

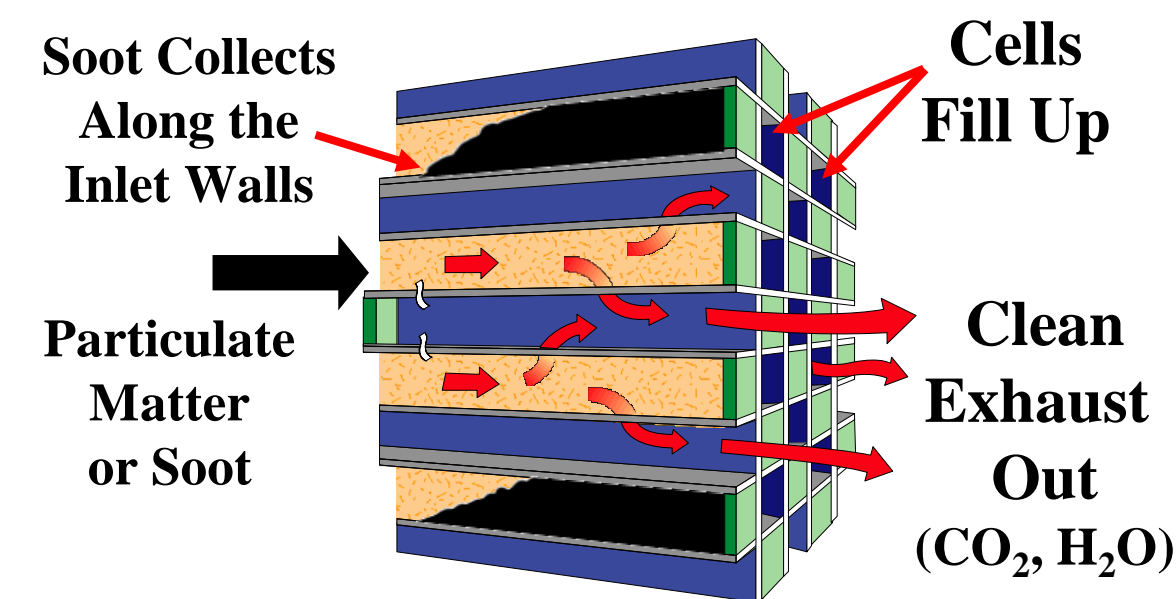
The Effect of Ca^{2+} and Al^{3+} Additions on Potassium Disilicate Glass Soot Oxidation Catalyst Stability



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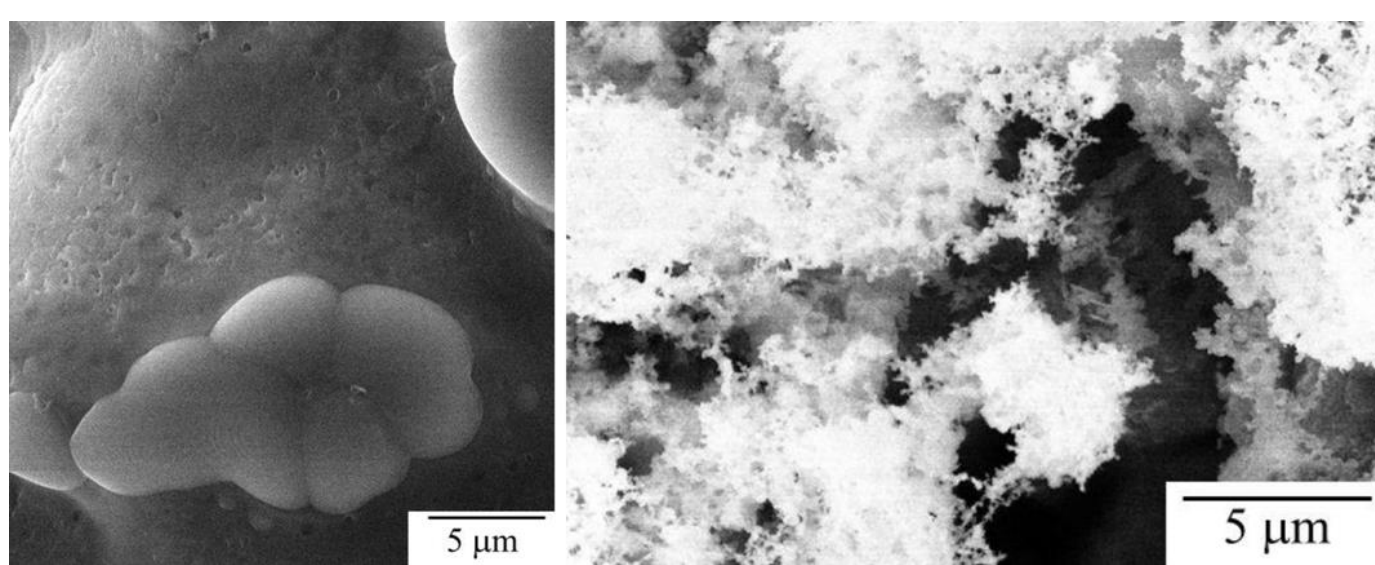
BACKGROUND

