

Supplemental Information

Development of Robust Sulfur Quantification and Speciation Method for SBA-15

Supported Sulfonic Acid Catalysts

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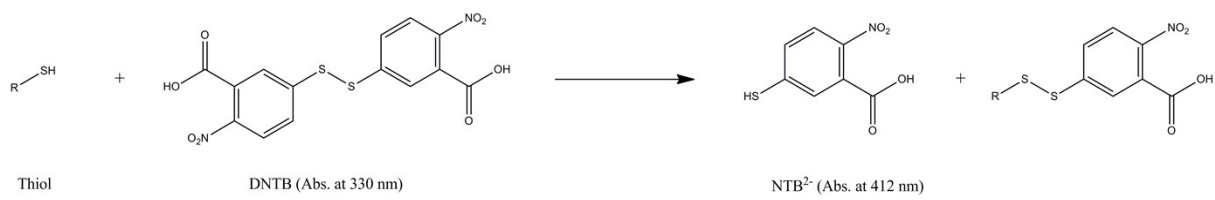
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Scheme S1. Detection of SH by Ellman's reaction.

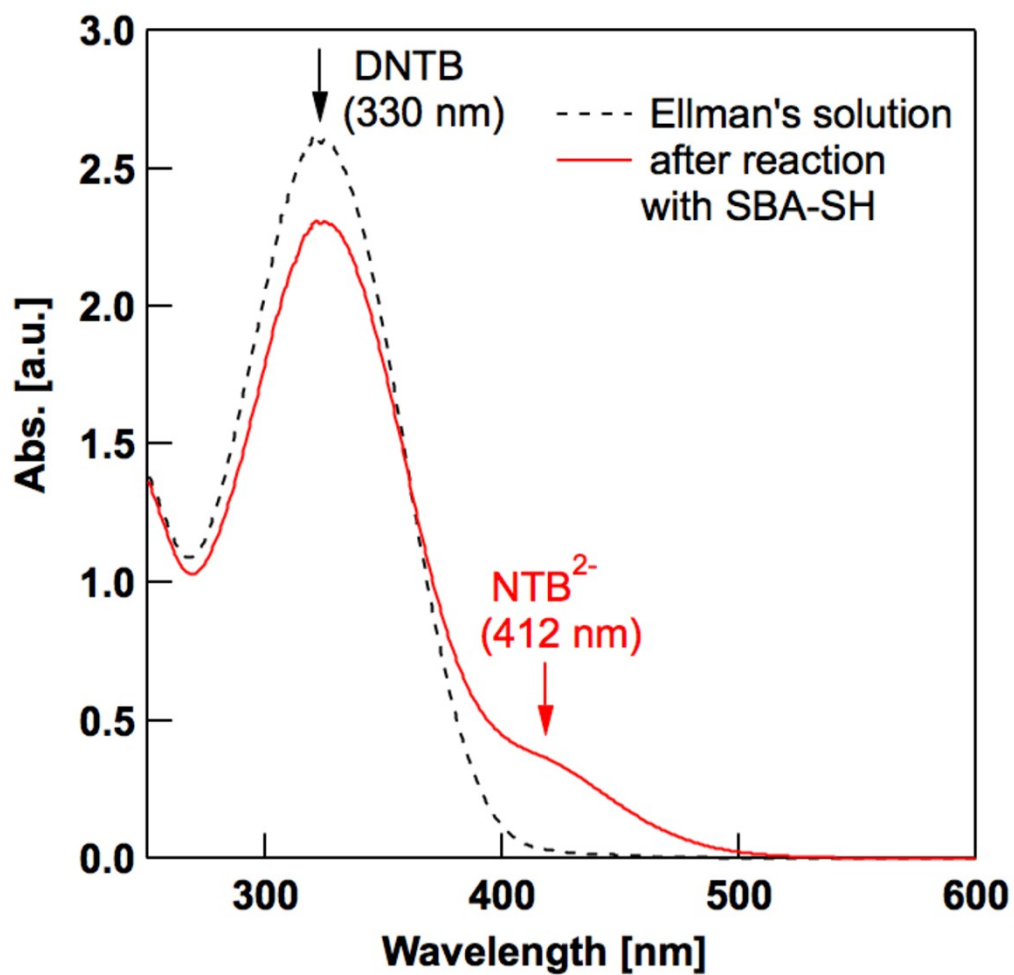


Figure S1. UV-Vis spectra of Ellman's solution before and after reaction with SBA-SH.

