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PREPARATION AND CHARACTERIZATION OF ZRO2 STABILIZED
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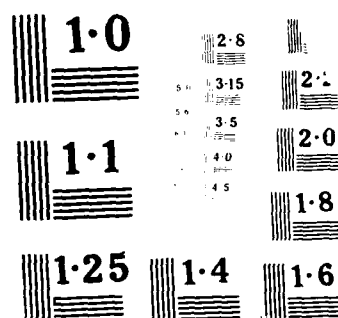
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TECHNICAL REPORT NO. 14

Preparation and Characterization of ZrO_2 Stabilized with Ru(IV) and La(III)

by

Y-C. Long, Z-D. Zhang, K. Dwight and A. Wold

Prepared for Publication in
MATERIALS RESEARCH BULLETIN

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Brown University
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REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED			1b. RESTRICTIVE MARKINGS	
2a. SECURITY CLASSIFICATION AUTHORITY			3. DISTRIBUTION/AVAILABILITY OF REPORT APPROVED FOR PUBLIC RELEASE DISTRIBUTION UNLIMITED	
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE				
4. PERFORMING ORGANIZATION REPORT NUMBER(S) # 14			5. MONITORING ORGANIZATION REPORT NUMBER(S) N000 14 86 0234	
6a. NAME OF PERFORMING ORGANIZATION AARON WOLD BROWN UNIVERSITY		6b. OFFICE SYMBOL (if applicable)	7a. NAME OF MONITORING ORGANIZATION OFFICE OF NAVAL RESEARCH DR. DAVID NELSON	
6c. ADDRESS (City, State, and ZIP Code) DEPARTMENT OF CHEMISTRY PROVIDENCE, RI 02912			7b. ADDRESS (City, State, and ZIP Code) CODE 472 800 N. QUINCY STREET ARLINGTON, VA 22217	
8a. NAME OF FUNDING/SPONSORING ORGANIZATION		8b. OFFICE SYMBOL (if applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER	
8c. ADDRESS (City, State, and ZIP Code)			10. SOURCE OF FUNDING NUMBERS	
			PROGRAM ELEMENT NO	PROJECT NO
			TASK NO	WORK UNIT NO
11. TITLE (Include Security Classification) PREPARATION AND CHARACTERIZATION OF ZrO₂ STABILIZED WITH Ru(IV) AND La(III)				
12. PERSONAL AUTHOR(S) Y-C. Long, Z-D. Zhang, K. Dwight and A. Wold				
13a. TYPE OF REPORT Technical		13b. TIME COVERED FROM TO		14. DATE OF REPORT (Month/Year) January 26, 1988
15. SUPPLEMENTARY NOTATION SUBMITTED TO MATERIALS RESEARCH BULLETIN				
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
FIELD	GROUP	SUB-GROUP		
19. ABSTRACT (Continue on reverse if necessary and identify by block number) Ruthenium oxide, dispersed on oxide supports such as TiO₂, SiO₂ and ZrO₂, are known to shown Fischer-Tropsch activity. Little is known about the catalyst-support interactions which must play an important role in the catalytic activity of dispersed ruthenium oxide. The strength of catalytic support interaction may be directly related to the stability of the dispersed catalyst towards reduction. Hence, solid solutions of Ru(IV)/ZrO₂ have been prepared, and the resulting stability of Ru(IV) toward reduction with hydrogen was measured and compared with that of bulk RuO₂. The observed increase in stability toward reduction was related to interaction between RuO₂ and ZrO₂. The introduction of a small amount of La₂O₃ with the ZrO₂ produced further stabilization of the Ru(IV) toward reduction.				
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT ☐ UNCLASSIFIED ☐ CONFIDENTIAL ☐ SECRET			21. ABSTRACT SECURITY CLASSIFICATION	
22. NAME OF PERSONS/ORGANIZATION			23. TELEPHONE (include area code)	

