Supporting Information

Aldehydes rather than alcohols in oxygenated products from light-driven Fischer-Tropsch synthesis over Ru/SiC catalysts

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Materials and methods

SiC with a specific surface area of ~ 50 m^2/g was prepared according to our reported route [1]. Ruthenium (Ⅲ) chloride, Polyvinyl Pyrrolidone (PVP) (molecular weight ~ 30000), cyclohexane, decahydronaphthalene, octanal, 5,5-Dimethyl-1-pyrroline N-oxide (DMPO) and triethanolamine (TEOA) were commercial available. The reagents were of analytical grade and used as received without further purification.

Synthesis of catalysts

For the preparation of 10 wt.% Ru/SiC catalyst, 41 mg of $RuCl_3$, 180 mg of SiC and 1200 mg of Polyvinyl Pyrrolidone (PVP) were dispersed into 20 ml deionized water under sonication for 0.5 h. Then, the above mixture was transferred in a 100 ml stainless steel autoclave and purged with H_2 for six times, followed by reduced under 2.0 MPa of H_2 at 150 °C for 2.5 h with a stirring speed of 800 rpm. At last, the product was obtained by filtration and washed with distilled water and ethanol repeatedly for 6 times.

The preparation of Ru nanoparticles and other Ru/SiC catalysts with different loadings was similar to that of 10 wt.% Ru/SiC, except that the amount of $RuCl_3$, SiC and PVP was changed to 20.5 mg, 0 mg, and 600 mg; 30.75 mg, 185 mg and 900 mg; 20.5 mg, 190 mg and 600 mg; 10.25 mg, 195 mg and 300 mg, respectively.

Characterization

The microstructures of the catalysts were investigated by high-resolution transmission electron microscope (HRTEM, JEM-2010). X-ray photoelectron spectroscopy (XPS) was measured on a Kratos XSAM800 spectrometer, using Al Ka (hk=1486.6 eV) X-ray source as the excitation source. The UV-visible absorption spectra of the catalyst were examined by a HITACHI U-3900 spectrometer with Al2O3 as a reference. The photoluminescence (PL) spectra of Ru/SiC and SiC were examined by a HITACHI F-7000 spectrometer

Photocatalytic experiments of FTS

To test the photocatalytic performance of Ru/SiC catalysts, an aqueous suspension containing 0.1 mmol Ru was placed in a 100 ml stainless steel autoclave (total volume is about 140 ml) with a round quartz window (the diameter is 3 cm) and a high-precision pressure gauge (0.4%). The syngas (CO/H_2 mole ratio of 1:2) was passed through activated 5A molecular sieves before use, and the purity is 99.9% at least. The reactor was purged for six times with syngas and then sealed at a syngas pressure of 3.0 MPa. The photocatalytic experiments of FTS were carried out strictly at 150 °C with stirring speed at 800 rpm under the irradiation of a 300 W Xe lamp with 0.3 W/cm^2 of light intensity for 5 h. The gas products were online analyzed by an Agilent 6890N (HP) gas chromatograph (GC) with a 5A molecular sieve column (Ar carrier gas) and an Al_2O_3 column (N_2 carrier gas) equipped with TCD and FID using ethane as internal standard. Then, 10 mL of cyclohexane and 5 μL of decahydronaphthalene were added into the autoclave and heated at 150°C for 2 h. After the autoclave was cooled to room temperature, the upper phase products were analyzed by GC-MS (BRUKER SCION SQ 456).

The approach for evaluating the thermal-catalytic FTS performance was the same as that for photocatalytic evaluation system, except no irradiation was added in thermal reaction. For aldehyde hydrogenation ability test, photocatalytic reactions were performed under H_2 and syngas atmosphere with a pressure of 3.0 MPa for 3 hours. In order to explore the aldehyde hydrogenation ability in different CO concentrations, photocatalytic reactions were measured under different mole ratio of CO/H_2.

