

Hydrogen Production from CO₂ Reforming of Methane Using Zirconia Supported Nickle Catalyst

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Table S1: The hydrogen production by various investigators

Catalyst	Study performed	Reaction (T)	Production Target	Ref
Ni-Co/ γ -Al ₂ O ₃ + La ₂ O ₃	Biogas reforming	800°C	H ₂ -Yeild	[13]
Ni/MgO	Dry reforming of CH ₄	600-800°C	H ₂ -Yeild	[15]
Ni/ZrO ₂ and Ni/CaO	Dry Reforming of Glycerol	700°C	H ₂ -Yeild	[17]
Ni-Co/MgO-ZrO ₂	Dry reforming of CH ₄	700-800°C	H ₂ -Yeild	[18]
Ni/Ce-ZrO ₂	ORM, SRM and OSRM	700-850°C	H ₂ -Yeild	[19]
Ni-ZrO ₂ @SiO ₂	Dry reforming of CH ₄	800°C	H ₂ -Yeild	[20]
Fe/ZrO ₂ , Fe-Ni/ZrO ₂	CH ₄ Decomposition	800°C	H ₂ -Yeild	[24]
Ni/ZrO ₂	Dry reforming of CH ₄	700°C	H ₂ -Yeild	[25]
Ni-Si/ZrO ₂	Dry reforming of CH ₄	400-450°C	H ₂ -Yeild	[26]
Ni/Al ₂ O ₃	Dry reforming of CH ₄	700°C	H ₂ -Yeild	[27]
Co/CeO ₂ and Co/ZrO ₂	Dry reforming of CH ₄	700°C	H ₂ -Yeild	[28]
Ni/CeO ₂ +ZrO ₂	Dry reforming of CH ₄	600°C	H ₂ -Yeild	[29]
Ni/PO ₄ +ZrO ₂	Dry reforming of CH ₄	800°C	H ₂ -Yeild	[30]
Ni _x Co _y /H-ZrO ₂	Dry reforming of CH ₄	700°C	H ₂ -Yeild	[31]
Ni-Co/Al ₂ O ₃ -ZrO ₂	Dry reforming of CH ₄	700°C	H ₂ -Yeild	[33]
Ni/ZrO ₂	Dry reforming of CH ₄	650°C	H ₂ -Yeild	[34]
Co+Ce/Al ₂ O ₃	Dry reforming of CH ₄	750°C	H ₂ -Yeild	[35]

Catalyst preparation

Ni supported catalysts employed in this study were synthesized using the wet-impregnation. The support used were $[\text{ZrO}_2, x\% \text{Y}_2\text{O}_3 + \text{ZrO}_2, (x= 5, 10, 15, 20)]$, $[\text{ZrO}_2, 5\% \text{MgO} + \text{ZrO}_2]$. Nickel nitrate hexahydrate $[\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$, Gallium nitrate hydrate $[\text{Ga}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}]$, Strontium nitrate tetrahydrate $[\text{Sr}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}]$, and Cesium nitrate $[\text{CsNO}_3]$ with 99% purity was purchased from Sigma-Aldrich. The zirconia (ZrO_2) support was obtained from Anhui Elite industrial with 99 % purity. Yttria (Y_2O_3 , 99.9%) were bought from MKnano Co. Magnesium oxide (MgO , 99.9%) was purchased from Sigma-Aldrich. Distilled water was used for impregnation. The stoichiometric amount of active metal was measured and introduced into distilled water (30 ml), thereafter the supports were added. The support-active metal mixtures, present in separate crucibles, were stirred and dried at 80 °C for 3 hrs over different hot plates. Subsequently, the samples were positioned inside an oven, for overnight drying at 120 °C. Calcination of the samples was done at 700 °C for 3 hrs in the oven. In the case of the promoted catalysts, 3wt.% promoter was mixed with Ni and the same procedure was adopted to final catalysts. Table S1 gives the catalyst designation used in this paper.

Table S2 Catalysts and their Designations

Catalyst-Name	Designation
5wt.%Ni/ ZrO_2	5NiZr
5wt.%Ni/5wt.%MgO+ ZrO_2	5Ni5MgZr
5wt.%Ni/x wt.% Y_2O_3 + ZrO_2	5NixYZr
Where x = 5, 10, 15, 20	
5wt.%Ni+ 3 Cs wt.%/15 wt.% Y_2O_3 + ZrO_2	5NiCs15YZr
5wt.%Ni+ 3 Ga wt.%/15 wt.% Y_2O_3 + ZrO_2	5NiGa15YZr
5wt.%Ni+ 3 Sr wt.%/15 wt.% Y_2O_3 + ZrO_2	5NiSr15YZr

