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**Test and Characterization of Some Zeolite Supported Gas
Phase Desulfurization Sorbents**

by Charles Rong, Deryn Chu, and John Hopkins

ARL-TR-4859

June 2009

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| 14. ABSTRACT This report presents the results of sulfidation and regeneration of mixed metal oxide supported on zeolite-Y for hydrogen sulfide (H ₂ S) at 650 and 800 °C, along with results for unsupported mixed metal oxide. The capacity for the unsupported oxide was higher than that for the supported oxide, but the unsupported mixed metal oxide showed evidence of sintering at higher temperatures, which resulted in a decreased desulfurization capacity. The sulfidation capacity of the zeolite supported mixed metal oxide, although it started with a lower capacity, was found to be independent of temperature at both 650 and 800 °C, suggesting the mixed metal ions supported on zeolite are resistant to sintering at higher temperature, and they appear to have only surface interaction with H ₂ S. | | | | | |
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1. Introduction

The development of fuel cell technology and logistics fuel reformation technology for power generation in the battlefield has received much attention in the Science & Technology (S&T) community in recent years (1–5). One of the key issues to be understood and addressed is the desulfurization of logistics fuels such as JP-8, in which the sulfur content may be up to a few thousands ppm while commercial fuels contain less sulfur due to strict Environmental Protection Agency (EPA) requirements for low sulfur fuels. The sulfur contents in the logistics fuel must be reduced to a near zero level since fuel cells require a clean and essentially sulfur-free fuel stream for proper operation. The Army relies on JP-8 as a major logistics fuel; thus, the desulfurization of JP-8 becomes a unique problem to be solved for advanced energy conversion technology development. Technically, sulfur removal from the fuel can be achieved by either liquid phase desulfurization or gas phase desulfurization, and in most cases with high sulfur contents in the fuel, both of the liquid and gas phase processes may be required.

Advanced energy conversion technology includes components such as fuel reformation and solid oxide fuel cell (SOFC) development. SOFCs have the advantages of using a non-noble-metal catalyst and working at high temperatures, and they are more versatile, being able to run on different fuels, than polymer electrolyte membrane fuel cells. JP-8 reformation converts liquid hydrocarbon fuel to a gaseous reformat consisting of hydrogen, carbon monoxide, carbon dioxide, water, and some lower molecular weight hydrocarbon molecules such as methane. SOFCs can be fed with this gas mixture as a suitable fuel stream as long as it is sulfur free. From a system integration and heat management point of view, SOFCs should be coupled closely with the fuel reformer. Therefore, gas phase desulfurization should be accomplished at a temperature range of 600 to 800 °C, the temperature at which both of the reformer and SOFC operate. Although the sulfur tolerance of the-state-of-the-art SOFC electrode material is improving, the gas phase desulfurization step at high temperature is still essential to SOFCs. Our report focuses on gas phase desulfurization at these high temperature conditions.

2. Experimental

2.1 Materials

2.1.1 Mixed Metal Oxide

The copper (Cu) and cerium (Ce) mixed metal oxide was prepared by hydrothermal synthesis and is described as follows. A 5% (in molar ratio) of copper to cerium (CuO/CeO₂) was formed by reaction of copper nitrate (Cu(NO₃)₂), cerium nitrate (Ce(NO₃)₃), and potassium hydroxide

(KOH) in aqueous solution at 180 °C for 48 h. The product was then filtered out and washed with water thoroughly. It was further calcined at 650 or 800 °C for 4 h before the corresponding sulfidation test.

2.1.2 Zeolite Supported Mixed Metal Oxide

The copper and cerium oxide incorporated in zeolite-Y was prepared by ion-exchange method as described:

- *Cu-zeolite*: 2 g of zeolite-Y was placed in 20 ml 0.5 M $\text{Cu}(\text{NO}_3)_2$ solution and stirred for 48 h at room temperature. It was then filtered out, washed with water, and dried at 110 °C for 2 h.
- *Ce-zeolite*: 2 g of zeolite-Y was placed in 20 ml 0.5 M $\text{Ce}(\text{NO}_3)_2$ solution (with a few drops of HNO_3 added) and stirred for 48 h at room temperature. It was then filtered out, washed with water, and dried at 110 °C for 2 h.
- *Cu-Ce-zeolite*: 1 g of Cu-zeolite was placed in 20 ml 0.014 M of $\text{Ce}(\text{NO}_3)_3$ solution with 10^{-3} M HNO_3 , which is close to $\frac{1}{4}$ of the exchangeable site of the zeolite, and stirred overnight. It was filtered out, washed with water, and dried at 110 °C for 2 h. The copper to cerium ratio on the zeolite support is expected to be larger than 0.05.