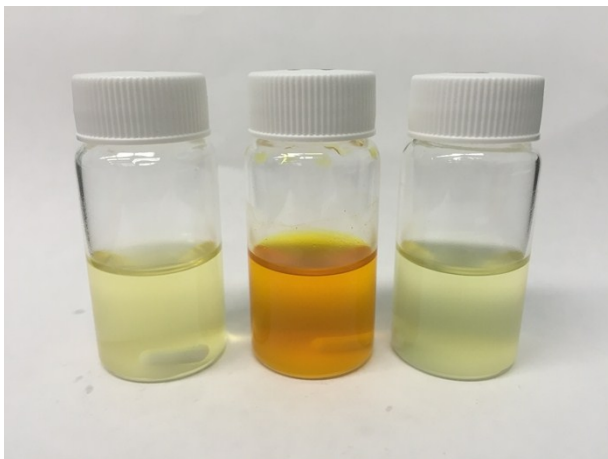


Figure S2. Photograph of Ellman's solution after reaction with SBA-15, SBA-SH and SBA-SH-ox-a (From left to right).

A clear color distinction between the samples demonstrates the successful incorporation and detection of SH in SBA-SH, as well as complete SH conversion after oxidation with a 30% H_2O_2 solution.

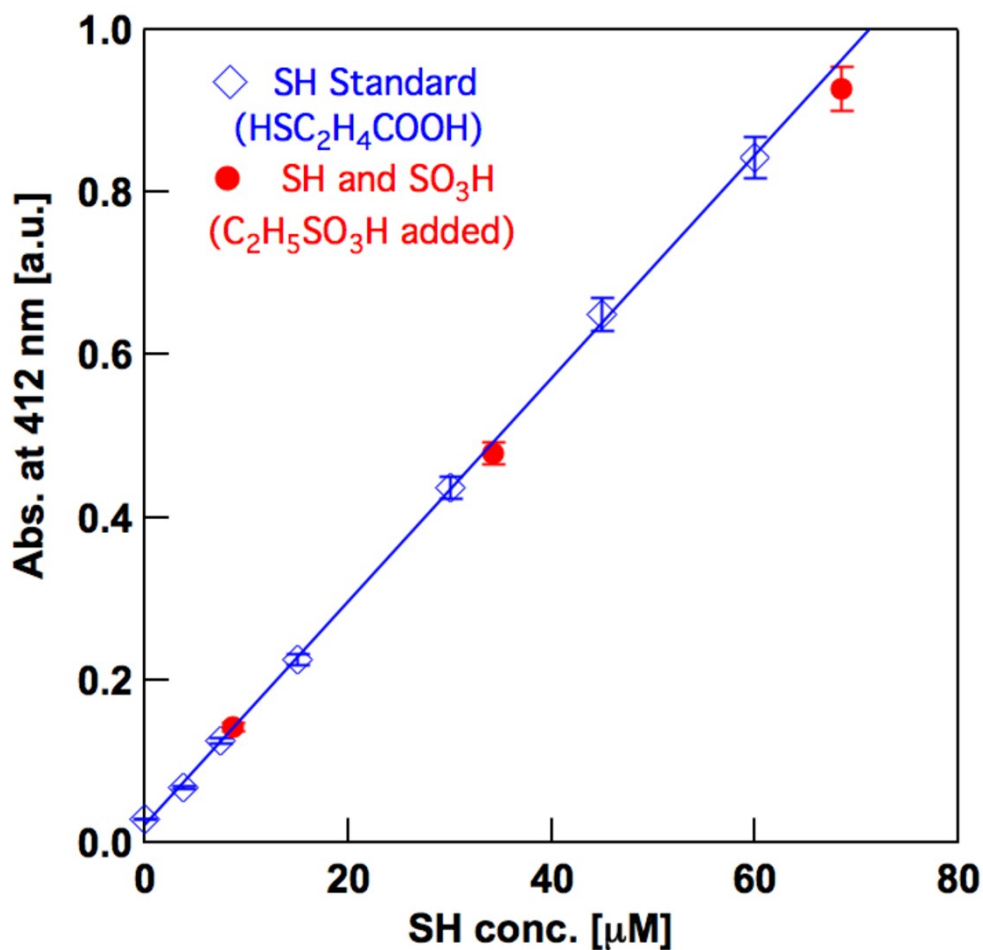


Figure S3. Determination of extinction coefficient from absorption at 412 nm due to Ellman's reaction product, NTB^{2-} with 3-mercaptopropionic acid solutions (homogeneous SH standard). The addition of sulfonic acid (ethanesulfonic acid 3 mM) to the SH standard solution did not disrupt Ellman's test results.

Although the peak for NTB^{2-} (412 nm), the product of Ellman's reaction with SH, overlapped with the Ellman's reagent peak (330 nm), a linear calibration curve ($R^2 > 0.99$) was obtained from the absorbance reading at 412 nm with 3-mercaptopropionic acid solutions with varying

concentrations (0-80 μM). The extinction coefficient of the NTB^{2-} (412 nm) was determined experimentally to be 13800 M^{-1} . Ellman's test is not disrupted by the presence of the sulfonic acid groups in solution. This was verified as shown in **Figure S4** by a control Ellman's test using a mixture of 3-mercaptopropionic acid (SH) and 3 mM ethanesulfonic acid (SO_3H), where the absorbance at 412 nm was not influenced.

Table S1. Reaction time dependence of Ellman's test for SH-SBA-15 samples.

Ellman's test reaction time (h)	SH Quantity (MPTMS:OH = 10) (mmol/g _{cat})
0.5	0.665
2	0.715
4	0.708
24	0.667
48	0.664

Varying the reaction time (0.5-48 h) showed that Ellman's test on solid samples was sensitive to this time, and the maximum NTB²⁻, the Ellman's test reaction product, was determined after 2 h. Prolonged reaction greater than 4 h resulted in a decrease in NTB²⁻ concentration. We speculate the decrease was caused by a combined effect of the decomposition of NTB²⁻ and adsorption of NTB²⁻ onto SBA-15 mesoporous silica. Riddles et al.¹ reported that NTB²⁻ can be oxidized back to the original Ellman's reagent (DNTB) under the presence of oxygen. A similar decrease in NTB²⁻ for longer reaction time (16 h) was also observed in Ellman's test with homogeneous SH standard (3-mercaptopropionic acid) under similar reaction conditions.