Diesel particulate filters (DPF) are an effective method to control particulate emission from diesel engines. A significant technical challenge is reducing the temperature needed for regeneration of DPF systems via soot combustion. Alkali metals oxidize soot at low temperatures (300-325°C) but are problematic because there can be consumption/loss by sublimation. *Our novel approach is to use a glass to supply alkali metal ions on an active basis via ion exchange from a glass (i.e. employ a glass catalyst).*



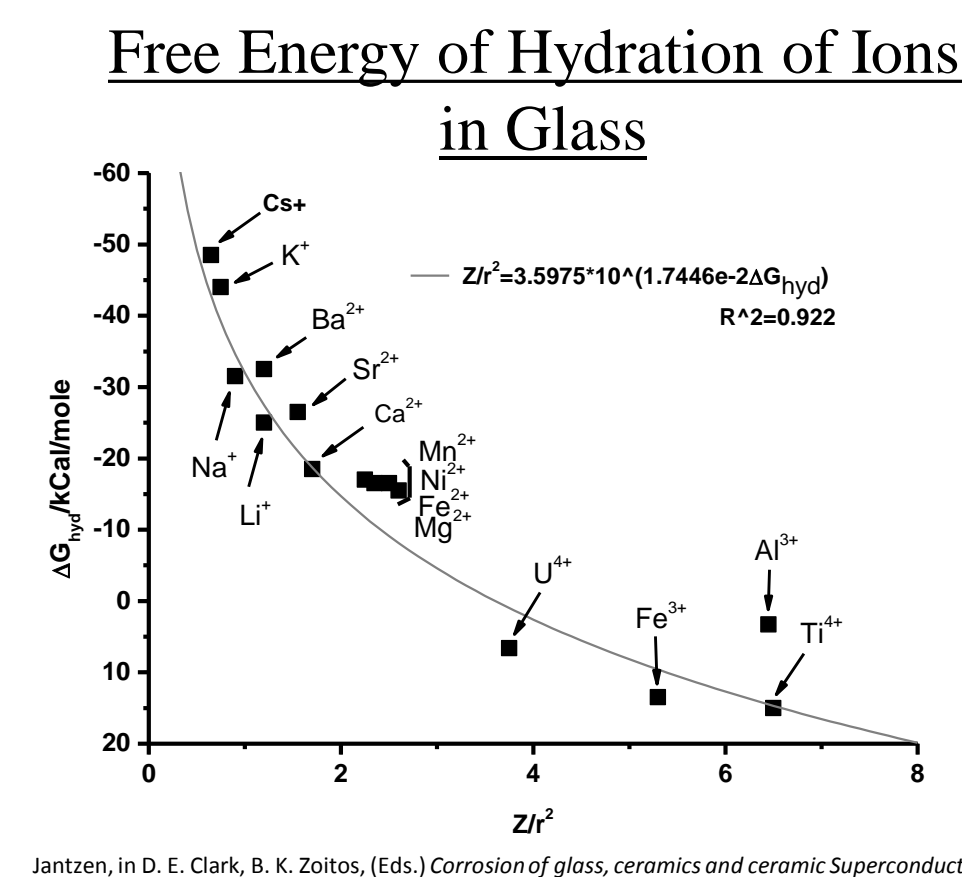
Potassium disilicate ($\text{K}_2\text{Si}_2\text{O}_5$) glass undergoes rapid degradation due to environmental interactions and K loss after only a few cycles of soot oxidation. Elements can be added to the glass to tune the stability of K in the glass matrix.

