Traditional Aqueous Routes

Advantages

Simple Equipment
Inexpensive Materials
Well Studied

Disadvantages

Difficult control of hydrolysis and condensation rates
Inhomogeneity introduced by homocondensation
Reversibility of condensation step
Phase Separation

$$\text{M-O-M'} + \text{H-O-H} \rightleftharpoons \text{M-OH} + \text{HO-M'}$$

$$2\ \text{M-OH} + 2\ \text{HO-M'} \rightleftharpoons \text{M-O-M} + \text{M'-O-M'} + 2\ \text{HOH}$$

Nonaquoeus – Nonhydrolytic – Organometallic Methods

Advantages

Inhomogeneity and phase separation prevented
absence of water, volatile organic byproducts cannot cleave M-O-M’ bonds and cause homocondensation, irreversible condensation step

M = mononuclear, polynuclear clusters, building blocks

$$\text{M-O-X} + \text{Z-M'} \longrightarrow \text{X-Z} + \text{M-O-M'}$$

Chemical control of reactivity by selecting X, Z groups

Wide choice of solvents, medium polarity, reaction temperature

Simplified drying to aerogels, lower surface tension

Nonaquoeus – Nonhydrolytic – Organometallic Methods

Advantages

Synthesis of hybrid materials
incorporation of water sensitive and water insoluble compounds:
organometallics, coordination compounds, long aliphatic chains, clusters
hydrophobic hybrid materials

Template syntheses
use of water sensitive and water insoluble compounds, polymers
microporous and mesoporous

Retention of lower coordination numbers (Al, TM), low-hydroxyl surfaces – catalysis

