

Effect of Support Microstructure on Observed Activity in the Henry Reaction



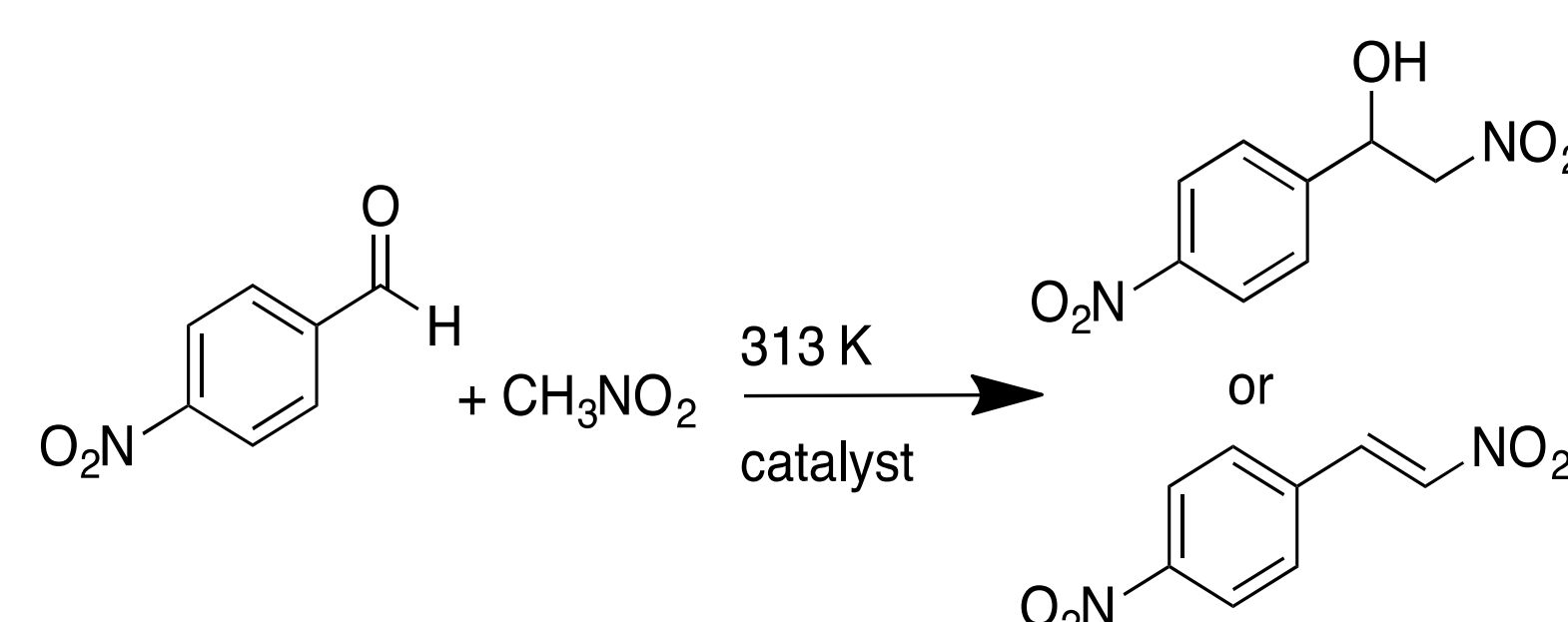
Leandra Caywood¹, Yueyun Lou², Daniel Shantz²

¹Department of Chemical and Materials Engineering, University of Alabama in Huntsville, Huntsville, AL

²Department of Chemical and Biomolecular Engineering, Tulane University, New Orleans, LA

Introduction

Organic ligands tethered to ordered mesoporous silica (OMS) hybrid materials have been the focus of many catalytic studies. More specifically the Henry reaction (or Nitroaldol reaction) has been widely used as a probe reaction to investigate OMS-hybrids containing a range of functional groups but predominantly amines. The issue of how product selectivity is influenced or controlled by the presence of surface silanols (i.e. cooperativity), how the amine linker impacts reactivity, and the presence of multiple functional groups have all been investigated. In this work we look at how the morphology and microstructure of the OMS support impacts the rate and selectivity in the Henry reaction (shown below), with the goal of ultimately quantifying how mass transfer impacts the observed catalytic properties.



