Supporting Information

Comparing the Performance of Supported Ru Nanocatalysts Prepared by Chemical Reduction of $RuCl_3$ and Thermal Decomposition of $Ru_3(CO)_{12}$ in the Sunlight-Powered Sabatier Reaction

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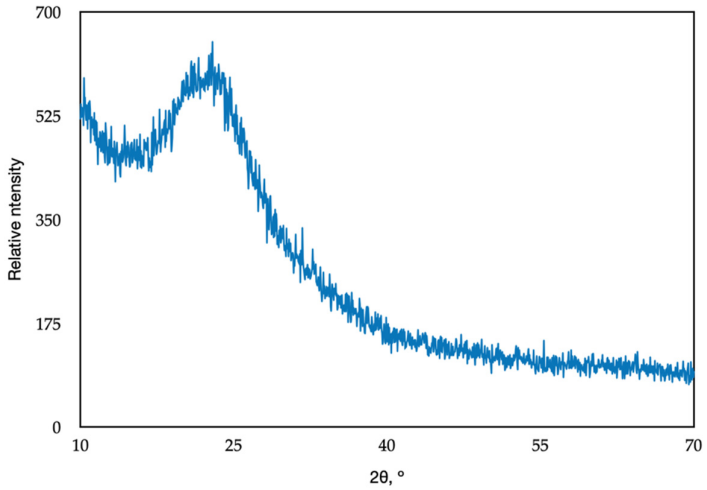
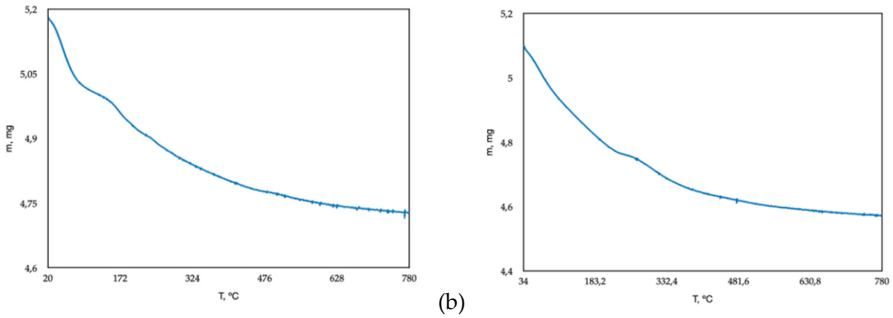


Figure S1. X-ray diffractogram of SiO_2 supported Ru catalyst prepared by reduction of $RuCl_3$.

The powder X-ray diffraction pattern was recorded using a Bruker AXS D8 Discover diffractometer (Cu Kα radiation, LynxEye detector). The broad peak centered at $2\theta = 23.8°$ represents the short range order in amorphous SiO_2. The X-ray diffraction analysis neither shows diffraction peaks of crystalline Ru nanoparticles on the SiO_2 support (expected at $2\theta \approx 37°$ and $2\theta \approx 45°$ [1]), nor reflections corresponding to crystalline RuO_2 [1] (expected at $2\theta \approx 28°$, $2\theta \approx 35°$ and $2\theta \approx 54°$). *Ergo*, due to the low Ru loading and small particle size, Ru reflections could not be detected.

[1] JCPDS reference patterns: Ru 00-006-0663; RuO_2 00-040-1290.



(a) (b)

Figure S2. Thermogravimetric analyses of (**a**) SiO_2-supported and (**b**) Al_2O_3-supported Ru catalyst prepared by reduction of $RuCl_3$, under air.

The thermal decomposition profiles of the samples were studied by thermogravimetric analysis (TGA, TA instruments Q500). The samples (~5 mg) were heated up to 800 °C at a heating rate of 10 °C/min under the air atmosphere. In both cases, the TGA analysis shows a mass loss of about 10%, which is likely due to loss of adsorbed water and progressive condensation of Si-OH and Al-OH groups.

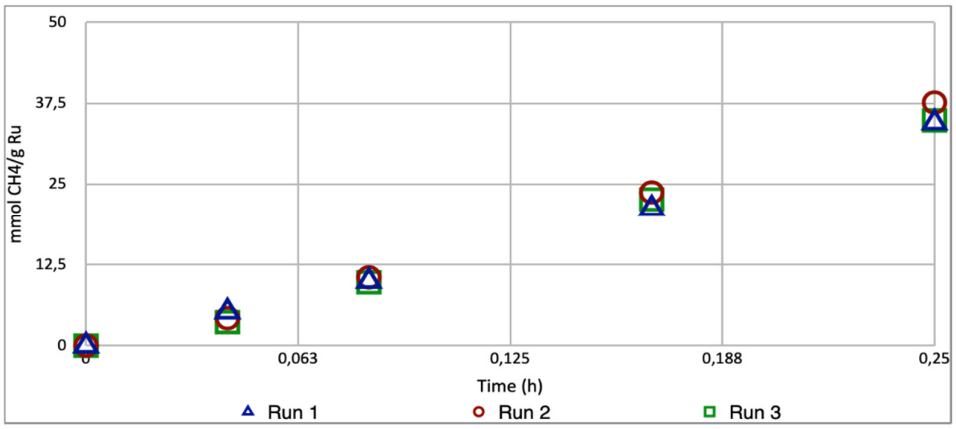


Figure S3. Conversion-time profile for three sequential runs of the sunlight-powered Sabatier reaction with Ru/SiO_2-TD. Ru loading is 3.49% w/w. Reaction conditions for all experiments: reaction mixture of $H_2/CO_2/N_2$ (4.5:1:1) at 3.5 ± 0.2 bar pressure, 200 mg of Ru/SiO_2-TD catalyst, light intensity of 6.66 suns, catalyst bed temperature approximately 220°C.