Nonaquoeus – Nonhydrolytic – Organometallic Methods

Disadvantages

- Elaborate procedures and expensive precursors

- Organic solvents

- Exclusion of moisture

- Ligand scrambling vs. elimination

Nonaquoeus – Nonhydrolytic – Organometallic Methods

Solid-state: solid-state thermolysis

Liquid-state: sol-gel, solventless, sonochemical reactions, solution thermolysis

Gas-phase: CVD, pyrosol

Preparation of Oxides, Mixed Oxides, and Silicates

Alkylhalide Elimination

Ester Elimination

Alkene Elimination

Acetamide Elimination

Ether Elimination

Ketene Elimination

Ketimine Elimination

Alkylhalide Elimination Reactions

M = Si, Al, Ti, Zr, V, Nb, Mo, W, Fe

M-X + R-O-M' ⟶ M-O-M' + R-X

M-X + R-O-R ⟶ M-O-R + R-X

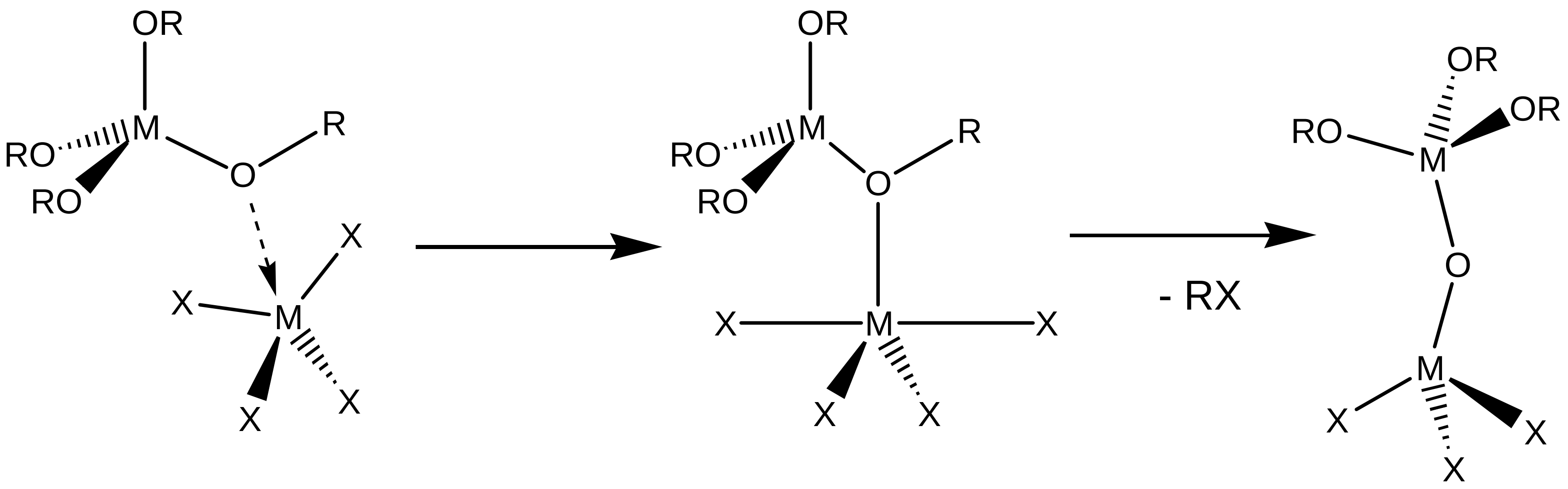
M-O-R + X-M' ⟶ M-O-M' + R-X

M-X + H-O-R ⟶ M-O-R + HX

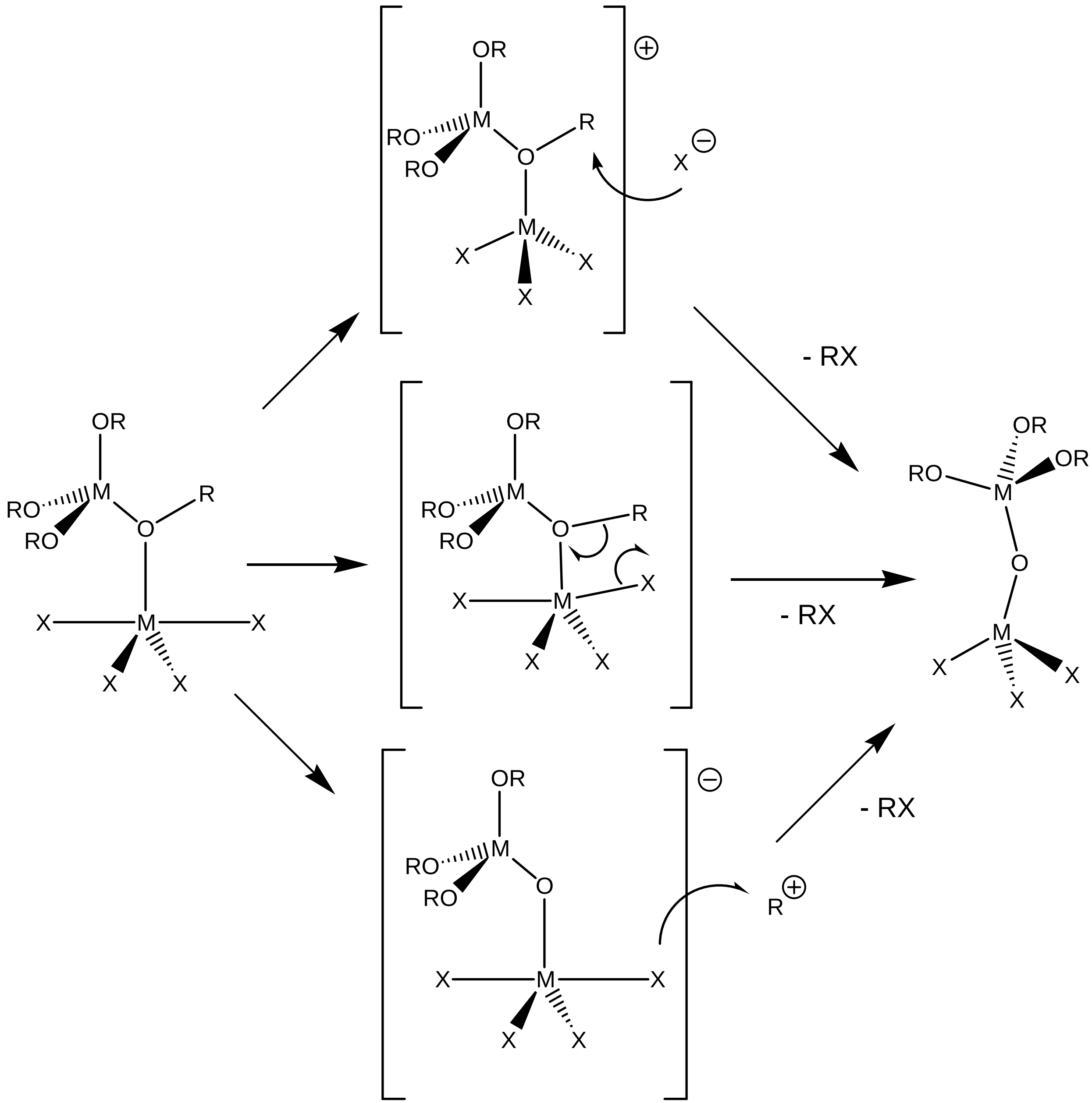
M-O-R + X-M' ⟶ M-O-M' + R-X

Corriu, Vioux, Leclercq, Mutin, Montpellier
Hay et al., Surrey

Alkylhalide Elimination Reactions



C-O bond cleavage



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Alkylhalide Elimination Reactions

$$TiCl_4 + Ti(OR)_4 + TOPO \xrightarrow[]{\text{heptadecane, 300 °C}} TiO_2 \text{ anatase, 10 nm} + RCl$$

R = Me, Et, *i*-Pr, *t*-Bu

Colvin et al., *J. Am. Chem. Soc.*, **1999**, *121*, 1613

Alkylhalide Elimination Reactions

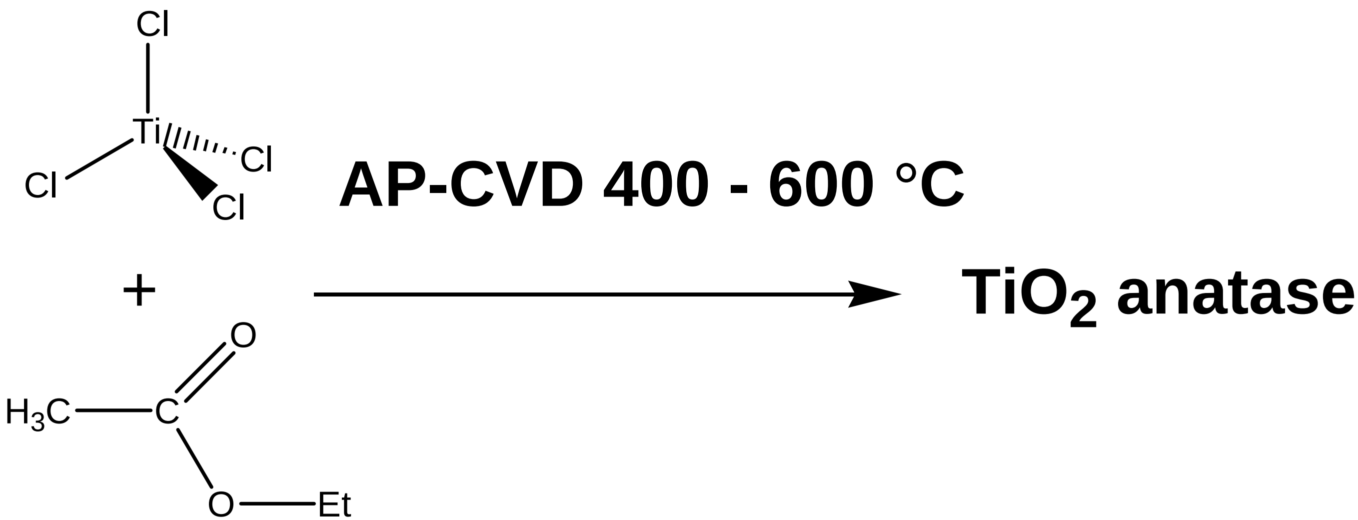
$$AlCl_3 + Si(OEt)_4 + Et_2O \xrightarrow{CCl_4,\ 110\ °C} \text{Al-O-Si gel}$$

$$\text{Al-O-Si gel} \xrightarrow{900\ °C} 3Al_2O_3 \cdot 2SiO_2$$

mullite

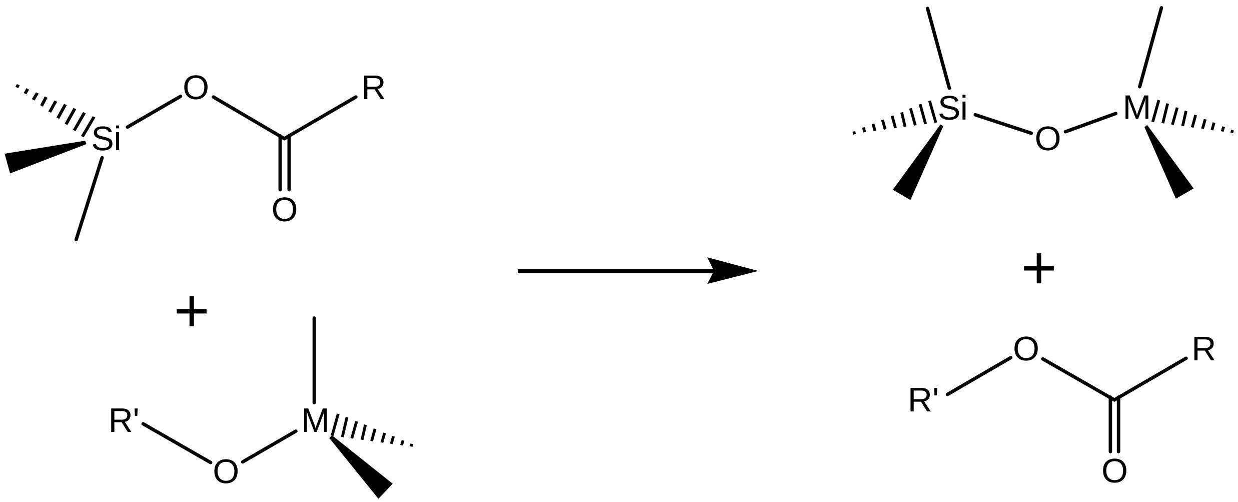
Janackovic et al., *NanoStructured Materials*, **1999**, *12*, 147