5,5-Dimethyl-1-pyrroline N-oxide (DMPO) as electron-trapping agent and triethanolamine (TEOA) as hole-trapping agent were used as the sacrificial regents to quench photocarriers. After adding 0.3ml DMPO or 0.36ml TEOA (keeping the mole amount as a constant), the conversion of CO was reduced to 40% and 30% comparing to the reaction without sacrificial agents. These results indicate that the electrons and holes have a important influence of the activity of Fischer Tropsch Synthesis.

To explore the influence of the support, we employed Ru/C_3N_4 catalyst for the reaction under the same reaction conditions with Ru/SiC catalyst, but no oxygenates were detected and all products were hydrocarbons. We also did the experiments using Ru/TiO_2, and found that the distribution of the reaction products was similar to that of Ru/SiC. Among Ru/C_3N_4, Ru/TiO_2 and Ru/SiC catalysts, the Ru/SiC catalyst exhibits the highest catalytic activity. The reason may be related to the bandgap of SiC (2.4 eV for β-SiC), which makes it absorb more light irradiation.

Figure S1-S10

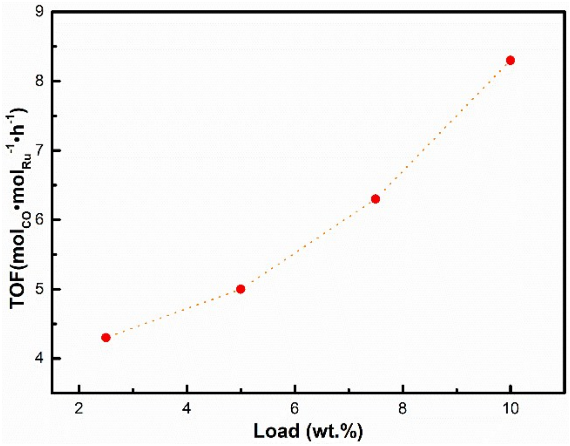

Figure S1: TOF values of catalysts with different Ru loadings.

The Ru/SiC catalysts with the 2.5 wt.%, 5 wt.%, 7.5 wt.% and 10 wt.% of Ru, exhibits the TOF value of 4.3, 5.0, 6.3 and 8.3 mol$_{CO}$·mol$_{Ru}^{-1}$·$_h^{-1}$, respectively.

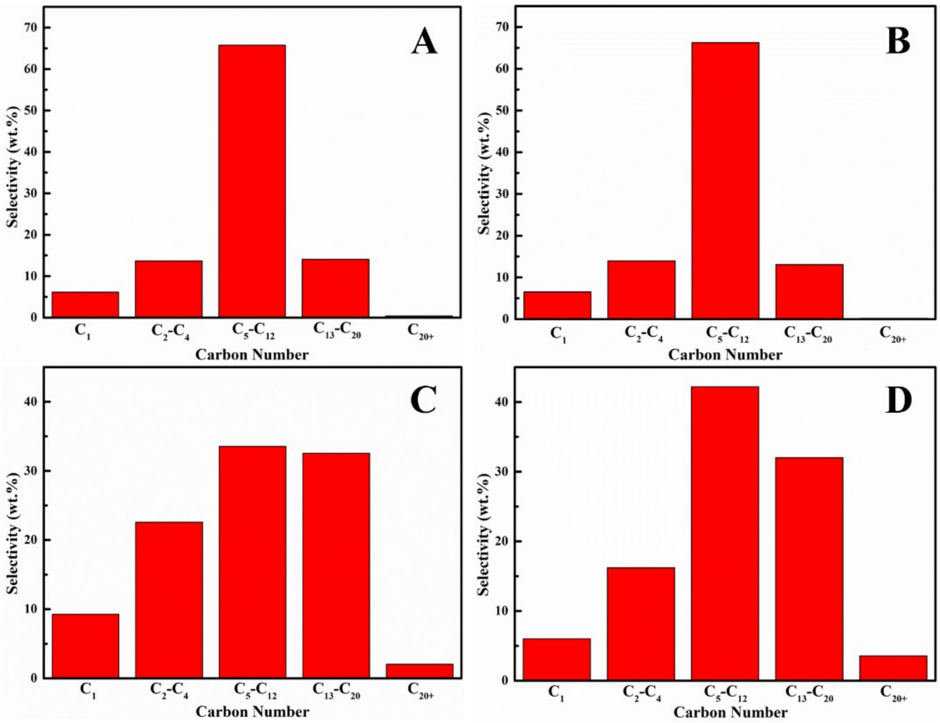

Figure S2: The selectivity of Ru/SiC with different Ru content: A. 2.5 wt.%; B. 5 wt.%; C. 7.5 wt.%; D. 10 wt.%.

