Supplementary Information

Effect of ceria promotion on the catalytic performance of Ni/SBA-16 catalysts for CO₂ methanation

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The CO₂ methanation activity of 10Ni/10Ce/SBA-16 at different reduction condition



Fig. S1. The CO₂ methanation test of 10Ni/10Ce/SBA-16 catalyst reduced at different temperatures; a) CO₂ conversion (%), b) CH₄ selectivity (%)

As shown in **Fig. S1**, the 10Ni/10Ce/SBA-16 catalyst reduced at 500 °C showed better CO_2 conversion and CH_4 selectivity compared to that reduced at 800 °C. This could be assigned to the shrinkage of support at high temperature, resulting in less accessible sites of Ni and Ce.

The CO₂ methanation activity of 10Ni/5Ce/SBA-16 at different reduction condition





Fig. S2. The CO₂ methanation test of 10Ni/5Ce/SBA-16 catalyst reduced at different temperatures; a) CO₂ conversion (%), b) CH₄ selectivity (%)

As shown in Fig. S2c, the 5 wt.% Ce modified Ni/SBA-16 catalyst shows a worse activity compared to other catalysts at the testing temperature range. In Fig. S2 a and b, it also can be seen that the activity and CH_4 selectivity decrease as the increase of reduction temperature until 900 °C. Thus, it can be concluded that 10 wt.% Ce is an appropriate

content for Ce-promoted Ni/SBA-16 catalyst in CO_2 methanation and 500 °C is the best condition for reduction process.

The low-angle XRD of the synthesized SBA-16 support

As shown in **Fig. S3**, two small peaks at 2θ =1.25 and 1.56 were observed for SBA-16 support, representing (200) and (211) reflection, respectively, indicating the existence of ordered mesopores in SBA-16 with body-centered cubic symmetry (*Im3m*).¹



Fig. S3. Low-angle XRD of the synthesized SBA-16 material

The supplementary TEM images of reduced catalysts



Fig. S4. TEM micrographs of the reduced catalysts; Condition: 500 °C for 1 h (H₂/Ar=5/95, 100 mL/min); a, b) 10Ni/SBA-16, c) 10Ni/10Ce/SBA-16, d) 10Ni/20Ce/SBA-16

The supplementary TEM images were displayed in Fig. S4. As shown in Fig. S4, indeed these images presented a cubic array of uniform channels when the incident electron beam was parallel to the main axis of the mesopores (a, c, d) and also unidirectional or hexagonal channels when the electron beam took different orientations with respect to the sample (b), which demonstrates that the order structure of SBA-16 was preserved despite the incorporation of Ce and Ni into the pores.

Characterization of the catalysts after CO₂ methanation test



Fig. S5. XRD patterns of the spent Ni/SBA-16 based catalysts with varying Ce loading

The XRD of the catalysts after test were also performed and the patterns were displayed in **Fig. S5**. As show in **Fig. S5**, the spent catalysts showed similar Ni and CeO₂ crystallites like reduced catalysts (**Fig.2b**). The broad peaks of Ni species indicate that no sintering of Ni active metal happened during reaction. The structure of CeO₂ also remains stable for Ce-doped catalysts.

References

1 D. Zhao, Q. Huo, J. Feng, B. F. Chmelka and G. D. Stucky, J. Am. Chem. Soc., 1998, **120**, 6024–6036.