Intrinsic and Extrinsic Paramagnetic Centers in Zirconia

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In the literature two intrinsic paramagnetic centers have been identified by EPR in pure zirconia: Zr^{3+} ions, yielding an axial signal ($g_{\parallel} = 1.958$ and $g_{\perp} = 1.979$) and electrons trapped in oxygen vacancies ($V_{\ddot{O}}$). In this study we investigated by quantitative-EPR pure and doped ZrO_2 heated in air and redox treated at various temperatures. In pure and in doped zirconia the axial signal has similar spectral features, including the satellite line due to the most intense component of ^{53}Cr hyperfine structure, and the signal intensity yielded the same redox trend. In doped zirconia the concentration of the species yielding the axial signal was a constant fraction (about 50%) of the total chromium content. In pure zirconia samples, the concentration determined by EPR was also about 50% of the Cr impurity level determined by GFAAS. These findings attribute this signal to the extrinsic center, Cr^{5+} ion, arising from chromium impurity. In reduced zirconia a signal of Lorentzian shape ($g = 2.002$; $\Delta H_{pp} = 4-5$ G) arises from the only intrinsic defect detected by EPR in zirconia bulk, namely $V_{\ddot{O}}$ center. This signal could easily be confused with another having the same g value, but a different line width ($\Delta H_{pp} = 0.5-1$ G) and line shape that forms in some vacuum-activated zirconia samples and arises from an extrinsic center, carbon paramagnetic impurity.

Introduction

The thermal stability and acid−base and redox properties make zirconia an interesting material.[1] A recent review has addressed the use in catalysis of zirconia, as pure oxide and as support for transition metal ions (tmi).[2] Zirconia mixed oxides are used for automotive exhaust catalysis.[3]

ZrO_2-based catalysts often operate in reducing atmosphere at temperature ≤1273 K and so that the nonstoichiometric oxide, ZrO_{2-x}, can form. After reduction in H_2 at 1173−1373 K, pure zirconia reaches a degree of nonstoichiometry, $x \leq 0.03$.[4−5] At temperatures ≤1273 K, the reduction extent depends mainly on kinetic factors, the most important being temperature, time, particle size, and texture. In reduced zirconia, the phase composition remains unchanged and anion vacancies form.[6] The released electrons can occupy the conduction band and/or intrinsic defects.

Many papers have centered on the electron paramagnetic resonance(EPR) characterization of reduced zirconia and have identified two intrinsic paramagnetic centers: (i) electrons trapped in oxygen vacancies (in Kröger-Vink notation: $V_{\ddot{O}}$) and (ii) Zr^{3+} ions in bulk or surface cationic sites.

In ZrO_2 outgassed in a vacuum at 623 K, Torralvo et al.[6] assigned a slightly asymmetric signal ($g_{\parallel} = 2.002$ and $g_{\perp} = 2.004$) to $V_{\ddot{O}}$ center, formed in the bulk during the crystallization process. After subsequent heating in air at 873 K the signal vanished and an axial signal ($g_{\parallel} = 1.956$ and $g_{\perp} = 1.981$) appeared. The investigators tentatively assigned this signal to Zr^{3+} ions, without discarding the possibility it to be due to an extrinsic center (tmi impurity).

In zirconia heated in air at temperatures less than 973 K, Matta et al.[7] found a signal at $g = 2.0018$; even though the signal formed in a non reducing atmosphere, they assigned it to $V_{\ddot{O}}$.

Studying the formation and reactivity of paramagnetic centers in a vacuum-activated ZrO_2, Morterra et al.[8] definitely assigned the axial signal ($g_{\parallel} = 1.953$ and $g_{\perp} = 1.978$, with a second component at $g = 1.975$) previously detected by Torralvo et al. to Zr^{3+} ions on the surface of monoclinic zirconia. After vacuum treatment at 870 K the signal formed and after treatment in O_2 at the same temperature its intensity appreciably increased. Although the assignment to a reduced surface state of zirconium conflicts with the increase of signal intensity in oxidizing atmosphere, several researchers accepted the assignment.[9−13]

In single crystal of yttrium- and calcium-stabilized cubic zirconia, after irradiation with X-rays or reduction in H_2 at 1370 K an axial signal having slightly different g values ($g_{\parallel} = 1.989$ and $g_{\perp} = 1.852$) was also assigned to Zr^{3+} species.[14−15] Studying yttrium-stabilized zirconia doped with titanium, Merino et al.[16] rejected this assignment because the intensity of the axial signal correlated with the titanium concentration, thus indicating that the signal arose from a Ti^{3+} extrinsic center.

In the reoxidation process of reduced zirconia by oxygen adsorption at room temperature (RT), the superoxide ion (O_2^-) adsorbed on surface Zr^{4+} cation ($g_{zz} = 2.0336$, $g_{yy} = 2.0096$, and $g_{xx} = 2.0034$) formed.[10,17−18] When the oxygen was adsorbed at 423 K, the O_2^- concentration strongly increased (more than 25 times), suggesting that the zirconia oxidation is an activated process.[10]

To find out what intrinsic or extrinsic paramagnetic centers form in bulk or on the surface of zirconia, in this study we investigated by EPR pure zirconia and doped ZrO_2 heated in air and redox treated at various temperatures.

