Silicon Alkoxides and Lunar Development

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In Situ Resource Utilization

- Necessary for establishing a space infrastructure
  - for bulk commodities especially
  - mass prohibitive!
- Regolith unpromising feedstock
  - comminuted common rock
  - mostly silicates
  - not used on Earth!

Regolith at Apollo 11 site

High-Temperature Silicate Processing, I

- DIRECT PYROLYSIS – “brute force” (~2500 C!)
  - On cooling, get O_2 plus elements and oxides from disproportionation of high-temperatue oxides
- At least it’s simple!
  - minimal reagent importation
  - but some obvious issues...

High-Temperature Silicate Processing, II

- “MAGMA ELECTROLYSIS”
  - electrolyze silicate melt, e.g.
  - $(Mg,Fe)_2SiO_4 \rightarrow Fe + MgO + ½\ O_2 + SiO_2$
    olivine
- Conceptually elegant
  - but again some obvious issues...

A note on regolith…

- Largely fine-grained--*already* comminuted!
  - grinding, crushing a major expense in ore processing
  - nice to have *something* easier…
- Fine grain size leads to higher reactivity
  - should make chemical processing approaches easier!

Low-Temperature Silicate Processing?

- Hindered by familiar unreactivity of silicates
  - consider macroscopic labware!
  - strong base only common etchant
    - slow reaction rates
- Motivated considering F-based reagents
  - *serious* handling and safety concerns
  - SiF_4 also a very stable and not immediately useful product

Low-Temperature Silicate Processing, II

HOWEVER!

- Certain organic-based reagents can attack silicates
  - surprising and not well known
- Potential advantages:
  - considerably less toxic
    - byproducts such as H_2O and alcohols recycled by life-support system
  - immediately useful products
  - Also lead to hydrometallurgical extraction of metals

Silicon Alkoxides

- Focus of this talk
- Motivations:
  - immediately useful for several potential applications
  - can be synthesized *directly* from silicate feedstock
  - synthesis by-products also potentially useful feedstock

So, what are they?

Silicon Alkoxides (“alkyl silicates”)

- Esters of monomeric or polymeric “silicic acids”
  - volatile liquids, many relatively low toxicity
- General Formulas
  - alkoxysilanes, “silicon alcoholates”
    - $Si(OR)_4$, R an alkyl group such as ethyl (C_2H_5)
  - alkoxysiloxanes, “silicate alcoholates”
    - siloxane (“silicone”) “backbone”, such that at least one Si-O-Si link is present
      - “already condensed”
    - simplest example: $(RO)_3SiOSi(OR)_3$

So, what are they good for?

Sol-Gel Processing

Alkoxides are immediately useful products!

Hydrolysis of alkoxides, e.g.

$$Si(OR)_4 + 2\ H_2O \rightarrow SiO_2 + 4\ ROH$$

provides a low-temperature pathway to ceramics

- less energy intensive

- Lunar advantage: The organic reagent (alcohol) is regenerated on curing!

Enormous current (terrestrial) interest!

Most relevant alkoxide

$Si(OR)_4$, where "R" = ethyl (C_2H_5, Et)

i.e., $Si(OEt_4)$

- *tetraethyoxysilane* ("tetraethyl silicate" in the older literature)
- "TEOS" either way!
- *Considerably* less toxic
  - byproduct of hydrolysis is just ethanol

Conventional Alkoxide Synthesis

- Directly from elemental silicon via $SiCl_4$ (tetrachlorosilane, silicon tetrachloride)

NOT relevant to lunar conditions!!

Low-Temperature Routes to Si Alkoxides, I a

- "Esterification" in acidic alcohol solution, e.g.:

  Mg_2SiO_4 + 4 ROH + 4 H^+ $\rightarrow$
(olivine) (alcohol) (acid)

  $Si(OR)_4$ + 2 Mg^{++} + 4 H_2O
- Direct synthesis from inorganic silicates
- Driven to right by “scarce water” conditions
- Works for silicates having isolated anions (as with SiO_4 here)
  - such silicates are “gelatinized” by strong acid—a traditional mineralogical test

Low-Temperature Routes to Si Alkoxides, I b.

- The "backbone" of a more complex anion is commonly preserved, e.g.
  $Ca_2ZnSi_2O_7 + 6\ EtOH + 6\ H^+ \rightarrow$
  hardystonite   ethanol
  $Et_3SiOSiEt_3 + 2\ Ca^{2+} + Zn^{2+} + 6\ H_2O$

- REFS: Goodwin & Kenney, 1988, 1989, 1990

Low-Temperature Routes to Si Alkoxides, I c.

