

Report Title: **DEVELOPMENT OF IMPROVED CATALYSTS FOR THE SELECTIVE
CATALYTIC REDUCTION OF NITROGEN OXIDES WITH HYDROCARBONS**

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ABSTRACT

Significant work has been done by the investigators on the cerium oxide-copper oxide based sorbent/catalysts for the combined removal of sulfur and nitrogen oxides from the flue gases of stationary sources. A relatively wide temperature window was established for the use of alumina-supported cerium oxide-copper oxide mixtures as regenerable sorbents for SO₂ removal. Preliminary evaluation of these sorbents as catalysts for the selective reduction of NO_x gave promising results with ammonia, but indicated low selectivity when methane was used as the reductant. Since the replacement of ammonia by another reductant is commercially very attractive, in this project, four research components will be undertaken.

The investigation of the reaction mechanism, the first component, will help in the selection of promoters to improve the catalytic activity and selectivity of the sorbents in the SCR with methane. This will result in new catalyst formulations (second component). If this research is successful, the combined SO₂-NO_x removal process based on alumina-supported copper oxide-ceria sorbent/catalysts will become very attractive for commercial applications. The objective of the third component of the project is to develop an alternative SCR process using another inexpensive fuel, residual fuel oil, instead of natural gas. This innovative proposal is based on very scant evidence concerning the good performance of coked catalysts in the selective reduction of NO and if proven to work the process will certainly be commercially viable. The fourth component of the project involves our industrial partner TDA Research, and the objective is to evaluate long- term stability and durability of the prepared sorbent/catalysts.

In the first year of the project, the catalysts were investigated by the temperature-programmed reduction (TPR) technique. The results from TPR indicated that the interaction with support appears to promote reduction at lower temperatures. Copper oxide in excess of monolayer coverage reduces at temperatures close to the reduction temperature of the unsupported copper oxide. Increased dispersion increases the support effect. Low activity of ceria in NO reduction may be due to its resistance to reduction at low temperatures.

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EXECUTIVE SUMMARY

Significant work has been done by the investigators on the cerium oxide-copper oxide based sorbent/catalysts for the combined removal of sulfur and nitrogen oxides from the flue gases of stationary sources. A relatively wide temperature window was established for the use of alumina-supported cerium oxide-copper oxide mixtures as regenerable sorbents for SO₂ removal. Preliminary evaluation of these sorbents as catalysts for the selective reduction of NO_x gave promising results with ammonia, but indicated low selectivity when methane was used as the reductant. Since the replacement of ammonia by another reductant is commercially very attractive, in this project, four research components will be undertaken:

- Investigation of the adsorption-reaction mechanism for the reduction of NO_x by methane using temperature programmed desorption and temperature programmed reaction studies.
- Improvement of the activity and selectivity of alumina supported cerium oxide-copper oxide-based sorbent catalysts for the reduction of NO_x by methane by the addition of promoters to enhance NO chemisorption, NO oxidation, intermediate stabilization, or methane activation. Alternative catalyst preparation methods will also be tried to enhance metal aluminate formation over the formation of oxide crystals.
- Investigation of the possibility of using inexpensive and widely available residual fuel oils as an alternate reductant to replace ammonia in the SCR reaction.
- Long term testing of the sorbent catalysts in a pilot size setup by TDA Research, our industrial partner.

The investigation of the reaction mechanism will help in the selection of promoters to improve the catalytic activity and selectivity of the sorbents in the SCR with methane. If this research is successful, the combined SO₂-NO_x removal process based on alumina-supported copper oxide-ceria sorbent/catalysts will become very attractive for commercial applications. The objective of the third component of the project is to develop an alternative SCR process using another inexpensive fuel, residual fuel oil, instead of natural gas. This innovative proposal is based on very scant evidence concerning the good performance of coked catalysts in the selective reduction of NO and if proven to work the process will certainly be commercially viable. The fourth component of the project involves our industrial partner TDA Research, and the objective is to evaluate long- term stability and durability of the prepared sorbent/catalysts.

