Supporting information

High Surface Area Siloxene for Photothermal and Electrochemical Catalysis

Yize Su,^{‡a} Shenghua Wang,^{‡a} Liang Ji,^{‡a} Chengcheng Zhang,^a Haiting Cai,^b Hui Zhang^a and Wei Sun^{*a}

^aState Key Laboratory of Silicon Materials, School of Materials Science and Engineering, Zhejiang University, Hangzhou, Zhejiang 310027, P. R. China.

^bInstitute of Industrial Catalysis, College of Chemical Engineering, Zhejiang University of Technology, Hangzhou 310014, China

‡These authors contributed equally to this work.

*Corresponding author: Wei Sun



Fig. S1 (a) XRD patterns of CaSi₂ and CaSi₂-NaOH. The peaks are labelled according to the standard SiO₂, the standard Si, the standard FeSi₂ and the standard CaSi₂. Subtle peaks of FeSi₂ and SiO₂ could be observed in the pattern, but all of them were far less pronounced than the Si peaks. (b) Raman spectra of CaSi₂ and CaSi₂-NaOH. (c) SEM image of CaSi₂. (d) SEM image of CaSi₂-NaOH.



Fig. S2 FTIR spectra of siloxene prepared with different reaction time.



Fig. S3 Raman spectra of siloxene-4.5d and siloxene (no NaOH).



Fig. S4 N_2 adsorption-desorption isotherms of (a) CaSi₂, (b) 2DSi, (c) C-siloxene-7.5d, (d) siloxene (no NaOH), (e) siloxene-2.5d, (f) siloxene-4.5d, and (g) siloxene-5.5d.



Fig. S5 Pore size distribution curves of (a) CaSi₂, (b) 2DSi, (c) C-siloxene-7.5d, (d) siloxene (no NaOH), (e)siloxene-2.5d, (f) siloxene-4.5d, and (g) siloxene-5.5d.



Fig. S6 (a) XRD patterns of 17.7%Cu_{im}-2DSi and 18.3%Cu_{im}-Siloxene-4.5d. (b) XRD patterns of 2.4%Pd_H-2DSi, 3.6%Pd_H-2DSi and 3.8%Pd_H-Siloxene-4.5d. The peaks are labelled according to the standard SiO₂, the standard Si, the standard FeSi₂, the standard Cu, and the standard Pd.



Fig. S7 TEM images of (a) 17.7%Cu_{im}-2DSi, (b) 18.3%Cu_{im}-Siloxene-4.5d, (c) 2.4%Pd_H-2DSi, (d) 3.6%Pd_H-2DSi, and (e) 3.8%Pd_H-Siloxene-4.5d.



Fig. S8 EDS mappings of (a-d) 18.3%Cu_{im}-siloxene-4.5d and (e-h) 3.8%Pd_H-siloxene-4.5d.



Fig. S9 HRTEM image of 3.8%Pd_H-siloxene-4.5d.



Fig. S10 CO production rates of different samples in thermocatalytic reactions (testing condition: 30 mg of the catalyst, $CO_2/H_2/N_2 = \sim 5/20/5$, ambient pressure).



Fig. S11 (a) N₂ adsorption-desorption isotherms and (b) pore size distribution curves of commercial SiO₂.



Fig. S12 CO production rates of 17.1%Cu_{im}-SiO₂ and 18.3%Cu_{im}-siloxene-4.5d in thermal catalytic reactions (testing condition: 30 mg of the catalyst, CO₂/H₂/N₂ = $\sim 5/20/5$, ambient pressure).



Fig. S13 Diffuse reflectance spectra of 17.7%Cu_{im}-2DSi and 18.3%Cu_{im}-Siloxene-4.5d.



Fig. S14 Surface temperature profile of 18.3%Cu_{im}-Siloxene-4.5d under 34.3-suns illumination.



Fig. S15 (a) Polarization curves of the 2.4% Pd_{H} -2DSi and 3.8% Pd_{H} -siloxene-4.5d catalysts. (b) Comparison of overpotential at 10 mA/cm² and onset potential of the catalysts. (c) Tafel plots of the catalysts. (d) chronoamperometry tests of the catalysts.



Fig. S16 (a) O 1s, (b) Si 2p, and (c) Pd 3d XPS spectra of the different Pd catalysts.

Table S1 Crystallite size of the metals in different samples estimated using theScherrer Equation based on the XRD patterns.

| Samples | 18.3%Cu _{im} -Siloxene-4.5d | 17.7%Cu _{im} -2DSi | 3.8%Pd _H -Siloxene-4.5d | 3.6%Pd _H -2DSi | 2.4%Pd _H -2DSi |
|-----------------------------------|--------------------------------------|-----------------------------|------------------------------------|---------------------------|---------------------------|
| Metallic crystallite size (nm) | 9 | 11 | 11 | 17 | 13 |
| | | | | | |

| Light Illumination (suns) | 17.7%Cu _{im} -2DSi | 15.9%Cu _{im} -Siloxene (no NaOH) | 18.3%Cu _{im} -Siloxene |
|---------------------------|-----------------------------|---|---------------------------------|
| 20.0 | 0.000 | 0.628 | 1.245 |
| 24.2 | 0.483 | 0.875 | 3.040 |
| 34.3 | 1.898 | 3.818 | 8.403 |

Table S2 CO rates of different samples in photothermal catalytic reactions (testing condition: 15 mg of the catalyst, $CO_2/H_2/N_2 = \sim 2.5/10/2.5$, ambient pressure).