Advanced Byproduct Recovery:

Direct Catalytic Reduction of Sulfur Dioxide to Elemental Sulfur

Sixth Quarterly

Technical Progress Report

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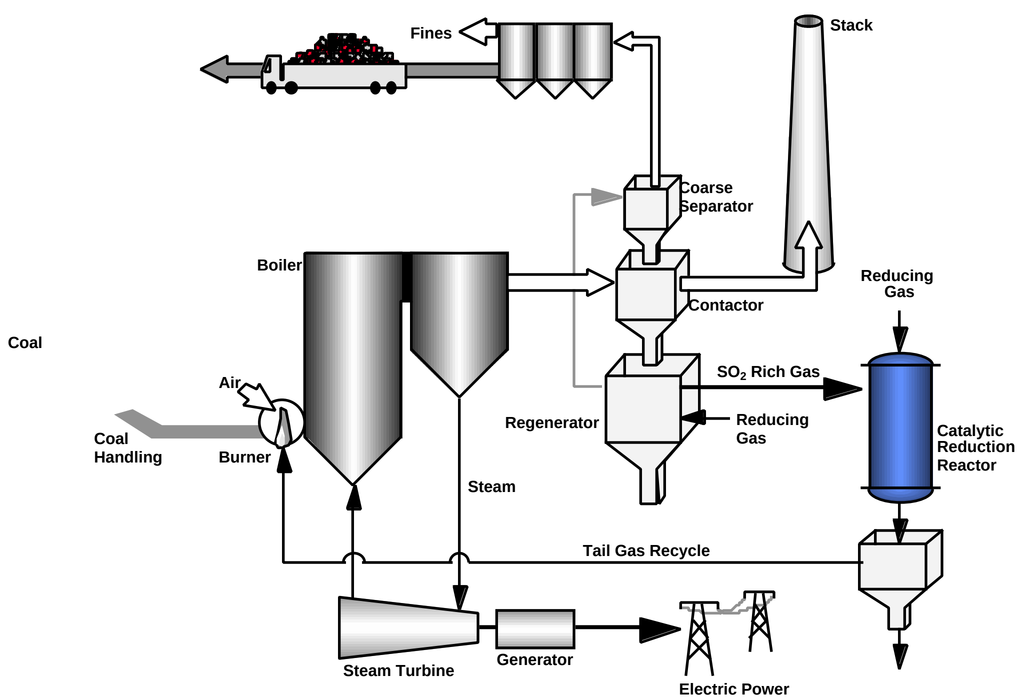
Introduction

Background

More than 170 wet scrubber systems applied, to 72,000 MW of U.S., coal-fired, utility boilers are in operation or under construction.[1] In these systems, the sulfur dioxide removed from the boiler flue gas is permanently bound to a sorbent material, such as lime or limestone. The sulfated sorbent must be disposed of as a waste product or, in some cases, sold as a byproduct (e.g. gypsum). Due to the abundance and low cost of naturally occurring gypsum, and the costs associated with producing an industrial quality product, less than 7% of these scrubbers are configured to produce useable gypsum[2] (and only 1% of all units actually sell the byproduct). The disposal of solid waste from each of these scrubbers requires a landfill area of approximately 200 to 400 acres. In the U.S., a total of 19 million tons of disposable FGD byproduct are produced, transported and disposed of in landfills annually.[3]

The use of regenerable sorbent technologies has the potential to reduce or eliminate solid waste production, transportation and disposal. In a regenerable sorbent system, the sulfur dioxide in the boiler flue gas is removed by the sorbent in an adsorber. The SO_2 is subsequently released, in higher concentration, in a regenerator. All regenerable systems produce an off-gas stream from the regenerator that must be processed further in order to obtain a saleable byproduct, such as elemental sulfur, sulfuric acid or liquid SO_2. A schematic of a regenerable sorbent system is shown below.

Figure 1-1: Regenerable Sorbent System



In addition to reducing solid waste, many regenerable systems have other benefits compared to non-regenerable scrubbing technologies, including higher sulfur removal efficiencies, and the capability of combined SO_2/NO_x removal.

Description of Byproduct Recovery System

The team of Arthur D. Little, Tufts University and Engelhard Corporation are conducting Phase I of a four and a half year, two-phase effort to develop and scale-up an advanced byproduct recovery technology that is a direct, single-stage, catalytic process for converting sulfur dioxide to elemental sulfur. This catalytic process reduces SO_2 over a fluorite-type oxide (such as ceria and zirconia). The catalytic activity can be significantly promoted by active transition metals, such as copper. More than 95% elemental sulfur yield, corresponding to almost complete sulfur dioxide conversion, was obtained over a Cu-Ce-O oxide catalyst as part of an on-going DOE-sponsored, University Coal Research Program (at MIT with Dr. Flytzani-Stephanopoulos). This type of mixed metal oxide catalyst has stable activity, high selectivity for sulfur production, and is resistant to water and carbon dioxide poisoning. Tests with CO and CH_4 reducing gases indicate that the catalyst has the potential for flexibility with regard to the composition of the reducing gas, making it attractive for utility use. The performance of the catalyst is consistently good over a range of SO_2 inlet concentration (0.1 to 10%) indicating its flexibility in treating SO_2 tail gases as well as high concentration streams.

Research and Development Activity

Arthur D. Little, Inc., together with its industry and commercialization advisor, Engelhard Corporation, and its university partner, Tufts, plans to develop and scale-up an advanced, byproduct recovery technology that is a direct, catalytic process for reducing sulfur dioxide to elemental sulfur. The principal objective of our Phase I program is to identify and evaluate the performance of a catalyst which is robust and flexible with regard to choice of reducing gas.

