Cu–Cr–O and Cu–Ce–O Regenerable Oxide Sorbents for Hot Gas Desulfurization

Zhijiang Li and Maria Flytzani-Stephanopoulos*

Department of Chemical Engineering, Tufts University, Medford, Massachusetts 02155

Binary Cu–Cr–O and Cu–Ce–O oxides were studied in this work as regenerable sorbents for high-temperature fuel gas desulfurization. CuO–Cr2O3 and CuO–CeO2 sorbents can remove H2S from simulated coal-derived fuel gas to less than 5–10 ppmv in the temperature range of 650–850 °C. The presence of stable CuCr2O4 in CuO–Cr2O3 solids retains some copper in the Cu2+ or Cu3+ oxidation state, which can account for the high H2S removal efficiency. In CuO–CeO2 sorbents, however, CuO is easily reduced to copper metal. Participation of reduced cerium oxide in sulfidation can explain the observed high desulfurization efficiency. TGA tests and XRD analysis indicate that sulfidation proceeds through partial initial reduction of the CuO–Cr2O3 sorbents: CuO → Cu/Cu2O → Cu2S (x < 2). Reduction kinetics were studied in the TGA over temperature ranges of 550–850 and 350–850 °C, respectively, for the CuO–Cr2O3 and CuO–CeO2 materials. The sulfidation kinetic parameters were measured in the temperature range of 450–850 °C after preoxidation of both sorbents. The sulfidation of metal copper in Cr2O3 and CeO2–x matrices is a fast reaction with low activation energy, 19.8 and 16.6 kJ/mol, respectively. Both types of sorbents can be fully regenerated with diluted air. The regeneration temperature affects the reaction pathway and the regenerability of the solid composition.

Introduction

High-temperature, regenerative desulfurization of fuel gases is under development to improve the thermal efficiency of advanced coal-based power generation systems, such as integrated gasification combined-cycle (IGCC) power plants. One of the crucial factors for the successful application of the high-temperature desulfurization technology is the development of sorbents which can efficiently remove sulfur compounds, mainly H2S, from fuel gases in the temperature range of 600–800 °C. The search for sorbents with high H2S removal efficiency, good sulfur-loading capacity, high regenerability, and sufficient strength has continued unabated since the early 1980s. Early studies of single metal oxides, such as Fe2O3 and ZnO, were soon followed by the development of mixed metal oxides to increase the H2S removal efficiency and regenerability of the sorbent. The mixed-oxide sorbent zinc ferrite, ZnFe2O4, combining ZnO and Fe2O3 has been developed as an improvement over each of its component oxides, primary in the work performed at the Department of Energy [1,2]. Zinc ferrite, however, is prone to reduction of both its component oxides at high temperatures. Work at the Massachusetts Institute of Technology in the middle and late 1980s established zinc titanates as improved ZnO-based sorbents that could also impart stability to ZnO against reduction to elemental zinc. Formation of the latter is followed by zinc migration and/or evaporation, which cause undesired structural modifications of the sorbent in highly reducing coal gas streams [3–9]. Because of their higher stability, zinc titanates lean-in-zinc may be used at higher desulfurization temperatures than ZnO or ZnFe2O4 [6].

In parallel with the development of ZnO-based sorbents, other sorbent studies have been conducted with various mixed metal oxides, predominantly based on copper oxide, which can be used at much higher temperature than ZnO [4,10–16]. The low vapor pressure of copper oxides and copper metal ensures operation without volatilization. Among all metal oxides, copper oxides (CuO and Cu2O) have the highest sulfidation equilibrium constants; for example, at T = 900 K, \( K_e = 6.3 \times 10^{17} \) and \( 8.9 \times 10^8 \), respectively, for CuO and Cu2O [17] sulfidation according to the reactions:

\[
2\text{CuO} + \text{H}_2\text{S} + \text{H}_2 = \text{Cu}_2\text{S} + 2\text{H}_2\text{O} \\
\text{Cu}_2\text{O} + \text{H}_2\text{S} = \text{Cu}_2\text{S} + \text{H}_2\text{O}
\]

Thus, copper oxides can reduce H2S from several thousand ppm to sub-ppm levels. However, CuO in uncombined form is readily reduced to metallic copper by the H2 and CO contained in fuel gases [13,15]. The reduction of Cu2+ or Cu3+ to metallic Cu lowers the desulfurization efficiency, since the sulfidation equilibrium constant of CuO is about 10 orders of magnitude higher than that of Cu. Metallic copper has an inferior desulfurization efficiency to ZnO. Another disadvantage of uncombined copper oxide is its low utilization in sulfidation caused by sintering of onion-like dense sulfide layers which dramatically increase the solid diffusion resistance and cause structural degradation of the pellet [18]. To improve the performance of CuO-based sorbents, research has focused on two approaches: (i) to maintain part of copper at the +2 or +1 oxidation state during sulfidation and (ii) to provide CuO in highly dispersed form to reduce the diffusion resistance.

