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X-ray powder diffraction study of monoclinic V^{4+}-ZrO_2 solid solutions obtained from gels

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Abstract

Rietveld refinement of six monoclinic $V_xZr_{1-x}O_2$ solid solutions, with $x = 0$, 0.01, 0.02, 0.05, 0.075 and 0.1, prepared by heating dried gel precursors at 1300°C in air atmosphere, has been characterized using X-ray powder diffractometer data. The present results confirm that crystal structure of these solid solutions contain $V^{4+}(Zr^{4+})$ cations surrounded by seven oxygens, four at a distance between 2.13 and 2.28 Å (referred as to O(2) in the tetrahedrally coordinated oxygens) and other three at a distance between 2.03 and 2.20 Å (denoted as O(1) in the triangularly coordinated oxygens). The trends in the lattice parameter variation of $V_xZr_{1-x}O_2$ solid solutions specimens with the nominal vanadium amount are in accordance with previous results obtained by experiments measured using an internal standard.

Keywords: Sol–gel chemistry; Solid solution; X-ray powder diffraction; Crystal structure; Rietveld refinement; Ceramic pigment

1. Introduction

Materials in the ZrO_2–V_2O_5 binary system have received considerable attention because of their interesting optical and catalytic properties [1–3]. The well-known vanadium-zirconia yellow baddeleyite ceramic pigmenting system has been used for years in the ceramic industry. However, some controversial aspects of the mechanism of color formation have remained unresolved until now [4–6]. Likewise, it has been found that catalysts based on zirconia-supported vanadia are more active than vanadia dispersed on other supports in the oxidative dehydrogenation of alkanes. Efforts aimed at relating the structure of the vanadia dispersed on zirconia to its catalyst activity and selectivity suggest a strong relationship between both.

Recently, we have prepared monoclinic and tetragonal vanadium-containing zirconia solid solutions by using sol–gel techniques [7,8]. The characterization of the solid solutions by X-ray powder diffraction, and diffuse reflectance and electron spin resonance spectroscopies revealed that the chemical state of vanadium was 4+ in both solid solutions based on zirconia crystalline forms. The structural refinement of the tetragonal V^{4+}-ZrO_2 has also been recently reported, confirming the location of the V^{4+} in octa-coordinated sites in the tetragonal ZrO_2 [9]. Recently, we have reported on the ability of these synthetic monoclinic vanadium-doped zirconias to promote a decrease in the reduction potential of oxygen and hydrogen peroxide dissolved in water and a significant increase in the currents with respect to unmodified carbon electrodes [10,11].

The formation of these tetragonal and monoclinic vanadium-containing zirconia solid solutions was also detected some years ago in compositions of the SiO_2–ZrO_2–V_2O_5 system [12–14]. The preparation technique used was also the sol–gel method but gel precursors were synthesized by gelling mixtures of zirconia and vanadia colloidal solutions and tetraethylorthosilicate. The characterization of the final V^{4+}-ZrO_2 solid solutions was carried out by X-ray powder diffraction, and diffuse reflectance and electron spin resonance spectroscopies, as well as by selected area diffraction, and scanning and transmission electron microscopies.

Since the formation of monoclinic V^{4+}-containing ZrO_2 solid solutions has been well established, it seems reasonable to determine their structure and to relate

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them to their pigmenting and catalytic properties. In this respect, it would be of interest to determine the nature of the distribution of V^{4+} cations in the monoclinic ZrO_2 lattice. The results would help to understand some crystallochemical and spectroscopic aspects of the widely used vanadium-zirconia yellow baddeleyite ceramic pigmenting system.

The purpose of this work is, therefore, the Rietveld refinement of the structure of the monoclinic V^{4+}-ZrO_2 solid solutions by X-ray powder diffraction obtained on heating gels with compositions in the ZrO_2–V_2O_5 binary system.

