## **Supporting Information for**

## Collateral Hydrogenation over Proton-Conducting Ni/BaZr<sub>0.85</sub>Y<sub>0.15</sub>O<sub>3-δ</sub> Catalysts for Promoting CO<sub>2</sub> Methanation

Sungjun Choi,<sup>ab</sup> Sung Min Choi,<sup>a</sup> Kyung Joong Yoon,<sup>a</sup> Ji-Won Son,<sup>a</sup> Jong-Ho Lee,<sup>a</sup> Byung-Kook Kim,<sup>a</sup> Byoung-In Sang<sup>b</sup> and Hyoungchul Kim\*<sup>a</sup>

<sup>a</sup>High-Temperature Energy Materials Research Center, Korea Institute of Science and Technology, 5 Hwarang-ro 14-gil, Seongbuk-gu, Seoul 02792, Republic of Korea. <sup>b</sup>Department of Chemical Engineering, Hanyang University, 222 Wangsimni-ro, Seongdong-gu, Seoul 04763, Republic of Korea.

\*Corresponding author (email: hyoungchul@kist.re.kr)



**Fig. S1** CO<sub>2</sub> methanation performances of BZY and BZY-supported BaCO<sub>3</sub>. All tested powders did not yield CH<sub>4</sub> gas at 400 °C.



Fig. S2 XRD patterns and TEM images of Al<sub>2</sub>O<sub>3</sub>-containing powders. (a) XRD patterns of the Al<sub>2</sub>O<sub>3</sub> support and the Ni/Al<sub>2</sub>O<sub>3</sub> catalyst reduced at 600 °C for 2 h. (b) TEM image and EDS analysis result of the reduced Ni/Al<sub>2</sub>O<sub>3</sub> catalyst, with Ni and Al elements denoted by red and cyan colors, respectively. Although the Al<sub>2</sub>O<sub>3</sub> support exhibited a complex XRD spectrum, peaks of metallic Ni could be discerned at 44.5 and 51.8°. In addition, the reduced Ni catalysts featured an average particle diameter of 8.80 nm (standard deviation = 3.10 nm), while the spherical particles of the Al<sub>2</sub>O<sub>3</sub> support had a diameter of ~50 nm.



**Fig. S3** Temperature-dependent (a)  $X_{CO_2}$  and (b)  $X_{H_2}$  values of Ni/BZY and Ni/Al<sub>2</sub>O<sub>3</sub>. The dashed line represents the thermodynamic equilibrium performance of each conversion under the chosen experimental conditions (H<sub>2</sub>/CO<sub>2</sub> = 4.0).



**Fig. S4** XRD pattern (a) and TEM-EDS images (b) of Ni/Al<sub>2</sub>O<sub>3</sub> subjected to 150 h CO<sub>2</sub> methanation at 400 °C. The average particle diameter of Ni on the Al<sub>2</sub>O<sub>3</sub> support equaled ~9.06 nm (standard deviation = 3.50 nm).



**Fig. S5** O 1*s* core level XPS spectra of Ni/Al<sub>2</sub>O<sub>3</sub> (a) before and (b) after CO<sub>2</sub> methanation. Red, green, and blue lines correspond to lattice oxygen, weakly adsorbed H<sub>2</sub>O, and adsorbed carbon-containing species, respectively. The main peak centered at ~531 eV was assigned to the lattice oxygen of Al<sub>2</sub>O<sub>3</sub>.