Sulfur Removal from Reformate

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Objectives

Develop a sulfur removal process for on-board fuel processing to meet DOE targets for hydrogen sulfide (H₂S) removal to <10 ppbv H₂S in reformate by 2010, a reactor volume of <0.06 L/kWₑ and weight of <0.06 kg/kWₑ, and operation at a gas-hourly space velocity (GHSV) of 50,000 h⁻¹.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- J. Durability
- L. Hydrogen Purification/Carbon Monoxide Cleanup

Approach

- Identified Cu oxides as candidate materials based on the H₂S equilibrium partial pressure for candidate adsorbents (metal sulfide-H₂S equilibrium).
- Synthesize mixed metal oxides consisting of CuO/Cu₂O and another transition metal oxide to stabilize copper in its oxide forms.
- Conduct experimental studies in a microreactor system to evaluate the H₂S concentration in the effluent as a function of temperature, flow rate, water content, and the gas composition for candidate mixed metal oxides.

Accomplishments

- Synthesized various mixed metal oxides consisting of CuO/Cu₂O and screened them for H₂S uptake in a microreactor system.
- Determined the effects of operating temperature, flow rate, water content, and gas composition on the performance of H₂S removal by a copper oxides-based composition.
- Demonstrated that a copper oxides-based composition reduced H₂S concentration from 10 ppmv to <50 ppbv from a simulated reformate.

Future Directions

- Evaluate H₂S uptake for the materials supported on the structured form.
- Characterize materials to improve performance and address stability issues.
- Optimize the composition and materials processing and work with industrial collaborator.
Introduction

On-board reforming of gasoline is one option being considered for supplying H$_2$ for polymer electrolyte fuel cell (PEFC) powered propulsion systems for automobiles and light-duty vehicles. Under reforming conditions, the sulfur present in gasoline is converted to H$_2$S. Although new Environmental Protection Agency (EPA) regulations will reduce the sulfur content of gasoline to <80 ppmv beginning in 2006, reformate produced from these gasolines will still contain ~10 ppmv H$_2$S. Concentrations of H$_2$S as low as 50 ppbv have been shown to irreversibly poison the PEFC catalysts.\textsuperscript{1} As a consequence, DOE has established a target of <10 ppbv H$_2$S in reformate by 2010.

Two different approaches, liquid-phase desulfurization of the fuel prior to reforming\textsuperscript{2} and gas-phase desulfurization of reformate after reforming, are being considered for on-board sulfur removal. There is a concern with liquid-phase desulfurization that H$_2$S will still need to be removed from reformate. Gas-phase desulfurization requires that the reforming catalyst be sulfur-tolerant. Our focus is on developing adsorbents for gas-phase desulfurization.

Zinc oxide (ZnO) is used for sulfur removal in the production of H$_2$ from natural gas for ammonia and methanol synthesis. For on-board fuel processing using ZnO, thermodynamic equilibrium predicts that a temperature of <250°C is required to reduce the H$_2$S concentration to <10 ppbv. We have observed that the concentration of H$_2$S in reformate increased as the temperature decreased below 300°C due to unfavorable kinetics, making ZnO unsuitable for on-board fuel processing.\textsuperscript{3} Copper oxides (CuO and Cu$_2$O) have among the highest sulfidation equilibrium constants for metal oxides and can potentially achieve parts-per-billion concentrations of H$_2$S in reformate. However, under fuel processing conditions, Cu$_2$O/CuO are reduced to metallic Cu. The sulfidation equilibrium for metallic Cu is significantly less than that of Cu oxides, resulting in reduced desulfurization efficiency. Research has focused on combining CuO/Cu$_2$O with other metal oxides to stabilize the oxide form,\textsuperscript{4} which is the approach that we are investigating.

Approach

Compositions consisting of Cu and a second transition metal oxide dispersed on a high surface area support, such as γ-Al$_2$O$_3$, were prepared by either co-impregnation or successive impregnation methods using nitrate salts as precursors. The H$_2$S desulfurization performance of these compositions was evaluated in a microreactor system. In a typical test, a sample of up to 2 mL was exposed to a synthetic reformate (10-40 ppmv H$_2$S, 29% H$_2$, 20% H$_2$O, 6% CO, 6.1% CO$_2$, 0.2% CH$_4$, balance N$_2$) at temperatures ranging between 200-400°C and at GHSV's ranging between 2000-50,000 h$^{-1}$. The H$_2$S concentration in the effluent from the reactor was measured using a gas chromatograph (GC) equipped with a flame photometric detector (FPD) with a detection limit of 200 ppbv H$_2$S and an on-line lead-acetate based H$_2$S analyzer with a detection limit of 20 ppbv H$_2$S.

