Desulfurization / Tar Removal for Gasifier and Biogasifier Effluents with Mixed Rare Earth Oxides

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Abstract

Current materials for high temperature H_2S removal from gasifier effluents are Zn- and Ca-based sorbents. These work at temperatures less than typical gasifier (especially biogasifier) effluent temperatures. We are examining sorbents based on Ce/La/M (M = transition metal) oxides and Ce/La/RE (RE = a rare earth) oxide. Reduced Ce/La oxides adsorb H_2S at temperatures of 600°C and above, and are regenerable in O_2 mixtures. But addition of group VII-VIII transition metals to Ce/LaOx increases the sulfur removal capacity significantly. Addition of oxides such as ZrO_2 or a third rare earth oxide increases surface area, sintering resistance of CeO_x/La_2O_3 at high temperatures, and sulfur capacity. These sorbents can be regenerated at temperatures near the operating conditions of gasifiers. They can also be used as tar cracking catalysts for tars formed in the gasifier. The results of some characterization tests, including H_2S adsorption / TPD, are presented.

Introduction

We are developing novel rare earth oxide (REO) $CeO_2/M_1O_x/M_2O_x$ and $CeO_2/M_1O_x/M_2O_xAl_2O_3$ (M_1 is a REO and M_2 is either a third REO or a group VIIB-VIIIB transition metal oxide) materials for two applications: hot gas desulfurization/ tar cracking/ secondary reforming, or nanoparticle-promoted combustion. Potential biomass gasification processes result in high (up to 10%) methane breakthrough and tars. In order to reform the CH_4, and to adjust the CO content by water-gas shift, one must first adsorb the sulfur (mostly H_2S), crack the tars to C_1-C_2, 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. A typical feed composition of biomass (wt%) is C = 49-52%, H = 5-7%, N = 0.1-2% , O = 40-43%, S = 0.02-0.3% , Cl < 0.1%.[2-5] A typical composition from a primary gasifier operating at 850°C (vol%) is H_2 47-53%, CH_4 1-3.5%, CO 13-16%, CO_2 26-31%, others 2-4%, tars 1.5-3%.[4] A hot gas cleanup catalyst/adsorbent must be able to work at low partial pressures of H_2S, with little interference from the NO_x, Cl, H_2O, H_2, CO or CO_2. Some reforming/water-gas shift may also occur.

REOs such as CeO_2 show promise as adsorbents/catalysts in these combined applications. Intimate mixtures of REOs function better in these applications than any single (e.g., CeO_2) oxide. The mixture composition is the chief variable affecting hydrothermal stability of the materials. Synthesizing REOs such that only mesopores are present may also reduce pore mouth poisoning. We are building upon existing synthetic expertise to prepare and characterize (pore distribution, hydrothermal stability, surface structure, H_2S adsorption capacity, tar cracking activity) these materials at LSU.

As temperature and steam to biomass ratio (usually ~2.5 steam/C) are increased, less tar is formed.[6-7] A steam/C increase is undesirable economically, while a temperature increase benefits the reaction kinetics.[8] When temperature is increased from 1000 to 1200 K there is ~35% decrease of in tar production.[6] The temperature range around 1100 K is favorable for gasification of several types of biomass.[9] Therefore the incentive exists for hot gas cleanup catalysts /adsorbents that can function effectively even at 1100 K.

While Ni (on Al_2O_3, e.g.) can crack tars to CH_4 and CO_x at 1100 K, there is rapid coking of the catalyst. However, Ni promoted by CeO_2 shows improved coking resistance.[1] Mixed REOs have also been proposed as future autothermal reforming or catalytic partial oxidation carriers or first stage catalysts,[8,10] being more active than Mg-Al spinels. In these applications they must also be able to work for extended periods at temperatures exceeding 1000 K. A further application of mixed REOs is as a hydrocarbon combustion additive, in furnaces and gas turbine combustors. Acharya has demonstrated that the addition of <0.5 wt% CeO_2 nanoparticles to an ethanol flame enhances volumetric heat release by a factor of $\geq$3 depending on loading.[11-12] Because of their enhanced stability and improved oxygen storage capacities, further benefits in combustion performance can be realized with mixed REO's.

Mixed REOs (e.g., $CeO_2/La_2O_3/Tb_2O_3$) may therefore be able to simultaneously adsorb H_2S (to give M_2O_2S), crack tars and reform slip methane – a one stop gasifier effluent cleanup shop. The oxide can be regenerated with O_2 at ~900 K.[13] For H_2S removal ZnO can also be used, but there are difficult issues here with regeneration and Zn volatility. While CeO_2/La_2O_3 by itself is an effective H_2S sorbent at these conditions initially, it rapidly loses surface area and so sulfur adsorption capacity (>80% after 3 redox cycles);[14] Another problem is the formation of sulfate during oxidative regeneration. While these problems may be alleviated by operating at high space velocities and low sorbent loadings,[15] such conditions are not practical for long-term operation. Therefore there exists a great need for more stable mixed REOs that are still active for hot gas cleanup, tar cracking, and as reforming or combustion catalysts.