Scheme 1. Reaction Mechanism of Nitroaldol (Henry) reaction.

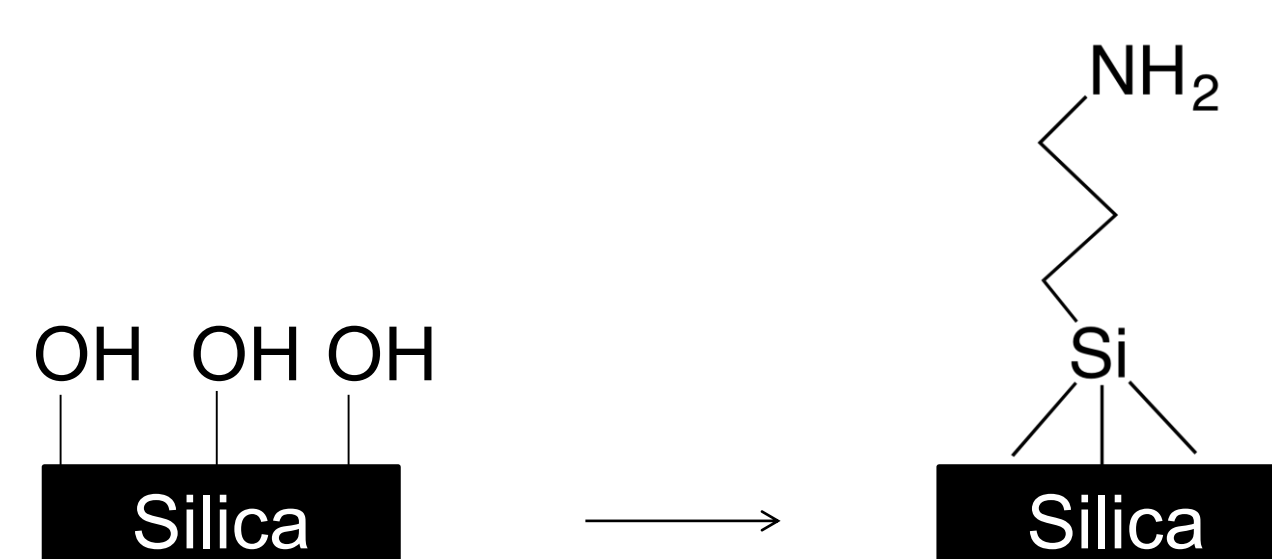
Synthesis

Particle Synthesis

- SBA-15 was synthesized with Pluronic P123, HCl, water, and TEOS at a stoichiometric ratio of 1TEOS: 0.17 P123: 80.7 HCl: 40.8 H₂O per Zhao and coworkers.¹
- Similarly, Silica spheres 1 was prepared with Pluronic P123 and F127, CTAB, ethanol, water, HCL, and TEOS according to work by Ai.²
- To vary the size and morphology of the SBA-15 prior work by Wan³ was used with the aim of making SBA-15 spheres. Silica spheres 2 – 4 were achieved using this work by varying the amount of salt in the synthesis. Using a molar ratio of 1 TEOS: 0.017 P123: 0.6 TMB: x KCl: 5.85 HCl:165 H₂O, x was set equal to 1, 1.25, and 1.5 for Silica spheres 2, 3, and 4, respectively.
- Non-porous Stöber silica was made using ethanol, water, NH₃, and TEOS following the protocol of Bogush et al.

