INVESTIGATION OF MIXED METAL SORBENT/CATALYSTS FOR THE SIMULTANEOUS REMOVAL OF SULFUR AND NITROGEN OXIDES

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ABSTRACT

Simultaneous removal of SO_2 and NO_x using a regenerable solid sorbent will constitute an important improvement in the removal processes for these two pollutants from stack gases and possibly eliminate several shortcomings of the individual SO_2 and NO_x removal operations. The DOE-funded investigation of the sulfation and regeneration of alumina-supported cerium oxide sorbents has shown that these materials can perform well at relatively high temperatures (823-900 K) as regenerable desulfurization sorbents. Recent literature shows the following interesting features: 1. addition of copper oxide to ceria lowers the sulfation temperature of ceria down to 773 K; 2. sulfated ceria-based sorbents can function as a catalyst for selective catalytic reduction (SCR) even at elevated temperatures; 3. SO_2 can be directly reduced to sulfur by CO on CuO-ceria catalysts; 4. ceria-based catalysts may have a potential for selective catalytic reduction of NO_x by methane. These observations indicate the possibility of developing a ceria-based sorbent/catalyst which can remove both SO_2 and NO_x from flue gases over a wide temperature range of 773-973 K, producing significant amounts of elemental sulfur during regeneration, and using methane for the selective catalytic reduction of NO_x.

The objective of this research is to reduce NO_x to N_2 and H_2O by selective catalytic reduction with NH_3 and CH_4 over alumina-supported cerium oxide and copper oxide-cerium oxide sorbent/catalysts, investigate SO_2 removal at lower temperatures by supported copper oxide-cerium oxide sorbents, and investigate the possibility of elemental sulfur production during regeneration with CO or with CH_4-air mixtures.

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EXECUTIVE SUMMARY

This research project was proposed in response to the Program Solicitation Number DE-PS22-96PC96200 for the support of advanced coal research at U.S. colleges and universities. It relates to the Technical Topic 6. Environmental Science of the solicitation and involves the elimination of gaseous pollutants arising from coal utilization processes. It is expected that this research will constitute a step in the commercial application of a new technology for the simultaneous removal of SO_2 and NO_x.

The objective of this research project is to reduce NO_x to N_2 by SCR with NH_3 and CH_4 over alumina-supported ceria and copper oxide-ceria sorbent/catalysts, investigate SO_2 removal at lower temperatures by supported copper oxide-ceria sorbents, and investigate the possibility of elemental sulfur production during regeneration with CO or with CH_4-air mixtures.

The expected contributions from the research are the following:

- Evaluation of supported ceria-based catalysts for the selective reduction of NO with methane and the determination of the kinetic parameters.
- Evaluation of using methane-air mixtures for direct reduction of SO_2 to selectively produce elemental sulfur and the determination of the kinetic parameters.
- Determination of the kinetic parameters for sulfation and regeneration of copper oxide-cerium oxide sorbents at temperatures below 823 K.

INTRODUCTION

Air pollution arising from the emission of sulfur and nitrogen oxides as a result of combustion taking place in boilers, furnaces and engines, has increasingly been recognized as a problem. Acid rain is not the only concern. Nitrogen oxides are involved in photochemical reactions that lead to oxidants such as ozone that are highly toxic to plants and trees. One third of man-made NO_x comes from the power generation industry and manufacturing industries contribute an additional 20%. The current federal NO_x emission limits for combustion sources such as process heaters, industrial and utility boilers, and combustion turbines can be readily achieved by most of control techniques in general use. Since a significant lowering of these limits is anticipated in the near future, new methods must be developed to remove SO_2 and NO_x emissions economically to much lower levels. It has been mentioned[1] that the pollutant emissions from coal-fired burners will be limited to one tenth of the current regulations, corresponding to about 0.06 lb pollutant per 10^6 BTU. This will demand about 99% SO_2 and 95% NO_x removal from stack emissions.

Several approaches may be taken to reduce the SO_2 and NO_x emissions from power generation plants, such as using low sulfur fuel, removing sulfur prior to or during combustion, lowering the combustion temperature to reduce NO_x formation, increasing the efficiency of the power generation systems, and removing the pollutants after combustion (stack gas cleanup).