Experimental

The catalysts/sorbents we used for sulfidation tests were prepared using either a Templated sol-gel method or by incipient wetness impregnation (IWI). Ceria and lanthanum oxide mixtures were prepared using ceric (IV) ammonium nitrate ($Ce(NH_4)_2(NO_3)_6$, Aldrich, 99.99%) as ceria precursor and La nitrate ($La(NO_3)_3\bullet 6H_2O$**),** Aldrich, 99%) as lanthana precursor. The desired amounts of precursors were dissolved in deionized water in 1 L beakers by magnetic stirring without heating. To this mixture a sufficient amount of 25% TMAOH solution was added as the surfactant template. Then NH_4OH (Alfa, 28–30% NH_3) was added dropwise until a pH of ~10.5, at which point no more precipitation occurred. The temperature was slowly increased to 363 K and left stirring for four days with periodic NH_4OH addition to maintain the pH. The precipitate was centrifuged and washed with water - acetone – water, then dried overnight at 373 K and calcined in flowing air at 773 K for 6 h, with a 2 K ramp to 773 K.

REOs and transition metal/REO mixtures supported on alumina or zirconia were prepared by IWI using commercial extrudates from Engelhard (now BASF). They were dried and calcined as above. For comparison purposes a commercial low temperature sulfur sorbent (BASF Selexsorb CDX, 7x14 mesh) was also tested. Its composition is Al_2O_3/Zeolite with 15-40% zeolite of unspecified phase.

The surface areas of the sorbents were measured using a Quantachrome AS-1 BET apparatus. To measure the sintering of some sorbents at high temperature hydrothermal conditions, 0.5 g was placed in a calcining furnace and contacted with flowing (165 mL/min at NTP) 3% H_20, 97% air at 323-973 K, 5 K/min, with a hold at 973 K for 12 h. Then the surface area of the sorbent was measured again.

Sulfur adsorptions were carried out at 873 K using a reacting gas composition of 23.4 mol% H_2, 41.4% N_2, 3.1% water, 32.0% CO_2, and 0.1% H_2S. The total reacting gas flow rate was ~100 mL/min at NTP. A ½" U-tube of 316 stainless steel contained the sample; the blank space was filled with quartz wool. Before sulfidation the sorbents were heated in air (60 mL/min) to remove volatile materials and kept at 873 K for 40 min, then 5 min in He flow (60 mL/min), then switched to the reaction mixture. Samples of the exit gas were taken every 15 s and analyzed by a sulfur- specific detector (PFPD) attached to a Varian 3800 GC. The reacting gas was passed through the reactor until the detector measured a total exit sulfur concentration equal to the inlet concentration for at least 1 min.

After switching from reacting gas to He at 60 mL/min, the temperature was raised from 873-1073 K at 10 K/min. The gas exiting the reactor was sampled every 15 s for total sulfur. The reactor was maintained at 1073 K until no sulfur was observed in the exit gas, then cooled down under flowing He. Final regeneration of the sorbent was with air (industrial grade) at 60 mL/min for 40 min at 873 K.

Results and Discussion

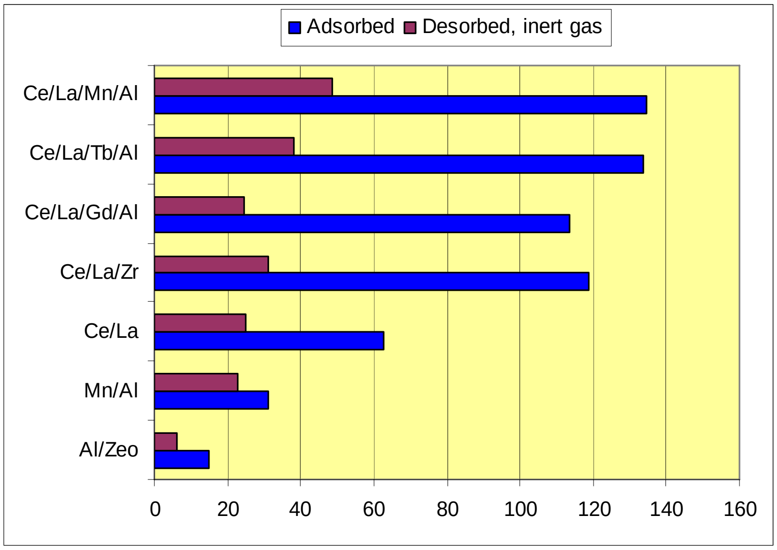
In order to understand the sintering effects of water vapor and temperature, the sorbents were sintered for 12 h at 973 K in flowing air/water (3% water). It was observed for unsupported REOs that the surface area decreased significantly (Table 1, all ratios are molar). Among the unsupported REOs, Ce/La =6 had the highest percentage decrease in surface area and Ce/La =0.9 had the lowest (Table 1), indicating that the rate of sintering increases with the Ce/La ratio. It is known that the thermal stability of CeO_2 is increased by the addition of La up to some point.[14] The sintering results coincided with DSC measurements of the crystallization exotherms showing increasing exotherms (more crystallization) with increasing Ce/La. However, for the REOs supported on Al_2O_3 or ZrO_2 there is much less sintering, and this is especially true when a small amount of Gd is added to form a ternary supported oxide (Table 1).