Amino Silane Grafting

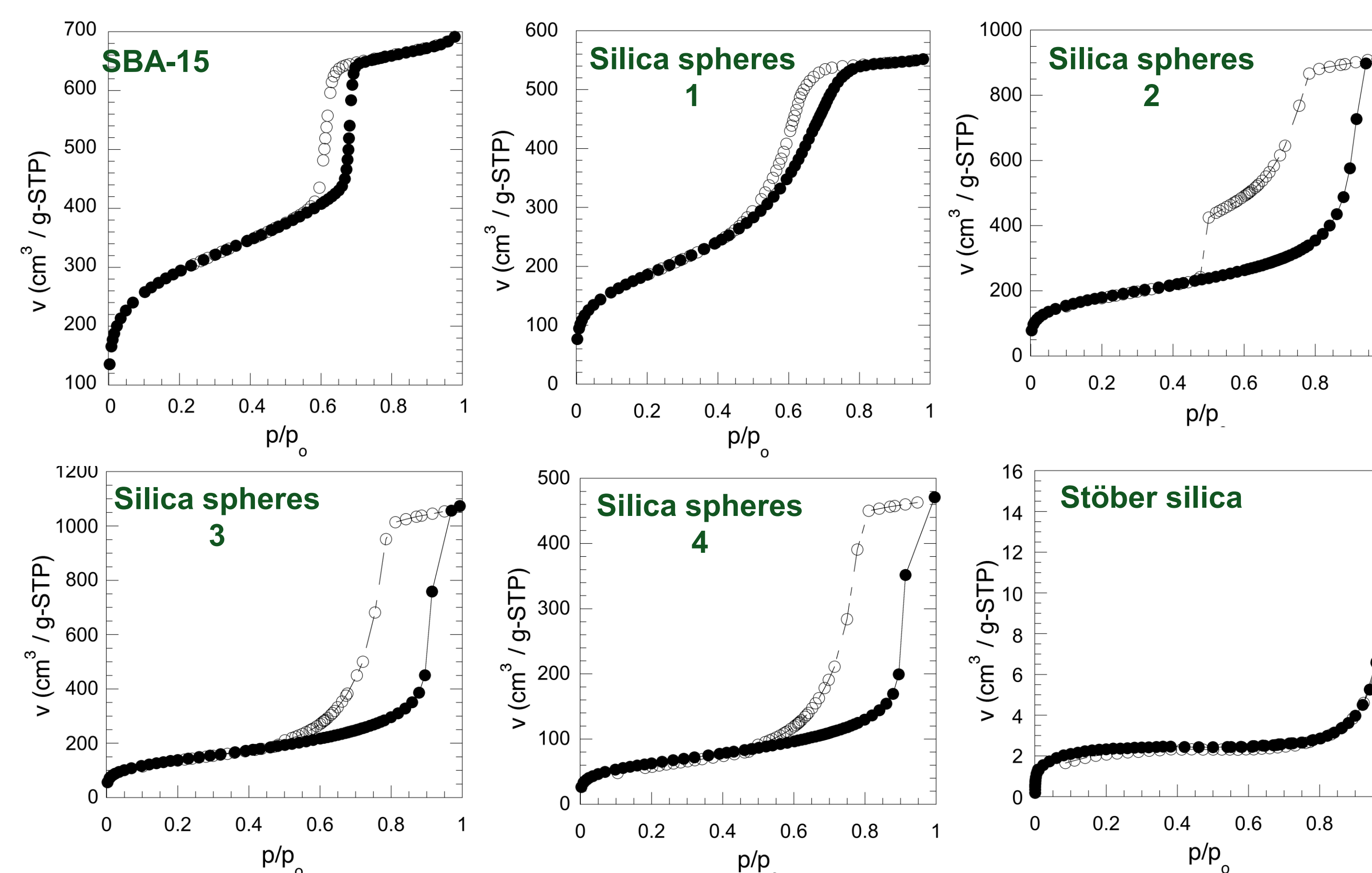
Amino silane grafting was performed on SBA-15 and Silica spheres 1 - 4 by adding dry toluene to the silica spheres along with 0.5 mmol of 3-aminopropyldimethylethoxysilane per gram of silica and mixed overnight. Stöber silica was prepared with a loading of 0.05 mmol/g.



Scheme 2. Amino Silane Grafting

Textural Properties

The silica textural properties were determined using nitrogen physisorption.

