

SiGNa™ Materials for Chemical Synthesis

Overview

Alkali metals are known to have limited uses in chemical synthesis owing to their pyrophoric character in the presence of trace amounts of moisture and air. Current work-arounds to alkali metal volatility are difficult to scale up due to low reaction efficiency, complications in handling, and adverse reaction conditions.

SiGNa's new alkali metal – porous oxide (**M-SG**) products are free-flowing powders that solve the problems surrounding the use of alkali metals by:

- **Yield:** retains reducing ability of parent alkali metal in both batch and continuous reactions
- **Reaction Kinetics:** performs fastest reductions at room temperature
- **Ease of Use:** removes impurities
- **Safety:** does not ignite or oxidize in air
- **Cost:** lower insurance, shipping, and safety expenses



Na₂K coated silica gel

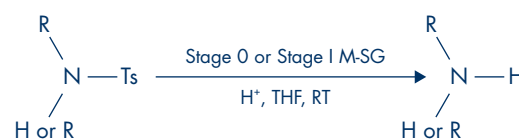


SiGNa Na₂,K-silica gel

Example Reactions

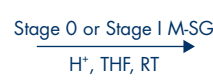
Detosylation of Amines: Current detosylation methods suffer from limitations of poor yield, lack of generality and functional group tolerance, and excessively harsh reaction conditions.

SiGNa M-SG products carry out detosylations of primary and secondary amines with a suitable proton source. This process undergoes selective removal and is much more versatile and high yielding (75-90%).



Transfer Hydrogenations: Current hydrogenations employ toxic and expensive transition metal-based catalysts and costly hydrogen gas.

SiGNa M-SG products initiate fast reduction of double and triple bonds at room temperature with quantitative yields, using cheap proton sources such as HMDS or ammonium salts. Birch reductions at room temperature can be carried out, avoiding the use of liquid ammonia.



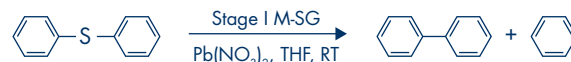
Dehalogenation / Wurtz Coupling: Typical Wurtz coupling uses sodium in refluxing toluene, which is too harsh for industrial processes. For dehalogenations, Pd on carbon with hydrogen gas is used.

SiGNa M-SG products can accomplish efficient Wurtz coupling in both batch and continuous reactions at room temperature. These reactions often go to completion in < 1 hour.



Desulfurization: Standard methods of desulfurization involve expensive catalysts and stoichiometric reagents. Also, most desulfurization reactions do not work at all for diaryl-sulfides.

SiGNa M-SG products avoid all harsh conditions (high temperature and pressure) and expensive catalysts. All sulfur species are removed using these mild conditions.

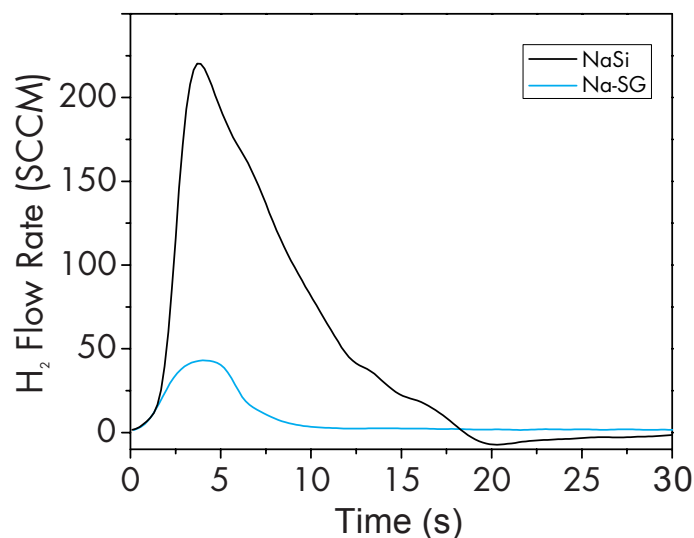
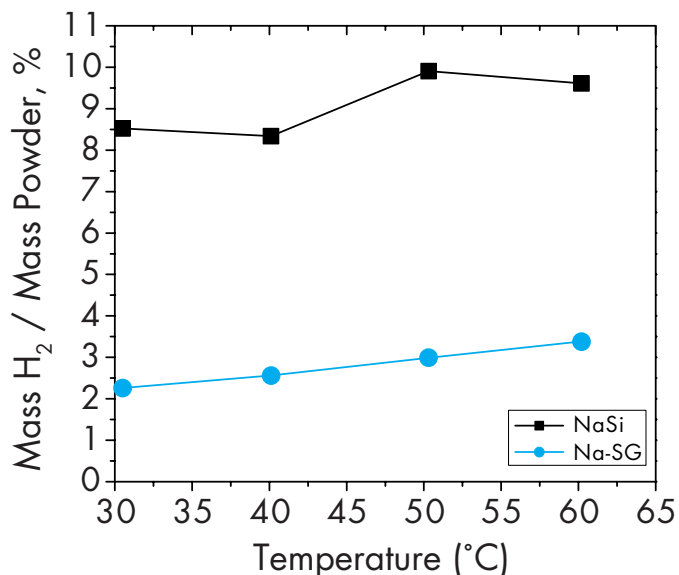


SiGNa™ Materials for Hydrogen Production

Overview

SiGNa's new sodium silicide (**NaSi**) and sodium silica gel (**Na-SG**) products are air stable powders that are high yielding, convenient sources of clean hydrogen gas. Their key advantages include:

- **Yield:** produces greater than 9 wt.% clean hydrogen gas at pressures above 5000 psi
- **Reaction Kinetics:** produces instant hydrogen upon addition to any water
- **Ease of Use:** does not require a catalyst to produce hydrogen gas
- **Safety:** does not ignite or oxidize in air
- **By-products:** generates non-toxic waste, such as sodium silicate



Applications

Slow or fast hydrogen production can be achieved in situ, or in a separate reaction vessel, to be utilized within a reaction mixture. Both Stage I and Stage II Na-SG can be used for this purpose, as well as NaSi. In this way, one can avoid the use of a high pressure hydrogen cylinder or even a deuterium cylinder, which is expensive and unnecessary for some experiments.

H ₂ source	weight	pressure	yield
H ₂ cylinder	60 kg	2200 psi	250 mol
Na-SG	29 kg	>5000 psi	250 mol
NaSi	6.3 kg	>5000 psi	250 mol

James L Dye, Kevin D. Cram, Stephanie A. Urbin, Mikhail Y. Redko, James E. Jackson, and Michael Lefenfeld. "Alkali Metals Plus Silica Gel: Powerful Reducing Agents and Convenient Hydrogen Sources." SiGNa Chemistry, LLC, New York, NY, Journal of the American Chemical Society 127(26), 9338-9339 (2005)

TO ORDER: Research quantities of SiGNa materials may be purchased from Sigma-Aldrich or Alfa Aesar.

For scale up, contact SiGNa chemistry directly at 212.933.4101 or visit www.signachem.com