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Naval Surface Weapons Center
Code 5617
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Department of Chemistry
James Franck Institute
5640 Ellis Avenue
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Chemistry Department
University of California
Irvine, California 92717

Dr. R. E. Jensen
Chemistry Department
University of California
Rochester, New York 14627

Dr. S. R. Koff
Naval Surface Weapons Center
Code 5617
Silver Spring, Maryland 20910

Dr. J. C. Salamone
Chemistry Department
University of California
Irvine, California 92717

Dr. R. E. Jensen
Chemistry Department
University of California
Rochester, New York 14627

Dr. John F. Tolles
Department of Chemistry
University of Pittsburgh
Pittsburgh, Pennsylvania 15260

Dr. R. Stephen Williams
Department of Chemistry
University of California, San Diego
San Diego, California 92024

Dr. R. E. Jensen
Materials Characterization Lab
General Electric, Schenectady
Schenectady, New York 12307

Dr. J. P. Jensen
Department of Chemistry
University of Birmingham
Birmingham, England B15 2TT

Dr. R. E. Jensen
Department of Chemistry
University of Pennsylvania
Philadelphia, Pennsylvania 19104

Dr. J. C. Salamone
Chemistry Department
University of California
Irvine, California 92717

Dr. R. E. Jensen
Chemistry Department
University of California
Rochester, New York 14627

Dr. R. E. Jensen
Chemistry Department
University of California
Rochester, New York 14627

Dr. R. E. Jensen
Chemistry Department
University of California
Rochester, New York 14627

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Chemistry Department
University of California
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Chemistry Department
University of California
Rochester, New York 14627

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Naval Research Laboratory
2222 Ralston Road
Bethesda, Maryland 20814

Dr. J. M. Hoverson
Department of Chemistry, Engineering
and Materials Science
University of Minnesota
Minneapolis, Minnesota 55455

Dr. A. Reardon
Naval Research Laboratory
Research Triangle Park, North Carolina
27709

Dr. W. J. Kricheldorf
Laboratory for Surface Science
and Catalysis
University of Maine
Orono, Maine 04469

Dr. J. C. Salamone
Naval Research Laboratory
Code 6073
Washington, D.C. 20375-5000

Dr. L. T. Farnham
Chemistry Department
Rensselaer Polytechnic Institute
Troy, New York 12181

Dr. J. C. Salamone
Chemistry and Physics Department
University of Pennsylvania
Philadelphia, Pennsylvania 19107

Dr. R. E. Jensen
Department of Chemistry
University of California
Berkeley, California 94720

Dr. R. E. Jensen
Department of Chemistry
University of California
Berkeley, California 94720

Dr. R. E. Jensen
Department of Chemistry
University of California
Berkeley, California 94720

Dr. R. E. Jensen
Chemistry Department
University of California
Berkeley, California 94720

Dr. J. M. Hoverson
Department of Chemistry
University of Minnesota
Minneapolis, Minnesota 55455

Dr. A. Reardon
Naval Research Laboratory
Research Triangle Park, North Carolina
27709

Dr. W. J. Kricheldorf
Laboratory for Surface Science
and Catalysis
University of Maine
Orono, Maine 04469

Dr. J. C. Salamone
Naval Research Laboratory
Code 6073
Washington, D.C. 20375-5000

Dr. L. T. Farnham
Chemistry Department
Rensselaer Polytechnic Institute
Troy, New York 12181

Dr. J. C. Salamone
Chemistry and Physics Department
University of Pennsylvania
Philadelphia, Pennsylvania 19107

Dr. R. E. Jensen
Department of Chemistry
University of California
Berkeley, California 94720

Dr. R. E. Jensen
Department of Chemistry
University of California
Berkeley, California 94720

Dr. R. E. Jensen
Department of Chemistry
University of California
Berkeley, California 94720

Office of Naval Research
Attn: Code 1113
800 N. Quincy Street
Arlington, Virginia 22217-5000