Alkylhalide Elimination Reactions



Parkin I. et al., *Chem. Mater.*, **2003**, *15*, 46

Ester Elimination Reactions: acetates + alkoxides



M = Zr, Si, Ti, Ba, Sn, Pb

Jansen, Guenther, *Chem. Mater.*, **1995**, *7*, 2110

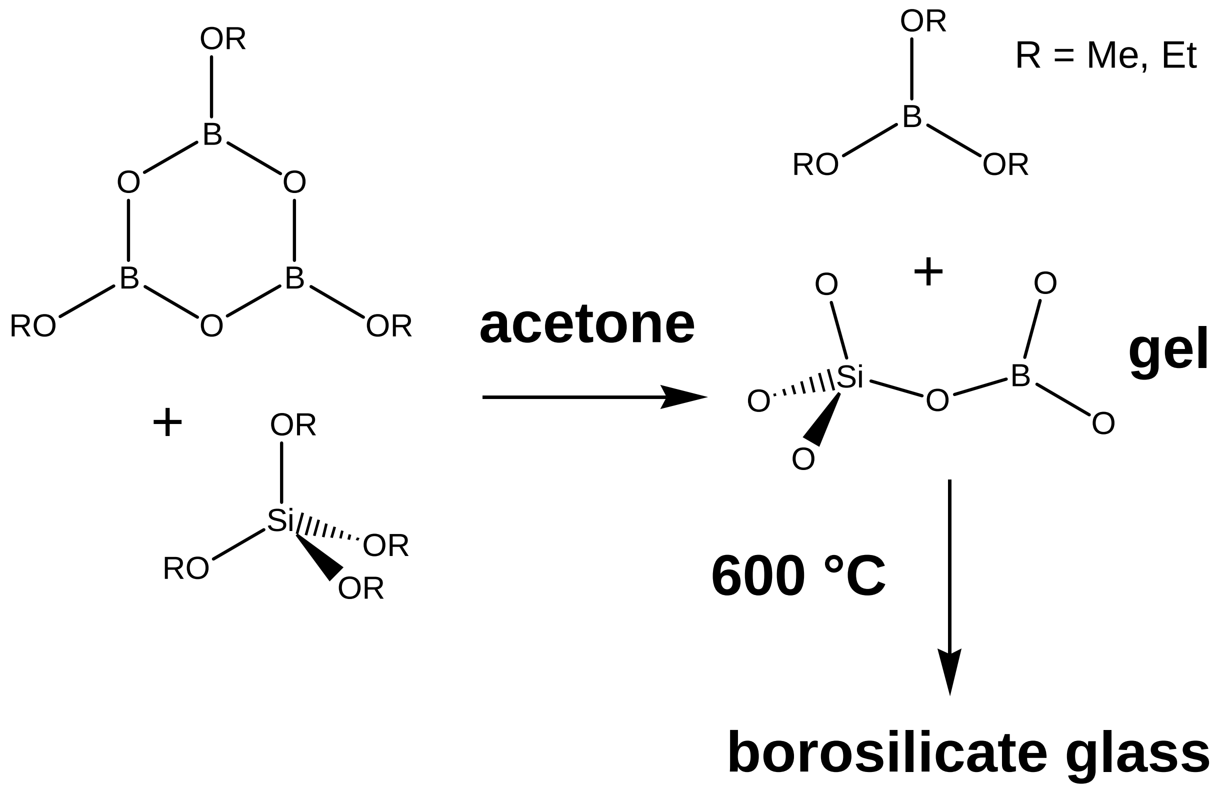
Hampden-Smith et al., *Chem. Comm.*, **1995**, 157

Ester Elimination Reactions: alkoxides + acid anhydrides

M = Si,   M' = Ti

Fujiwara et al., *Chem. Mater.*, **2002**, *14*, 4975

Ester Elimination Reactions: alkoxides + acid anhydrides



Becket et al., *Chem. Comm.*, **2000**, 1499

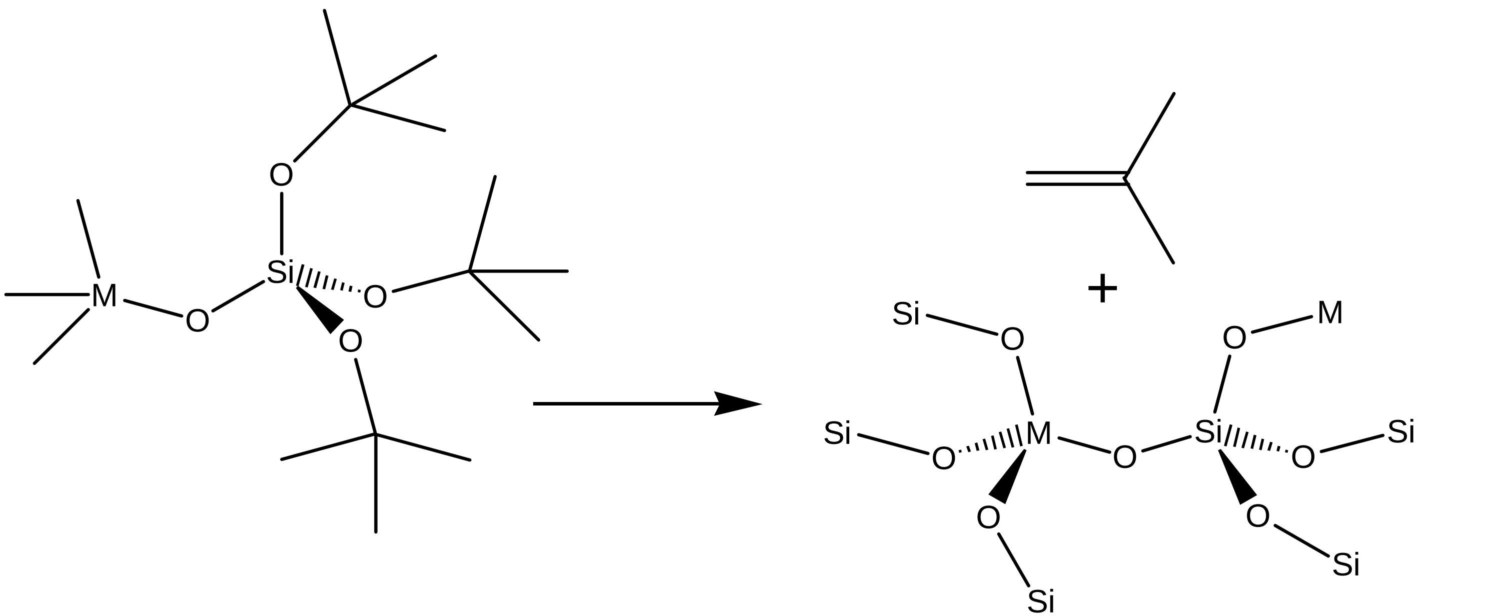
Ester Elimination Reactions

$$Ti(NO_3)_4 + Si(OEt)_4 \xrightarrow{\text{CVD , 300 - 535 °C}} SiO_2/TiO_2 + 4\ EtONO_2$$

