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Alkali Metals Plus Silica Gel: Powerful Reducing Agents and Convenient Hydrogen Sources

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Alkali metals absorbed into silica gel yield three types of loose black powders (M−SG) that are strong reducing agents. All react nearly quantitatively with water to form hydrogen. Liquid NaK alloys form air-sensitive powders at room temperature that can be converted at 150 °C to a form that is sensitive to moisture but not to dry air. Slowly heating sodium and silica gel to 400 °C yields a third type that can be handled in ambient air with only slow degradation by atmospheric moisture. These materials eliminate many hazards associated with pure alkali metals by providing easily handled reducing agents and hydrogen sources. In continuous-flow reactors, they could reductively protonate aromatics, dechlorinate alkyl and aryl halides, and desulfurize various compounds.

Synthetic and industrial chemistry has long tried to take full advantage of the reducing power of alkali metals. They have been used as dispersions, or on inert supports, or as solutions in liquid ammonia[1] to carry out Birch reductions, Wurtz reactions, and many others.[2] Although industrially useful, these reactions can be difficult to scale up because of low reaction efficiencies or rates and complications in handling such pyrophoric reagents.

Alkali metals, at concentrations up to 12 mol %, can be absorbed from the vapor phase into aluminosilicate[3] or pure silica zeolites.[4] This report describes the incorporation of up to 60 mol % alkali metals from the liquid metal phase into amorphous silica gel (porous SiO_2). Three different preparations of alkali metal−silica gel adducts (designated M−SG, stages 0, I, II) provide a range of reducing abilities and air-sensitivities.

Liquid sodium−potassium alloys are readily absorbed by silica gel (SG) to form shiny black stage 0 powders. Figure 1 shows the conversion of SG particles, initially coated with 35 wt % of a liquid Na_2K alloy, to a powder that has absorbed all the alloy. Some nanoscale alkali metal particles are present, as shown by the characteristic reduction of the melting point commonly seen for small particles.[5] The differential scanning calorimetry (DSC) trace for stage 0 Na_2K (Figure 2A) shows that melting begins at −25 °C rather than the normal value of −12.6 °C. Stage 0 powders must be handled in an inert atmosphere (e.g., within a nitrogen-filled glovebag) to avoid hydrogen ignition in high humidity air. However, they are loose powders that can easily be packed in chromatographic columns to provide a medium for continuous-flow chemical reductions. Of course, the solvent used must not be reducible by M−SG.

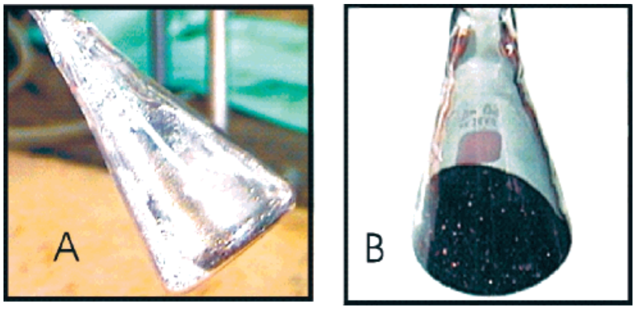

Figure 1. Room-temperature absorption of Na_2K alloy into Davisil Grade 646 silica gel (Aldrich, 15-nm nominal pore size) in a 50-mL modified Erlenmeyer flask. (A) The SG coated with alkali metal alloy just after mixing. (B) The final loose black powder (stage 0) formed by shaking the sample shown in A for a few minutes.

Stage 0 samples, when heated to about 150 °C, form stage I powders that show little or no melting endotherm by DSC (Figure 2B). Exposure to dry oxygen for up to a day does not change the *reducing capacity* (the amount of hydrogen produced by reaction with water). Stage I samples are stable in closed columns and have been stored for up to eight months in screw-cap vials without any change in the reducing capacity.

Uniform black powders of stage I Na−SG can be made by heating Na with SG to ~165 °C with continual agitation. DSC traces show no melting endotherm of Na metal but only a broad exotherm ($\Delta H \approx -25$ kJ/mol of Na) from 100 to 450 °C. When heated slowly to 400 °C with intermittent agitation, sodium metal and SG react to form uniform powders of stage II Na−SG. The bulk density at this concentration is about 0.7 g/cm^3. DSC traces of Na with SG (Figure 2C) show that the process is exothermic, with ΔH in the range of −75 kJ/mol of metal. The melting endotherm of Na metal, present in the initial trace at 98 °C, is absent in the subsequent run, showing that the metal has reacted with the silica gel. The highest concentration at which all of the Na reacts is ~40 wt % Na. Stage II Na−SG shows no peaks in the DSC up to 450 °C.

