



Catalyst design for methane steam reforming



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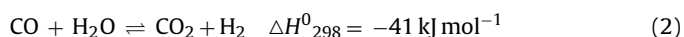
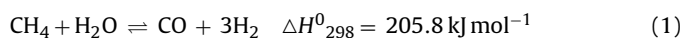
ABSTRACT

Commercial syngas production via methane steam reforming is conventionally carried out over Ni catalyst supported on semiconductor oxides such as Al_2O_3 and SiO_2 . The present work reports empirical verification of catalyst design for methane steam reforming carried out at relatively low steam-to-carbon feed ratio (2:1–2:1) and compares the behavior among SiO_2 , SBA-15 (mesoporous silica), $\gamma\text{-Al}_2\text{O}_3$ and $\alpha\text{-Al}_2\text{O}_3$ supported Ni catalyst. In addition promoters such as B, Ce, Mo and Zr were assessed. SBA-15 and Ce emerged to be significant support and promoter respectively. However there seems to be an optimum Ni wt% loading for a given support which was found to be 10 wt% for SBA-15. The investigations revealed that MSR over 1 wt% Ce/10 wt% Ni/SBA-15 at S:C = 1–2 at atmospheric pressure and 1073 K resulted in 92–99% methane conversion with higher H_2 to CO ratio and highly resistant to carbon deposition.

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1. Introduction

Methane steam reforming (MSR) is the most important route for the production of hydrogen or syngas (cf. reaction (1)) [1] employed in the manufacturing of methanol, ammonia and the Fischer-Tropsch synthesis of hydrocarbons. Industrial reforming employs Ni-based catalyst.



Exact formulation however, vary due to the need for carbon deposition control and minimization as well as the procurement of high catalyst activity, product selectivity and stability. Moreover, other reaction metrics for MSR also contribute toward the favorable performance explained earlier. Namely, temperature, pressure, steam-to-carbon (S:C) ratio, $W_{\text{CAT}}/F_{\text{CH}_4}$, time-on-stream and catalyst reduction temperature [2–7].

In order to address this multi-objective optimization problem similar to that of MSR, in recent times artificial neural network (ANN) approach had been utilized for catalyst design [8–10]. Where, the ANN inputs in those studies were only the % composition of the individual components present in a multi-component

catalyst. In particular, Umegaki et al. [10] used the ANN learning to predict optimal combination of the component percentage to derive the Cu/Pr/Ti catalyst which provided 96% methanol conversion in oxidative methanol steam methane reforming experiments. Hattori and Kito demonstrated the ability of ANN to learn the complex relationships between reaction rates to factors like heat of formation, ionization potential, electronegativity, etc. for propene oxidation [11]. Likewise, Chesterfield and Adesina established correlations between catalyst-treatment, -properties, reaction conditions and organic pollutant concentration to photo catalytic activity via reliable ANN models for photo degradation of aqueous organics [12].

In our previous study [13] we have employed ANN analysis of available MSR data [2–7] namely, catalyst design variables such as Ni loading, support types such as SBA-15, SiO_2 , $\alpha\text{-Al}_2\text{O}_3$ and $\gamma\text{-Al}_2\text{O}_3$; promoters – B, Mo, Zr, Ce, catalyst reduction temperature using H_2 , in addition to reactor operating factors for instance S:C ratio, $W_{\text{cat}}/F_{\text{CH}_4}$, reforming temperature and pressure to determine the overall methane conversion. The ANN model with significant model adequacy was used to assess whether a factor has positive influence or detrimental effect and the magnitude of effect against methane conversion.

