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Stabilization of Cubic ZrO_2 with Rh(III) and/or La(III)*

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Samples of stabilized cubic ZrO_2 were prepared containing Rh(III), La(III), and both La(III) and Rh(III). The properties of these compounds were studied by X-ray analysis and temperature-programmed reduction. These studies indicated that the cubic phase becomes stabilized with the incorporation of La(III) or Rh(III) into the ZrO_2 structure. © 1988 Academic Press, Inc.

Introduction

Supported rhodium catalysts and Rh-containing mixed catalysts have been extensively studied for the Fischer–Tropsch process, particularly for their ability to produce different distributions of oxygenated products (*1–6*). It was shown previously (*7*) that, when neutral or acidic metal oxides such as SiO_2 or Al_2O_3 were used as the support, more than 95% of the CO consumed was converted to non-oxygen-containing hydrocarbons. However, when basic metal oxide supports such as ZnO, MgO, or CaO were used, more then 95% of the CO consumed was converted to methanol (*7*). When Rh was supported on ZrO_2 or La_2O_3, ethanol and methanol were produced, although the yield was low (*8*). When $LaRhO_3$ was used as catalyst for the CO hydrogenation process, methanol, ethanol, and some other oxygenates were produced (*3, 6*).

It has been shown that, when the Rh is in an oxidation state higher than zero, oxygen-containing products are produced (*1–4, 6*). Ichikawa *et al.* used X-ray photoelectron spectroscopy measurements to show that both Rh^0 and Rh^+ were necessary for producing oxygenated products (*1, 2*). Somorjai *et al.*, using Auger electron spectra, also found that a mixture of oxidized (probably Rh^+) and reduced rhodium species were required to produce oxygenated products (*3, 4*). Monnier *et al.* studied the electronic states of rhodium in a $LaRhO_3$ catalyst by photoelectron spectra and temperature-programmed reduction (*6*), but their results were different from those of Ichikawa and Somorjai. They found that Rh^+ was absent in the active catalyst which produced the oxygenated products. Instead, they observed the presence of Rh^{3+} in the active catalyst. However, all of these studies indicate that oxidized rhodium is required for producing oxygenated products. Bulk Rh_2O_3 is not stable toward reduction by hydrogen. It reduces completely below 130°C (*9*). Watson and Somorjai (*3*)

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and Monnier and Apai (*6*) have indicated that oxidized Rh can be stabilized by incorporating rhodium ions into a stable oxide lattice such as La_2O_3. Rhodium can also be stabilized as a result of its interaction with ZrO_2 (*9, 10*). When Rh(III) is incorporated into the ZrO_2 structure to form a solid solution, the Rh^{3+} ions should be stabilized.

It is the purpose of this paper to study the Rh_2O_3 and ZrO_2 solid solution. Since La_2O_3 may have an important influence on the yield of oxygen-containing products, the interaction between La_2O_3 and ZrO_2 as well as the stabilization of cubic ZrO_2 by the introduction of both Rh(III) and La(III) in the fluorite structure should be studied.

Experimental

Samples of members of the system Rh(III)/ZrO_2 were prepared to give compositions containing 5, 10, and 15 at.% Rh(III). Calculated quantities of Rh $(NO_3)_3 \cdot 2H_2O$ and $ZrO(NO_3)_2$ (*11*) were dissolved in water. The solution then was dried at 150°C for 12 hr and predecomposed at 400°C for 24 hr in order to drive off nitrogen oxides. Decomposition of the double nitrates was not complete until 900°C (*9*); hence, the samples were heated at 900°C for 48 hr. Samples were air quenched to room temperature in order to prevent the transformation of the ZrO_2 to the monoclinic phase.

Samples of the system La(III)/ZrO_2 were prepared by double decomposition of La $(NO_3)_3$ and $ZrO(NO_3)_2$ to give compositions containing from 0 to 50 at.% La(III). The lanthanum nitrate was prepared by dissolving high-purity La_2O_3 in 8 M nitric acid and drying the product at 90°C. The molecular weight was determined by thermogravimetric analysis to be 372. Required quantities of the lanthanum nitrate and zirconyl nitrate were dissolved in water. For each gram of the total nitrates, 10 ml of water was used. The solution was dried at 150°C for 12 hr, ground, ignited at 400°C for 24 hr, and heated at 900°C for an additional 48 hr.

