

Performance Study of Methane Dry Reforming on Ni/ZrO₂ Catalyst

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Supplementary

Catalyst Preparation

The wet impregnation method was used to prepare the zirconium-supported nickel catalyst. 1-An aqueous solution of (5 wt.%) nickel nitrate precursor using 0.03 L of purified water was prepared. then the zirconium support was placed in it.

2-The prepared mixture was stirred at 80°C until it became slurry and dried at 120°C overnight in an oven. Subsequently, the dried product was calcined at 700°C for 3 h.

Steps 1 & 2 were repeated three times to guarantee homogeneous distribution within each sample. In the case of the modified supported Ni catalysts, the zirconium oxides and the oxide of a modifier such as MgO or Y₂O₃ were mixed together mechanically in desired proportion. Then, steps 1 and 2 are repeated. In the case of promoted Ni-based catalysts, an aqueous solution of (5 wt.%) nickel nitrate precursor and 3 wt.% promoter (Ce, Ga, and Sr) nitrate precursor using purified water was then added to the support. Then step 2 is repeated.

Table S1 Catalysts and their Designations

| Composition of Catalyst | Catalyst Denotation |
|--------------------------|---------------------|
| 5wt.%Ni/ZrO ₂ | 5Ni-ZO ₂ |

| | |
|---|---------------------------|
| 5wt.%Ni/5wt.%MgO+ZrO ₂ | 5Ni-5MgZO ₂ |
| 5wt.%Ni/5 wt.%Y ₂ O ₃ +ZrO ₂ | 5Ni-5YZ O ₂ |
| 5wt.%Ni/10 wt.%Y ₂ O ₃ +ZrO ₂ | 5Ni-10YZ O ₂ |
| 5wt.%Ni/15 wt.%Y ₂ O ₃ +ZrO ₂ | 5Ni-15YZ O ₂ |
| 5wt.%Ni/20 wt.%Y ₂ O ₃ +ZrO ₂ | 5Ni-20YZ O ₂ |
| 5wt.%Ni+ 3 Cs wt.%/15 wt.%Y ₂ O ₃ +ZrO ₂ | 5NiCs-15YZ O ₂ |
| 5wt.%Ni+ 3 Ga wt.%/15 wt.%Y ₂ O ₃ +ZrO ₂ | 5NiGa-15YZ O ₂ |
| 5wt.%Ni+ 3 Sr wt.%/15 wt.%Y ₂ O ₃ +ZrO ₂ | 5NiSr-15YZ O ₂ |

Catalyst Characterization

The pore size distribution and catalyst's surface area were evaluated by N₂ -physisorption of nitrogen at −196 °C by employing a Micromeritics Tristar (II) 3020, porosity and surface area analyzer. The distribution of the pore size was computed by Barrett, Joyner, and Halenda (BJH) method. A step of 0.02° and scanning 2θ range of 10–85° were used. The software X'Pert high score plus was used to examine the data acquired from the instrument. Different phases were harmonized via the JCPDS data bank. The procedure of Barrett-Joyner-Halenda (BJH) was applied for the estimation of pore size distribution, and surface area.

The crystalline phases, present in the samples, were identified by their diffraction of X-ray by using a Bruker D8 Advance X-ray diffractometer, fitted with a source of Cu K α radiation which is run at 40 kV and 40 mA. The XRD patterns were recorded in the 2θ range of $10\text{--}85^\circ$ with a scanning rate of θ $0.01^\circ/\text{step}$. The XRD patterns, corresponding to the catalyst phases, were recognized by matching them with those on the standard powder XRD cards of the Joint Committee on Powder Diffraction Standards (JCPDS).

The reducibility of catalysts was determined by TPR. A sample weighing 0.07 g was put in the TPR cell consisting of a Micromeritics Auto Chem II. Then the furnace temperature was increased from 24°C to 1000°C with a ramping rate of $10^\circ\text{C}/\text{min}$, under 40 ml/min, the flow of 10 vol. % H_2/Ar mixture. The H_2 consumption was checked by a TCD unit.