In the first year of the project, investigation of the reduction mechanism of the catalysts used for the reduction of NO_x by a reductant (methane or propylene) using temperature-programmed reduction (TPR) was undertaken. This is the first step in the investigation of the adsorption-reaction mechanism on the catalysts being studied. The conclusions drawn from these TPR experiments can be summarized as follows:

Interaction with support appears to promote reduction at lower temperatures. Copper oxide in excess of monolayer coverage reduces at temperatures close to the reduction temperature of the unsupported copper oxide. Increased dispersion increases the support effect. Low activity of ceria in NO reduction may be due to its resistance to reduction at low temperatures.

WORK DONE

I. Background Information

The sorbents (Table 1) consisting of cerium oxide and copper oxide impregnated on alumina were prepared and characterized during a previous research project funded by DOE (DE-FG22-96PC96216). Their sulfation performance was 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.

The 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. In the reduction of NO with NH_3 , the conversion passes through a maximum at 573 K. Selective catalytic reduction studies with methane indicated that NO conversions between 10% and 17% could be obtained in the temperature range 648-748 K on catalysts containing both copper and cerium oxides for the space velocity used in the experiments (13700/hr).

Since propylene is known to be a more active and selective reductant for NO with other SCR

catalysts and since hydrocarbons are much more desirable reductants for NO removal, the performance of Cu-Ce catalysts for SCR of NO with propylene was also investigated. Although propylene was found to be very active in the absence of oxygen, the NO conversions obtained in wet oxygen-containing gases was limited to the same range observed using methane. With propylene, the temperature for maximum NO conversion decreased as the Cu/Ce ratio increased. Maximum conversion obtained was 17.5 % at 713 K on the catalyst with Cu/Ce=3 (Cu_{7.5}Ce_{2.5}). For Cu₈Ce₂ and Cu₂Ce₆ catalysts, the NO conversions obtained in wet oxygen-containing gases were limited to about 12.5% and 10.5% respectively, for the space velocities employed in this research (about 13,700/hour). This was due to low selectivity at high temperatures and low activity at low temperatures. In fact, the NO conversion passes through a maximum at around 730 K and 740 K for Cu₈Ce₂ and Cu₂Ce₆ catalysts, respectively. It was observed that water has a negative effect on NO conversion for Cu-Ce catalysts; NO conversion reduces from 21% in the absence of water to 12.5% in the presence of 7% water on Cu₈Ce₂ catalyst.

Table 1. Physical Properties of the Sorbent/Catalysts

Sorbent	Cerium Loading, mass %		Copper Loading, mass %		Surface Area, m ² /g
	Nominal	Actual	Nominal	Actual	
SOR10-II	5	4.58	5	5.54	122
SOR10-III	2.5	2.26	7.5	8.42	134
SOR10-IV	7.5	6.49	2.5	2.77	122
SOR10-V	2	1.90	8	8.76	130
SOR10-VI	0	0	10	10.36	105
SOR 10-VII	10		0	0	126

II. Experimental

In the first year of the project, investigation of the reduction mechanism of the catalysts used for the reduction of NO_x by a reductant (methane or propylene) using temperature-programmed reduction (TPR) was undertaken. This is the first step in the investigation of the adsorption-reaction mechanism on the catalysts being studied. For temperature-programmed experiments, a Micromeritics Pulse Chemisorb 2705 with TPD/TPR Option was used. This equipment was installed and calibrated. A mass spectrometer-gas chromatograph system (SATURN 2000MS/3800GC) from Varian was purchased for the identification of desorbed species and reaction products.