Necessity for K-Stabilization in Glass



K-glasses substituted with additions of Ca^{2+} and Al^{3+} have been prepared, characterized and tested as diesel soot oxidation catalysts. Ca and Al modify the silicate glass network, resulting in glass catalysts that remain active for soot oxidation in a diesel exhaust environment.

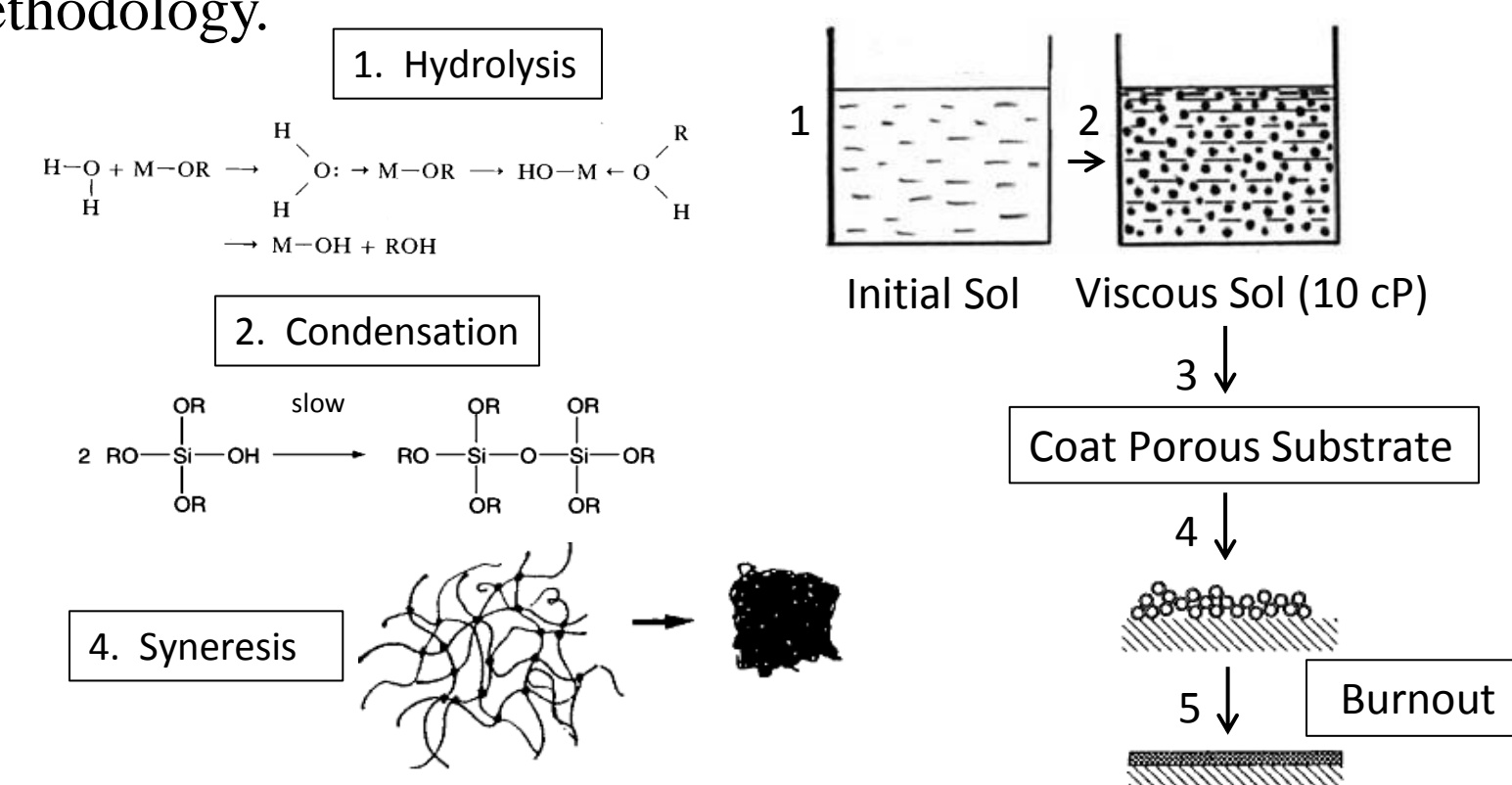
The potassium in a silicate glass is subject to leaching in a humid environment by ion exchange. The rate can be controlled by adding ions to the glass with less affinity to hydrate. Additions such as Ca^{2+} or Al^{3+} increase bonding energy of K^+ in the glass matrix. The composition must be tuned to sustain desired leaching over a suitable lifetime for the glass catalyst and DPF.