Gladfelter et al., *Chem. Mater.*, **2000**, *12*, 2822

Alkene Elimination: *tris*(tert-butoxy)silanolates

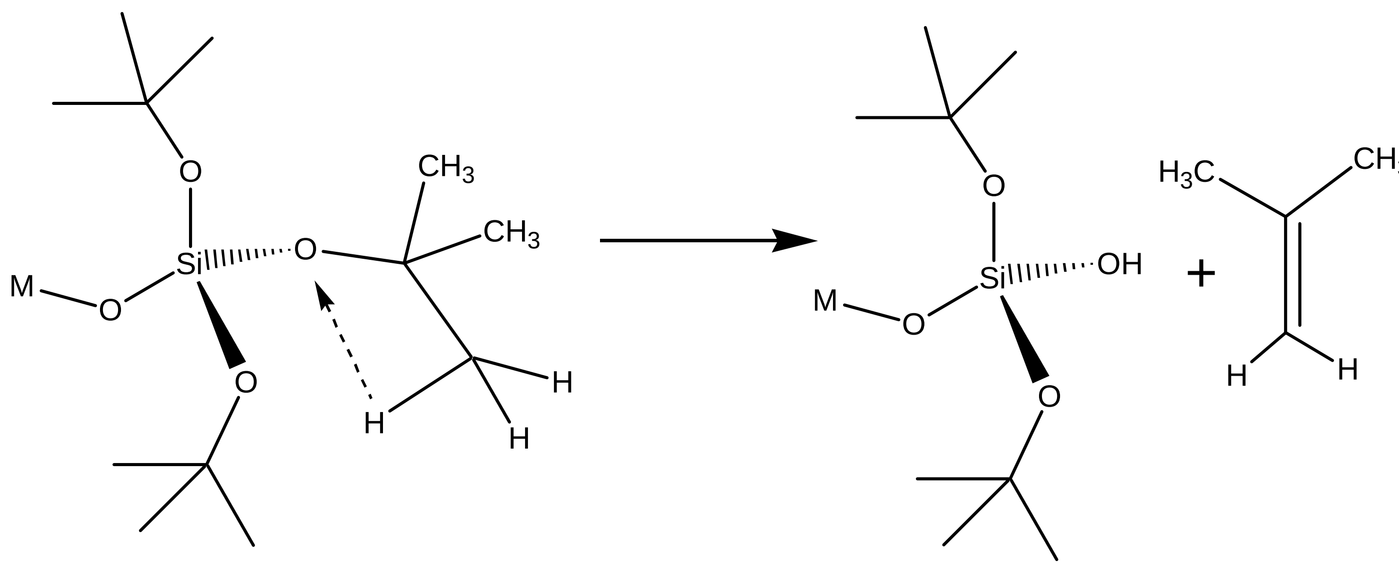
M = Ti, Zr, Hf, Al, Cr, Cu, Zn, Mo, W, V



