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

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PRINCIPAL INVESTIGATOR: Ates Akyurtlu

CO-INVESTIGATOR: Jale F. Akyurtlu

Department of Chemical Engineering
Hampton University
Hampton, VA 23668

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EXECUTIVE SUMMARY

Simultaneous removal of SO_2 and NO_x using a regenerable solid sorbent will constitute an important improvement over the use of separate processes for the removal of these two pollutants from stack gases and possibly eliminate several shortcomings of the individual SO_2 and NO_x removal operations. The work done at PETC and the DOE-funded investigation of the investigators on the sulfation and regeneration of alumina-supported cerium oxide sorbents have shown that they can perform well at relatively high temperatures (823-900 K) as regenerable desulfurization sorbents. Survey of the recent literature shows that addition of copper oxide to ceria lowers the sulfation temperature of ceria down to 773 K, sulfated ceria-based sorbents can function as selective SCR catalysts even at elevated temperatures, SO_2 can be directly reduced to sulfur by CO on CuO-ceria catalysts, and ceria-based catalysts may have a potential for selective catalytic reduction of NO_x by 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, produce significant amounts of elemental sulfur during regeneration, and use methane for the selective catalytic reduction of NO_x .

The original objective of this research was to conduct kinetic and parametric studies of the selective catalytic reduction of NO_x 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.

The first two objectives were realized, SCR with NH_3 was limited to a few number of experiments;

instead propylene was investigated as a reductant in SCR due to the several shortcomings of NH_3 as a reductant. The last objective, elemental sulfur production, was not accomplished because it was found that CO formation from partial oxidation of CH_4 was not observed under all reaction conditions studied in this research and thus, no elemental sulfur formation could be obtained with CH_4 and O_2 . Runs with CO as reductant produced almost 100% conversion of NO in gases containing stoichiometric amount of oxygen at 573 and 673 K, but considering the feasibility of using CO in commercial power plants, it was decided not to pursue this objective any further.

The sorbents consisting of cerium oxide and copper oxide impregnated on alumina have been prepared and characterized. Their sulfation performance has been investigated in a TGA setup, studying mainly the effects of temperature, sorbent composition, metal loading and support type. As a result of the sulfation experiments, a relatively wide temperature window was established for the use of alumina-supported cerium oxide-copper oxide as regenerable sorbents for sulfur dioxide removal. In the 723-823 K temperature range, cerium oxide-copper oxide sorbents have specific sorbent capacities (mass of sulfur removed per unit mass of metal sorbent) and sulfation rates significantly higher than those of cerium oxide and copper oxide sorbents used alone. Best sulfation performance was exhibited by the sorbent containing 1:1 molar ratio of cerium and copper. Specific sulfur capacities decreased as the coverage of the support surface by the metal oxides approached monolayer coverage. Sorbents appeared to be resistant to cycling. No loss of sulfation capacity was observed after the third cycle.

Preliminary evaluation of these sorbents for the selective reduction of NO_x gave promising results with ammonia. In the reduction of NO by ammonia, the conversion passes through a maximum at 573 K. These results have to be viewed with caution due to the difficulties of the measurement of NO. Even

though the chemiluminescence analyzer was modified to measure NO_x in the presence of ammonia by incorporating a low temperature converter, the measured NO conversions in the presence of ammonia were still somewhat unreliable.

In the SCR experiments, NO conversions show a maximum with temperature due to the effect of temperature on the rates of reductant + NO and reductant + O₂ reactions, indicating that the reductant+NO reaction has a smaller activation energy, on the sulfated catalysts, and catalysts from sulfate salt precursors, as has been observed with the original catalysts. Cerium oxide and copper oxide by themselves are not good catalysts for the reduction of NO with methane, especially at low temperatures. Maximum NO conversion at the space velocities used in the experiments (13700/hr) is 9 % at 748 K with cerium oxide and about 8 % at 723 K for copper oxide.

Catalysts containing both copper and cerium oxides have better activities for NO reduction with methane, regardless of the Cu/Ce metal ratio. The maximum NO conversion at the space velocity used is 17 % obtained at 723 K.

The maximum NO conversions with propylene occur at lower temperatures on the catalyst containing only copper oxide compared to that with methane. Catalyst containing only cerium oxide exhibited almost constant NO conversion of about 6 % between 648 and 848 K with propylene.

The effect of Cu/Ce metal ratio on the NO conversion is more significant with propylene. The temperature for maximum NO conversion moves towards higher temperatures as the Cu/Ce ratio decreases. The maximum conversion obtained also changes with the Cu/Ce ratio. The catalyst with Cu/Ce =3 exhibited the highest NO conversion with propylene, which is about the same as that obtained with methane.

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I. INTRODUCTION

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 is related to the "Technical Topic 6. Environmental Science" cited in the program solicitation and it involves the elimination of gaseous pollutants arising from coal utilization. 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 .

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 the NO_x formation control techniques in general use. Since a significant lowering of these limits is anticipated in the near future, new methods to remove SO_2 and NO_x emissions significantly and economically must be developed. It has been mentioned¹ 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. The more common of these are: (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 $\text{V}_2\text{O}_5/\text{TiO}_2/\text{SiO}_2$). 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 over the use of separate processes for 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 SO₂ clean-up. Department of Energy's Pittsburgh Energy Technology Center (PETC) has been involved with the development of a regenerative fluidized bed process using copper oxide-impregnated alumina spheres for simultaneous removal of SO₂ 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 which uses a cyclic fixed-bed contactor and the Rockwell International Moving-Bed Process use alumina-supported copper-oxide as the sorbent/catalyst.

More recent studies at PETC considered cerium oxide as an alternate sorbent to CuO^{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 and can bind 1.5 atoms of sulfur per atom. It is readily available at a moderate cost. Although it is more expensive than copper oxide, since the cost of metal oxide is a small fraction of the total sorbent cost, this may not be a significant factor. 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 NH₃ at the relatively high temperatures (above 500°C) used for SO₂ removal. A DOE funded investigation⁹ of unsupported ceria and copper oxide-ceria sorbent/catalysts report that with Cu-Ce sorbents, 90% NO_x removal efficiencies could be obtained at 400°C in the presence of SO₂. The same study used an unsupported ceria catalyst to directly reduce the SO₂ in the regeneration gases by CO to selectively produce elemental sulfur. A more recent study¹⁰ indicated that the best results were obtained with a Cu/CeO₂ catalyst which produced 97% elemental sulfur yield and 99% SO₂ conversion with dry gas and 73% sulfur yield and 91% conversion with wet gas at 510°C.