Dr. Bernard Duda
Naval Weapons Support Center
Code 520
Crane, Indiana 47522-5050

Naval Civil Engineering Laboratory
Attn: Dr. R. W. Drisko, Code 52
Port Hueneme, California 93040

Defense Technical Information Center
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Dr. David Young
Code 1113
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Arlington, Virginia 22217-5000

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PREPARATION AND CHARACTERIZATION OF ZrO_2 STABILIZED WITH Ru(IV) AND La(III)

Y-C. Long, Z-D. Zhang, K. Dwight and A. Noid*

Department of Chemistry, Brown University, Providence, RI 02912

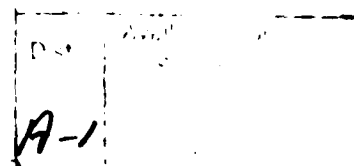
ABSTRACT

Ruthenium oxide, dispersed on oxide supports such as TiO_2 , SiO_2 and ZrO_2 , are known to show Fischer-Tropsch activity. Little is known about the catalyst-support interactions which must play an important role in the catalytic activity of dispersed ruthenium oxide. The strength of catalytic support interaction may be directly related to the stability of the dispersed catalyst towards reduction. Hence, solid solutions of Ru(IV)/ ZrO_2 have been prepared, and the resulting stability of Ru(IV) toward reduction with hydrogen was measured and compared with that of bulk RuO_2 . The observed increase in stability toward reduction was related to interaction between RuO_2 and ZrO_2 . The introduction of a small amount of La_2O_3 with the ZrO_2 produced further stabilization of the Ru(IV) toward reduction.

MATERIALS INDEX: Ruthenium oxide/zirconium oxide solid solution; ruthenium oxide/(lanthanum oxide/zirconium oxide) solid solution

Introduction

In order to determine the stability of dispersed ruthenium oxide on ZrO_2 , it is first necessary to investigate the properties of solid solutions containing Ru(IV) oxide. Such studies would result in optimizing the conditions necessary for the use of this catalyst in Fischer-Tropsch conversions of carbon monoxide to either hydrocarbons or alcohols. Solid solutions of ZrO_2 and various metal ions have been widely investigated. Collins and Ferguson (1) reported the formation of monoclinic phases when ZrO_2 reacts to form solid solutions with Fe_2O_3 , SnO_2 and Cr_2O_3 . Stocker and Collongues (2) prepared cubic solid solutions of ZrO_2 with MO (M = Mg, Ni, Cd, Zn, Fe, Mn) and M_2O_3 (M = Fe, Mn, Cr, Al, V). Recently Nu (3) indicated that a tetragonal phase formed between Cr_2O_3 and ZrO_2 with less than 7.5 mole percent Cr_2O_3 and changed to cubic when the chromium content was above this level. There have been additional studies concerning the preparation and characterization of a series of cubic ZrO_2 solid solutions stabilized by Rh(III) (4), Fe(II) and Fe(III) (5), and Ni(II) (6) which were prepared by double decomposition of the nitrates. In all of these recent studies (3-6), a tetragonal form of ZrO_2 was first stabilized by the introduction of metal ions and transformed to the cubic form of ZrO_2 as the concentration of these ions was increased.



Despite the fact that ruthenium oxide shows a high catalytic activity in Fischer-Tropsch reactions (7), very little has appeared concerning the preparation and stabilization of ruthenium(IV) oxide under reducing conditions. A number of other transition metals have been shown to be stabilized when reacted with zirconium oxide. Hence this study of solid solutions between RuO_2 and ZrO_2 was undertaken. Such studies are essential in order to optimize the conditions necessary for the conversion of carbon monoxide to useful fuels.