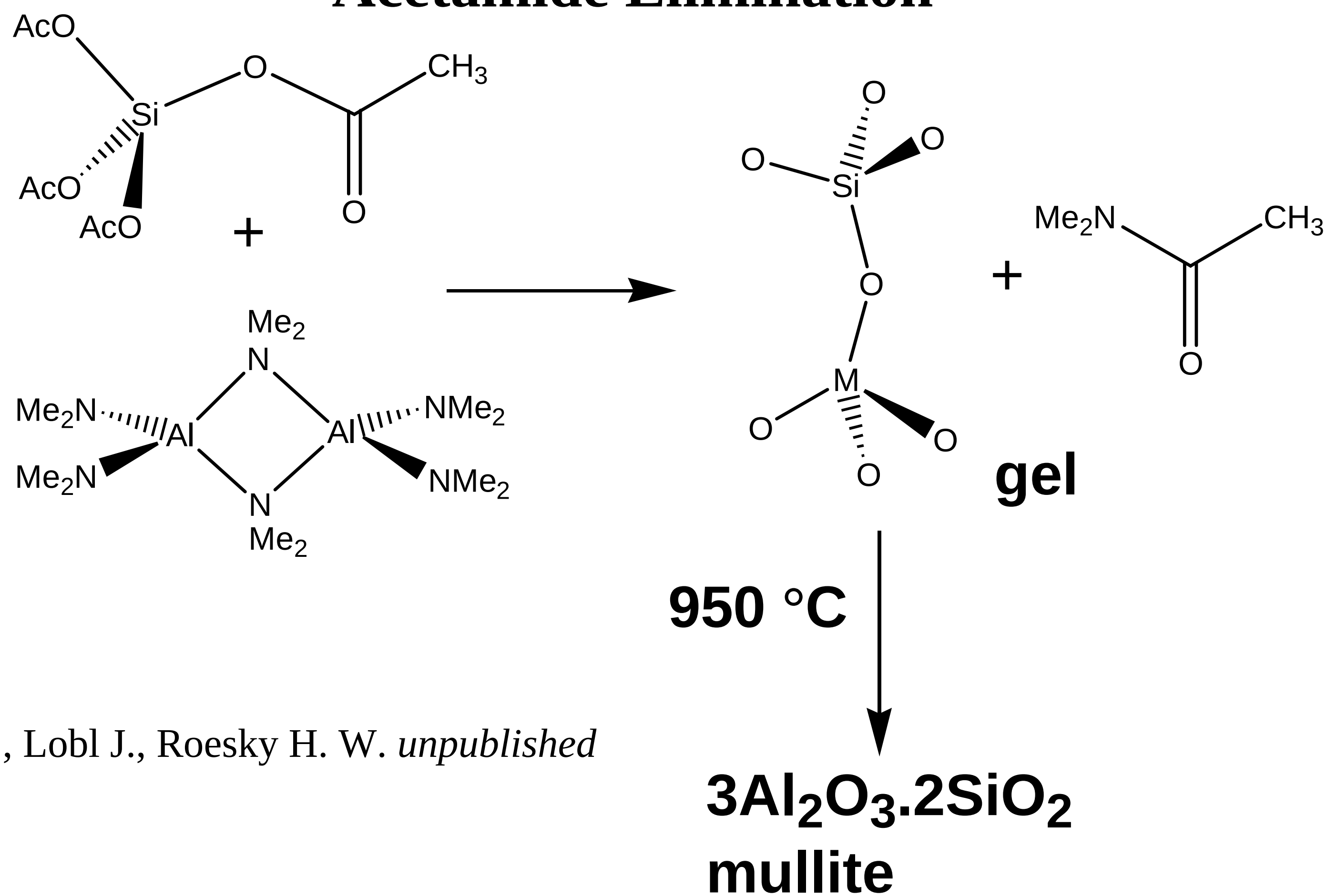
Tilley et al., Berkely

Alkene Elimination: *tris*(tert-butoxy)silanolates

β-Hydrogen Elimination

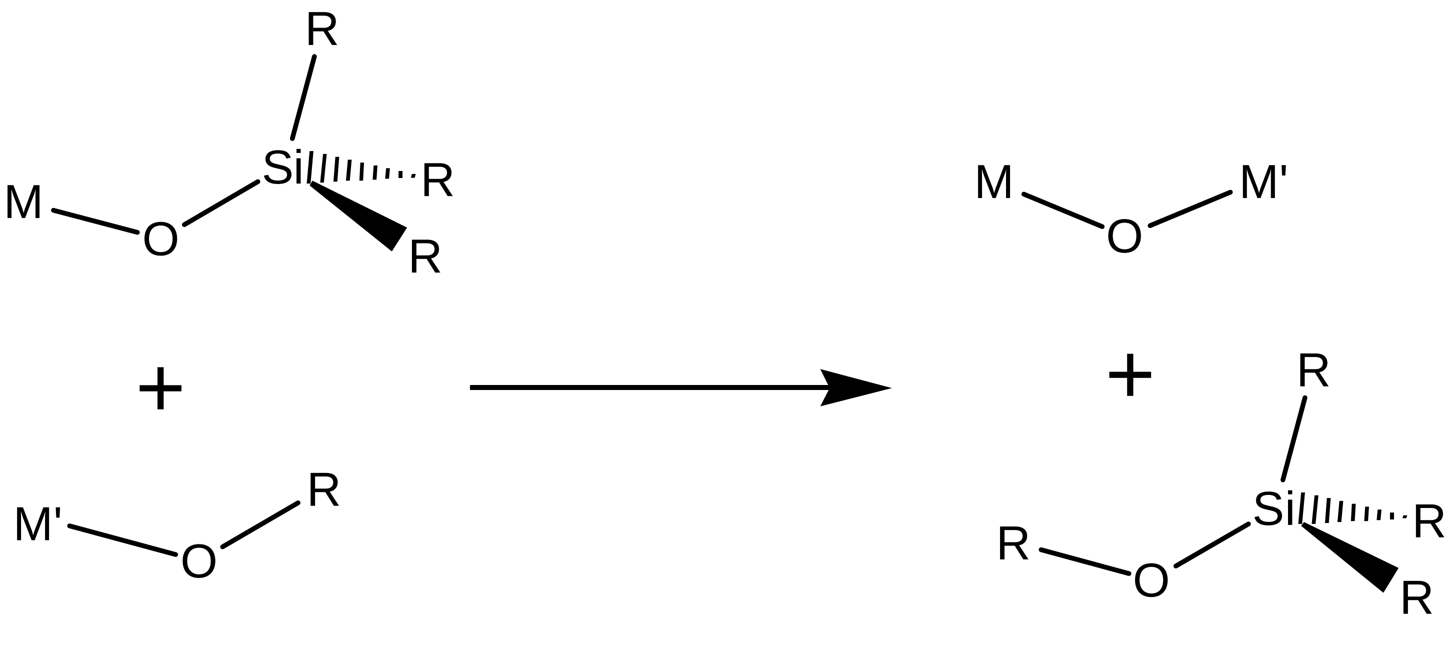


Acetamide Elimination



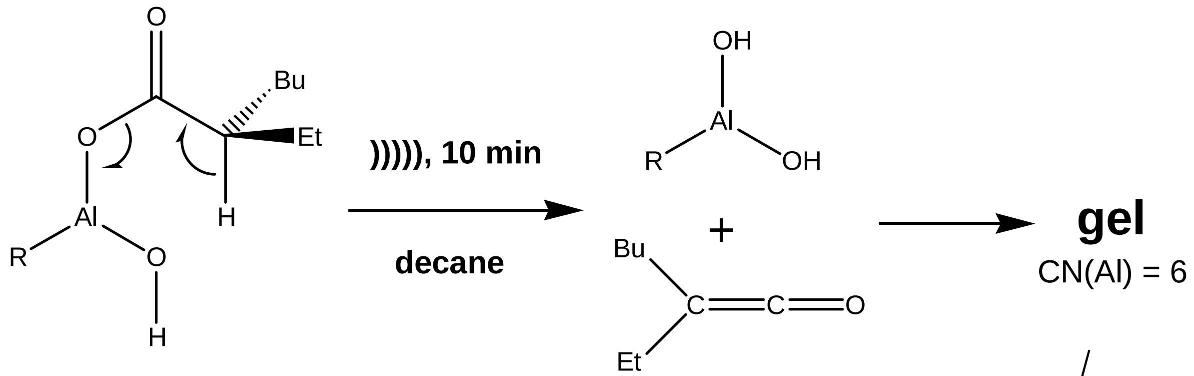
Pinkas J., Lobl J., Roesky H. W. *unpublished*

Ether Elimination



Hampden-Smith et al.,

Ketene Elimination



Ulman et al., *J. Am. Chem. Soc.*, **2003**, *125*, 4010

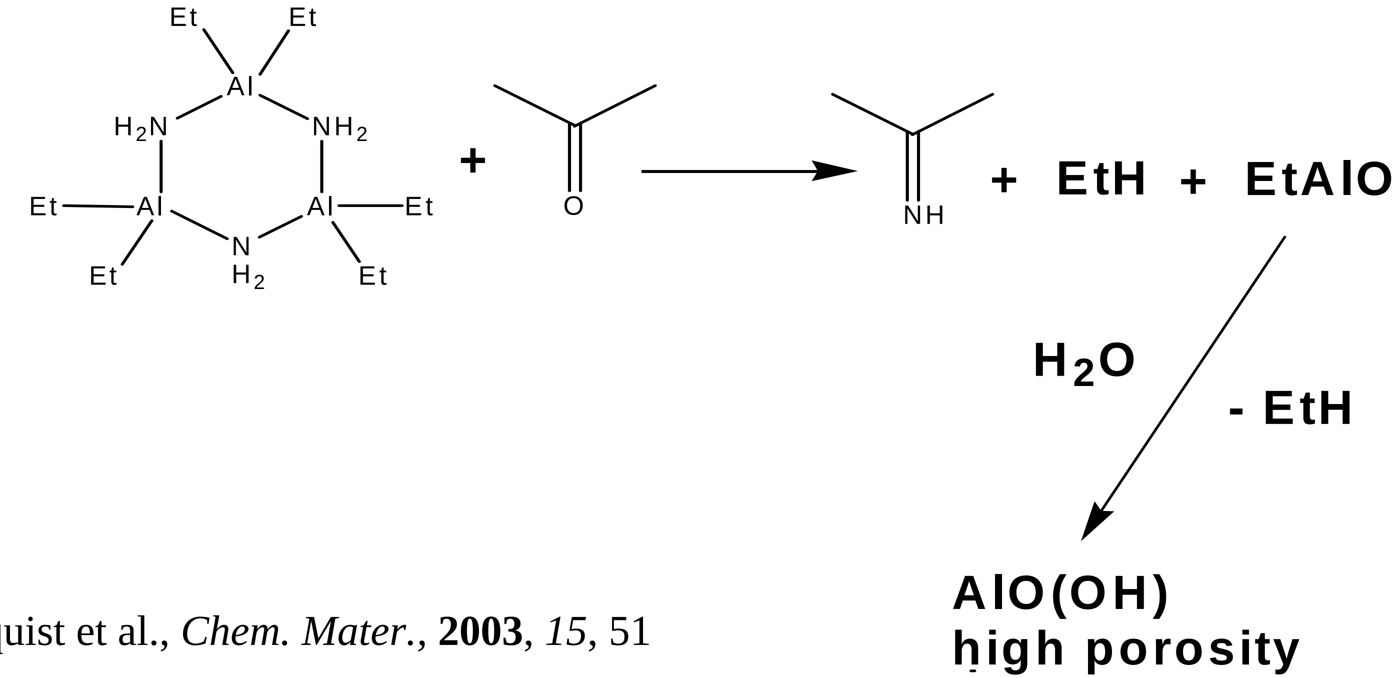
700 - 900 °C

γ-Al_2O_3 (10 nm)