2.2 Characterization

The x-ray diffraction (XRD) results were obtained using a Rigaku Ultima III instrument with $\text{Cu K}\alpha$ radiation with a Bragg-Brentano Configuration, and a Philips PW1840 X-ray Diffractometer with iron (Fe) $\text{K}\alpha$ radiation. A Micromeritics ASAP 2010 instrument was used to measure the surface area of the samples.

2.3 Sulfidation and Regeneration Test

The sulfidation and regeneration test was carried out at Tufts University, a Collaborative Technology Alliance (CTA) Power and Energy consortium member of the Army, as part of a CTA staff rotation effort. The schematic of the reactor system is shown in figure 1. About 0.2 g of sorbent materials was used for the test. After the test, the material was recovered for further characterization. The sorbent was first subjected to pre-reduction under the conditions of 50% H_2 -10% H_2O -balanced helium (He) for 1 h. Then it was subjected to sulfidation under the conditions of 0.1% H_2S -50% H_2 -10% H_2O -balanced He with a space velocity of 80,000/h. When the concentration of H_2S in the stream after the reactor reached 30 ppm, which is the pre-defined breakthrough point, the reactor conditions were changed to regeneration mode of 50% H_2 -10% H_2O -balanced He, space velocity 80,000/h. The sulfidation and regeneration test was conducted at two temperatures, 650 and 800 °C. The hydrogen sulfide (H_2S) level in the exit gas was measured in real time using an AMETEK 922 UV Photometric Analyzer.

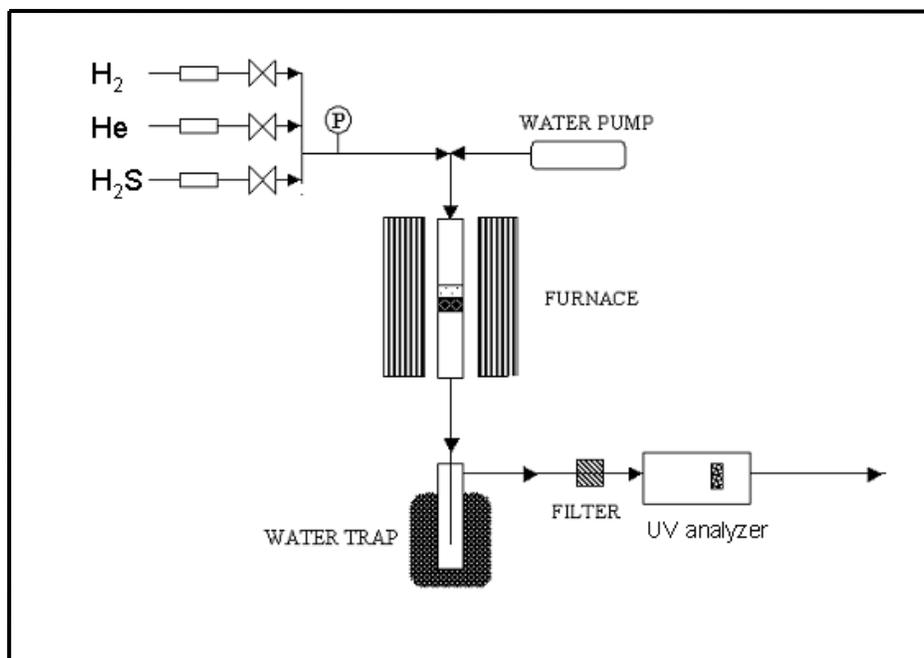


Figure 1. The schematic of the desulfurization reactor system.