CO_2 -TPD was employed to assess the amount of O_2 vacancies. The CO_2 -TPD was measured by Micromeritics Autochem II. First, 0.005 g of catalyst was treated with He flow rate of 30 mL/min at a temperature of 600°C over a period of 1 h and then cooled to 50°C . The flow of CO_2 was continued for 1 h, and the sample was then flushed with He to eliminate any physisorbed CO_2 . The peaks of desorption were noted while the temperature was varied by $10^\circ\text{C}/\text{min}$. The CO_2 concentration in the output stream was calculated employing a detector of thermal conductivity, while the areas under the curves gave the quantity of desorbed CO_2 during TPD.

The TGA was performed under airflow at 50 ml/min, using a TGA15 SHIMADZU analyzer, to compute the amount of carbon formed on the catalyst surface after the reaction, where 0.010–0.015 g of the used catalyst was filled into a platinum pan of the thermo-balance. Then the temperature was raised to 103°C with a ramping rate of $20^\circ\text{C min}^{-1}$ and the mass reduction was computed.

Transmission electron microscopy (TEM) measurements of fresh and spent samples were performed on a JEOL JEM-2100F transmission electron microscope operated at 200 kV accelerating voltage to check the active metal particle sizes of Ni and to analyze the morphology of the deposited carbon. Prior to TEM analysis, the samples were first dispersed ultrasonically in ethanol at room temperature. Then, a drop of the suspension was put on a lacey carbon-coated Cu grid to take images.

Elemental analysis was determined using EDX (SEM, MERLIN® VP Compact, Co. Zeiss, Oberkochen) equipped with an energy dispersive X-ray detector (XFlash 6130, Co. Bruker, Berlin). Representative areas of the samples were analyzed by QUANTAX ESPRIT Microanalysis software (version 2.0).

Catalytic Performance Evaluation

The evaluation of the catalytic performance of all prepared catalysts was done by feeding 0.1 g of a sample into the reactor containing glass wool. Temperature measurement, during the reaction, was evaluated by K-type thermocouple, which was injected axially in the center of the catalyst bed. Then the catalyst was activated in situ by reduction under the flow of hydrogen gas (20.0 ml/min) at 700°C for 1h. After the activation step, the hydrogen gas valve was switched off and nitrogen gas valve was switched at a rate of 10 ml/min for 15 minutes to remove the hydrogen. The reactor was taken to the desired reaction temperature in the presence of N₂, after that, the reactants (CH₄ and CO₂) are were pumped at a rate of 30 ml/min and nitrogen at a rate of 10 ml/min with a space velocity of 42,000 ml h⁻¹gcat⁻¹ for at least 440 min to perform the DRM test. Then the reactor temperature was lowered to ambient temperature for characterizing the spent catalyst.

The equations below were used for calculating the conversion of reactants.

$$\text{Reactant (R) conversion \%} = \frac{\text{mol (R)}_{in} - \text{mol (R)}_{out}}{\text{mol (R)}_{in}} \times 100 \quad (\text{S1})$$

The test stand of the experimental setup contains cylinders of methane, carbon dioxide nitrogen and hydrogen. The reactant gases from regulators are passed to the mass flow controllers (MFC). The CH₄ and CO₂ are being consumed as the reactant with nitrogen as an inert gas. The hydrogen is used for the activation process to reduce the metallic oxide form of the catalyst to pure metal. The output from the reactor is connected to online gas chromatography (GC-2014 Shimadzu) with argon as the carrier gas for analysis. The GC having a thermal conductivity detector and a switchable combination of two columns, Porapak Q and Molecular Sieve 5A, was used to have a complete online analysis of the reaction products. The maximum total carbon balance and hydrogen balance at the end of the run do not exceed 2.5% and 1.2 % respectively.

