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PROPERTIES OF LANTHANIDE OXIDES AS SUPPORTS FOR TRANSITION METAL CATALYSTS. PROGRESS REPORT, MAY 1, 1985-APRIL 30, 1986

TEXAS A AND M UNIV., COLLEGE STATION.
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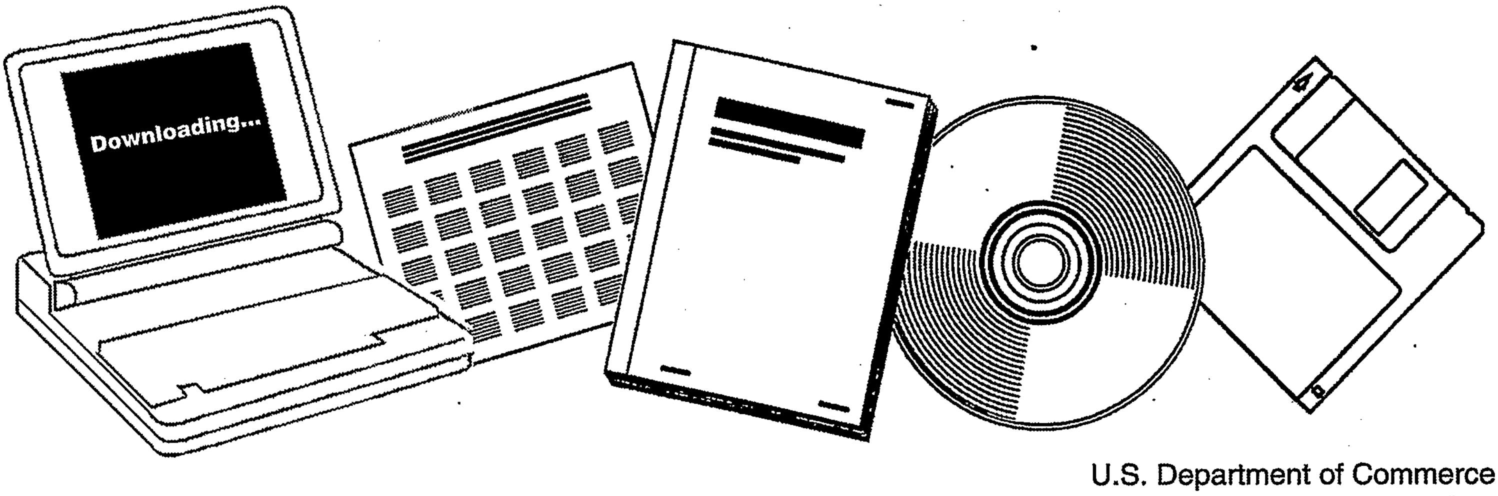

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PROPERTIES OF LANTHANIDE OXIDES AS SUPPORTS FOR TRANSITION METAL CATALYSTS

Progress Report for the Period
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Objective

The overall objective of this project is to determine the role played by oxidic support materials, particularly lanthanide oxides, in influencing the catalytic behaviors of dispersed transition metals. Our investigation is currently focused primarily on studies of support-induced effects on the chemical nature and reactivity of hydrocarbon-derived coke deposited on these catalysts.

Multi-Technique Catalyst Characterization System

An essential facet of this study is a thorough and systematic characterization of the reduction and surface behaviors of each of the catalysts being investigated. For this reason, we have devoted a portion of our time during the past year to the design, construction, and testing of a multi-technique pulse/flow system, depicted schematically in Fig. 1. This extremely versatile system has the capabilities to perform quantitative measurements involving temperature-programmed reduction (TPR) and re-oxidation cycles, pulse reaction studies of coke deposition and subsequent reaction, dynamic chemisorption and temperature-programmed desorption (TPD) of a variety of adsorbates, as well as routine flow-type surface area experiments. Thus, extensive information about several important physical/chemical parameters can be obtained from a single sample of each catalyst.

The system is constructed entirely of stainless steel valves, fittings, and components, with the exception of the sample-containing reactor vessel, which is made of quartz to ensure inertness at the high temperatures employed. Low-volume, shear-type sampling and switching valves have been employed throughout to minimize system dead volume and pulse spreading. Several carrier and reactant gases are available, and each can be independently regulated by electronic mass flow controllers to ± 0.1 cm³/min. A variable-power temperature programmer/controller is used with a very low thermal mass furnace to provide highly reproducible linear temperature ramping over a wide range of rates. A heated-filament thermal conductivity detector (TCD), energized by a constant-voltage generator, is used, either separately or in conjunction with an auxiliary switchable gas chromatographic column, to monitor processes occurring in the reactor as a result of injected reactant pulses or temperature ramping. The detector is interfaced to an X-Y recorder, digital integrator, and microcomputer-based data acquisition system to enable subsequent data processing, storage, and display. An on-line bleed of the detector effluent into the inlet system of a quadrupole mass spectrometer provides continuous real-time chemical identification of consumed and emitted flow stream components.