In order to retain copper at the +2 or +1 oxidation state, copper oxides have been combined with other metal oxides, forming metal oxide compounds [4,10,11,14,15,18,19]. Flytzani-Stephanopoulos et al. [4,10] and Patrick et al. [14,15] studied various bulk CuO-based sorbent systems, such as Cu–Fe–O, Cu–Al–O, Cu–Fe–Al–O, and Cu–Mo–Al–O. In metal oxide compounds, such as CuFe2O4 or CuAl2O4, the reduction of CuO to Cu by H2 or CO was much slower than that of pure CuO. This is due both to the thermodynamic stability of these spinels and to slow kinetics. The slow reduction of CuO in these mixtures retained a portion of copper in +2 and/or +1 oxidation state and, therefore, achieved sub-ppm H2S breakthrough levels at temperatures as high as 650–700 °C depending on the fuel gas composition. Even higher
stability is provided to CuO by combining it with chromium oxide. Thus, CuCr2O4 was found to possess the best thermodynamic stability and slowest reduction kinetics among all oxide compounds of copper [17,19].

Dispersed CuO-containing sorbents can generally be synthesized by carrying copper oxides on a support at low temperatures. For high-temperature application, however, the choice of support is crucial. Alumina, for example, will react with copper, forming stable copper aluminates at high temperature (≥ 600 °C) either during calcination or during the sorbent regeneration step. Compound formation prevents good dispersion.

During calcination or during the sorbent regeneration, aluminate phases at high temperature (example, will react with copper, forming stable copper aluminates at high temperature (≥ 600 °C). For high-temperature application, the choice of support is crucial. Alumina, for example, will react with copper, forming stable copper aluminates at high temperature (≥ 600 °C) either during calcination or during the sorbent regeneration step. Compound formation prevents good dispersion.

While, as mentioned above, CuO-based sorbents are expected to retain oxidic copper in reductivesulfidation, both types of sorbents were better than 99%, and complete CuO conversion was attained at 750 °C. The H2S removal efficiency and high reactivity in both sulfidation and regeneration was confirmed that bulk gas diffusion limitations were eliminated at this flow rate.

In all TGA tests 2–3 mg of sorbent was placed in a hemispherical quartz pan suspended by a quartz hang-down wire. A thin layer of quartz wool was used to partially fill the quartz pan. The typical size of solid particles used was 125–180 μm. After loading the sample, the furnace was heated to a set point at a rate of 22 °C/min under pure N2 and was maintained at the set value throughout the experiment. Typically, reduction lasted for 10 min, sulfidation for 20 min, and regeneration for 10 min. An intermittent nitrogen purge for 20 min was used between sulfidation and regeneration tests.

**Packed-Bed Microreactor Tests.** Sulphidation and regeneration tests were performed in a packed-bed microreactor to evaluate the overall H2S removal efficiency and regenerability of the synthesized sorbents. The packed-bed microreactor system and experimental procedure were the same as those previously described by Lew et al. [5–8]. About 50 mg of sorbent of 420–800 μm in diameter was used. Dry gas mixtures containing H2S–H2–N2 were used to screen the sorbents. The gas hourly space velocity, SV, was 3000 h⁻¹ (NTP). H2S and SO2 concentrations in the exit gas were measured by a HP 5880A gas chromatograph (GC), equipped with a flame photometric detector (FPD) and a thermal conductivity detector (TCD) used respectively during sulfidation and regeneration.

**Results and Discussion**

**Characterization of Fresh Sorbents.** Table 1 lists the physical properties of fresh binary Cu–Cr–O and Cu–Ce–O sorbents prepared in this work. At a calcination temperature of 1000 °C, the specific surface area of the two types of sorbents decreased with the CuO content. X-ray diffraction identified that cupric chromite, CuCr2O4, was formed in the CuO-lean Cu–Cr–O sorbent, while the excess chromium oxide was in the form of Cr2O3. For the equimolar CuO–Cr2O3 material, CuCr2O4 was the only crystalline phase formed and no separate CuO or Cr2O3 phases were identified. Cuprous chromite, CuCrO2, and CuO phases coexisted in the CuO-rich sorbent, 3CuO–Cr2O3. For Cu–Ce–O sor-
bents, the XRD data in Table 1 show that no compounds were formed for all three Cu–Ce–O sorbents. CuO and CeO₂ existed in separate phases in all sorbent compositions.

Parts A and B of Figure 1 show scanning electron micrographs of the fresh equimolar CuO–Cr₂O₃ and CuO–CeO₂ sorbents. As can be seen from Figure 1A, well-formed CuCrO₄ crystals were produced after calcination at 1000 °C. These crystals have a uniform size of ~0.5 μm. Figure 1B shows a very different structure for the CuO–CeO₂ sorbent. No separate phase of CuO could be discerned on ceria by SEM. By the use of high-resolution scanning transmission electron microscopy and EDS, however, Liu et al., have identified CuO particles and clusters in Cu–Ce–O materials.

