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TECHNICAL REPORT NO. 14

Preparation and Characterization of ZrO<sub>2</sub> 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



Brown University Department of Chemistry Providence, RI 02912

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PREPARATION AND CHARACTERIZATION OF 2rO7 STABILIZED WITH Ru(IV) AND La(III)

Y-C. Long, Z-D. Zhang, K. Dwight and A. Nold\* Department of Chemistry, Brown University, Providence, RI 02912

#### ABSTRACT

Ruthenium oxide, dispersed on oxide supports such as  $TiO_2$ ,  $SiO_2$ and  $2rO_2$ , 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  $Ru(IV)/2rO_2$  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  $2rO_2$ . The introduction of a small amount of  $La_2O_3$  with the  $2rO_2$  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 2r02, 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-Tronsch conversions of carbon monoxide to either hydrocarbons or alcohols. Solid solutions of 2r02 and various metal ions have been widely investigated. Collins and Ferguson (1) reported the formation of monoclinic phases when True reacts to form solid solutions with Fep03, SnOp and Cr203. Stocker and Collongues (2) prepared cubic solid solutions of 2rO2 with MO (M = Mg, Ni, Cd, Zn, Fe, Mn) and M<sub>2</sub>O<sub>3</sub> (M = Fe, Mn, Cr, A1, V). Recently Nu (3) indicated that a tetragonal phase formed between Cro03 and 2r09 with less than 7.5 mole percent Cro03 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 2r02 solid solutions stabilized by Rh(III) (4), Fe(II) and Fe(III) (5), and Ni(II) (6) which were provated by double decomposition of the nitrates. In all of these recent studies (3-6), a tetragonal form of ZrO2 was first stabilized by the introduction of metal ions and transformed to the cubic form of Irdy 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  $Ru(IV)/2rO_2$  were prepared to give compositions containing 5, 10 and 15 atomic percent Ru(IV). Calculated quantities of  $Ru(NO)(NO_3)_3$  and  $2rO(NO_3)_2$  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  $Ru(NO)(NO_3)_3$ , lanthanum nitrate, and zirconyl nitrate  $ZrO(NO_3)_2$ . 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  $85\%Ar/15\%H_2$  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 La(III) - Ru(IV) - ZrO<sub>2</sub> 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 nonochromated high intensity CuK is radiation () 1.5405 Å). Polycrystalline samples were unalyted by s-ray diffraction. Fast scans were recorded at a speed of 1° 197min and slow scans it i speed of 0.25 2°/min. The lattice parameters were determined by a least sources 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)/IrOb were prepared by louble lecomposition of  $Ru(NO)(NO_3)_3$  and  $ZrO(NO_3)_2$ . 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) /IrOn 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 IrO2. 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 Å and c = 5.16 A. In order to determine whether the ruthenium oxide actually reacted to form a solid solution with IrO, 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 RuO2 and IrO2. 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 RuO2 and the second step is due to the gradual reduction of the stabilized RuO<sub>2</sub>. This is also consistent with the appearance of diffraction lines due to excess RuO<sub>2</sub> in the x-ray pattern of the 15%  $RuO_2/2rO_2$  sample.

A part of the system  $RuO_2/(La_2O_3/2rO_2)$  was studied in order to determine the effect of lanthanum oxide on the stabilization of ruthenium(IV) in  $2rO_2$ . Samples of  $2rO_2$  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  $2rC_2$  since this level of solid solution with  $2rO_2$  has previously been studied for the system  $Rh_2O_3/(La_2O_3/2rO_2)$ . Therefore, the preparations which were studied can best be represented by the general formula: mole%  $RuO_2/(5 mole% La_2O_3/2rO_2)$ .

At five mole percent lanthanum oxide, the stabilized cubic structure of IrOp is maintained for ruthenium(IV) sxide loading up to 10 mole percent. 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 RuOp at 90°C. The sample at 5 atomic percent ruthenium loading shows that a part of the ruthenium oxide behaves just as  $RuO_2/(2\pi O_2)$  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 muthenium. Mig. 4 summarizes the change of cell parameters as a function of reduction temperature for each sample studied. It can be seen that there is toos reduction of the ruthenium - lanthanum - miconium oxide supples polos (2007. But at 850°C all of the mithenium is reduced, and the cell minameters moturn 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 3 mole 5 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. Mhereas 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<sub>2</sub> and members of the system  $Ru_x 2r_{1-x}O_2$  in  $85^{\circ}Ar/15^{\circ}H_2$ .



Fig. 2. Change of cell parameter with  $RuO_2$  concentrations in the system  $RuO_2/(5 \text{ mole} \ln 2_0 3/2rO_2)$ .



Fig. 3. Variation of relative weight with increasing temperature buring temperature programmed reduction of Ruby and members of the system Ruby((5 mole) Lisoz(1905) in 851%r 12145.



Fig. 4. Cell parameters of members of the system  $RuO_2(5 \text{ mole} La_2O_3/ZrO_2)$  as prepared and after reduction in  $85\%Ar/15\%H_2$  at  $400^\circ$  and  $850^\circ$  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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