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Supplementary Information

Hydrogen yield from CO_2 reforming of methane: impact of La_2O_3 doping on supported Ni catalysts

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S1. Catalyst testing

The DRM reactions were performed using a stainless steel fixed reactor (9.1 mm diameter and 300 mm long) operated at 1 atm. The reactor was from PID Eng. & Tech Microactivity Reference Company. A 0.1 g of the catalyst was reduced by a H_2 flow of 20 mL/min for 1 h at 700 °C. Then, N_2 admitted to the bed for 15 min to remove the physisorbed H_2. In a typical test, the proportion $CO_2/CH_4/ N_2$ was set to 3/3/1 at 4.2 L/h, generating 42 L $(h{\cdot}gcat)^{-1}$ of gas hourly space velocity. A conductivity detector "GC-2014 SHIMADZU" computed the compositions of the gases in and out. Afterward, N_2 gas was used to cool the reactor. Then, the characterization of the catalysts was performed. Finally, the reproducibility was maintained by taking the mean value of three runs. The expressions for the hydrogen yield is given as:

$$\%H_2 \text{ yield } = \frac{moles\ of\ H_2\ (out)}{2 \times moles\ of\ CH_4\ (in)} \text{ x } 100 \quad \text{(S1)}$$

S2. 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). 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), furnished with energy dispersive X-ray spectroscopy (EDXS) for surface elemental analysis. 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. Temperature programmed reduction (TPR) was attained from the Micromeritics AutoChem II to assess the reducibility of the fresh catalysts, where a thermal conductivity detector (TCD) was employed to follow the H_2 consumption. 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 air via an EXSTAR SII TG/DTA 7300 analyzer. For assessing catalyst reducibility, the H_2-TPR measurements were carried out on Micromeritics Auto Chem II 2920 apparatus. 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 spent samples was monitored using a transmission electron microscope "JEOL JEM-2100F". Transmission electron microscopy (TEM) micrographs were recorded at 120 kV.

Table S1. Textural properties of different catalysts supported Ni catalysts: BET specific surface area (S_{BET}), pore volume (P_V), and pore diameter (D_P).

Catalyst	BET-Surface area (m^2/g)	Pore Volume (cm^3/g)	Pore Diameter (nm)
5Ni-ZrO_2	16.1	0.15	43.3
5Ni-10La_2O_3-ZrO_2	21.6	0.18	36.3
5Ni-15La_2O_3-ZrO_2	18.4	0.15	36.1
5Ni-20La_2O_3-ZrO_2	17.3	0.13	33.5
5Ni-Al_2O_3	185.6	0.64	12.4
5Ni-10La_2O_3-Al_2O_3	161.7	0.55	12.2
5Ni-15La_2O_3-Al_2O_3	162.2	0.61	12.9
5Ni-20La_2O_3-Al_2O_3	135.0	0.50	12.2

Table S2. The quantitative analysis of H_2 consumption during H_2-TPR.

Catalyst	Region I-H_2 uptake (μmol/g)	Region II-H_2 uptake (μmol/g)	Region III-H_2 uptake (μmol/g)	Total-H_2 uptake (μmol/g)
5Ni-ZrO_2	142.3	1903.6	38.7	2084.6
5Ni-10La_2O_3-ZrO_2	964	86	0.0	1050
5Ni-15La_2O_3-ZrO_2	1688.2	0.0	0.0	1688.2
5Ni-20La_2O_3-ZrO_2	2230.6	0.0	0.0	2230.6
5Ni-Al_2O_3	0.0	0.0	1651.2	1651.2
5Ni-10La_2O_3-Al_2O_3	0.00	0.00	830.6	830.6
5Ni-15La_2O_3-Al_2O_3	0.00	0.00	1161.4	1161.4
5Ni-20La_2O_3-Al_2O_3	0.00	0.00	1564.6	1564.6