Table 1: Surface area of the fresh sorbents before and after sintering

Composition (fresh)	**Surface area (m^2/g)**	**Surface area (m^2/g) after sintering**
Ce/La = 0.9	110	40
Ce/La = 3	242	55
Ce/La = 6	205	25
La/Zr = 1/2.8	65	55
Ce/La/Al = 3/1/53	165	120
Ce/La/Al = 0.9/1/25	160	110
Gd/Ce/La//Al = 0.2/0.9/1/28	160	140
Tb/Ce/La/Al = 0.2/0.9/1/28	170	115
Mn/Al = 0.2/1	150	NA
Fe/Al = 0.24/1	170	NA
Mn/Ce/La/Al = 0.6/0.9/1/29	60	NA
Mn/Ce/La/Al = 0.4/3/1/56	170	NA

The best lab tests to gauge utility in gasifier cleanup operations are temperature-programmed desorptions (TPDs), after H_2S adsorption. We used a realistic adsorbate of H_2, N_2, water, CO_2, and 0.1% H_2S. From these data, the sulfur adsorptive capacity in the presence of competing adsorbates is determined. Our evolutionary development of adsorptive materials is depicted in Figure 1; a commercial zeolite/Al_2O_3 sulfur adsorbent is shown for comparison. The data show that going to more complex disordered mixed REOs in order to enhance hydrothermal stability greatly improves desulfurization activity. Note that the amounts desorbed in N_2 from the more complex oxides are increasing along with the amounts adsorbed, which augurs well for ease of regeneration of the better materials.

Figure 1. Sulfur adsorption capacity and amount desorbed (both in μmol/g), using synthetic gasifier effluent, adsorption at 873 K, TPD 873-1073 K in N_2. Average of three cycles with air regeneration at 873 K.



La, Pr, Sm, and Nd are all more stable oxysulfides than Ce_2O_2S,[16] and therefore more effective for H_2S removal. This has already been proven for La_2O_3, where intimate mixing with CeO_2 greatly improves regeneration to the oxides under either oxidizing or reducing conditions.[15,17] This is also the case for ZnO-based sorbents under oxidizing conditions.[18] We hypothesized that supported (on Al_2O_3, BaO/Al_2O_3 or YSZ) mixtures of CeO_2/La_2O_3/third REO would prove superior to the mixed oxides alone, because these supports can better stabilize (less crystalline ripening) the mixed REO phase when local hot spots occur during regeneration. These ternary supported oxides can be made by impregnation or templated co-precipitation methods. Optimal Ce/La ratios will differ from that of the simpler mixed Ce/La oxides. The solubility limit for the CeO_2 fluorite phase is ~60-70 at% La, usually with no phase separation upon reduction.[19]

The problem with CeO_2 as sole REO is its slow reaction with H_2S in the Ce(IV) state, and its relatively poor reduction (to Ce(III)) thermodynamics - only ~30-40% reduction at 1000 K. However, the reducibility of CeO_2 can be enhanced if intimately mixed with certain other oxides. For example, CeO_2 films can be completely reduced at 900 K when supported on YSZ, and the process is reversible even at higher temperatures.[20] For 10-30 at.% La with CeO_2, the rate constant for reduction increases by more than ten times, with reduction substantial at 1070 K.[21-22] Mixtures with La are not long term stable under reducing conditions at >1200 K.[22] However, more stable Gd_2O_3, Tb_2O_3 and Sm_2O_3 dopants similarly increase the rate of reduction (Gd_2O_3[23-24]; Sm_2O_3[24]; Tb_2O_3[25]) and can be used as alternatives or in combination with La_2O_3. They can also convert to a bulk sulfide at relatively low temperatures.[26] The conclusion is that while it is not necessary to depart entirely from CeO_2 in order to obtain an oxide mixture active for desulfurization, other REOs are necessary. The mixed CeO_2 phase should be more active for tar cracking and further reforming of slip methane because of ceria's excellent redox behavior relative to La_2O_3 and other REOs.

Mixed Ce/Al oxides also exhibit superior (at ~1000 K) reduction ("oxygen storage capacity") behavior compared to CeO_2 alone, if the mixture is intimate and either nanocrystalline or as a monolayer dispersion on Al_2O_3.[27-31]

For simple or binary REOs, total capacities from 45-1000 μmol/g have been reported, but in the absence of CO_2 and H_2O.[14] Only the larger (near 1000 μmol/g) amounts match the capacities of Zn-based sorbents,[32] so further evolutionary development of REO-based materials is needed, although recall that Zn-based materials are not thermally stable at >870 K.

We will further charactere more promising materials by:

- TEM and porosimetery;
- XAS and XRD;
- H_2S adsorption / desorption (TPD) tests, for many repeat cycles.
- Regeneration tests using CO, CO_2 and other non-traditional regenerating media.
- Cracking of naphthalene, a typical tar molecule, included as a small amount (~0.1%) in a simulated gasifier stream.

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