

## Preparation and Characterization of Cubic ZrO<sub>2</sub> Stabilized by Fe(III) and Fe(II)\*

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Samples of cubic ZrO<sub>2</sub> containing 2.5–40 at% Fe(III) were prepared by codecomposition of the nitrates. X-ray powder diffraction analysis and magnetic measurements indicated that  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub> form a solid solution up to 25 at% Fe/Zr in the product. At this point, the solubility limit of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> in ZrO<sub>2</sub> is exceeded. The reduction of cubic zirconia samples containing 2.5–20 at% Fe(III) leads to the stabilization of iron(II) in the zirconia lattice. Reduction to metallic iron occurs at much higher temperatures than the reduction of bulk  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. © 1988 Academic Press, Inc.

### Introduction

The cubic form of ZrO<sub>2</sub> crystallizing with the fluorite structure can be stabilized when impurity cations are introduced into the monoclinic or tetragonal ZrO<sub>2</sub> structures. Stöcker (1) has shown that transition metal cations may form solid solutions with ZrO<sub>2</sub>, thus producing cubic ZrO<sub>2</sub>. The exact extent of solid solution formation depends on the precursors used, temperature of preparation, and the transition metal cation. Although the properties of the cubic stabilized phases have received much attention, little has appeared in the literature concerning the magnetic properties or thermal stabilities toward reduction of solid solutions containing transition metals such as iron. It is the purpose of this investigation to carry out such studies and to determine also the

stability of iron(III) toward reduction in view of zirconia's use as a support in Fischer-Tropsch catalysis (2, 3).

### Experimental

#### *Preparation of Samples*

Samples of cubic ZrO<sub>2</sub> containing iron(III) were prepared by thermal decomposition of a double salt of iron(III) nitrate and zirconyl nitrate. Zirconium basic nitrate was obtained from zirconium basic carbonate (Noah Chemical) by dissolving the basic carbonate in nitric acid (5.3 g basic carbonate per 20 ml 16 M nitric acid) and evaporating to dryness at 100°C (4). The iron nitrate (Baker analyzed reagent) and zirconium basic nitrate were analyzed by converting them to their constituent oxides in flowing O<sub>2</sub>. A weight of 1.5 g of the zirconium basic nitrate was then dissolved in 15 ml of water to give a zirconyl nitrate solution and the exact amount of iron nitrate was added to give the desired

\* This paper is dedicated to Professor Albrecht Rabeneau in honor of his 65th birthday.

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amount of iron(III) in  $ZrO_2$ . Two successive heatings were used; the sample was dried at  $150^\circ C$  for 12 hr and then ground to a fine powder. The resulting product was heated at  $600^\circ C$  for 24 hr. This final firing temperature of  $600^\circ C$  was determined by thermogravimetric analysis which showed that complete decomposition occurred at  $600^\circ C$ .

### Magnetic Susceptibility Measurements

Magnetic susceptibilities were measured using a Faraday balance at a field strength of 10.4 kOe (5, 6). Honda-Owens (field dependency) plots were also made to determine the presence of parasitic ferromagnetism, which would be due to bulk iron oxide. The data was corrected for the theoretical core diamagnetism. (7).

### Thermogravimetric Analysis

Thermogravimetric analysis was performed using a Cahn electrobalance (Model RG). An atmosphere of 85% Ar/15%  $H_2$  was used for reduction in these studies. The gas was predried by passing it through a  $P_2O_5$  column and the samples were preheated in argon at  $500^\circ C$  to remove any water before reduction. Thermogravimetric analysis experiments required about 70 mg of sample and the gas flow rate was  $50\text{ cm}^3/\text{min}$ . The heating rate was  $50^\circ C/\text{hr}$  up to a maximum temperature of  $1000^\circ C$ .

### X-ray Diffraction Studies

Powder diffraction patterns of the samples were obtained with a Philips diffractometer using monochromated high-intensity  $CuK\alpha_1$  radiation ( $\lambda = 1.5405\text{ \AA}$ ). For qualitative identification of the phases present, the patterns were taken from  $30^\circ < 2\theta < 80^\circ$  with a scan rate of  $1^\circ 2\theta/\text{min}$  and a chart speed of 30 in./hr. Cell parameter data was obtained using a scan rate of  $0.25^\circ 2\theta/\text{min}$  and a chart speed of 30 in./hr. Cell parameters were obtained from a least-squares refinement of the data with the aid

of a computer program which corrected for the systematic experimental errors.