$Y_3Al_5O_{12}$

$LaAlO_3$

Ketimine Elimination



Lindquist et al., *Chem. Mater.*, **2003**, *15*, 51

Thermolysis of a single-source precursor

Fischer et al., *J. Mater. Chem.* **2002**, *12*, 1625

Preparation of Phosphates and Phosphonates

Alkane/Hydrogen Elimination

Alkene Elimination

Alkylhalide Elimination

Alkylsilane Elimination

Aklylamine Elimination

Alcohol Elimination

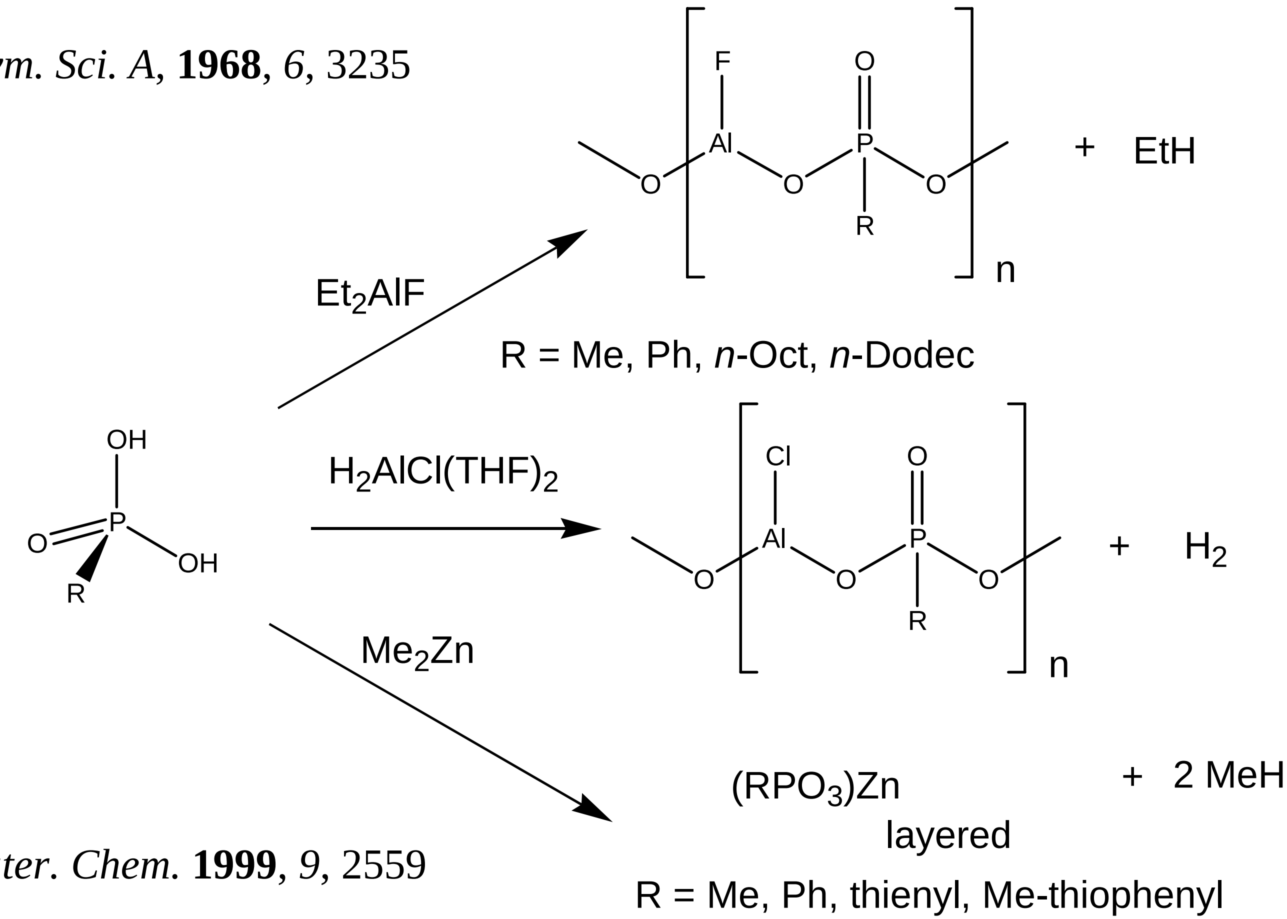
Ether Elimination

Chlororsilane Elimination

Diketone/Ester Route

Alkane/Hydrogen Elimination

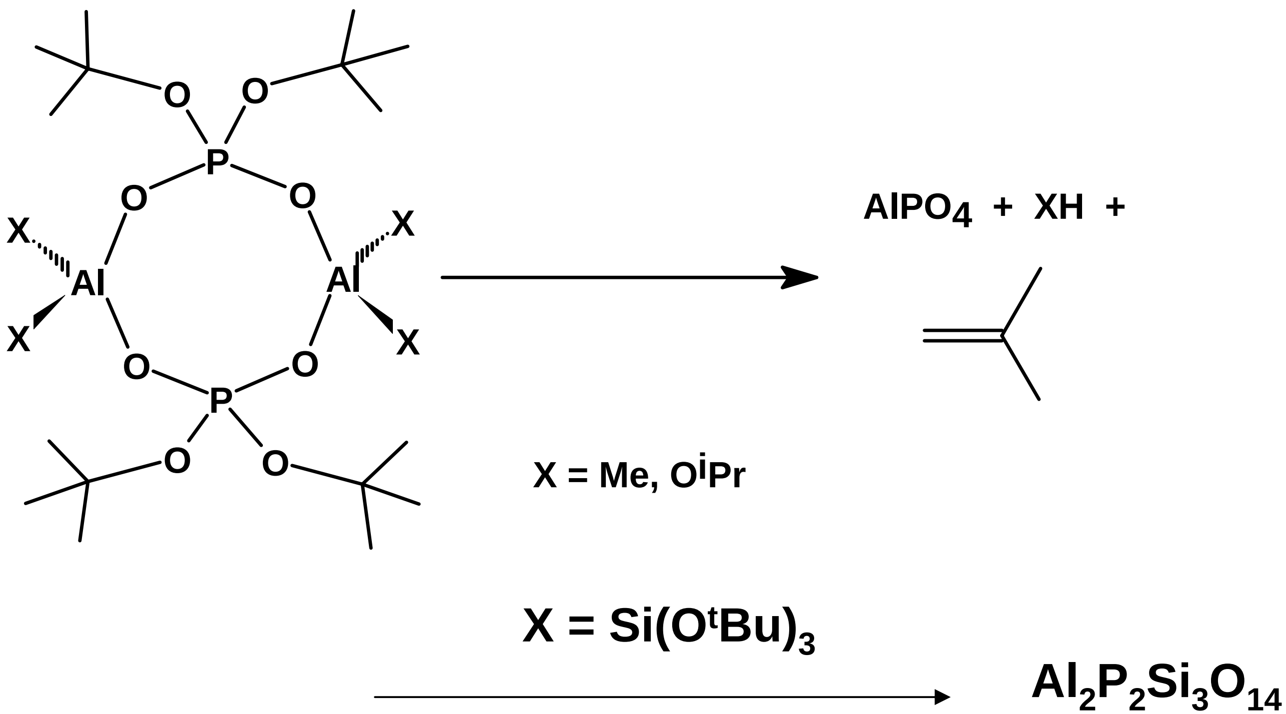
Schmidt et al., *J. Polym. Sci. A*, **1968**, *6*, 3235