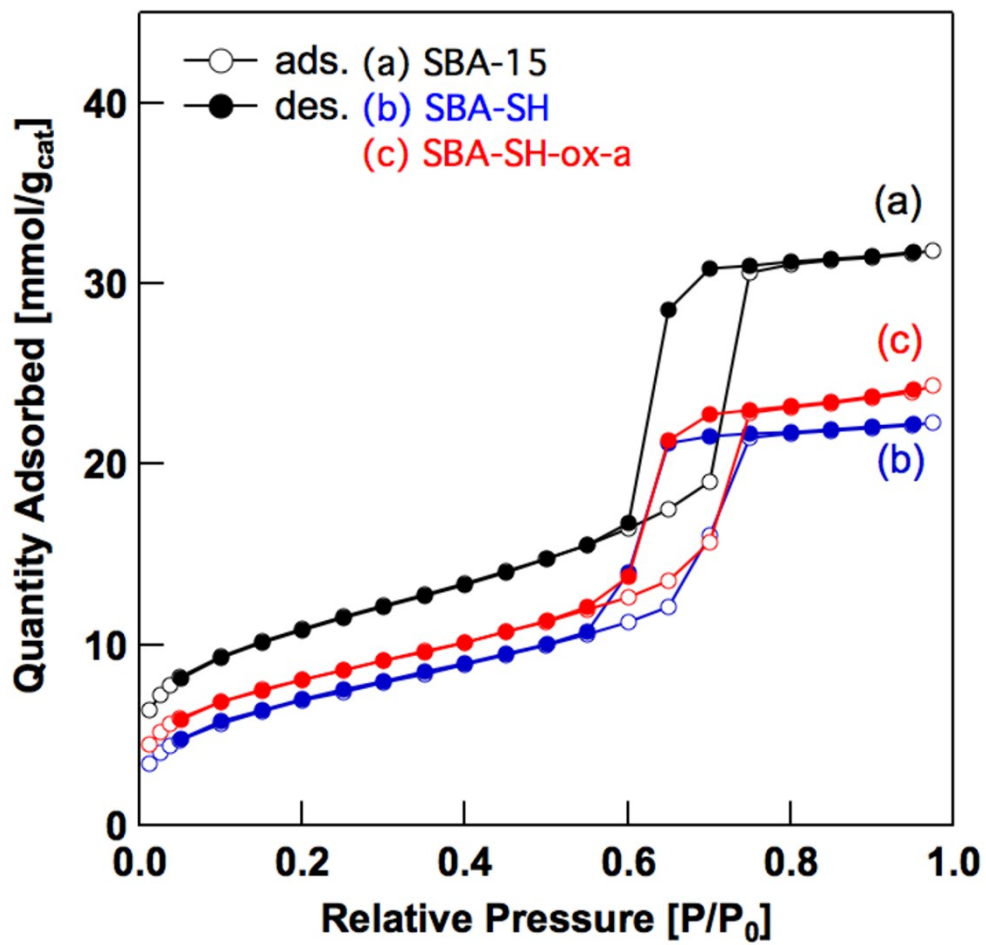


Figure S4. N₂ adsorption-desorption isotherms of (a) SBA-15, (b) SBA-SH, and (c) SBA-SH-ox-a.