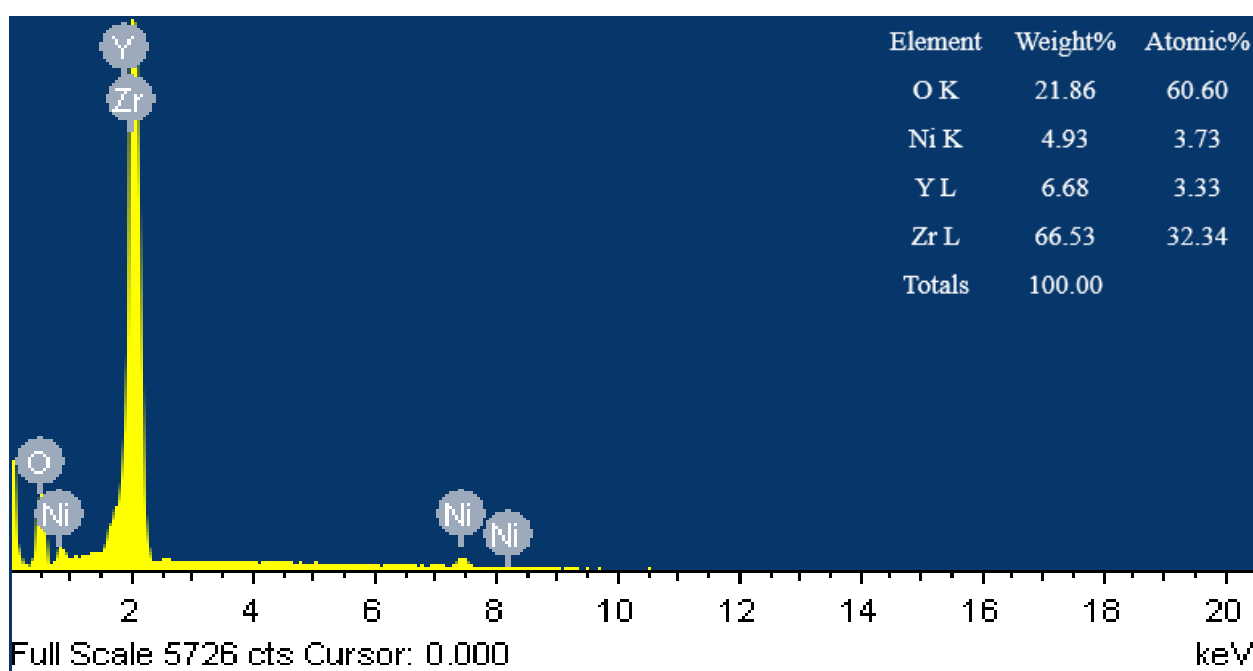


Figure S1 EDX image of fresh 5Ni10YZr catalyst.

