HCl solution (pH ≈ 1) for 2 h at 313 K in order to completely dissolve the P-123 template. The tetraethyl orthosilicate (TEOS, procured from Merck Millipore) silica precursor was then added to resulting crystal clear solution and vigorously mixed at similar temperature about 24 h. Afterward, the resulting mixture was subjected to hydrothermal treatment in an autoclave (possessing an inner Teflon-lined container) for 24 h at 373 K and the achieving milky slurry was filtered as well as rinsed with purified water to pH value ≈ 4. The obtained white solid powder was further dried at 323 K for 24 h and calcined in furnace at 823 K (ramping rate: 2 K min⁻¹) with flowing air for 5 h to yield the mesoporous SBA-15 support.

X%B-10%Ni/SBA-15 (X%: 0-5 wt%) catalysts were synthesized using a sequential incipient wetness impregnation (SIWI) approach employing as-prepared SBA-15 support, Ni(NO₃)₂·6H₂O metal precursor and boric acid (H₃BO₃) promoter precursor solutions (supplied by Sigma-Aldrich Chemicals). Accurately balanced amounts of Ni (NO₃)₂·6H₂O solution and original SBA-15 support were mixed and thoroughly stirred at 333 K for 3 h in a rotary evaporator (BÜCHI Rotavapor R-200) at vacuum conditions.

The mixture was further dehydrated by heating up to 373 K for 24 h before being air-calcined for 5 h at 1073 K with a heating rate of 2 K min⁻¹ to produce an unpromoted 10%Ni/SBA-15 catalyst. The incipient wetness impregnation approach between abovementioned unpromoted 10%Ni/SBA-15 catalyst and different calculated quantities of H₃BO₃ aqueous solution was further conducted using the same aforementioned experimental procedure in order to synthesize B-promoted catalysts.

2.2. Characterization of catalyst

The physical attributes (*viz.*, Brunauer-Emmett-Teller (BET) surface area, average pore diameter and total pore volume) of unpromoted, B-promoted Ni-based catalysts and SBA-15 support were measured in Micromeritics ASAP-2010 equipment using N₂ adsorption-desorption isotherms data obtained at 77 K. Before conducting any BET measurements, the specimen was pretreated at 573 K for about 1 h in N₂ flow to remove traced moisture and possibly volatile contamination on sample surface. The attenuated total reflectance Fourier-transform infrared (ATR-FTIR) spectroscopy of support and catalysts was recorded within 400–4000 cm⁻¹ with spectral resolution of 4 cm⁻¹ and scan number of 100 on a Thermo Fisher Scientific Nicolet iS5 FTIR spectrometer attached with iD7 ATR component.

The low-angle X-ray diffraction (XRD) experiments for fresh SBA-15 support and catalysts were conducted on a Philips X'Pert MPD (3 kW) diffractometer employing Cu Kα as radiation source (with a wavelength, λ, of 1.5405 Å). All samples were scanned from 2θ of 0.5° to 5° with a step size of 0.005°. In addition, the Rigaku Miniflex II system with a Cu monochromatic X-ray radiation (λ = 1.5418 Å) was utilized for wide-angle XRD measurements. This system was operated at 15 mA and 30 kV. Fairly small scan speed (1° min⁻¹) and step size (0.02°) were applied for all samples to obtain high-resolution patterns during 2θ scanning range from 3° to 80°. In order to calculate average NiO crystallite size, *d*(NiO), Scherrer equation given in Eq. (8) was employed

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