Experimental

Samples of members of the system Ru(IV)/ZrO_2 were prepared to give compositions containing 5, 10 and 15 atomic percent Ru(IV) . Calculated quantities of $\text{Ru(NO)(NO}_3)_3$ and $\text{ZrO(NO}_3)_2$ were dissolved in water. The solution then was dried at 150°C for 12 hours and predecomposed at 550°C for 24 hours in order to drive off nitrogen oxides, and then allowed to cool to room temperature.

Ternary oxide samples of La_2O_3 , RuO_2 and ZrO_2 were prepared by decomposing the required mixture of ruthenium nitrosyl nitrate $\text{Ru(NO)(NO}_3)_3$, lanthanum nitrate, and zirconyl nitrate $\text{ZrO(NO}_3)_2$. The triple salt was decomposed by the same procedure as described above except that the samples were finally heated at 850°C for 24 hours.

In order to make certain of the proper decomposition conditions, temperature programmed decompositions of both the double salt of ruthenium nitrosyl nitrate and zirconyl nitrate, and the triple salt of lanthanum nitrate, ruthenium nitrosyl nitrate, and zirconyl nitrate were carried out in a Cahn System 113 thermal balance. Both the double salt and the triple salt were dissolved in water and dried at 150°C for 12 hours. The partially decomposed products were then decomposed under a predried oxygen atmosphere at a flow rate of 60 cc/min. The samples were heated to 1000°C at a rate of 100°C/hr .

Temperature programmed reductions (TPR) of ruthenium-containing samples were carried out using the same balance. Before reduction was started, the sample was preheated in dry oxygen up to 600°C in order to drive off any adsorbed water. After the sample was allowed to cool to room temperature, the gas was changed from oxygen to a 85% $\text{Ar}/15\%\text{H}_2$ mixture predried over P_2O_5 . The flow rate over a 25 mg sample was 60 cc/min. The temperature was then increased to 600°C at a rate of 50°C/hr . For the system of $\text{La(III) - Ru(IV) - ZrO}_2$ the reduction was carried out to 1000°C .

Characterization of the Products

X-ray powder diffraction patterns of the samples were obtained using a Philips diffractometer and monochromated high intensity $\text{CuK}\alpha$ radiation ($\lambda = 1.5405 \text{ \AA}$). Polycrystalline samples were analyzed by x-ray diffraction. Fast scans were recorded at a speed of $1^\circ/2\text{ min}$ and slow scans at a speed of $0.25^\circ/2\text{ min}$. The lattice parameters were determined by a least squares refinement of the observed peak positions by a computer program which corrected for the systematic errors inherent in the measurement.

Results and Discussion

Samples of the system Ru(IV)/ZrO_2 were prepared by double decomposition of $\text{Ru(NO)(NO}_3)_3$ and $\text{ZrO(NO}_3)_2$. A previous study (8) has indicated that the nitrates decompose completely at 900°C . In this study, however, complete decomposition occurred at 550°C . Therefore, the samples were heated at 550° for 24 hours. Compositions of Ru(IV)/ZrO_2 up to 10 atomic percent ruthenium crystallized in the tetragonal system. These phases were stable in air up to 700°C . At 800°C , x-ray analysis indicated the formation of monoclinic ZrO_2 . Because of poor crystallinity, the cell parameters of the tetragonal phases up to 10 atomic percent ruthenium appeared to remain constant with $a = 5.07 \text{ \AA}$ and $c = 5.16 \text{ \AA}$. In order to determine whether the ruthenium oxide actually reacted to form a solid solution with ZrO_2 , temperature programmed reduction of each sample was carried out. The results of these studies are shown in Fig. 1. It can readily be seen that there is stabilization of the ruthenium toward hydrogen reduction, and this must be related to an interaction between RuO_2 and ZrO_2 . The temperature programmed reduction of the 15 mole percent ruthenium oxide sample shown in Fig. 1 indicates a two-step reduction. The first plateau is achieved by the reduction of unreacted excess RuO_2 and the second step is due to the gradual reduction of the stabilized RuO_2 . This is also consistent with the appearance of diffraction lines due to excess RuO_2 in the x-ray pattern of the 15% $\text{RuO}_2/\text{ZrO}_2$ sample.