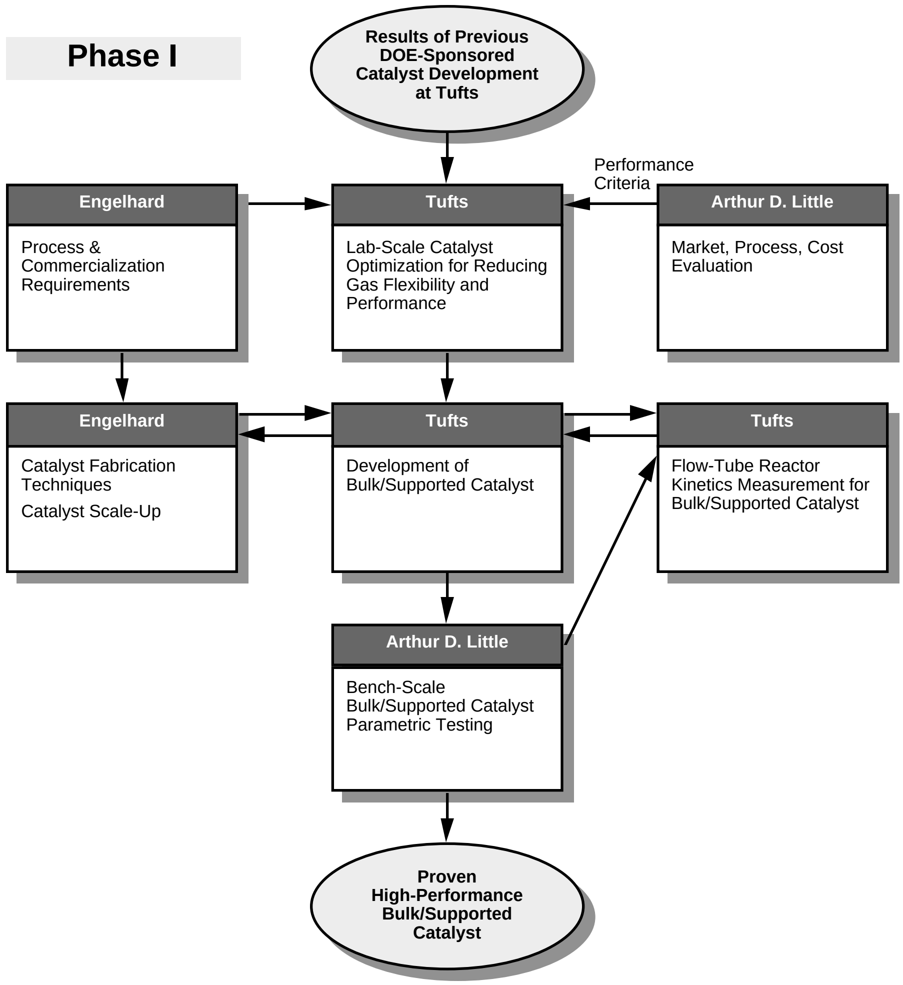
In order to achieve this goal, we have planned a structured program including:

Market/process/cost/evaluation;
Lab-scale catalyst preparation/optimization studies;
Lab-scale, bulk/supported catalyst kinetic studies;
Bench-scale catalyst/process studies; and
Utility Review

The flow of and interaction among the planned work elements are illustrated in for Phase I. A description of the methods of investigation to be used for these program elements is described below.

Market, Process and Cost Evaluation. Interviews will be conducted with electric utilities and regenerable sorbent system developers to define key market issues, such as: preferred reducing gas; variability of off-gas stream composition; system contaminants; emissions limitations; cost constraints; and reliability/durability issues. From the interview responses, key performance criteria for the system will be defined. The performance and cost of the proposed catalytic process will be evaluated and compared to these criteria. In addition, these performance criteria will be used to define milestones and to focus catalyst and process development.

Figure 1-2: Work Elements



Lab-scale Catalyst Preparation/Optimization Studies. Catalyst will be prepared using a variety of methods (such as co-precipitation, sol-gel technique) from two candidate fluorite oxides (CeO_2, ZrO_2) and four candidate transition metals (Cu, Co, Ni, Mo). These catalyst materials will be tested at Tufts in the same apparatus as was used in the previous work discussed above with a variety of reducing gases (CO, $CO+H_2$, CH_4). Data will be gained in order to determine the key underlying reaction mechanisms. Parametric tests will determine the relative effects of temperature, concentration, space velocity, catalyst preparation method, and reducing gas. To reduce the amount of screening work, statistical experiment design methods will be used and catalyst characterization will be used to discriminate between active compositions. Some catalyst characterization work (x-ray diffraction, microscopy) will be conducted by Tufts staff at MIT laboratories.

Lab-scale, Bulk/Supported Catalyst Kinetic Studies. The best-performing catalysts will then be either appropriately supported (pellet, tablets, honeycomb, etc.) or formulated in bulk form. The bulk/supported catalyst will be tested in a laboratory-scale flow-tube reactor at Tufts to determine kinetic data.

Bench-scale Catalyst/Process Studies. Larger quantities of the bulk/supported catalyst will be tested in a bench-scale flow tube reactor at Arthur D. Little. Parametric tests will be conducted to assess the influence of temperature, inlet SO_2 concentration, space velocity, and choice of reducing gas on performance. Some cyclic and duration testing will also be conducted at this scale.

Utility Review. A utility review team will be assembled, consisting of one or more utilities that have experience with regenerable desulfurization technologies or are considering their application in the near future. We will work closely with the utilities to inform them of the developments and solicit their perspective on utility needs and development issues.

Work Breakdown Structure

Phase I Task 1: Market, Process and Cost Evaluation

Lead Contractor: Arthur D. Little

Objectives:

To identify the critical market forces, technical requirements and cost constraints in order to focus the catalyst/byproduct recovery process research effort;
To evaluate the costs and benefits of the advanced byproduct recovery process, and to compare these attributes to those of state-of-the-art technologies;
To determine the extent to which application of the advanced byproduct recovery process improves the competitiveness of regenerable sorbent systems.

Approach:

This task is being conducted by Arthur D. Little. We are interviewing utilities, leading architect/engineering companies, regenerable sorbent system developers, industry consultants and EPRI to define key market issues, including: preferred reducing gas; variability of SO_2-rich off-gas stream composition; compatibility/flexibility in coupling with the adsorption/regeneration step; system contaminants; emissions limitations; cost constraints; and reliability/durability issues. Based on these interviews, we will define the key performance criteria for the system. We will estimate the potential market for advanced, catalytic reduction of SO_2 to elemental sulfur in utility and industrial applications.

