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

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

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DISCLAIMER

ABSTRACT

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 research 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 objective of this research is 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 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, but indicated low selectivity when methane was used as a reductant. The catalyst containing equimolar amounts of cerium and copper is not active for NO reduction by CH_4 at low temperatures and is not selective at high temperatures. In the reduction of NO with NH_3, the conversion passes through a maximum at 573 K.

Since propylene is known to be a more active and selective reductant for NO with other SCR catalysts, in this reporting period we evaluated the performance of Cu-Ce catalysts for SCR of NO with propylene. Although propylene is very active in the absence of oxygen, the NO conversions obtained in wet oxygen-containing gases was limited to about 12 % for the space velocities employed in this research (about 46,000/hr). This was due to the low selectivity at high temperatures and low activity at low temperatures. In fact, the NO conversion passes through a maximum around 730 K. It was found that the presence of water vapor decreases the maximum conversion that can be obtained, and that up to a Cu/Ce ratio of 4, increasing Cu/Ce ratio increases the NO conversion. Although the catalyst with Cu/Ce ratio of 4 exhibited some loss of activity upon prolonged use, this observation was not yet confirmed for other catalysts.

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WORK DONE

Since our previous studies showed the Cu-Ce catalysts to be non-selective for NO reduction with methane in the presence of oxygen, in this period, the main focus was on the SCR studies with selected catalyst samples at different temperatures and using propylene as the reductant. Since high activity at temperatures below 700 K would be a good indication of selectivity, first the catalytic activities of some selected catalysts for NO reduction with propylene were evaluated at different temperatures in the absence of oxygen. In the subsequent runs, the effects of oxygen and SO_2 were investigated.

I) Experimental

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

Experimental variables in a standard SCR experiment with propylene:

temperature = 473 - 773 K

Propylene/NO ratio = 0.5, 1.0

concentration of O_2 = 0, 1.5 %

concentration of H_2O = 0, 7 %

concentration of SO_2 = 0, 3000 ppm

total gas flow rate = 750 cc/min

catalyst amount = 1, 2 g

A typical reactant gas composition was 650-900 ppm NO, which contains a maximum of 5 ppm NO_2, 1.5% O_2, 7% H_2O, propylene (propylene/NO_x = 1), balance He.

Gas samples were analyzed using a Varian 3400 Gas Chromatograph for CO, CO_2, N_2 , O_2

(with TCD detector, propylene (with FID detector) and Thermo Environmental Instruments Model 42H Chemiluminescence NO- NO_2- NO_x analyzer for NO and NO_2. In the presence of a reductant, the high temperature (923 K) converter in the instrument led to side reactions and gave erroneous NO_2 and NO_x readings. To overcome this shortcoming a low temperature (623 K) Mo converter was purchased. With this converter reliable NO_2 measurements could be made.

II) Results and Discussion

Figure 1 presents the results of the NO reduction experiments with wet gas feed containing no oxygen and sulfur dioxide. It can be seen 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. Also it can be seen that decreasing the Cu to Ce ratio below 4 decreased the activity. Based on these results, catalysts Cu4Ce1 and Cu3Ce1 were selected for further studies with gases containing oxygen.

Figure 2 shows the NO conversions obtained in gases containing 1.5 % oxygen with the selected catalysts. Maximum NO conversions were obtained around 730 – 740 K, and this conversion was about 12.5 % for Cu4Ce1 and about 10.5 % for Cu3Ce1.

From Figure 3 it can be seen that the low temperature conversion was significantly higher in dry gases. With the Cu4Ce1 catalyst, the maximum conversion was about 21 % and occurred at a lower temperature, 700 K.

Both with and without oxygen, addition of 3000 ppm SO_2 almost completely and irreversibly poisoned the Cu4Ce1 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. Therefore it is planned to test the Ce3Cu1 catalyst and partially sulfated Cu4Ce1 and Cu3Ce1 catalysts for their low temperature activity and sulfur resistance. Unfortunately, our NO-NO_x analyzer's ozone generator malfunctioned and these tests could not be completed. At the present we are waiting for the replacement part to arrive.

Figure 1. Effect of Space Velocity on NO Reduction with Propylene for Various Catalyst Samples. Wet gases without oxygen.

