

# Alkali Metal-Silica Gels



The use of metallic sodium and potassium used to be fundamental in such reactions as the Birch reduction or C-C bond formation in the Wurtz reaction. However, the inherent handling and fire risks associated with the metallic alkali metal reagents has restricted their large-scale use. SiGNa Chemistry has developed a range of stabilized alkali metal-silica gel powders (M-SG)

capable of performing reduction chemistries in a safe, streamlined process. These powders are free-flowing, non-pyrophoric and retain the reactivity equivalent of their parent alkali metal. Moreover, SiGNa Chemistry's powders eliminate the need for elevated temperatures and pressures and the associated handling equipment.

SiGNa's alkali metal-silica gels have metal loadings up to 60 mol% and are available in 3 varieties:

- Stage 0 M-SG: Pyrophoric, free-flowing, shiny black powder capable of reducing Teflon® in its solid state. This material is easily handled under Nitrogen.
- Stage I M-SG: Dry air-stable, free-flowing, non-pyrophoric black powder that retains the reactivity equivalent of its parent alkali metal.
- Stage II M-SG: Air-stable, free-flowing, non-pyrophoric black powder that contains nano-crystalline domains of metal silicide. The reactivity is strong enough to reduce simple molecules and water.

Alfa Aesar has entered into collaboration with SiGNa Chemistry, for the distribution of research quantities of these metal-silica gel powders. Alfa Aesar is pleased to announce our standard catalog range of SiGNa Chemistry products directly from stock.

**44890** Sodium potassium (K2Na)-silica gel, 35-40% alkali metal in silica gel, Stage I  
Standard Catalog Sizes: 5g, 25g, 100g, bulk

**44892** Sodium potassium (Na2K)-silica gel, 35-40% alkali metal in silica gel. Stage I  
Standard Catalog Sizes: 5g, 25g, 100g, bulk

**44893** Sodium-silica gel, 35-40% alkali metal in silica gel, Stage I  
Standard Catalog Sizes: 5g, 25g, 100g, bulk

**44894** Sodium-silica gel, 35-40% alkali metal in silica gel, Stage II  
Standard Catalog Sizes: 5g, 25g, 100g, bulk

# Alkali Metal-Silica Gels

## Birch reduction

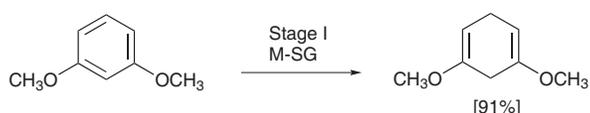
### Classical Method

The Birch reduction is a one-electron reduction of aromatic rings with alkali metals (Li, Na, K) dissolved in liquid ammonia. This reaction provides an alternative to catalytic hydrogenation, which is difficult to achieve with aromatics due to their extended conjugation. However, Birch reductions are generally avoided for scale-up due to the complexities of the large-scale process.

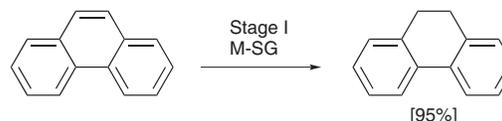
### SiGNa's Method

A Birch reduction performed using SiGNa material removes the hazards of alkali metals and does not require liquid ammonia or cryogenic temperatures. The SiGNa method improves yields, shortens reaction times, and simplifies workup procedures.

#### Dimethoxybenzene Reduction



#### Phenanthrene Reduction



### Benefits

- Shorter reaction times
- No liquid ammonia or cryogenic temperatures required
- No special equipment needed for handling
- By-products are non-hazardous and environmentally friendly

## C-C Bond Formation

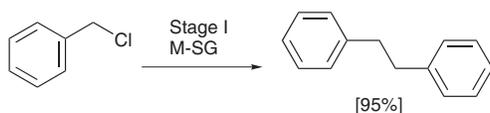
### Classical Method

Radical carbon-bond forming reactions (i.e. Wurtz reaction, acyloin condensation, etc.) are fundamental to organic synthesis. The majority of carbon-centred radicals undergo dimerization but these reactions are usually not atom economical or chemically selective, increasing the costs for synthesis.

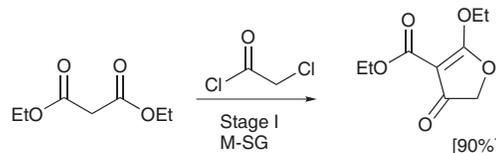
### SiGNa's Method

Carbon bond formations with SiGNa materials are able to be performed in both atom and process efficient syntheses in turn reducing cost to the end-user. The reaction conditions afford much cleaner products, safer reactive species, and milder conditions.

#### Benzyl Chloride Reduction



#### Diethyl Malonate Acylation



### Benefits

- Provides a smooth solution process at room temperature
- Can be performed in either batch or continuous-flow reactor setup
- Enhanced selectivity and kinetics of reaction
- By-products and salts removed through binding to SiGNa material

# Alkali Metal-Silica Gels

## Deprotections

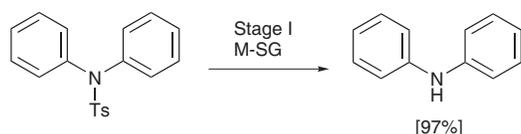
### Classical Method

Nitrogen is central to medicinally-oriented organic synthesis, therefore it is important to be able to protect and deprotect them throughout a synthesis. However, the most useful nitrogen protecting groups, like sulfonamides, which provide high crystallinity are extremely difficult to remove in high yield through simple non-toxic methods.