3. Results and Discussion

3.1 Mixed Metal Oxide

A 5% in molar ratio of CuO in CeO₂ (5%CuO/CeO₂) was tested at 650 and 800 °C for sulfidation and regeneration. The results are shown in table 1 and figure 2 for a total of eight cycles. The initial capacity was higher than the subsequent runs at both 650 and 800 °C, but they were all stabilized to about the same values after several cycles. The percentage of the desorbed H₂S from the sorbent was found to be over 80% for most cycles, as shown in table 1, indicating the reversibility of the sorbent. Although the capacity was basically the same for both temperatures, the temperature effect on the sorbent was obvious when the XRD measurements were taken to examine the tested samples. As shown in figure 3, narrower peaks were observed for the 800 °C tested sorbent, which means the 5%CuO/CeO₂ mixed metal oxide crystalline size increased due to a high temperature sintering effect.

Table 1. Sulfidation/regeneration cycling results of 5% CuO/CeO₂ at 650 and 800 °C.

| Cycled at 650 °C | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|--|------|------|------|------|------|------|------|------|
| Capacity (mg S /g sorbent) | | 4.18 | 3.34 | 2.85 | 3.18 | 2.85 | 2.51 | 2.34 | 2.34 |
| Desorbed /adsorbed H ₂ S (%) | | 81 | 88 | 89 | 95 | 91 | 95 | 98 | 95 |
| Cycled at 800 °C | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| Capacity (mg S /g sorbent) | | 2.45 | 2.45 | 2.18 | 2.45 | 2.18 | 2.18 | 2.18 | 2.45 |
| Desorbed /adsorbed H ₂ S (%) | | 81 | 83 | 81 | 79 | 83 | 84 | 82 | 73 |

Note: Experimental conditions: pre-reduction at 650 and 800 °C, respectively, 50%H₂-10%H₂O-balanced He, 1 h; Sulfidation at 650 and 800 °C, respectively, 0.1%H₂S-50%H₂-10%H₂O-balanced He, space velocity 80,000/h; regeneration: 650 and 800 °C, respectively, 50%H₂-10%H₂O-balanced He, space velocity 80,000/h.

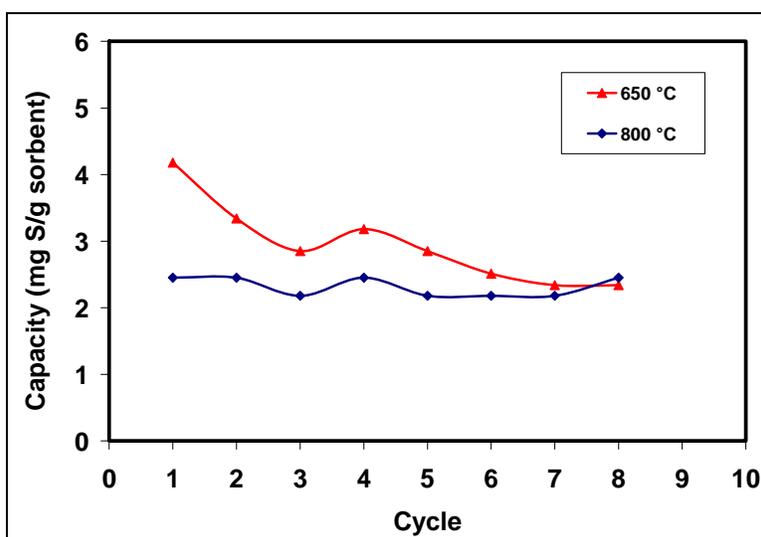


Figure 2. Sulfidation capacity of 5% CuO/CeO₂ tested at 650 and 800 °C.