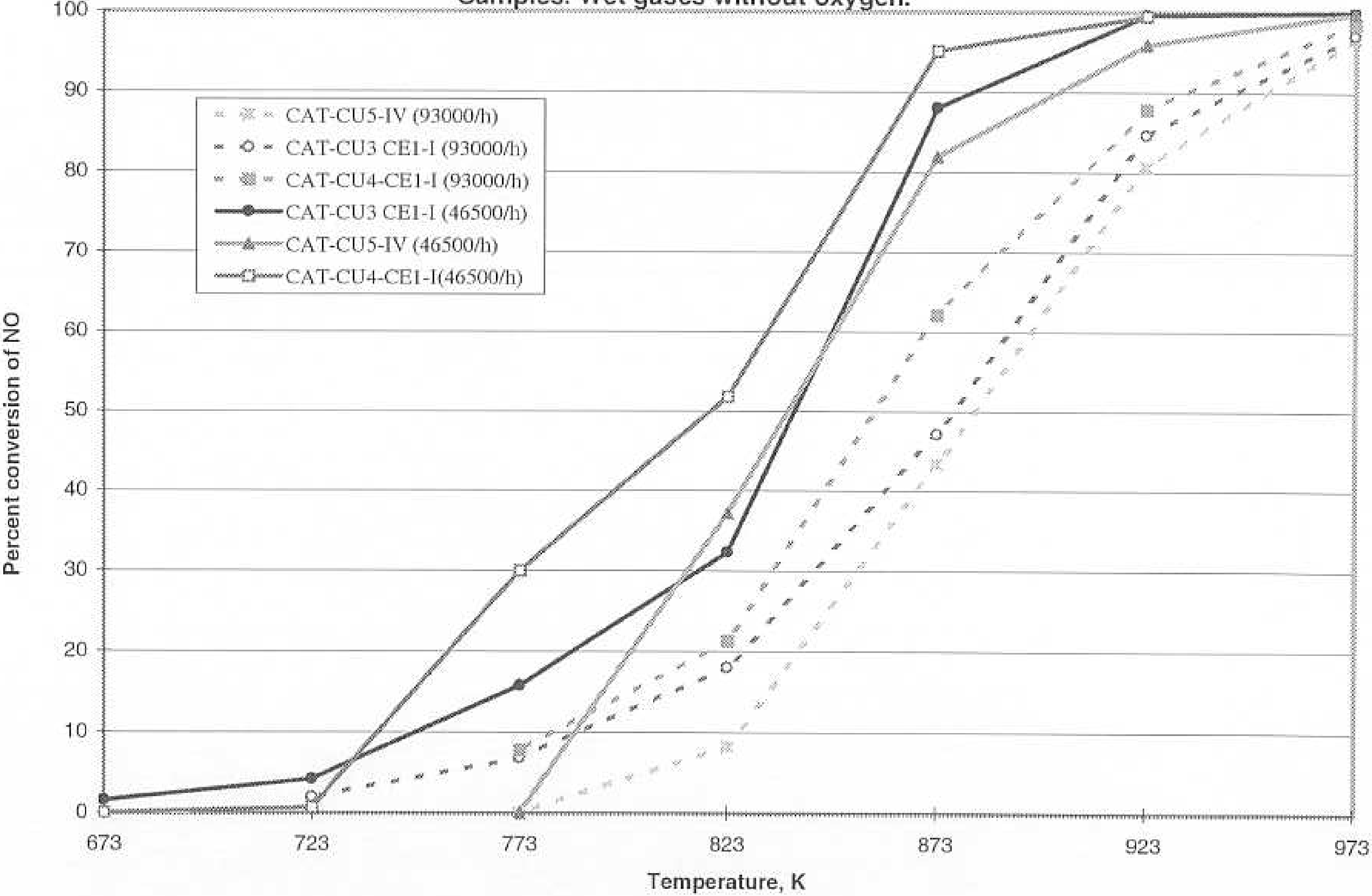


Figure 2. Effect of Temperature on NO Reduction with Propylene. Wet gas with 1.5 % oxygen