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 due to its availability at most electricity generation sites. A recent development in this area is the use of metal-exchanged zeolites as catalysts for this purpose. 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 range for nitric oxide reduction around 700-800 K. 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 re-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.

Some 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 temperature¹⁵. The selectivity for N_2 production was 60% at 893 K and increased with temperature. In another study¹⁶, 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.

Since it is known that lattice oxygen promotes partial oxidation while surface oxygen leads to complete oxidation and considering the fluorite structure of ceria it might be possible to replace CO as the reducing gas with an appropriate mixture of methane and air. These observations indicated 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, produce significant amounts of elemental sulfur during regeneration, and use methane for the selective catalytic reduction of NO_x .

Therefore, the objectives of the proposed research were established to be the following: to conduct kinetic and parametric studies of SCR of NO_x 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.

II. PROJECT SUMMARY

II.A. Catalyst/Sorbent Preparation and Characterization

The standard method for the preparation of the sorbents was selected to be the incipient wetness impregnation technique using aqueous solutions of metal salts on an ALCOA alumina as support material. The resulting solid was dried in air at 393 K and calcined in nitrogen at 923 K for 6 hours. Copper oxide-cerium oxide sorbents were prepared by co-impregnation of nitrate salts of the metals.

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 $\text{Cu}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$.

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 $\text{Cu}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$.

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 $\text{Cu}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$.

Calcined at 923 K for 6.5 hours (heating rate=10°C/min).
5. **SOR10-V:** 8% Cu+2% 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)

6. **SOR10-VI:** 10% Cu+0% Ce on alumina

prepared by the co-impregnation of ALCOA alumina by $\text{Cu}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$.

Calcined at 923 K for 6.5 hours (heating rate=10°C/min)

7. **SOR10-VII:** 0% Cu+10% Ce on alumina

prepared by the co-impregnation of ALCOA alumina by $\text{Cu}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$.

Calcined at 923 K for 6.5 hours (heating rate=10°C/min).

These sorbents were prepared on ALCOA CSS200 Alumina, which has a surface area of 200 m²/gram, and they have a total metal loading of 10 % by mass (designated by the number after 'SOR'). Since alumina plays an important role in sulfation, additional sorbents were prepared at monolayer coverage of the support, which is about 8 % by mass on the ALCOA CSS200 alumina. Another type of ALCOA alumina, LD350 with a surface area of 360 m²/gram, was also used. A monolayer on the second support corresponds to about 14.4% by mass of metal loading.

Ammonia is an interfacial solvent; therefore, the diffusion of copper in the support may be affected by the ammonium ion in $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$. Actually, during preparation, the investigators have noticed that its aqueous solution is oily and thus, may influence the relative distribution of the two metals on the alumina.

These samples were analyzed for their metal contents by ICP in a local laboratory. Their surface areas have been measured by nitrogen adsorption; these results are presented in Table 1.

Additionally, X-ray diffraction measurements for the identification of the crystalline phases, and SEM and EDAX analysis were performed on the sorbent/catalysts. XRD results are presented below:

SOR10-V(Cu8Ce2): Major chi-Al₂O₃; major CuO type structure (Tenorite); major CeO₂

SOR10-II(Cu5Ce5): Major chi-Al₂O₃; major CeO₂; trace possible CuO type structure (Tenorite)

SOR10-III(Cu7.5Ce2.5): Major chi-Al₂O₃; major CuO type structure (Tenorite); major CeO₂

SOR10-IV(Cu_{2.5}Ce_{7.5}): Major chi-Al₂O₃; major CeO₂; trace possible CuO type structure

(Tenorite)

SOR10-VI(Cu₁₀Ce₀): Major chi-Al₂O₃; major CuO type structure (Tenorite)

SOR10-VII(Cu₀Ce₁₀): Major chi-Al₂O₃; major CeO₂

Table 1. Physical Properties of the Sorbents

Sorbent	Cerium Loading, mass %		Copper Loading, mass %		Nominal Metal Loading, mass %	Surface Area, m ² /g	Support
	Nominal	Actual	Nominal	Actual			
SOR10-II	5	4.58	5	5.54	10	122	CSS200
SOR10-III	2.5	2.26	7.5	8.42	10	134	CSS200
SOR10-IV	7.5	6.49	2.5	2.77	10	122	CSS200
SOR10-V	2	1.90	8	8.76	10	130	CSS200
SOR10-VI	0	0	10	10.36	10	105	CSS200
SOR 10-VII	10	8.84	0	0	10	126	CSS200
SOR 10-VIII	2	1.35	8	7.52	10		LD350
SOR 05-I	1	0.99	4	4.18	5		CSS200
SOR 08-I	6	5.56	2	2.01	8		CSS200
SOR 08-II	6	4.16	2	2.00	8		LD350
SOR14.4-I	10.8	7.81	3.6	3.47	14.4		LD350

Table 2. Results from EDAX Measurements

	Mass % of components at different locations on Cu ₆ Ce ₁ pellet			
	Mass % at 0	Mass % at 1	Mass % at 2	Mass % at 3
Cu₆Ce₁				
O	20.44	7.76	14.78	15.10
Al	54.44	54.23	54.90	56.16
Ce	6.56	9.66	6.57	0.46
Cu	18.56	28.35	23.75	28.29
Cu/Ce	2.83	2.93	6.57	61.50
Cu_{7.5}Ce_{2.5}				
O	29.8	21.5	21.76	
Al	41.00	54.00	52.41	
Ce	11.27	7.62	10.72	
Cu	17.86	16.88	15.12	
Cu/Ce	1.58	2.21	1.41	
Cu₈Ce₂				
O	22.53	14.67		
Al	50.82	52.13		
Ce	10.04	11.30		
Cu	16.79	21.91		
Cu/Ce	1.67	1.94		

Table 3. Summary of EDAX Results

	Cu/Ce Mass Ratio			
Sorbent	0	1	2	3
Cu_{7.5}Ce_{2.5}	1.58	2.21	1.41	
Cu₈Ce₂	1.67	1.94		
Cu₆Ce₁	2.83	2.29	6.57	61.5

I.B. Sulfation

i) Experimental Setup and Procedure

For this purpose, a CAHN instruments TG121 thermal analysis system was employed to record the weight of the sorbent as it underwent sulfation. The weight and the sample temperature were monitored and stored continuously using a microcomputer. Reactant gas mixture was prepared from high purity bottled gases without further purification.

The effect of temperature on the sulfation performance of the sorbents was done under standard sulfation conditions with temperature being varied from 723 to 823 K. The standard sulfation gas composition was 0.3% SO₂, 3% O₂, and balance N₂, the gas flow rate being 200 cc(NPT)/min. About 3 mg of sorbent particles in the 75-150 µm size range, was used in each run. All the sorbents (SOR10-II to SOR 10-VII) were crushed and sieved and the 75-150 µm range was saved for sulfation experiments. It has been established that under these conditions mass transfer effects are negligible.

