Supplementary Information

Dry reforming of CH₄ using zirconia supported Ni catalyst: The effect of different sources of zirconia

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Materials

Hydrated nickel(II) nitrate $Ni(NO_3)_2.6H_2O$; 98% was procured from Riedel-De Haen AG, Seelze, Germany. The zirconia supports, RC-100 and Z-3215, were acquired from Japan (DAIICHI KIGENSO KAGAKU KOGYO C., LTD); MKnano was acquired from Canada (K Impex Corp. Division: MKnano 6382 Lisgar Drive Missisauga, ON L5N 6X1); ELTN was obtained from China (Room 2301, Building 20, CBD inner Ring Zhengdong New District, Zhengzhou).

Catalyst preparation

The wet impregnation technique was implemented for the formation of the catalysts. The different supports of zirconium oxide along with the Ni acquired from the nickel nitrates

[Ni(NO$_3$)$_2 \cdot$6H$_2$O; 99.7% pureness] formed the desired ingredients. Distilled water was used to dissolve the ingredients. A 5 wt. % Ni was fixed in the catalyst preparation. The solution temperature was raised to 90 °C. The mixing of the solution was kept for 3 h. After that, the drying and the calcination of the samples were performed at 125 °C for 12 h and at 700 °C for 3 h, respectively. For simplicity, Ni supported on zirconium oxide catalysts will be designated as 5Ni–Z-3215; 5Ni–RC-100; 5Ni–Mknano; 5Ni–ELTN

Catalyst Characterization.

The catalysts were characterized by numerous experimental skills.

The specific surface area of catalysts was computed via nitrogen (N$_2$) physisorption at −197 °C. A Micromeritics Tristar II 3020 unit was used to obtain the surface area via standard Brunauer−Emmett−Teller (BET). The Barrett, Joyner, and Halenda (BJH) method was employed in the calculation of pore size distribution.

X-ray diffraction of Rigaku (Miniflex), using the radiations of Cu Kα, was considered to inspect the configuration of the produced catalysts. Diffraction peaks registered in a 2θ range between 11 and 81° were used to sort the phases of the catalysts.

The morphology of the used catalyst samples was examined by using a field emission scanning electron microscope (FE-SEM, model: JEOL JSM-7100 F)

Temperature-programmed reduction (TPR) was carried out with the Micromeritics AutoChem II, Atlanta, GA, USA. 0.07 g of the sample (in sample holder) was degassed using argon at 150 °C for 60 min and then cooled to 25 °C. Further, it was heated to 800 °C at the rate of 10 °C/minute under 10% H$_2$ in argon flow. The flow rate of 10% H$_2$ in argon was set at 40 mL/minute. At the reactor outlet, thermal conductivity detector (TCD) monitors the gas mixture and peaks corresponding to the consumption of H$_2$ as a function of temperature were obtained.

The Fourier transform infrared (FTIR) measurements were performed by using IR Prestige-21 SHMADZU, spectrophotometer, Kyoto, Japan. The spectra were read in the range 400–4000 cm^{-1} with 4 cm^{-1} energy resolution, using KBr pellet.

H_2 temperature programmed desorption (H_2-TPD) experiments were measured on the same reactor. Before each test, the sample (100 mg, 20–40 meshes) was reduced at 700C for 60 min under the flow of 10 vol% H_2/Ar (30 ml/ min). After cooling the reactor down to room temperature (30°C) under Ar flow (30 ml/min), the sample was exposed on the flow of 10 vol% H_2/Ar (30 ml/min) for 30 min. Finally, the reactor was heated up to 600°C (10°C/min) under Ar flow. The signals of H_2 consumption and desorption were recorded by an online thermal conductivity detector.

Temperature programmed desorption of carbon dioxide (CO_2-TPD) was acquired from automatic chemisorption equipment (Micromeritics AutoChem II 2920) with a TCD.

Carbon deposition over the surface of used catalysts was measured by means of thermogravimetric analysis (TGA) in atmospheric air via an EXSTAR SII TG/DTA 7300 analyzer. A platinum pan was filled with 10–15 mg of the used catalysts and carefully positioned inside the device. Heating was done from room temperature up to 1000 °C at a 20 °C min^{-1} temperature ramp. The change in mass was continuously monitored as the heating progressed.

Raman spectroscopy gave the graphitization degree and the type of carbon deposited over the spent catalysts. A laser Raman (NMR-4500) spectrometer (JASCO, Japan) was used to register the Raman spectra of the spent catalysts. An excitation beam with a 532 nm wavelength was employed.