In this study catalysts derived from support types; SiO_2 , $\gamma\text{-Al}_2\text{O}_3$, $\alpha\text{-Al}_2\text{O}_3$ and SBA-15, promoters; Ce, Zr, B and Mo were compared in order to design an efficient catalyst for MSR employing existing suggestions from literature [2–7] and thereby experimentally validating the ANN model from our previous analysis [13]. This investigation also evaluated the optimum Ni metal loading namely

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Nomenclature

b	inert volume fraction of bed
C_{As}	concentration of reactant at the catalyst surface (mol m^{-3})
C_{Ab}	concentration of reactant in bulk stream (mol m^{-3})
C_{A_0}	initial concentration of methane (mol L^{-1})
C_A	concentration of methane at time 't' (mol L^{-1})
d_p	catalyst particle diameter (m)
d_r	reactor tube diameter (m)
D_{eff}	effective diffusivity ($\text{m}^2 \text{s}^{-1}$)
E_A	activation energy (kJ mol^{-1})
h	heat transfer coefficient between gas and catalyst ($\text{kJ m}^{-2} \text{s}^{-1} \text{K}^{-1}$)
ΔH_r	heat of reaction (kJ mol^{-1})
k'	kinetic constant with respect to activity ($\text{mol m}^{-2} \text{s}^{-1} \text{L}^{-1}$)
k_d	kinetic constant with respect to deactivation ($\text{mol m}^{-2} \text{s}^{-1} \text{L}^{-1}$)
k	rate constant ($\text{mol m}^{-2} \text{s}^{-1} \text{kPa}^{(\alpha+\beta)}$)
k_c	mass transfer coefficient (m s^{-1})
n	apparent reaction order
R	ideal gas constant ($\text{J mol}^{-1} \text{K}^{-1}$)
$-r$	reaction rate ($\text{mol s}^{-1} \text{g}_{\text{cat}}^{-1}$ (or) $\text{mol m}^{-2} \text{s}^{-1}$)
t	time-on-stream (s)
T_b	bulk gas-phase temperature (K)
T_s	particle temperature (K)

Greek alphabets

ρ_c	catalyst bulk density (kg m^{-3})
ρ_b	catalyst bed density (kg m^{-3})
τ	space time (s)
λ_{eff}	effective bed thermal conductivity ($\text{W m}^{-1} \text{K}^{-1}$)

catalyst with 5, 10, 20 and 40 wt% were subjected to MSR activity tests. Hence, to procure a catalyst with optimum Ni loading sustained on a significant support with most favorable promoter in perspective of methane consumption and resistance to coking under low S:C ratio feed composition for MSR carried out at atmospheric pressure.

2. Experimental

2.1. Supports and catalysts preparation

The SBA-15 support was synthesized as detailed by Zhao et al. [14], a mixture of HCl and triblock copolymer (EO₂₀-PO₇₀-EO₂₀) (Pluronic P123) (chemicals used in this study are procured from Sigma-Aldrich, unless otherwise specified) was stirred continuously at 308 K until the copolymer was dissolved completely. Tetraethyl orthosilicate was added to the mixture and the stirring was continued for another 20 h, at 308 K, later the mixture was subjected to drying for 48 h at 373 K. Upon filtration, the solid obtained was calcined at 773 K for 6 h, to remove the template resulting in pristine white SBA-15. Precipitated amorphous SiO₂ and γ -Al₂O₃ (obtained from Saint Gobain NorPro (USA) as pellets) were grinded and sieved required particle size (90–425 μm) whereas, the SBA-15 support is pelletized at 6 ton pressure followed by size reduction. SBA-15, SiO₂ and γ -Al₂O₃ were pre-treated at 1073 K for 6 h. However, α -Al₂O₃ is prepared by elevating γ -Al₂O₃ to 1523 K and held for 6 h [15].

Aqueous solutions of Ni(NO₃)₂·6H₂O, Ce(NO₃)₃·6H₂O, Zr(NO₃)₄·(NH₄)₆Mo₇O₂₄·4H₂O and H₃BO₃ were used as precursors for Ni, Ce, Zr, Mo and B respectively. The catalysts 10 wt% Ni/90 wt% X (where

X stands for SiO₂, SBA-15, γ -Al₂O₃ and α -Al₂O₃) were prepared via wet impregnation of corresponding support using Ni precursor. However, the promoted catalysts 1 wt% Y-10 wt% Ni/89 wt% SBA-15 (where Y = Ce, Zr, Mo and B) were prepared by wet co-impregnation of SBA-15 with Ni and promoter precursors simultaneously. After impregnation the wet solid samples were dried at 375 K for 24 h followed by calcination in air at 1123 K for 6 h to obtain the oxide catalysts.