The selectivity of C$_{13+}$ hydrocarbons is ~ 14 % for 2.5 wt.% and 5 wt.% catalysts, while it is ~ 35 % for 7.5 wt.% and 10 wt.% catalysts.

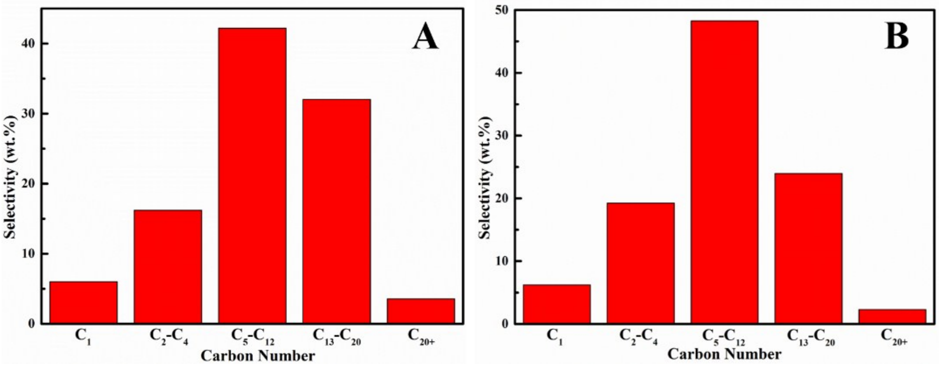

Figure S3: The hydrocarbon selectivity of 10 wt.% Ru/SiC with irradiation (A), without irradiation (B).

The main products were C_5-C_{12} hydrocarbons with or without irradiation. However, compared with the dark reaction, the light reaction has a higher proportion of C_{13}-C_{20}, which means light reaction has a better ability to increase hydrocarbon chains growth than dark reaction.

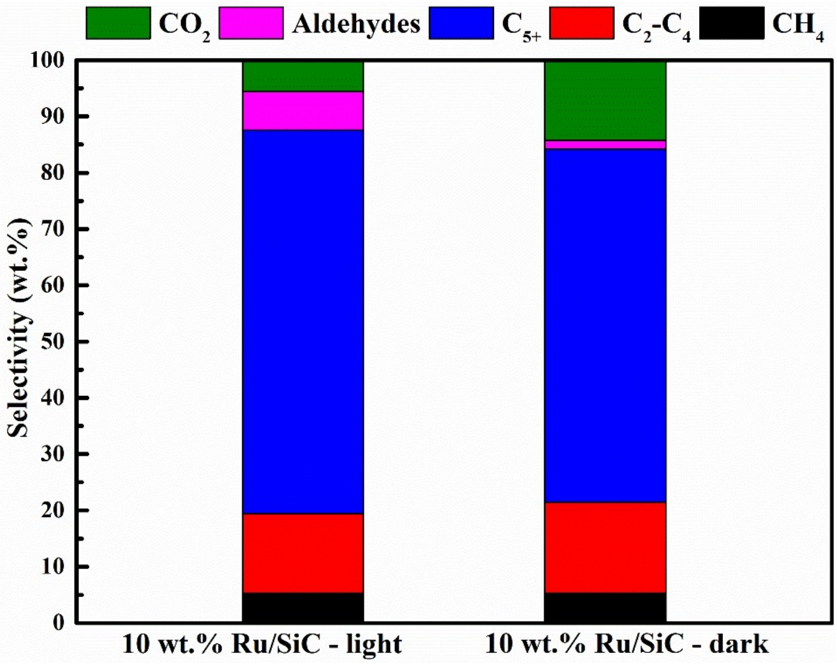

Figure S4: The selectivity of all products of 10 wt.% Ru/SiC with or without irradiation.

