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## SUPERCONDUCTOR METAL OXIDE CATALYST IN A CHEMILUMINESCENCE CHROMATOGRAPHY DETECTOR

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### SUMMARY

The superconducting oxygen-deficient perovskite,  $\text{YBa}_2\text{Cu}_3\text{O}_7$ , was used to catalyze redox reactions between organic species and  $\text{NO}_2$  in a chromatography detector based upon chemiluminescence. The reactions were studied at catalyst temperatures ranging from  $200^\circ\text{C}$  to  $350^\circ\text{C}$  and at make-up gas flow-rates of 3.5–36.5 ml/min. By changing the flow-rate or the catalyst temperature, one can alter the sensitivity of analyte response in redox chemiluminescence and the selectivity ratios. Alcohols and alkenes responded the most strongly, with ethanol being detected at the level of 0.5 ng. Ammonia, acetaldehyde, acetone, methylethylketone, acetonitrile and nitromethane were also sensitively detected. Chromatographic analyses of oxygenates, e.g., methyl *tert.*-butyl ether or alcohols, in paraffinic matrices such as gasoline were demonstrated.

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### INTRODUCTION

Selective detectors for gas chromatography are widely used for the quantitative analysis of specific compounds that are present in complex matrices. A recent review of selective detectors<sup>1</sup> describes many that are currently in use and the range of compounds that can be detected selectively. Chemiluminescence offers many advantages upon which chromatography detectors can be based. Among the new detectors that are especially effective is the redox chemiluminescence detector, the selectivity of which depends on the post-column reaction of  $\text{NO}_2$  with eluted analytes over a heated gold catalyst to produce  $\text{NO}^{2-8}$ . The pulses of  $\text{NO}$  formed are subsequently detected downstream through the chemiluminescent reaction with ozone.

While gold is the catalyst that has shown the best selectivity for oxygenated compounds, other catalysts such as palladium may be employed to achieve differing degrees of selectivity<sup>7</sup>. We now report on the catalytic properties of a new catalyst that will be of particular value to chromatographers. The superconducting characteristics of the oxygen-deficient perovskite,  $\text{YBa}_2\text{Cu}_3\text{O}_7$ , and its oxygen-exchange properties are now well known<sup>9,10</sup>. Other perovskites have been studied for use in the catalytic oxidation of  $\text{CO}$  and hydrocarbons in auto exhaust, and as fuel cell components<sup>11</sup>.

Chauvin and Michel<sup>1,2</sup>, studied three perovskites and found that the greater the oxygen mobility in the structure, the greater is the catalytic activity of the perovskite for the oxidation of CO. Our experiments have now demonstrated that  $\text{YBa}_2\text{Cu}_3\text{O}_7$  is a strongly active catalyst in the redox chemiluminescence detector system, and that alcohols are particularly sensitively detected.

## EXPERIMENTAL

The chromatographic system used in these studies is shown in Fig. 1. The gas chromatograph was a Hewlett-Packard (Avondale, PA, U.S.A.) Model 5710A that was modified with a Grob-type split/splitless injection port<sup>1,3</sup>. Analytical separations were made with a 25 m  $\times$  0.32 mm I.D. fused-silica column from Hewlett-Packard with a 5% cross-linked phase of phenylmethylsilicone (0.52  $\mu\text{m}$  film thickness). The column was operated at a linear velocity of 21 cm/s of helium carrier gas.

At D in Fig. 1, the effluent from the column was mixed with  $\text{NO}_2$  in a heated, 2-mm I.D. quartz, "T" shaped catalyst chamber. The source (C) of  $\text{NO}_2$  was a permeation tube fabricated from fluorinated ethylene propylene (FEP) tubing (Galtek, Chaska, MN, U.S.A.), over which diluent helium was passed. Approximately 10 mg of the  $\text{YBa}_2\text{Cu}_3\text{O}_7$  catalyst was held in place by plugs of quartz wool at either end of the 3-mm long catalyst bed in the tube. The reduction of  $\text{NO}_2$  and oxidation of analyte occurs rapidly on the catalyst bed in the reaction zone, and the NO produced is detected downstream in the ozone reaction chamber (F) of a Model 207 redox chemiluminescence detector (Sievers Research, Boulder, CO, U.S.A.).