A part of the system $\text{RuO}_2/(\text{La}_2\text{O}_3/\text{ZrO}_2)$ was studied in order to determine the effect of lanthanum oxide on the stabilization of ruthenium(IV) in ZrO_2 . Samples of ZrO_2 containing Ru(IV) and La(III) were prepared by decomposing mixtures of nitrates at 850°C for 24 hours. Temperature programmed decomposition studies indicated that decomposition of the mixtures was not complete below this temperature. The concentration of La_2O_3 was kept constant at 5 mole percent relative to that of ZrO_2 since this level of solid solution with ZrO_2 has previously been studied for the system $\text{Rh}_2\text{O}_3/(\text{La}_2\text{O}_3/\text{ZrO}_2)$. Therefore, the preparations which were studied can best be represented by the general formula: mole% $\text{RuO}_2/(5 \text{ mole\% } \text{La}_2\text{O}_3/\text{ZrO}_2)$.

At five mole percent lanthanum oxide, the stabilized cubic structure of ZrO_2 is maintained for ruthenium(IV) oxide loading up to 10 mole percent. The variation in the cell constants with increased ruthenium concentration is shown in Fig. 2. The temperature programmed reduction studies were carried out with the Cahn balance using predried gas, and the results are shown in Fig. 3. It can be seen that 2.5 atomic percent ruthenium loading is completely stable towards reduction up to 800°C ; this may be compared to the reduction of bulk RuO_2 at 90°C . The sample at 5 atomic percent ruthenium loading shows that a part of the ruthenium oxide behaves just as $\text{RuO}_2/\text{ZrO}_2$ did under reducing conditions. However, the effect of lanthanum on the further stabilization of ruthenium(IV) towards reduction is evident for the compositions containing both 5 and 10 atomic percent ruthenium. Fig. 4 summarizes the change of cell parameters as a function of reduction temperature for each sample studied. It can be seen that there is some reduction of the ruthenium - lanthanum - zirconium oxide samples below 100°C . But at 850°C all of the ruthenium is reduced, and the cell parameters return to that of lanthanum oxide/zirconium oxide not containing ruthenium.

Conclusions

Solid solution of Ru(IV) oxide in ZrO_2 increases the stability towards hydrogen reduction from under 90° to over 200°C . The further addition of 5 mole % of lanthanum(III) oxide significantly increases the stability of dispersed RuO_2 to 800°C . The Fischer-Tropsch process depends upon the presence of oxide as well as reduced metal. Whereas pure RuO_2 is catalytically inactive because of the low temperature at which it can be reduced, it is possible that a proper combination of La_2O_3 , RuO_2 and ZrO_2 might result in optimal conversion of carbon monoxide to useful hydrocarbons.