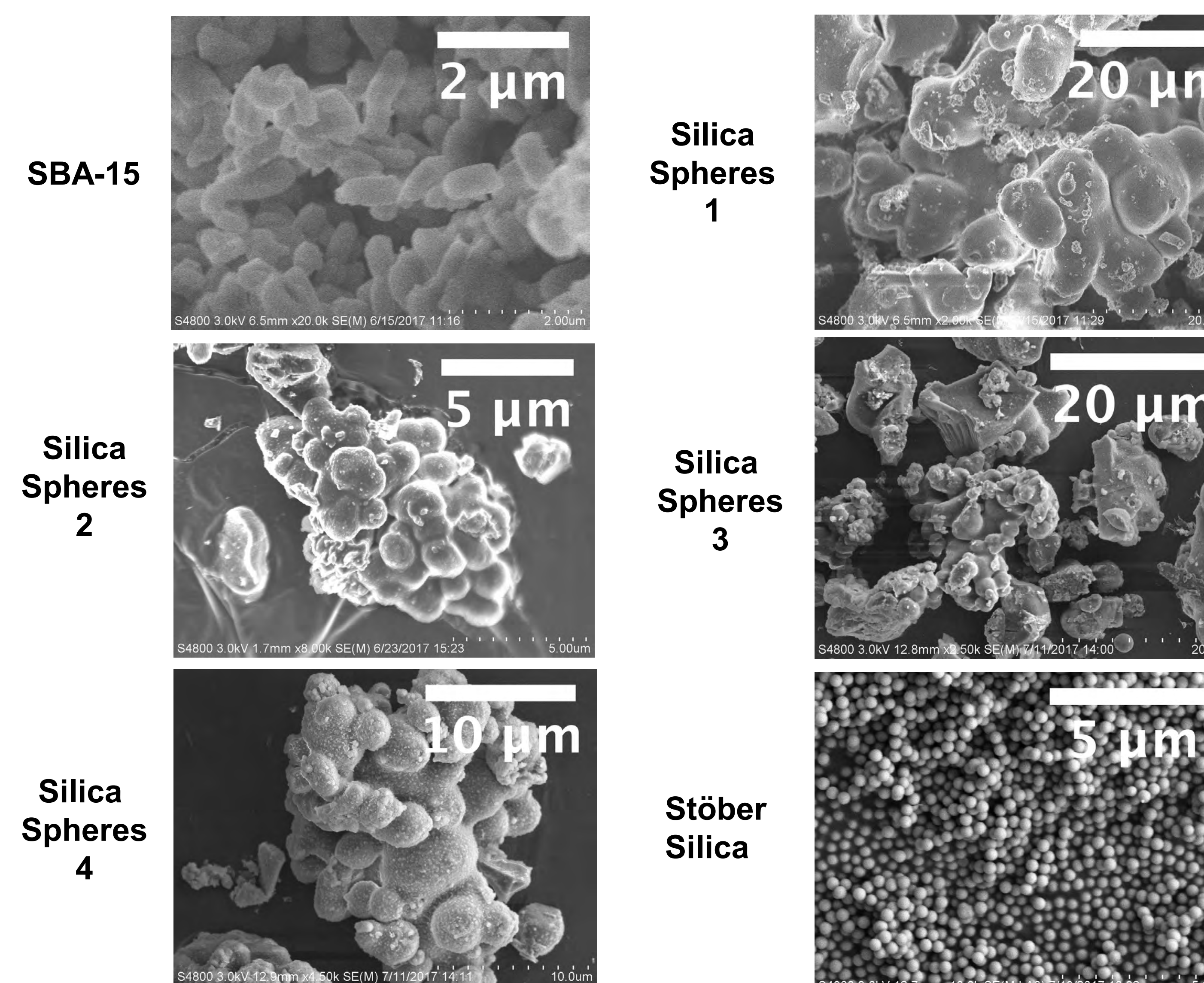


Sample	S _(a-s) [m²/g]	v _{meso} [cm³/g]	d _p (BJH) [nm]
SBA-15	808	0.92	7.56
Silica spheres 1	653	0.78	6.5 (broad)
Silica spheres 2	634	1.22	25
Silica spheres 3	501	1.43	21
Silica spheres 4	225	0.77	22
Stöber silica	12	N/A	N/A

Pore size of spheres 2-4 appear similar based on this data. The PSD for spheres 1 is very broad.

Particle Morphology

Field-Emission scanning electron microscopy (FE-SEM) was used to assess crystal size and shape.