- Acidified alcohol may also work for high-aluminum aluminosilicates
  - where Al substitutes for Si in the 3D silicate framework
  - such silicates *also* gelatinize in acid sol'n
    - K. J. Murata, 1943, 1946
  - H^+ attacks the O-Al-O link
  - Relevant to lunar anorthite, $CaAl_2Si_2O_8$
    - makes up much of highlands regolith
  - might yield a mixture of oligomeric species (small alkoxysiloxanes)
    - if necessary, could be fractionally distilled
    - has never been tested experimentally!

Low-Temperature Routes to Si Alkoxides, II

- Si alkoxides from dialkyl carbonates:
  - $SiO_2 + 2\ (RO)_2CO \rightarrow Si(OR)_4 + 2\ CO_2$
    ~ 300º C
    - route to silicon alkoxides directly from silica
    - possibly also from other polymeric silicates (e.g., regolith glass, pyroxenes)
      - has also not been tested experimentally!

  - *REF: Akiyama, Ono, & Suzuki, 1992, 1993*

Low-Temperature Routes to Si Alkoxides, III

- Through triethanolamine [$(C_2H_4OH)_3N$, $teaH_3$]
  - $SiO_2 + 2\ teaH_3 \xrightarrow{\sim 200°C,\ NaOH} Si(tea)(teaH_2) + 2\ H_2O$
- followed by reaction in acidified alcohol:
  - $Si(tea)(teaH2) + 4\ ROH \xrightarrow{HCl,\ ROH} Si(OR)4 + 2\ teaH3$
- Another route to Si alkoxides directly from silica
  - Also other polymeric silicates?

- *REF: Kemmitt & Henderson, 1998*

Stretching Resources: Alkoxides as Glues and Binders

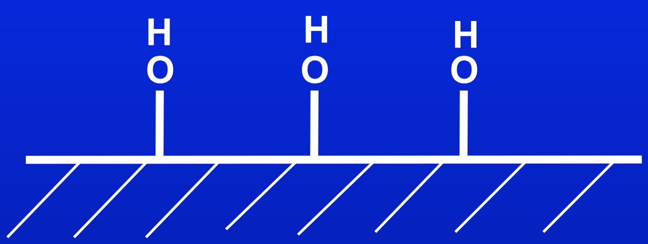
- Alkoxide-derived ceramics impractical for large structures
  - at least in near term!
- Therefore, must stretch the lunar-manufactured alkoxide by using as a glue, binder, or sealer
  - “Ethyl silicate” (i.e., TEOS) used to make “adhesive silica” decades ago
    - early application of sol-gel technology
- One idea: “bricks” from a slurry of raw regolith and alkoxide
  - cure indoors, so regolith particles are hydroxylated and alcohol vapor recycled

Hydroxylation of oxide/silicate surfaces

+ H_2O (trace)