Ternary oxide samples of La_2O_3, Rh_2O_3, and ZrO_2 were prepared by decomposing the required mixture of rhodium nitrate, lanthanum nitrate, and zirconyl nitrate. The triple salt was decomposed by the same procedure as described above except that the samples were finally heated at 950°C for 48 hr.

Temperature-programmed decomposition of both the double salt of lanthanum nitrate and zirconyl nitrate, and the triple salt of lanthanum nitrate, rhodium 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 hr. 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 950°C at a rate of 100°C/hr.

Temperature-programmed reductions (TPR) of the rhodium-containing samples were carried out using the same balance. Before reduction was started, the sample was preheated in dry oxygen up to 800°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 700 °C at a rate of 50°C/hr.

Characterization of the Products

X-ray powder diffraction patterns of the samples were obtained using a Philips diffractometer and monochromated high-intensity Cu$K\alpha_1$ radiation (λ = 1.5405 Å). Polycrystalline samples were analyzed by X-ray diffraction. Fast scans were recorded at a speed of 1° 2θ/min and slow scans at a speed of 0.25° 2θ/min. The lattice parame-

TABLE I

Chemical composition	Phase	Cell volume (Å^3)
ZrO_2[a]	Tetragonal	133.7
5% Rh(III) in ZrO_2	Tetragonal	132.6
10% Rh(III) in ZrO_2	Pseudocubic + Rh_2O_3	130.8
15% Rh(III) ZrO_2	Pseudocubic + Rh_2O_3	130.7

[a] Prepared by decomposing $ZrO(NO_3)_2$ at 400°C (*11*).

ters 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 Rh(III)/ZrO_2 were prepared by double decomposition of $Rh(NO_3)_3 \cdot 2H_2O$ and $ZrO(NO_3)_2$. A previous study (*9*) has indicated that the nitrates decompose completely at 900°C. Therefore, the samples were heated at 900°C for 48 hr. The phases formed and the cell volumes of pure ZrO_2 as well as those containing varying amounts of rhodium are given in Table I. The X-ray patterns of 5 at.% Rh(III) in ZrO_2 can be indexed on the basis of a tetragonal cell. An increase in the concentration of Rh(III) in ZrO_2 resulted in a structural change from tetragonal to pseudocubic. This was accompanied by a decrease in the cell volume. Pure tetragonal ZrO_2 is stable below 600°C and begins to transform to a monoclinic structure above this temperature (*11*). The presence of rhodium stabilizes a pseudocubic ZrO_2 which does not transform until the temperature is greater than 900°C. It is likely that a solid solution is formed. However, there is no change in the cell volume of the pseudocubic ZrO_2, indicating a maximum solubility of at most 10 at.% Rh(III) in ZrO_2. It was decided that temperature-programmed reduction studies might be significant in demonstrating the interaction of rhodium(III) and ZrO_2 resulting from solid solution formation.

The temperature-programmed reduction studies of ZrO_2 samples containing Rh(III) are compared with the study of bulk Rh_2O_3 in Fig. 1. Pure Rh_2O_3 is reduced to rhodium metal at 90°C and this process is complete at 130°C. The reduction of 5 at.% Rh(III) in ZrO_2 begins at 220°C and is complete at 550°C. This reduction process takes place more gradually and at higher temperatures than the reduction of bulk Rh_2O_3. The initial increase in weight for the ZrO_2-samples containing Rh(III) is due to gas adsorption of ZrO_2. Both the 10 and 15 at.% Rh(III) samples show a two-step reduction process. The first step begins at about 100°C and the second at about 200°C. The reduction to rhodium metal and tetragonal ZrO_2

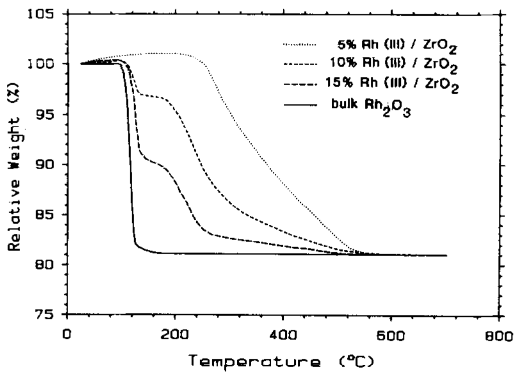

FIG. 1. Temperature-programmed reductions of Rh(III) in ZrO_2. The weight of ZrO_2 was subtracted. The initial rise in the weights of samples is due to gas adsorption on the ZrO_2.