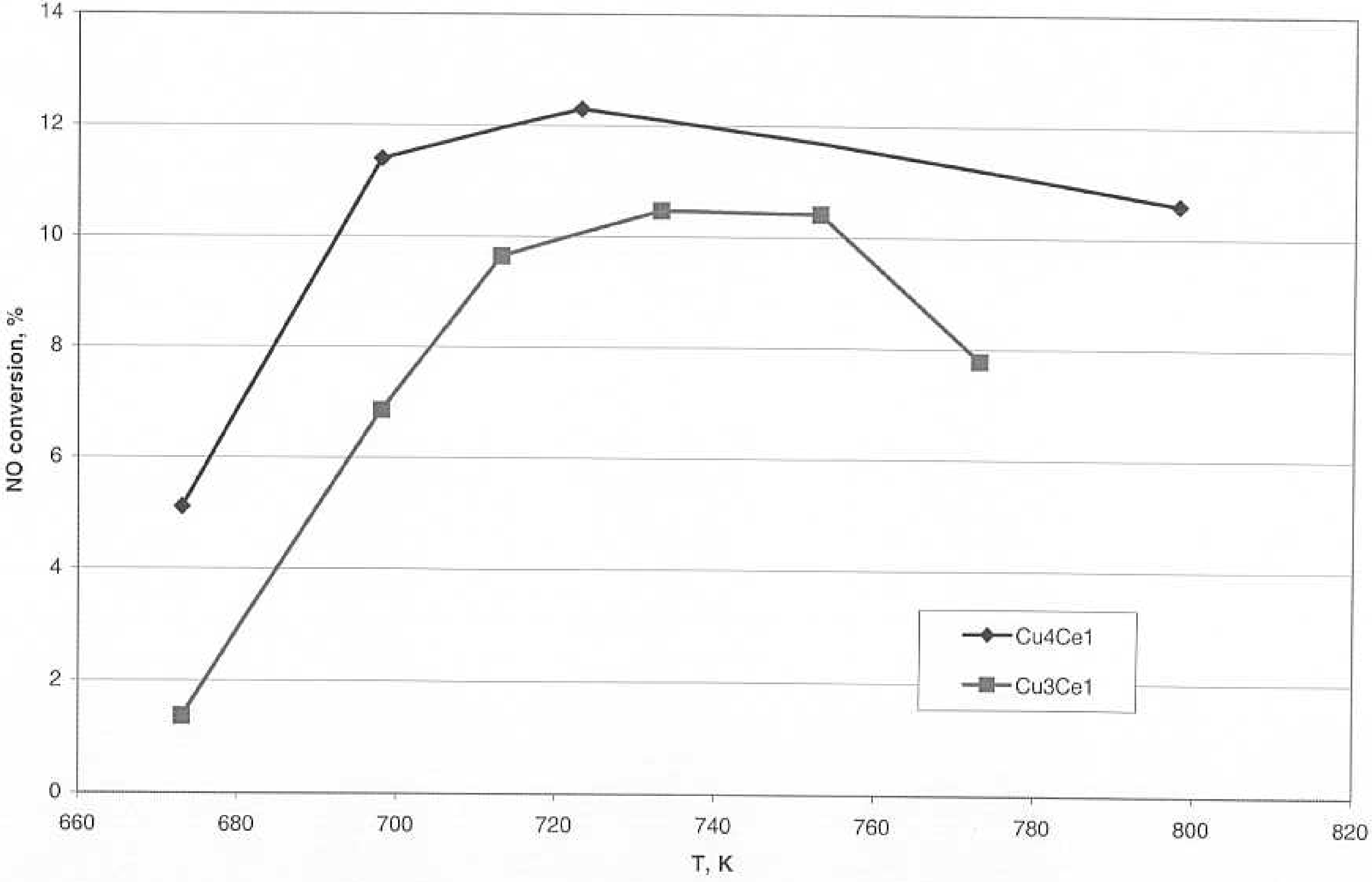
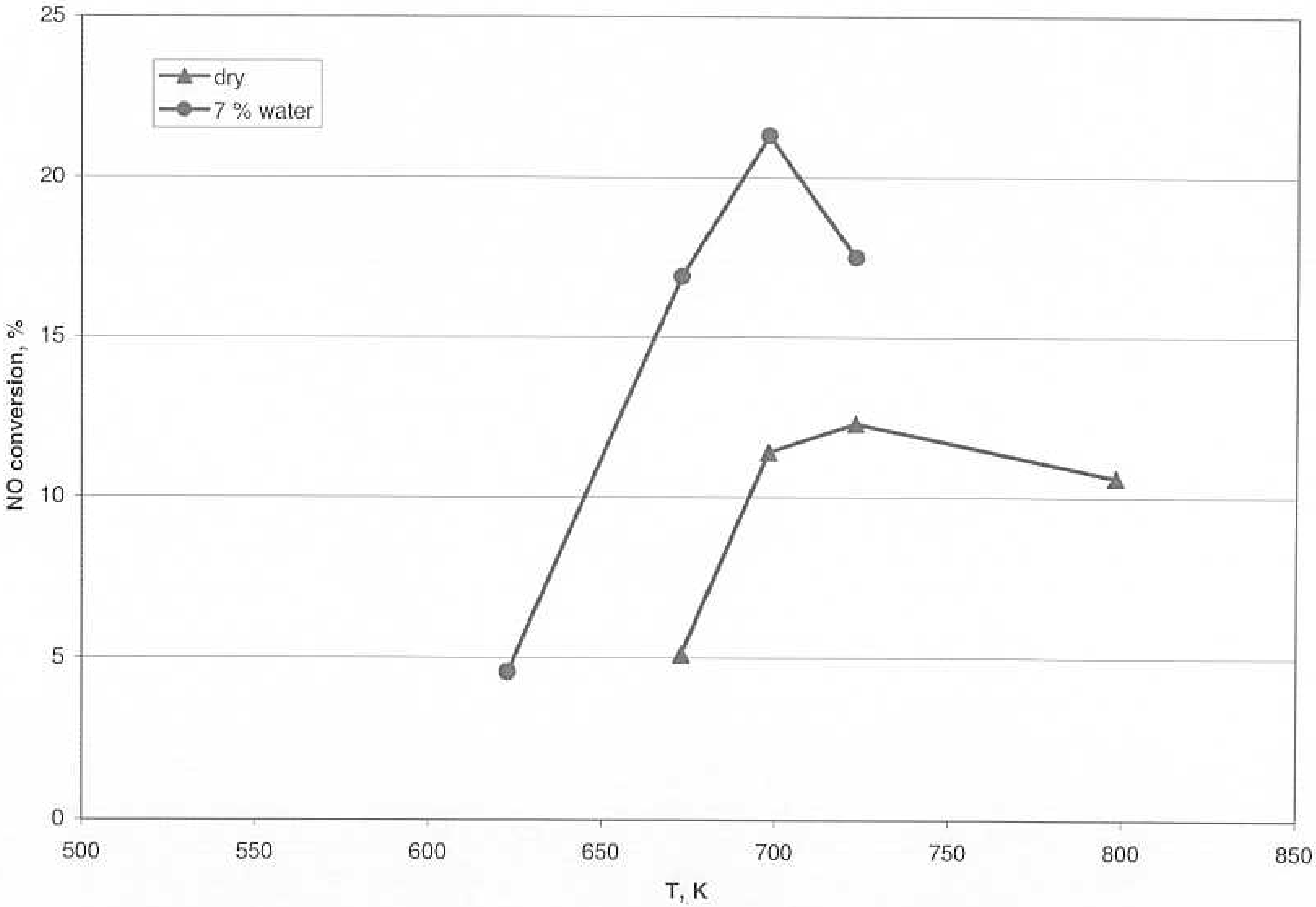