2. Experimental procedure

Gels have been prepared following methods previously described [7,8]. Basically, gels have been obtained by gelling mixtures of vanadyl acetylacetonate ($C_{10}H_{14}O_5V$, $VO(acac)_2$) and zirconium *n*-propoxide ($Zr(OCH_3)_4$, ZnP), both from Merck. The process involved two steps. First, a solution of ZnP was added to a solution of *n*-propanol (*n*-PrOH) and acetylacetone (acacH) kept under an atmosphere of Ar. The resulting solution was held in continuous stirring, and the required stoichiometric amount of $VO(acac)_2$ was then added in order to obtain the desired V:Zr ratio in the final material. Second, to hydrolyze the above resulting solution, the required amount of water was added and the final solution was sealed in a vessel and placed in an oven at 60°C. The molar ratios of *n*-PrOH/ZnP, AcacH/ZnP and H_2O/ZnP were 8.1, 1.1, and 11.2, respectively. Gels appeared after varying amounts of time, depending on the amount of vanadium in the final solution. Six monoclinic $V_xZr_{1-x}O_2$ solid solutions, with $x = 0$, 0.01, 0.02, 0.05, 0.075 and 0.1, were prepared by heating dried gel precursors up to 1300°C at a rate of 10°C/min in an air atmosphere. Specimens were annealed at this temperature for 3 h. After annealing, the samples were cooled in air in the furnace.

For the preparation of X-ray powder diffraction specimens, the crystallized zirconia gels were ground with an agate mortar and pestle. The X-ray diffraction patterns of the powder samples were recorded using Bragg–Brentano geometry at room temperature by means of a Siemens D-500 X-ray powder diffractometer. The experimental conditions used were Cu$K\alpha$ radiation (40 kV, 20 mA, 1° divergence slit, 0.05° detector slit), scintillation detector, and a secondary graphite monochromator.

The peak positions and the integral intensities of the observed reflections were collected by step-scanning from 15° to 75° (2θ) with a step size of 0.02° (2θ) and a counting time of 10 s for each step.

The crystal structure was resolved from the integrated intensities extracted from the powder data set using the whole-pattern profile technique. Rietveld refinement was performed with FULLPROF98 [15], available in the software package WINPLOTR [16]. The refinement was started using the $P2_1/c$ space group and structure parameters derived from Smith and Newkirk [17]. The pseudo-Voight function was used for modeling diffraction profiles. Peaks below 35° (2θ) were corrected for asymmetry effects. In the final refinement the following parameters were refined: a scale factor; 2θ zero; four parameters from the background; unit cell parameters; peak profile parameters using a pseudo-Voight function; two parameters from asymmetry parameter and positional *x*-, *y*- and *z*-parameter of O and Zr(V). Due to some instabilities in atomic thermal displacement parameters above $x = 0.05$, an overall B factor was fixed (0.10 Å^2). The details of the Rietveld refinement are given in Table 1.

3. Results and discussion

On heating gel precursors at around 450°C, the first crystalline phase formed was tetragonal ZrO_2 [7,8]. An increase in temperature was required to produce the

Table 1
Crystallographic data and details of the Rietveld refinement for monoclinic V^{4+}-ZrO_2 solid solutions with nominal composition $V_xZr_{1-x}O_2$ ($x = 0$, 0.01, 0.02, 0.05, 0.075 and 0.1)

	ZrO_2	$V_{0.01}Zr_{0.99}O_2$	$V_{0.02}Zr_{0.98}O_2$	$V_{0.05}Zr_{0.95}O_2$	$V_{0.075}Zr_{0.925}O_2$	$V_{0.10}Zr_{0.90}O_2$
a (Å)	5.1510(4)	5.1451(2)	5.1441(1)	5.1435(2)	5.1447(2)	5.1432(4)
b (Å)	5.2031(4)	5.2082(2)	5.2072(1)	5.2059(2)	5.2064(2)	5.2052(4)
c (Å)	5.3151(4)	5.3139(2)	5.3147(1)	5.3143(2)	5.3156(2)	5.3138(4)
β (°)	99.197(2)	99.208(1)	99.194(1)	99.191 (1)	99.198(1)	99.200(2)
V (Å^3)	140.62(2)	140.56(1)	140.53(1)	140.47(1)	140.55(1)	140.43(2)
R_p (%)	6.41	5.16	5.38	7.73	7.00	3.91
R_{wp} (%)	8.87	7.97	7.35	10.40	9.60	4.93
R_{wp} (expected) (%)	4.59	4.89	4.85	4.75	5.21	3.78
R_B (%)	1.66	1.97	2.24	3.85	2.88	9.52
R_F (%)	3.73	2.66	2.30	4.83	3.40	7.04

tetragonal to monoclinic phase transformation. The temperature range for which the phase transformation took place was dependent on the nominal vanadium loading. Thus, as previously shown [7], the undoped monoclinic zirconia was first detected at 600°C, but the complete transformation was observed only after heating at 900°C for 24 h. In contrast, for the specimen with nominal composition $V_{0.05}Zr_{0.95}O_2$, the complete transformation to the monoclinic phase was observed at 700°C for 12 h, i.e. at lower temperatures.