More experiments were conducted for CuO-rich and CuO-lean Cu–Cr–O and Cu–Ce–O sorbents. The crystals in 3CuO–Cr₂O₃ and CuO–3Cr₂O₃ solids were not as uniform as those in equimolar samples, and the average crystal sizes were ~2 and ~0.3 μm, respectively. The 3CuO–CeO₂ and CuO–3CeO₂ samples had structures similar to that of the CuO–CeO₂ sorbent.

Sulfidation of the Cu–Cr–O and Cu–Ce–O Solids. Packed-Bed Microreactor Tests. Sulfidation tests were performed in the packed-bed microreactor with each of the six Cu–Cr–O and Cu–Ce–O sorbent compositions listed in Table 1. A gas mixture containing (mol) 2% H₂S–20% H₂–78% N₂ at SV = 3000 h⁻¹ (NTP) was used in these tests. The resulting performance is shown in Figure 2 in terms of H₂S breakthrough curves at 850 °C. The normalized time, t/t*, is defined as the ratio of the real reaction time, t, to the theoretical time, t*, required for complete sulfidation of the amount of sorbent used in each test to form Cu₂S. Thus, t/t* corresponds to active sorbent conversion. This assumes that neither Cr₂O₃ nor CeO₂ forms bulk sulfides under the tested conditions. It also assumes the absence of nonstoichiometric sulfides of copper. The H₂S breakthrough time is reported here for 100 ppmv H₂S in the effluent gas.

More experiments were conducted for CuO-rich and CuO-lean Cu–Cr–O and Cu–Ce–O sorbents. The crystals in 3CuO–Cr₂O₃ and CuO–3Cr₂O₃ solids were not as uniform as those in equimolar samples, and the average crystal sizes were ~2 and ~0.3 μm, respectively. The 3CuO–CeO₂ and CuO–3CeO₂ samples had structures similar to that of the CuO–CeO₂ sorbent.

Table 1. Characterization of Fresh and Sulfided Sorbents

<table>
<thead>
<tr>
<th>sorbent</th>
<th>BET surface area [m²/g]</th>
<th>max. theoretical sulfur loading a (g of sulfur/100 g of sorbent)</th>
<th>crystalline phases c/sulfided d</th>
<th>fresh</th>
<th>sulfided</th>
</tr>
</thead>
<tbody>
<tr>
<td>3CuO–Cr₂O₃</td>
<td>0.6</td>
<td>12.2</td>
<td>CuCrO₂, CuO</td>
<td>Cr₂O₃, Cu₆S₅, Cu₂O</td>
<td></td>
</tr>
<tr>
<td>CuO–Cr₂O₃</td>
<td>2.2</td>
<td>6.7</td>
<td>CuCrO₂, CuO</td>
<td>Cr₂O₃, Cu₆S₅</td>
<td></td>
</tr>
<tr>
<td>CuO–3Cr₂O₃</td>
<td>3.7</td>
<td>3.0</td>
<td>CuCrO₂, Cr₂O₃</td>
<td>Cr₂O₃, Cu₆S₅</td>
<td></td>
</tr>
<tr>
<td>3CuO–CeO₂</td>
<td>1.1</td>
<td>17.7</td>
<td>CuO, CeO₂</td>
<td>CeO₂, Cu₆S₅, CeS₃</td>
<td></td>
</tr>
<tr>
<td>CuO–CeO₂</td>
<td>4.4</td>
<td>6.4</td>
<td>CuO, CeO₂</td>
<td>CeO₂, Cu₆S₅, CeS₃</td>
<td></td>
</tr>
<tr>
<td>CuO–3CeO₂</td>
<td>5.8</td>
<td>2.7</td>
<td>CuO, CeO₂</td>
<td>CeO₂, Cu₆S₅, CeS₃</td>
<td></td>
</tr>
</tbody>
</table>