The flow of  $\text{NO}_2$  in helium was controlled by adjusting a needle valve (E) downstream of the catalyst zone and was measured with a flow meter (B) (Brooks Instrument, Hatfield, PA, U.S.A.) that had been previously calibrated. Flow-rates ranged from 3.5 to 36.5 ml/min when the helium head pressure was set at 4 p.s.i.g. The  $\text{NO}_2$  was research purity grade (Matheson, Secaucus, NJ, U.S.A.), and was purged with oxygen at approximately 0°C to oxidize any residual NO to  $\text{NO}_2$ , prior to filling a permeation device that was constructed from 2 mm I.D., 6 mm O.D. FEP. At room temperature the permeation device supplies a constant mass of  $\text{NO}_2$  per unit time that

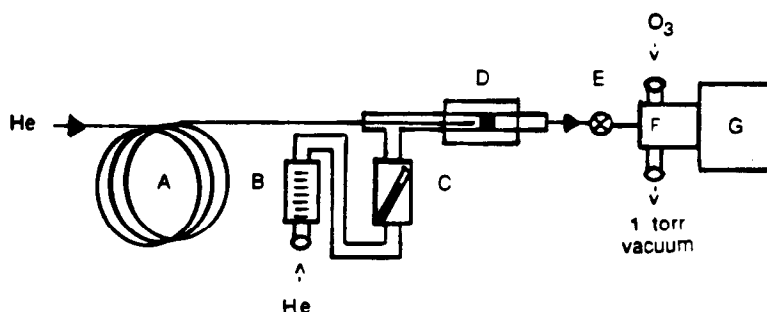


Fig.1. Experimental apparatus: (A) gas chromatography column, (B) flow meter to measure the rate of helium make-up gas flow over the  $\text{NO}_2$  permeation tube, (C)  $\text{NO}_2$  permeation tube, (D) reaction zone containing the catalyst bed in a quartz tube surrounded by a heater block, (E) needle valve to control the flow of make-up gas through the reaction zone, (F)  $\text{NO}-\text{O}_3$  chemiluminescence chamber, (G) photomultiplier tube and electronics of the Model 207 RCD.

yields a concentration of about 200 ppm when the flow of diluent gas is maintained at approximately 30 ml/min.

The helium used as NO<sub>2</sub> diluent and column carrier (U.S. Welding, Denver, CO, U.S.A.) was purified by scrubbing with Hopcalite (Mine Safety Appliances, Pittsburgh, PA, U.S.A.) to remove CO, R3-11 copper catalyst (Chemical Dynamics, South Plainsfield, NJ, U.S.A.) to remove oxygen, and molecular sieve 4A (Fisher Scientific, Fair Lawn, NJ, U.S.A.) to remove water.

The chemicals used in the test mixture were obtained from the following vendors: methyl *tert.*-butyl ether (MTBE) (97%), toluene (99 + %), and 1-octene (97%) were obtained from Aldrich (Milwaukee, WI, U.S.A.). Benzene (99%) and methanol (certified ACS Spectranalyzed grade) were obtained from Fisher Scientific, ethanol (absolute) from AAPER Alcohol and Chemical Co. (Shelbyville, KY, U.S.A.), *tert.*-butanol (analytical-reagent grade from Mallinckrodt (St. Louis, MO, U.S.A.), methylcyclohexane from J. T. Baker (Phillipsburgh, NJ, U.S.A.), octane from Eastman-Kodak (Rochester, NY, U.S.A. and isooctane (2,2,4-trimethylpentane) from EM Science (Gibbstown, NJ, U.S.A.). The benzene used as solvent in the dilutions of ethanol for detection limit studies was pesticide quality obtained from MCB (Norwood, OH, U.S.A.).