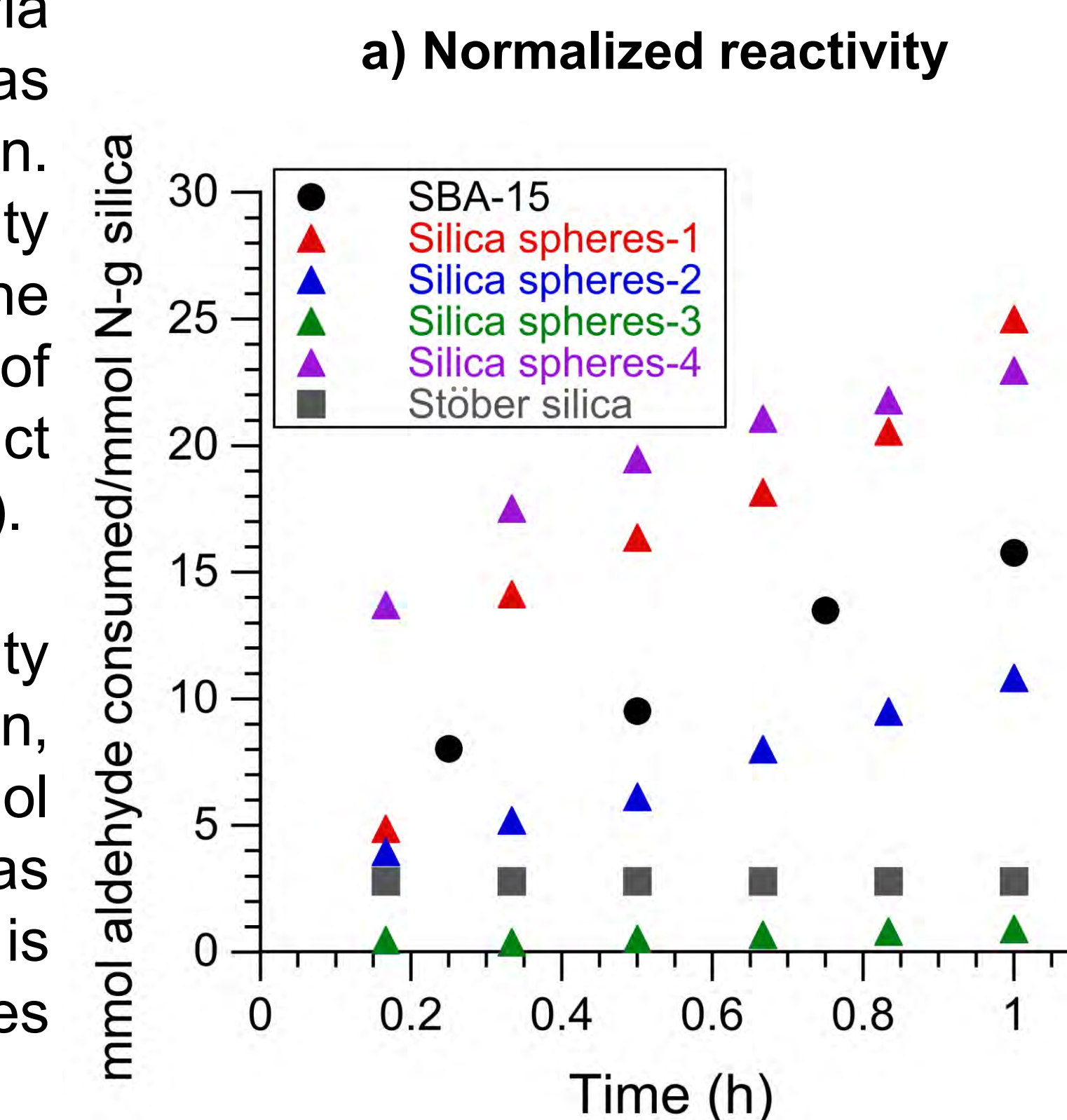


Clearly many of the literature preps (1, 3, 4) did not lead to uniform spheres.

