

### Advances in Gas Filtration Materials Research: Fuel Cell Air Purification Challenge?

#### **AFS: FILTCON 2019 Conference**

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Ionic Liquid Based Sorbents for Acidic Gas Capture.

### Outline

- Current state of Art: Acidic Gas Pollutant Mitigation Approaches
   ➢ Industrial Flue Gas
   ➢ Air Purification
- Advances in Acidic Gas Sorbent Materials Development.
  - Improvements in state of art [composites, promoters, supports]
     MOFs
  - □Ionic Liquids

□Hybrid Materials

- □Supported Sorbents
- HNEI-Severa Lab: Acidic gas sorbent materials research.
- Acknowledgements

### **Types of Air Pollutants**

<u>Particulate Pollutants</u>: Ash, dust, metallic (Hg, etc) and nonmetallic (sulfates, nitrates, etc) compounds.



<u>Gas Pollutants</u>: Sulfur oxides (SO<sub>x</sub>), Nitrogen oxides (NO<sub>x</sub>), carbon oxides (CO<sub>x</sub>), Volatile organic compounds (VOCs), ground-level ozone (O<sub>3</sub>).

EPA: http://www3.epa.gov/airquality/urbanair/

### **Detrimental Effects of Air Pollutants**

#### Gas Pollutants:

- Detrimental to human healthy
- Toxic to environmental- cause acid rain, endanger marine life
- Technology effects: hinder use of unfiltered air in fuel cells

#### Particulate Pollutants:

- Causes respiratory problems, premature deaths.
- Detrimental to ecosystem especially mercury.
- Reduce visibility
- Technological effects: reduce efficiency







### **Classic Flue Gas Pollutants Removal Approaches**

Pollutants	Pollutant Mitigation Technology
Sulfur dioxides, SO <sub>2</sub>	Flue gas desulfurization, Dry sorbent injection with fabric filter.
Other acid gases (H <sub>2</sub> S, HCl)	Flue gas desulfurization, Dry sorbent injection-fabric filter
Nitrogen oxides, NO <sub>x</sub>	Selective catalytic reduction (SCR), Activated carbon injection with fabric filter
Carbon dioxide, $(CO_2)$	Solvents, membranes, solid sorbents
Mercury (Hg)	Selective catalytic reduction with FGD, Activated carbon injection (ACI), ACI with Fabric Filter
Non-mercury metals	Fabric Filter or electrostatic precipitators.

### Flue Gas Pollutants Mitigation Approaches

#### Advantages:

- Cheap
- Proven technology
- Some reversibility at high temperature (e.g. ethanol amines)

#### <u>NO<sub>x</sub> Mitigation</u>

Selective reduction of  $NO_x$  using  $NH_3$  at high temperatures (300-500 °C)

 $NO + 2NH_3 + 1/2O_2 \rightarrow H_2O + 2N_2$ 

#### <u>SO<sub>2</sub> mitigation (Desulfurization)</u>

Sorbents: Metal Compounds (CaO/CaCO<sub>3</sub>)



#### Disadvantages:

- Issues of reversibility with sorbent cycling
- Bulky solid waste
- Waste water
- High energy usage

### Acidic Gas Air Pollutant Removal Approaches

#### • Pure Activated carbons

- Impregnated activated carbons/silica:
  - Metal hydroxides (e.g. KOH, Mg(OH)<sub>2</sub>)
  - Metal oxides (e.g. CaO, MgO, ZnO, KMnO<sub>4</sub>)
  - Metals (e.g. Cu, Fe, K, V, Ca)
- Disadvantages of current approaches:
  - Non reversible at moderate conditions
  - Bulky waste
  - Pollutes environment
  - Low breakthrough capacity under harsh conditions









Classic PEM Fuel Cell Air Filtration contains activated carbon impregnated with chemicals. Chemicals effective for removal of acidic gases.