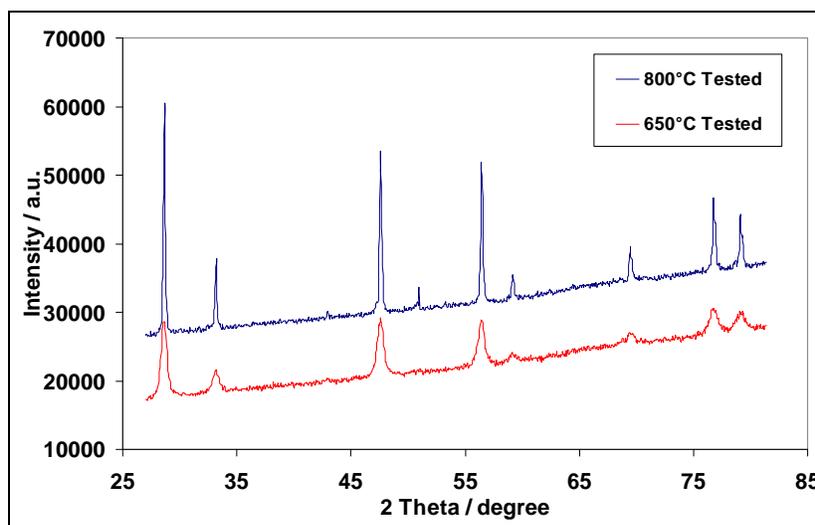


Figure 3. XRD of 5% CuO/CeO₂ after being tested at 650 and 800 °C.

In addition to the XRD measurements, Brunauer-Emmett-Teller (BET) surface area measurements were also conducted for the samples before testing and after being tested. The results are listed in table 2. The surface area of the samples was reduced from 54 m²/g before the sulfidation test to 30 m²/g after being tested at 650 °C, and severely reduced to 1.6 m²/g after being tested at 800 °C. The BET surface area results are in agreement with the XRD results in figure 3. To further investigate if composition change will affect the sintering, 3%, 10%, and 50% CuO/CeO₂ were made and their surface area was measured after being calcined at 650 °C. The results are listed in table 3, and the surface areas were found to be basically independent on the ratio of copper to cerium. However, when the sample of 50% CuO/CeO₂ was calcined at the higher temperatures of 800 and 950 °C, the surface area was decreased from 52 m²/g (calcined at 650 °C) to 13.5 m²/g and 0.49 m²/g, respectively, as shown in table 4. This shows that neither copper nor cerium oxide were able to resist sintering at the temperature above 650 °C. Furthermore, a sample of 50% CuO/Al₂O₃ calcined at the same temperatures had a similar degree of reduction of the surface area, as shown in figure 4.

Table 2. BET results of 5% CuO/CeO₂ before and after testing at 650 and 800 °C.

| | BET Surface Area (m²/g) | Micropore V (cm³/g) | Micropore Area (m²/g) |
|----------------|---|---|---|
| Before testing | 54 | 0.00133 | 1.55 |
| 650 °C tested | 30 | 0.00088 | 2.05 |
| 800 °C tested | 1.6 | 0.00036 | 0.67 |

Table 3. BET surface area (m²/g) of CuO/CeO₂ oxides calcined at 650 °C.

| | 3% CuO/CeO₂ | 10% CuO/CeO₂ | 50% CuO/CeO₂ |
|-----------------|-------------------------------|--------------------------------|--------------------------------|
| 650 °C calcined | 45.7 | 45.6 | 52.0 |

Table 4. BET surface area (m²/g) of oxides calcined at different temperatures.

| | 650 °C Calcined | 800 °C Calcined | 950 °C Calcined |
|--|------------------------|------------------------|------------------------|
| 50% CuO/CeO ₂ | 52.0 | 13.5 | 0.49 |
| 50% CuO/Al ₂ O ₃ | 42.1 | 24.9 | 3.13 |