## Results and Discussion

Members of the system  $Fe_2O_3-ZrO_2$  were prepared by double decomposition of  $ZrO(NO_3)_2$  and  $Fe(NO_3)_3 \cdot 9H_2O$ . The temperature programmed decomposition of bulk iron nitrate, zirconyl nitrate, and the double salt of iron nitrate and zirconyl nitrate were carried out in order to ascertain their decomposition temperatures. Pure iron nitrate and zirconyl nitrate decomposed completely to the oxides at  $290$  and  $500^\circ C$ , respectively. The complete decomposition of the double salt occurred at  $550^\circ C$ . All sample preparations were carried out at  $600^\circ C$  for 24 hr to ensure complete decomposition of the nitrates to the

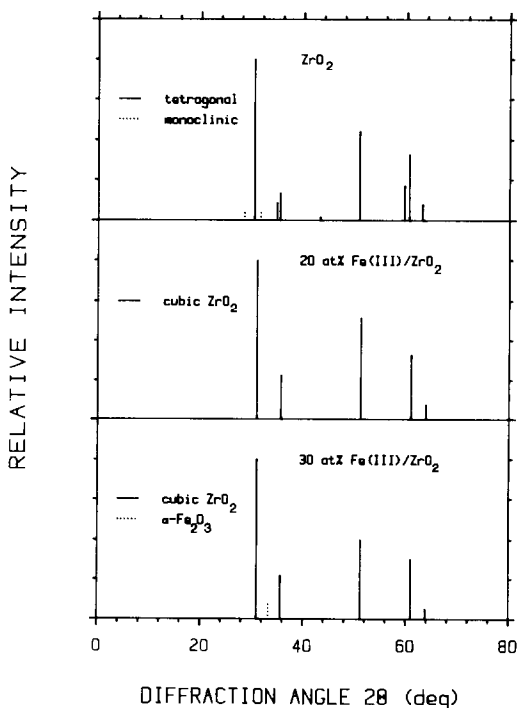


FIG. 1. X-ray phase analysis of samples of pure  $ZrO_2$ ,  $ZrO_2$  with 20 at% Fe(III), and  $ZrO_2$  with 30 at% Fe(III) prepared by decomposition of the nitrates at  $600^\circ C$ .

TABLE I  
Fe(III)/ZrO<sub>2</sub> DECOMPOSED AT 600°C

Compound at% Fe(III)/ZrO <sub>2</sub>	Phases present	Lattice parameter ( <i>a</i> )
0	Tetragonal ZrO <sub>2</sub> and monoclinic	5.081(2) ( <i>c/a</i> = 1.02)
2.5	Tetragonal ZrO <sub>2</sub>	5.076(2) ( <i>c/a</i> = 1.02)
5	Tetragonal ZrO <sub>2</sub>	5.076(2) ( <i>c/a</i> = 1.01)
10	Cubic ZrO <sub>2</sub>	5.067(2)
15	Cubic ZrO <sub>2</sub>	5.059(2)
20	Cubic ZrO <sub>2</sub>	5.049(2)
25	Pseudo cubic + $\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	
30	Pseudo cubic + $\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	
40	Pseudo cubic + $\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	

oxides. This was confirmed by X-ray analysis, which indicated that the pure end members,  $\alpha$ -iron oxide and predominantly the tetragonal phase of ZrO<sub>2</sub> (Fig. 1), were formed on decomposition of the nitrates. Decomposition of the double salts resulted in the formation of cubic ZrO<sub>2</sub> (Fig. 1) with loadings of iron greater than 5 at%. X-ray analysis indicated the absence of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> in the diffraction patterns until the introduction of 25 at% Fe or more into ZrO<sub>2</sub> was attempted. At the nominal composition of

30 at%, the 100% peak at  $2\theta = 33.28$  could just be detected in the diffraction pattern (Fig. 1). Table I summarizes the X-ray analysis results and reports the *a* parameter and *c/a* of ZrO<sub>2</sub> samples containing 0–20 at% of iron. The formation of cubic ZrO<sub>2</sub> at concentrations greater than 5 at% Fe(III)/ZrO<sub>2</sub> confirms earlier studies concerning the change of structure of ZrO<sub>2</sub> upon the introduction of foreign ions such as Fe(III) (5).

Temperature programmed reduction

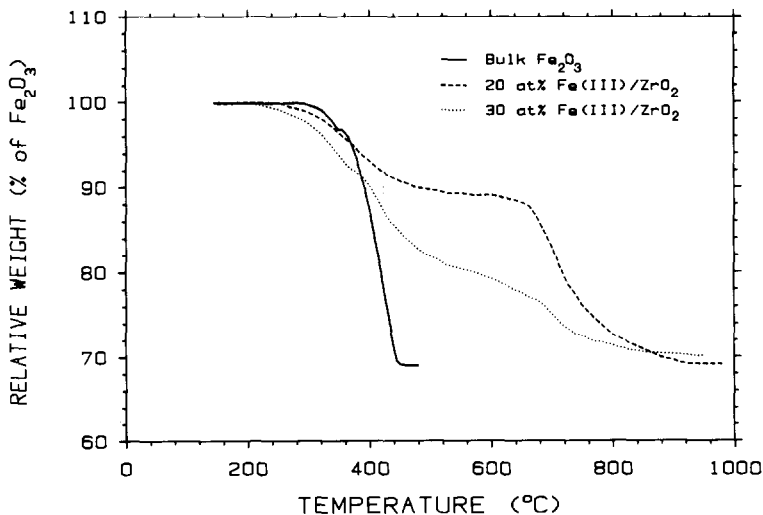


FIG. 2. Comparison of the stability toward reduction in 85% Ar/15% H<sub>2</sub> of samples of bulk  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub> with 20 at% Fe(III), and ZrO<sub>2</sub> with 30 at% Fe(III) prepared by decomposition of the nitrates at 600°C.