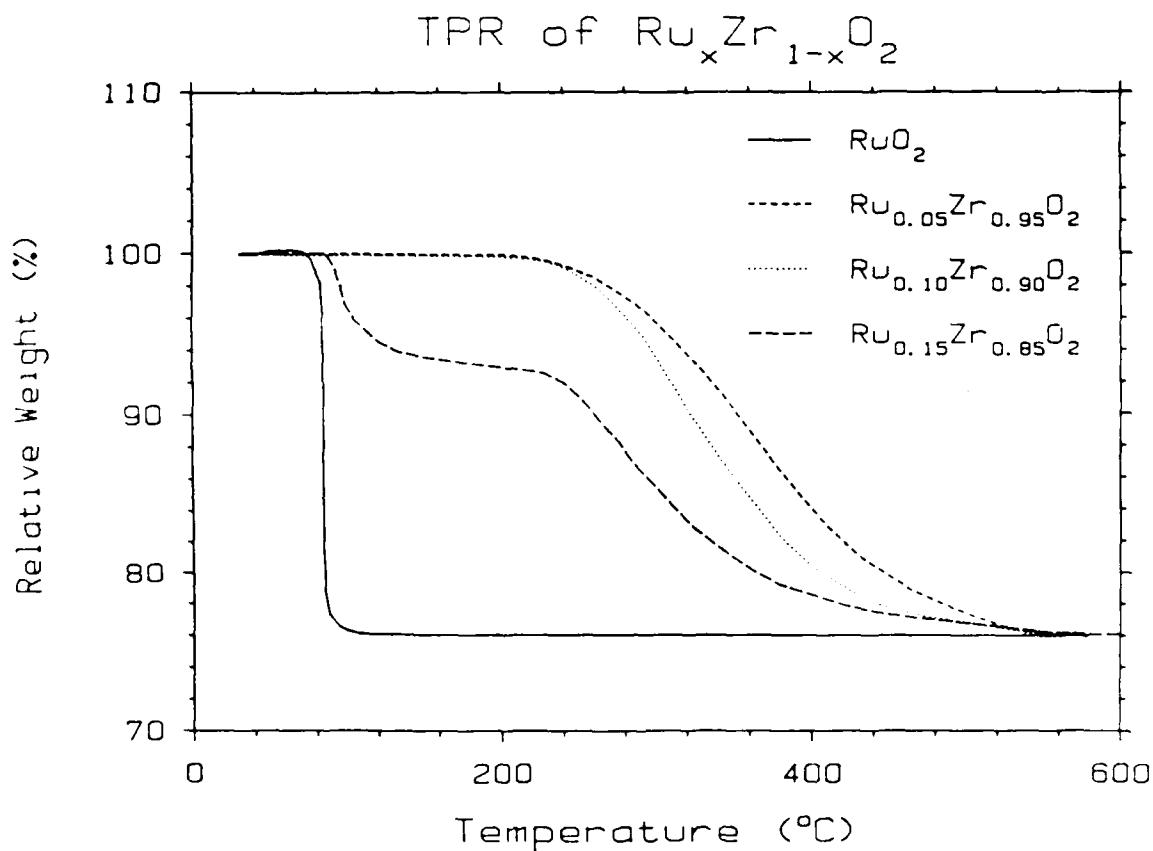


Fig. 1. Variation of relative weight with increasing temperature during temperature programmed reduction (TPR) of RuO_2 and members of the system $\text{Ru}_x\text{Zr}_{1-x}\text{O}_2$ in $85\% \text{Ar}/15\% \text{H}_2$.

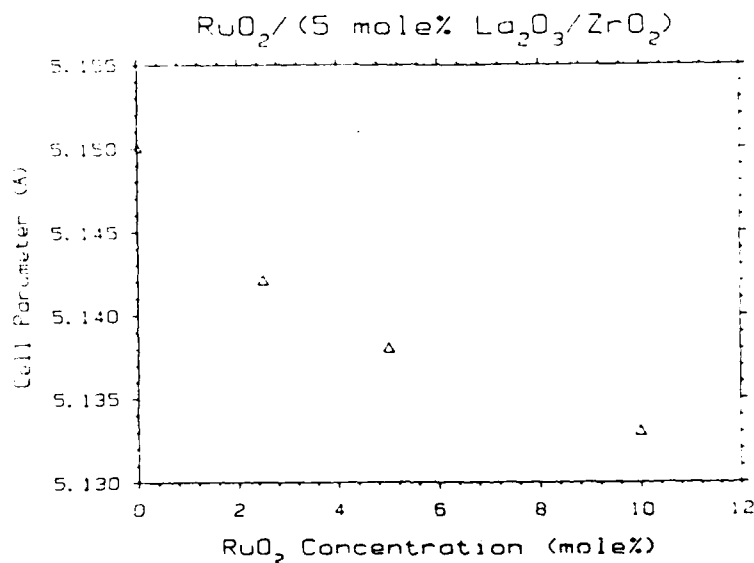


Fig. 2. Change of cell parameter with RuO_2 concentrations in the system $\text{RuO}_2/(5 \text{ mole\% } \text{La}_2\text{O}_3/\text{ZrO}_2)$.