We are preparing a Process Evaluation, in which we will prepare or specify process energy balances, temperature requirements, reactor volumes, and recycle rates, for one or more reducing gas production methods. These analyses will be tied to the requirements of utilities and the various regenerable sorbent technologies under development. We are also preparing a Cost Evaluation of the byproduct recovery system in the context of its use with one or more regenerable SO_2 removal systems and compare the costs of the proposed technology to that of state-of-the-art technology.

Deliverables:

Market, process and cost analyses of the proposed byproduct recovery system; definition of key areas to focus research efforts; assessment of the potential market for the process.

Phase I Task 2: Lab-Scale Catalyst Testing/Optimization

Lead Contractor: Tufts

Objectives:

To optimize catalyst composition and preparation method for use with a variety of reducing gas compositions and qualities, including syn-gas and natural gas.

Approach:

This task is being carried out by Tufts University, a subcontractor to Arthur D. Little. Under four subtasks, Tufts will prepare and characterize the catalysts, conduct adsorption/desorption studies, measure catalytic activity in a packed-bed microreactor, and conduct parametric tests and kinetic measurements. Specifically, Tufts will optimize the catalyst composition and preparation method for use with a variety of reducing gas compositions and qualities, including synthesis gas and natural gas.

The transition metal-promoted fluorite-type oxides previously identified as very active and selective catalysts for the reduction of SO_2 to elemental sulfur with carbon monoxide will be tested with other reductants, namely synthesis gas (H_2 and CO mixed with H_2O and CO_2) and natural gas. Various transition metals (including Cu, Co, Ni, and Mo) will be examined as promoters to obtain a catalyst composition active in various reducing gases. The fluorite oxides to be used in this work are ceria (CeO_2) and zirconia (ZrO_2).

Arthur D. Little, with assistance from Tufts, will develop a detailed Test Plan for the laboratory-scale catalyst testing and optimization activities. The Test Plan will be submitted as an amendment to the Management Plan. No testing will begin until the Test Plan has been approved by the DOE Project Manager.

Catalyst Preparation and Characterization Tufts will prepare the catalysts by the co-precipitation method to produce a surface area in the range of 20 - 60 m^2/g. To achieve high surface area, high elemental dispersion, and uniform pore-size distribution, other preparation techniques (such as gelation and impregnation of high surface area supports) will also be examined.

Catalysts will routinely be characterized by X-ray powder diffraction for crystal phase identification and by nitrogen adsorption/desorption for BET surface area and pore size distribution measurements. The elemental composition of the catalyst will be analyzed Inductively Coupled Plasma Atomic Emission Spectrometry. Selected active catalysts will be further characterized by X-ray Photoelectron Spectroscopy (XPS) and Scanning Transmission Electron Microscopy (STEM).

Adsorption/Desorption Studies In parallel with the preparation of the new catalyst composition, the Cu-Ce-O catalyst will be evaluated in adsorption/desorption studies with CO, COS, and SO_2 to determine the reaction mechanism. These experiments will lead to an understanding of the low selectivity of this catalyst to the undesirable byproduct COS and facilitate catalyst optimization. A thermo-gravimetric analyzer, coupled with a residual gas analyzer, will be used for these tests.

Catalytic Activity Measurements in a Packed-Bed Microreactor Tufts will conduct catalyst activity tests under steady conditions in an existing packed- bed microreactor. Screening tests will be conducted with a reducing gas consisting of 1% SO_2 and 0.5% CH_4. Additional tests of the most promising catalysts will be conducted with two additional synthesis reducing gases. However, final selection of reducing gases will be made based on input from regenerable sorbent system developers and utilities (the Task 1 findings). We currently envision the two additional synthesis test gases to be:

(i) wet feed gas mixture containing 1% SO_2 and stoichiometric amount of synthesis gas with $H_2/CO = 0.3$, 2% H_2O and 2% CO_2; and

(ii) wet feed gas mixture containing 1% SO_2, stoichiometric amount of synthesis gas with $H_2/CO = 3$, 2% H_2O, and 2% CO_2.

The existing data on performance with pure CO and the new data to be developed using methane and wet synthesis gases will cover the range of possible regeneration gases available. It is not necessary to test dry synthesis gases since the tests with CO and methane provides information on ideal performance without water. For each reacting gas mixture, the reactor temperature will be increased and then reduced to establish light-off and fall-off behavior of each catalyst. Elemental sulfur yield, catalyst activity and catalyst selectivity will be used to identify the most promising catalysts.

Parametric Studies and Kinetic Measurements After identifying promising catalysts, an extensive parametric study and kinetic measurements will be carried out to provide reactor design information. The parametric studies will address:

(i) the effects of water vapor and/or carbon dioxide on catalyst activity and elemental sulfur yield; and

(ii) effect of reducing gas composition (H_2/CO ratios/CH_4) on catalyst activity and sulfur yield.

Long-term and hydrothermal catalyst stability will be evaluated for the preferred catalyst composition in Task 4, Bench-Scale Testing.

The parametric studies will be conducted at space velocities in the range 1,000 to 100,000 h^{-1}, SO_2 concentrations from 0.1% to 10%, H_2O contents from 0 to 10%, H_2/CO ratios from 0 to 3, and CH_4 concentrations from 0.1% to 10%. The temperature will be in the range 50 to 700°C. A kinetic model will be developed from the data obtained at short contact time (< 0.1g s/cc) in a small diameter catalytic reactor. This will include the effects of H_2O and CO_2 on the specific activity.

Deliverables:

An optimized catalyst composition/preparation method for bench-scale catalyst tests. Kinetic data for use in reactor design.

Phase I Task 3: Catalyst Preparation and Costing

Lead Contractor: Engelhard

Objectives:

Provide guidance regarding the establishment of activity and simulated aging tests to quickly and efficiently determine performance characteristics of catalyst formulations;
To prepare supported or bulk (extruded) catalysts in the form of pellets or honeycombs for bench-scale testing;

To provide catalyst manufacturing and cost analysis for inclusion in the analysis of process economics.