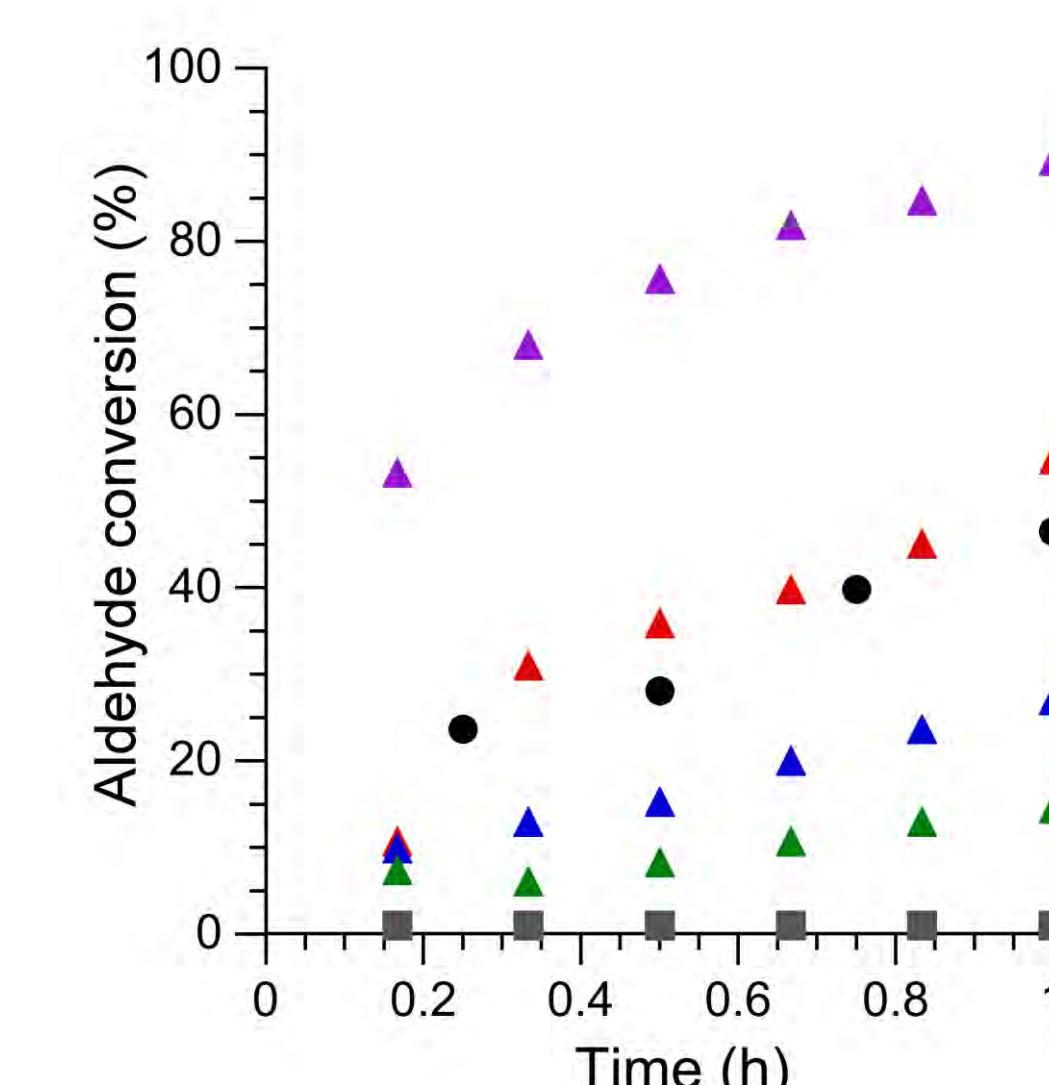
Catalysis

The silane loading was verified via TGA. All samples were used as catalysts in the Henry reaction. The conversion and selectivity were calculated based on the integration of ¹H NMR peaks of reactant (aldehyde), main product (alkene) and by-product (alcohol).