There are a number of stack gas desulfurization processes being used commercially. They usually require 5% to 10% of the generated power for operation. Following are the more common of these processes: (1) wet scrubbing using lime, limestone, soluble alkali, or dual alkali and (2) dry absorption with sodium, lime, or limestone. The efficiency and cost of the wet scrubbing systems are usually higher than those of the dry absorber systems. Dry absorption can have over 90% SO_2 removal efficiency. All of these flue gas desulfurization methods produce waste material that must be collected, stored, and disposed. Except for sodium sorbent systems which can remove 10-20% of NO_x, these SO_2 scrubbers are not effective in capturing NO_x. Some additives to the scrubbing solution such as chelating agents or phosphorous have been proposed to enhance NO_x removal.

Selective Catalytic Reduction (SCR) is an important process for controlling power plant NO_x emissions. This process removes NO_x in flue gas by catalytically reacting oxides of nitrogen with ammonia to form nitrogen and water. The catalyst used is either an alumina supported noble metal (such as Pt) or a mixed oxide (such as $V_2O_5/TiO_2/SiO_2$). A major constraint imposed on the heat transfer equipment by a SCR installation is the narrow operating range of the SCR catalysts. Minimum acceptable temperatures usually range between 200°C to 350°C and the maximum operating temperatures are around 400°C to 425°C. Post-combustion NO_x removal processes such as selective catalytic and noncatalytic reduction are relatively expensive and are economically feasible only for large-scale combustors.

Simultaneous removal of SO_2 and NO_x using a regenerable solid sorbent will constitute an important improvement is the removal of these two pollutants from stack gases and possibly eliminate several shortcomings of the individual SO_2 and NO_x removal operations. This process will allow simple and reliable cleanup of large volumes of stack gases at a competitive cost, produce a concentrated stream of SO_2 which can easily be converted into valuable by-products, and eliminate the waste materials generated in some other sulfur removal processes. Thus, post-combustion NO_x removal may become economical even for small scale combustors if it can be combined with SO_2 clean-up. Department of Energy's Federal Energy Technology Center (FETC) has been involved in the development of a regenerative fluidized bed process using copper oxide-impregnated alumina spheres for simultaneous removal of SO_2 and NO_x since late 1960's. These efforts have been summarized by Yeh et. al[2,3]. This process is expected to operate around 400°C. The UOP/Shell Process involving a cyclic fixed-bed contactor and the Rockwell International Moving-Bed Process also use alumina-supported copper-oxide as the sorbent/catalyst.

More recent studies at FETC considered cerium oxide as an alternative to CuO sorbent[4,5]. Ceria improves the resistance of the alumina support to thermal sintering and produces a regeneration off-gas stream that can be easily converted to elemental sulfur. Ceria can bind 1.5 mols of sulfur per mol and is readily available at a moderate cost. Although it is more expensive than copper oxide, this may not be a significant factor since the cost of metal oxide is a small fraction of the total sorbent cost. There are a few patents[6,7,8] which indicate that

ceria possesses sufficient activity and selectivity as a catalyst for the reduction of NO with NH_3 at the relatively high temperatures (above 500ºC) used for SO_2 removal. A DOE-funded investigation[9] of unsupported ceria and copper oxide-ceria sorbent/catalysts report that with Cu-Ce sorbents, 90% NO_x removal efficiencies could be obtained at 400ºC in the presence of SO_2. The same study used an unsupported ceria catalyst to directly reduce the SO_2 in the regeneration gases by CO to selectively produce elemental sulfur. A more recent study[10] indicated that the best results were obtained with a CuO/CeO_2 catalyst which captured 99% of the sulfur dioxide in the stack gas and the elemental sulfur yield was 97% with the dry gas at 510ºC. When wet gas was used, 91% sulfur dioxide capture and 73% sulfur yield were realized at the same temperature. It might be possible to replace CO as the reducing gas with an appropriate mixture of methane and air, since the lattice oxygen promotes partial oxidation while surface oxygen leads to complete oxidation in the ceria structure.