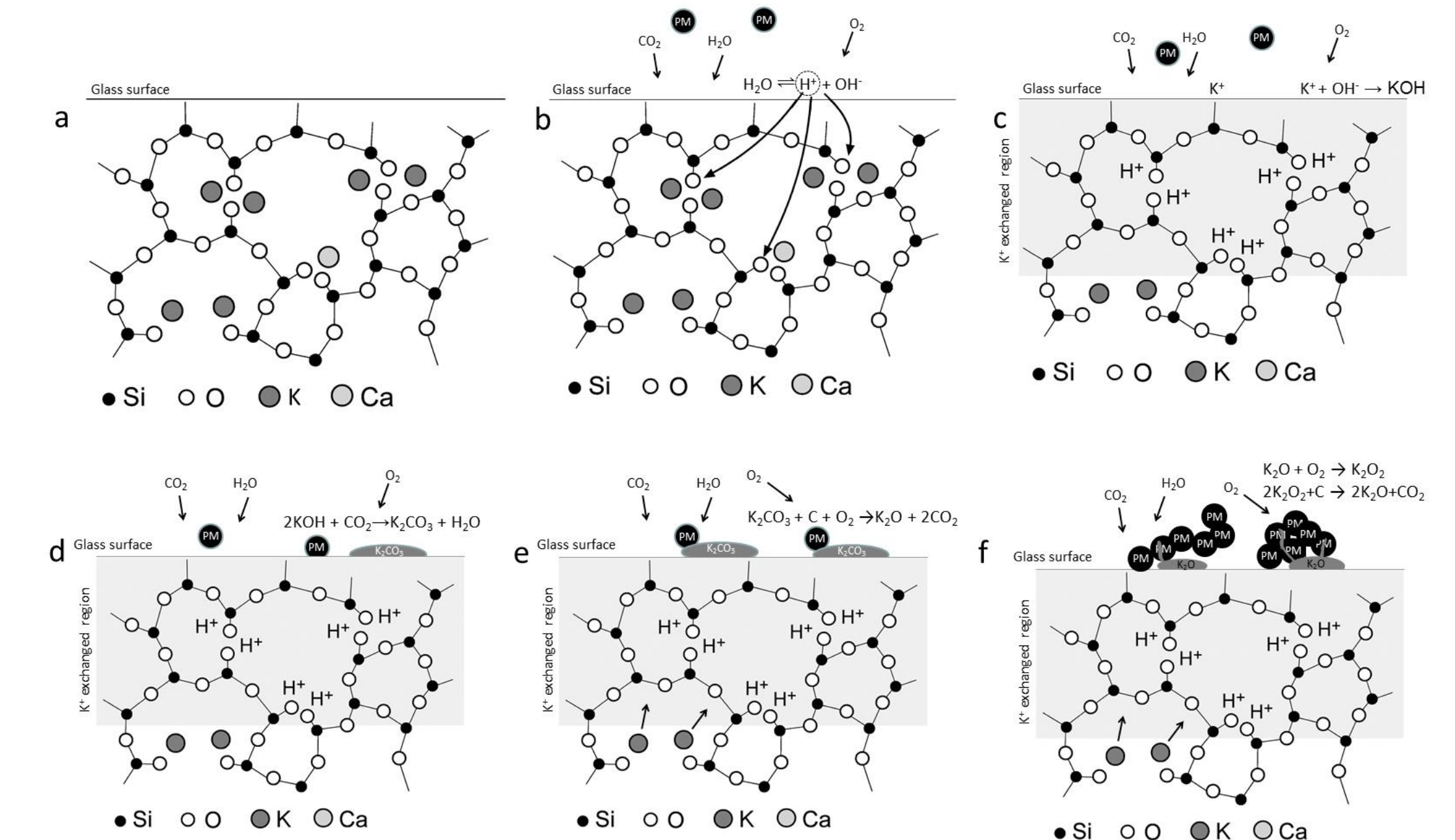
MATERIALS AND METHODS

Sol-gel Glass Synthesis

A liquid based precursor containing TEOS and metal salts undergoes inorganic polymerization to form a 3D gel matrix, which houses the catalytic K and stabilizing ions, and forms an amorphous catalytic glass upon burnout. Complex shaped substrate materials such as cordierite and mullite can be coated by this dip coating methodology.



