Supplementary Information

The influence of Ce incorporation on integrated CO_2 capture and in situ methanation performance of Ni/CaO-Al_2O_3 dual functional materials

Le Wang , Xinyue Su , Laihong Shen *

Key Laboratory of Energy Thermal Conversion and Control of Ministry of Education, School of Energy and Environment, Southeast University, Nanjing 210096, China

**Corresponding Author: Laihong Shen, Email address: lhshen@seu.edu.cn*

Text S1. Details of XRD, BET,SEM and XPS.

The crystal structure of prepared materials were characterized via X-ray diffraction (XRD) with a Bruker D2 Phaser X-ray diffractometer (Germany). First, the samples were meticulously ground. Subsequently, using a Cu Kα source, the diffraction range from 10° to 90° was measured at a scanning speed of 5 °/min. The average grain size of Ni in the prepared samples was estimated by means of the Scherrer equation. The surface properties and pore size distribution of the materials were accurately measured via N_2 adsorption-desorption experiments. These analyses were performed on a Micromeritics ASAP 2460 analyzer (USA). Prior to analysis, the samples were subjected to degassing at 200 °C for 8 h. The surface area values were calculated using Brunauer-Emmett-Teller (BET) model. The surface morphology of the materials were characterized by high-resolution scanning electron microscopy (Hitachi Regulus 8100, Japan). The surface composition of the materials was measured via an X-ray photoelectron spectrometer (Thermo Scientific K-Alpha, USA). The binding energy of the 1s peak of adventitious carbon is 284.80 eV, which serves as the calibration standard.

Text S2. Details of CO_2-TPD, H_2-TPD and H_2-TPR.

During the CO_2-TPD test, 100 mg of the sample was weighed and placed in the reaction tube for each test. The sample was dried and pretreated by heating from room temperature to 150 °C at a rate of 10 °C/min under a helium flow (50 mL/min) for 1 hour. After cooling to 50 °C, a 10% CO_2/He mixture (50 mL/min) was introduced for 1 hour until saturation. Then, the helium flow was switched on to blow for 1 hour to

remove the weakly physically adsorbed CO_2 on the surface. Finally, the sample was desorbed at a rate of 10 °C/min to 900 °C under a helium atmosphere, and the concentration change of CO_2 in the desorbed gas was detected by a thermal conductivity detector (TCD).

In the H_2-TPD experiment, a 100 mg sample was loaded into a reactor tube and subjected to a drying pretreatment process by heating from room temperature to 200 °C at a ramp rate of 10 °C/min under a He flow (50 mL/min) for 1 h. After cooling to 50 °C, the sample was exposed to a 10% H_2/Ar mixture (50 mL/min) for 1 h to achieve saturation. Subsequently, the system was purged with an Ar flow (50 mL/min) for 1 h to remove weakly physically adsorbed H_2. Finally, the temperature was increased to 800 °C at a heating rate of 10 °C/min under Ar flow, and the desorbed H_2 was monitored using a TCD.

For the H_2-TPR measurement, 100 mg of the sample was placed in a quartz reactor and subjected to thermal pretreatment under a helium flow (50 mL/min) by ramping the temperature from ambient to 200 ℃ at 10 ℃/min and holding for 1 hour. After cooling to 50 ℃, the sample was treated with a 10% H_2/Ar mixture (50 mL/min) for half an hour. Upon stabilization of the baseline, the sample was heated to 850 °C at a rate of 10 °C/min in a 10% H_2/Ar flow. The consumed reducing gas H_2 during the experiment was recorded by a TCD detector.

Text S3. Specifications on the detection limit and sampling frequency of the flue gas analyzer (MRU, Germany) employed in this work.

The minimum detection limits for CO and CH_4 are 0.001%, and for CO_2 it is 0.01%. The sampling frequency of the flue gas analyzer is 1 Hz.