Selective catalytic reduction of nitrogen oxides with hydrocarbons has been limited to mobile sources because of their low selectivity for the SCR reactions and hence excessive hydrocarbon use. If the ammonia used for the SCR of NO_x in the stationary source flue gas treatment processes can be replaced by a hydrocarbon, the problems associated with the use of ammonia, namely the difficulties in the transport and storage , equipment corrosion, and the ammonia slip can be eliminated. It will be especially advantageous if methane can be used for this purpose since it is available at most electricity generation sites. A recent development in this area is the use of metal-exchanged zeolites as catalysts for this purpose[11,12,13]. In particular Cu/ZSM-5 and Co/ZSM-5 have shown significant activity for NO_x reduction by hydrocarbons. Although Cu/ZSM-5 is very effective with higher hydrocarbons, it has no selectivity for the SCR reaction with methane . One disadvantage of the zeolite-based catalysts is that they have a limited temperature range (700-800 K) for nitric oxide reduction. Another is the severe deactivation by the water present in the flue gas. Also, since they cannot be used for SO_2 removal, they are not suitable for combined removal of SO_2 and NO_x. Recently Zhang et al.[14] reported that the incorporation of cerium ions into Cu/ZSM-5 stabilized the active copper sites for NO decomposition in wet gases by suppressing CuO formation and improved the hydrothermal stability of the catalyst. The high selectivity of cerium for SCR with methane combined with the high activity of copper resulted in improved catalyst

performance.

Other metal oxides were also shown to possess sufficient activity and selectivity for NO reduction with methane. The activity of Li/MgO catalyst for NO reduction with methane was equal to that of Co/ZSM-5 but required higher temperatures and did not exhibit a NO conversion bend-over with temperature[15]. The selectivity for N_2 production was 60% at 893 K and increased with temperature. In another study[16], La_2O_3 was found to be more active and selective for nitric oxide reduction by methane than the magnesium oxide-based catalysts, with essentially 100% selectivity toward nitrogen production. Its activity increased continuously with temperature with no bend-over up to 973 K. The specific activity (based on the catalyst area) of La_2O_3 at 773 K was comparable to that of Co/ZSM-5. Ceria is a fluorite-type oxide like $La_2O_{3,}$ with superior oxygen vacancy and mobility properties. This suggests that ceria-based catalyst may have a potential for the reduction of nitrogen oxides with methane.

These observations indicate a possibility of developing a ceria-based sorbent/catalyst which can remove both SO_2 and NO_x from flue gases within a relatively wide temperature window, producing significant amounts of elemental sulfur during regeneration, and using methane for the selective catalytic reduction of NO_x.

WORK DONE

In the first six months of the project, the main focus was on the planning of the research work which would include the selection of standard procedures for sorbent preparation; preparing three new sorbents; development of the experimental setup and the specifications for the equipment and the chemicals to be purchased. The overall objectives of the proposed research are summarized under the following work elements:

1. To investigate the sulfation of alumina-supported copper oxide-cerium oxide sorbents at temperatures below 823 K.
2. To perform kinetic and parametric studies of the sulfated and fresh alumina-supported cerium oxide and copper oxide-cerium oxide sorbents as catalysts for the selective reduction of nitric oxide with ammonia.
3. To investigate the possibility of using alumina-supported cerium oxide and copper oxide-cerium oxide sorbents as a catalyst for the selective reduction of NO by methane.
4. To investigate the activity and selectivity of sulfated and fresh cerium oxide and copper oxide-cerium oxide sorbents as catalysts for the direct reduction of SO_2 by CO and by CH_4-oxygen mixtures.
5. To investigate the effect of the sulfate salts as precursors of cerium on the performance of ceria sorbents for the simultaneous removal of SO_2/NO_x.