Approach:

Engelhard will work closely with Tufts and Arthur D. Little to specify the appropriate catalyst structures to meet the engineering requirements for the targeted sulfur recovery systems. Included in this activity will be the training of scientists and engineers on the Tufts team by Engelhard staff members in the formulation of commercially viable catalyst structures. Engelhard staff will observe and participate in laboratory-scale and bench-scale testing at Tufts and Arthur D. Little to interpret/analyze results. The resulting analysis will be used to redesign catalysts which resist deactivation.

Engelhard will apply their expertise in process and cost evaluation of catalytic systems to the sulfur byproduct recovery system. Engelhard will provide catalyst manufacturing cost details to allow the process economics to be established.

Deliverables:

Catalysts for bench-scale testing; manufacturing/cost analysis of catalysts for inclusion in system evaluation task.

Phase I Task 4: Bench-scale Testing

Lead Contractor: Arthur D. Little

Objectives:

To conduct bench-scale, parametric tests to evaluate the performance of three to five supported/extruded catalyst preparations.

Approach:

Arthur D. Little will develop a Test Plan for the bench-scale parametric tests and will incorporate this plan into an amendment to the Management Plan. No work will begin on the bench-scale tests until the Test Plan has been approved by the DOE Project Manager. Arthur D. Little is designing, and will fabricate and commission a bench-scale SO_2 reduction reactor facility. The facility will consist of gas supply controls (for the simulated regenerator off-gas stream and the reducer gas stream); gas heaters; a catalytic reduction reactor (approximately 1-2 l in size); a heat exchanger for sulfur knock-out; gas analysis instrumentation (SO_2, H_2S on-line analyzers, gas chromatograph) and an afterburner for clean-up of off-gases. The system will be fabricated and shaken-down in the first 6 months of the program following approval of the Management Plan.

We will initiate bench-scale tests using the catalyst materials that have been proven as highly active and selective for sulfur production from the previous/ongoing catalyst development programs: a copper promoted ceria catalyst, Ce-Cu-O. Tests on supported materials will reveal the performance changes associated with the use of supported or bulk extruded materials compared to powders. We will investigate the effects of space velocity, temperature, and reducer gas and regenerator gas composition on catalyst performance.

Subsequent parametric tests will be performed on catalyst formulations selected from the lab-scale catalyst optimization work. The operating variables are expected to be as follows: space velocity: 10,000, 25,000, 50,000 hr^{-1}; temperature: 450, 500, 600°C; inlet stream composition: SO_2 concentration: 0.1 to 10%; H_2O concentration 2 to 30%; CO_2 concentration 2 to 30%; reducing gas composition: CO/H_2 ratio: 0.5 to 3.0; CO/CO_2 ratio: 0.5 to 3.0. Information developed from this task will provide insights for the process evaluation task, the catalyst optimization work, and the Phase II efforts in reactor scale-up.

Deliverables:

Performance map for 3 to 5 catalyst preparations; selection of catalyst preparation for dynamic response and pilot-scale testing.

Phase I Task 5: Utility Review

Lead Contractor: Arthur D. Little

Objectives:

To provide electric utility perspective and review of development program
To focus development effort on issues of key importance to utilities

Approach:

We will identify a utility review team, consisting of one or more utilities that have experience with regenerable desulfurization technologies or are considering their application in the near future. We will work closely with the utilities to inform them of the developments and solicit their perspective on utility needs and development issues. We plan to communicate through monthly meetings and will share data as it becomes available. Possible Utility Review Team members are Niagara Mohawk, Public Service of New Mexico, and Ohio Edison. All these utilities are participants in either regenerable sorbent programs or Clean Coal Development programs and would therefore have a valuable perspective to provide to our program, and would have a stake in the development of an improved byproduct recovery system.

Deliverables:

Utility review of the bench-scale developments; input to developments concerning issues of key importance to utilities.

Phase I Task 6: Management and Reports

Lead Contractor: Arthur D. Little

This task will be conducted by Arthur D. Little and will involve coordinating the catalyst/process development effort, coordinating the activities of the prime contractor and two subcontractors, and preparing the monthly, quarterly, topical, and final reports for DOE.

Objectives for Sixth Quarter Activity

The objectives for the sixth quarter were to:

Continue work on catalyst screening using the laboratory-scale packed bed reactor. Effects of dopant type, dopant level, reducing gas type, stoichiometry, and temperature on selectivity and activity of a range of fluorite-type catalysts will be assessed.

Continue to examine catalysts containing Cu, Co, Ni and Mo. High surface area (150 m^2/g) ceria samples recently obtained from Engelhard will be impregnated with nitrate salts of the metals under consideration. The performance of the supported catalysts will be compared to that of the bulk mixed oxide catalysts.

To examine the effect of water vapor on the best catalyst of each type. Other reducing gases, such as synthesis gas, will be tested.

To characterize catalysts by X-ray powder diffraction for crystal identification and by nitrogen adsoption/desorption for BET surface area and pore size distribution measurements. The elemental composition of the catalyst will be analyzed using Inductively Coupled Plasma Atomic Emission Spectrometry.

To complete fabrication of the bench-scale experiment, conduct shake-down tests and to refine the plan for the larger scale experiments.

To assemble a team of industry experts to assist in evaluating the results of our research in the context of practical experience.

This report summarizes the results of the catalyst screening experiments at Tufts and the progress on the larger scale reactor.

Sixth Quarter Technical Progress

Background

In previous DOE-supported work,[4] the activity and selectivity of fluorite-type oxides, such as ceria and zirconia, for reduction of SO_2 were investigated. A wide range of transition metal-impregnated ceria and zirconia catalyst formulations were evaluated in a packed bed reactor, under both dry gas and wet gas (2% H_2O) conditions. Under dry gas conditions, more than 95% yield of elemental sulfur and essentially complete SO_2 conversion were obtained for a variety of catalysts. Under wet gas conditions, Cu/CeO_2 catalyst showed the lowest light-off temperature, the greatest resistance to water, and gave over 90% SO_2 conversion and more than 70% elemental sulfur yield.