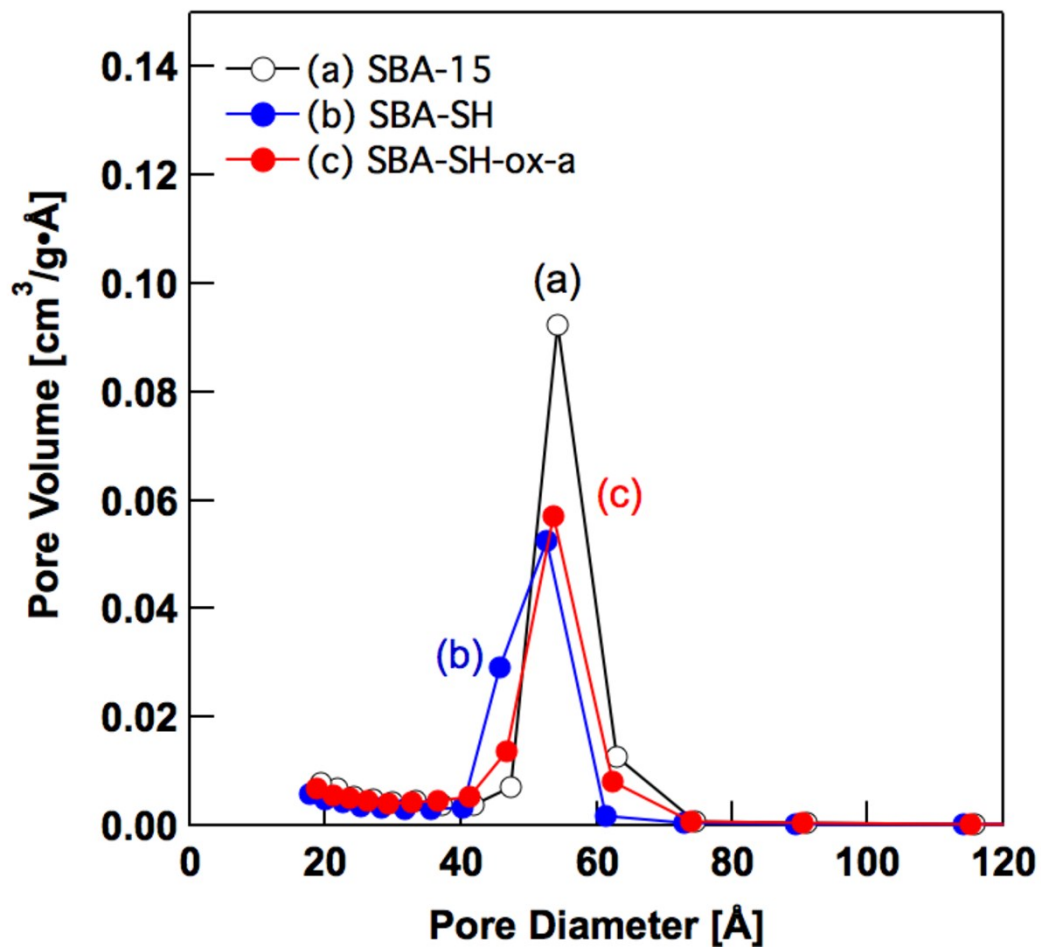


Figure S5. Pore diameter distribution (BJH plot) of (a) SBA-15, (b) SBA-SH, and (c) SBA-SH-ox-a.

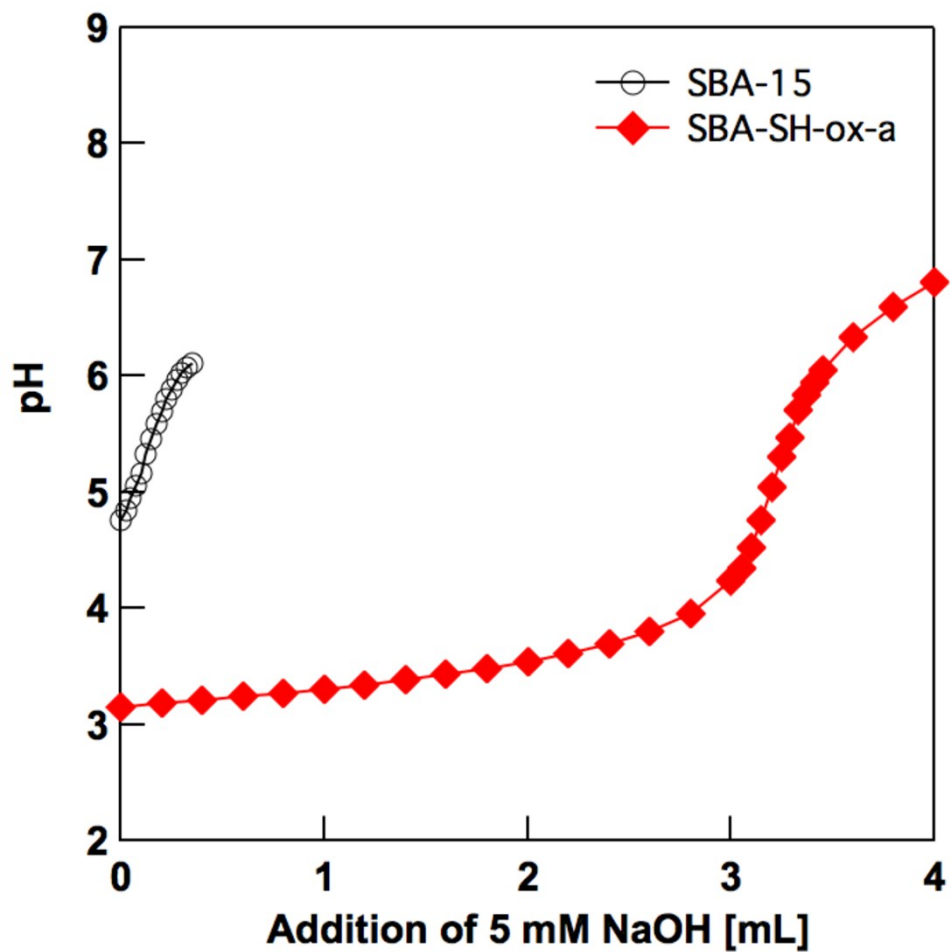


Figure S6. Acid-base titration profiles of SBA-15 and SBA-SH-ox-a. 50 mg SBA-15 sample; 10 mL of 10 mM NaCl. Each point was recorded after mixing for 5 min.