Gerbier et al., *J. Mater. Chem.* **1999**, *9*, 2559

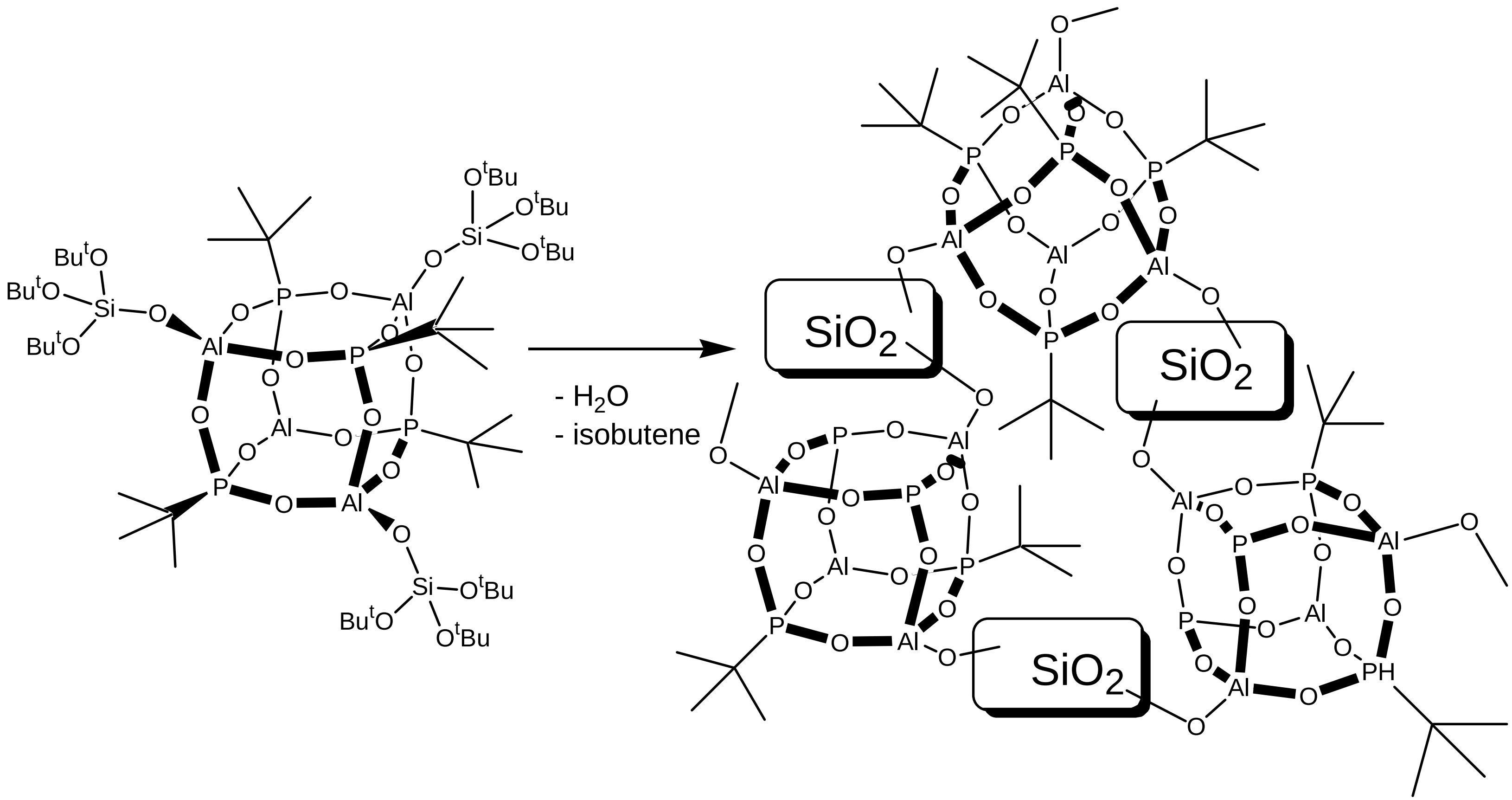
Knight et al., *J. Organometal. Chem.* **1999**, *585*, 162

Alkene Elimination



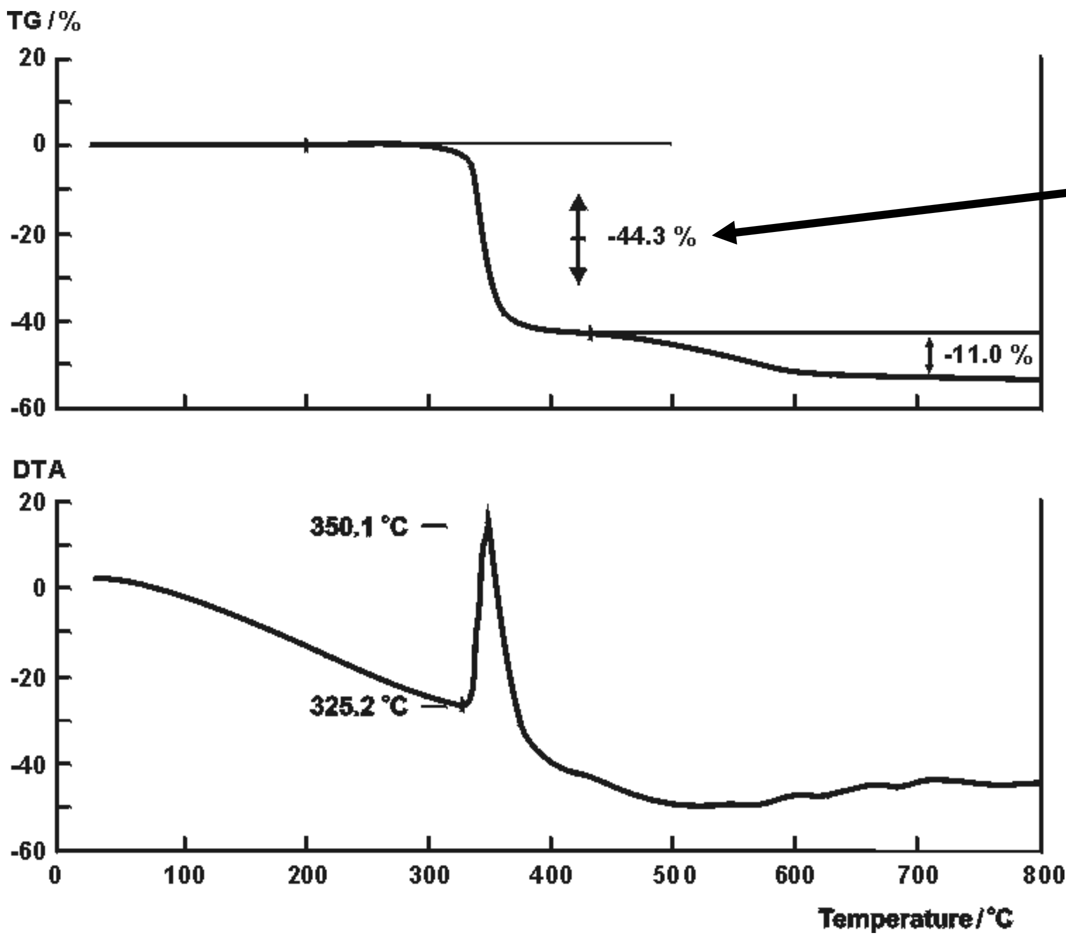
Tilley et al., *J. Am. Chem. Soc.* **2001**, *123*, 10133

Alkene Elimination: *tris*(tert-butoxy)silanolates



Pinkas J., Brlejova Z., Roesky H. W. *unpublished*

Alkene Elimination: *tris*(tert-butoxy)silanolates



isobutene + H_2O

Alkylhalide Elimination

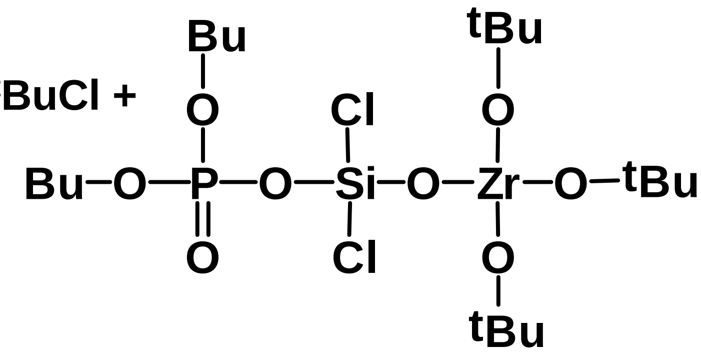
Nonhydrolytic synthesis of NASICON
$Na_3Zr_2Si_2PO_{12}$ solid electrolyte, high Na^+ ionic conductivity