Based on these results, and the fact that a 25 hour test indicated that the Cu/CeO_2 catalyst was stable at the reacting conditions, the Cu-Ce-O system was selected for detailed studies of the SO_2 reaction with CO. The effects of copper content, temperature, presence of water, and presence of CO_2 on the selectivity and activity of this catalyst system were evaluated. This work led to the selection of bulk $Cu_{0.15}Ce_{0.85}(La)O_x$ for further study. More than 95% elemental sulfur yield, corresponding to almost complete sulfur dioxide conversion, was obtained over a Cu-Ce-O oxide catalyst with a feed gas of stoichiometric composition ($[CO] / [SO_2] = 2$) at temperatures above 450°C. This catalyst showed no apparent deactivation during a 35-hour run in the presence of 2% water at 470°C. In addition, the performance of this catalyst with other reducing gases was briefly investigated. Elemental sulfur yields of 50 - 66% were obtained using H_2 at 600°C and an elemental sulfur yield of 72% was obtained using CH_4 at 800°C. It is noteworthy that all tests mentioned above were conducted at high space velocities, on the order of 40-50,000 h^{-1} (STP).

Thus previous work has shown that the catalytic activity of fluorite-type oxides, such as ceria and zirconia, for the reduction of sulfur dioxide by carbon monoxide to elemental sulfur can be significantly promoted by active transition metals, such as copper. This type of mixed metal oxide catalyst has stable activity and is resistant to water and carbon dioxide poisoning. The performance of the catalyst was consistently good over a range of SO_2 inlet concentration (0.1 to 10%) indicating its flexibility in treating SO_2 tail gases as well as high concentration streams.

The overall objective of the current two-phase program is build on the results described above to advance the SO_2-reduction technology from the laboratory to commercial scale. The principal objective of our Phase I program is to identify and evaluate the performance of a catalyst which is robust and flexible with regard to choice of reducing gas (methane, carbon monoxide, or syn-gas).

Tufts

Work to date at Tufts University has focused on screening tests of a variety of catalyst formulations. The catalyst preparation technique used consists of mixing a solution of nitrate salts and urea and heating the solution to 100°C under strong stirring. Co-precipitation occurs as the solution is heated for 8 hr. The precipitate is then filtered, washed twice with hot deionized water, dried overnight, and then calcined in air at 650°C for 3 hr.

Previously reported results have indicated that:

Ni-Ce(La)-O catalysts show the highest activity, even at relatively low Ni concentrations (2%).

La_2O_3 dopant plays a more important role in the reduction of SO_2 by CH_4 than in the reduction of SO_2 by CO.

Low metal contents are necessary to avoid agglomeration and sintering of the metal oxides at high temperatures.

Use of synthesis gas as the reducing agent can shift the catalyst light-off temperatures back to the values previously reported for pure CO.

The catalysts were prepared by urea gelation/coprecipitation. This method provides well dispersed and homogeneous mixed oxides or mixed oxide compounds, and was used in previous work and for some of the catalysts examined during this reporting period. This preparation consists of the following steps: (i) Mixing nitrate salts of metals with urea and heating the solution to 100°C under continuously stirring, (ii) After coprecipitation, boiling the resulting gels of Ce or Zr vigorously for 8 hours; (iii) Filtering and washing the precipitate twice with hot deionized water; (iv) Drying the precipitate overnight in a vacuum oven at 80-100 °C; (v) Crushing the dried lumps into smaller particles and calcining in air for a few hours at 650 °C for CeO_2-based catalysts and 500°C for ZrO_2-based catalysts. The typical surface area of the thus prepared CeO_2-based catalyst was about 70-120 m^2/g. However, the surface area of CeO_2 and La-Ce-O catalysts was not stable even after 750 °C calcination, and the typical surface area after reaction up to 750 °C was around 35 m^2/g (Table 1).

Table 1. Physical Properties and Activity of Ceria and Doped Ceria

Sample	Surf. area of fresh sample (m^2/g)		Surf. area of used sample* after reaction at 750 °C		Activity of Sample (T=700 °C)	
	650 °C calcination	750 °C calcination	dry	wet	X-SO_2	Y-[S]

CeO_2	75	40	29 (20)	33	0.255	0.255
4.5%La-Ce-O	70	59	33		0.221	0.211
10%La-Ce-O	106	69	37		0.236	0.226
20%La-Ce-O	120	58	34 (30)	28	0.299	0.291
30%La-Ce-O	78	59	35		0.206	0.198

*all catalysts were pre-reduced (at 600 ^{o}C in 10% CO/He for 1 hr).
The values in parenthesis are the surface area of the samples calcined at 750 ^{O}C.

All catalysts were tested in a laboratory-scale, quartz tube packed bed flow reactor with a porous quartz frit supporting the catalyst, which was in powder form. A 0.5 in. O.D. x 18.5 in. long bed was used in catalyst tests. The experiments were carried out under nearly atmospheric pressure. A cold trap connected at the outlet of the reactor was used to separate and collect the elemental sulfur and water from the product stream. The product gas was analyzed by a HP5880A Gas Chromatograph (GC) with a Thermal Conductivity Detector(TCD). A 1/4 in. O.D. x 6 in. long packed glass column of Chromosil 310 was used in the GC to detect CO, CO_2, COS, SO_2 ,CS_2 and H_2S.

The results are shown in terms of sulfur dioxide conversion, X-SO_2, and elemental sulfur yield, Y-[S], defined as follows:

$$X(SO_2) = \frac{([SO_2]_0 - [SO_2])}{[SO_2]_0}$$

$$Y(S) = \frac{[S]}{[SO_2]_0}$$

where $[SO_2]_0$ and $[SO_2]$ are the inlet and outlet sulfur dioxide concentrations, respectively, while [S] is the outlet elemental sulfur concentration. [S] is calculated from the difference:

$$[S] = [SO_2]_0 - [H_2S] - [COS] - [SO_2]$$

From the previous work, we have found that the 5%Ni-Ce(La)-O catalyst was also an active catalyst for the SO_2 reduction by CH_4. Due to the difficulty to activate methane, the activity of pre-reduced (metal + support) and that of the support were almost indistinguishable. However, in the presence of water vapor, the metal may help to improve the resistance to water vapor. Figure 1 shows the activity of 5%Ni-Ce(La)-O catalyst in the presence of 3% H_2O with the stoichiometric amount of CH_4 and SO_2. A typical activation profile at 700°C shown in Figure 2 indicates that H_2S concentration first reached a maximum due to the introduction of water vapor, then went down and gradually reached a value which was slightly higher than the dry level. SO_2 concentration increased, while some of the activity of the catalyst was suppressed by water adsorption on the catalyst surface. Similar to the CeO_2 catalyst, the activity of 5%Ni-Ce(La)-O catalyst could be recovered upon removal of the water.