The structure of the fresh samples was monitored using a transmission electron microscope "120 kV JEOL JEM-2100F". Transmission electron microscopy (TEM) micrographs were recorded at 120 kV.

Ni Reduction and Dispersion

The reduction degree is calculated from the ratio of total amount of experimental H_2 consumption to that of theoretical amount of H_2 consumption multiplied by 100. The experimental H_2 consumption is obtained from the TPR unit, while the theoretical value is calculated as:

During the reduction $NiO + H_2 = Ni + H_2O$; 1 mole H_2 generates 1-gram atom of Ni

Therefore, for 5% Ni; with atomic weight of 58.6934 g produces 0.05/58.6934 =0.852mmole/g_{cat} = 852 µmole/g_{cat} equivalent to 852 µmole/g_{cat} of hydrogen.

 % Reduction = 100 X (total amount of experimental H_2 consumption)/theoretical amount of hydrogen consumption.

For the Ni dispersion (D_{Ni}) was calculated using the following equations based on the H_2-TPD

% D_{Ni} = (H_2 uptake $\times M_{Ni} \times \delta$)/ mf $\times$ 100% where

H_2 uptake (µmol/g) is obtained from the H_2- TPD results;

M_{Ni} is the molar mass of Ni = (58.69 g/ mol);

mf is the mass fraction of Ni= 5;