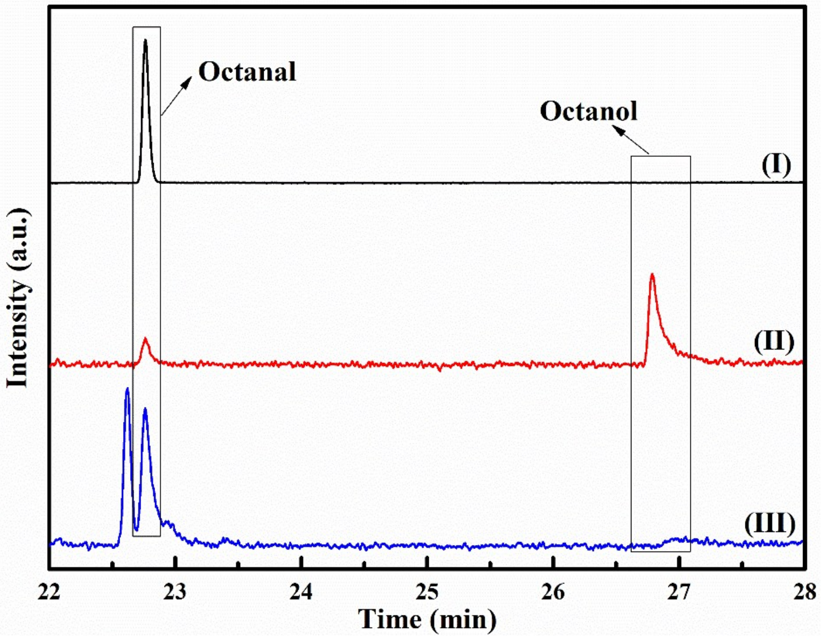

Figure S5: The activity of Ru/SiC catalyst in aldehyde hydrogenation. (Ⅰ) Octanal standard sample; (Ⅱ) React 3 h in 3 Mpa H_2; (Ⅲ) React 3 h in 3 Mpa syngas (CO/H_2=0.5).

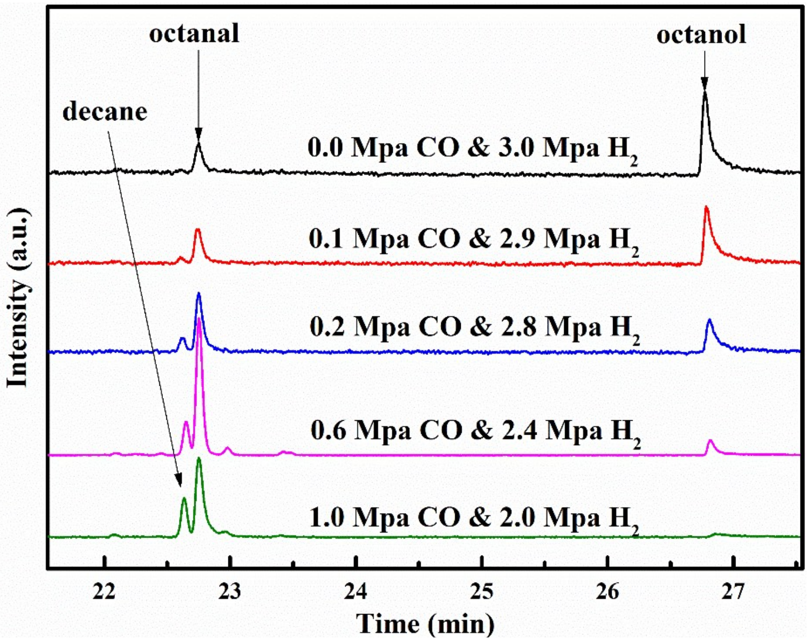

Figure S6: The chromatogram results of different concentration of CO in aldehyde hydrogenation using 10 wt.% Ru/SiC catalyst.

The conversion of aldehyde to corresponding alcohol was 78.1%, 66.6%, 38.2%, 11.6% and 5.8% when the partial pressure of CO was 0 bar, 1 bar, 2 bar, 6 bar, 10 bar, respectively. The total pressure of syngas was 3 Mpa. When the conversion of CO became higher, the activity of FTS reaction became higher, either. So the chromatographic peak of the decane became higher accordingly.

