

## Electronic supplementary information (ESI)

### Continuous CO<sub>2</sub> capture and methanation over Ni-Ca/Al<sub>2</sub>O<sub>3</sub> dual functional materials

Lingcong Li,<sup>1</sup> Ziyang Wu,<sup>1</sup> Shinta Miyazaki,<sup>1</sup> Takashi Toyao,<sup>1</sup> Zen Maeno,<sup>\*2</sup> Ken-ichi Shimizu<sup>\*1</sup>

<sup>1</sup> Institute for Catalysis, Hokkaido University, N-21, W-10, Sapporo 001-0021, Japan

<sup>2</sup> School of Advanced Engineering, Kogakuin University, 2665-1, Nakano-cho, Hachioji, 192-0015, Japan

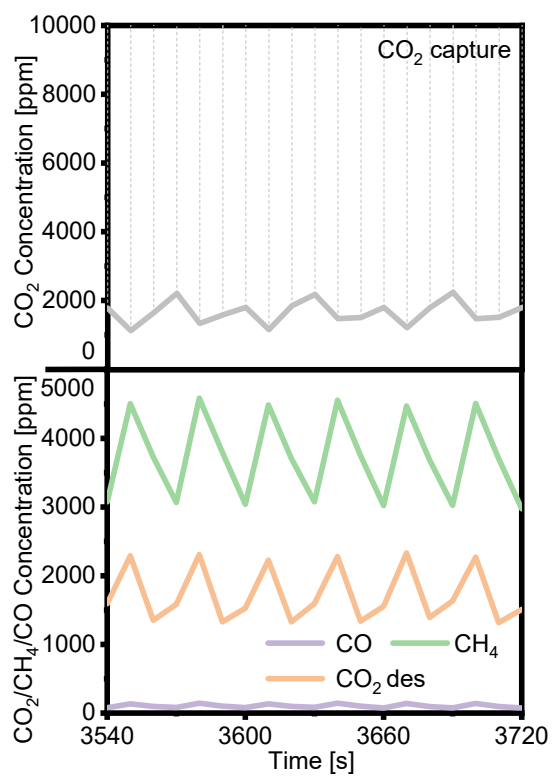
\*Corresponding authors

Zen Maeno, E-mail: zmaeno@cc.kogakuin.ac.jp

Ken-ichi Shimizu, E-mail: kshimizu@cat.hokudai.ac.jp

## Figures

(a) Double reactor



(b) Single reactor

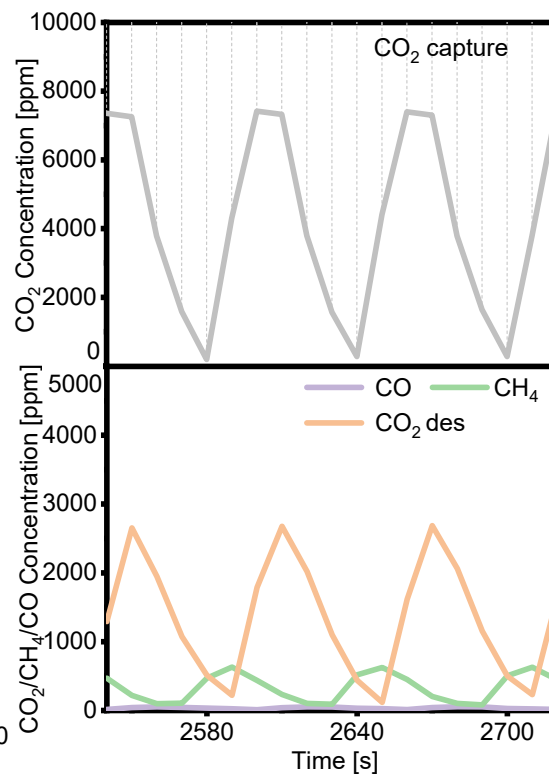


Figure S1. Effluent gas compositions for CCR over Ni(10)–Ca(30)/Al<sub>2</sub>O<sub>3</sub> in (a) double reactor and (b) single reactor systems. Conditions: 100 mg of catalyst, 450 °C, 100 mL min<sup>-1</sup> of 1% CO<sub>2</sub>/10% O<sub>2</sub>/N<sub>2</sub> for 30 s, switched to 100 mL min<sup>-1</sup> of H<sub>2</sub> for 30 s.

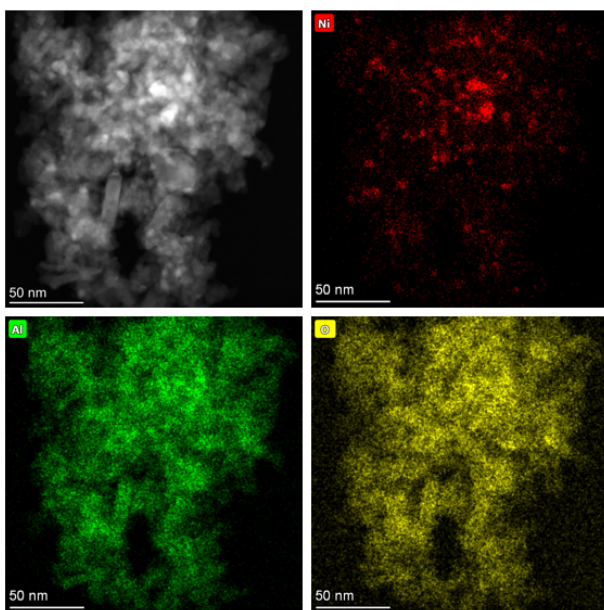


Figure S2. STEM images and EDS mapping of Ni(10)/Al<sub>2</sub>O<sub>3</sub>.