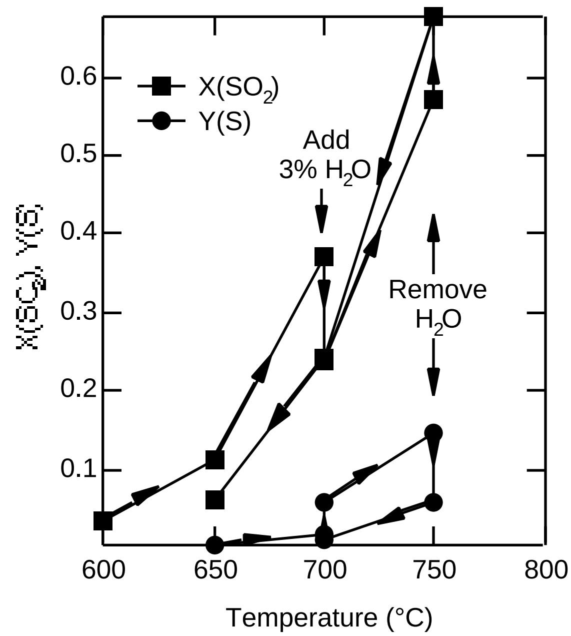


Figure 4-1. Activity profile of 5% Ni-Ce(La)-O catalysts in the presence of 3% H_2O, 1.18% SO_2, 0.5% CH4, at a contact time of 0.36 gs/cm^3.

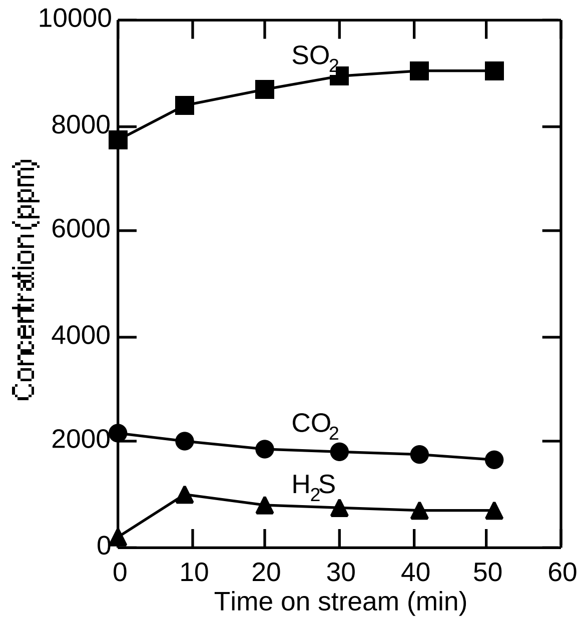


Figure 4-2. Product slate at 700°C of a 5% Ni-Ce(La)-O catalysts in the presence of 3% H_2O, 1.18% SO_2, 0.5% CH_4, at a contact time of 0.36 gs/cm^3.

By increasing the ratio of CH_4 to SO_2, the SO_2 conversion and sulfur yield of 5%Ni-Ce-O catalyst were improved both in dry and wet conditions at temperatures lower than 750°C (Figure 5). Figure 3 illustrates the activation profile at 700°C, which shows that the concentration of H_2S passed through a maximum and went back to dry-gas level. COS formation was suppressed by introducing water.

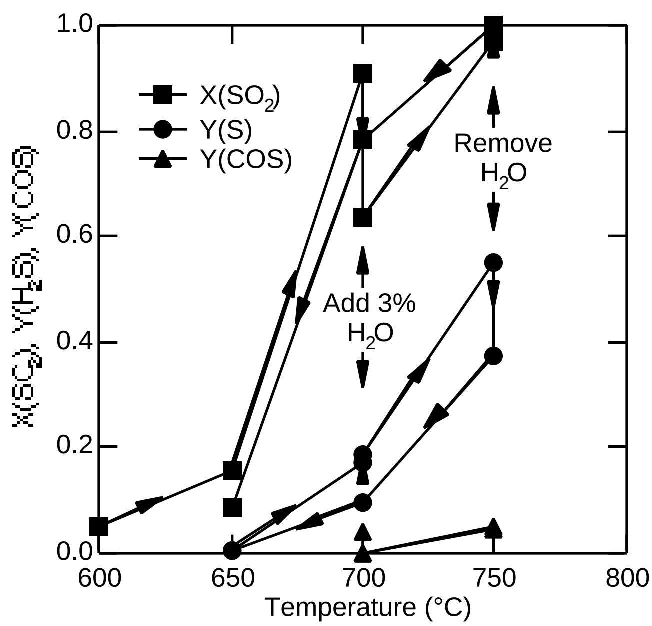


Figure 4-3. Activity profile of 5% Ni-Ce(La)-O catalysts at at higher concentration of reducing gas: 3% H_2O, 1.18% SO_2, 0.5% CH_4, at a contact time of 0.36 gs/cm^3.

TPR is one of the temperature programmed reaction methods in which a chemical change is monitored while temperature increases linearly with time. The TPR experiment employs a reductant, usually CO or H_2, to reduce the catalyst during increasing temperature. Here, methane was employed since it is one of the reactant, and the weight change of catalysts in a TGA or the effluent gas composition analyzed by Mass Spectrometry was monitored. Theoretically, interpretation of the reduction rate profile obtained from TGA is straightforward on a qualitative basis: number of peaks represents different precursors; the higher the reduction temperature, the less reducible the catalyst is; and the total peak area is proportional to the amount of reacted oxygen. In this work, TPR experiments were conducted both in a thermal gravimetric analyzer (TGA) apparatus and a packed bed reactor with on-line mass spectrometry. In both cases, 5%CH_4/He or 5% H_2/He was used as the reductant.