a After calcination in air at 1000 °C for 1 h. b Assuming Cu₂S as the only sulfidation product. c Identified by X-ray diffraction analysis. d Sulfided under 2% H₂S–20% H₂–78% N₂ at 850 °C.
The H$_2$S breakthrough curves in Figure 2 show that complete desulfurization of the feed gas stream can be obtained for all the Cu–Cr–O and Cu–Ce–O sorbents even at the high temperature of 850 °C. The conversion of copper at breakthrough was higher in the Cu-lean sorbents, CuO–3Cr$_2$O$_3$ and CuO–3CeO$_2$. As the CuO content was increased, H$_2$S breakthrough occurred earlier, with corresponding lower CuO utilization. For example, the normalized prebreakthrough time decreased from 1.5 to 0.65 to 0.2 as the CuO/Cr$_2$O$_3$ molar ratios changed from 1/3 to 1/1 to 3/1, respectively. A plausible explanation for this is that, in higher CuO-containing sorbents, CuO exists in larger crystals, which provide increased diffusion resistance to the reactant gas through a shell of product Cu$_2$S. Assuming the Cu$_2$S stoichiometry, the calculated sulfur loading of the sorbents at 100 ppmv H$_2$S breakthrough level was approximately 2.2, 3.7, and 4.3 g of sulfur per 100 g of sorbent for the 3CuO–Cr$_2$O$_3$, CuO–Cr$_2$O$_3$, and CuO–3Cr$_2$O$_3$ sorbents and 4.4, 4.2, and 2.2 g of sulfur per 100 g of sorbent for the 3CuO–Ce$_2$O$_3$, CuO–Ce$_2$O$_3$ and CuO–3CeO$_2$ sorbents, respectively. Compared to the theoretical values listed in Table 1, the actual utilization of copper in Cu-rich sorbents is very low. On the other hand, in Cu-lean sorbents full utilization of copper has been achieved. Interestingly, the actual sulfur loading exceeds the theoretical value for the CuO–3Cr$_2$O$_3$ sorbent (see also Figure 2A). As discussed below, this may be due to formation of nonstoichiometric sulfides.

Figure 2 shows prebreakthrough levels of H$_2$S (<5 ppm) that are much lower than the equilibrium H$_2$S levels corresponding to reaction of metallic copper with H$_2$S, i.e., 2Cu + H$_2$S = CuS + H$_2$. Under the conditions of these experiments (850 °C, 20% H$_2$), the equilibrium H$_2$S level is ~300 ppmv [17]. Hence, the active sorbent phase is not copper metal under these conditions. Similar observations were made with other gas compositions and temperatures both in this lab and in bench-scale reactor tests conducted at the Institute of Gas Technology using the equimolar CuO–Cr$_2$O$_3$ and CuO–Ce$_2$O$_3$ sorbents [22]. The presence of various amounts of hydrogen, water vapor, and carbon oxides in the reactant gas does not affect the H$_2$S prebreakthrough level, although it can shift the breakthrough time [19,22].

Characterization of Sulfided Solids. Sulfided solids from the packed-bed microreactor tests were analyzed by XRD and SEM. As shown in Table 1, Cu$_9$S$_5$ is the major phase of copper sulfides for all three Cu–Cr–O compositions after sulfidation. Cr$_2$O$_3$ was also identified by XRD, while no chromium sulfides were found. A small amount of Cu$_2$O (based on signal intensity) was observed for the sulfided 3CuO–Cr$_2$O$_3$ solid, in agreement with the low Cu utilization of this sorbent composition in the microreactor test. For the Cu–Ce–O mixtures, Cu$_9$S$_5$ was the major sulfide phase. Also, CeO$_2$ appeared to have reacted with H$_2$S to form cerium sulfides, since Ce$_2$S$_3$ was consistently identified by XRD in the sulfided Cu–Ce–O sorbents. This is in agreement with the report that reduced cerium oxides, CeO$_{2-x}$, are good sulfidation materials at high temperatures [23]. In regards to Figure 2, it is not accurate to estimate t* on the basis of only Cu$_9$S$_5$ formation. However, even if approximate, the normalized time used in Figure 2 provides a measure of sorbent conversion. In practice, a more meaningful measure is that of sulfur loading, which can be used as the abscissa when comparing H$_2$S breakthrough profiles [22].
is the reduction of Cu²⁺ oxides to Cu¹⁺ oxides or metal copper, with concomitant weight decrease; the second is sulfidation of metal copper or copper oxides to copper sulfides, leading to weight increase. Although both reduction and sulfidation reactions occurred simultaneously once the sorbents were contacted with the inlet gas containing H₂ and H₂S, reduction was much faster than sulfidation and dominated the earlier part of the reaction. As the reaction proceeded, sulfidation began to dominate the entire reaction. Thus, the reaction path for sulfidation of these copper oxide-containing sorbents appears to be CuO − Cu₂O/Cu − CuₓS (x < 2) over the tested temperature range.

Comparing parts A and B of Figure 4, it is seen that the reduction of CuO−Cr₂O₃ sorbent was much slower when the temperature was decreased from 850 to 650 °C. However, temperature had little effect on the CuO−CeO₂ sorbent. In other words, reduction of CuO−CeO₂ took place to the same extent at all temperatures in the range of 650–850 °C. For the CuO−Cr₂O₃ sorbent consisting of CuCr₂O₄ compound, the stability of CuCr₂O₄ suppresses reduction, especially at T ≤ 750 °C. This can explain why the H₂S removal efficiency obtained in the packed-bed microreactor was higher than that of copper metal (Figure 2A). On the other hand, the reducibility of the Cu−Ce−O sorbents shown in Figure 4B does not match the Cu₂O/Cu − CuₓS reaction (x < 2) over the tested temperature range.