The standard procedure for running a sulfation-regeneration experiment was as follows:

1. Turn on the TGA computer; select or build the method.
2. Go to 'Run' mode on TGA; tare and calibrate under flowing nitrogen.
3. Put the sample in the pan; close the reactor tightly. Record the sample weight.
4. Turn on the purge gas (helium) to TGA.
5. Turn on nitrogen gas to the TGA reactor.
6. Turn on the fan and furnace on TGA; turn the furnace air on.
7. Start the run on the TGA.
8. While the reactor is being heated up to the reaction temperature, prepare the reactant gas mixture

for sulfation; vent it.

9. When the reaction temperature is reached and the mass reading is stable, switch from nitrogen to the reactant gas mixture.

10. After 65 minutes, switch from the reactant gas mixture to nitrogen. Turn off all the reactant gases except nitrogen in the sulfation mixture.

[Prepare the regeneration mixture in the meantime.

[11. After 10 minutes, switch to the regeneration mixture.

In the meantime, prepare (nitrogen + air) mixture on the sulfation line.

12. After 30 minutes of regeneration, switch to the (nitrogen + air) mixture.

Continue until oxidation is complete.

[In the case of performing cyclic experiments, do the steps 8-12.]

Once the experiments to study the effect of temperature are completed, five sulfation/regeneration cycles were run to establish the effect of cycling.

ii) Evaluation of Sulfation Data:

The following sulfation reactions were used to analyze the data obtained using sorbents consisting of ceria and copper oxide on alumina:

Other Probable Sulfation and Oxidation Reactions:

Regeneration Reactions:

Since the selectivity of the reactions (1) and (2) is not known, the following evaluation method is being used to evaluate the sulfation data:

1. Mass versus time data is obtained from the TGA results.
2. Maximum mass change (Δm_{max}) due to the complete sulfation of copper and cerium oxides is calculated from the reaction stoichiometry of the two above-mentioned reactions and the composition and initial mass of the sorbent loaded to TGA.
3. Mass (m) versus time data during sulfation is obtained from the TGA results and $\Delta m = m - m_0$ is calculated at each time value. m_0 is the mass of the sorbent at the start of sulfation.
4. Conversion, X_s , defined as $\Delta m / \Delta m_{\text{max}}$, is calculated for each time value and plotted as a function of time. These plots will be used to compare the sorbents of different compositions and also the dependence of the performance of a sorbent on temperature.
5. The conversion data will be used to fit a reaction model with X_{ce} and X_{cu} as adjustable parameters.

At this time, the researchers are working on this model.

iii) Results and Discussion of Sulfation Experiments

The effect of temperature on the sulfation of sorbents is shown in Figures 1-6. The following observations can be made:

1. All curves exhibit two regions:
 - (a) a rapid sulfation region which is generally confined to the first 600 seconds of sulfation and
 - (b) a slow sulfation region in which the conversion either levels off or continues at a slow and almost constant rate due to the bulk sulfation of alumina. This behavior is indicative of the significance of the bulk sulfation of alumina at 773 K. The sulfation rate in the rapid sulfation region is not significantly affected by cycling.
2. The effect of temperature on the rate of rapid sulfation becomes more significant as the cerium content of the sorbent increases. On the other hand, the conversion at one hour of sulfation for the sorbent containing more cerium than copper by mass is about the same at all temperatures.
3. Above 773 K, the bulk sulfation of alumina becomes significant indicated by the rate of sulfation in the slow sulfation region. At 723 K, the bulk sulfation of alumina effectively stops after about one hour of sulfation.
4. For sorbents with high copper content, the conversion curves at different temperatures cross over as the result of the decreasing sulfur capacity of copper due to the dissociation of sulfate and increasing sulfation rate of alumina.

The effect of sorbent composition on sulfation behavior is shown at 823 K and 723 K in Figures 7 and 8, respectively. At 823 K, the conversion in the rapid sulfation region increases with increasing cerium content up to 7.5% cerium by mass. All sorbents show the same rate in the sulfation region indicating that

cerium and copper are about equally effective in facilitating the SO_3 formation and hence the bulk sulfation of alumina at this temperature. The sorbent containing 7.5 % cerium reaches its theoretical capacity, based on ceria and copper oxide, within about 400 seconds of sulfation while the conversion of the sorbent containing only ceria is about 80 % for the same sulfation time. After one hour of sulfation, the ceria sorbent reaches a conversion of about 125 %. The conversion of other sorbents after one hour of sulfation depends on the cerium content, with the copper oxide sorbent giving the lowest conversion around 70 % and the 7.5 % cerium-containing sorbent exhibiting 120 % conversion.

Curves 1 through 6 in Figure 8 show the sulfation at 723 K of the same sorbents as in Figure 7. Copper oxide and ceria sorbents show the lowest sulfur capacities at this temperature. Mixed metal oxide sorbents demonstrated much higher sulfur capacities than single oxide sorbents with the conversions at one hour of sulfation increasing with increasing ceria content up to 7.5 % cerium (curve 5). The sorbent containing about equal amounts of cerium and copper has a higher sulfation rate in the rapid sulfation region but does not exhibit significant levels of bulk aluminum sulfation and, thus, the conversion levels off at about 90 %.

Figures 7 and 8 indicate that the best sorbent composition in the 723 - 823 K temperature range is the sorbent containing 7.5 % cerium and 2.5 % copper. This ratio roughly corresponds to a 1.1 molar ratio of copper and cerium and indicates that the interaction of each cerium atom with one copper atom is needed to produce the highest specific sulfur capacity.

Curves 7 and 8 in Figure 8 correspond to different total metal loadings. If curve 7, which corresponds to about 60 % of monolayer coverage, is compared to curve 3, which corresponds to a coverage of slightly above monolayer, it is seen that the specific sulfur capacity (mass of sulfur per unit mass of metal oxide) is higher for lower surface coverage as expected. Lower surface coverages provide well-

dispersed metal ions and available sites for the formation of surface sulfate species (Centi, et al, 1992 a). Curve 8 is for a sorbent prepared using a higher surface area support ($350 \text{ m}^2/\text{g}$) and has about 70 % of monolayer coverage with the metal oxides. Specific sulfur capacity of this sorbent falls between the sorbent with 60 % of monolayer coverage (curve 7) and the sorbent with slightly more than a monolayer coverage (curve 3). The conversion of this sorbent levels off in the slow sulfation region possibly due to pore closure and surface area loss. The results of the porosity measurements are not available yet, however, to confirm this reasoning.