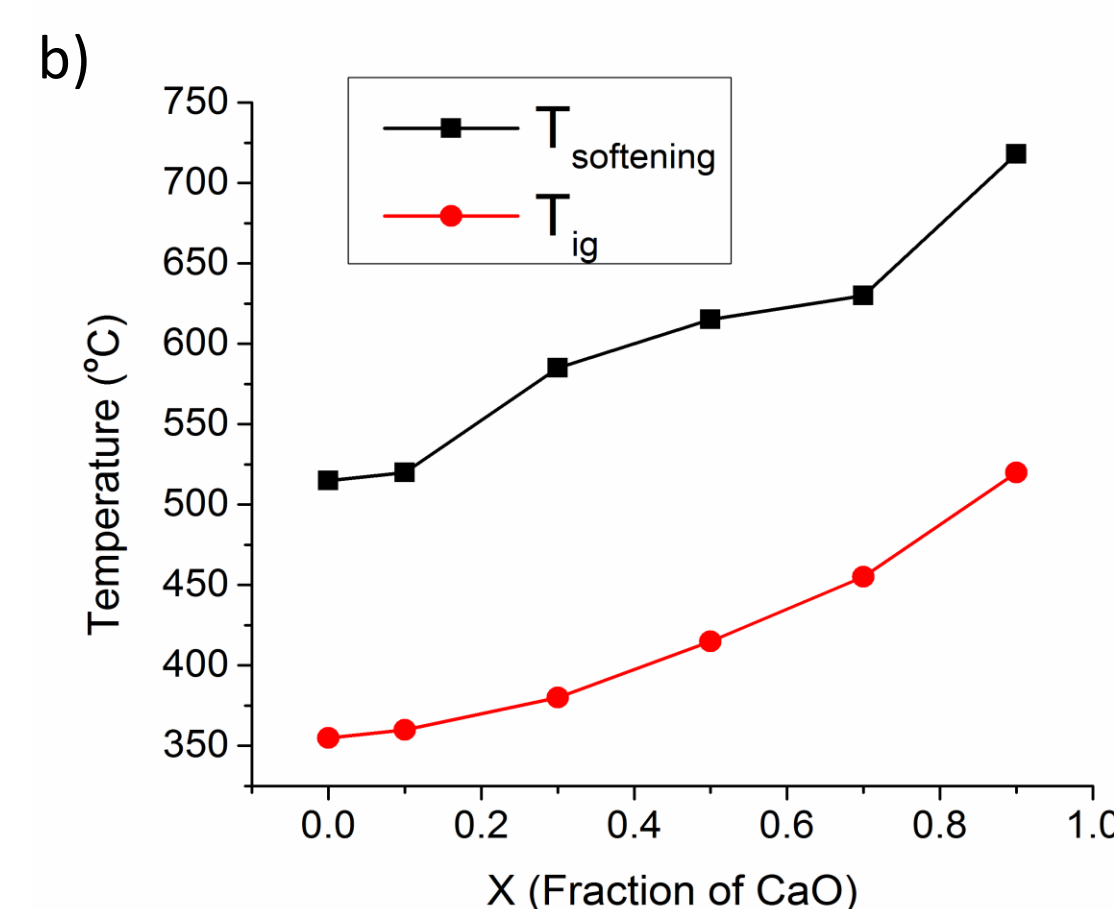
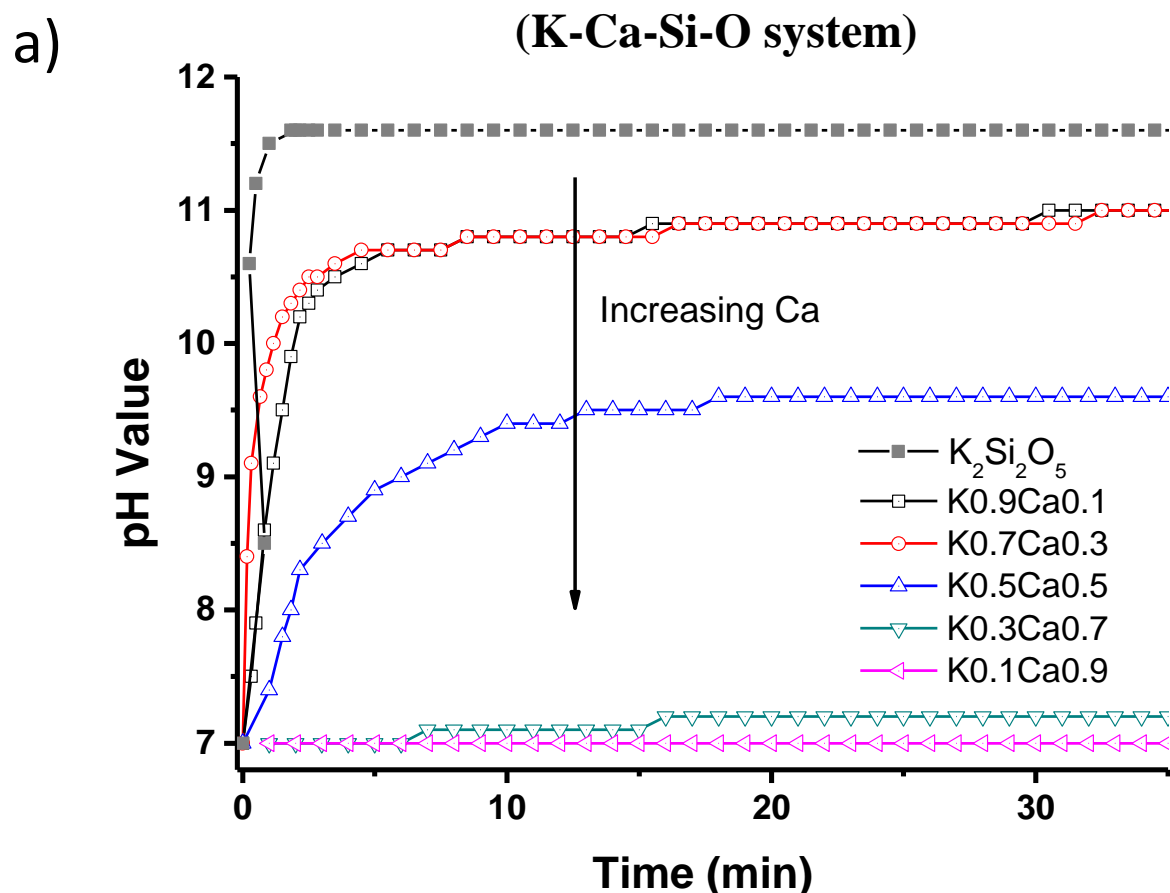
K⁺ EXCHANGE MECHANISM FOR CATALYTIC SOOT OXIDATION