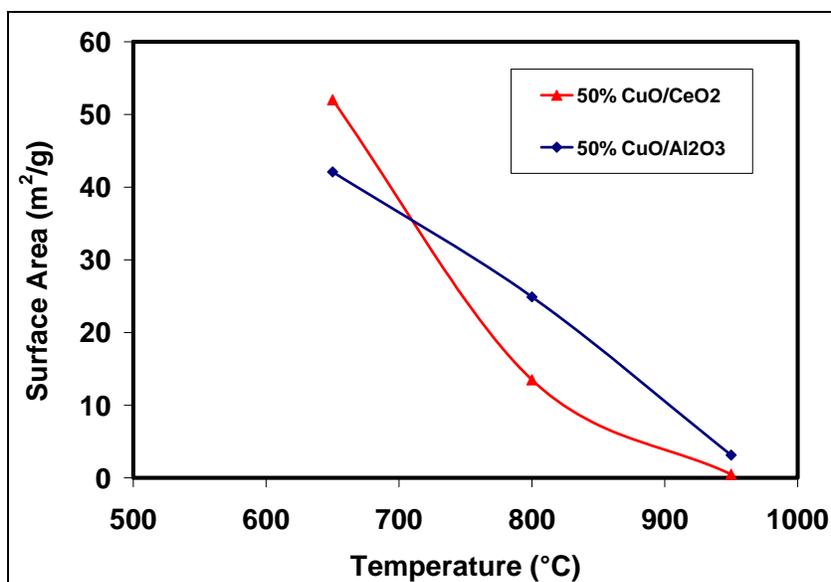


Figure 4. BET surface area of 50% CuO/CeO₂ and 50% CuO/Al₂O₃ calcined at different temperatures.

3.2 Mixed Metal Oxide Supported on Zeolite

In order to better understand the sulfidation behavior of the active copper and cerium ions that were supported on high surface area porous materials in comparison to the corresponding oxide itself, zeolite-Y was chosen as the support. Through ionic exchange reactions, the mono positively charged sodium ion in the zeolite structure was easily replaced by a double positively charged copper ion in solution. The copper exchanged zeolite can be further exchanged by a triple positively charged cerium ion so that a mixed metal supported sorbent can be prepared. The sulfidation experiment was conducted as discussed previously for the mixed metal oxide under the same conditions. The results are shown in figure 5 and table 5. This zeolite supported sorbent has a lower sulfidation capacity than the oxide, and the capacity seemed to be independent of the number of the sulfidation and regeneration cycles, especially for the initial run that was the same as the last run, indicating a near perfect reversible process. Unlike the unsupported oxide, the capacity of this supported sorbent is also temperature independent at both 650 and 800 °C. The XRD in figure 6 demonstrates that the zeolite support structure remained intact after being tested; although, we suspect that some extent of dealumination (6) of zeolite-Y may have happened during the sulfidation test in which water vapor was present at 650 and 800 °C. The BET results in table 6 show a slight decrease in surface area from 575 to 521 m²/g. Table 5 also shows the adsorbed H₂S can be desorbed completely during the regeneration process. Based on these experimental observations, we may characterize it as surface only activity with the supported copper and cerium oxide. For using unsupported 5% CuO/CeO₂ oxide as sorbent, the activity may involve both surface and some bulk domains of the oxide.

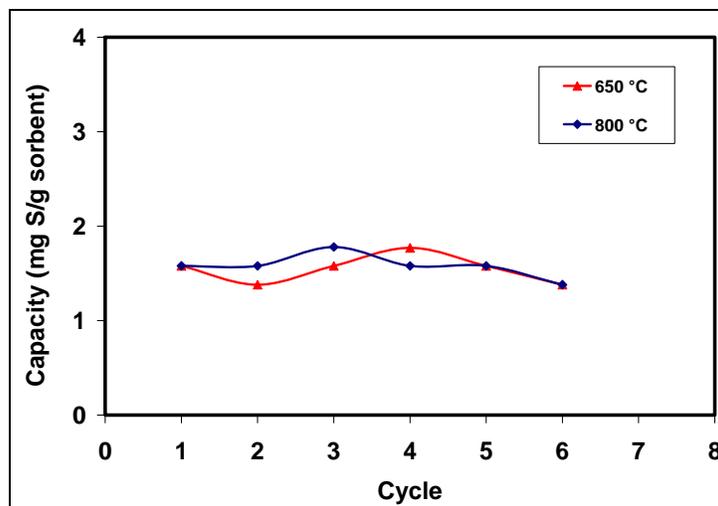


Figure 5. Sulfidation capacity of Cu-Ce-zeolite tested at 650 and 800 °C.