First, temperature-programmed reduction (TPR) studies were undertaken to investigate the effect of reduction and reoxidation on the catalysts used for selective catalytic reduction of NO. The main goal for TPR studies is to determine the number of reducible species on the catalyst and the temperature at which the reduction occurs. The conditions employed for reduction and reoxidation are summarized below:

Reduction:

Reductant: 6.96 % H_2 in Ar
Flow rate: 40 ml/min
Temperature range: 35°C – 900°C
Temperature ramp: 10 °C/min

Reoxidation Conditions

Oxidizer: 3.60 % O_2 in He
Flow rate: 40 ml/min
Oxidation temperature: 500°C and 100°C
Oxidation time: 1 hr

A typical TPR run is described below⁽¹⁾:

1. Insert a small amount of quartz in the right side of a clean and empty sample tube. Weigh the sample tube.
2. Pour approximately 50 mg catalyst sample into the sample tube.
3. Weigh the sample tube with the sample. Subtract the sample weight obtained in the first step to determine the initial sample weight.
4. Turn the 'PATH SELECT' knob on the TPR equipment to 'BYPASS' position.
5. Connect the sample tube to the analysis ports and tighten the fittings.
6. Install the thermocouple into the sample tube.
7. Adjust the gas carrier flow rate.
8. Turn the 'SAMPLE SELECT' knob to 'TEST' for the appropriate station to start the carrier gas flowing over the sample. Allow the detector baseline to stabilize. Place a Dewar flask filled with liquid nitrogen mixed with isopropyl alcohol around the loop of the cold trap to ensure that the moisture formed during reduction does not reach the detector.
9. Close the furnace around the sample tube. Set the furnace controls to ramp the furnace from room temperature to the desired temperature.
10. As the temperature increases, the catalyst is reduced and the amount of hydrogen consumed is displayed on the computer screen as a function of time.
11. After the TPR, reoxidize the catalyst and subject it to another cycle of TPR.

III. Results and Discussion

Figures 1- 9 present the results from the TPR experiments. They are developed from the temperature versus time and amount of hydrogen consumed versus time data from the TPR equipment. The following observations were made from those figures:

1. Copper oxide supported on alumina has two reduction peaks indicating the presence of two different types of copper oxide, appearing at 518 and 563 K. This is due most probably to the transition state of the copper ion: Cu^{+2} Cu^{+1} Cu^0
2. Reoxidation at 773 K lowers the reduction temperatures of both oxides by about 50 K.
3. The copper oxide with the lower reduction temperature appears to be almost fully regenerated by reoxidation at 773 K, while the second oxide appears to be only partially regenerated at this temperature. Reoxidation of the reduced copper oxide at 373 K partially regenerates the oxide with the lower reduction temperature and its reduction at the second cycle occurs at 448 K. The second oxide does not form upon reoxidation at this temperature.
5. The alumina support and the catalyst with 10 % CeO_2 on alumina do not have any reduction peaks up to 1173 K.
6. Fresh catalyst containing 2.5 % copper oxide and 7.5% cerium oxide shows only the lower temperature reduction peak. Reoxidation of this catalyst lowers the reduction temperature by about 100 K. Reoxidation at 773 K regenerates some of the second oxide.
7. The catalyst containing 7.5 % copper oxide and 2.5% cerium oxide shows similar behavior to the 10% copper oxide on alumina both during the first reduction and the subsequent reoxidation/reduction cycle.

IV. CONCLUSIONS

Catalyst support, metal oxide loading, and the degree of dispersion of the metal oxide affect the reduction temperature of the metal oxide.

- Interaction with support appears to promote reduction at lower temperatures. Copper oxide in excess of monolayer coverage reduces at temperatures close to the reduction temperature of the unsupported copper oxide.
- Increased dispersion increases the support effect.
- Low activity of ceria in NO reduction may be due to its resistance to reduction at low temperatures.

V. Additional Activities

Vaughnery Ammons and Taikelia Battle were employed as undergraduate research students. They were trained in the laboratory to use the TPR/TPD equipment and the reactor setup for the SCR experiments. They have learnt how to use the gas chromatograph and the NO_x Chemiluminescence equipment.