Sequence of the suggested soot combustion process by a glass catalyst
(a) Clean catalyst (K-Ca-Si-O) surface. (b) Exposure to water vapor in diesel exhaust leads to ion exchange, bringing K^+ to the surface. (c) Exchanged potassium ions at the surface react to form KOH while a near surface K depleted region slowly develops in the glass. (d) Further reaction of the KOH with CO_2 leads to formation of K_2CO_3 . (e) K_2CO_3 reacts with carbon to form K_2O ; K ions diffuse into depleted region from glass interior. (f) K_2O tunnels into surface soot deposits, catalyzing soot combustion, with CO_2 being evolved and K potentially being lost. [figure adapted from Melcher et al., Accounts of Chemical Research 43 (2010).]

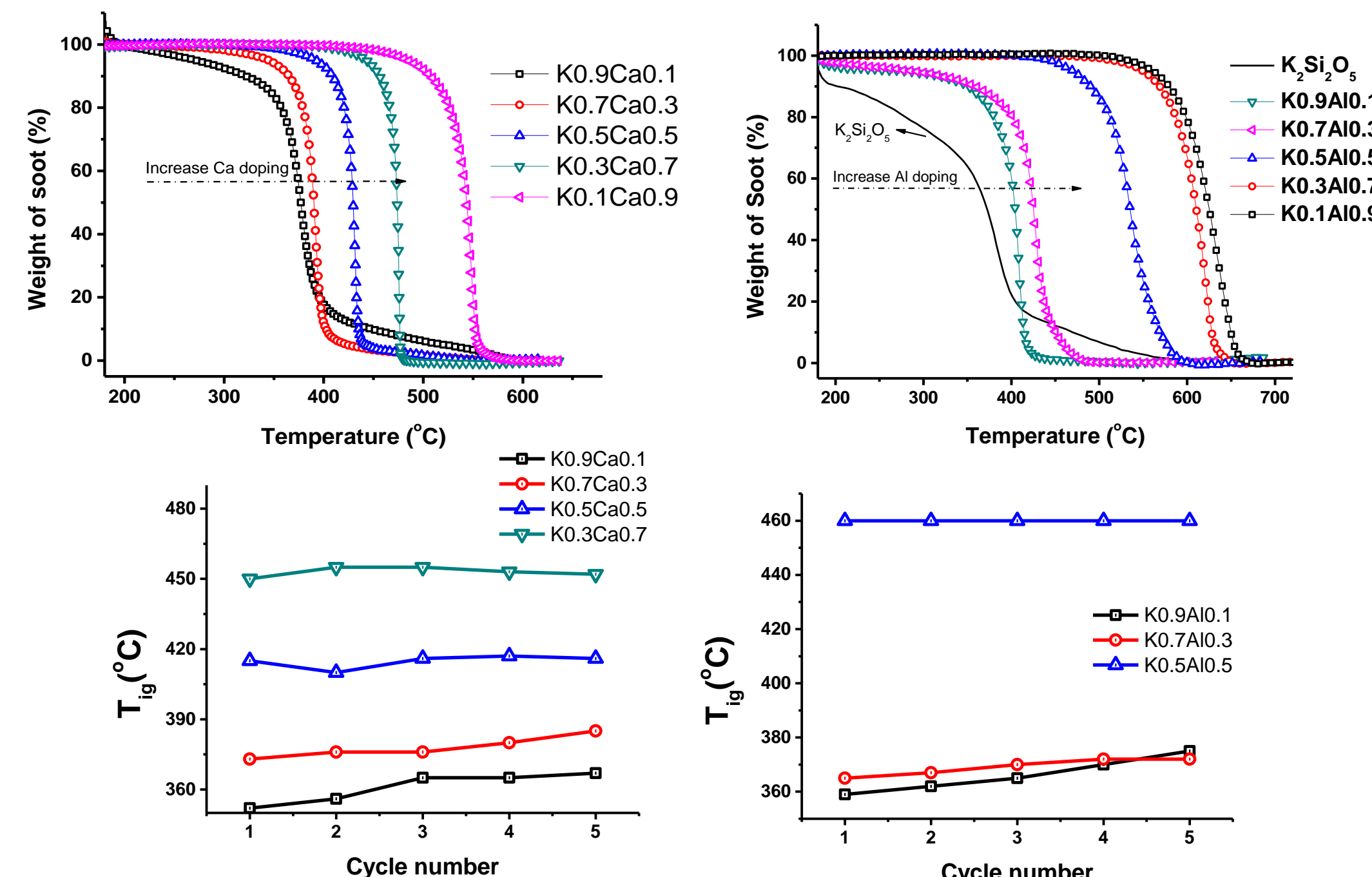
LEACHING & SOFTENING TEMPERATURE vs. COMPOSITION

pH of water with catalyst powders (K-Ca-Si-O system)



a) Leaching rate of K with varying levels of Ca content in $(\text{K}_2\text{O})_{(1-x)}(\text{CaO})_x(\text{SiO}_2)_2$ ternary silicates; b) $T_{\text{softening}}$ and T_{lg} as a function of CaO composition (where $x=0.1, 0.3, 0.5, 0.7, 0.9$) for $(\text{K}_2\text{O})_{(1-x)}(\text{CaO})_x(\text{SiO}_2)_2$ ternary silicates.