The refinements for the V^{4+}-ZrO_2 solid solutions were performed on a single phase with monoclinic symmetry. No other phases were detected in all samples studied.

Table 1 displays the unit-cell parameters derived from the refinement using all the observed reflections and the structure-refined parameters. The trends in the lattice parameter variation of solid solutions specimens with the nominal vanadium amount are in agreement with previous results obtained from experiments using an internal standard [7]. It can be noted, as shown in Table 1, that the *a*-axis has the largest contraction with increasing the vanadium nominal amount in the solid solution series. However, an anomalously large lattice volume is shown for the specimen with nominal vanadium amount of $x = 0.075$. In order to understand this fact, it is interesting to look at the lattice volume variation as a function of the vanadium occupancy, obtained in the Rietveld refinement, shown in Fig. 1. As a matter of fact, the occupancy in this specimen corresponds to a low nominal amount of vanadium. Obviously, the very small increases in the amount of vanadium for successive specimens in the series of solid solutions may give rise to experimental errors in the real stoichiometry of the prepared samples. The decrease in lattice volume with increasing vanadium occupancy is consistent with a substitutional mechanism of the solid solution formation, i.e. the Zr^{4+} is replaced by V^{4+} in the seven coordinates sites of the monoclinic zirconia structure. Surprisingly, the lattice volume obtained for the specimen with nominal amount of vanadium $x = 0.1$ is strikingly small. As shown in Fig. 1, the lattice volume is in agreement with the decrease observed along the series. So, the limit of solubility of V^{4+} in monoclinic ZrO_2 would be extended at least up to nominal amounts of vanadium of $x = 0.1$. A close look at the R_B and R_F reliability factors for the specimen with $x = 0.1$ reveals a large increase compared with the values for the specimens with lower amounts of vanadium. These results indicate that the structural model put forward for this specimen does not fit the experimental results. From the above facts and in accordance with both the continuous decrease of lattice volume as the vanadium occupancy raises in the solid solutions series up to the nominal vanadium amount of $x = 0.05$ and previously reported electrochemical studies [11], it can be assumed that the limit of solubility of V^{4+} in monoclinic ZrO_2 is around $x = 0.05$.

The final Rietveld plot for the solid solution $V_{0.02}Zr_{0.98}O_2$, shown in Fig 2, is representative of all samples. Comparison of the observed and the calculated pattern for the sample displayed in the lower trace of Fig. 1 shows a good agreement in the range of diffraction angles between 15° and 75° (2θ).

The present Rietveld analysis confirms the monoclinic structure of $V_xZr_{1-x}O_2$ solid solutions obtained by thermal treatment of vanadium-containing amorphous zirconia gels.

The structure parameters of stable monoclinic V^{4+}-ZrO_2 solid solutions, i.e., final atomic positions of Zr(V), O(1) and O(2), and occupancy are given in Table 2.

Table 3 shows the Zr(V)–O interatomic distances in the six monoclinic $V_xZr_{1-x}O_2$ solid solutions. The

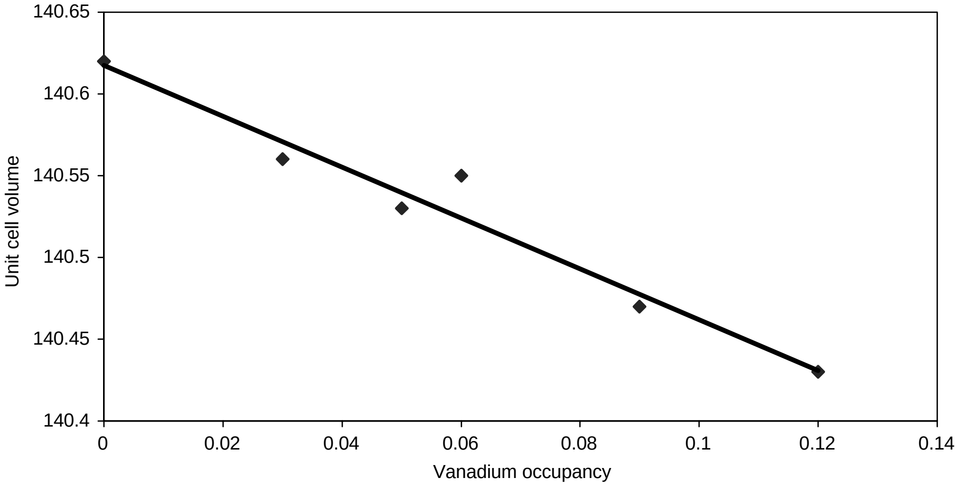

Fig. 1. Variation of the lattice volume as a function of the vanadium occupancy for monoclinic V^{4+}-ZrO_2 solid solutions with nominal composition $V_xZr_{1-x}O_2$ ($x = 0$, 0.01, 0.02, 0.05, 0.075 and 0.1).