FUTURE PLANS

During next year, it is planned:

1. to do TPD and TPR_xN experiments; and
2. to prepare the promoted catalysts.

BIBLIOGRAPHY

1. Pulse ChemiSorb 2705 Operator's Manual by Micromeritics

FIGURE 1. TPR OF ALUMINA SUPPORT

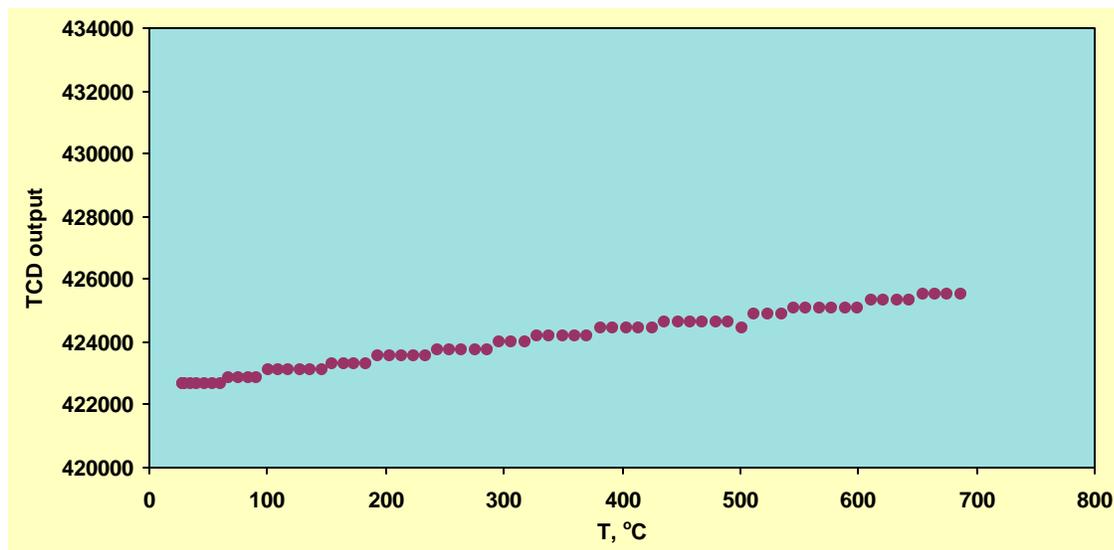


FIGURE 2. TPR OF 10% CuO on ALUMINA

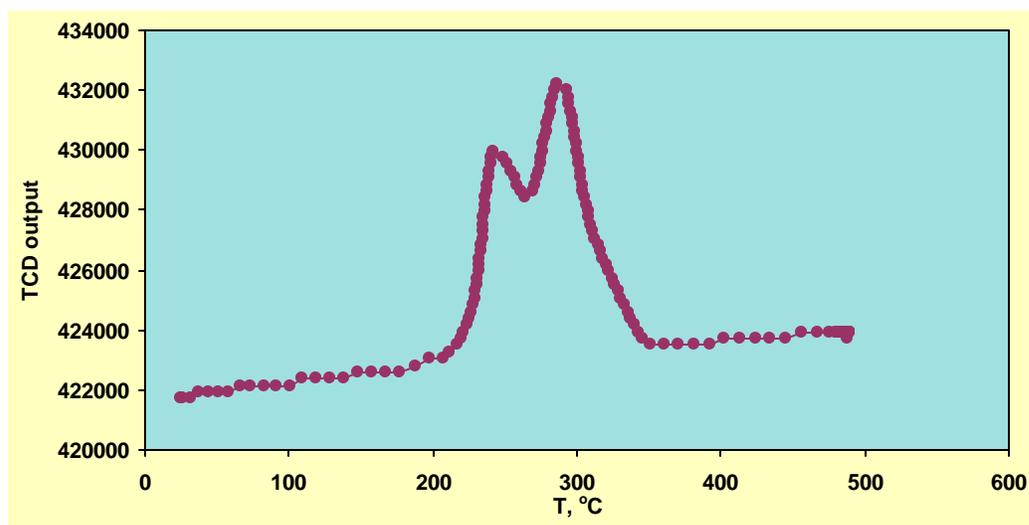


FIGURE 3. TPR OF 10% CeO₂ on ALUMINA

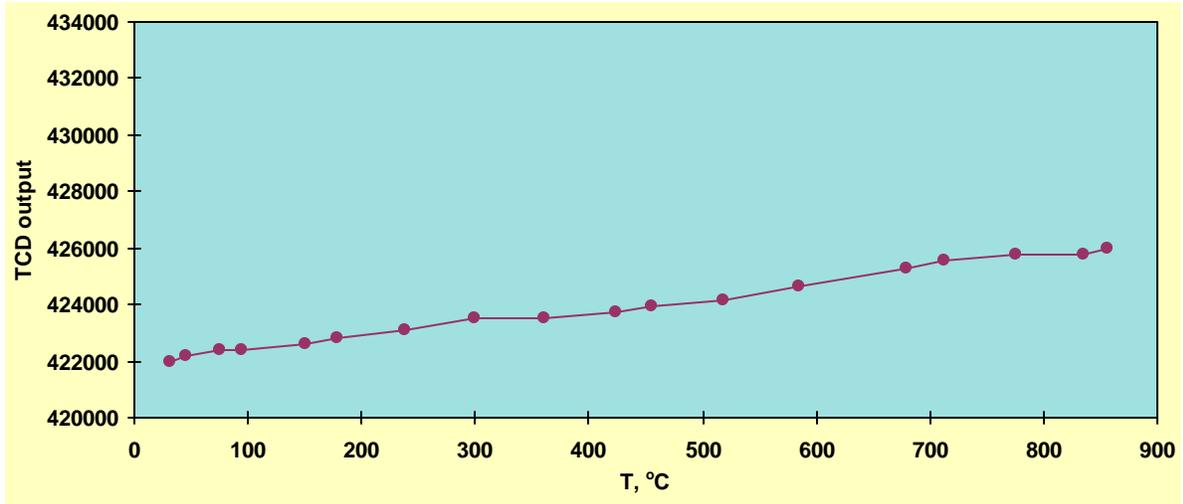