Additional studies of catalyst materials were performed with a system that allowed for continuous flow of NO<sub>2</sub> and/or an organic compound over the catalyst<sup>6</sup>. The products of reactions that occurred were monitored by mass spectrometry. High-purity grade helium (O<sub>2</sub> less than 5 ppm, v/v) was used as the diluent gas in these studies. The temperature of the catalyst was maintained with a modified oven control unit from a Hewlett-Packard Model 402 gas chromatograph. Downstream of the catalyst, a portion of the flow was diverted to a Hewlett-Packard Model 5980A mass spectrometer that had been modified to allow for direct introduction of the sample into the ion source. The remaining flow was sampled to determine NO concentrations by a Sievers Research Model 207 redox chemiluminescence detector.

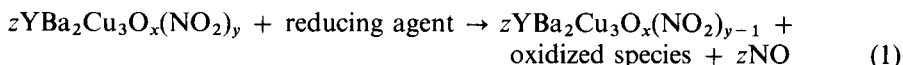
The chemicals used to synthesize the catalyst were 99.9% Y<sub>2</sub>O<sub>3</sub> (American Potash and Chemical Co., West Chicago, IL, U.S.A.), BaCO<sub>3</sub> (Mallinckrodt) and CuO (J. T. Baker). The superconductor catalyst was prepared by a solid-state reaction of powders of the compounds listed above using established techniques<sup>10</sup>. Presence of the superconducting phase was verified by observation of the Meissner effect, in which a sample of the material is repelled by a magnet at temperatures below the superconducting transition temperature. Analysis by X-ray diffraction indicated the presence of the superconducting, orthorhombic phase.

## RESULTS AND DISCUSSION

The catalytic reactions that occur in a redox chemiluminescence detector determine the selectivity of the detector; thus, studies of new catalysts are important for the development of new applications for this detector. Oxidation of CO and organic compounds on various perovskites has been investigated and reviewed<sup>11</sup>. Other mechanistic studies indicate that a two-step redox mechanism often plays a major role in the catalytic oxidation of compounds over perovskites<sup>14,15</sup>. In the first step, lattice or adsorbed oxygen is responsible for the catalytic oxidation. Regeneration of the oxygen vacancy occurs in the second step as the catalyst is reoxidized by molecular oxygen in the gas phase.

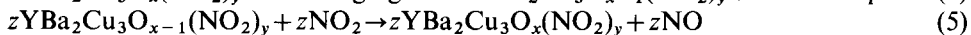
In our present system, our studies indicate that NO<sub>2</sub> can act as the oxidant that regenerates the oxidized lattice. When excess NO<sub>2</sub> is allowed to react with ethanol over this catalyst, oxidation occurs at a temperature identical to that at which it occurs in the absence of NO<sub>2</sub>. The yields and identities of product are also the same for NO<sub>2</sub> oxidation as for O<sub>2</sub> oxidation, except that substantial amounts of NO are also produced as the oxidation occurs. These results suggest that the superconducting perovskite may act catalytically in two different ways. In one way (reactions 1–3), the perovskite may promote the direct oxidation of analytes by lattice NO<sub>2</sub>, under similar conditions as employed for reaction with lattice oxygen. In the other (reactions 4–6), the redox reaction may occur directly with the oxide catalyst to form an oxygen vacancy which is then cyclically refilled in a second step by reaction with NO<sub>2</sub>. After exposure to NO<sub>2</sub> in the analytical system the catalyst is still superconducting, as evidenced by observation of the Meissner effect. However, the resulting material is different from YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub>, and has NO<sub>2</sub> incorporated into the lattice. Temperature-programmed desorption mass spectrometry experiments indicate that the stoichiometry of this material is YBa<sub>2</sub>Cu<sub>3</sub>O<sub>x</sub>(NO<sub>2</sub>)<sub>y</sub>, where  $x = 7.4 \pm 0.4$  and  $y = 1.3 \pm 0.2$  (ref. 16).

Reactions 1–3:



In these reactions  $z$  is determined by the extent of reduction in reaction 1. In reaction 1, the analyte eluting from the chromatographic column reacts directly with NO<sub>2</sub> at the catalyst surface and becomes oxidized, creating an NO<sub>2</sub> vacancy and generating NO which is measured by chemiluminescence (reaction 3). In reaction 2, NO<sub>2</sub> refills the vacancy.

