Synergistic Effect of Ce-Mg Promoted Ni Catalysts on 3D structured open cell Foams for CO_2 hydrogenation to Methane

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1. Experimental Section

1.1. Catalytic procedure

The catalytic activity was evaluated in a fixed-bed tubular borosilicate glass U-shaped reactor designed and prepared in-house (Sorbonne University, France), equipped with a K-type thermocouple mounted on the outer wall within a heating furnace to monitor the reaction temperature. The modified foams as catalysts were placed inside the U-shaped reactor, while preparing glass reactors to fit them inside the reactor. Before the reaction, all catalysts were reduced at 550 °C under a 5% H_2/Ar flow (100 mL/min) for 1 hour. The gas hourly space velocity (GHSV) was estimated using the volume of catalyst in the reactor, and the obtained GHSV was 7000 h^{-1}. Following reduction, the reactor was cooled to 250 °C, and a gas mixture of Ar/CO_2/H_2 = 25:15:60 was introduced at a total flow rate of 100 mL/min. The temperature was then ramped from 250 °C to 450 °C at a rate of 10 °C/min. At each temperature point, the reaction was held for a minimum of 30 minutes to ensure steady-state conditions.

The conversion and selectivity of the desired product were analyzed using an online gas chromatograph (Agilent Varian GC4900) equipped with a thermal conductivity detector (TCD). For equilibrium calculations, a CO_2:H_2 molar ratio of 1:4 was considered at 1 bar pressure across the 100–450 °C temperature range. Equilibrium CO_2 conversion and selectivity to CH_4 were calculated with HSC Chemistry 5.0 software. The calculations for equilibrium were done considering 1 bar pressure, CO_2/H_2 ratio in feed of 1:4, and temperature range from 100 to 500 ℃.

The conversion (X_{CO2}) and selectivity (S_{CH4}) were calculated based on the following formulas:

$$CO_2 \text{ conversion (\%) } {}^{X}CO_2 = \frac{[CO_2]_{in} - [CO_2]_{out}}{[CO_2]_{in}} \times 100\%$$

$$CH_4 \text{ selectivity (\%) } {}^{S}CH_4 = \frac{[CH_4]_{out}}{[CH_4]_{out} + [CO]_{out}} \times 100\%$$

$$STY_{CH4} = \frac{SV \; X \; [CO_2]_{in} \; X \; x_{CO2} \; X \; S_{CH4}}{V_m} = \frac{[CH_4]_{out}}{[CH_4]_{out} + [CO]_{out}}$$

In the above-mentioned reactions, in and out refer to the concentrations of the gas at the reactor inlet and outlet, respectively. xCO_2 and xCH_4 denote the CO_2 conversion and CH_4 selectivity, respectively. STY represents the space-time yield of methane, while SV indicates the space velocity (h^{-1}). V_m corresponds to the molar volume at a specific temperature (mL/mol).

1.2 Physicochemical characterizations

Powder x-ray diffraction (PXRD) measurements of the fresh and reduced crushed foams were recorded on Bruker D8_Advance diffractometer, equipped with a LynxEye XE-T detector, and Cu anticathode (Cu Kα radiation (0.154 nm)) with a sampler at the UCCS, University of Lille, France. To analyze the data, recorded XRD patterns were compared with the database of the Joint Committee on Powder Diffraction Standards (JCPDS) and the crystallite size was calculated using Debye Scherrer equation. It is a Bruker D8_Advance diffractometer, equipped with a LynxEye XE-T detector, copper anticathode, with a sampler.

Temperature-programmed reduction (H_2-TPR) and CO_2 temperature-programmed desorption (CO_2-TPD) experiments were conducted using a BELCAT-M instrument (BEL Japan, Japan) equipped with a thermal conductivity detector (TCD). All these tests were performed using quartz tube equipped with a thermocouple in a furnace. For the H_2-TPR study, 55-60 mg of crushed modified open cell foams were outgassed at 100 °C for 1 hour to remove the moisture under helium flow (50 mL/min) with 10 °C/min ramping temperature, and then the sample was cooled down to 50 °C, and the reactor was flushed with He for another 20 minutes to remove physically adsorbed hydrogen. Further, catalyst was then heated with 10 °C/min heating rate from 50 to 700 °C under 5% H_2:Ar (50 mL/min flow). The estimation of consumed H_2 was done in terms of TCD signal values with increasing temperature.

Just after H_2-TPR, the samples were directly utilized for CO_2-TPD analysis. Initially, the samples were treated under He for 20 minutes, with the temperature increasing from room temperature (RT) to 100 °C. Then, the gas flow was switched to 10% CO_2/He for 1 hour to adsorb CO_2 on the surface of the catalysts. After this, the sample was cooled down to 50 °C under 10% CO_2/He flow (50 mL/min) and then switched to He flow and kept for 20 minutes to remove weakly adsorbed CO_2 from the surface. Afterward, the analysis was carried out under He flow from 50 to 700 °C with 10 °C/min ramping temperature. The basicity calculation was done by considering the area under the curve, with comparison of the standard calibrated samples area for precise values.

Microstructural/morphological features were investigated using field emission gun scanning electron microscopy (FEG-SEM) (Zeiss, Supra 55) equipped with an energy dispersive spectrometer (EDS).

Table S1. Determination of basic sites for active phase of foams using the CO_2-TPD profile

Catalysts	Basic sites (µmol/g of active phase of the catalyst)			
	I (100-280 °C)	**II (300-500 °C)**	**III (500-700 °C)**	**Total**
CeNi	4.20	0.26	1.46	5.92
CeNiMg-5	4.09	3.03	2.18	9.31
CeNiMg-10	0.67	5.92	2.15	8.75
CeNiMg-15	0.21	4.98	0.91	6.09