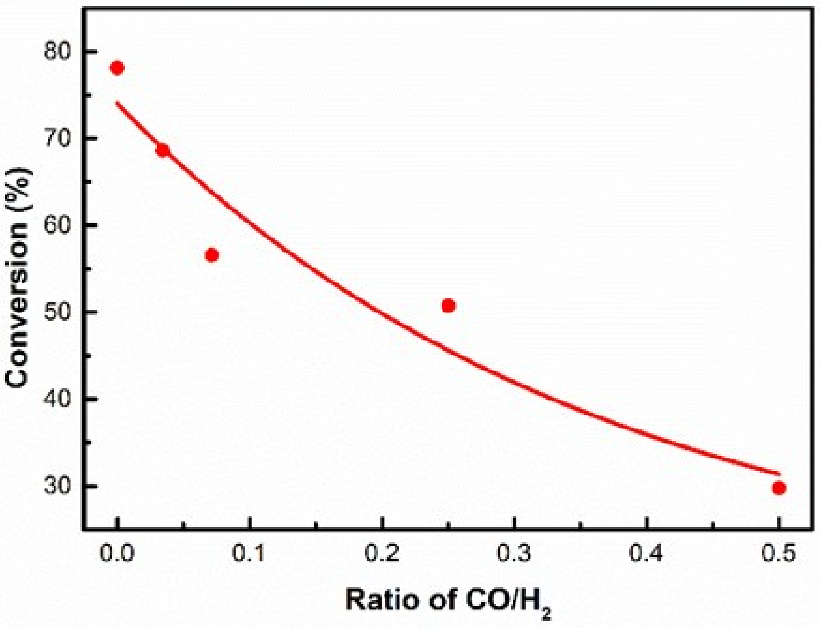

Figure S7. The conversion of aldehyde hydrogenation in different mole ratio of syngas using 10 wt.% Ru/SiC. (Keep the amount of H_2 as a constant.)

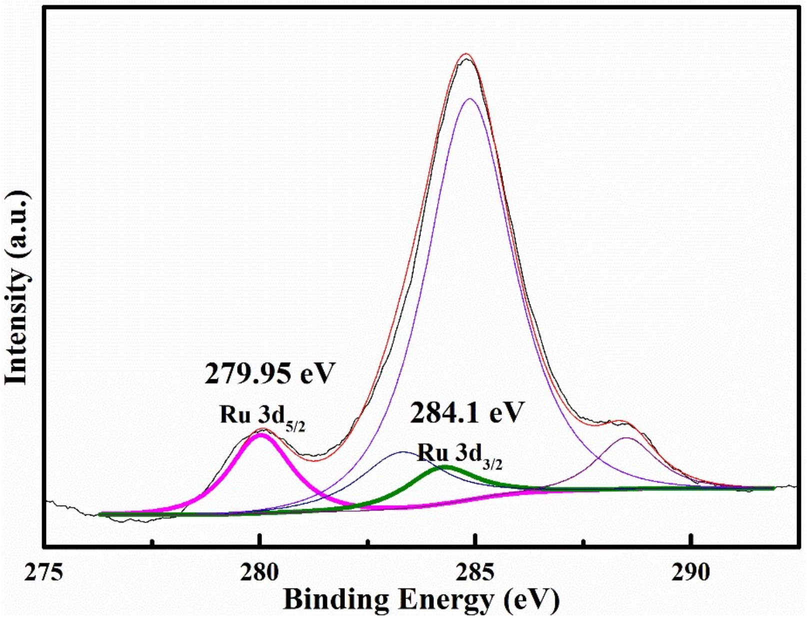

Figure S8: The XPS spectrum of 10 wt.% Ru/SiC.