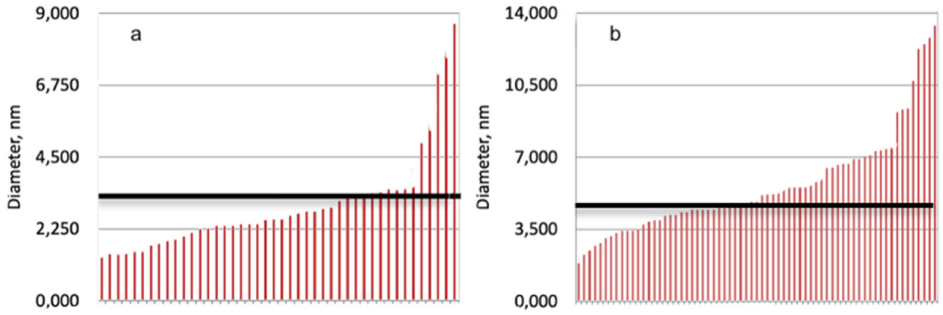


Figure S4. Comparison of mean diameter of Ru nanoparticles and numbers of agglomerates before (**a**) and after (**b**) reaction for Ru/SiO_2-CR catalysts with a Ru loading on silica of 3.34% w/w. The black line in both diagrams indicates the border between single particles and agglomerates.

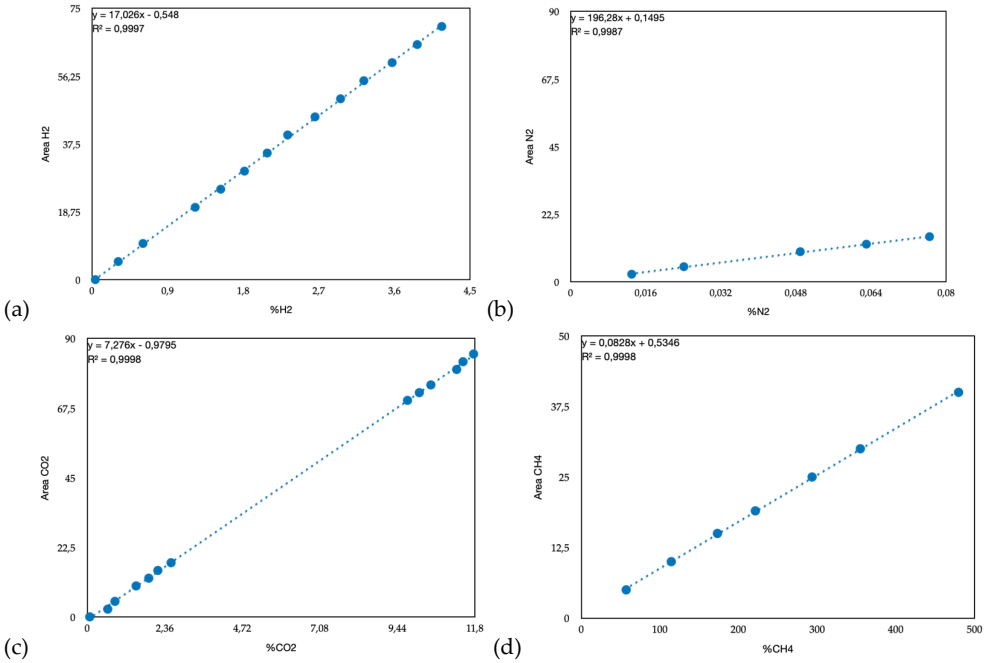


Figure S5. Calibration curves for GC detection of (**a**) H_2, (**b**) N_2, (**c**) CO_2 and (**d**) CH_4.

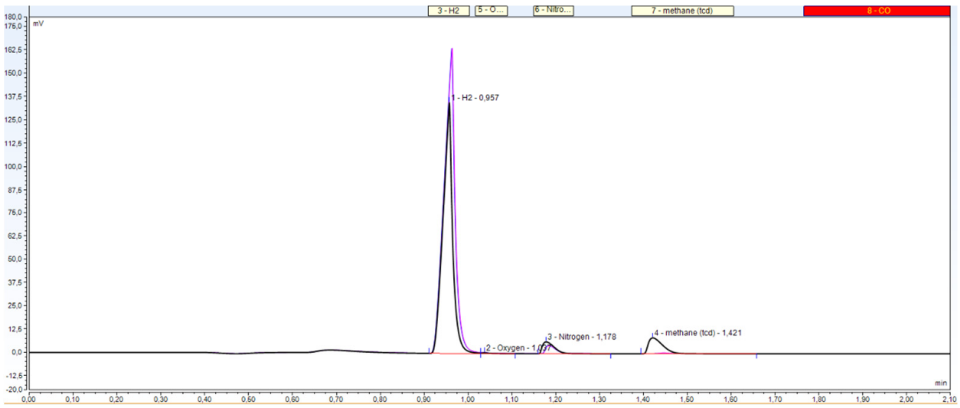


Figure S6. Prototypical gas chromatogram for catalytic conversion of CO_2 and H_2 to CH_4 in a mixture diluted with N_2.