In reactions 4–6, the catalyst acts as an oxidizing agent:



In reaction 4, the analyte reacts at the catalyst surface to form an oxygen vacancy, and becomes oxidized. In reaction 5 the oxygen vacancy is re-filled with oxygen by NO<sub>2</sub> reacting with the catalyst to form NO. Reaction 6 occurs outside the catalyst chamber in front of the photomultiplier tube (F in Fig. 1), where the NO formed by each analyte reacts with ozone to produce chromatographic peaks.

The size of each peak is related to the amount of the analyte, and the yield of O or NO<sub>2</sub> vacancies it created under the conditions in the catalyst chamber (D). Compounds that have been tested in this system and produce a relatively large response include methanol, ethanol, *tert.*-butanol, MTBE, 1-octene, toluene, ammonia, acetaldehyde, acetone, methylethylketone, cyclohexene, acetonitrile and nitromethane. Hydrogen and carbon monoxide produce weak responses in this system.

### *Chromatographic studies*

A mixture of the following composition (prepared by volumetric dilution) was studied to provide information about selectivity of response to various classes of compounds: methanol, 0.1%; ethanol, 0.1%; *tert.*-butanol, 0.1%; MTBE, 5.0%; benzene, 5.0%; isooctane (2,2,4-trimethylpentane), 73.7%; methylcyclohexane, 5.0%; 1-octene, 1.0%; toluene, 5.0%; and octane, 5.0%. These compounds are present in various commercially available gasolines. In a test program, either 10% ethanol or 8% MTBE is being added to gasolines in Colorado in order to evaluate the effect of these additives on reducing the ambient concentration of CO resulting from automobile exhaust, so a rapid method for checking the concentration of either of these is needed. Oxygenates in feedstocks also poison some catalysts, so the detection of alcohols in hydrocarbon matrices is important.

A systematic study was made of the effect of catalyst temperature and flow-rate through the catalyst on the detector response for each component in the mixture. Flow-rates through the catalyst bed were varied from 3.5 to 36.5 ml/min at a catalyst temperature of 325°C in one set of experiments, and, in another set, the catalyst temperature was varied from 200 to 375°C with the flow-rate fixed at 6.0 ml/min. The chromatographic separations were all performed isothermally and with split injections of the sample at a split ratio of 25:1.

### *Effects of flow-rate*

Two important experimental conditions are dependent on the flow-rate of helium in the system. The permeation device emits a constant amount of NO<sub>2</sub> per unit time; therefore, the concentration of NO<sub>2</sub> in the flow stream is dependent on the rate of helium flow. The flow-rate of gas over the catalyst bed also affects the residence time of reactants in the reaction zone of the detector. For all compounds studied, an increase in the flow-rate of NO<sub>2</sub> in helium through the catalyst zone caused a decrease in the observed chemiluminescence response, without altering the order of relative responses. However, the degree of selectivity with which certain compounds respond is highly dependent on the flow-rate. These data, relative to the response for benzene, are shown in Table I. Above a flow-rate of 18.8 ml/min, benzene response was not detectable. The data were calculated as photon counts per mole of analyte/photon counts per mole of benzene. Relative standard deviations for replicate measurements ranged from 1 to 10% for the various compounds. The absolute responses of the alcohols decrease less with increased flow than any of the other compounds. Since the relative rates of reactions determine, in part, the relative responses, it can be concluded that the response of the alcohols suffers least from shorter catalyst contact time at the higher flow-rates because they react most rapidly.