TPR of Cobalt/Silica Catalysts

Our initial studies with this system during the past year have involved TPR characterization of various supported cobalt catalysts, materials which we have previously investigated extensively for carbon monoxide hydrogenation. All TPR experiments reported here were performed using a 5 mole% H_2/N_2 reductant stream at a total flow rate of 60 cm³/min and a pressure of 3 psig. The temperature program rate in all cases was 30°C/min, and typical catalyst sample sizes were 10 to 50 mg. The solid curve in Fig. 2 shows the initial reduction profile for a $Co(NO_3)_2/SiO_2$ catalyst containing 2 wt% cobalt. The dashed TPR profile in this Figure was obtained after re-oxidizing in O_2 at 500°C the sample resulting from the preceding experiment. Several features are apparent in these TPR curves that demonstrate the extensive information that is obtainable from measurements of this kind.

The intense peak at 230°C in the $Co(NO_3)_2/SiO_2$ profile is due to a combination of nitrate decomposition to CoO and/or Co_3O_4 (with concomitant release of NO_x) and direct reduction of the nitrate to metallic cobalt. The unaided TCD cannot be used to distinguish between released NO_x and consumed H_2 from the H_2/N_2 stream, since both phenomena give rise to a positive TPR peak. However, simultaneous monitoring of the event by mass spectrometry confirms that both consumption of H_2 and emission of NO occur and, in fact, that onset of thermal decomposition slightly precedes that of reduction. The much weaker peak at 270°C in Fig. 2 may be due to reduction/decomposition of small amounts of $Co(OH)_2$ that is almost certainly generated during impregnation of the support with the aqueous nitrate solution. Both of these peaks are absent from the TPR profile of the re-oxidized sample, an observation that is consistent with their assignment to reduction/decomposition of non-oxidic precursors.

The weak, but very broad peak having a maximum at about 370°C is ascribed to the partial reduction of Co_3O_4 that was either present in the original sample or, more likely, was generated by prior nitrate decomposition. Consistent with this interpretation, the re-oxidized sample also displayed this peak, although at a somewhat lower temperature (320°C), as did a Co_3O_4/SiO_2 sample (obtained by prior oxidation of $Co(NO_3)_2/SiO_2$ in air at 500°C), shown in Fig. 3. The final, broad peak in Fig. 2, having a maximum at about 670°C is probably due to the last stage of residual CoO reduction to metallic cobalt. This peak is present in approximately the same temperature range, although with varying relative intensity, in all three of the TPR profiles shown in Figs. 2 and 3.

The significance and potential usefulness of the type of information shown in Figs. 2 and 3 can be realized by correlating these TPR results with data that we have obtained previously for the catalytic and surface behaviors of dispersed cobalt. The x-ray photoelectron spectrum (XPS), for example, of a $Co(NO_3)_2/SiO_2$ sample that had been directly reduced in H_2 at 400° without prior high-temperature exposure to O_2 showed less than 10% of the surface cobalt to be completely reduced, with the remainder present as Co^{2+}. Although this XPS result was puzzling at the time it was originally observed, the recently-obtained TPR profile of such a sample (Fig. 2) indicates that complete reduction to zero-valent cobalt may only occur at a temperature greater than 600°C. By contrast, reduction in H_2 at 400°C of $Co(NO_3)_2/SiO_2$ that had first been converted into Co_3O_4/SiO_2 by exposure to air at 500°C resulted in a material whose XPS spectrum showed an intense Co° peak and almost complete absence of residual unreduced Co^{2+}. Again, the TPR curve for a sample treated in this manner (Fig. 3) is consistent with the XPS result and shows that reduction is virtually complete at less than 500°C.

In a broader sense, the TPR data in Figs. 2 and 3 suggest that direct reduction of $Co(NO_3)_2/SiO_2$ in H_2 results in a surface oxide layer that is considerably more difficult to reduce completely than when the nitrate is first decomposed into Co_3O_4 prior to reduction. Fragmentary results obtained for reduction of $Co(NO_3)_2$ dispersed on various other supports, including TiO_2, La_2O_3, Eu_2O_3, and CeO_2 indicate that this phenomenon is not limited to silica-supported cobalt, but is a more general feature of $Co(NO_3)_2$-derived catalysts. Such behavior, if generalized, would have a significant impact on the preparation and pretreatment of catalysts intended for reactions such as CO hydrogenation and methanation.