Temperature programmed reduction (TPR) of the nickel-containing catalyst in 5%CH_4/He in the TGA shows a sharp peak around 500 °C (Figure 1). This is due to the surface reduction by H_2 which comes from the methane dissociation on Ni. Hydrogen was identified in the similar experiment in the reactor by MS. The initial report of the activity of Ni-Ce(La)-O catalyst was for the pre-reduced state by heating at 600 °C in 10%CO/He, which possibly reduced the nickel oxide to Ni metal providing sites for methane dissociation during the reaction. For Cu-Ce-O catalysts, the TPR results did not show such behavior (Figure 2). Additional tests of the pre-reduction effect on the activity and selectivity of these two catalysts are planned.

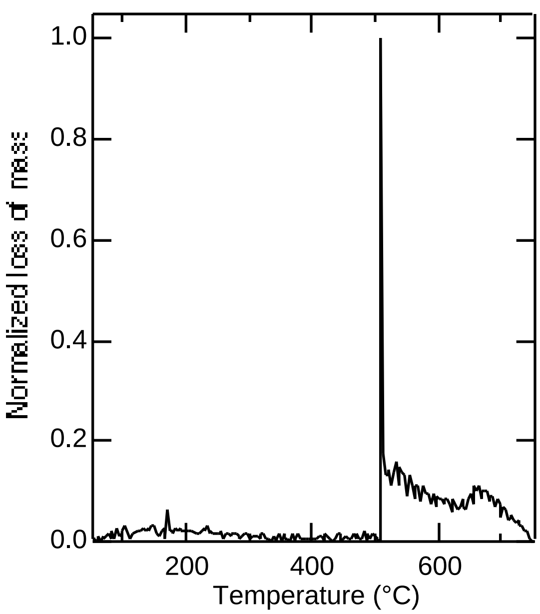


Figure 4-4. Temperature programmed reduction of 5% Ni-Ce(La)-O catalyst in 5% CH_4/He

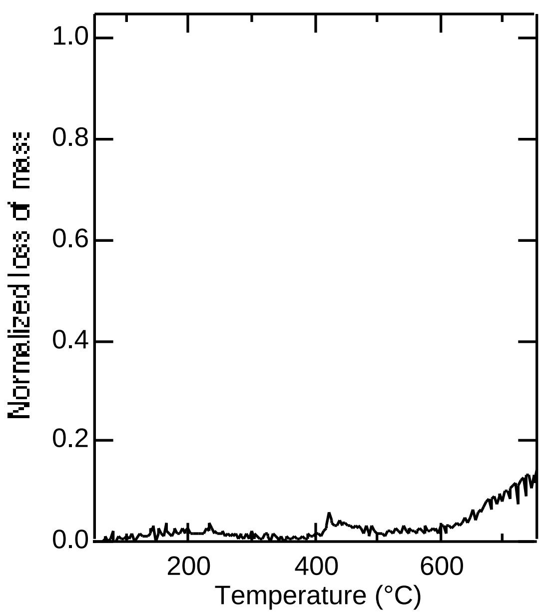


Figure 4-5. Temperature programmed reduction of 5% Cu-Ce(La)-O catalyst in 5% CH_4/He

The activity of doped CeO_2 catalysts for the SO_2 reduction by CO, as well as activity of undoped ceria prepared by a different method and having different crystallinity is shown in Figure 1. Urea precipitated CeO_2 had higher activity (light-off temperature for 50% conversion of SO_2 around 400°C) than CeO_2 prepared by acetate decomposition (520°C). The most active catalyst was Ce(10%Zr)O_2 with 50% SO2 conversion at 380°C. The activity of Ce(10%La)O_2 catalysts was slightly lower.

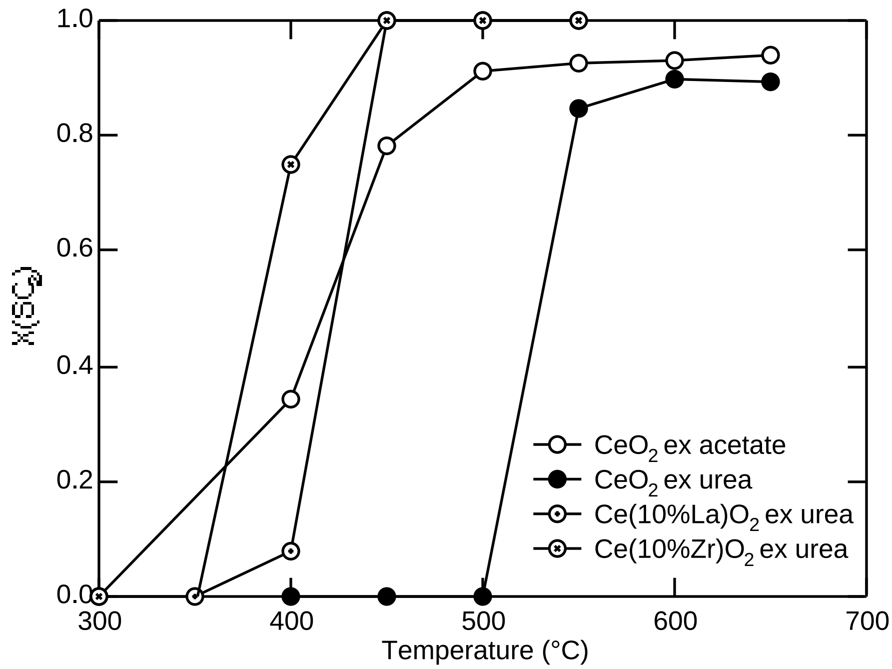


Figure 4-6. Activity of doped CeO_2 catalysts for reduction of SO_2 by CO.

The characteristics of doped CeO_2 catalyst, such as BET surface area and crystal size determined from the <111> and <220> XRD peaks using Scherrer equation are shown in Table 2. All catalysts have cubic crystal structure. Results indicate that doping stabilizes the ceria crystal size and its resistance to sintering. Zr-doped ceria calcined at 500°C had smaller crystal size (around 5 nm) than the undoped CeO_2 (10nm) and a corresponding higher activity. The La-doped CeO_2 had crystal size 20% lower (~8 nm) than the undoped CeO_2 (both after 650°C calcination).

Table 4-2. BET surface area and crystal size of pure and doped CeO_2.