### *Effects of catalyst temperature*

Selectivity of response factors for each compound studied, relative to benzene, as a function of catalyst temperature are listed in Table II. The ratios were calculated from area responses on a molar basis (integrated photon counts per mole). Typical relative standard deviations for replicate measurements of the components of the test mixture using the peak area percent for each compound ranged from 2 to 10%, with benzene often showing the highest variability because it produces the smallest peak in the chromatogram. With a make-up gas flow-rate of 6.0 ml/min and a catalyst

TABLE I

THE EFFECT OF MAKE-UP REAGENT GAS FLOW-RATE ON SELECTIVITY OF DETECTOR RESPONSE TO VARIOUS ANALYTES AT 325°C

Compound	Flow-rate through the catalyst (ml/min)		
	3.5	6.0	18.8
Methanol	50	153	200
Ethanol	182	379	582
<i>tert.</i> -Butanol	452	839	1430
MTBE	28	31	22
Benzene	1	1	1
Methylcyclohexane	6	10	5
1-Octene	207	227	253
Toluene	51	48	59
<i>n</i> -Octane	17	16	12

TABLE II

THE EFFECT OF TEMPERATURE ON SELECTIVITY OF DETECTOR RESPONSE TO ANALYTES AT A MAKE-UP GAS FLOW-RATE OF 6.0 ml/min

Compound	Temperatures of catalyst (°C)				
	275	300	325	350	375
Methanol	264	138	153	158	147
Ethanol	681	408	379	366	383
<i>tert.</i> -Butanol	1180	819	839	879	890
MTBE	32	28	31	35	30
Benzene	1	1	1	1	1
Methylcyclohexane	9	8	10	9	7
1-Octene	191	182	227	227	241
Toluene	47	45	48	49	54
<i>n</i> -Octane	19	15	16	13	11

temperature of 275°C the relative standard deviations of the peak areas were: methanol, 6.9%; ethanol, 5.6%; *tert.*-butanol, 4.7%; MTBE, 2.8%; benzene, 8.6%; methylcyclohexane, 4.0%; 1-octene, 3.5%; toluene, 3.5%; *n*-octane, 3.5%. At temperatures below 225°C, benzene was not detectable; therefore, the data for selectivity are tabulated starting at 275°C. The alcohols were most selectively detected at 225°C, because at higher temperatures, the other compounds studied produced proportionately larger peaks than the alcohols. Changes in selectivity ratios with temperature are greatest for the alcohols and 1-octene, while the other compounds studied show only small changes in the selectivity.

The components in the mixture all exhibited a maximum response at 325°C and a slight decrease in response with increased temperature above 325°C. While this was not expected, it may arise from partial loss of the most active O or NO<sub>2</sub> in the superconductor catalyst at higher temperatures. Temperature-programmed desorption experiments have shown that NO<sub>2</sub> and O<sub>2</sub> begin to evolve from the catalyst at

350°C. This results in lower concentrations of active oxidants in the catalyst at these temperatures, which may result in lower yields of NO.

The most sensitively detected compounds were the alcohols. Toluene, 1-octene and MTBE also responded, but much less sensitively than the alcohols, at a catalyst temperature of 200°C. Methylcyclohexane responded when the catalyst temperature was raised to 225°C, while the remaining compounds in the mixture responded only at 250°C or greater. For the oxygenated compounds studied at temperatures below 325°C, the responses observed for MTBE and *tert.*-butanol were more dependent upon the temperature of the catalyst than were those observed for methanol and ethanol. At 200°C the response for ethanol is 100-fold greater than that for MTBE and 10-fold greater than that for *tert.*-butanol. However, at 325°C, the response for ethanol is only 10-fold greater than that for MTBE and half that for *tert.*-butanol. This order of relative responses is maintained at catalyst temperatures of 300°C and above. The order of response for all compounds studied (area counts/mole) at 300°C is: *tert.*-butanol > ethanol > 1-octene > methanol > toluene > MTBE > *n*-octane > methylcyclohexane > isooctane > benzene.

It is interesting to compare the selectivity of the catalytic reactions for alcohols and MTBE with those for octane and methylcyclohexane, because it is desirable to detect these oxygenated compounds in the presence of hydrocarbons. The alcohols and MTBE are detected most selectively, relative to *n*-octane and methylcyclohexane at 225°C; however, peaks tend to be broader at the lower temperatures.