studies in an atmosphere of 85% Ar/15% H<sub>2</sub> were also carried out on all samples. Bulk iron oxide showed a reduction profile in which the initial  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> phase reduced first to Fe<sub>3</sub>O<sub>4</sub> and then to iron metal by 450°C. This is in agreement with an earlier study (8). The reduction plot of the bulk iron oxide prepared from the nitrates at 600°C is shown in Fig. 2. Samples with 2.5–20 at% Fe present in cubic ZrO<sub>2</sub> showed increased stability toward reduction.

The weight loss at the first and final plateaus in the reduction process of the 20 at% Fe(III) sample corresponded to the reduction of Fe(III) to Fe(II) and then to metallic iron (Fig. 2). The 20 at% Fe(III) substituted samples showed a plateau which extends from 400–700°C. This is consistent with an increase in the stability of iron(II) when it is inserted in the fluorite structure compared to iron(II) formed on reduction of bulk  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. When an attempt was made to introduce 30 at% Fe(III) into ZrO<sub>2</sub> there was evidence both for reduction of bulk  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and for the more

gradual reduction of the stabilized iron(II). The stabilization of iron(II) in cubic zirconia samples was confirmed by X-ray analysis for the 20 at% Fe(III)/ZrO<sub>2</sub> samples by showing that only cubic ZrO<sub>2</sub> was present at the first plateau. Upon reduction of the Fe(III)/ZrO<sub>2</sub> samples at elevated temperatures, X-ray analysis also indicated that both metallic iron and predominantly monoclinic ZrO<sub>2</sub> were observed to form.

Magnetic susceptibility and field dependency measurements were carried out on all samples in order to differentiate iron(III) present in the cubic ZrO<sub>2</sub> structure from bulk  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. Samples with loadings of 25 at% Fe(III)/ZrO<sub>2</sub> and above showed field dependent susceptibilities, indicating the presence of bulk  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. At loadings of 2.5–20 at% Fe(III)/ZrO<sub>2</sub>, no field dependency of the magnetic susceptibility (characteristic of the parasitic ferromagnetism of bulk  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) was observed and the samples showed paramagnetic behavior (Fig. 3). It can be seen from Table II that the observed moments increase with a decrease in the concentration of Fe(III) and

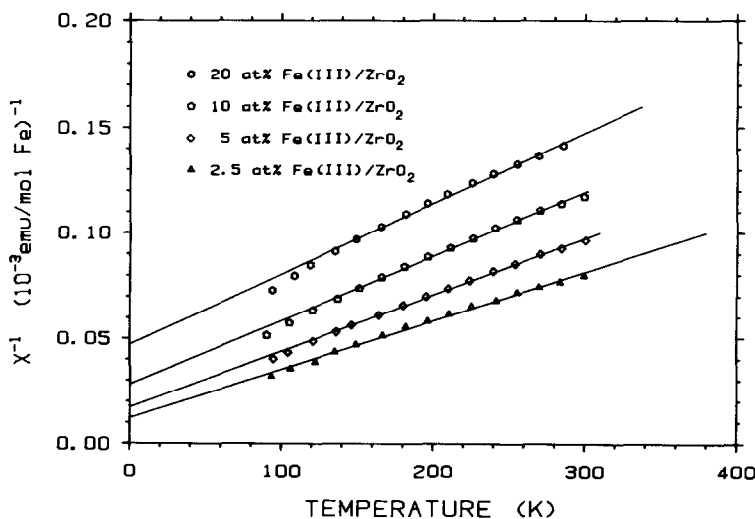


FIG. 3. Variation with temperature of the magnetic susceptibility of samples of ZrO<sub>2</sub> with 2.5, 5, 10, and 20 at% Fe(III) prepared by decomposition of the nitrates.

TABLE II  
Fe(III)/ZrO<sub>2</sub> DECOMPOSED AT 600°C

Compound at% Fe(III)/ZrO <sub>2</sub>	Parasitic ferromagnetism (bulk iron oxide)	$\mu^a$ (BM)	$\theta^a$ (K)
0 Fe(III)	None	5.90	0
2.5	None	5.89	-52
5	None	5.48	-64
10	None	5.14	-92
20	None	4.90	-145
25	Present	—	—
30	Present	—	—
40	Present	—	—
$\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	Present	5.90	-1900

<sup>a</sup> Determined from measurements above the Néel points.

approach the spin only value of 5.9 BM for Fe(III). At the lower concentrations of Fe(III) (2.5–20 at% Fe), the magnetic data indicates a tendency toward the formation of isolated iron(III) ions.

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