The effects of cycling on the sulfation of the sorbents are presented in Figures 9- 12. Conversion of sorbents containing more copper than cerium improved upon cycling, with cycle 5 giving the highest specific sulfur capacity. The sulfation capacity of sorbents containing higher amounts of cerium decreased for the second and third sulfations, then increased for the fourth sulfation cycle to settle at a conversion level slightly below the fresh sorbent. This observation is similar to the behavior of ceria sorbents reported earlier (Akyurtlu and Akyurtlu, 1995).

Figures 13-16 indicate that the monolayer coverage on the sorbents studied is dependent on the cerium to copper ratio. Figure 13 shows the effect of metal loading for sorbents containing a Cu/Ce mass ratio of 4:1. Since the conversion plotted on the ordinate is a normalized specific sulfur capacity, it is expected that it will increase with decreasing surface coverage because lower surface coverages provide well-dispersed metal ions and sites available for the formation of surface sulfate species¹⁷. The results shown in Figure 13 confirm this expectation. Curve 1 is for a sorbent with a surface coverage of a little over a monolayer. Curves 2 and 3 are for sorbents having about 60% and 70% surface coverages, respectively. The highest conversions are obtained for the sorbent with 60% coverage. Figure 14 shows the sulfation behavior of the same sorbents at 823 K as in Figure 13. The behavior is similar to that at 723 K.

Figure 15 shows the effect of metal loading for a sorbent containing a 3:1 Ce/Cu mass ratio. Curve 1 is for a sorbent with a monolayer coverage; curve 3 is for a sorbent which has a metal loading 20% over monolayer; and curve 2 is for the sorbent with 70% surface coverage. In this case, the sorbent with the monolayer coverage exhibits the highest sulfur capacity. Since the sorbent in curve 2 has a higher surface area, pore blockage may be causing the conversion to be limited at high sulfation levels. It can be observed that the coverages in excess of a monolayer retard the bulk sulfation of alumina and it appears that the excess ceria, which is expected to be present as microcrystals unassociated with alumina, are not as reactive as the cerium aluminate species present in the monolayer. Also, microparticles of metal oxides form above monolayer coverages; these form bulklike metal sulfates, which inhibit sulfation of sub-surface layers because the specific volume of the sulfates is higher than that of the oxides, which will also result in pore closure. Thus, the metal loading affects the metal oxide crystallite size and the bonding interaction between the metal oxide and the support. Figure 16 shows the sulfation behavior of the same sorbents at 823 K as in Figure 15. The behavior is similar to that at 723 K.

Table 4 indicates that the conversion at 3000 seconds of sulfation for the sorbent containing roughly equimolar amounts of cerium and copper (SOR 10-IV) is about the same at all temperatures while that of the sorbent containing ceria only (SOR10- VII) increase with temperature due to the increased reaction rate.

The conversion at 3000 seconds of the sorbent containing only copper oxide is affected by two phenomena: limitation of copper oxide conversion by chemical equilibrium above 773 K (copper sulfate decomposition) and the resulting increase in the bulk sulfation of the alumina sites due to the presence of unsulfated copper, which catalyzes the SO_3 formation. Above 773 K, the bulk sulfation of alumina effectively stops after 3000 seconds of sulfation. For sorbents with high copper content, the conversion curves at different temperatures cross over as the result of the decreasing sulfur capacity of copper and

increasing sulfation rate of alumina as the temperature increases. As the coverage is decreased below monolayer, the two regions of sulfation become less distinct and vice versa.

Table 4. Effects of Temperature and Sorbent Composition on Sulfation

Sorbent	Specific Conversion at 3000 s	Temperature, K
SOR10-VI (10%Cu by mass)	0.56	723
	0.65	748
	0.64	773
	0.73	798
	0.66	823
SOR 10-IV (7.5%Ce, 2.5%Cu by mass)	1.14	723
	1.16	748
	1.20	773
	1.20	798
	1.19	823
SOR10-VII (10%Ce by mass)	0.70	723
	1.00	773
	1.25	823

Figure 1. Effect of temperature on the sulfation of **SOR10-VI** (0% Ce, 10% Cu)

Figure 2. Effect of temperature on the sulfation of SOR10-V (2% Ce, 8% Cu)

Figure 3. Effect of temperature on the sulfation of SOR10-III (2.5%Ce, 7.5%Cu)

Figure 4. Effect of temperature on the sulfation of SOR10-II (5% Ce, 5% Cu)

Figure 5. Effect of temperature on the sulfation of SOR10-IV (7.5% Ce, 2.5% Cu)

Figure 6. Effect of temperature on the sulfation of SOR10-VII (10% Ce, 0% Cu)

Figure 7. Effect of sorbent composition on the sulfation behavior at 823K

Figure 8. Effect of sorbent composition on sulfation behavior at 723K

Figure 9. Cycling behavior of SOR10-VI (0% Ce, 10% Cu) at 773 K

Figure 10. Cycling behavior of SOR10-V (2% Ce- 8% Cu) at 773K

Figure11: Cycling behavior of SOR10-II (5% Ce, 5% Cu) at 773K

Figure 12. Cycling behavior of SOR10-IV (7.5% Ce, 2.5% Cu) at 773K

Figure 13. Effect of Metal Loading at 723K. Ce/Cu mass ratio = 1:4

Figure 14. Effect of Metal loading on Sulfation at 823K. Ce/Cu mass ratio=1:4

Figure 15. Effect of Metal Loading at 723K. Ce/Cu mass ratio = 3:1

Figure 16. Effect of Metal Loading on Sulfation at 823K. Ce/Cu mass ratio=3:1

II.C. **NO_x Removal**

i) Experimental Setup and Procedure

The experimental setup used for the selective catalytic reduction of NO is presented in Figure 17.

For NO_x removal experiments, 2 grams of the catalyst/(sorbent) (particle size of 250 - 425 μm) is weighed and placed in the quartz microreactor. The reactant gas mixture is prepared from high purity bottled gases without further purification.

Experimental variables in a standard SCR experiment:

temperature = 773 - 973 K

NH₃/NO ratio = 0.5 - 1.2 or CH₄/NO ratio = 0.25-1.0

concentration of O₂ = 0.5 - 4%

concentration of H₂O = 2 - 10%

concentration of SO₂ = 0 - 5000 ppm

degree of sulfation of the sorbent;

The reactant gas composition for the standard SCR experiments is 650-900 ppm NO, 0-250 ppm NO₂, 3.0% O₂, 7% H₂O, 3500 ppm CH₄ (or NH₃/NO_x = 1), balance He. Initially, experiments were performed with both CH₄ and NH₃ as the reducing agent.