Catalyst (calcination temperature)	BET surface area (m^2/g)	Crystal size (nm)*	
		<111>	<220>
CeO_2 (650°C)-urea	46.4	10.9	10.4
CeO_2 (700°C)-acetate	18	20.0	-
Ce(10%Zr)O_2 (500°C)	138.5	5.3	4.9
Ce(10%La)O_2 (650°C)	91.7	7.7	7.1

* XRD analysis

Three different factors are considered to be important for the catalytic activity of doped ceria in redox reactions: ceria microcrystallinity, defect formation and reducibility. Doping of ceria leads to defect formation and in some cases to the reduction of ceria crystal size.[5]

On the other hand microcrystalline materials are known to be highly defective. The reduction behavior of ceria depends on its surface area (surface oxygen reduction) and also on oxygen ion conductivity (bulk reduction). Both surface and bulk reduction of ceria can be modified by doping.

The TPR profiles of undoped CeO_2 and La and Zr doped CeO_2 are shown in Figure 2 in the form of weight change and derivative of the weight change vs. temperature. As was previously reported, surface reduction of CeO_2 starts about 300°C, with maximum reduction rate at 500°C. Bulk reduction of CeO_2 occurs at higher temperatures with maximum rate at about 700°C. Doping of CeO_2 changes both surface and bulk reaction properties. La doped CeO_2 shows a higher degree of surface reduction due to the higher surface area and also the bulk oxygen reduction temperature is slightly lower. Similarly Zr-doped catalyst has lower reduction temperature than the undoped CeO_2. Reduction at lower temperatures may be attributed to the higher oxygen mobility (oxygen conductivity) of Ce-Zr-O mixed oxides, due to structural changes introduced by doping.[5]

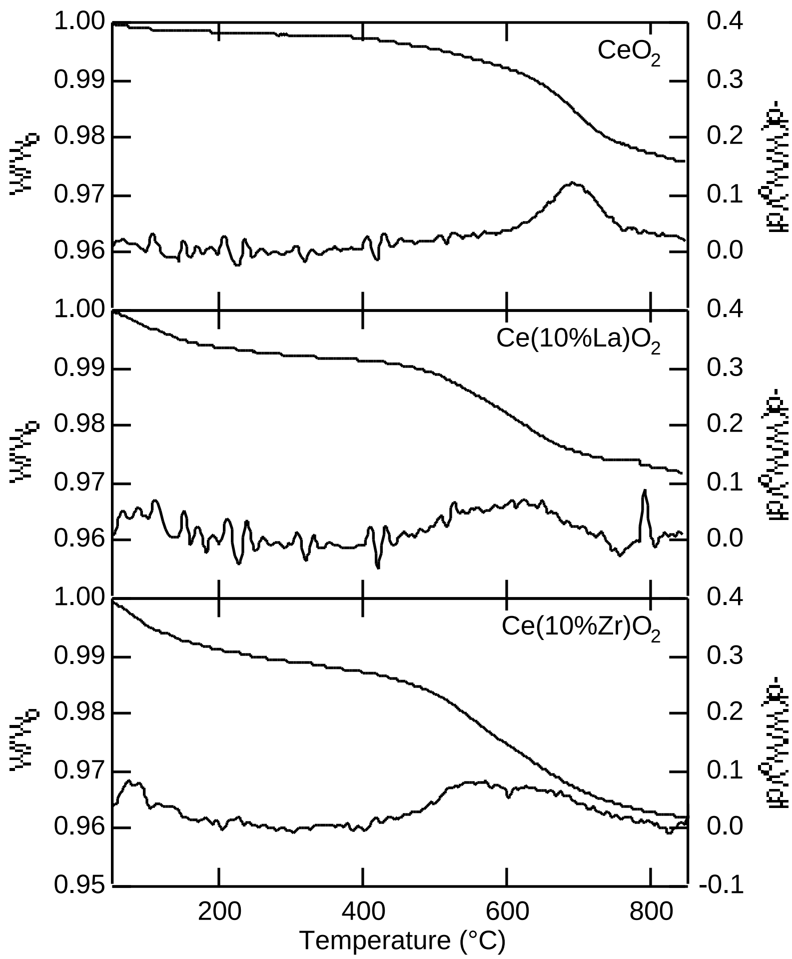


Figure 4-7. H_2-TPD of doped CeO_2. Conditions: 5% H_2/He, 500 ml/min, 10°C/min.

H_2-TPR results are summarized in Table 3. Reduction extent is expressed as x in CeO_x. Results show that Zr-doped ceria is more reducible than La doped ceria, which can be correlated to the higher activity of these catalysts for the SO_2-CO reaction.

Table 4-3. Reduction extent based on H_2-TPR data expressed as stoichiometry x of oxygen in CeO_x

Catalyst	reduction temperature (°C)

	170	200	300	400	450	500	600	850
CeO_2 (650°C)-urea	1.996	1.994	1.989	1.983	1.973	1.961	1.926	1.752
Ce(10%Zr)O_2 (500°C)	1.962	1.952	1.928	1.907	1.890	1.862	1.760	1.613
Ce(10%La)O_2 (650°C)	1.970	1.965	1.957	1.940	1.931	1.914	1.840	1.729

Future plans include testing the wet activity, effect of CO_2, and long term performance stability of these materials in reduction of SO_2 by CO or $CO+H_2$.

Arthur D. Little

Reactor. The reactor has been completed and we have started to calibrate its gas flows, the analysis train and the control system. We have also received an initial catalyst sample, prepared by Engelhard according to the specifications provided by Tufts. This sample was prepared by washcoating 2% Cu supported on Ceria to a loading of 1.7 g/in^3. A portion of the catalyst tested at Tufts exhibited a comparable specific activity (per unit mass of Cu) as did the progenitor washcoating material.

Industry contact. We had a preliminary discussion with Jeri-Catherine Penrose, of Sargent-Lundy, about the potential application of this process in a modern power generating plant. Ms. Penrose said that the pilot plant being built at the University of Southern Illinois initially will use an ammonium sulfate process to dispose the sulfur dioxide that comes from the regenerative system. There may be an opportunity in Phase 2 of this project to test a direct catalytic reduction process in that pilot facility. In addition, we have initiated conversations with other people who are likely candidates for our industrial review panel.

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