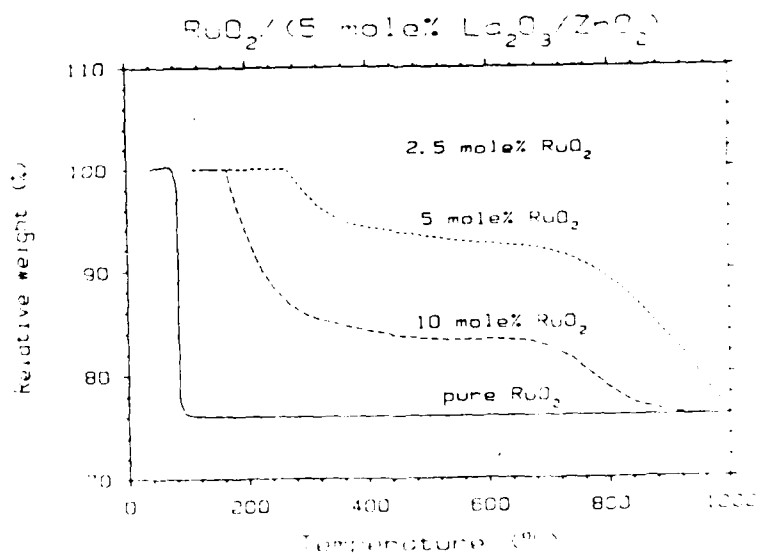


Fig. 3. Variation of relative weight with increasing temperature during temperature programmed reduction of RuO_2 and members of the system $\text{RuO}_2/(5 \text{ mole\% } \text{La}_2\text{O}_3/\text{ZrO}_2)$ in 85% Ar-15% H_2 .

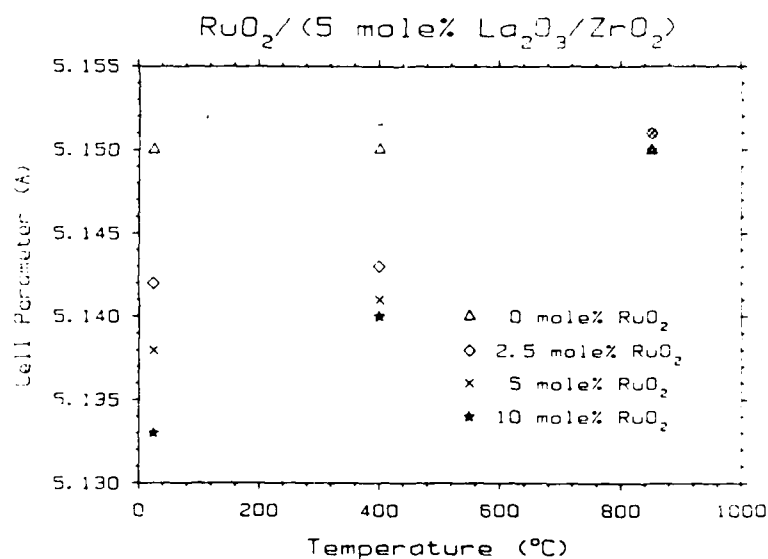


Fig. 4. Cell parameters of members of the system $\text{RuO}_2(5 \text{ mole\% } \text{La}_2\text{O}_3 / \text{ZrO}_2)$ as prepared and after reduction in 85%Ar/15% H_2 at 400° and 850° C.

Acknowledgments

This research was supported in part by the Office of Naval Research and Eastman Kodak Company, Rochester, NY. The authors also wish to acknowledge the support of the National Science Foundation for the partial support of K. Dwight and the use of the Materials Research Laboratory at Brown University which is funded by the National Science Foundation.

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