Stage II powders of Na−SG are easily handled in an open ambient environment and do not change with time when kept in a closed container. They are slightly less reducing than stages 0 and I but react rapidly with water to yield the same amounts of pure hydrogen gas, as measured by a method described elsewhere.[4b] Because of its significantly lower reactivity toward air, even in the presence of mild humidity, stage II Na−SG reduced silica would be the material of choice for hydrogen production, solvent drying, and those reduction reactions that do not require the stronger reducing properties of stages 0 or I.

Preliminary atomic pair distribution function measurements similar to those applied to "inorganic electrides"[4c] suggest that stage I samples retain mostly SiO_2 character and that stage II Na−SG contains nanoparticles of Na_4Si_4.[6] The fate of the released electrons in stage I M−SG remains a mystery. Are they delocalized in a high energy band of silica, or have they partially reduced the silica, or are they present in the void spaces along with partially ionized cations, as with "inorganic electrides"?

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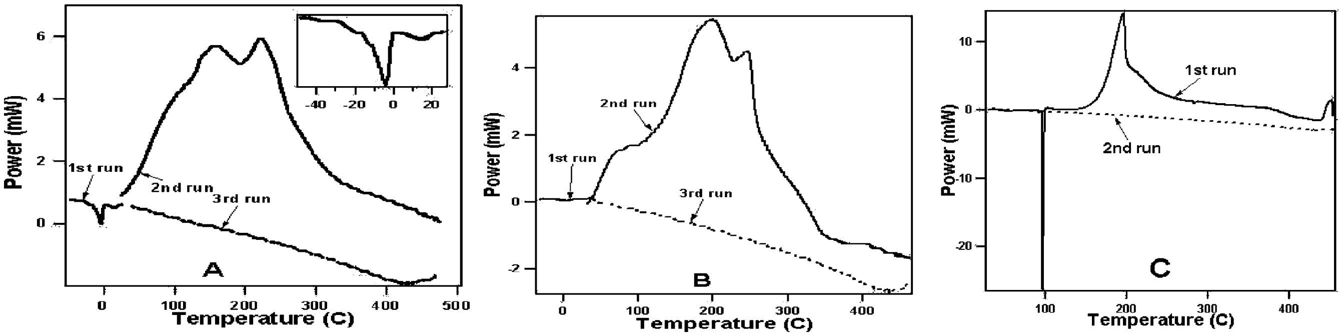

Figure 2. (A) DSC traces for 9.2 mg of stage 0 Na_2K in SG. The inset shows the region of melting. The overall value of ΔH is ~ -100 kJ/mol of metal. (B) DSC traces for 12.5 mg of stage I NaK_2 in SG. Note the absence of a melting endotherm. The overall value of ΔH is ~ -35 kJ/mol of metal. (C) DSC traces for a mixture of 4.6 mg of Na and 6.6 mg of SG, which react exothermically to form stage II material. The endothermic heat of melting of Na (113 J/g Na), which appears at 98 °C in the initial scan, is absent in the repeat scan.

Organic reductions in tetrahydrofuran (THF) were carried out *at room temperature* in a nitrogen-filled glovebag, either by stirring batch reactions with M−SG or by passing the solution through a 2-mL Pasteur pipet that had been plugged with Pyrex glass wool and filled with M−SG. Analyses before and after reaction were made by ^{1}H and ^{13}C NMR and GC−MS. The effective reduction potentials of the various stages of M−SG can be determined by comparing their ability to form highly colored aromatic radical anions with the reduction potentials listed by Szwarc[7] (biphenyl = 0). Stage 0 M−SG can reduce biphenyl to its radical anion. Stage I powders reduce naphthalene (0.043 V) and phenanthrene (0.142 V). Even stage II materials, which can be handled in air, are able to reduce pyrene (0.529 V) and anthracene (0.642 V) to their radical anions. M−SG materials can serve as effective drying agents and anti-oxidants for aprotic solvents such as THF. Care must be taken not to expose flammable solvents that contain particles of M−SG to air, since spontaneous ignition could occur.