Gas samples were analyzed using a Varian 3400 Gas Chromatograph for CO, CO₂, N₂, O₂, CH₄ and C₃H₆. For the first five components, TCD detector with a 15' Carboxen 1000 column from Supelco was used. The column was temperature-programmed for the optimum resolution of the components; it was kept at 35°C for 5 minutes, then heated to 225°C at 20°C/minute and kept at that temperature for 10 minutes. Under these conditions, the retention times were 5.5 min for O₂, 6 min for N₂, 7.7 min for CO, 11.5 min for CH₄, and 13.8 min for CO₂. FID detector was used to analyze

FIGURE 17. Experimental Setup for NO_x Removal Experiments

C₃H₆ with a 2' Carboxen column from Supelco. The temperature program for this column was keeping it 165°C for 1 min, then heating it to 220°C at 16°C/min and keeping it at that temperature for 15 minutes. The retention time for propylene under those conditions is 5 minutes.

A Thermo Environmental Instruments Model 42 H Chemiluminescence NO-NO₂-NO_x analyzer was employed for the quantitative analysis of NO₂ and NO. To avoid the wet analysis methods for the determination of NH₃, a low temperature molybdenum converter was purchased for the chemiluminescence analyzer. In the standard high temperature NO₂ to NO converter, ammonia is also converted to NO and therefore, is measured as NO, while in the low temperature converter negligible ammonia conversion is expected. Thus, by alternately using the high and low temperature converters, we expected to determine ammonia from the difference in the NO measurements.

Unfortunately the initial experimental measurements gave inconsistent results and did not allow the determination of ammonia as intended. A decision was then made to remove the ammonia from the gas stream before it enters the chemiluminescence unit by absorption and then determine the ammonia by titration. We also checked the operation of both the low temperature and the high temperature converters. Further inconsistencies were observed in the NO and NO₂ measurements. This led us to open up the low temperature converter to find the cause of the faulty measurements. It was then noticed that the NO/NO₂ switch on the instrument was connected wrong and the NO readings indicated NO₂, and NO₂ readings indicated NO. Even after the switch connections were corrected, reliable NO measurements could not be obtained.

The results reported in Figure 18 for the SCR of NO by ammonia were obtained using the high temperature reactor and therefore are only rough estimates. In the calculation of conversions, since at the reactor exit for full NO₂ conversion, the amounts of NO and NO_x were roughly equal, it was assumed that

the amount of ammonia at the reactor exit was negligible and the difference between the NO_x and NO measured at the reactor inlet was due to both NO₂ and NH₃. This figure indicates that the conversion passes through a maximum at 573 K in the reduction of NO with NH₃ on sulfated SOR08-I sorbent/catalyst.

Since it was proposed to use sulfated sorbents as NO_x removal catalysts, SOR08-I and SOR10-V samples were sulfated in the quartz microreactor at the conditions used for standard sulfation experiments at 823 K for one and two hours. These samples were sent to a local laboratory for sulfur analysis. For one hour of sulfation, the sulfur mass percentage on SOR08-I and SOR10-V were 0.03 and 0.04, respectively and these values are 0.12 and 0.09, respectively for two-hour sulfation. The higher results correspond to about 4.2% and 2.1% sulfation of the respective sorbents. Based on these results, sorbent/catalysts were subsequently sulfated to different extents for NO_x removal experiments. In the preliminary experiments reported above the behavior of the sulfated catalysts were very similar to that of the oxide catalysts.

The pertinent SCR reactions with ammonia and methane are, respectively,

Since the interest in ammonia as a reductant in the SCR process has waned due to the shortcomings of ammonia in industrial applications, we have decided to use propylene in addition to methane instead of ammonia as a reductant in the SCR of NO. The new set of SCR experiments were performed in a

modified setup, presented in Figure 17. A typical reactant gas composition was 650-900 ppm NO, which contains a maximum of 5 ppm NO₂, 1.5% O₂, 7% H₂O, propylene or methane as reductant (reductant/NO_x = 1), balance He.

Gas samples were analyzed using a Varian 3400 Gas Chromatograph for CO, CO₂, N₂, O₂ (with TCD detector, propylene (with FID detector) and Thermo Environmental Instruments Model 42H Chemiluminescence NO- NO₂- NO_x analyzer for NO and NO₂ as mentioned above. In the presence of a reductant, the high temperature (923 K) converter in the instrument led to side reactions and gave erroneous NO₂ and NO_x readings. To overcome this shortcoming the low temperature (623 K) Mo converter was utilized. With this converter reliable NO₂ measurements could be made.

The pertinent SCR reactions with propylene are:

The results from the NO_x removal experiments are interpreted by calculating the conversion of NO_x as:

$$\text{NO conversion (X}_{\text{NO}}) = [\text{NO in feed} - \text{NO in reactor effluent}]/[\text{NO in feed}]$$

(ii) Results and Discussion of NO_x Removal Experiments

Some preliminary SCR experiments were performed with methane as reductant in a simulated flue gas with no oxygen. The results of these NO reduction experiments showed that although copper oxide catalysts do not have any catalytic activity below 773 K, catalysts containing some Ce exhibit some activity at lower temperatures above 673 K and that this activity increases as the space velocity is lowered. It was also observed that decreasing the Cu to Ce ratio below 4 decreased the activity. Subsequent SCR experiments were performed on various catalysts using the simulated flue gas composition reported above.

Figures 19 and 20 present the comprehensive results for the NO reduction with methane and propylene

on different catalysts. Both NO/CH₄ and NO/C₃H₆ molar ratios are one. The conclusions that may be drawn from these figures are:

1. NO conversions show a maximum with temperature due to the effect of temperature on the rates of reductant + NO and reductant + O₂ reactions, indicating that the reductant+ NO reaction has a smaller activation energy.
2. Cerium oxide and copper oxide by themselves are not good catalysts for the reduction of NO with methane, especially at low temperatures. Maximum NO conversion at the space velocities used in the experiments (13700/hr) is 9 % at 475°C with cerium oxide and about 8 % at 450°C for copper oxide.
3. Catalysts containing both copper and cerium oxides have better activities for NO reduction with methane, regardless of the Cu/Ce metal ratio. The maximum NO conversion at the space velocity used is 17 % obtained at 425°C.
4. The maximum NO conversions with propylene occur at lower temperatures on the catalyst containing only copper oxide compared to that with methane. Catalyst containing only cerium oxide exhibited almost constant NO conversion of about 6 % between 350 and 550°C with propylene.
5. The effect of Cu/Ce metal ratio on the NO conversion is more significant with propylene. The temperature for maximum NO conversion moves towards higher temperatures as the Cu/Ce ratio decreases. The maximum conversion obtained also changes with the Cu/Ce ratio.
6. The catalyst with Cu/Ce =3 exhibited the highest NO conversion with propylene, which is about the same as that obtained with methane.