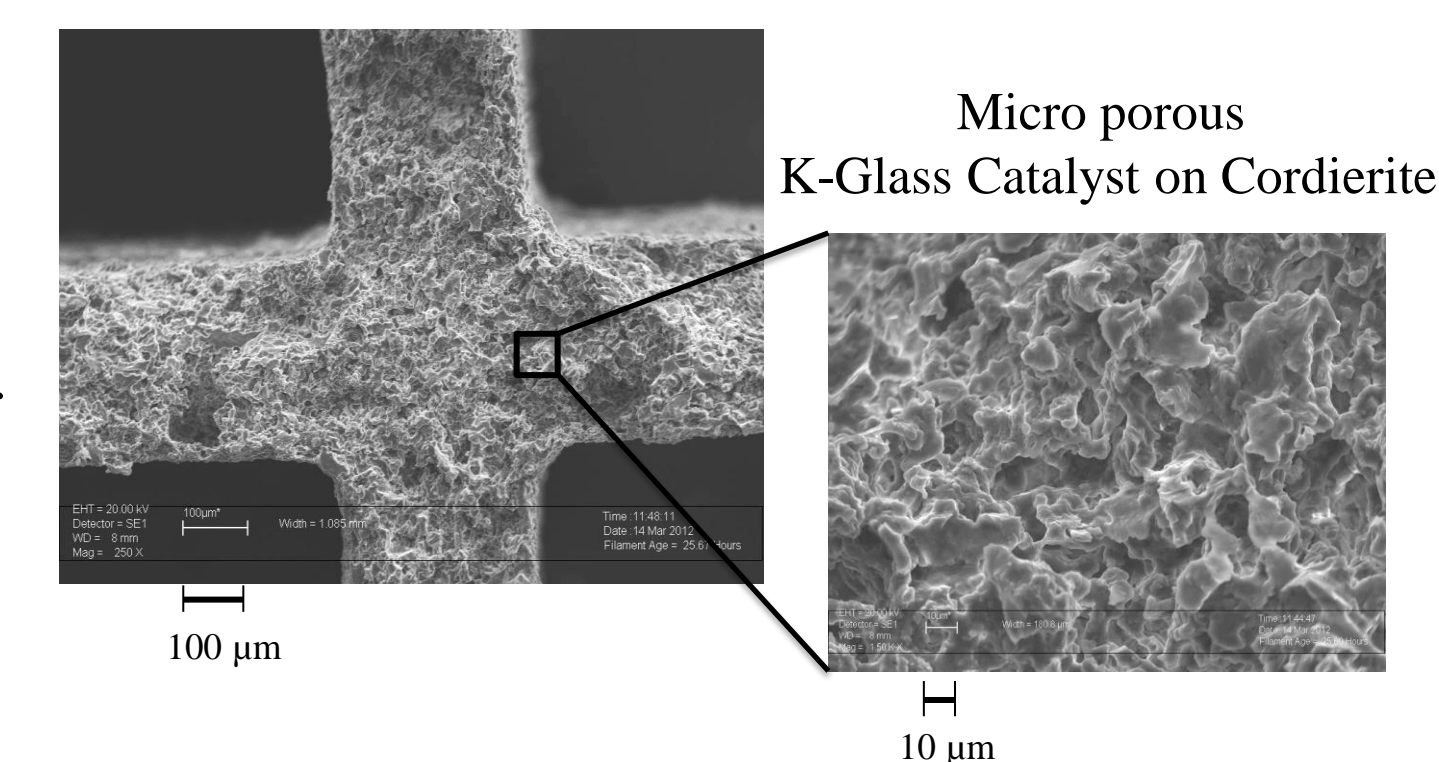
CATALYTIC PERFORMANCE



Soot oxidation performance was tested with high resolution thermogravimetric analysis in simulated diesel gas (10% O_2 -5% CO_2 -3% H_2O - N_2 balance) and carbon black was used to build a comparable diesel soot contact condition by methanol deposition. T_{lg} : soot ignition temperature

COATING OF CORDIERITE FILTERS

Substrates such as cordierite have been coated with K-glass compositions by a sol-gel dip coating method. Filters have been coated with various compositions of the glass and are currently undergoing testing for commercial application.



CONCLUSIONS

- Substitutions of Ca^{2+} and Al^{3+} for K^+ in the catalytic K-glass tune the catalytic activity for soot oxidation and environmental stability.
- $(\text{CaO})_{0.5}(\text{K}_2\text{O})_{0.5}$ showed less catalytic activity than $\text{K}_2\text{Si}_2\text{O}_5$ ($T_{\text{lg}} \sim 410^\circ\text{C}$) but also significantly improved catalytic stability.
- Substituting with Al^{3+} gave improved stability, with $(\text{K}_2\text{O})_{0.7}(\text{Al}_2\text{O}_3)_{0.3}(\text{SiO}_2)_2$ exhibiting a T_{lg} around 370°C and better stability than $\text{K}_2\text{O} \cdot 2\text{SiO}_2$.
- Commercial testing of K-glass coated filters is currently underway.

Further details: Appl. Catal. B: Environ., 138-139, 17 July 2013, pp. 70-78