#### *Detection limit for ethanol*

The limit of detection for ethanol was determined using splitless injection techniques with samples of known amounts of ethanol in benzene. The standards were prepared volumetrically by serial dilution of stock solutions of ethanol in benzene. At 325°C, with a reagent gas flow-rate of 6.0 ml/min, the detection limit (signal-to-noise ratio = 3) was 0.5 ng of ethanol. If the oxidation of ethanol is complete, producing only CO<sub>2</sub> and H<sub>2</sub>O, then 6 mol NO per mol ethanol should be produced if this is the only reaction product. Although the mechanism for oxidation of ethanol on superconductor catalyst is unknown, we have investigated the reaction by mass spectrometric techniques and have shown the reaction products to be CO<sub>2</sub> and H<sub>2</sub>O although some acetaldehyde formation was observed at low catalyst temperatures.

#### *Analysis of gasoline for MTBE*

A sample of a commercial gasoline containing 8% MTBE by volume was analyzed by redox chemiluminescence detection, employing YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> as the catalyst, at 325°C (Fig. 2). Temperature programmed chromatography was used for the analysis of this sample. Split injections (30:1) of undiluted gasoline samples were made at an initial oven temperature of 25°C for 6 min, and subsequently programmed at 8°C per min to a final temperature of 150°C.

The sensitivity of the system to isooctane, octane and methylcyclohexane decreases more rapidly at higher flows than does the sensitivity for MTBE; therefore, higher make-up gas flows may be used advantageously to detect MTBE selectively in the complex hydrocarbon matrices of gasolines. The selectivity factor for MTBE compared to methylcyclohexane at the highest flow-rate studied (36.5 ml/min) was its greatest value of 3.65, compared to a value of 2.25 at a flow-rate of 3.5 ml/min. Neither

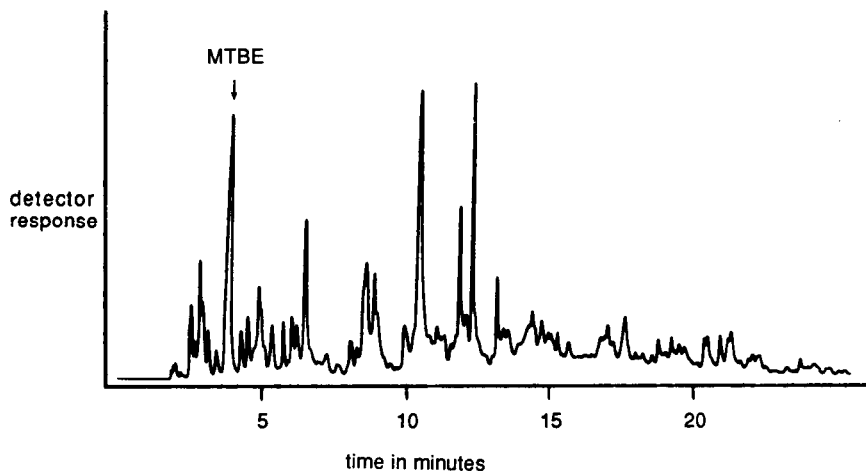


Fig. 2. Chemiluminescence detection of methyl *tert.*-butyl ether in a commercial gasoline sample.

isooctane nor octane was detected at the highest flow-rate. The chromatogram shown in Fig. 2 was obtained using a make-up gas flow-rate of 18.8 ml/min. By Colorado law, the concentration of MTBE in the gasoline is required to be 8% (v/v) during the wintertime when atmospheric inversions are common. The area of the peak for MTBE is the largest of any peak in the chromatogram. The percent response for this peak, based on peak height, in the matrix was reproducible within  $\pm 8\%$  relative S.D. for four determinations that were made over a period of two days.

## CONCLUSIONS

The perovskite,  $\text{YBa}_2\text{Cu}_3\text{O}_7$ , exhibits strong catalytic activity, particularly toward oxidation of alcohols and other organic compounds in reactions with  $\text{NO}_2$  to form NO. The selectivity of the catalyst can be modified by changing the temperature or the flow-rate of the reagent gas to selectively detect compounds of interest. The response to *tert.*-butanol is 1000 times greater than to benzene. Olefins and alkyl-aromatic compounds are detected with greater sensitivity than benzene or aliphatic hydrocarbons measured in gasoline with this detector.

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