After these experiments, it was focused on the SCR performance of sulfated catalysts with different

Cu/Ce ratios; and CuO-Ce oxide catalysts, made from the corresponding sulfate salt precursors, with respect to their activities for the reduction of NO with methane and propylene. The same experimental conditions as given above were used.

Preparation of new catalysts: Two new catalysts were prepared using cerium ammonium sulfate ($\text{Ce}(\text{NH}_4)_4(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$) and copper sulfate (CuSO_4) precursors, to observe the effect of precursor on the SCR performance of the catalysts. We had mentioned in the proposal that preparing the catalysts from nitrate salts entails an industrial problem; namely, that the calcinations step in the preparation procedure results in the emission of nitrogen oxides. Since during the simultaneous removal of SO_2/NO_x , the oxides on alumina support are converted to sulfates, sulfate species are not foreign to the process environment. That is why, it was decided to use sulfate salts of copper and cerium as catalyst precursors. The same preparation method as had been used for the catalysts from nitrate precursors was employed; one catalyst has a Cu/Ce ratio of 1/3 (XIS) and the other a Cu/Ce ratio of 3 (XIIS), with 10% (by mass total metal loading). They were calcined by the same procedure, too.

Sulfation of Catalysts: The catalysts were placed in a quartz reactor, which was heated to 550°C under nitrogen. At this temperature, a gas mixture composed of air, SO_2 and nitrogen was introduced, starting sulfation. The mole fraction of SO_2 in the sulfation gas was 0.3%. The catalyst with 7.5% Cu and 2.5% Ce loading (SOR10-III) was sulfated for 72 hours, while the catalyst with 2.5% Cu and 7.5% Ce loading (SOR10-IV) was sulfated for 48 hours. The times correspond to about 80% sulfation of the catalysts according to the calculations made and the previous experience from the sulfation of some samples as mentioned above. However, the results from the laboratory reported only about 2.5% sulfation. We got in touch with the laboratory, but they are standing by their results. We do not have enough samples for further analysis.

Figures 21 and 22 present the comprehensive results for the NO reduction with methane and propylene on different catalysts, respectively. Both NO/CH₄ and NO/C₃H₆ molar ratios are one. The conclusions that may be drawn from these figures are:

1. NO conversions show a maximum with temperature due to the effect of temperature on the rates of reductant + NO and reductant + O₂ reactions, indicating that the reductant+ NO reaction has a smaller activation energy, on the sulfated catalysts, and catalysts from sulfate salt precursors, as has been observed with the original catalysts.

SCR with Methane (Space velocity=13700/hour) (Figure 21)

2. Sulfated catalysts show an SCR activity with methane comparable to their unsulfated counterparts, which show slightly higher activity. The temperatures where the maximum activity with methane occurs are comparable, too. The catalysts with a Cu/Ce metal ratio of 1:3 have slightly higher activity than those with a Cu/Ce metal ratio of 3.
3. The catalysts prepared from sulfate salt precursors have very low SCR activity with methane as the reductant. For the catalyst with a Cu/Ce ratio of 1:3, maximum NO conversion is 0.7% at 525°C; for that with a Cu/Ce ratio of 3:1, maximum NO conversion is 4.3% at 500°C.

SCR with Propylene (Space velocity=13700/hour) (Figure 22)

4. The effect of Cu/Ce metal ratio on the NO conversion is more significant with propylene for sulfated catalysts, in the same fashion as with their unsulfated counterparts. Higher Cu/Ce metal ratio exhibits enhanced SCR activity as can be observed on Figure 2, for both sulfated and unsulfated catalysts. For a Cu/Ce metal ratio of 3:1, SCR activity is higher for unsulfated catalysts than for sulfated ones, while for a Cu/Ce metal ratio of 1:3, this behavior is reversed.
5. The SCR activity of the catalysts prepared from sulfate salt precursors with propylene is much more

appreciable than in the case of SCR with methane. For the catalyst with a Cu/Ce ratio of 1:3, maximum NO conversion is 5.7% at 420°C; for that with a Cu/Ce ratio of 3:1, maximum NO conversion is 6.5% at 340°C and 8% at 525°C. The source of the occurrence of the double maxima cannot be accounted for at this time.

From Figure 23, it can be seen that the low temperature conversion was significantly higher in dry gases. With the SOR10-V (Cu₈Ce₂) catalyst, the maximum conversion was about 21 % and occurred at a lower temperature, 700 K.

Effect of SO₂ on the SCR performance on these catalysts was also studied. Both with and without oxygen, addition of 3000 ppm SO₂ almost completely and irreversibly poisoned the SOR10-V (Cu₈Ce₂) catalyst. This was tentatively attributed to the sulfidation of copper in the presence of a reducing species. Since ceria is not reduced to metallic cerium easily upon reduction and hence does not form a sulfide, and since it is known to retard the reduction of copper oxide under reducing conditions, it is expected that catalysts containing larger amounts of ceria might be more resistant to sulfur poisoning. The same experiment was repeated with the SOR08-I (Cu₂Ce₆) catalyst: Activity was lost with the introduction of the sulfur dioxide, however, it was restored partially with oxygen at the reaction temperature, and completely with increasing temperatures. This is due to the fact that ceria is not reduced to metallic cerium easily and hence, does not form a sulfide. It is also expected to retard the reduction of copper under reducing conditions. Therefore, the sulfidation of copper will also be retarded.

Figures 24 and 25 present the results for the effect of oxygen to methane ratio on NO reduction on two catalysts, SOR10-IV (Cu_{2.5}Ce_{7.5}) and SOR10-III (Cu_{7.5}Ce_{2.5}), respectively. O/M ratio on the figures designates the molar ratio of oxygen to methane. The stoichiometric ratio of O/M for the complete oxidation of methane is 2. The conclusions that may be drawn from these figures

are:

1. As the oxygen to methane ratio increases, the conversion of NO reduction decreases.
2. For oxygen to methane ratios less than the stoichiometric, NO conversions start at higher temperatures.
3. For oxygen to methane ratios less than the stoichiometric, copper content is important in the behavior of activity of NO reduction. There is no bendover for the catalyst with a Cu/Ce ratio of 1/3, while there is bendover for Cu/Ce ratio of 3. This observation may be explained by the fact that copper is a good oxidizing catalyst; therefore, as the copper to cerium ratio of the catalyst increases, selectivity of NO reduction to methane oxidation decreases.