Catalyst activity

The CO₂ reforming of methane (CRM) was performed using Ni supported catalysts in an upright, fixed-bed, stainless steel tubular micro-reactor (PID Eng&Tech microactivity reference), 9.1 mm I.D. and 30 cm long, at atmospheric pressure. Catalyst testing was performed using catalyst mass of 0.1 g which was carefully positioned over a bed of glass wool inside the reactor. The actual reactor temperature was read by an axially positioned thermocouple (K-type), sheathed in stainless steel. The total time of analysis for each of the catalysts was 440 min. Before the start of reaction, each of the catalysts was reduced under the flow of H₂ at 20 ml/min for 90 min. at 700 °C. Thereafter the system was purged with N₂ for 15 min., to remove any remnant of H₂. The temperature of the reactor was raised to the reaction (i.e. 700 °C) in the flow of N₂. The feed gas mixture, was maintained at a total flow rate of 20 ml/min (30/30/10 ml/min for CH₄, CO₂, and N₂ respectively) and equivalent space velocity of 42,000 ml/h/g-cat. The product gas composition was analysed by a gas chromatography (Shimadzu GC 2004) that was connected on-line. The GC is equipped with a thermal conductivity detector (TCD). The following expressions were used to determine the methane conversion and hydrogen yield:

$$H_2\text{Yield: } Y_{H_2} = \frac{\text{moles of } H_2\text{ produced}}{2 \times \text{moles of } CH_4 \text{ in the feed}} \times 100\%$$

Catalyst characterization

The N₂- physisorption was used to estimate Brunauer-Emmet-Teller specific surface area per unit mass of the samples (BET) by using a Micromeritics Tristar II 3020. The

X-ray powder diffraction patterns (XRD) for the samples were recorded on a Bruker D8 Advance (Bruker, Billerica, MA, USA) XRD diffractometer by using Cu K radiation source and a nickel filter, operated at 40 kV and 40 mA. The step size and scanning range for analysis was set to 0.01 and 5–100, respectively. The obtained phases were documented using standard powder XRD cards (JCPDS). Automatic chemisorption equipment (Micromeritics Auto Chem II 2920, USA) was used to study temperature programmed reduction (TPR) and temperature programmed desorption (CO₂-TPD) of the catalysts. 70 mg of the sample was

subjected to a heat treatment for TPR at 10 °C/min up to 900 °C under atmospheric pressure and gas flow (40 ml/min) of 10% H₂/Ar or CH₄/Ar mixture. For CO₂-TPD, 70 mg of sample was used. The sample was first kept at 200 °C for 1 h under helium flow to remove physically adsorbed species from the catalyst surface. Then, CO₂ adsorption was accomplished at 50 °C for 30 min by passing 10% CO₂/He mixture gas with a flow rate of 30 ml/min. Then, the CO₂ desorption signal was recorded by TCD with a linear increase in temperature up to 800 °C with a temperature ramp rate of 10 °C/min. The Laser Raman (NMR-4500) Spectrometer (JASCO, Japan) was used to obtain Raman spectra of the catalyst samples. The wavelength of the excitation beam was set to 532 nm and an objective lens of 100× magnification was used for the measurement. The laser intensity was adjusted to 1.6 mW for 10 seconds exposure time at 3 accumulations. This was to protect the sample from being damaged by laser irradiation. Measurement was done in the range 500–1200 cm⁻¹ (Raman shift) and the spectra were processed using Spectra Manager Ver.2 software (JASCO, Japan). The morphology of the catalysts was captured via 120 kV JEOL JEM-2100F transmission electron microscope (TEM). The amount of carbon deposition on the spent catalysts was evaluated by thermal gravimetric analysis (TGA) under air by using a Shimadzu TGA-51.