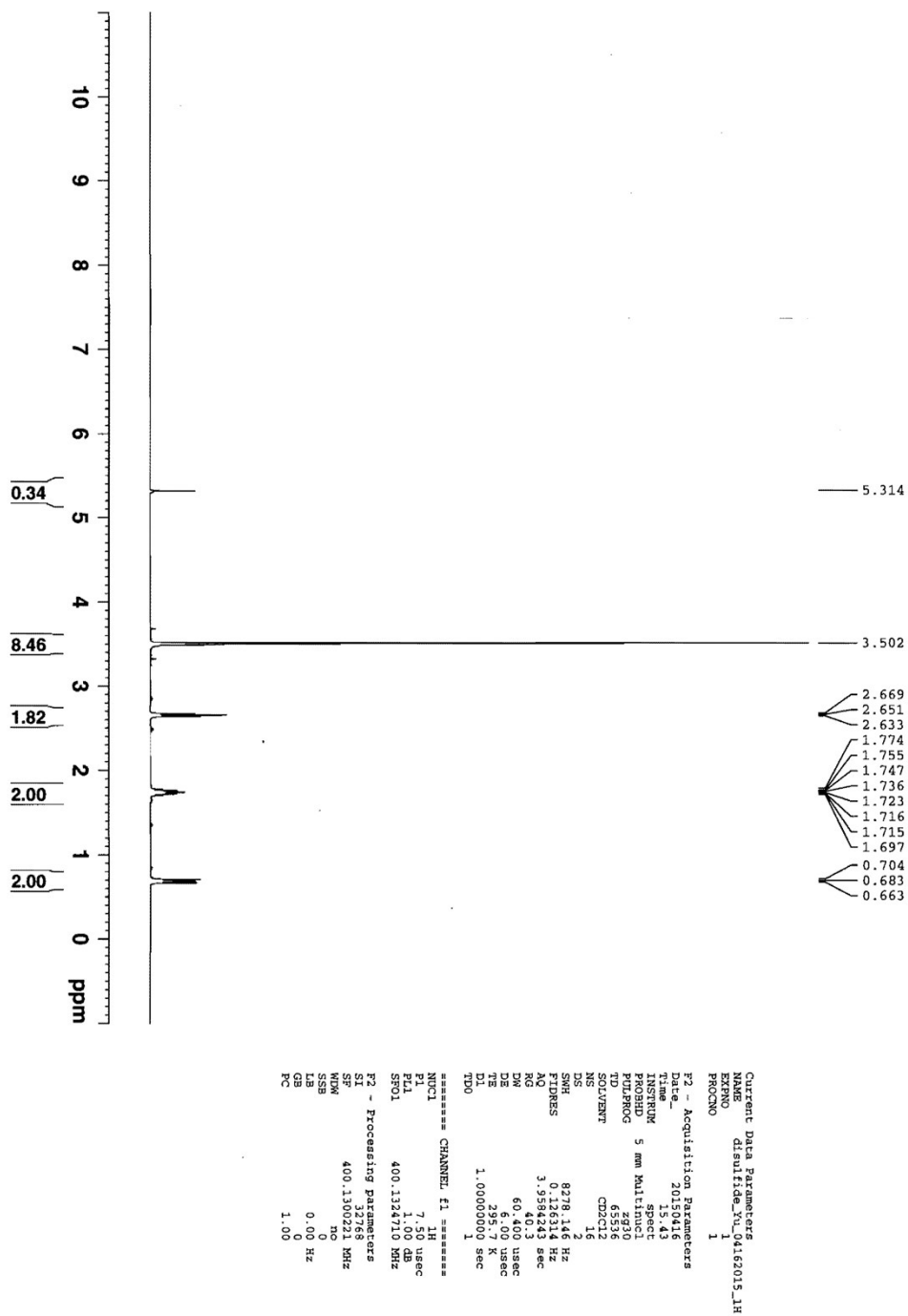


Figure S7. ¹H NMR spectrum of disulfide dipropyl silane (SS precursor).