### Future Approaches to Acid Gas Pollutants Mitigation



Cu-BTC 400 ppm CO₂ @ 25 °C 1.50 mmol/g Ar @ 120 ° C

#### **Regenerable Materials**

- Mixed metal compounds
- Metal Organic frameworks
  - Zeolite imidazolium frameworks (ZIFs)
- Permanent porous liquids
  - Ionic Liquids
  - Hybrid materials
  - Supported materials





#### Potential for higher performance, cost savings and waste reduction

http://www.rsc.org/chemistryworld/2015/11/first-permanently-porous-liquids-created Bollini et al. J. Mater. Chem., 2011,21, 15100-15120; Sun et al. AIChE Journal, Vol. 60, No. 6, 2314

### **Recent Advances in State-of-Art: Metal Oxides for H<sub>2</sub>S and SO<sub>2</sub> Capture.**

- Composites and supports for H<sub>2</sub>S:
  - ZnO supported on SBA-15, higher capacity compared to commercial ZnO.
  - Mesoporous metal oxides (e.g. Cr<sub>2</sub>O<sub>3</sub> and CuO) show better performance, up to 200 times, compared to corresponding none porous oxides.
- Incorporation of dopants: Effect on H<sub>2</sub>S and SO<sub>2</sub> sorption.
  - Copper doping in ZnO supported on silica improves ZnO conversion to ZnS from 64% to 93%.
  - Doping of MgFeAl mixed metal oxide derived from hydrotalcites, with Cu results in 1600 mg SO<sub>2</sub>/ g sorbent compared to about 1110 mg/g.

#### Challenges

- Sorbent regeneration results in loss of capacity with cycling.
  - Agglomeration of oxides with cycling, loss in surface area and porosity
- High temperatures >400 °C needed for regeneration.

### Metal Organic frameworks (MOFs)

#### **Characteristics of MOFs**

- Tunable porosity
   Size, shape
   Large surface area
   Tunable composition
  - functionality, selectivity

#### Advantages of MOFs in gas sorption

- Room temp gas sorption
- Reversible gas sorption
- High gas pollutant sorption kinetics
- ➢ High gas selectivity

Forse et al. J. Am. Chem. Soc. 2018, 140, 18016–18031 Sun et al. AIChE Journal, Vol. 60, No. 6, 2314 Li et al., Materials Today, Volume 21, Number 2, March 2018



### Metal Organic frameworks (MOFs)

#### **MOFs for SO<sub>2</sub> and H<sub>2</sub>S capture**

- > Defected MOFs and amine functionalized/appended MOFs show high SO<sub>2</sub> sorption, 11 mmol SO<sub>2</sub>/g at 293K.
- $\rightarrow$  MOF MIL-101 absorbed 38 mmol H<sub>2</sub>S/g sorbent.
- Selective functionalization of MOFs with basic groups



#### More studies needed for evaluation of MOFs for SO<sub>x</sub> H<sub>2</sub>S and NO<sub>x</sub> capture

Bares et al. Chem. Soc. Rev., 2014, 43, 5419—5430; Glomb et al. ACS Appl. Mater. Interfaces 2017, 9, 37419- 37434; Mansi S. Shah et a., Chem. Rev. 2017, 117, 9755–9803; Marleny Rodri guez-Albel et al. Nature communication, 2017, 1-10. DOI: 10.1038/ncomms14457.

### MOFs: Zeolite imidazolate frameworks

### **Challenges of MOFs**

- Adsorption performance may be affected by water, require activation for enhanced capacity
  - H<sub>2</sub>S breakthrough capacity increased by 38% on activation at 180 °C.
- Partial reversibility, MIL 101
- Stability issues
  - Thermal stability concerns
  - Susceptible to Hydrolysis
  - Poor stability under acid environments

#### Characteristics of ZIF-MOFs

- ➢ High thermal stability
- ➢ High surface area
- Tunable porosity
- ➢ High chemical stability

### **Ionic Liquids**

#### Characteristics of ionic liquids

- Negligible volatility
- Large liquidus range: 25-400 °C
- High viscosity
- Non flammable
- Tunable chemical properties