The results of NO reduction by methane on sulfated (extent of sulfation=4.2%) SOR08-I (Cu₂Ce₆) are presented on Figure 26. At this extent of sulfation, the effect of sulfation of the catalyst on the extent of NO reduction is not significant.

Figures 27 and 28 present the effect of oxygen to propylene ratio on the extent of NO reduction on two catalysts, SOR10-V (Cu₈Ce₂) and SOR08-I (Cu₂Ce₆), respectively. These two catalysts have been selected for these experiments since copper is a good oxidizing catalyst and cerium is expected to make the copper catalyst more resistant to sulfur poisoning. O/P ratio on the figures designates the molar ratio of oxygen to propylene. The stoichiometric O/P ratio is 4.5 when propylene is used as a reductant. The O/P ratio of 18.75 corresponds to 1.5% (molar) oxygen in the reactant gases

The following conclusions are drawn from these figures:

1. As the oxygen to propylene ratio increases, the conversion of NO reduction decreases and the temperature where the catalysts become active for NO reduction increases. The second observation is opposite to what has been observed in the case of methane as the reductant.

2. In the absence of oxygen, there is no bendover in NO conversion for either of the catalysts. However, the light-off temperature for the catalyst with the higher copper to cerium ratio is lower than that with the lower Cu/Ce ratio. The bendover occurs with the O/P ratio of 18.75 due to the competition between NO reduction and propylene oxidation reactions. This behavior indicates that the activation energy of the former reaction is lower than that of the latter.
3. The light-off temperatures with propylene as the reductant are lower than those with methane. Therefore, one can conclude that propylene activates NO at lower temperatures than methane, and thus, is a better reductant for NO reduction.

A simple model was used to estimate the values of the activation energy for the NO reduction by propylene on the SOR10-V and SOR08-I catalysts. The assumptions used in deriving the model are that the reactor operates in the plug flow regime; the reaction kinetics is rate-limiting; and the reaction is first order with respect to NO concentration and zero order with respect to oxygen since oxygen is in large excess.

$$-r_{\text{NO}} = kC_{\text{NO}}$$

Therefore, the mole balance on NO in the reactor after integration gives:

$$k = -[U_g/(1-\epsilon)L] \ln(1-X_{\text{NO}})$$

Where: k = reaction rate constant

U_g = superficial gas velocity, m/s

ϵ = porosity of the bed

L = bed height, m

X_{NO} = NO conversion

The dependence of k on temperature is expressed by using the Arrhenius relationship:

$$k = k_0 \exp[-E/RT]$$

The values of the activation energy, E, from experimental NO conversion versus temperature data are as follows:

For Cu₈Ce₂ catalyst: E = 131 kJ/mol

For Cu₂Ce₆ catalyst: E = 199 kJ/mol

The performance of our catalysts were compared with the results of some work in literature. Kiel, et al ⁽¹⁸⁾ reported 45% NO conversion at 643 K on fresh CuO/SiO₂ catalyst with an activation energy of 68 kJ/mol and 65% NO conversion at 643 K on sulfated CuO/SiO₂ catalyst with an activation energy of 73 kJ/mol with ammonia used as reductant. Our catalysts showed similar behavior with ammonia. Our activation energies are larger with propylene used as reductant, indicating that ammonia is a more effective reductant than propylene.

Shimizu, et al⁽¹⁹⁾ reported 20% NO conversion at 610 K with propylene used as reductant, with NO/P=0.5 and O₂/P=67 and dry reactant gases on a 8% CuO/alumina catalyst. Our Cu₈Ce₂ catalyst exhibited 21% NO conversion at 700 K under dry conditions and 12.5% NO conversion at 720 K with 7% water, with NO/P=1 and O₂/P=18.75. These are very comparable results.

FIGURE 18. NO Reduction by Ammonia on Sulfated SOR08-I (Ce/Cu=3)

FIGURE 19. NO Reduction by CH₄ in the Presence of oxygen, 7% water

FIGURE 20. NO Reduction by C_3H_6 in the Presence of oxygen, 7% water

FIGURE 21. NO Reduction by CH₄ in the presence of oxygen, 7% water

FIGURE 22. NO Reduction by C₃H₆ in the presence of oxygen, 7% water

Figure 23. Effect of water on NO Reduction with C_3H_6 . Catalyst: SOR10-V (Ce_8Cu_2),
with 1.5 % oxygen. NO/Propylene=1

FIGURE 24. NO Reduction by CH₄ on catalyst SOR10-IV (Cu_{2.5}Ce_{7.5}) in the presence of oxygen, 7% water

FIGURE 25. NO Reduction by CH₄ on catalyst SOR10-III (Cu_{7.5}Ce_{2.5}) in the presence of oxygen, 7% water

FIGURE 26. NO Reduction by CH₄ on sulfated catalyst SOR08-I (Cu₂Ce₆) in the presence of oxygen, 7% water, (O₂/CH₄=5.25)

FIGURE 27. NO Reduction by C_3H_6 on catalyst SOR10-V (Cu_8Ce_2) in the Presence of Oxygen, 7% water

FIGURE 28. NO Reduction by C_3H_6 on Catalyst SOR08-I (Cu_2Ce_6) in the Presence of Oxygen, 7% water

III) Conclusions

The sulfation results show that in the 723 - 823 K temperature range, cerium oxide-copper oxide sorbents have specific sorbent capacities (mass of sulfur removed per unit mass of metal sorbent) and sulfation rates significantly larger than those of cerium oxide or copper oxide sorbents used alone. Best sulfation performance was shown by the sorbent containing 1:1 molar ratio of cerium and copper. Specific sulfur capacities decreased as the coverage of the support surface by the metal oxides approached monolayer coverage. At 823 K, specific sulfur capacities more than 20% over the theoretical value were obtained by sorbents with Ce/Cu molar ratios over five sulfation-regeneration cycles without significant loss of sulfation capacity.

The results presented above indicate that temperature of operation and the cerium/copper ratio of the sorbent should be optimized to achieve the best sulfation performance. Additionally, metal loading below monolayer coverage must be optimized due to the tradeoff between higher sulfation efficiency and larger sorbent amounts needed at lower loadings. These optimization procedures should also take the NO_x removal activity into consideration.

In the SCR experiments, NO conversions show a maximum with temperature due to the effect of temperature on the rates of reductant + NO and reductant + O_2 reactions, indicating that the reductant+NO reaction has a smaller activation energy, on the sulfated catalysts, and catalysts from sulfate salt precursors, as has been observed with the original catalysts. Cerium oxide and copper oxide by themselves are not good catalysts for the reduction of NO with methane, especially at low temperatures. Maximum NO conversion at the space velocities used in the experiments (13700/hr) is 9 % at 748 K with cerium oxide and about 8 % at 723 K for copper oxide.