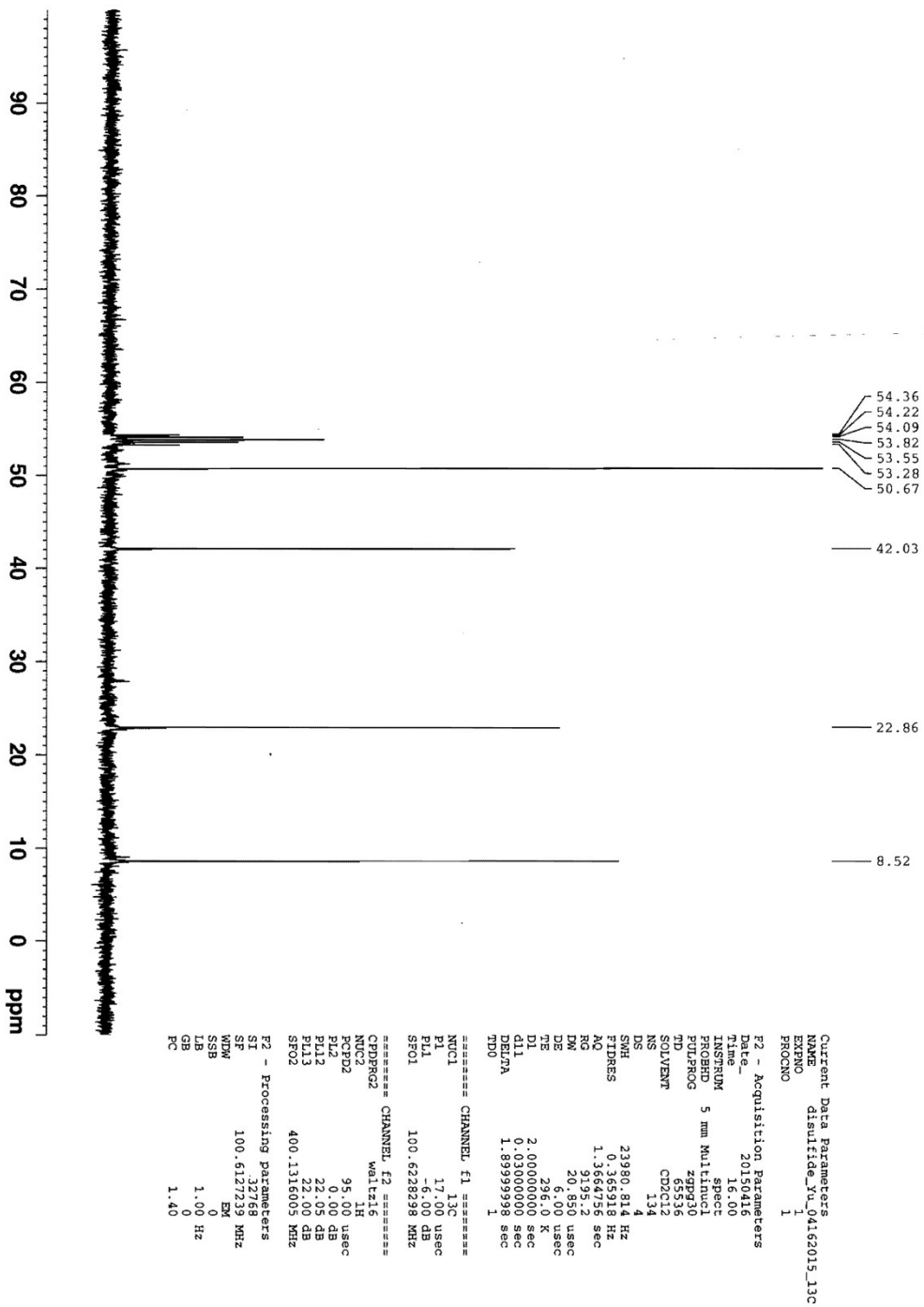


Figure S8. ¹³C NMR spectrum of disulfide dipropyl silane (SS precursor).

