

Desulfurization of and Tar Removal from Gasifier Effluents Using Mixed Rare Earth Oxides

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Introduction

Biomass gasification/reforming results in high (up to 10%) CH₄ breakthrough - too much potential H₂ to lose. In order to further reform the CH₄ using commercial Ni catalysts, and to make more H₂ by water-gas shift, one must adsorb the sulfur (H₂S), crack the tars, and either adsorb or reduce the NO_x [1-2]. There are also small amounts of K, Na and Cl which would deactivate most transition metals [3]. A hot gas cleanup catalyst/adsorbent must be able to work at low partial pressures of H₂S, with little interference from the NO_x, Cl, H₂O, H₂, CO or CO₂. The temperature range around 1100 K is favorable for gasification of coal and several types of biomass with high conversions to CO and H₂ [4-5]. Therefore the incentive exists for hot gas cleanup catalysts /adsorbents that can function effectively at or near 1100 K.

Rare-earth mixed oxides (REOs) have demonstrated their multifunctionality and versatility in addressing some energy-related challenges: (a) cleanup of gasifier effluents in H₂ generation or synfuel applications; (b) support materials for transition metal catalysts in exhaust gas cleanup, high temperature reforming and water-gas shift; (c) enhancing combustion efficiencies of gaseous and liquid fuels.

Materials and Methods

We have developed novel REOs, CeO₂/MO_x/M₂O_x and CeO₂/MO_x/M₂O_x/Al₂O₃ (M is a REO and M₂ is either a third REO or a group VIIB-VIIIB transition metal oxide), for two applications: hot gas desulfurization/ tar cracking/ secondary reforming, or nanoparticle-promoted combustion. These materials were prepared by sol-gel and microemulsion methods. To determine the sulfur adsorption capacity of the sorbents, sorption tests at 873 K were performed using a simulated effluent gas containing 0.1 % H₂S, 24% H₂, 32% CO₂, 3.3 % H₂O, balance N₂. The purpose of these experiments is to determine which sorbent has the highest sulfur removal capacity and can retain its capacity in successive runs. We are also examining the simultaneous tar cracking capability of the materials by adding naphthalene (~0.5%) to the simulated effluent and cracking it during the adsorption cycle.

Results and Discussion

Sorbents containing pure Ce/La oxides have low sulfur capacities (Fig. 1) and are not very effective in removing H₂S from a real gasifier effluent. Supporting the REOs on Al₂O₃ (20 wt% REO) or ZrO₂, and addition of a small amount of a third REO known to enhance the thermal stability of CeO₂ (either Tb₂O₃ or Gd₂O₃), greatly increased the total sulfur capacities of the REOs (Fig. 1). These ternary REOs maintained their capacity in a minimum of four successive runs and were regenerated in air. Addition of certain transition metal oxides to Ce/La/Al₂O₃ increased the total sulfur adsorption capacity by even more, even though the pure supported transition metal oxides were ineffective. Among sorbents impregnated with transition metal oxides (Mn, Fe, Cu), those containing Mn showed the highest capacities (about

three times that of pure Ce/La oxides), and it is noteworthy that MnO_x has lower solubility in the REOs. TPR data show that intermediate Ce/La ratios, which are best for long-term sulfur removal, also give the most reduced Ce/La mixed oxide at these temperatures; reduction of CeO_x favors sulfide formation both kinetically and thermodynamically.

Most of the adsorbed sulfur cannot be removed by inert gas (N₂) alone, as indicated by the desorption capacities in Fig. 1; alternative regenerations to either air or inert gas are being tested. The Ce/La-based sorbents are stable at up to 1070 K in N₂.

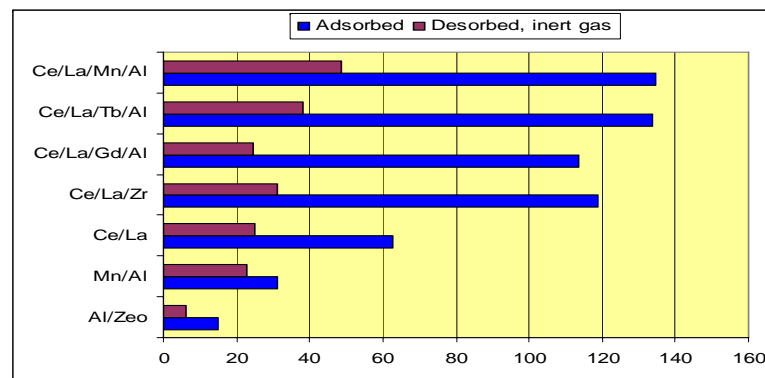


Figure 1. Sulfur adsorption capacity to breakthrough and amount desorbed (both in μmol/g), using synthetic gasifier effluent for adsorption and N₂ for desorption. The Al/Zeo is a commercial sulfur adsorbent typically used at lower temperatures.

Significance

The modified Ce/La sorbents/catalysts showed much higher sulfur adsorption capacities at realistic conditions, and are relatively stable at the high operating temperatures of gasifiers. These materials are capable of simultaneous tar cracking and sulfur removal.

References

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