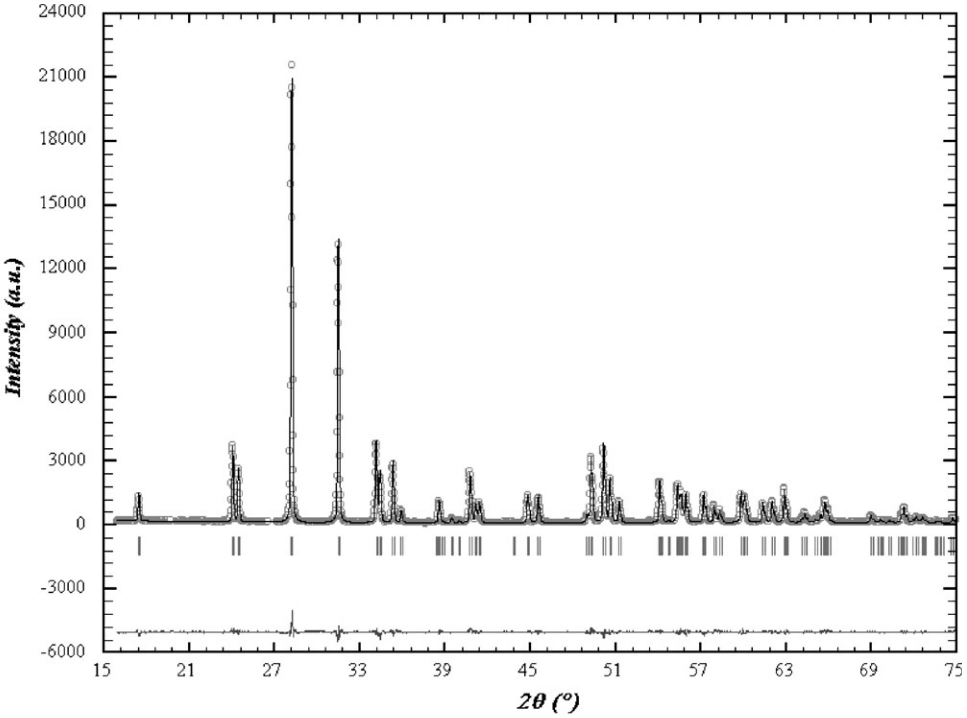

Fig. 2. Final Rietveld plot of monoclinic $V_{0.02}Zr_{0.98}O_2$. The calculated pattern is compared with observed data. The small vertical bars indicate the positions of allowed *h k l* reflections. The difference between the observed and the calculated profiles is the lower trace plotted below the diffraction pattern.

Table 2
Atomic parameters for monoclinic V^{4+}-ZrO_2 solid solutions with nominal composition $V_xZr_{1-x}O_2$ ($x = 0$, 0.01, 0.02, 0.05, 0.075 and 0.1)

		ZrO_2	$V_{0.01}Zr_{0.99}O_2$	$V_{0.02}Zr_{0.98}O_2$	$V_{0.05}Zr_{0.95}O_2$	$V_{0.075}Zr_{0.925}O_2$	$V_{0.10}Zr_{0.90}O_2$
Zr(V)	*x*	0.2744(2)	0.2751(2)	0.2750(2)	0.2757(2)	0.2752(2)	0.2752 (4)
	y	0.0394(2)	0.0405(2)	0.0405(1)	0.0406(2)	0.0403(2)	0.0401(3)
	z	0.2084(2)	0.2087(2)	0.2090(2)	0.2091(2)	0.2087(2)	0.2085(3)
O(1)	*x*	0.0614(11)	0.0671(10)	0.0711(9)	0.0624(12)	0.0582(11)	0.0699(20)
	y	0.3263(11)	0.3314(9)	0.3362(9)	0.3289(11)	0.3266(10)	0.3290(18)
	z	0.3404(11)	0.3420(19)	0.3483(9)	0.3384(11)	0.3294(10)	0.3476(19
O(2)	*x*	0.4495(12)	0.4483(10)	0.4471(9)	0.4491(12)	0.4420(11)	0.4493(21)
	y	0.7575(9)	0.7561(8)	0.7581(8)	0.7542(10)	0.7532(10)	0.7564(15)
	z	0.4757(15)	0.4766(12)	0.4771(12)	0.4817(14)	0.4725(13)	0.4738(30)
Bov (Å^2)		0.41(5)	0.46(4)	0.85(4)	0.10(fixed)	0.10(fixed)	0.10(fixed)
Occupancy	V	0	0.03(1)	0.05(1)	0.09(1)	0.06(2)	0.12(3)
	Zr	1	0.97(1)	0.95(1)	0.91(1)	0.94(2)	0.88(3)