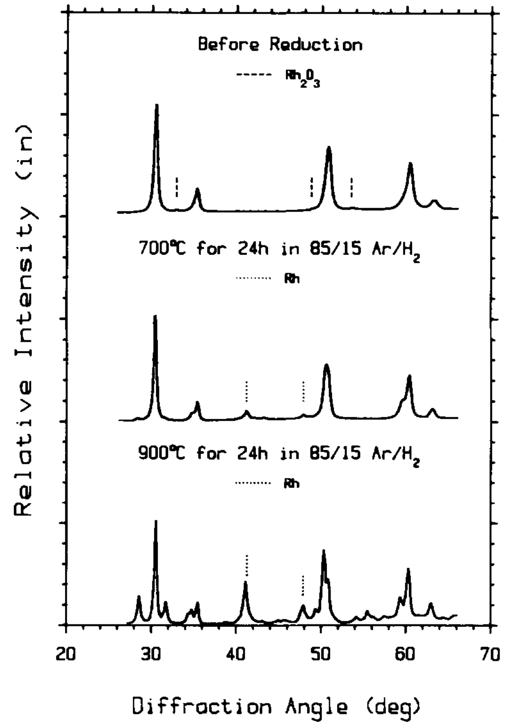

FIG. 2. X-ray diffraction patterns of ZrO_2 containing 10 at.% Rh(III) under various conditions: (top) before reduction, (middle) reduced in 85% Ar/15% H_2 at 700°C for 24 hr, (bottom) reduced in 85% Ar/15% H_2 at 900°C for 24 hr.

is complete at 550°C. The initial reduction step corresponds to the reduction of bulk Rh_2O_3. The second step corresponds to the reduction process observed for the 5 at.% sample of Rh(III) substituted into the ZrO_2 structure. From the ratio of the weight losses observed in the two-step reduction process for both 10 and 15 at.% samples, the maximum solubility of Rh(III) in ZrO_2 can be estimated to yield the composition $Rh_{0.08}Zr_{0.92}O_{1.96}$. This is consistent with the X-ray results described above.

The formation of the solid solution of Rh(III) in ZrO_2 is confirmed by X-ray analysis of the 10 at.% sample heated under various conditions (see Fig. 2). The sample heated in air at 900°C for 48 hr showed the presence of both a pseudocubic ZrO_2 phase and a hexagonal Rh_2O_3 phase. Only the Rh_2O_3 or Rh^0 peaks are identified in Fig. 2; all of the other peaks belong to the cubic, tetragonal, or mixed monoclinic tetragonal ZrO_2 system. When this sample was reduced at 700°C for 24 hr in 85% Ar/15% H_2, there was evidence for the formation of tetragonal ZrO_2. The absence of monoclinic ZrO_2 in these samples heated at 700°C compared to the formation of a monoclinic phase when bulk ZrO_2 was heated to 600°C indicated that a small percentage of the rhodium remained in the tetragonal structure, resulting in its stabilization. After heating at 900°C in 85% Ar/15% H_2 for 24 hr, the rhodium no longer remained in the structure and the ZrO_2 began to transform to the monoclinic phase.

Samples of La(III)/ZrO_2 were prepared by a procedure similar to that used for Rh(III)/ZrO_2. ZrO_2 can be stabilized either in a tetragonal or pseudocubic structure, depending upon the amount of La(III) inserted into the structure. ZrO_2 containing 4 at.% La(III) appeared to be tetragonal. When the concentration of La(III) was equal to or exceeded 10 at.% the ZrO_2 was stabilized as a pseudocubic ZrO_2 phase. The characteristic splittings of tetragonal phase formation are evident for the sample containing 4 at.% La(III). When the La(III) concentration is increased to 10 at.%, the split reflections of the tetragonal phase coalesce to form the reflections of the cubic phase.

The cell constant of the cubic ZrO_2 increases linearly with increasing La(III) insertion up to 37 at.% (Fig. 3). When the insertion of La(III) exceeds 37 at.%, there is no further increase in the cell constant and La_2O_3 reflections appear in the X-ray pattern. It is evident that La(III) may be inserted into the fluorite ZrO_2 structure, and the maximum solubility of La(III) in ZrO_2 is approximately 37 at.%. This phase may be represented by the formula $La_{0.37}Zr_{0.63}O_{1.815}$. Upon extrapolating to 0%

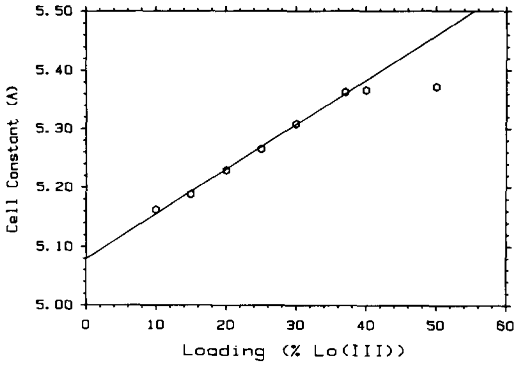

FIG. 3. Influence of La(III) loading on cell parameters of ZrO_2.