Further direct sulfidation tests of the fresh sorbent samples were conducted in the TGA under various conditions. The effect of H₂ concentration on sulfidation at T = 750 °C is shown in parts A and B of Figure 5 for CuO−Cr₂O₃ and CuO−CeO₂, respectively. For both sorbents, the reduction rate and extent of reduction increased with the H₂ concentration. At temperatures above 750 °C complete reduction of CuO to metallic copper during sulfidation took place for CuO−Cr₂O₃ sorbents when H₂ was above 30 mol% (Figure 5A). For CuO−CeO₂ sorbents, a lower H₂ concentration of 10 mol% was sufficient to reduce the sorbent to an extent corresponding to all oxidic copper reduced to the metal state. As can be seen in Figure 5A,B, a small weight decrease was measured even when the inlet gas did not contain H₂ (H₂₀% curves). Two factors could contribute to the weight decrease at this condition. One is the reduction of CuO by H₂ produced by the decomposition of H₂S, while the other is the oxidation of H₂S by CuO or CeO₂ to form SO₂. The former was verified by the condensation of elemental sulfur on the cooler walls of the quartz tube and in the water trap located downstream of the TGA. The equilibrium H₂ concentration for H₂S decomposition at 750 °C is calculated to be ~1400 ppm in the absence of hydrogen in the inlet gas. On the other hand, the oxidation of H₂S to SO₂ has been reported to be catalyzed by ceria [25]. To check for this, we analyzed the TGA off-gas in the GC-FPD. The measurement showed that approximately 50 ppm SO₂ could be obtained in the TGA outlet gas when a low H₂ concentration (<10 mol %) was used. Thus, under some conditions, other reactions, such as decomposition and/or oxidation of H₂S, can also take place in addition to the main sulfidation reaction.
Sulfidation of fresh sorbent samples at various H$_2$S concentrations is shown in Figure 6 for the CuO–CeO$_2$ sorbent. Similar results were found for the CuO–Cr$_2$O$_3$. Increasing the H$_2$S concentration led to faster sulfidation rate. Thus, at higher H$_2$S concentrations fresh sorbents were less extensively reduced and showed an early weight increase. For example, at 2% H$_2$S, the weight loss due to reduction is 77% of that observed at 0.5% H$_2$S and the weight gain begins 5 s earlier. From Figure 6, it is also obvious that H$_2$S has little effect on the reduction rate at 750 °C, as indicated by the overlapping of the reduction segments of the normalized weight profiles at various H$_2$S concentrations.

**Comparative Kinetics of Reduction and Sulfidation of Cu–Cr–O and Cu–Ce–O.** To better study the above reductive sulfidation behavior, separate tests of reduction and sulfidation of prereduced sorbent samples were performed in the TGA. The kinetics of reduction of CuO–Cr$_2$O$_3$ and CuO–CeO$_2$ were compared. Also, comparative studies of the kinetics of prereduced Cu–Cr$_2$O$_3$ and Cu–CeO$_2$–x materials were conducted as described below.

**Reduction Kinetics.** Reduction tests were conducted over a wide temperature range from 350 to 850 °C in a gas mixture containing (mol) 10% H$_2$–10% H$_2$O–bal N$_2$. The effect of temperature on reduction is shown in Figure 7. When the temperature was decreased from 850 to 550 °C, the reduction rate of CuCr$_2$O$_4$ decreased dramatically, (Figure 7A), but for CuO–CeO$_2$, no appreciable change of reduction rate was found even over a wider temperature range (350–850 °C). In temperature-programmed-reduction (TPR) experiments with Cu–Ce–O, Liu et al. [24] have found a bimodal reduction by hydrogen. A 15(at)% Cu-containing cerium oxide showed a TPR profile with a first peak at 120–145 °C corresponding to CuO reduction and a broader second peak from 450 to 850 °C corresponding to CeO$_2$ reduction. Notably, each phase alone is less reducible.

Reduction of the CuO–Cr$_2$O$_3$ and CuO–CeO$_2$ solids under various H$_2$ concentrations was conducted at 750 °C with [H$_2$] = 2–40 mol %. Figure 8 shows the profiles of the normalized weight vs time at three H$_2$ concentrations: 2, 10, and 40%. Over the tested H$_2$ concentration range, the reduction of both sorbents was rather fast at 750 °C. As can be seen from this figure, the reduction rate of both sorbents increased with the H$_2$ concentration in the feed stream. The CuO–Cr$_2$O$_3$ material showed a stronger dependence on H$_2$ concentration than CuO–CeO$_2$, apparently due to the stability of the CuCr$_2$O$_4$ compound.