Figure 3. Effect of water on NO Reduction with Propylene. Catalyst Cu4Ce1. With 1.5 % oxygen



III) Additional Activities

Publication

1. Akyurtlu, J.F., and Akyurtlu, A., "Behavior of Ceria-Copper Oxide Sorbents under Sulfation Conditions", accepted for publication in **Chemical Engineering Science 54**, pp. 2991-2997, 1999.

Presentations:

1. Akyurtlu, J. F., and Akyurtlu, "Catalytic Reduction of Nitrogen Oxides Over Supported Ceria-Copper Sorbents", presented at the 16th North American Meeting of the Catalysis Society, Boston, MA, May 30-June 4, 1999.
2. 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.
3. 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.

FUTURE PLANS

In the next six months, it is planned:

1. to complete the SCR studies with propylene using the catalysts that might be more resistant to sulfur poisoning.
1. to complete the modeling of sulfation reaction on mixed metal oxides;
2. to investigate the regeneration of sorbent with CO and the possibility of elemental sulfur production;
3. to evaluate all the data;
4. to write the final report.

REFERENCES

1. **Akyurtlu, J. F., and Akyurtlu, A. (1995),** □Investigation of Combined SO_2/NO_x Removal by Ceria Sorbents", Paper presented at the *Eleventh Annual Coal Preparation, Utilization,*

and Environmental Control Contractors Conference, Pittsburgh, PA July 12-14.

2. **Centi, G., Passarini, N., Perathoner, S., and Riva, A. (1992),** "Combined DeSO_2/DeNO_x Reactions on a Copper on Alumina Sorbent/Catalyst-1. Mechanism of SO_2 Oxidation-Adsorption", *Industrial and Engineering Chemistry Research,* **31**, 1947-1955.