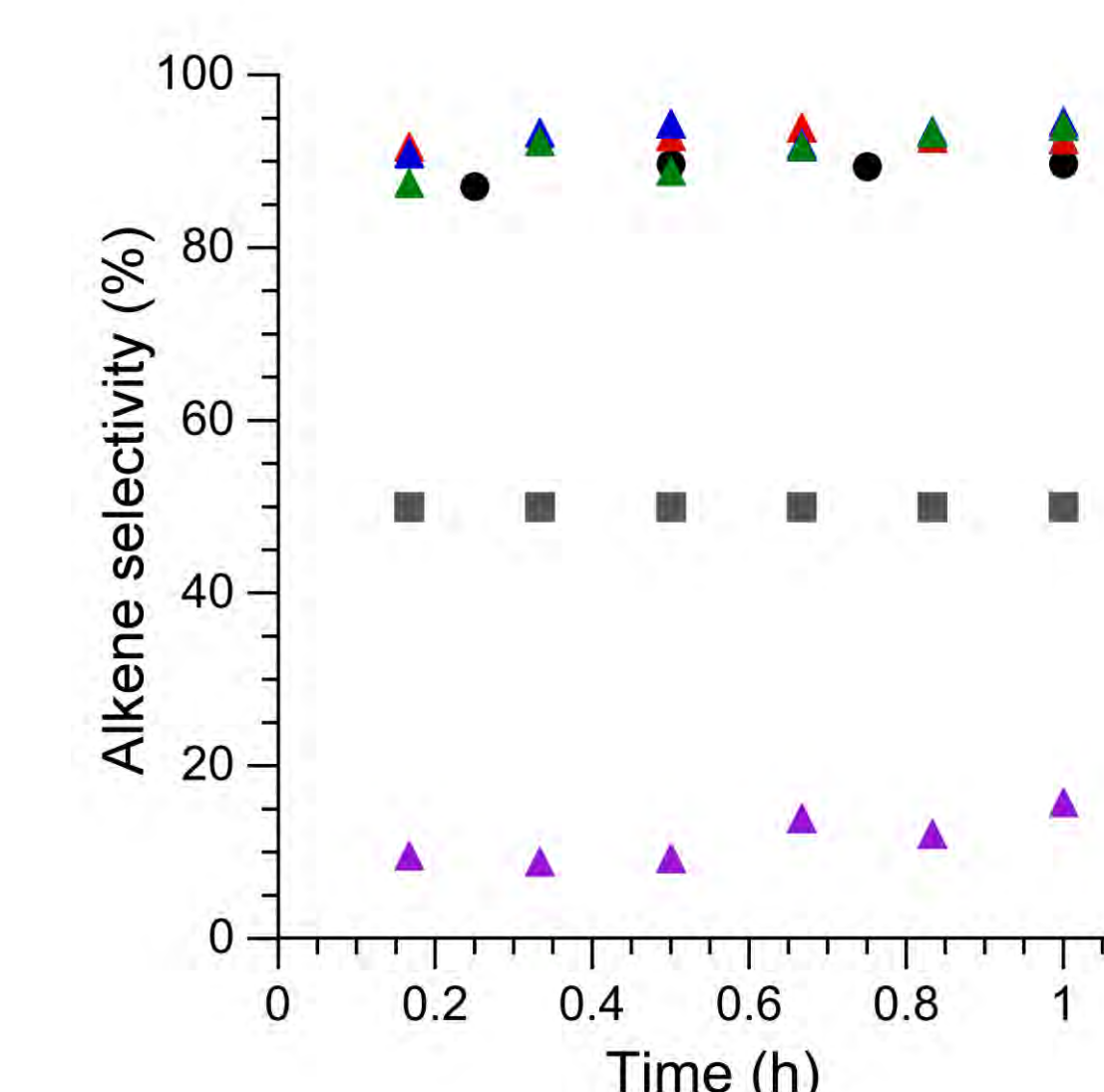
The wide differences in reactivity were not anticipated. In addition, The high selectivity to nitroalcohol for the most active catalyst was unexpected and ongoing work is investigating the microstructures of the sample in more detail.



b) Aldehyde Conversion



c) Alkene Selectivity



Conclusions

The synthesis of several OMS materials was performed and the materials were tested in the nitroaldol reaction. Two samples appeared more active than SBA-15, which is surprising. There were no clear correlations at this point between material properties and reactivity. It is clear that we had difficulties replicating the spheres from Wan and Ai. Ongoing work is attempting to understand the spheres made using TEM to better comprehend the observed reactivity. We are also exploring new synthesis protocols to make improvements in the sphere uniformity.

References

- 1) D. Zhao, Q. Huo, J. Feng, B. F. Chmelka, and G. D. Stucky, *J. Am. Chem. Soc.*, 1998, **120**, 6024-6036.
- 2) F. Ai, L. Li, S. C. Ng, and T. T. Tan, *J Chromatogr A*, 2010, **1217**, 7502-7506.
- 3) H. Wan, L. Liu, C. Li, X. Xue, and X. Liang, *J Colloid Interface Sci*, 2009, **337**, 420-426.

Acknowledgements

Special thanks to Daniel Shantz for his lab materials, guidance, and expertise; and to Yueyun Lou and Aibolat Koishybay for their time, assistance and advice. We thank the National Science Foundation for financial support through grants.

DMR-1460637 and IIA-1430280