Anhydrous oxide surface

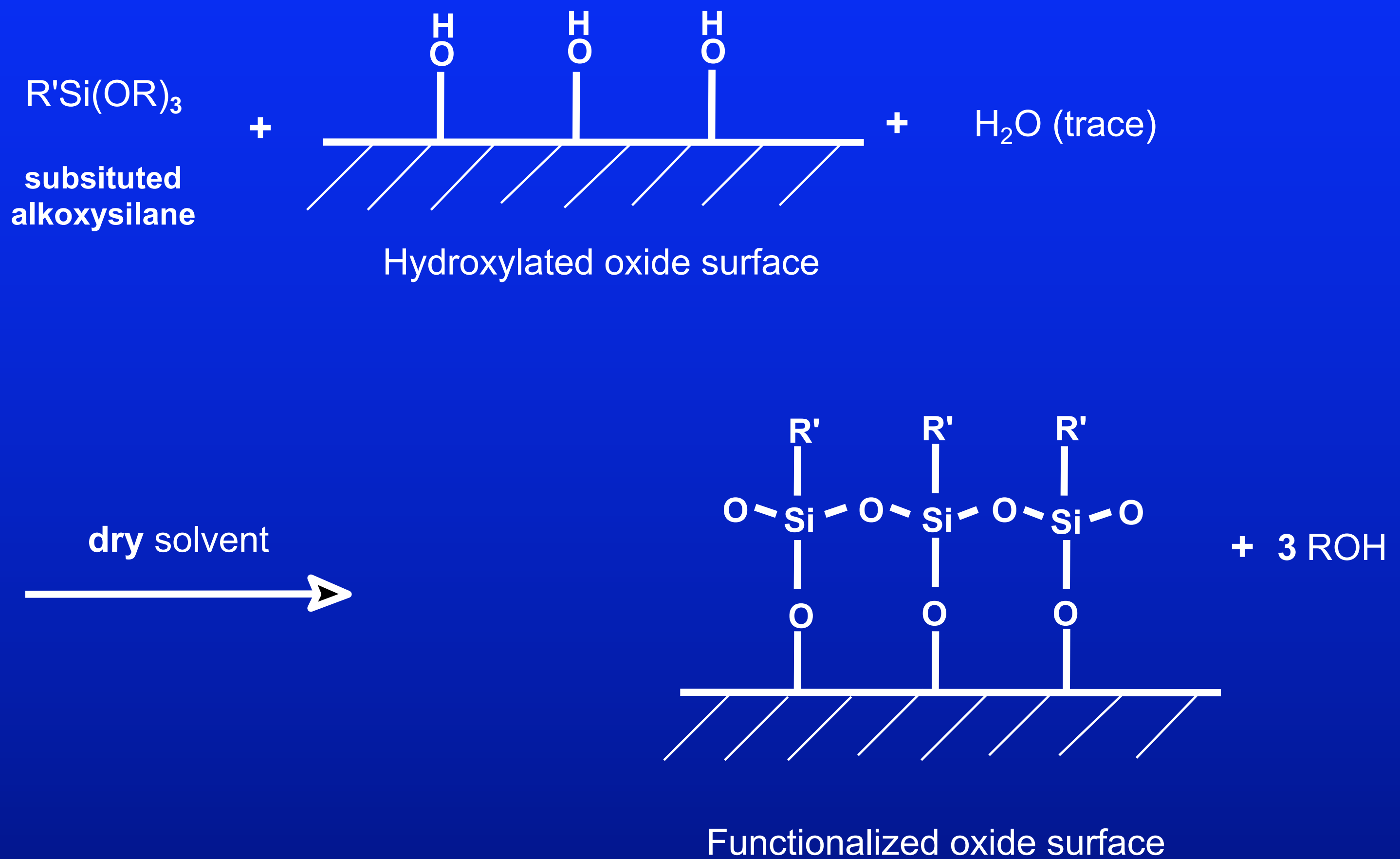
Hydrolysis by
unsatisfied valences



Hydroxylated oxide surface

Hydroxylation happens automatically in the presence of a trace of water vapor.

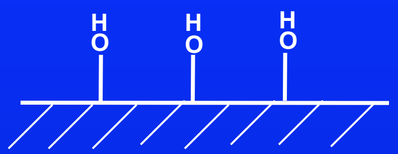
Functionalization of oxide surfaces



Binding silicate particles with alkoxides

x $Si(OR)_4$ +

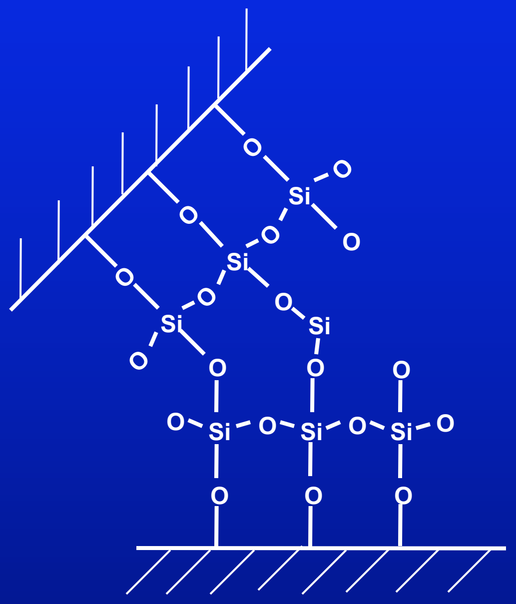
alkoxysilane



+ H_2O (trace)

Hydroxylated silicate particle surfaces

$\longrightarrow$



+ x ROH

Particles crosslinked by disiloxy links

Si Alkoxides as Feedstock, I a

- For ultrapure semiconductor-grade Si
  - TEOS liquid, can be purified by distillation
- Pyrolysis
  - for CVD?
    - some experiments
      - SiO_2 interfering product
    - further work seems promising

Si Alkoxides as Feedstock, I b

- Chemical reduction
  - by (lunar-derived?) electropositive metal, e.g.
  - $Si(OR)_4 + 2\ Mg \rightarrow Si + 2\ Mg(OR)_2$
  - may also be route to producing Grignard reagents (more anon)

Si Alkoxides as Feedstock, II

- Siloxane ("silicone") manufacture
  - e.g.,
    $n\ Si(OR)_4 + 2n\ R'MgX \rightarrow$
    Grignard reagent; X = Cl, Br, I
    $[SiO(R')_2]n + n\ Mg(OR)_2 + n\ Mg(OR)X$
    (as well as side reactions)
  - If siloxanes prove sufficiently useful, lunar manufacture and recovery of the Grignard reagent may prove attractive

By-products as feedstocks

- Alkoxide synthesis yields metal salts corresponding to mineral acid used
  - e.g., chlorides for HCl
  - $MgCl_2$ from olivine processing
- Chlorides are *much* easier to electrolyze than oxides!
  - Cl_2 recovered
    - straightforward to reconstitute HCl
  - and metal extracted!

Let’s go back!