Table 3
Selected interatomic distances (Å) in the six monoclinic $V_xZr_{1-x}O_2$ solid solutions

	ZrO_2	$V_{0.01}Zr_{0.99}O_2$	$V_{0.02}Zr_{0.98}O_2$	$V_{0.05}Zr_{0.95}O_2$	$V_{0.075}Zr_{0.925}O_2$	$V_{0.10}Zr_{0.90}O_2$
Zr (V)–O(1)	2.042(6)	2.046(5)	2.066(5)	2.042(6)	2.027(6)	2.042(10)
	2.036(6)	2.051(5)	2.054(5)	2.040(6)	2.028(6)	2.068(10)
	2.198(6)	2.173(5)	2.132(5)	2.204(6)	2.252(6)	2.147(10)
Zr (V)–O(2)	2.138(6)	2.147(6)	2.139(5)	2.169(7)	2.133(6)	2.137(12)
	2.171(6)	2.169(5)	2.181(5)	2.174(6)	2.172(6)	2.157(12)
	2.255(6)	2.248(5)	2.251(5)	2.226(6)	2.235(6)	2.257(12)
	2.280(7)	2.277(6)	2.273(6)	2.259(7)	2.314(6)	2.284(13)

Zr(V)–O distances range from 2.03 to 2.28 Å in the sevenfold coordination polyhedron of Zr(V). It should be noted that the O(1) atoms form a triangle whose plane is nearly parallel to the plane of the O(2) atoms which form a planar, square group that corresponds to one-half of a normal eightfold cubic array. It is interesting to comment on some details of the coordination configurations of the two oxygen atoms. The O(1) is only slightly shifted from the plane defined by the three Zr(V) atoms to which it is coordinated. The average distances in these triangular arrangements do not change significantly with the solid solution formation. Likewise, for the O(2) with nearly tetrahedral coordination the average distance O(2)–Zr(V) does not experience appreciable changes.

The above results prove the distribution of vanadium in vanadium-zirconia yellow baddeleyite ceramic pigmenting system. In this vanadium-zirconia solid solutions series, vanadium substitutes for Zr^{4+} in monoclinic ZrO_2. Results previously reported indicated that the chemical state of vanadium in these solid solutions is 4+ [7,8]. Therefore, the present and previous studies [7,8] answer some questions concerning the formation mechanism of this ceramic pigment, mainly those related to a structural point of view. The color of vanadium-zirconia yellow is produced by the dissolved vanadium, as V^{4+}, in monoclinic ZrO_2.

With respect to the electrocatalytic activity of monoclinic vanadium-doped zirconias in the reduction of oxygen and hydrogen peroxide [10,11], it seems to be associated with seven-coordinated vanadium centers isomorphously substituting zirconium ones in the ZrO_2 lattice. It is to be noted that tetragonal vanadium-doped zirconias and V_2O_5 remained catalytically silent. The confinement of the electrocatalytic activity to monoclinic V^{4+}-ZrO_2 denotes high selectivity.

4. Conclusion

The crystal structure of six monoclinic V^{4+}-ZrO_2 solid solutions, in the range of compositions comprising the well-known vanadium-zirconia pigmenting ceramic system, was determined by Rietveld refinement on the basis of X-ray powder diffraction data. The Rietveld analysis confirmed the monoclinic structure of $V_xZr_{1-x}O_2$ solid solutions. The present study has also confirmed that the unit cell parameters of monoclinic V^{4+}-ZrO_2 solid solutions depend on the amount of vanadium in the monoclinic ZrO_2 lattice. On the basis of the present results, it can also be concluded that the V^{4+} is located in the sevenfold coordination polyhedron.

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