Advantages of IL in gas absorption

- Potential for reversible gas absorption
- Non volatile
- High gas pollutant sorption kinetics



Challenges of Bulky IL in gas sorption

- Poor gas contaminant permeation into the bulky
- Poor gas pollutant selectivity

B. Kirchner, Topics in current chemistry, in: B. Kirchner (Ed.) Ionic liquids, Springer-Verlag new york, 2009, pp. 40. P. Wasserscheid, T. Welton, Ionic Liquids in Synthesis, Wiley-VCH Verlag, Weinheim, 2003. <u>http://www.chem.uniromal.it</u>,

### Process of SO<sub>2</sub> Pollutant Removal by Ionic Liquids

• Reversible and selective removal of SO<sub>2</sub> from flue gas by ionic liquids.



#### High viscosity of IL and high flue gas temp limits practical applicability

### Hybrid Materials and Supported Sorbents

### Modification of Support for enhanced SO<sub>2</sub> or H<sub>2</sub>S capture.

- Basic chemicals or functionalities (eg PEI, urea, amines, hydroxl) incorporated
- Activated carbon and mesoporous silica popular supports.

#### Direct modification of support by grafting chemicals.

- Consistent capacity with sorbent cycling
- Low pore blockage
- Generally lower gas uptake, due to partial utilization of support surface for gas sorption.

#### Physical impregnation of sorbents on supports

- Generally higher gas uptake as whole surface of support is impregnated with sorbent.
- Sorbent leakage/stripping
- Pore blockage correlated with sorbent loading ratios

Hybrid Sorbents: Co-operative sorption (e.g. activated carbon-ionic liquid; MOF-Graphene, MOF-IL)

### **Fuel Cell Air Purification**

#### Development of advanced air filtration materials for fuel cell operations in harsh environments.





#### Stringent fuel cell air requirements

High air flow rates Low pressure drop Low acid gas pollutant tolerant levels

#### **Sorbent Implications:**

Low back pressure Effective acidic gas capture. High breakthrough capacity

#### Hybrid sorbents and Supported sorbents have potential in fuel cell air purification

#### HNEI-Severa Lab Approach Regenerable Materials for Acid Gas Capture

Hybrid materials and Supported sorbents. Ionic Liquids, Mixed Metal Materials, Nano-Confinement Effects





#### Air Pollutant Mitigation for Acidic Gas Fuel Cell Applications

### **Process of Physical Support of Ionic Liquid onto** Nano-Porous Materials



SEM images of pure and ionic liquid impregnated activated carbon (AC)



- Microporous and mesoporous activated carbon
  - Pore volume> 0.48 cm<sup>3</sup>/g
  - Surface area >1000 cm<sup>2</sup>/g

#### Impregnated AC maintains porosity after ionic liquid impregnation process.

Severa, G., et al.,  $SO_2$  sorption by activated carbon supported ionic liquids under simulated atmospheric conditions. Chemical Engineering Journal, 2015. **265**: p. 249-258.

### Best Performance: Nano-Confined [C<sub>2</sub>mim][Ac] Sorbent (EMA)



- Highest sorption capacity and break through time from 1-ethyl-3-methylimidazolium acetate impregnated activated carbon (EMA).
- EMA chosen as model impregnated ionic liquid sorbent for detailed study.
- Experimental conditions:
  \$15 LPM purified air
  \$15 ppm SO<sub>2</sub> contaminants
  \$50 % RH @ 25 °C.
  \$3 g samples.

- Break through times:
  - EMA>EML>HMN, EMS>AMC, HMS, BMHS >EMHS >BMF.

# Mechanism of SO<sub>2</sub> Capture by EMA Elucidated by combination of NMR, FT-ATR and TGA-DSC.



#### Mechanism derived from FTIR, thermal analysis and NMR data. S-O vibrational frequencies indicate presence of chemically bound SOx species.