La(III), a cell constant of 5.08 Å is obtained, which is in agreement with the value of 5.09 Å given for pure ZrO_2 (*12*). When the samples were heated to temperatures above 1050°C, a pyrochlore corresponding to the composition $La_2Zr_2O_7$ was formed. Initially the cubic ZrO_2 transforms to the tetragonal phase, but above 1200°C, only the pyrochlore and monoclinic ZrO_2 remain.

Samples of ZrO_2 containing Rh(III) and La(III) were prepared by decomposing mixtures of the nitrates at 950°C for 48 hr. Temperature-programmed decomposition studies of the mixture indicated that decomposition was not complete below this temperature. The concentration of La(III) was 15 at.% for all the samples. Loading La(III) to 15 at.% was chosen because the cell parameter does not change significantly for lower concentrations and the crystallinity is poor for higher. Samples containing 5, 10, and 15 at.% Rh(III) were prepared.

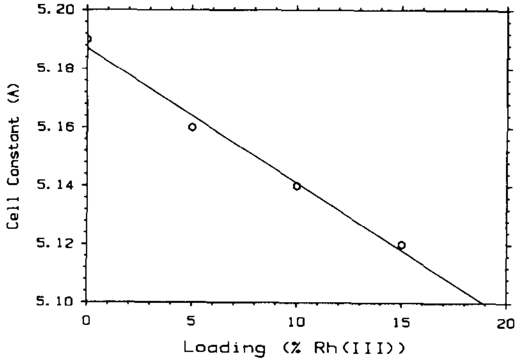

FIG. 4. Influence of Rh(III) loading on cell parameters of Rh(III)La(III)/ZrO_2 with 15 at.% La(III).

X-ray diffraction studies indicated that samples containing 5 or 10 at.% Rh(III) showed only the existence of pseudocubic ZrO_2. The sample containing 15 at.% Rh(III) consisted of pseudocubic ZrO_2 and a small amount of Rh_2O_3. The cell parameters of the Rh(III)La(III)/ZrO_2 solid solution decrease linearly with increasing Rh(III) concentration (Fig. 4), which indicates the Rh(III) is incorporated into the solid solution. It is also possible that some Rh_2O_3 can combine with La_2O_3 to form $LaRhO_3$ and that this phase might not be detected by X-ray diffraction analysis. However, temperature-programmed reduction studies can be used to detect the existence of bulk $LaRhO_3$ when the phase is not shown in X-ray diffraction patterns. Results from temperature-programmed reduction studies are shown in Fig. 5. It can be seen that ZrO_2 samples containing 5 or 10 at.% Rh(III) with 15 at.% La(III) show a one-step reduction process. For the at-

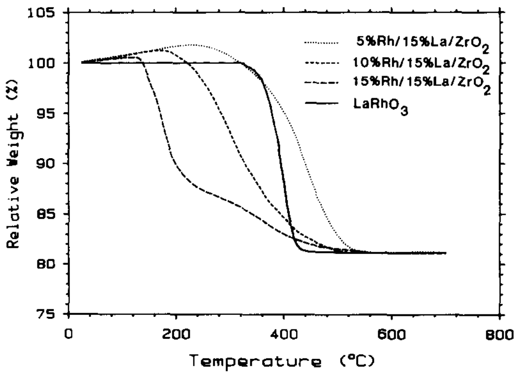

FIG. 5. Temperature-programmed reductions of Rh(III)La(III)/ZrO_2 with 15 at.% La(III) (*13*). The weight of La_2O_3 and ZrO_2 was subtracted. The initial rise in weights of samples is due to gas adsorption on the ZrO_2.

tempted substitution of 15 at.% Rh(III) in ZrO_2 with 15 at.% La(III), there is evidence for the presence of some bulk Rh_2O_3 (see Fig. 1) as well as Rh(III) stabilized in La_2O_3/ZrO_2.

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