Catalysts containing both copper and cerium oxides have better activities for NO reduction with methane, regardless of the Cu/Ce metal ratio. The maximum NO conversion at the space velocity used is 17 % obtained at 723 K.

The maximum NO conversions with propylene occur at lower temperatures on the catalyst containing only copper oxide compared to that with methane. Catalyst containing only cerium oxide exhibited almost constant NO conversion of about 6 % between 648 and 848 K with propylene.

The effect of Cu/Ce metal ratio on the NO conversion is more significant with propylene. The temperature for maximum NO conversion moves towards higher temperatures as the Cu/Ce ratio decreases. The maximum conversion obtained also changes with the Cu/Ce ratio. The catalyst with Cu/Ce =3 exhibited the highest NO conversion with propylene, which is about the same as that obtained with methane.

In order to explain some of these observations, temperature-programmed desorption and temperature-programmed reaction studies have to be performed. Under a recent funding obtained from DOE, we are in the process of conducting such experiments.

The behavior of the catalysts employed in this research may also be explained by a summary of some facts cited in literature: Ceria has super oxygen vacancy and mobility properties. Thus, it can stabilize copper in its active form. Redox phenomena is very important in this system. Active form of copper is CuO. It is very difficult to reduce ceria²⁰; it may only be reduced somewhere between Ce⁺⁴ and Ce⁺³. Therefore, it will prevent the reduction of copper under reducing conditions and its sulfidation in the presence of SO₂. These will affect selectivity in NO reduction and catalyst poisoning in the presence of SO₂, respectively. Also, oxygen vacancies in ceria may facilitate NO adsorption. Another important factor,

surface coverage, affects dispersion, particle size, and metal-support interactions. For example, coordination of copper (less oxygen) will be different in the bulk and on the surface. This will affect both sulfation and deNO_x properties.

Cu/Ce ratio affects the catalytic behavior due to electronic effects, coordination state, and metal-support interaction. Metal aluminates have higher bonding energies; therefore, they are highly selective for SCR of NO with methane. Metal aluminate suppresses reducibility of metal cations on the surface; therefore, reaction of hydrocarbon with oxygen is reduced.

In the absence of oxygen, NO dissociates on the surface (NO dissociation requires reduced surface); methane (and so does propylene more than propane) facilitate the removal of surface oxygen left behind. In the presence of oxygen, oxygen acts as a poison by competing with NO for the same active sites.

With respect to the selection of support, the following facts were considered: Alumina facilitates conversion of propylene to partially oxidized species. Alumina matrix suppresses the reducibility of metal cations not only by limiting the cluster size of transition metal oxide species, but also by changing the local environment of the cation (chemically inert tetrahedral cation having a strong interaction with alumina). Hence hydrocarbon combustion is reduced and desired SCR selectivity is achieved on M-Al₂O₃ catalysts¹⁹. Similar behavior was observed in the presence of sulfur dioxide.

During this research the following variables were observed to be the most important in the industrial application of the SCR process and they should be optimized: Cu/Ce ratio; oxygen to HC ratio; extent of sulfation; dependence between NO/P ratio and oxygen %; metal loading.

IV. Additional Activities:

Following activities were also undertaken during the project period:

1. Several undergraduate students (Estelle Rutledge, John McHugh, Courtney Amritt, Judith Cothorn, Franklyn Julien, Burnitta Johnson, Amy Bayer Gay, Taikelia Battle, Gerald Reed, John Davis, and Pamela Perkins) were hired and trained to use the research equipment in the laboratory. Some of them participated in the construction of the SCR experimental setup. They were involved in the data acquisition and evaluation.
2. **Publications:**
 1. Akyurtlu, J. F. and Akyurtlu, A., "Behavior of Ceria-Copper Oxide Sorbents under Sulfation Conditions", **Chem. Eng. Sci.** **54**, 2991-2997 (1999).
3. **Presentations:**
 1. "Behavior of Supported CuO/CeO₂ Sorbents under Sulfation Conditions", presented at the ISCRE 15 Conference held at Newport Beach, CA, on September 13-16, 1998,
 2. "Supported CuO/CeO₂ Sorbents for Gas Cleaning in Power Generation Systems", presented at the 15th Annual International Pittsburgh Coal Conference held at Pittsburgh, PA on September 14-18, 1998.
 3. "Behavior of Supported Ceria/CuO Sorbents under Sulfation Conditions" presented at Session 62 of the 2nd World Congress on Environment to be held at Miami, FL in November 15-19, 1998.
 4. "Investigation of Supported Ceria-Copper Oxide Sorbents for the Removal of SO₂ and NO_x from Flue Gases" presented at the DOE 1999 Seventh Annual Historically Black Colleges and Universities and Other Minority Institutions, Miami, FL, March 16-18, 1999.

5. "Catalytic Reduction of Nitrogen Oxides by Methane over Supported Ceria-Copper Oxide Sorbents", poster presentation at the 16th North American Catalysis Society Meeting held at Boston, MA on May 30- June 4, 1999.
6. Akyurtlu, A., and Akyurtlu, J. F., "Investigation of Supported Ceria-Copper Oxide Sorbents for the Removal of SO_2 and NO_x from Flue Gases", presented at the DOE 1999 Seventh Annual HBCU and OMI Annual Symposium, Miami, FL, March 16-18, 1999.
7. Akyurtlu, A., and Akyurtlu, J. F., "Investigation of Mixed Metal Sorbent/Catalysts for the Simultaneous Removal of Sulfur and Nitrogen Oxides" presented at the DOE-UCR Contractors' Review Meeting, Pittsburgh, PA, June 1, 1999.
8. "Selective Catalytic Reduction of NO by Hydrocarbons on Supported Copper-Oxide-Cerium Oxide Catalysts", presented at the AIChE Spring 2000 Meeting, Atlanta, GA, March 5-9, 2000.
9. A presentation, entitled "Selective Catalytic Reduction of NO_x by Hydrocarbons on Supported Copper Oxide-Cerium Oxide Catalysts" was made by Ms. Amy Gay, an undergraduate research student, at the National Technical Association 72nd National Conference, Hampton, VA, on October 18-21, 2000.
10. "Selective Catalytic Reduction of Nitrogen Oxides over Supported Copper Oxide-Cerium oxide Catalysts", poster presentation at the 17th North American Catalysis Society Meeting held at Toronto, Canada on June 3- 8, 2001.

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