Results

Figure 1 shows a typical H$_2$S breakthrough curve (i.e., H$_2$S concentration in the effluent as a function of time) for these sorbents at 350°C and a GHSV of 2000 h$^{-1}$ with a feed H$_2$S concentration of 40 ppmv. All compositions tested, including Cu alone, exhibited two stages of H$_2$S breakthrough. During the first stage, they reduced the H$_2$S concentration below detection limit of the FPD. During the second stage, they reduced the H$_2$S concentration to ~10 ppmv. The second stage is believed to be associated

![Figure 1. The H$_2$S Breakthrough Curve for Cu+B at 350°C and a GHSV of 2000 h$^{-1}$](image-url)
with the sulfidation of metallic copper since the observed \( \text{H}_2\text{S} \) concentration of 10 ppmv is close to that predicted by thermodynamic equilibrium (7.2-10.6 ppmv at 350-380\(^\circ\text{C}\)) for metallic Cu; however, this has not been experimentally confirmed. These materials did show different sulfur uptake capacities as shown in Table 1. The highest sulfur uptake capacities were shown by compositions identified as Cu+B and Cu+C.

The Cu+C system was chosen for further study to determine the effect of various operating parameters including temperature, GHSV, and the water content in reformate on \( \text{H}_2\text{S} \) removal. Temperature significantly affected \( \text{H}_2\text{S} \) removal performance, as shown in Figure 2. The \( \text{H}_2\text{S} \) concentration was reduced from 10 ppmv to \(<50\) ppbv at 200 and 300\(^\circ\text{C}\); however, a longer breakthrough time was observed at 200\(^\circ\text{C}\), indicating a higher \( \text{H}_2\text{S} \) uptake capacity. At 200\(^\circ\text{C}\), the reduction of copper oxides to metallic Cu is less favorable, suggesting more of the Cu may be in the oxide form, which would favor desulfurization.

The effect of GHSV at 200\(^\circ\text{C}\) is shown in Figure 3. Although breakthrough time decreased significantly as the GHSV was increased from 10,000 to 50,000 \( \text{h}^{-1} \), similar sulfidation efficiencies (~20 ppbv) and Cu utilizations (~60\%) were observed at both GHSVs. When the temperature was increased to 350\(^\circ\text{C}\), the performance decreased significantly at the higher GHSV. The sulfidation efficiency was 25 ppbv and the Cu utilization was 15\% at a GHSV of 10,000 \( \text{h}^{-1} \), which decreased to 200 ppbv and 5\%, respectively, at a GHSV of 50,000 \( \text{h}^{-1} \). This implies that lower operating temperatures are desirable if the GHSV target is to be met.

The effect of the \( \text{H}_2\text{O} \) concentration in the reformate on \( \text{H}_2\text{S} \) removal performance is shown in Figure 4. The pre-breakthrough \( \text{H}_2\text{S} \) concentration increased as the \( \text{H}_2\text{O} \) concentration increased from 11 to 30 vol\%, consistent with the reaction equilibrium (e.g., \( \text{Cu}_2\text{O} + \text{H}_2\text{S}(g) = \text{Cu}_2\text{S} + \text{H}_2\text{O}(g) \)). Since \( \text{H}_2\text{O} \) is a product of the sulfidation reaction, increasing the \( \text{H}_2\text{O} \) concentration in the reformate shifts equilibrium towards the reactants, leading to a higher \( \text{H}_2\text{S} \) concentration.

### Table 1. Copper Utilization for Sulfidation of Binary Oxides of Copper and a Second Transition Metal

<table>
<thead>
<tr>
<th>Sorbent formulation</th>
<th>Surface area (m(^2)/g)</th>
<th>Sulfur uptake (% based on Cu content)(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu+A/Al(_2)O(_3)</td>
<td>197.9</td>
<td>37.3</td>
</tr>
<tr>
<td>Cu+B/Al(_2)O(_3)</td>
<td>199.5</td>
<td>57.9</td>
</tr>
<tr>
<td>Cu+C/Al(_2)O(_3)</td>
<td>211.3</td>
<td>53.9</td>
</tr>
<tr>
<td>Cu+D/Al(_2)O(_3)</td>
<td>201.5</td>
<td>44.0</td>
</tr>
<tr>
<td>Cu+E/Al(_2)O(_3)</td>
<td>202.3</td>
<td>32.8</td>
</tr>
<tr>
<td>Cu/Al(_2)O(_3)</td>
<td>256.8</td>
<td>36.3</td>
</tr>
</tbody>
</table>

\(^a\)Calculated based on \( \text{H}_2\text{S} \) uptake until breakthrough occurs (1 ppmv \( \text{H}_2\text{S} \)).
Conclusions

- Binary oxides containing Cu are capable of reducing the H₂S concentration from 10 ppmv to <50 ppbv in reformates containing 30% H₂ and 20% H₂O at temperatures ranging from 200-350°C and GHSVs ranging from 10,000-50,000 h⁻¹.

- Lower operating temperatures, lower H₂O concentrations, and lower GHSVs are desirable to meet DOE targets.

References


FY 2003 Publications/Presentations