A) Sorbent Preparation:

The standard method for the preparation of the sorbents is selected to be the incipient wetness impregnation technique using aqueous solutions of metal salts on an ALCOA alumina as support material. The resulting solid is dried in air at 393 K and calcined in nitrogen at 923 K for 6 hours. Since alumina plays an important role in sulfation, majority of sorbents are loaded at monolayer coverage of the support (which is about 10 wt% for 200 m^2/g alumina). Copper oxide-cerium oxide sorbents were prepared by co-impregnation of nitrate salts of the metals. Majority of the sorbents will be prepared with a copper to cerium ratio of 1:1 (molar), which corresponds to a distribution of about 32 wt% CuO and 68 wt% CeO_2 on the support. The metal loadings correspond roughly to monolayer coverage. Some sorbents with higher and lower copper contents are also

prepared to study the effect of copper loading:

1. **SOR10-I**: 5%Cu+5%Ce on alumina

   prepared by impregnating a catalyst containing 5% copper on alumina by cerium ammonium nitrate. Calcined at 923 K for 6.5 hours (heating rate=10°C/min)

2. **SOR10-II**: 5%Cu+5%Ce on alumina

   prepared by the co-impregnation of ALCOA alumina by $Cu(NO_3)\cdot 2\frac{1}{2}H_2O$ and $(NH_4)_2Ce(NO_3)_6$. Calcined at 923 K for 6.5 hours (heating rate=10°C/min)

3. **SOR10-III**: 7.5%Cu+2.5%Ce on alumina

   prepared by the co-impregnation of ALCOA alumina by $Cu(NO_3)\cdot 2\frac{1}{2}H_2O$ and $(NH_4)_2Ce(NO_3)_6$. Calcined at 923 K for 6.5 hours (heating rate=10°C/min).

4. **SOR10-IV**: 2.5%Cu+7.5%Ce on alumina

   prepared by the co-impregnation of ALCOA alumina by $Cu(NO_3)\cdot 2\frac{1}{2}H_2O$ and $(NH_4)_2Ce(NO_3)_6$. Calcined at 923 K for 6.5 hours (heating rate=10°C/min).

These samples are being analyzed for their metal contents. They will further be characterized by the surface area and porosity measurements.

B) Plan for Experimental Work

The experimental work was planned in detail so that the experimental setup can be designed and the specifications for the required equipment can be prepared. Following is a summary of the steps to be undertaken in the experimental program:

I) SULFATION OF COPPER OXIDE-CERIA SORBENTS:

1. CAHN instruments TG121 thermal analysis system will be used. The gas manifold for this system already exists in our laboratory. A few modifications are being made to it. It will be ready for experimentation in the next two weeks. About 3 mg of sorbent particles in the 75-150 μm size range will be used in each run.

2. The standard sulfation gas composition will be 0.3% SO_2, 3% O_2, 14% CO_2, 4% H_2O, and balance N_2.

Water will be introduced by means of a syringe pump at the entrance of the reactor. The gas flow rate will be 200 cc(N.P.T.)/min.

3. Temperature = 723 to 823 K.

4. SO_2 concentration = 0.15% to 0.4%.

5. Five sulfation/regeneration cycles will be run to establish the effect of cycling. These runs will be performed at a temperature to be chosen after the temperature dependency is established.

6. Data obtained will be used to determine the intrinsic kinetics of the reactions and the sulfation capacity of the sorbents.

ii) SCR PERFORMANCE OF SORBENTS:

1. A fixed-bed micro reactor setup will be constructed. The following are needed:

a) a quartz tube equipped with a porous quartz frit or a stainless steel tube as the reactor;

b) automatically controlled tubular furnace;

c) chromel-alumel thermocouples placed in quartz or SS thermowells;

d) mass flow controllers for NO, NH_3, O_2, and He:

500 ppm NO, 500 ppm NH_3, 3% O_2 and the balance He

(water vapor and SO_2 will be added in some experiments)

e) a syringe pump for water;

f) gas chromatography for O_2, N_2, and N_2O;

g) chemiluminescence for inlet and outlet concentrations of NO (remove NH_3 and water vapor first);

h) ammonia analysis by NDIR.

Experimental variables in a standard SCR experiment:

temperature	= 773 - 973 K
NH_3/NO ratio	= 0.5 - 1.2
concentration of O_2	= 0.5 - 4%
concentration of H_2O	= 2 - 10%

concentration of SO_2 = 0 - 5000 ppm

degree of sulfation of the sorbent;

metal loading on the sorbent;

Cu/Ce molar ratio;

support material.