- Solid state preparation: dissolved ZrO_2

- Sol-gel from alkoxides: very slow hydrolysis necessary, different hydrolysis rates

- Nonhydrolytic route in CH_3CN

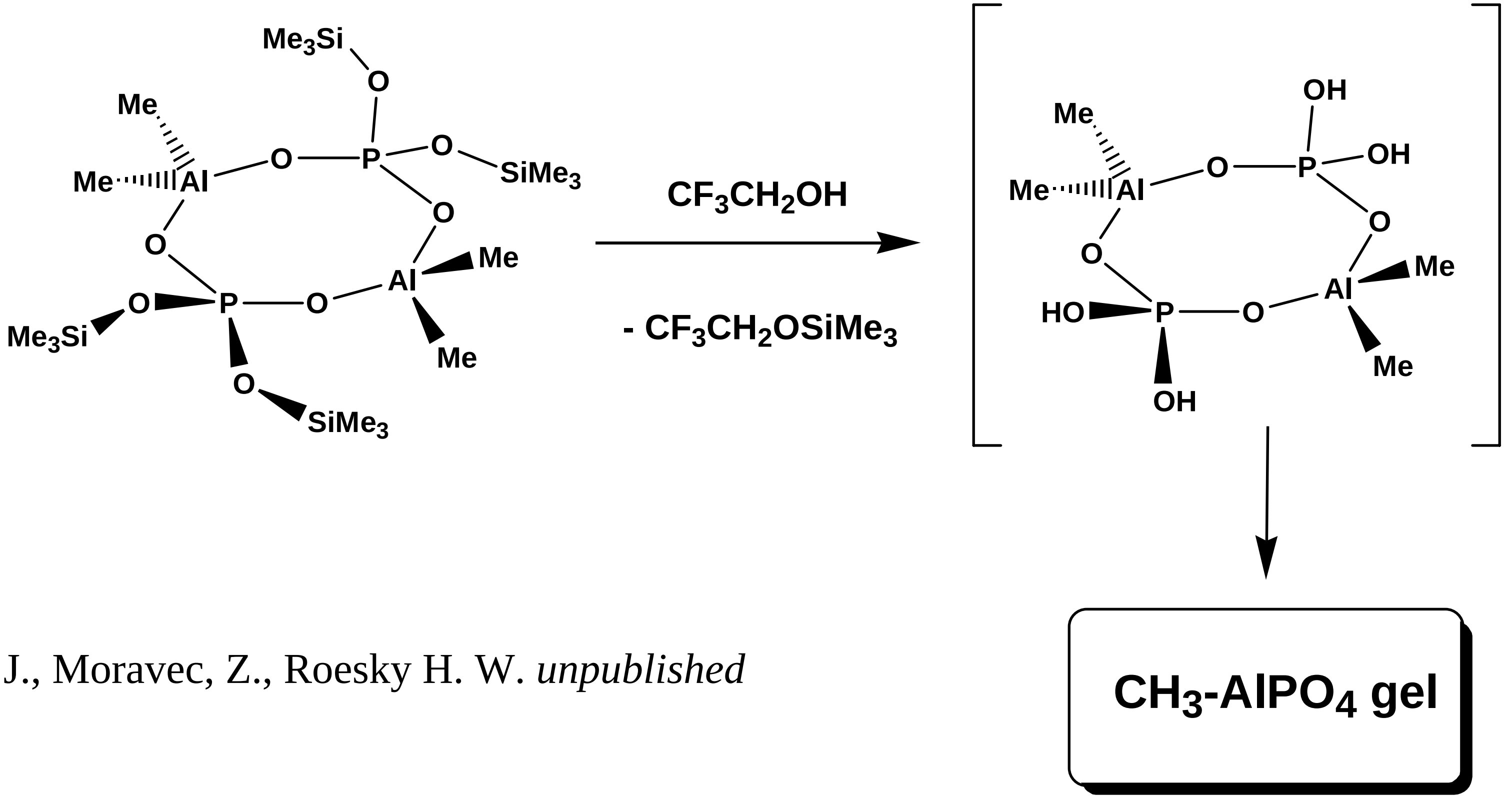
$OP(O^nBu)_3 + SiCl_4 + Zr(O^tBu)_4 + NaO^tBu \rightarrow {}^nBuCl + {}^tBuCl +$



Gel formation
Solvent and byproduct evaporation under vacuum
Drying at 120 °C for 15 h
Ball milling
Calcination at 800 °C gives NASICON

Di Vona et al., *J. Sol-Gel Sci. Technol.*, **2000**, *1/3*, 463

Ether Elimination



Pinkas J., Moravec, Z., Roesky H. W. *unpublished*

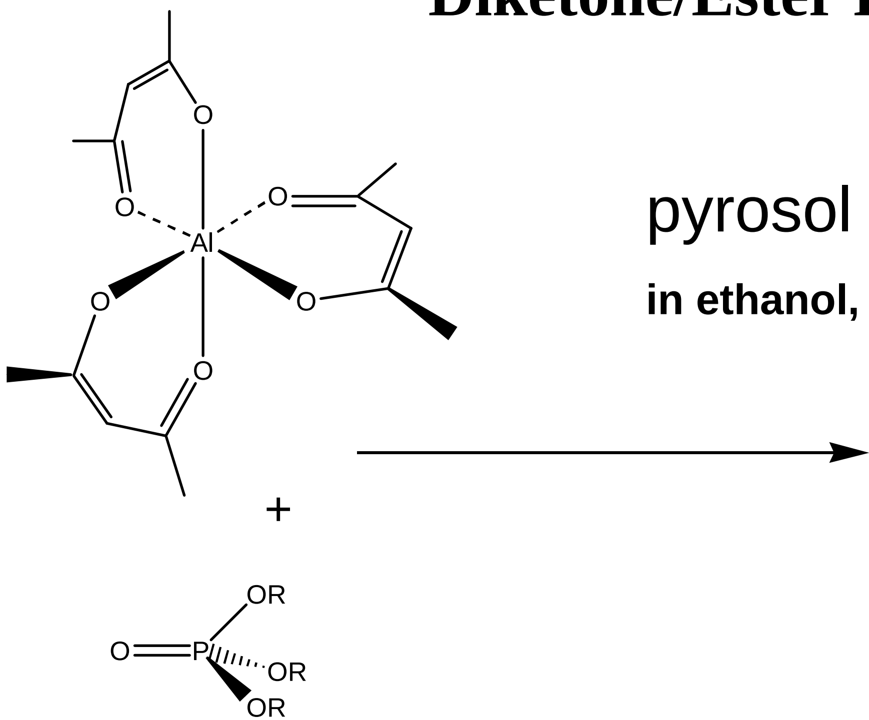
Chlororsilane Elimination

$$AlCl_3 + OP(OSiMe_3)_3 \xrightarrow{\text{THF, reflux}} \text{gel } AlPO_4 + ClSiMe_3$$

$$\text{gel } AlPO_4 \xrightarrow{800\ ^\circ C} AlPO_4 \text{ tridymite, } 13\%\ Si$$

Pinkas J., et al. *Inorg. Chem.* **1998**, *37*, 2450

Diketone/Ester Route



pyrosol CVD process

in ethanol, 300 – 400 °C

$AlPO_4$ amorphous

Daviero et al., *J. Non-Cryst. Solids*, **1992**, *146*, 279, *Thin Solid Films*, **1993**, *226*, 207