Anthracene in THF underwent Birch reduction[1a] (5 min elution time) to 9,10-dihydroanthracene in >99% purity upon elution through a chromatography column that contained either stage 0 or stage I M−SG mixed with an equal volume of silica gel (to provide a proton source). In the absence of a proton source, all three stages yielded stable THF solutions that contained anthracene radical anions, as verified by the optical spectrum (Supporting Information).

Reductions such as the Wurtz reduction of halogenated organic compounds[1b,c] can be violent with alkali metals but occur smoothly with M−SG. Benzyl chloride reacted by Wurtz coupling in both chromatographic (stages 0 and I) and batch (stage II) processes to form bibenzyl as the only product. Other dehalogenations include the dechlorination of chlorobenzene, 1,2-dichlorobenzene, and neopentyl chloride. Thus, both aromatic and aliphatic halocarbons can be dehalogenated by M−SG.

Slow alkali metal reduction of aromatic sulfur compounds in hydrocarbon solvents can occur at high temperatures.[8] With M−SG the reduction of dibenzothiophene in THF to biphenyl by continuous (stage 0) and batch reactions (0 and I) is readily accomplished at room temperature. Even the normally difficult desulfurization of 4,6-dimethyl dibenzothiophene occurred in a batch process with stage 0 material. Surprisingly, the historically difficult[9] reduction of diphenyl sulfide to biphenyl was also accomplished in 2 h via bulk reaction with stage I Na_2K−SG.

The powerful reducing properties of alkali metal−silica gel adducts should permit the use of continuous-flow columns for the reduction of organic and inorganic compounds that are now reduced by alkali metals. In addition, they provide the ability to provide hydrogen gas upon demand from air-stable, easily handled sources that can be stored indefinitely.

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Supporting Information Available: Materials and methods, reaction schemes, and product identification. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Savoia, D.; Trombini, C.; Umani-Ronchi, A. *Pure Appl. Chem.* **1985**, *57*, 1887−1896. (b) Levy, J.; Tamarkin, D.; Selig, H.; Rabinovitz, M. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 1033. (c) Rabideau, P. W. *Tetrahedron* **1989**, *45*, 1579−1603.
(2) (a) Birch, A. J. *Pure Appl. Chem.* **1999**, *68*, 553−556. (b) Billington, D. C. In *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon Press: New York, 1991; Vol. 3, pp 413−423.
(3) (a) Edwards, P. P.; Anderson, P. A.; Thomas, J. M. *Acc. Chem. Res.* **1996**, *29*, 23−29. (b) Rabo, J. A.; Angell, P. H.; Kasai, P. H.; Schomaker, V. *Discuss. Faraday Soc.* **1966**, *41*, 328−349. (c) Srdanov, V. I.; Stucky, G. D.; Lippma, E.; Engelhardt, G. *Phys. Rev. Lett.* **1998**, *80*, 2449−2452.
(4) (a) Ichimura, A. S.; Dye, J. L.; Camblor, M. A.; Villaescusa, L. A. *J. Am. Chem. Soc.* **2002**, *124*, 1170−1171. (b) Wernette, D. P.; Ichimura, A. S.; Urbin, S. A.; Dye, J. L. *Chem. Mater.* **2003**, *15*, 1441−1448. (c) Petkov, V.; Billinge, S. J. L.; Vogt, T.; Ichimura, A. S.; Dye, J. L. *Phys. Rev. Lett.* **2002**, *89*, 075502.
(5) Unruh, K. M.; Huber, T. E.; Huber, C. A. *Phys. Rev. B* **1993**, *48*, 9021−9027.
(6) (a) Witte, J.; Schnering, H. G. *Z. Anorg. Allg. Chem.* **1964**, *327*, 260−273. (b) He, J.; Klug, D. D.; Uehara, K.; Preston, K. F.; Ratcliffe, C. I.; Tse, J. S. *J. Phys. Chem. B* **2001**, *105*, 3475−3485.
(7) Szwarc, M. *Carbanions, Living Polymers and Electron-Transfer Processes*; Interscience: New York, 1968; p 314.
(8) Yu, Z.; Verkade, J. G. *Energy Fuels* **1999**, *13*, 23−28.
(9) Hauptman, H.; Walter, W. F.; Marino, C. *J. Am. Chem. Soc.* **1958**, *80*, 5832−5835.

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