

TITLE: Supported Liquid Catalysts for In-Situ Removal of High Temperature Fuel Cell Contaminants

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ABSTRACT

OBJECTIVE

The objective of this exploratory research is to develop a basic understanding of the behavior of supported liquid phase molten salts (SLPC) on fluidized particles in a fluidized bed reactor. The following three specific tasks have been defined:

1. Identify compatible non-reactive molten salt/support particle systems
2. Develop a model for liquid capillary forces affecting agglomeration and defluidization of the particle bed.
3. Carry out exploratory experiments, based on model parameters, for evaluating the effect of molten salt loading on fluidization hydrodynamics.

ACCOMPLISHMENTS TO DATE

Theoretical and experimental studies have been carried out per the 3 tasks listed above.

Free energy minimization calculations using the F*A*C*T (Facility for the Analysis of Chemical Thermodynamics) Software have identified at least 3 non-reactive compatible support materials for molten Na₂CO₃ at 1088 K (1500°F): Fe₂O₃, CaO, and ZrO₂. Similar thermodynamic calculations have shown that standard fluidizable support materials SiO₂ and Al₂O₃, typically used in fluidized bed combustors or catalytic processing, are not compatible as they react with sodium and alumina to produce sodium silicate (Na₆Si₉O₁₉) or β-alumina (Na*Al₉O₁₄), respectively. Additional calculations were carried out for evaluating the equilibrium products of combustion for a raw fuel gas [generated by gasifying Illinois No. 6 coal (10% excess air)] in the presence of supported molten Na₂CO₃ at 1088 K (1500°F). The product gas contained < 1 ppm SO_x and < 10 ppm NO_x. The residual sulfur from the feed COS and H₂S was captured in-situ as Na₂SO₄, while the low NO_x resulted from low combustion temperatures due to the catalytic oxidation enhancement of the molten Na₂CO₃.

Two approaches were taken to model liquid capillary forces: (1) a quasi-empirical dimensional analysis to relate liquid capillary forces (i.e. cohesive forces between SLPC particles) to other fluidization parameters through particle, gas, and liquid properties, and (2) a modified force balance that accounts for cohesive forces between particles. The modeling indicates that in order for the bed to remain fluidized in the presence of a liquid loading, the inertial forces must dominate over the viscous surface forces. Also, surface forces dominate for smaller particles since the number of particle contacts per unit volume is larger. The modeling indicates that the support particles should have high density and be large in diameter (Geldart Group D).

Preliminary experiments are in progress to validate the modeling. A 0.07 m (2-3/4 inch) I.D. InconelTM fluidized bed was constructed and heated via a 0.46 m (18 inch) long hot zone Thermal Technology AstroTM furnace. Differential pressure measurements are used to indicate the fluidization of the support as the salt is loaded at temperatures above its melting point. The approach taken was to start out at low temperatures using a low melting temperature salt (LiNO_3 , mp = 251°C) with fluidizable porous SiO_2 and non-porous glass ballotini. One simple 2^3 experimental design was established to determine the effect of temperature, linear gas velocity above minimum fluidization, and support particle size on fluidization hydrodynamics, liquid capillary forces, and agglomeration tendency. Experiments are in progress.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAMS

The envisioned application of this processing is in the DOE/FETC focus area of hot gas cleanup for (1) fuel cell contaminants, or (2) combining hot gas cleanup with low temperature selective oxidation processing for integrated combined cycle processes. One envisioned process is to develop methods for capturing trace impurities in fuel cell gas feeds, using small quantities of the same molten carbonate to be used in the fuel cell processing. The 2nd conceptualized process is to combine hot gas clean-up processing with low temperature catalytic combustion of raw syngas or fuel gas. The idea is to carry out selective oxidation reactions at reduced temperatures (taking advantage of the catalytic oxidation characteristics of molten Na_2CO_3) where NO_x formation is minimized, while simultaneously capturing trace gaseous contaminants (S, Cl, Hg, etc.) in-situ at temperatures of 1100 to 1200 K ($T > 1500^\circ\text{F}$). In both instances, the enabling factor is the ability to maintain fluidization of the bed in the presence of supported molten salt. Hence, the present studies are directed towards a basic understanding of inter-particle forces in such SLPC systems.

FUTURE WORK

Future work will focus on continuing to develop an understanding of supported molten salt fluidized systems with a target being the fluidization of molten Na_2CO_3 and the eventual experimental evaluation of a reactive system. Future work will depend upon continued support beyond this 1 year exploratory grant. A 3 year proposal is currently pending with DOE/FETC (DE-PS26-99FT40479).

STUDENTS SUPPORTED UNDER THIS GRANT

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