Initial reduction rates were measured from the slopes of the WW$_0$ profiles in Figures 7 and 8 at time $t = 0$. The initial reduction rates, $R_0$, can be expressed as surface rates of reduction of CuO, by dividing the slope $d$WW$_0$/dt at $t = 0$ by the surface area of the sorbent, $A_0$ (m$^2$/g), and by the molecular weight of the escaping species, considering the reaction stoichiometry. Here,
this is $\frac{1}{2}$ mol of oxygen for each 1 mol of CuO. In calculating the initial reduction rates for CuO–CeO$_2$, we assumed that CuO was the faster of the two oxides. Figure 9 shows Arrhenius-type plots for the initial reduction rates of CuO–Cr$_2$O$_3$ and CuO–CeO$_2$. The rates, expressed in mmol of CuO cm$^{-2}$ s$^{-1}$, were measured over the temperature range of 550–850 °C. The reaction order in H$_2$, $n$, was determined to be 0.58 and 0.42, respectively, for CuO–Cr$_2$O$_3$ and CuO–CeO$_2$ at 750 °C. Assuming constancy of this order with temperature, reaction rate constants can be calculated using the expression $R_0 = k_0 C_{H_2}$. Table 2 lists the values of the Arrhenius constants $k_{0,0}$ and $E_a$ for the reduction rate constants expressed in Arrhenius form: $k_0 = k_{0,0} \exp(-E_a/RT)$, for each of the two CuO-based sorbents.

From Figure 8, it is seen that at 750 °C the surface reduction kinetics (initial reduction rates) prevail also at large sorbent conversions in the presence of more than 10 mol % H$_2$ in the feed gas. However, under different conditions, the rate may become limited by gas diffusion through the solid. This is particularly so for the CuO–Cr$_2$O$_3$ sorbent, which is limited by diffusion at 750 °C when the hydrogen level is 2 or 10%, as shown in Figure 8A by the lower slope of the W/W$_0$–time curves at long times.

Sulfidation of Prereduced Sorbents. Sulfidation of reduced sorbents was conducted at 650, 750, and 850 °C by first reducing the sample at a fixed condition, i.e., at 750 °C with a gas mixture containing (mol) 10% H$_2$–10% H$_2$O–80% N$_2$, and then introducing the sulfidation gas mixture containing (mol) 10% H$_2$–10% H$_2$O–0.5% H$_2$S–bal N$_2$. As an example, Figure 10 shows the sulfidation of prereduced Cu–Cr$_2$O$_3$ at various temperatures. Similar profiles were obtained for Cu–CeO$_2$–x. As a result of complete prereduction, sulfidation of Cu in both samples was fast and almost independent of temperature in the range of 650–850 °C. Complete conversion of Cu to copper sulfides was achieved at all conditions tested except at 650 °C for Cu–Cr$_2$O$_3$ as shown in Figure 10, where the final normalized weight was slightly less than 1. From several comparisons of the overall kinetics at 750 and 850 °C, the Cu–CeO$_2$–x material appeared to have faster sulfidation. This difference may be caused by the different pore structure of the two sorbents and the potential participation of cerium oxide in sulfidation of the prereduced Cu–CeO$_2$–x material.

Parts A and B of Figure 11 show sulfidation profiles of prereduced Cu–Cr$_2$O$_3$ and Cu–CeO$_2$–x samples, respectively, at various concentrations of H$_2$S. Clearly, the rates increase appreciably with the H$_2$S concentration. With the exception of the Cu–Cr$_2$O$_3$ at 0.125% H$_2$S (Figure 11A), the W/W$_0$ increased linearly with the reaction time up to complete conversion, indicating that sulfidation rates were not limited by diffusion at 750 °C.

Initial rates of sulfidation of prereduced sorbents were obtained from the slopes of W/W$_0$–time profiles at t = 0 in Figures 10 and 11 and other similar data. The stoichiometry of the sulfidation of metallic copper was assumed: 2Cu + H$_2$S = Cu$_2$S + H$_2$, and the BET surface area of the prereduced solids was used to calculate the initial rate, $R_0$, in terms of moles of Cu$_2$S produced per unit time per unit area (Table 2). Figure 12 shows the Arrhenius-type plots of the initial sulfidation rates for Cu–Cr$_2$O$_3$ and Cu–CeO$_2$–x. The reaction order in H$_2$S, n, at 750 °C was 0.70 for the former and 0.83 for the latter. Assuming constancy of these orders with temperature, the sulfidation rate constant can be calculated for $R_0 = k_0 C_{H_2S}$. Table 2 shows the Arrhenius constants $k_{0,0}$ and $E_a$ for $k_0 = k_{0,0} \exp(-E_a/RT)$. The activation energies of copper metal sulfidation are much lower than the corresponding values for the reduction of the precursor oxides. Thus, sulfidation is a weak function of temperature. This finding is in agreement with sulfidation kinetics of other metals, e.g., iron in a matrix of silica [26] or the oxides of zinc, manganese, and calcium [8,27]. The most plausible explanation for these very low activation energies is that of H$_2$S adsorption limitation [26,28].