Publications

One publication, entitled "The Nature of Catalytic Sites on Lanthanum and Neodymium Oxides for Dehydration/Dehydrogenation of Ethanol," based on previous work on this project, has been accepted for publication in the Journal of Catalysis. Two other manuscripts, describing our XPS and TPR studies of cobalt catalyst reduction behaviors, are currently in preparation.

Personnel

The following graduate students, all doctoral candidates, are currently being supported by funding from this project:

William P. Addiego
Dale R. Palke
Christine A. Polansky

FIGURE 1

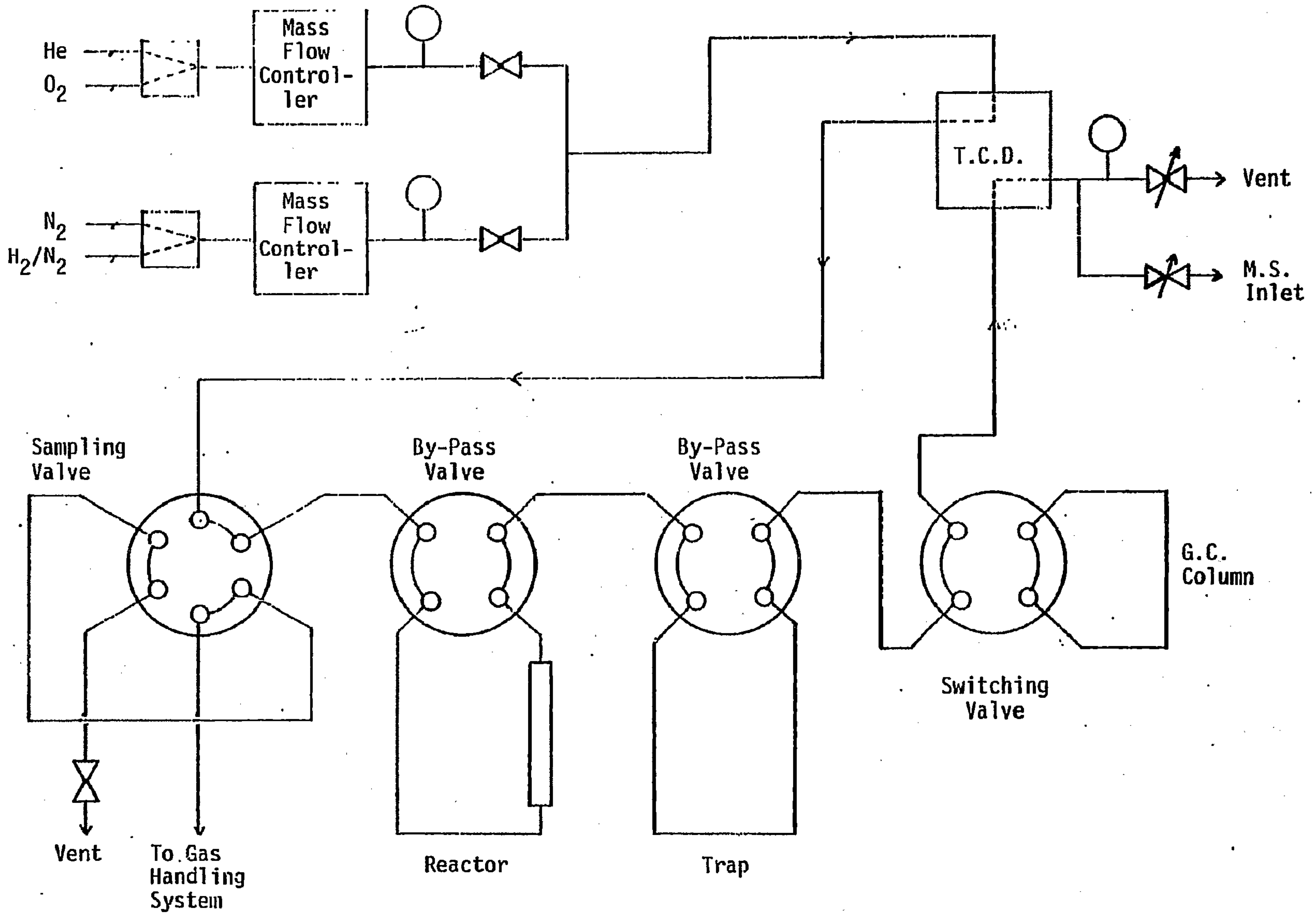

He
O_2
Mass Flow Control-ler
N_2
H_2/N_2
Mass Flow Control-ler
T.C.D.
Vent
M.S. Inlet
Sampling Valve
By-Pass Valve
By-Pass Valve
G.C. Column
Switching Valve
Vent
To Gas Handling System
Reactor
Trap