δ is the stoichiometric factor of Ni/H molar ratio in the chemisorption ($H_2 + Ni = 2N-H$) =2.
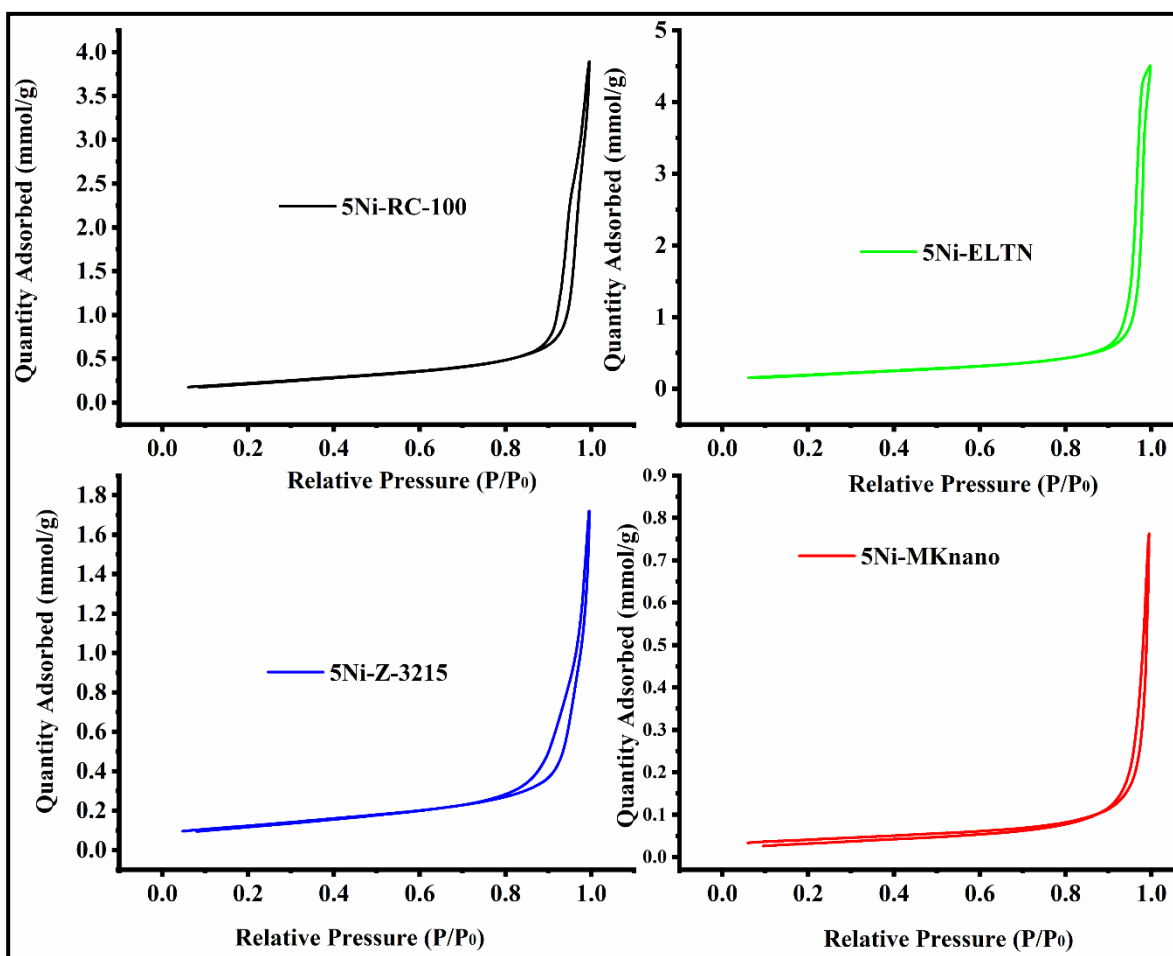
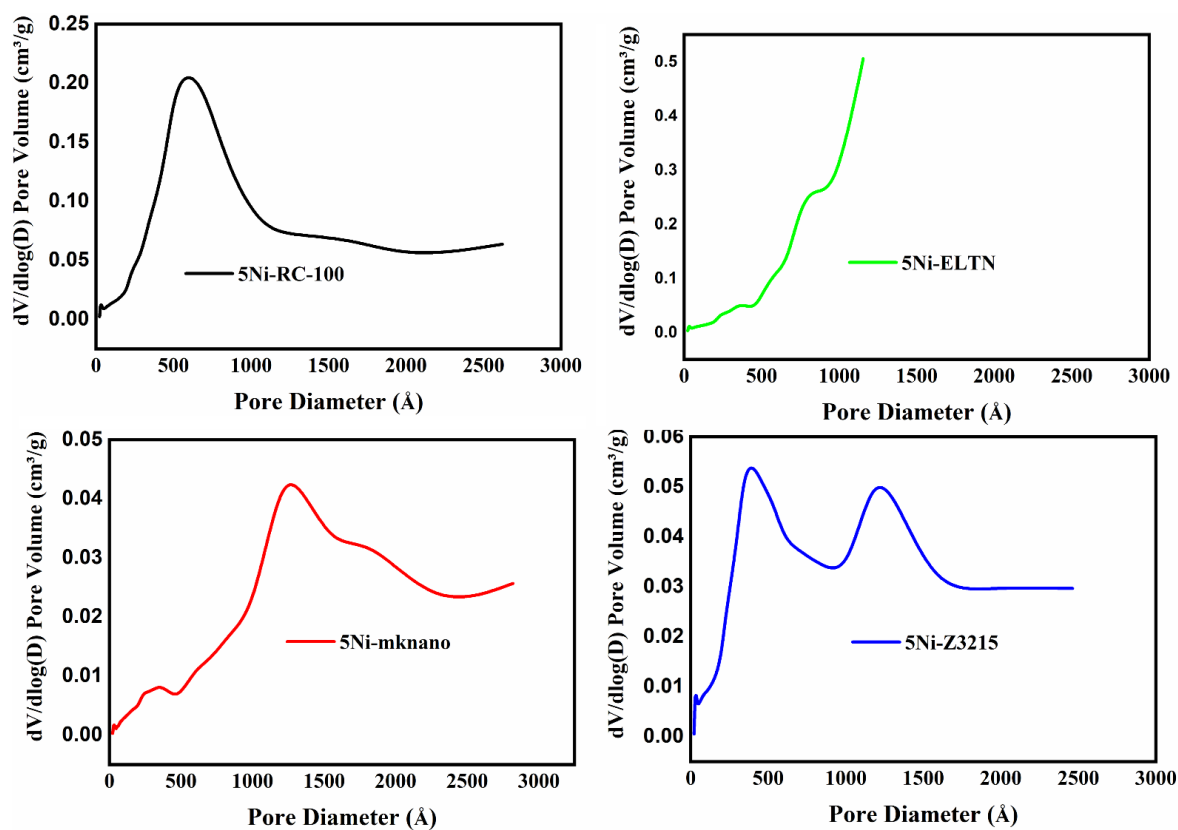**Figure S1.** N_2 adsorption and desorption isotherms.

Figure S2. Pore volume versus pore diameter of different ZrO_2 sources supported Ni catalysts.

Table S1. The analysis of CO_2 consumption during TPD

samples	Temperature	Quantity of CO_2 (μmole/g)	Total quantity of CO_2 (μmole/g)
5Ni-RC-100	78.7	52.0	75.5
	288.3	23.5	
5Ni-ELTN	84.1	58.6	69.7
	260.7	11.1	
5Ni-Z-3215	74.7	44.4	85.0
	283.5	41.4	
5Ni-MKnano	75.6	5.8	14.7
	289.0	8.9	