While there is a difference between the initial rates of sulfidation of Cu–CeO$_2$–x and Cu–Cr$_2$O$_3$, the difference is not large (Figure 12). This is anticipated if the reactive phase in both prereduced materials is metallic copper. In terms of fast intrinsic sulfidation kinetics, MnO and Cu metal are ranked the best, followed by ZnO, CaO, and Fe [28]. However, the overall reactivity of sorbents is the important parameter. Structural changes that may hinder regenerability and good cyclic performance often manifest themselves in reductive sulfidation of both single oxide sorbents as well as nonoptimized mixed oxides. Such is the case of ZnO–rich sorbents, as has been reported in the literature [6,8].

Regeneration Performance. Regeneration tests of sulfided CuO–Cr$_2$O$_3$ and CuO–CeO$_2$ were conducted with 6 mol % O$_2$ in nitrogen over the temperature range of 650–850 °C. The results are shown in parts A and B of Figure 13 for CuO–Cr$_2$O$_3$ and CuO–CeO$_2$, respectively, with the initial W/W$_0$ being slightly higher than 1 for the CuO–Cr$_2$O$_3$ as a result of sulfidation. All samples had been sulfided completely prior to regeneration under the same conditions, as indicated in the figure.

For the CuO–Cr$_2$O$_3$ sorbent in Figure 13A, a sharp weight decrease at the beginning of the regeneration was observed at all four temperatures, as shown in the inset of the figure. This weight loss was probably caused by the formation of intermediate Cu$_2$O. At the lower tested temperatures of 650 and 700 °C, the weight increased very rapidly following the initial weight drop and reached a maximum in each run, probably due to the formation of CuSO$_4$. After that the weight decreased gradually as the copper sulfate decomposed, but for the regeneration at 650 °C it did not go back to the
initial value after 20 min of regeneration. The most plausible regeneration path at low temperature, therefore, is \( \text{Cu}_2\text{S} \rightarrow \text{Cu}_2\text{O} \rightarrow \text{CuSO}_4 \rightarrow \text{CuO} \). At the high temperature of 750 and 850 °C, although the weight also increased after a quick drop, it did not exceed 1 and was almost constant after it reached that value, implying that direct regeneration \( \text{Cu}_2\text{S} \rightarrow \text{Cu}_2\text{O} \) took place, i.e., without sulfate formation, took place.

**Table 2. Kinetic Parameters of Sorbent Reduction and Sulfidation**

<table>
<thead>
<tr>
<th></th>
<th>( k_{r,0} (\text{mmol}^{1-n} \text{cm}^{3-n} \text{s}^{-1}) )</th>
<th>( E_a (\text{kJ mol}^{-1}) )</th>
<th>( n^b )</th>
<th>( k_{s,0} (\text{mmol}^{1-n} \text{cm}^{3-n} \text{s}^{-1}) )</th>
<th>( E_s (\text{kJ mol}^{-1}) )</th>
<th>( n^b )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuO–Cr(_2)O(_3)</td>
<td>( 1.07 \times 10^3 )</td>
<td>96.8</td>
<td>0.58</td>
<td>( 2.73 \times 10^{-2} )</td>
<td>19.8</td>
<td>0.70</td>
</tr>
<tr>
<td>CuO–Ce(_2)O(_2)</td>
<td>( 2.58 \times 10^{-2} )</td>
<td>26.2</td>
<td>0.42</td>
<td>( 7.50 \times 10^{-2} )</td>
<td>16.6</td>
<td>0.83</td>
</tr>
</tbody>
</table>

\(^a\) Samples used in sulfidation were prereduced at 750 °C with 10% H\(_2\)–10% H\(_2\)O–80% N\(_2\). The BET surface area of the prereduced sorbents was 7.43 and 4.98 m\(^2\)/g, respectively, for Cu–Cr\(_2\)O\(_3\) and Cu–Ce\(_2\)O\(_2\). \(^b\) Reduction and sulfidation order in H\(_2\) and H\(_2\)S, respectively, from measurements at 750 °C.
temperatures. For the CuO–CeO$_2$ sorbent, the final normalized weights were higher than 1 after 20 min of regeneration at all tested temperatures, including 750 and 850 °C. This means that the CuO–CeO$_2$ solid forms more stable surface sulfates than the CuO–Cr$_2$O$_3$ system. This is attributed to cerium sulfate rather than CuSO$_4$ [24].