Table 5. Sulfidation/regeneration cycling results of Cu-Ce-zeolite at 650 and 800 °C.

| Cycled at 650 °C | 1 | 2 | 3 | 4 | 5 | 6 |
|---|----------|----------|----------|----------|----------|----------|
| Capacity (mg S /g sorbent) | 1.58 | 1.38 | 1.58 | 1.77 | 1.58 | 1.38 |
| Desorbed /adsorbed H ₂ S (%) | 90 | 101 | 102 | 97 | 98 | 99 |
| | | | | | | |
| Cycled at 800 °C | 1 | 2 | 3 | 4 | 5 | 6 |
| Capacity (mg S /g sorbent) | 1.58 | 1.58 | 1.78 | 1.58 | 1.58 | 1.38 |
| Desorbed /adsorbed H ₂ S (%) | 100 | 99 | 92 | 99 | 102 | 97 |

Note: Experimental conditions: pre-reduction: 650 and 800 °C, 50%H₂-10%H₂O-balanced He, 1 h; sulfidation: 650 and 800 °C, 0.1%H₂S-50%H₂-10%H₂O-balanced He, space velocity 80,000/h; regeneration: 650 and 800 °C, 50%H₂-10%H₂O-balanced He, space velocity 80,000/h.

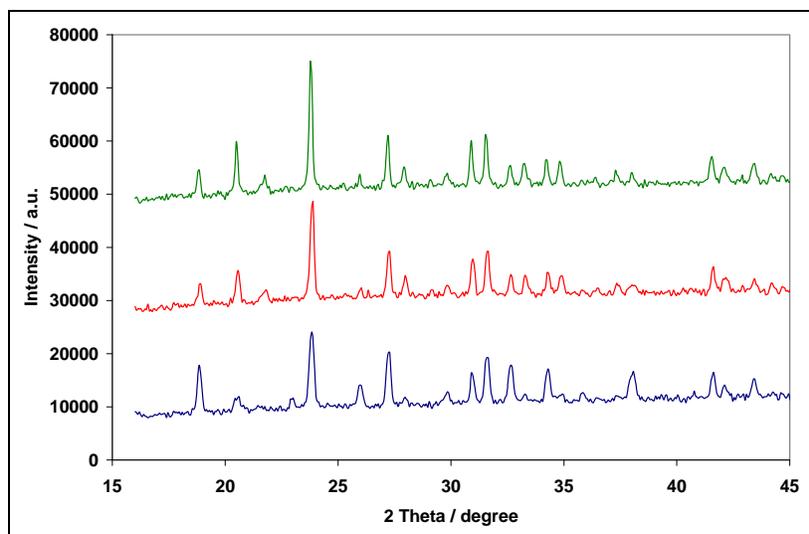


Figure 6. XRD of Cu-Ce-zeolite—upper: after being tested at both 650 and 800 °C; middle: after being calcined at 650 °C; and lower: as prepared.

Table 6. BET surface area (m^2/g) of Cu-Ce-zeolite.

| Cu-Ce-Zeolite | BET Surface Area (m^2/g) |
|----------------------|--|
| 650 °C calcined | 575 |
| 800 °C calcined | 540 |
| 800 °C tested | 521 |

3.3 Effect of Metal Ion on Zeolite Structure

Table 7 summarizes the sulfidation capacity of zeolite-Y, the supported copper, cerium, and copper/cerium sorbents, and table 8 summarizes their BET surface area changes after the test at 800 °C. From table 7, we see that zeolite-Y has a minimal capacity, but the incorporation of copper provided an additional more than 1 mg S/g in capacity, and the incorporation of cerium provided less than 1 mg S/g in capacity than zeolite-Y by itself as a sorbent. The supported copper and cerium mixed metal sorbent Cu-Ce-zeolite has a capacity between those of the Cu-zeolite and Ce-zeolite, as shown in table 7. Noticeably in table 8, the BET results show that (1) the surface area of zeolite-Y by itself was significantly reduced to 20 under the sulfidation conditions, (2) the surface area of copper supported on zeolite (Cu-zeolite) was reduced to an even lower value of 9.4 under the same conditions, and (3) only Ce-zeolite and Cu-Ce-zeolite can keep the surface area above 500 m^2/g after being tested, indicating the structure of the cerium ion exchanged zeolite was stable during the test, even if some extent of dealumination of zeolite-Y (7) may have occurred, as mentioned previously. XRD measurements of these zeolite samples (figures 7 and 8) after the test at 800 °C revealed that significant structural change only occurred for Cu-zeolite, as shown in figure 7. It shows the formation of copper metal (three narrow peaks between 40 and 80 degrees, and a broad peak centered around 22 degrees as possible aluminate and silicate amorphous phases. This is most likely due to the combined result of high temperature, highly reducing atmosphere, and the presence of water. The reduction of copper ions to copper metal within the structure of the zeolite and the high temperature steam may lead to the collapse of the zeolite structure. This suggests that both the cerium exchanged zeolite and the copper/cerium mixed metal exchanged zeolite should be better candidates than the copper only exchanged zeolite for H_2S desulfurization at 800 °C.