FIGURE 2

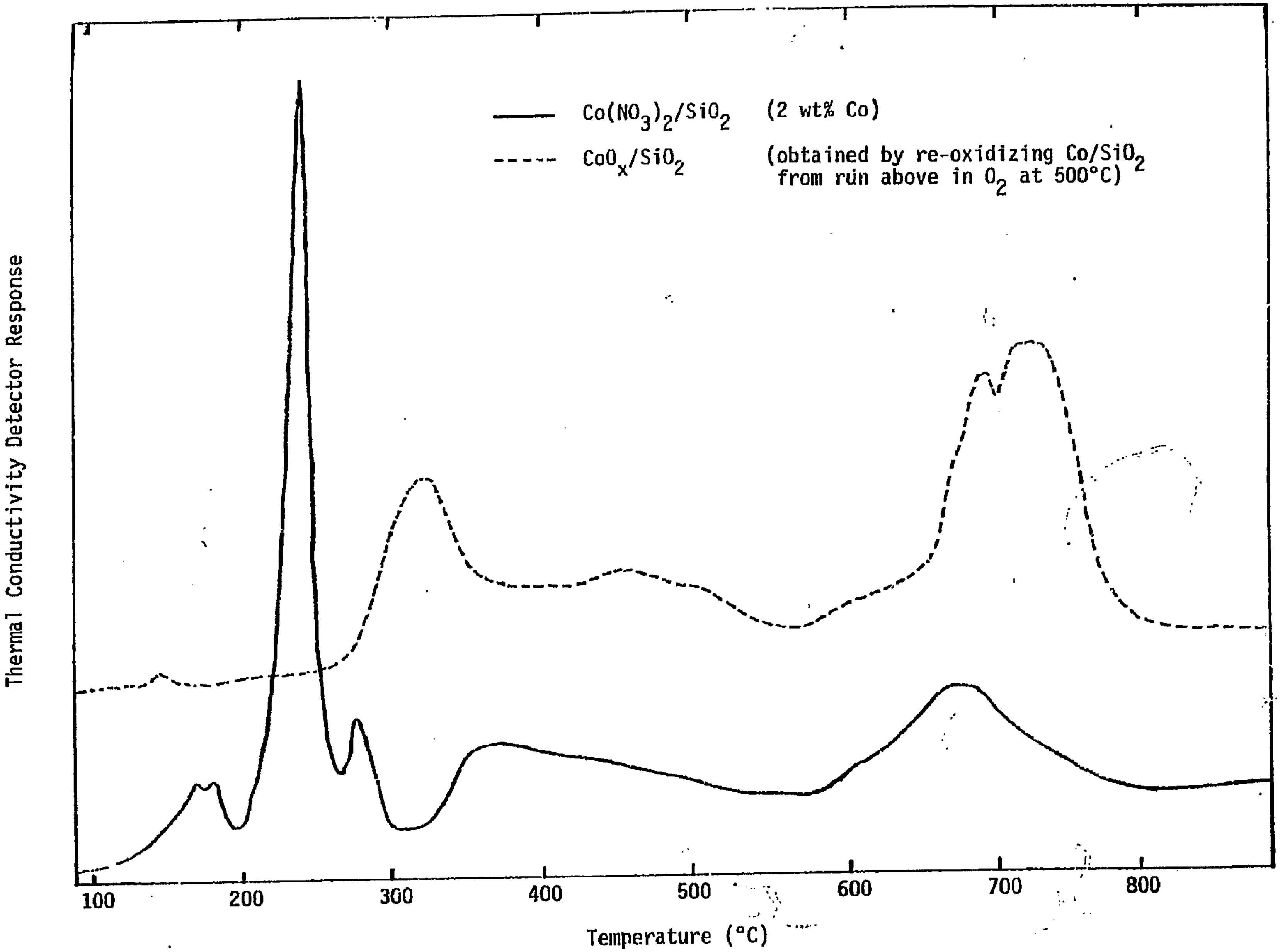
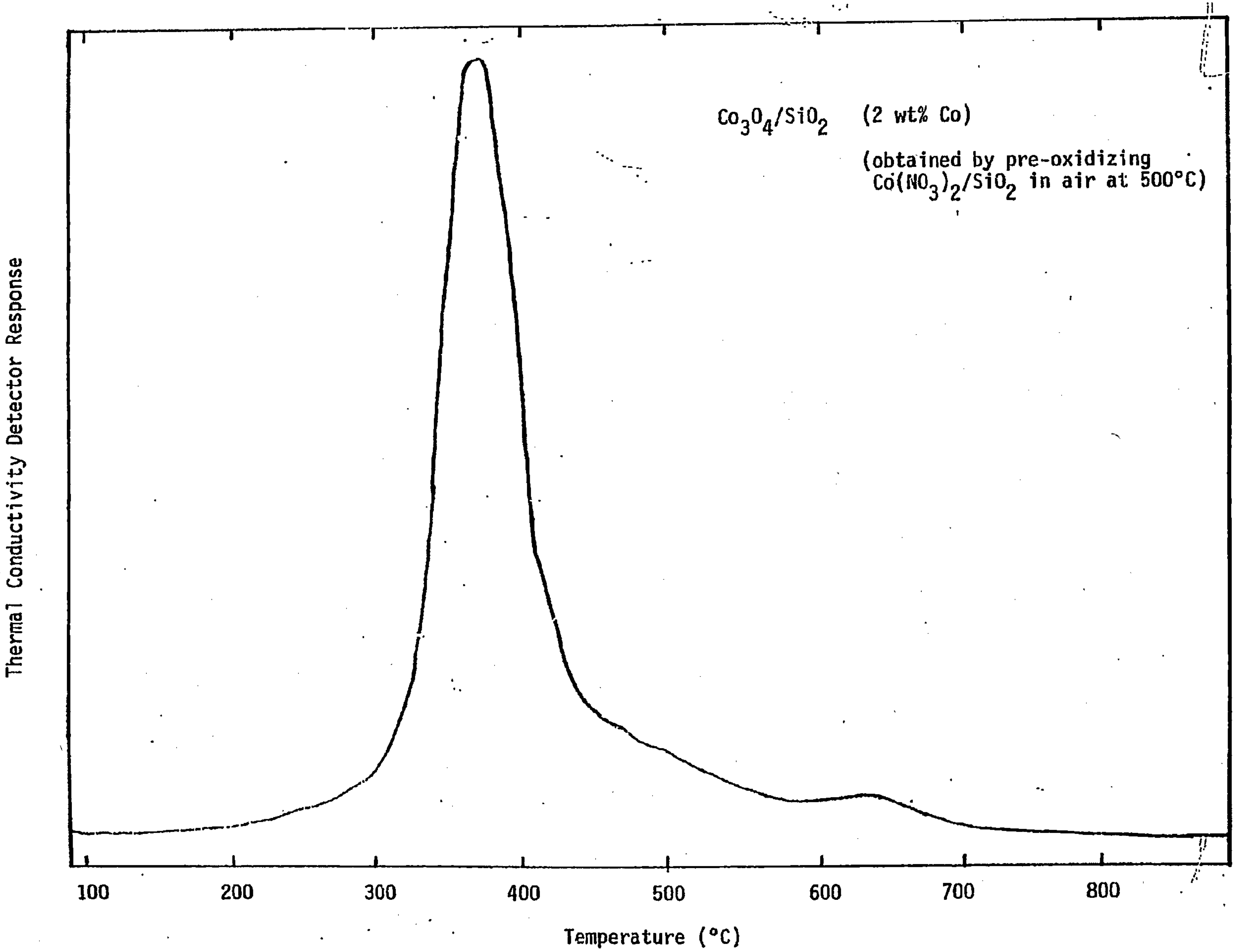

Co(NO$_3$)$_2$/SiO$_2$ (2 wt% Co)
CoO$_x$/SiO$_2$ (obtained by re-oxidizing Co/SiO$_2$ from run above in O$_2$ at 500°C)
Thermal Conductivity Detector Response
100
200
300
400
500
600
700
800
Temperature (°C)

FIGURE 3


Co_3O_4/SiO_2 (2 wt% Co)
(obtained by pre-oxidizing $Co(NO_3)_2/SiO_2$ in air at 500°C)
Thermal Conductivity Detector Response
100
200
300
400
500
600
700
800
Temperature (°C)