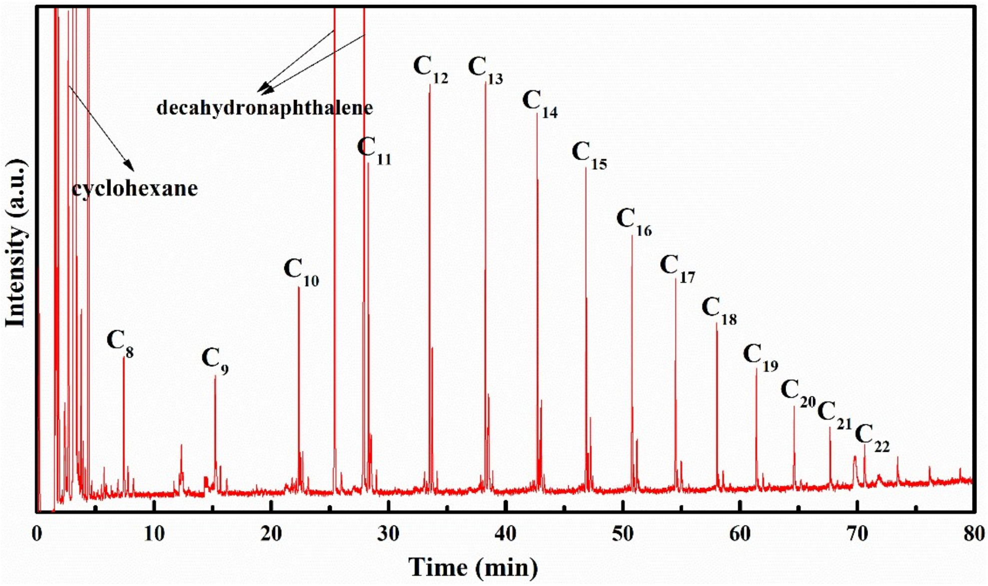

Figure S9: A typical GC spectrum of FTS products. Reaction conditions: 3.0 MPa syngas (CO:H_2=0.5), 100 mg 10 wt.% Ru/SiC catalyst, 20 ml water, reacted at 423 K for 5 h with the stirring speed of 800 rpm.

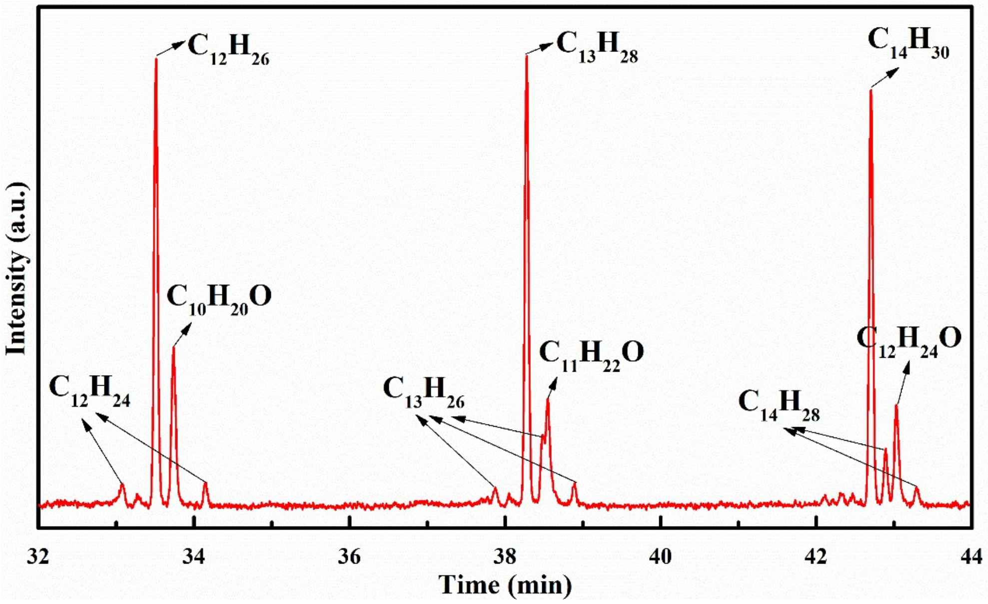

Figure S10: Details of Figure S8. Each group of products contained alkanes, olefins and aldehydes. None alcohol had been detected.

Reference

[1]. G. Q. Jin and X. Y. Guo, Micropor. Mesopor. Mater., 2003, 60, 207-212.