**Multicycle Tests.** From a practical viewpoint, the Cu–Cr–O and Cu–Ce–O sorbents should possess regenerability in cyclic operation. This was shown to be good in microreactor tests. In this work, to determine the sorbent regenerability, two and a half cycles of consecutive sulfidation–regeneration were performed with the CuO–Cr$_2$O$_3$ and CuO–CeO$_2$ sorbents. The results are shown in parts A and B of Figure 14, respectively. Sulfidation was carried out with a wet gas mixture containing (mol) 0.5% H$_2$S–10% H$_2$–10% H$_2$O–bal N$_2$ for 20 min. Sulfided solids were purged in nitrogen for 10 min and then regenerated with a 6 mol % O$_2$–bal N$_2$ mixture for 10 min. All reactions were performed at 750 °C. Since there was no significant weight change in the later period of sulfidation and regeneration, only the first 5 min in each of the processes are shown in Figure 14. As can be seen from this figure, no significant changes were found except the lower starting values of WW$_0$ for CuO–Cr$_2$O$_3$ sorbent in the second and third cycles as a result of the formation of Cu$_2$O in the regeneration step of the previous cycles. Thus, the activities of both CuO–Cr$_2$O$_3$ and CuO–CeO$_2$ are stable in cyclic operation.

**Summary/Conclusions**

CuO-based sorbents were compared in this work in terms of their desulfurization efficiency and reactivity for H$_2$S removal from coal gas streams by high temperatures (650–850 °C). Two very different sorbent structures were selected for study. In one, CuO–Cr$_2$O$_3$, the stable compound of copper chromite is formed, while the second, CuO–CeO$_2$, keeps copper in a dispersed state. CeO$_2$ and CuO are immiscible oxides. Copper chromite has the lowest reducibility of all copper oxide-containing compounds reported in the literature. On the contrary, in the CuO–CeO$_2$ system, the reducibility of both the CuO and CeO$_2$ phases is enhanced.

Sulfidation tests carried out in a packed-bed microreactor have shown that equimolar CuO–Cr$_2$O$_3$ and CuO–CeO$_2$ sorbents can remove H$_2$S in a fuel gas to less than 5–10 ppm in the temperature range of 650–850 °C and in the presence of 20 mol % H$_2$–10 mol % H$_2$O. This is well below the equilibrium H$_2$S level corresponding to sulfidation of metallic copper. The presence of stable CuCr$_2$O$_4$ in the CuO–Cr$_2$O$_3$ solids is believed to preserve copper in the Cu$^{2+}$ or Cu$^{3+}$ oxidation state and, therefore, to account for the high H$_2$S removal efficiency. However, a similar argument cannot be made for the CuO–CeO$_2$ sorbent, which is easy to reduce. Here the participation of reduced cerium oxide, CeO$_2$–x, in the sulfidation is invoked to explain the observed desulfurization efficiency.

In direct sulfidation of the two sorbents, in a TGA apparatus, we found that reduction and sulfidation were competing reactions. TGA tests and XRD solid analysis have indicated that sulfidation proceeds through partial initial reduction: CuO → Cu/Cu$_2$O → Cu$_2$S (x < 2) for the CuO–Cr$_2$O$_3$ sorbents. The extent of reduction depends on temperature and feed gas composition as well as the solid composition. The CuO–CeO$_2$ sorbent was reduced appreciably even with low H$_2$ gas concentrations.

Comparative kinetics of reduction and sulfidation of prereduced sorbents were conducted in the TGA under conditions free of mass-transfer limitations. The activation energy for reduction of the two sorbents is very different, i.e., 96.8 and 26.2 kJ/mol for CuO–Cr$_2$O$_3$ and CuO–CeO$_2$, respectively. The activation energy for sulfidation is very low, 19.8 and 16.5 kJ/mol, for prereduced Cu–Cr$_2$O$_3$ and Cu–CeO$_2$–x, respectively, indicating that the reaction may be adsorption limited.

In regeneration the reaction paths were complex over the tested temperature range. At low temperatures, intermediate sulfate formation is suggested by the data and the reaction path appears to be Cu$_2$S → CuO–Cr$_2$O$_3$ → CuSO$_4$/CuO → CuO for CuO–Cr$_2$O$_3$ and CuS → CuSO$_4$/CuO → CuO for CuO–CeO$_2$. At higher temperature a rather simple mechanism involving no intermediate sulfate is inferred from the data for CuO–Cr$_2$O$_3$: Cu$_2$S → Cu$_2$O/CuO. However, in the case of CuO–CeO$_2$, some sulfate still persists after regeneration at 750 °C with 6% O$_2$ in N$_2$. This is attributed to stable surface sulfates of cerium.

Overall, in this work we have shown that CuO-based sorbents of the type CuO–Cr$_2$O$_3$ and CuO–CeO$_2$ can be tailored to meet a wide range of applications in hot coal-gas desulfurization. Thus, the desulfurization efficiency and reactivity as well as the regenerability of the sorbent can all be optimized for a particular fuel gas composition—temperature—reactor design by suitable sorbent composition and structure selection.

**Acknowledgment**

We thank Ms. Lu Hong Bo and Ms. Li Li for assisting with the packed-bed microreactor tests and the SEM analyses. Financial support by the Illinois Clean Coal Institute and the U.S. Department of Energy through a contract to the Institute of Gas Technology/Contract...
Literature Cited


Received for review May 6, 1996
Revised manuscript received October 9, 1996
Accepted October 22, 1996

IE960245D