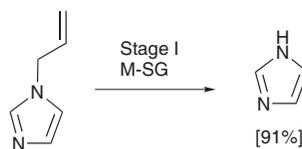
### SiGNa's Method

Nitrogen deprotection using SiGNa materials effects clean desulfonation and deallylation utilizing a safe, smooth solution process. The SiGNa method improves yield and reaction conditions, provides milder conditions, and simplifies process purification.

#### Diphenyl Sulfonamide Deprotection



#### N-Allylimidazole Deprotection



### Benefits

- Provides a smooth solution process at room temperature
- Highly selective allowing more options for substrate functionalization
- No toxic (e.g. mercury) or hazardous (e.g. liquid ammonia) materials needed
- No special equipment required for handling or processing

## Desulfurization

### Classical Method

A chemical approach to the removal of sulfur from organic molecules is of interest in several industries, specifically petroleum and natural gas refining as well as markets like pharmaceuticals. Today's desulfurization processes typically utilize very efficient catalysts that, however, often struggle to remove sulfur from highly aromatic and sterically-hindered organic sulfur systems.

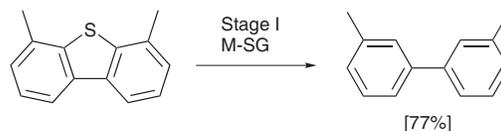
### SiGNa's Method

The SiGNa desulfurization method has the ability to remove sulfur from a wide range of sulfur species, including ones that are highly aromatic, due to its finely dispersed metal and high reactivity. SiGNa's method is capable of performing desulfurizations at room temperature and pressure with simpler and safer reaction conditions.

#### Diphenyl sulfide Reduction



#### Dimethyldibenzothiophene Reduction



### Benefits

- Can be performed in either batch or continuous-flow reactor setup
- Provides a smooth solution process at room temperature and pressure
- Enhanced selectivity and kinetics of reaction
- Capable of chemically removing sulfur from highly aromatic sulfur systems

# Alkali Metal-Silica Gels

## Hydrogenation

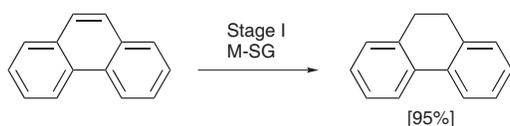
### Classical Method

Typical hydrogenation reactions result in the addition of hydrogen (H<sub>2</sub>) to unsaturated organic compounds in the presence of a metal catalyst. These hydrogenations are limited to specific equipment and expensive precious metal catalysts or difficult reaction conditions with cheaper catalyst alternatives.

### SiGNa's Method

The SiGNa hydrogenation method does not require expensive catalysts or high pressure hydrogen to complete the conversion due to its electron-donating mechanism. SiGNa's materials and method perform hydrogenations in a smooth solution process at room temperature and pressure utilizing simple sources of hydrogen (water, alcohol, ammonium phosphate, etc.).

#### Phenanthrene Hydrogenation



#### Stilbene Hydrogenation



### Benefits

- Performed in either batch or continuous-flow reactor setup in safe solvents
- Provides a smooth solution process at room temperature
- Hydrogen can be supplied by either homogeneous or heterogeneous sources
- Enhanced selectivity and kinetics of reaction

## Phosphine Reduction

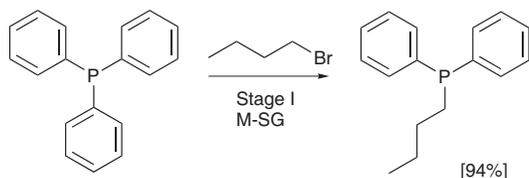
### Classical Method

Many phosphine derivatives are important industrial compounds with applications as synthetic intermediates or as ligands in a variety of homogeneous and heterogeneous synthetic processes. Their derivatization, however, has many difficulties associated with it, including the need for dissolving metal conditions, or a metal dispersion setup.

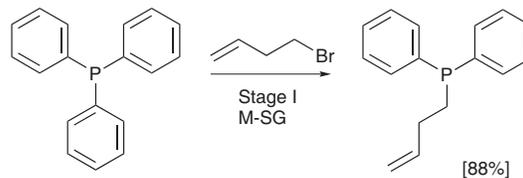
### SiGNa's Method

Phosphine reduction using SiGNa's method removes the reaction challenges and allows for improved reaction control with no need for low temperatures. The SiGNa method increases solvent choice, selectivity and yield and allows high concentration reactions at ambient conditions.

#### Triphenylphosphine Reduction



#### Triphenylphosphine Reduction



### Benefits

- Provides a smooth solution process at room temperature
- Can be performed in high concentrations to limit solvent requirements
- Can be performed in either batch or continuous-flow reactor setup in convenient and safe solvents
- Enhanced selectivity and kinetics of reaction