Electronic Supplementary Information (ESI)

## Ru nanoparticles supported on amorphous ZrO<sub>2</sub> for CO<sub>2</sub> methanation

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## S1 Stoichiometry of Ru to CO

Fig. S1a shows the TEM image of Ru/SiO<sub>2</sub> prepared by the SD\_NaOH method. Several darker spots can be observed and attributed to Ru nanoparticles. The average size of Ru nanoparticles was  $9.0 \pm$ 2.8 nm according to the particle size distribution (Fig. S1b). Furthermore, CO chemisorption measurement was also conducted for the catalyst. The CO uptake was 40 µmol g<sup>-1</sup>. If the stoichiometry of CO to Ru (*n* in Eq. 3) is 0.93, the Ru size estimated from TEM is equal to that calculated from CO chemisorption.



Fig. S1 (a) TEM image of Ru/SiO<sub>2</sub>. (b) Particle size distribution of Ru.



Fig. S2 Particle size distributions of Ru nanoparticles for (a) Ru/am-ZrO<sub>2</sub> (Imp), (b) Ru/am-ZrO<sub>2</sub> (SD\_NaOH), (c) Ru/am-ZrO<sub>2</sub> (SD\_NH<sub>3</sub>), and (d) Ru/cr-ZrO<sub>2</sub> (SD\_NaOH).



Fig. S3 TEM image in a yellow rectangle of Fig. 6 (b). Several black dots with the size < 5 nm are observed, indicated by arrows.



Fig. S4 FTIR spectra over (a) Ru/am-ZrO<sub>2</sub> (SD\_NH<sub>3</sub>), (b) Ru/am-ZrO<sub>2</sub> (SD\_NaOH), and (c) Ru/cr-ZrO<sub>2</sub> (SD\_NaOH) during desorption of CO<sub>2</sub>-derived species at 250 °C for 40 min.