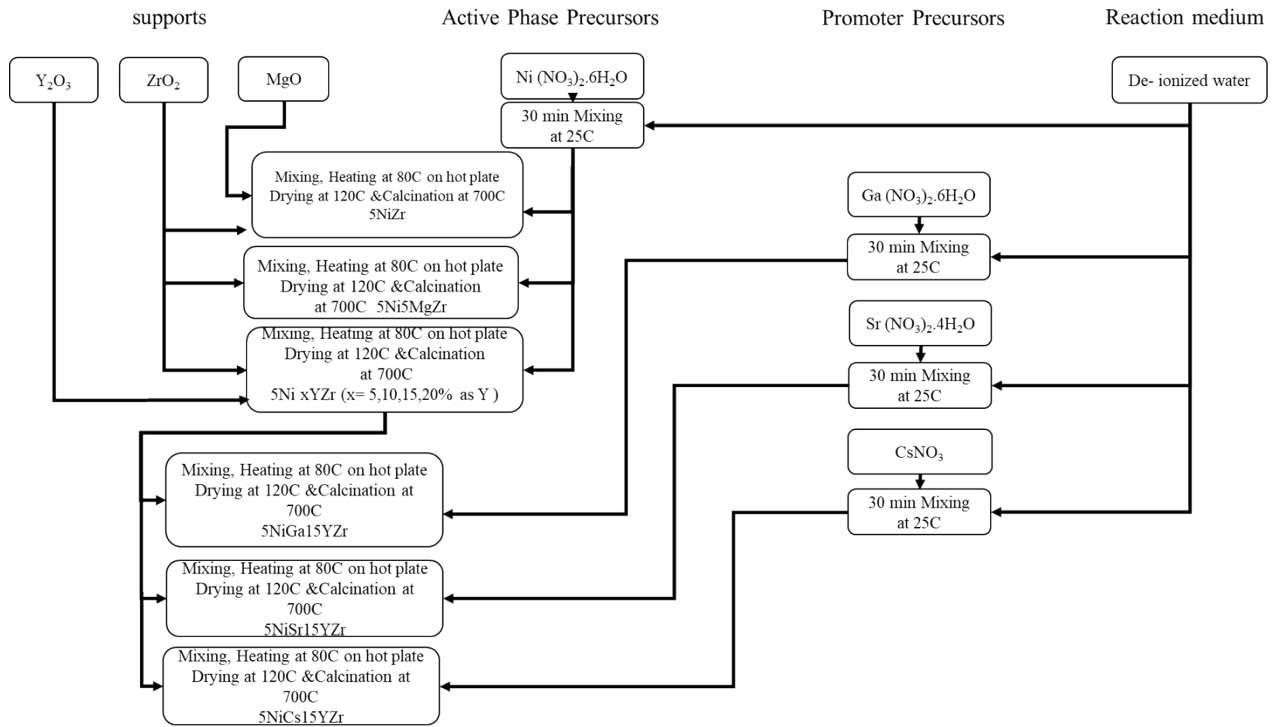


Figure S1 flow chart for the catalyst Preparation

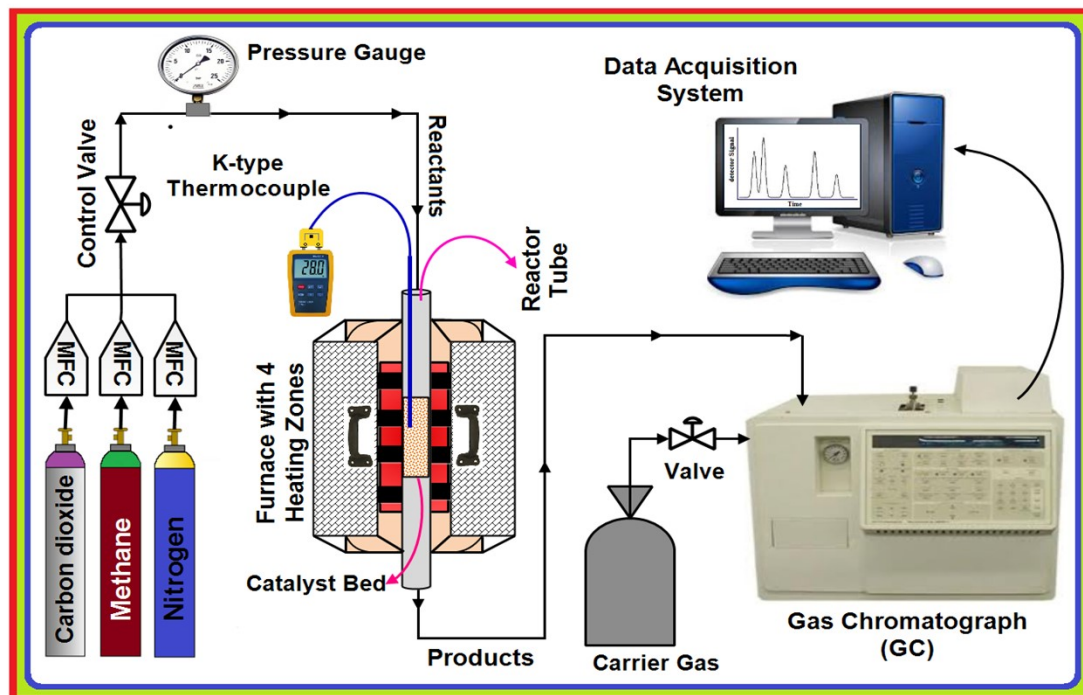


Figure S2 experimental Set-up