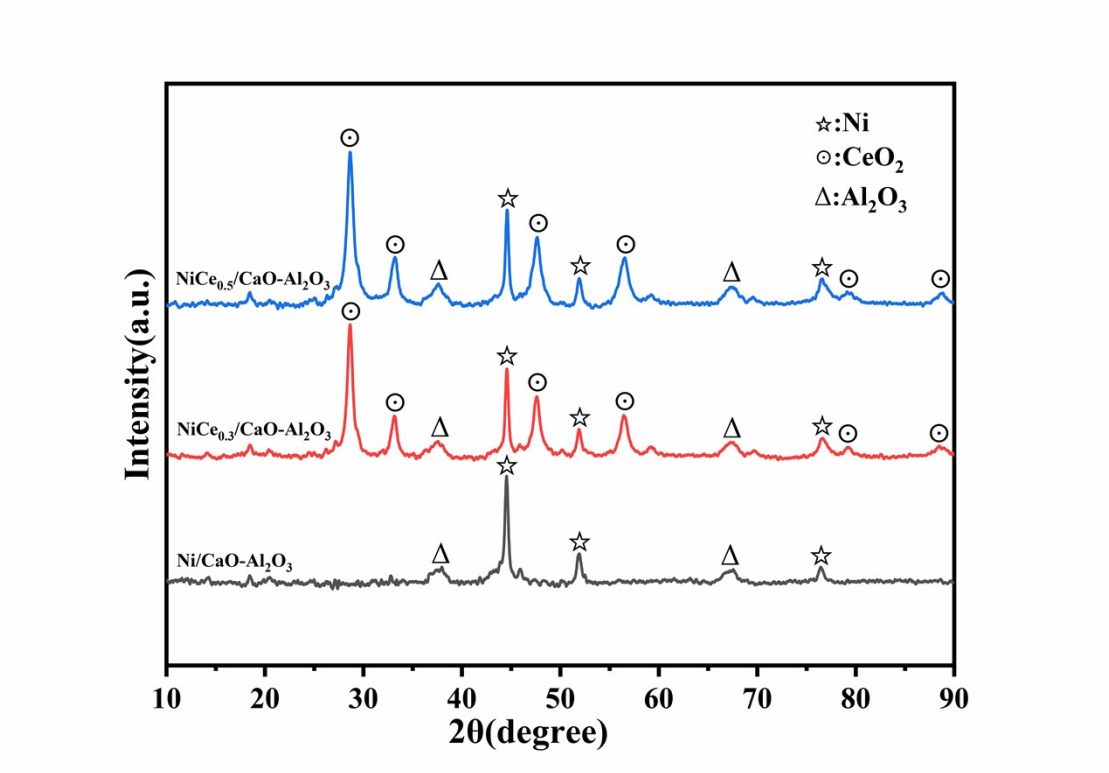

Fig. S1. XRD patterns of the spent DFMs.

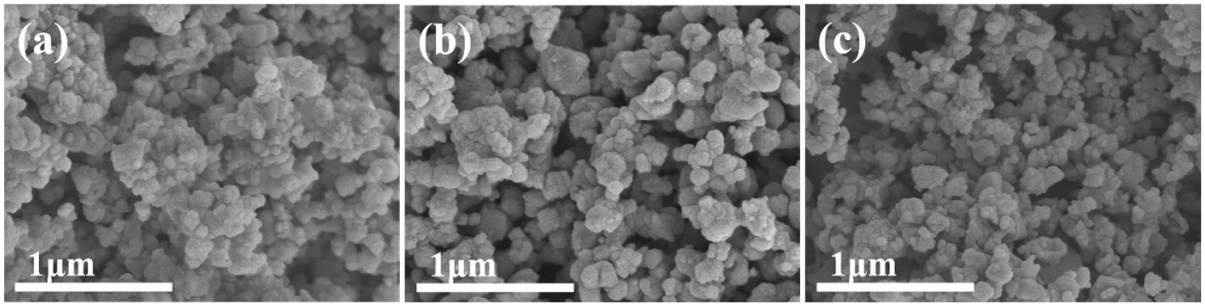

Fig. S2. SEM images of spent DFMs (a) $Ni/CaO\text{-}Al_2O_3$, (b) $NiCe_{0.3}/CaO\text{-}Al_2O_3$, and (c) $NiCe_{0.5}/CaO\text{-}Al_2O_3$.