Table 7. Sulfidation/regeneration cycling results of pure zeolite and metal ion exchanged zeolites tested at 800 °C.

| Tested at 800 °C | Capacity (mg S/g Sorbent) | Desorbed/Adsorbed H_2S (%) |
|-------------------------|----------------------------------|--|
| Zeolite-Y | 0.26 | 99 |
| Cu-zeolite | 1.80 | 87 |
| Ce-zeolite | 1.04 | 98 |
| Cu-Ce-zeolite | 1.58 | 98 |

Note: Experimental conditions: pre-reduction: 800 °C, 50% H_2 -10% H_2O -balanced He, 1 h; sulfidation: 800 °C, 0.1% H_2S -50% H_2 -10% H_2O -balanced He, space velocity 80,000/h; regeneration: 800 °C, 50% H_2 -10% H_2O -balanced He, space velocity 80,000/h.

Table 8. BET surface area (m^2/g) of pure zeolite and metal ion exchanged zeolites calcined at $800\text{ }^\circ\text{C}$ and tested at $800\text{ }^\circ\text{C}$.

| BET Surface Area (m^2/g) | $800\text{ }^\circ\text{C}$ Calcined | $800\text{ }^\circ\text{C}$ Tested |
|--|--------------------------------------|------------------------------------|
| Zeolite-Y | 581 | 20.3 |
| Ce-zeolite | 576 | 542 |
| Cu-Ce-zeolite | 575 | 521 |

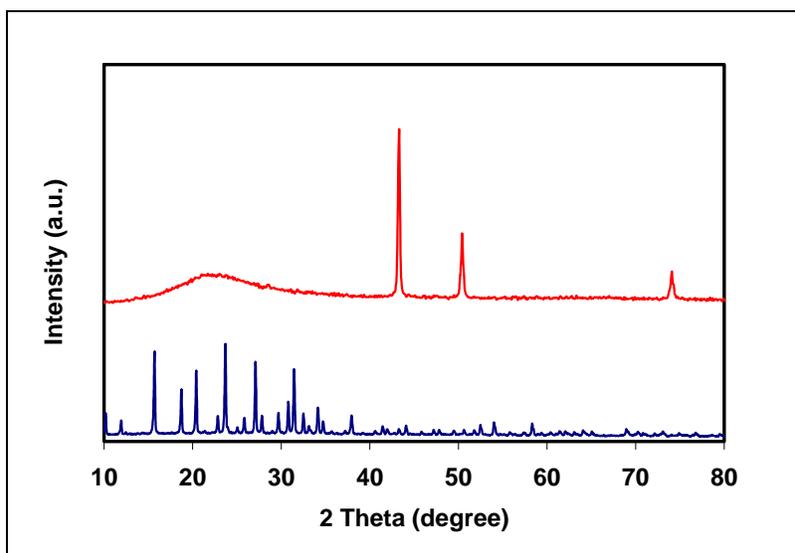


Figure 7. XRD of Cu-zeolite—upper: after being tested at $800\text{ }^\circ\text{C}$ and lower: after being calcined at $650\text{ }^\circ\text{C}$.