FIGURE 4. TPR OF 10% CuO on ALUMINA Reoxidized at 773 K

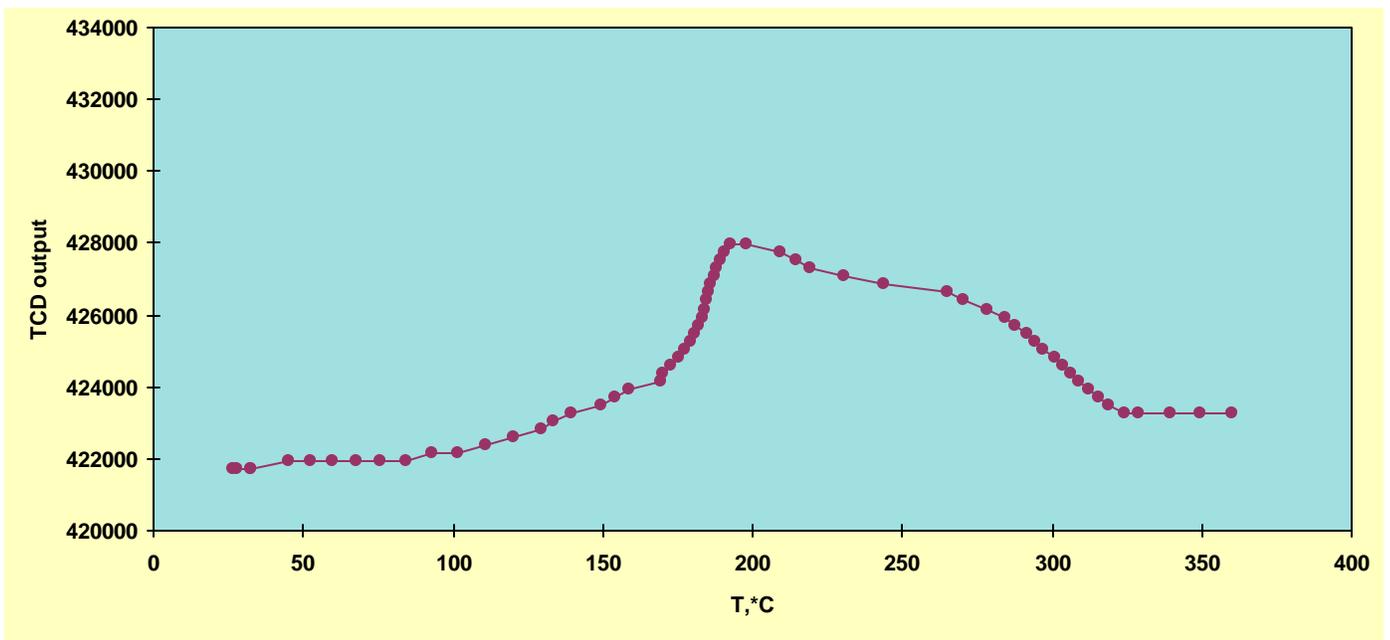


FIGURE 5. TPR OF 10% CuO on ALUMINA Reoxidized at 373 K

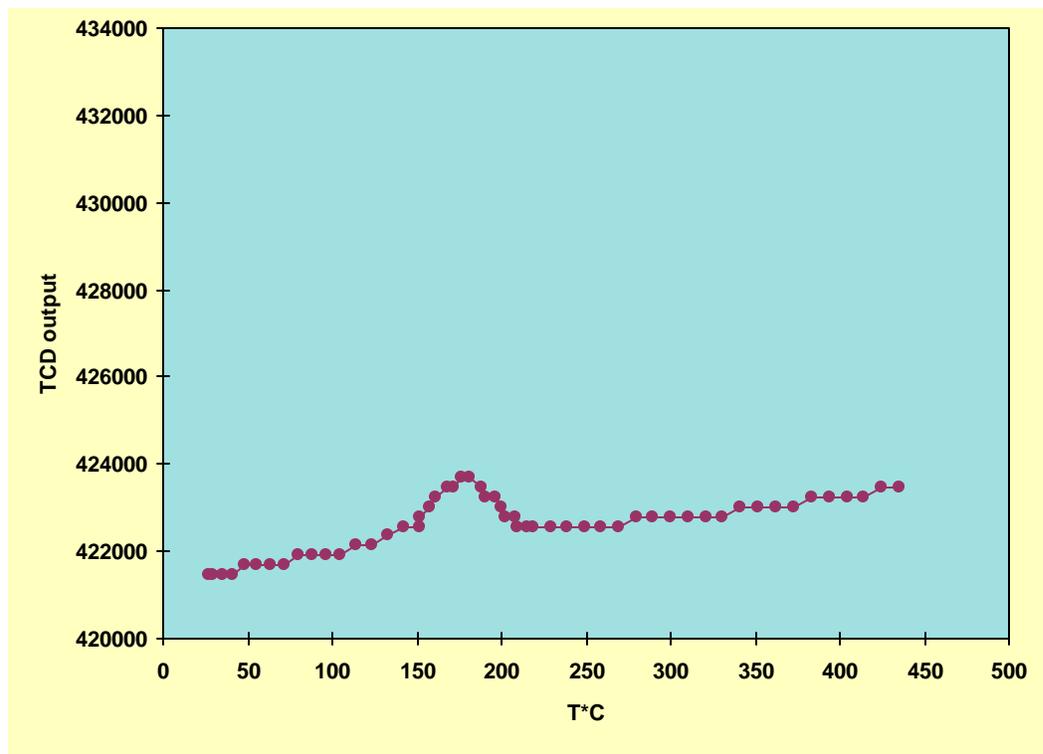


FIGURE 6. TPR OF 2.5% CuO and 7.5 % CeO₂ on ALUMINA