Severa, G., et al.,  $SO_2$  sorption by activated carbon supported ionic liquids under simulated atmospheric conditions. Chemical Engineering Journal, 2015. **265**: p. 249-258.

### **DFT Molecular Modelling of EMA Ionic Liquid**



Determine ionic liquid, [C<sub>2</sub>mim][Ac], binding affinity for SO<sub>2</sub> and NO<sub>2</sub>.

### Simultaneous Interaction of the ionic liquid [C<sub>2</sub>mim][Ac] with SO<sub>2</sub> and NO<sub>2</sub>

**Higher affinity for SO<sub>2</sub> than NO<sub>2</sub> for ionic liquid [C<sub>2</sub>mim][Ac]** 



C <sub>2</sub> mim][Ac]: Stronger SO <sub>2</sub> h	oinding
compared to NO <sub>2</sub>	

Substrate	Adsorbate YO <sub>2</sub>	ΔH (298 K)	ΔG (298 K)
[C <sub>2</sub> mim][Ac]	1 <sup>st</sup> NO <sub>2</sub>	-30	5
[C <sub>2</sub> mim][Ac] <sup>·</sup> NO <sub>2</sub>	2 <sup>nd</sup> NO <sub>2</sub>	-41	11
[C <sub>2</sub> mim][Ac] <sup>·</sup> SO <sub>2</sub>	$2^{nd} NO_2$	-31	12
[C <sub>2</sub> mim][Ac]	$1^{st} \operatorname{SO}_2$	-99	-48
[C <sub>2</sub> mim][Ac] <sup>·</sup> NO <sub>2</sub>	$2^{nd}$ SO <sub>2</sub>	-91	-34
[C <sub>2</sub> mim][Ac] <sup>·</sup> SO <sub>2</sub>	$2^{nd}$ SO <sub>2</sub>	-71	-25

Adsorption enthalpies and Gibbs energies (in kJ/mol) for  $YO_2$  binding with  $[C_2mim][Ac]$  and  $[C_2mim][Ac]^{\cdot}XO_2$  where X and Y are N or S atoms

### Design, Synthesis and Characterization of Metallo Ionic Liquids and Ionic Salts for Acid Gas Capture

- Targeting simpler scalable syntheses approaches.
  - Minimum use of solvent
  - Least number of syntheses steps
  - One pot approaches
  - Cost competitive materials
  - Relatively low reaction temperatures

Motivated by our previous work showing acetate anion of  $[C_2mim][Ac]$ having large effect on SO<sub>2</sub> capture and coordination potential of acid gas species on metal ions.

- Synthesized acetate based metallo ionic liquids/ionic salts with Fe, Mn, Zn, Mg, Co or Sc ions.
  - Still trying to crystallize discernible grains of Co and Sc metallo ionic liquids.











### Acetate Based Metallo Ionic Liquid

¢ C

• The metallo ionic liquid has potential for acidic gas capture



 $[C_2 mim][Fe]_2[Ac]_5H_2O$  Melting point: ~95 °C



Acidic gas (SO<sub>2</sub>, H<sub>2</sub>S and CO<sub>2</sub>) sorption testing planned

### Acetate Based Metallo Ionic Liquids/Salts

• The ionic salts have potential for acidic gas capture



### Different Topology and Stereochemistry Depending on Water Content



Anhydrous monoclinic Mn(II) compound Hydrous triclinic Mn(II) compound

Is activation required for acidic gas capture? Are Open metal sites formed on water removal?

#### **Conclusion: Main Takeaways**

- Composites, promoters and supports are effective for improving absorption capacity of metal oxide sorbents.
- Hybrid sorbents and supported sorbents have potential for fuel cell air filtration in future.
- More consistent studies of sorbents performance under simulated practical conditions are needed to understand their potential to meet fuel cell air filtration needs.
- The development of practical sorbents must take into account the effect of humidity and other gas components on sorbent performance.
- Metallo ionic liquid and ionic solids based on acetate anion with potential for acid gas capture have been developed.

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