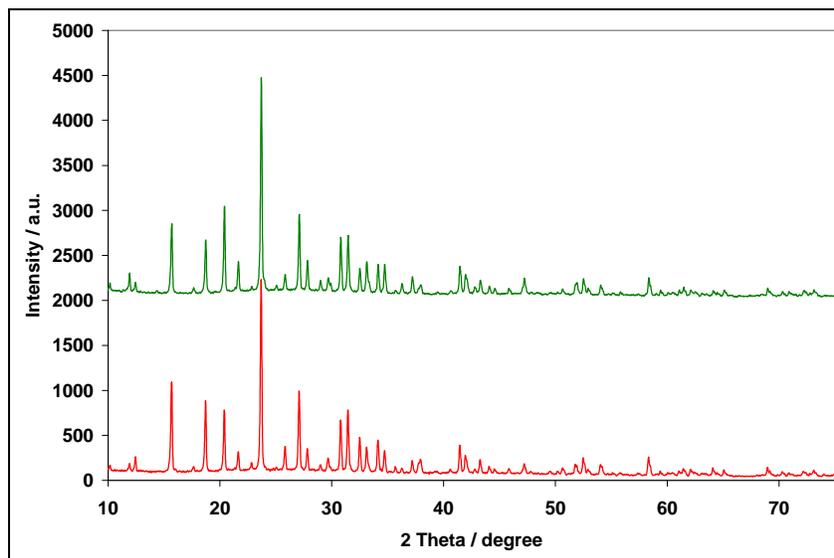


Figure 8. XRD of Ce-zeolite—upper: after being tested at $800\text{ }^\circ\text{C}$ and lower: after being calcined at $650\text{ }^\circ\text{C}$.

4. Conclusions

The overall sulfidation capacity of the mixed metal oxides was found to be higher than corresponding zeolite supported counterparts, but the mixed metal oxide also showed evidence of sintering at higher temperatures, which resulted in a decreased capacity. The sulfidation capacity of the zeolite supported mixed metal oxide, although started with a lower capacity, was found to be independent of the temperature at both 650 and 800 °C, suggesting the mixed metal ions supported on zeolite are resistant to the sintering at higher temperature. The experimental evidence confirmed that the mixed metal ions supported on zeolite have only surface interaction with H₂S.

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List of Symbols, Abbreviations, and Acronyms

| | |
|-----------------------------------|-----------------------------------|
| BET | Brunauer-Emmett-Teller |
| Ce | cerium |
| Ce(NO ₃) ₃ | cerium nitrate |
| CTA | Collaborative Technology Alliance |
| Cu | copper |
| Cu(NO ₃) ₂ | copper nitrate |
| CuS | copper sulfide |
| EPA | Environmental Protection Agency |
| Fe | iron |
| H ₂ S | hydrogen sulfide |
| He | helium |
| KOH | potassium hydroxide |
| S&T | Science & Technology |
| Si | elementary silicon |
| SOFCs | solid oxide fuel cells |
| XRD | x-ray diffraction |

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| 1 HC | US ARMY RSRCH DEV AND ENGRG CMND ARMAMENT RSRCH DEV AND ENGRG CTR ARMAMENT ENGRG AND TECHNLGY CTR ATTN AMSRD AAR AEF T J MATTS BLDG 305 ABERDEEN PROVING GROUND MD 21005-5001 | TOTAL: 15 (1 PDF, 1 CD, 13 HCS) | |
| 1 HC | PM TIMS, PROFILER (MMS-P) AN/TMQ-52 ATTN B GRIFFIES BUILDING 563 FT MONMOUTH NJ 07703 | | |
| 1 HC | US ARMY INFO SYS ENGRG CMND ATTN AMSEL IE TD F JENIA FT HUACHUCA AZ 85613-5300 | | |
| 1 HC | COMMANDER US ARMY RDECOM ATTN AMSRD AMR W C MCCORKLE 5400 FOWLER RD REDSTONE ARSENAL AL 35898-5000 | | |
| 1 HC | US GOVERNMENT PRINT OFF DEPOSITORY RECEIVING SECTION ATTN MAIL STOP IDAD J TATE 732 NORTH CAPITOL ST NW WASHINGTON DC 20402 | | |

INTENTIONALLY LEFT BLANK.