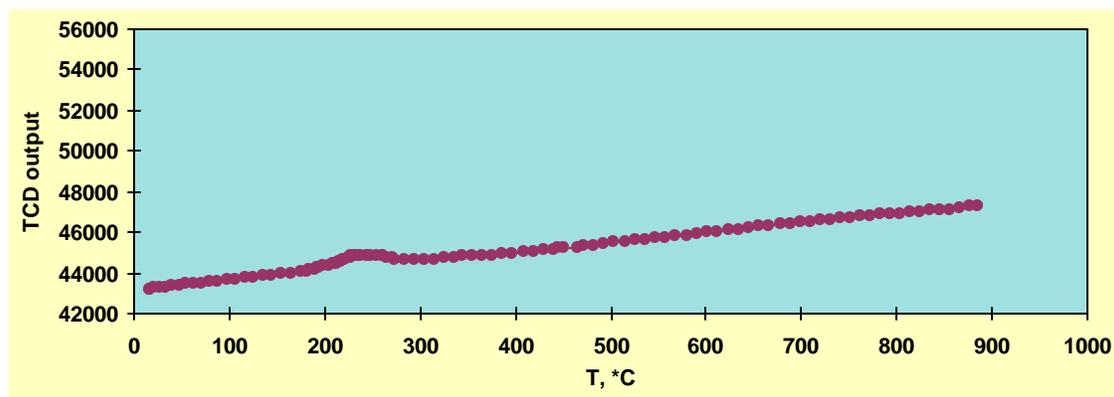


FIGURE 7. TPR OF 2.5% CuO and 7.5 % CeO₂ on ALUMINA Reoxidized at 773 K

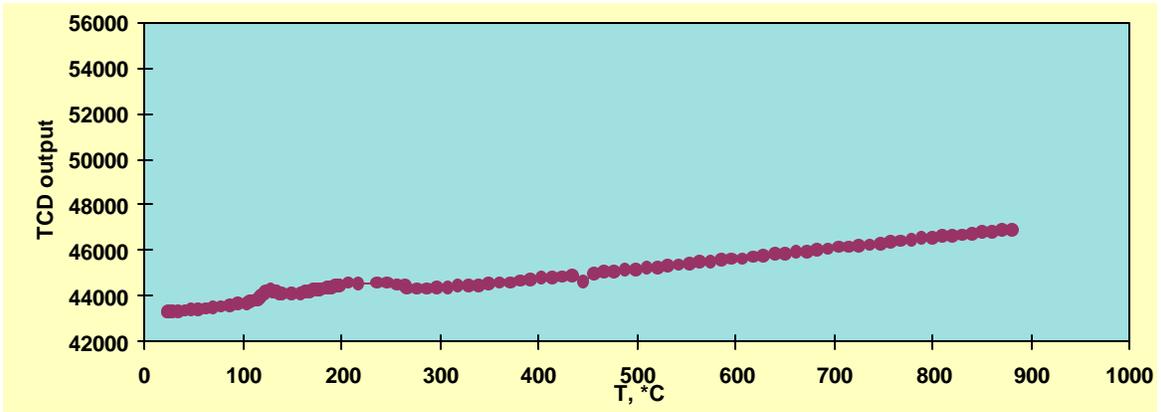


FIGURE 8. TPR OF 2.5% CuO and 7.5 % CeO₂ on ALUMINA Reoxidized at 373 K