2.2. Catalysts characterization

Multi-point BET surface area, pore volume and diameter of both fresh and used catalysts were measured via N₂ physisorption at 77 K using Quantachrome Autosorb unit and the samples were held at 573 K for 3 h before analysis. Powder X-ray diffraction (XRD) pattern of the calcined catalyst was obtained on X'pert Pro Multipurpose X-ray Diffraction (MPD) system using Cu K α radiation ($\lambda = 0.154 \text{ nm}$) operated at 40 mA and 45 kV. X-ray photoelectron spectroscopy (XPS) measurements were recorded using ESCALAB250Xi spectrometer, with Al K α radiation generated at 164 W. The analyses were carried out at pass energy of 100 eV for survey scans and 20 eV for surface region scans. Adventitious carbon C_{1s} at 285 eV was used as binding energy reference. The thermogravimetric analysis (TGA) involved temperature-programmed reduction (TPR) experiments (held at 1073 K for 2 h using a heating rate of 10 K min⁻¹) on fresh calcined catalysts and temperature-programmed reduction-oxidation (TPR-TPO conducted at 973 K for 1 h with a heating rate of 10 K min⁻¹ for both reduction and oxidation stages) on used catalysts were performed in a ThermoCahn TG-2121 unit to study the weight change transients and to estimate effectiveness of carbon gasification respectively. The TGA were carried out with 55 mL min⁻¹ of 50% H₂/Ar and air for TPR and TPO respectively.

NH₃-, CO₂-temperature-programmed desorption (TPD) and pulse H₂-chemisorption were conducted employing Micromeritics Autochem 2910. The calcined catalysts were reduced in situ with H₂ at 1073 K for 2 h after a heating rate of 10 K min⁻¹ and then cooled to 383 K under flowing N₂, followed by pulse injection of 10% H₂/N₂. While, the catalysts were cooled to 323 K after reduction for NH₃- and CO₂-TPD followed by flow of 10% NH₃/N₂ and 10% CO₂/He respectively, subsequently desorption was carried out at heating rates 10, 15, 20 and 30 K min⁻¹. A Shimadzu Total Organic Carbon (TOC) Analyser 5000A coupled to a Solid Sample Module SSM-5000A was employed to determine the total carbon content on used catalysts under the flow of 100% O₂ at 1173 K. The transmission electron microscope and scanning electron microscope images of as synthesized SBA-15 were obtained using FEI-Tecna G2-20 TEM and Hitachi S3400 instruments respectively.

2.3. Catalysts activity evaluation and reaction metrics

The catalyst activity tests were conducted in a stainless steel fixed-bed reactor operated under atmospheric pressure with an internal diameter of 10 mm using 0.25 g of catalyst supported on quartz wool. Distilled and deionized water was fed in specific quantities from a small concealed reservoir via Gilson Minipuls 3 M 312 peristaltic pump by passage through a steam generator and mixer maintained at 453 K to form steam-to-CH₄ (i.e. S:C) feed mixture with ratios varying from 1:2 to 2:1. This mixture was further diluted in Ar and supplied as feed stream (at a fixed gas-hourly space velocity, GHSV = 2.5 × 10⁴ h⁻¹) downwards from the top end of the reactor. Runs were carried out in the range 873–1073 K. Prior to each activity test the catalyst was reduced in a stream of 50% H₂/Ar flowing at 55 mL min⁻¹ for 2 h at 1073 K. Moisture was removed by passing the gas over a steam-trap maintained at 275 K and the

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