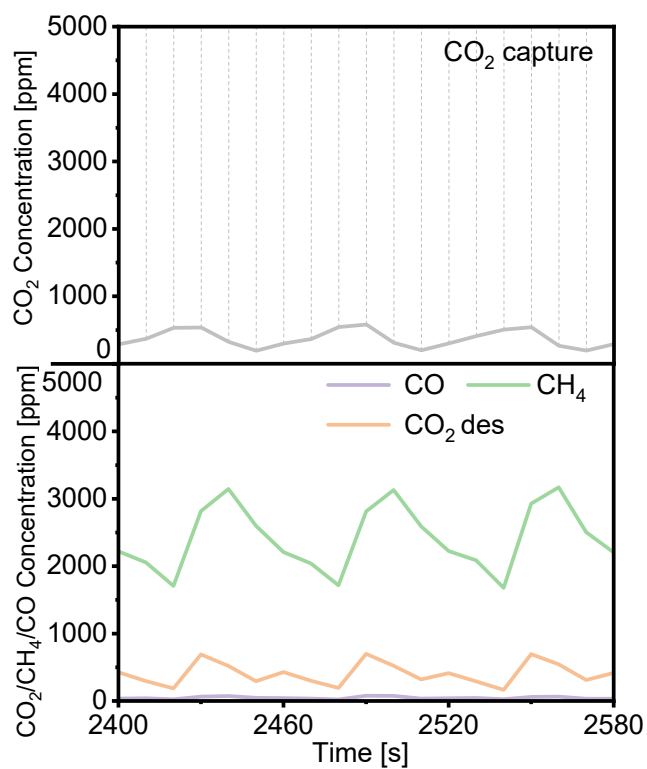


Figure S3 Effluent gas composition for continuous operated CCR over Ni(10)/Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub>. Conditions: 100 mg of catalyst, 450 °C, 100 mL min<sup>-1</sup> of 0.5% CO<sub>2</sub>/10% O<sub>2</sub>/N<sub>2</sub> for 30 s, switched to 100 mL min<sup>-1</sup> of H<sub>2</sub> for the other 30 s.

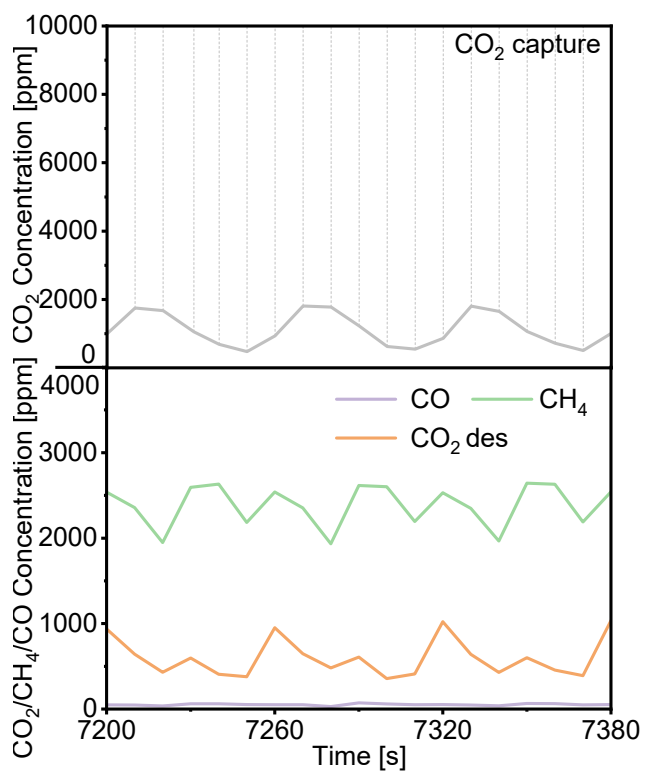


Figure S4 Continuous CCR operation with flowing steam over Ni(10)-Ca(30)/Al<sub>2</sub>O<sub>3</sub>. Conditions: 100 mg of catalyst for each reactor, 450 °C, 100 mL min<sup>-1</sup> of 1% CO<sub>2</sub>/10% O<sub>2</sub>/N<sub>2</sub> with 20% water vapor for 30 s, switched to 100 mL min<sup>-1</sup> of H<sub>2</sub> for the other 30 s.

Table S1. Comparison of CCR performance among the reported Ni-Ca based DFMs.

Ni-Ca DFM	Reaction Temperature [°C]	CO <sub>2</sub> capture [μmol g <sup>-1</sup> ]	CO <sub>2</sub> conversion (%)	CH <sub>4</sub> formation [μmol g <sup>-1</sup> ]	CH <sub>4</sub> selectivity (%)	Ref.
10% Ni-30% Ca/Al <sub>2</sub> O <sub>3</sub>	450	340	46	153	97	This work
1% Ni-CaO	550	9200	38	2000	58	Fuel <b>2021</b> , 286, 119308
10% Ni-CaO	550	8100	45	2500	69	Fuel <b>2021</b> , 286, 119308
10% Ni-15% Ca-Al <sub>2</sub> O <sub>3</sub>	450	73	82	58	97	<i>ACS Sustainable Chem. Eng.</i> <b>2021</b> , 9, 3452–3463
5% Ni/15%Ca-Al <sub>2</sub> O <sub>3</sub>	520	---	---	223	---	<i>J. CO<sub>2</sub> Util.</i> <b>2019</b> , 34, 576-587
10% Ni/15%Ca-Al <sub>2</sub> O <sub>3</sub>	520	---	---	225	---	<i>J. CO<sub>2</sub> Util.</i> <b>2019</b> , 34, 576-587
15% Ni/20%Ca-Al <sub>2</sub> O <sub>3</sub>	450	---	66.6	---	63.2	<i>J. CO<sub>2</sub> Util.</i> <b>2019</b> , 31, 143-151