The existing sulfation setup will be modified to accommodate the quartz reactor to sulfate the sorbents for SCR experiments.

Pertinent Reactions:

$4\ NO + 4\ NH_3 + O_2 \rightarrow 4\ N_2 + 6\ H_2O$

$2\ NO_2 + 4\ NH_3 + O_2 \rightarrow 3\ N_2 + 6\ H_2O$

iii) NO REMOVAL BY METHANE:

Same as (ii) above except item (1d):

1d) mass flowmeters or controllers for NO, CH_4, O_2, He and SO_2:

1000 ppm NO, 1000 ppm CH_4, 3% O_2 and the balance He.

(water vapor and SO_2 will be added in some experiments)

Experimental variables:

temperature = 773 - 973 K

CH_4/NO ratio = 0.25-1.0

concentration of O_2 = 0.5 - 4%

concentration of H_2O = 2 - 10%

concentration of SO_2 = 0 - 5000 ppm

degree of sulfation of the sorbent;

metal loading on the sorbent;

Cu/Ce molar ratio;

support material.

Pertinent Reactions:

$4\ NO + CH_4 \rightarrow 2\ N_2 + CO_2 + 2\ H_2O$

$CH_4 + 2\ O_2 \rightarrow CO_2 + 2\ H_2O$ (if O_2 is present)

iv) DIRECT REDUCTION OF SO_2 BY CO AND BY CH_4-O_2 MIXTURES:

1. The existing setup connected to the TGA will be modified to accommodate the quartz reactor for this reaction.

2. A) Pertinent Reaction:

$SO_2 + 2\ CO \rightarrow S + 2\ CO_2$

Reactant gas composition:

2-3% CO; 1.3% SO_2; 5% CO_2; balance: N_2

T = 773 - 923 K

B) Pertinent Reaction:

$SO_2 + CH_4 + O_2 \rightarrow S + CO_2 + 2\ H_2O$

Reactant gas composition:

2-3% CH_4; 1.3% SO_2; 2-3% O_2; balance: N_2

CH_4/O_2 = 0.5-1.5

T = 773 - 923 K

3. Gas chromatography for CO, CO_2, COS, and SO_2.

4. Condenser for elemental sulfur.

Based on the results of the above studies, the experimental setup for the NO-removal studies has been designed in detail. The calculations on the feed flow rates (Table 1) have been completed so that the specifications on the flow measurement devices can be initiated. We are in the process of determining the specifications for the required equipment for their acquisition.

Table 1. **FLOW RATES** (Total flow rate= 1 L/min)

Species	Conc., max	Flow rate, max sccm	Gas mixture	Total flow rate (He), sccm	Range of flowmeter
NO	1500 ppm	1.5	4% in He 2% in He 1% in He	37.5 (36) 75 (73.5) 150(148.5)	100ccm
NH_3	2250 ppm	2.25	4% in He 2% in He 1% in He	56.25(54) 112.5(110.25) 225 (222.75)	100ccm
O_2	0.5-4%	5 - 40	10% in He	50-400(45-360)	500ccm
CH_4	250-1000 ppm	0.25 - 1	4% in He 2% in He 1% in He	6.25-25(6-24) 12.5-50(12.25-49) 25-100(24.75-99)	100ccm
SO_2	3000 ppm	3	4% in He	75 (72)	100ccm
He	99.1%	991	100%		1 L/m

RESULTS AND DISCUSSION

This project is just starting. Therefore there are no results yet.

CONCLUSIONS

This project is just starting. Therefore there are no conclusions yet.

PLANS FOR THE NEXT REPORTING PERIOD

In the next six months, we plan to do the following:

1. To complete the acquisition of the equipment; and the construction of the experimental setup for NO removal.
2. To initiate the sulfation experiments.
3. To setup the non-dispersive infra red equipment and standardize the analysis methods.
4. To complete the characterization of the catalyst/sorbents prepared.

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