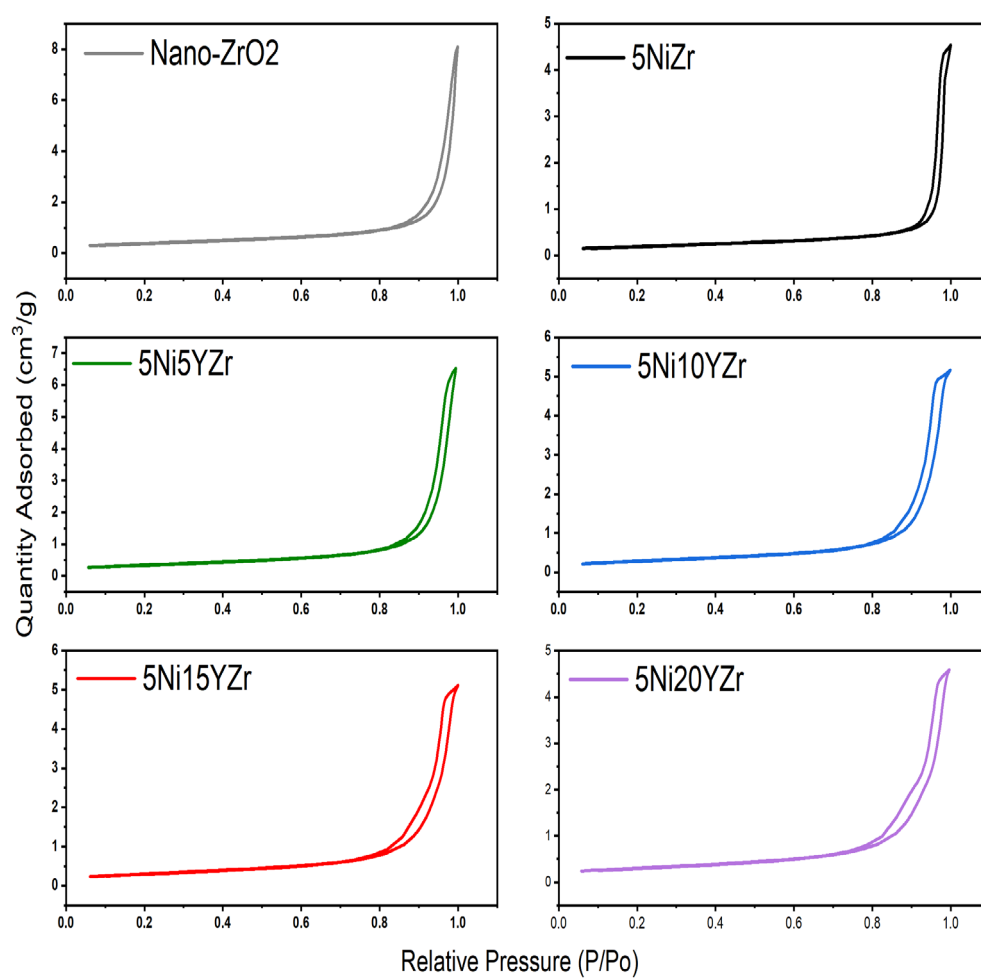


Figure S2 N₂ adsorption isotherm profiles

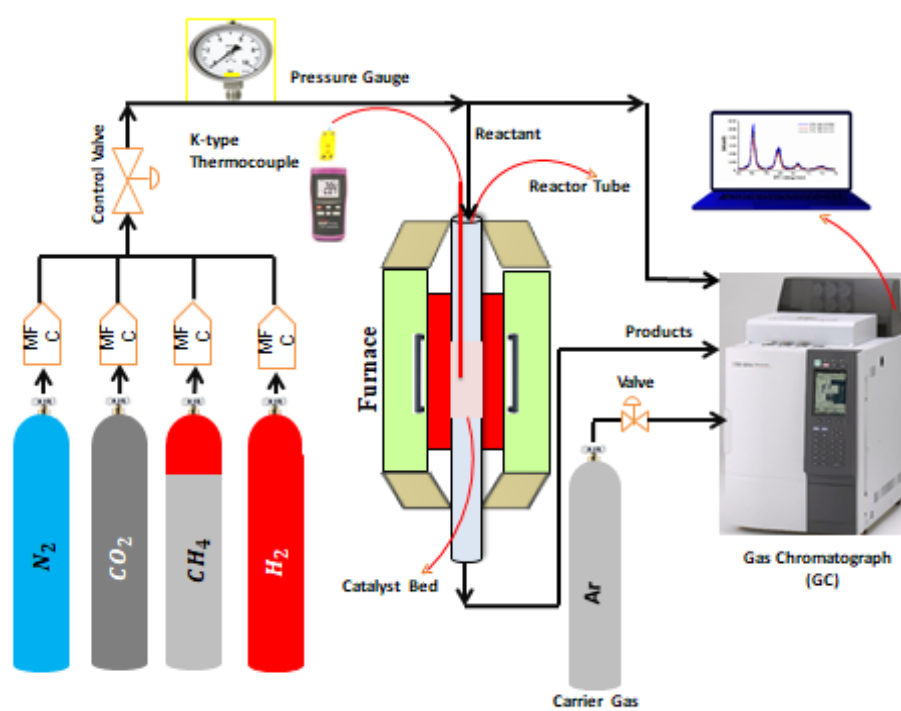


Figure S3 experimental Set-up

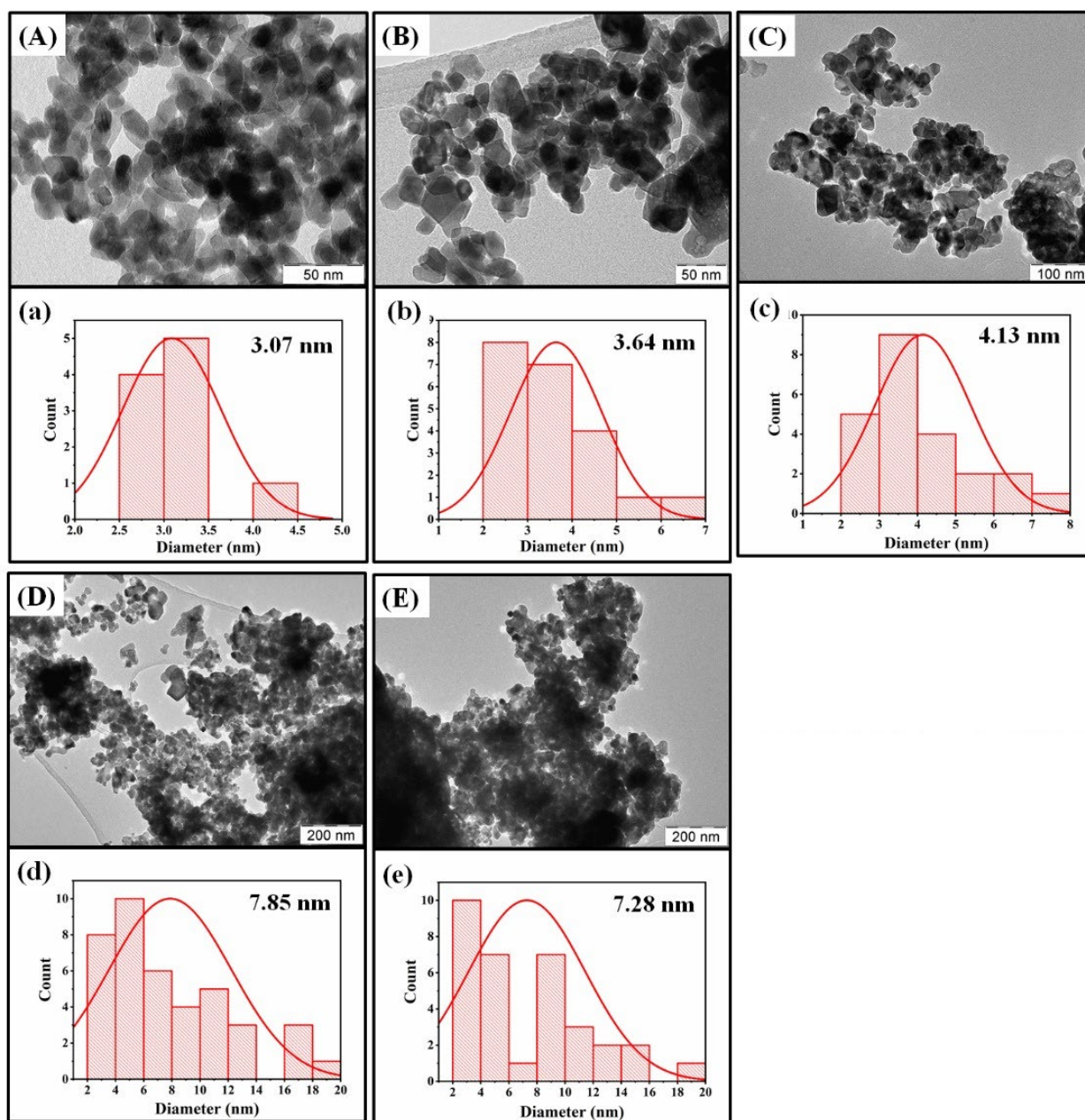


Figure S4 fresh TEM images and relevant particle size distributions for 5NiZr (A, a), 5Ni15YZr (B,b), 5Ni3Sr15YZr (C,c), 5Ni3Ga15YZr (D,d), and 5Ni3Cs15YZr (E,e).