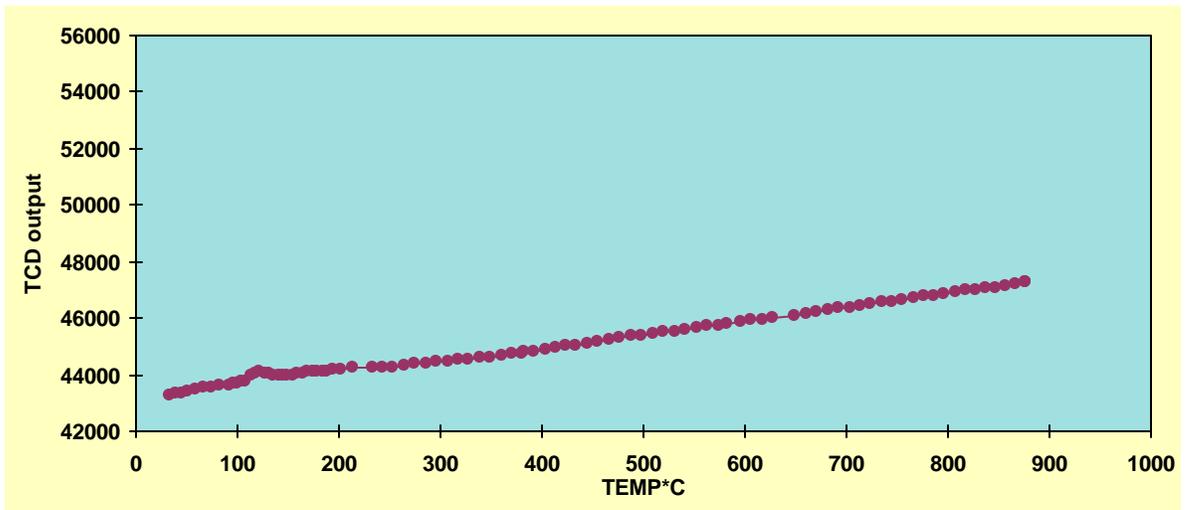


FIGURE 9. TPR OF 7.5% CuO and 2.5 % CeO₂ on ALUMINA

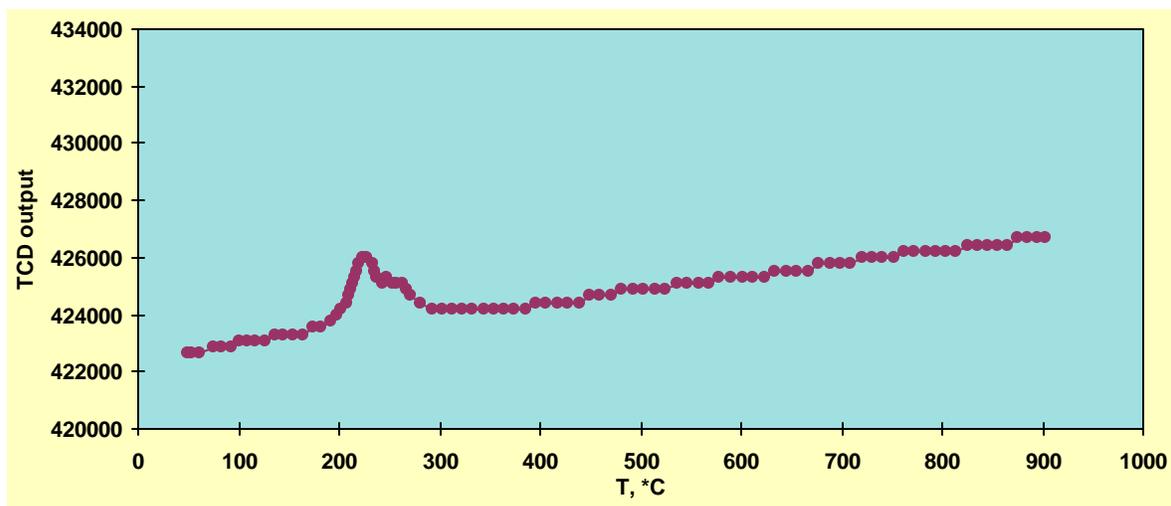


FIGURE 10. TPR OF 7.5% CuO and 2.5 % CeO₂ on ALUMINA Reoxidized at 773 K

