Ru nanoparticles supported on amorphous ZrO$_2$ for CO$_2$ methanation

Hironori Nagase $^a$, Rei Naito $^a$, Shohei Tada $^b$, Ryuji Kikuchi $^a$,*, Kakeru Fujiwara $^c$, Masahiko Nishijima $^d$, Tetsuo Honma $^e$

$a$ Department of Chemical System Engineering, Graduate School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

$b$ Department of Materials Science and Engineering, Ibaraki University, 4-12-1 Nakanarusawa-cho, Hitachi, Ibaraki 316-8511, Japan.

$c$ Department of Chemistry and Chemical Engineering, Yamagata University, 4-3-16 Jonan, Yonezawa, Yamagata 992-8510, Japan

$d$ The Electron Microscopy Center, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai, Miyagi 980-8577, Japan

$e$ Japan Synchrotron Radiation Research Institute, Sayo-cho, Sayo-gun, Hyogo 679-5198, Japan

S1 Stoichiometry of Ru to CO

Fig. S1a shows the TEM image of Ru/SiO$_2$ 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 ± 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$^{-1}$. 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$_2$. (b) Particle size distribution of Ru.

Fig. S2 Particle size distributions of Ru nanoparticles for (a) Ru/am-ZrO$_2$ (Imp), (b) Ru/am-ZrO$_2$ (SD$_{\text{NaOH}}$), (c) Ru/am-ZrO$_2$ (SD$_{\text{NH}_3}$), and (d) Ru/cr-ZrO$_2$ (SD$_{\text{NaOH}}$).
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$_2$ (SD_NH$_3$), (b) Ru/am-ZrO$_2$ (SD_NaOH), and (c) Ru/cr-ZrO$_2$ (SD_NaOH) during desorption of CO$_2$-derived species at 250 °C for 40 min.