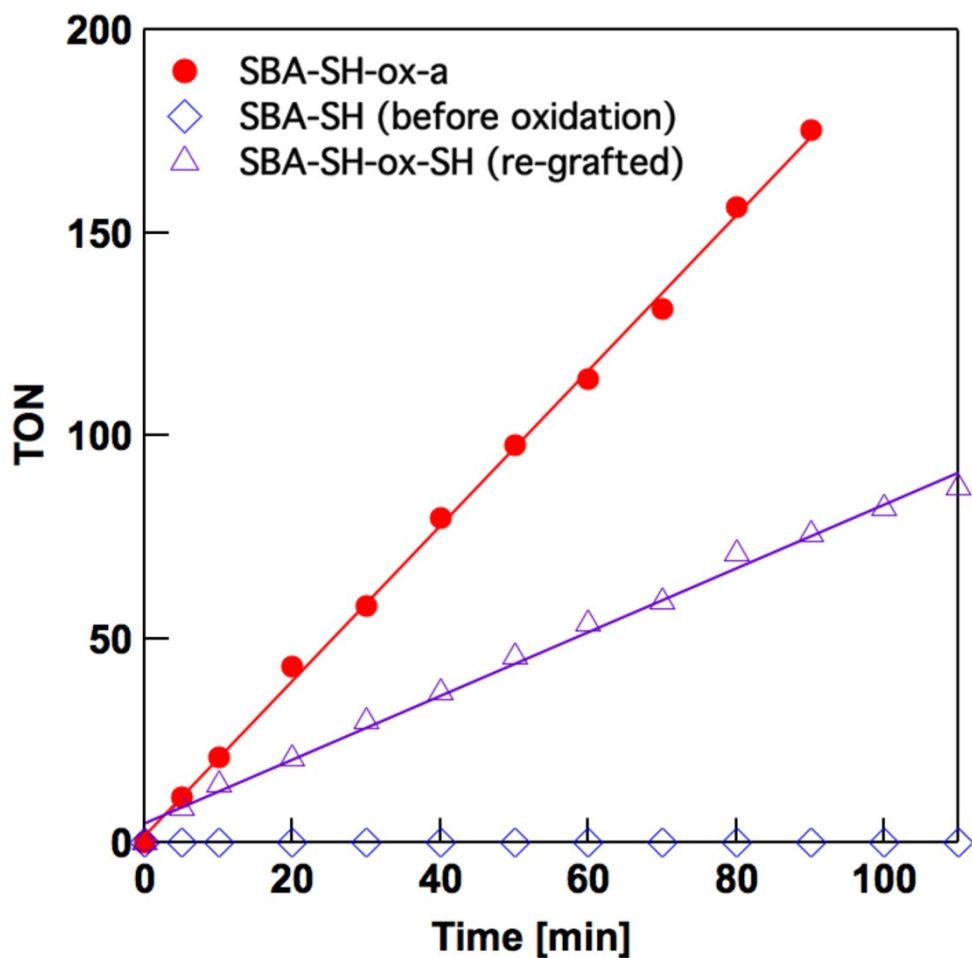


Figure S9. Time course of esterification reaction of acetic acid and methanol over three SBA-15 catalysts: SBA-SH, SBA-SH-ox-a, and SBA-SH-ox-SH. Reaction conditions were 3 M acetic acid, 6 M MeOH in 1,4-dioxane as a solvent, catalyst loading of 50 mg and $T = 323$ K.

References

- (1) Riddles, P. W.; Blakeley, R. L.; Zerner, B. Reassessment of Ellman Reagent. *Methods Enzymol.* **1983**, *91*, 49–60.