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Experimental Section

Sample Preparation and Treatments. To prepare samples of pure zirconia, we used hydrous zirconium oxide obtained from MEL Chemicals (code no. XZ0631/01) or prepared in our laboratory by precipitation from solutions of $ZrOCl_2 \cdot 8H_2O$ (Fluka, code n*o*. 96609) with ammonia, as previously described.[19] Both the precursors were dried at 383 K for 24 h and ground. The specimens from the MEL precursor are designated as Z(T)M and the others as Z(T)A, where *T* is the temperature of the final heating in air.

Two series of doped zirconia samples were prepared: the first contained all the tmi tested (Cr, Fe, Cu, Mn, and V) at 100 ppm level for each ion; the second ones contained chromium ion alone at very low concentrations (2, 5, and 10 ppm). The tmi-doped zirconia was prepared by wet impregnation at pH 2 (fixed by nitric acid) of Z(383)M with an aqueous solution of $(NH_4)_2Cr_2O_7$, $Fe(NO_3)_3 \cdot 6H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$, $Mn(NO_3)_2 \cdot 4H_2O$, and NH_4VO_3. All reactants were purchased from Carlo Erba (R. P. E.). The relative amounts of solid and solution and the solution concentration were calculated so that the final zirconia sample contained 100 ppm by weight of each tmi. After impregnation the solid was dried at 383 K for 24 h and ground. The specimens are designated as ZMe(T).

Three Cr-doped zirconia samples, containing 2, 5 and 10 ppm by weight of Cr were prepared by wet impregnation at pH 2 (fixed by nitric acid) of Z(383)M with an aqueous solution of Cr^{3+} (1.00 μg/mL). This solution was obtained by dilution of a Cr^{3+} standard solution (1.000 mg/mL, Fluka). To avoid contamination, particular care was taken in the preparation by using pure reagents (ultrapure H_2O from Milli-Q, Millipore and HNO_3 Suprapure, Merck). After impregnation the solid was dried at 383 K for 24 h, ground and calcined at 823 K for 5h.The specimens are designated as ZC(823)*x*, where *x* indicates the chromium content expressed in ppm.

After preparation, pure zirconia and tmi-doped zirconia specimens were heated in air at various temperatures (823−1273 K). The Z(383)A, Z(823)A, Z(383)M, Z(823)M, and ZMe-(823) samples were redox treated at increasing temperatures up to 1073 K.

For the redox treatments, the samples (about 0.5 g) were placed in a silica reactor equipped with a side EPR tube and connected to a circulating all-glass apparatus, described elsewhere.[19] The redox treatments consisted of vacuum activation at 773 K for 1 h; heating in O_2 (5−10 kPa) at 773 K; reduction in H_2 (5−10 kPa) at 573−1073 K; and reoxidation in O_2 (5−10 kPa) at RT, 773 or 873 K. In samples dried at 383 K, to control the gas desorption, the temperature of vacuum activation was raised slowly (for 6 h). All treatments in gas atmosphere were stopped after about 1.5 h, when monitoring showed that pressure remained appreciably unchanged ($\pm$5 Pa). Samples were then evacuated at the treatment temperature for 30 min at about 10^{-2} Pa.

The degree of nonstoichiometry in ZrO_{2-x} was calculated from O_2 and H_2 moles reacted per gram of ZrO_2 (n_{O_2} and n_{H_2}) by the equation: $x = 123(2n_{O_2} + n_{H_2})/2$, where 123 is the molecular weight of zirconia.

Characterization Techniques. *Chromium Analysis*. A weighted amount ($\sim$0.5 g) of Z(823)A and Z(823)M samples was dissolved in 5 mL of concentrated (40%) HF solution (Suprapure Merck) at 353 K. The Z(823)A solution was diluted with ultrapure H_2O (Milli-Q, Millipore) up to the final volume of 100 mL and the Z(823)M solution up to the final volume of 50 mL. The blanks of HF solution were prepared with the same reagents and concentration used for pure zirconia samples. To determine the chromium impurity a Perkin-Elmer AAnalyst 800 graphite furnace atomic absorption spectrometer (GFAAS) was used for absorbance measurements at 357.9 nm wavelength.

Surface Areas. BET surface areas (SA/m^{2}g^{-1}) were measured by N_2 adsorption at 77 K.

XRD Measurements. After thermal treatment in air, the pure and tmi-doped zirconia samples were analyzed by XRD with a Philips PW 1729 diffractometer (Cu Kα, Ni-filtered radiation) equipped with an IBM computer (software APD-Philips).

EPR Measurements. The EPR measurements were recorded at RT and at 77 K on a Varian E-9 spectrometer (X-band), equipped with an on-line computer for data treatment and spectra calculation (program SIM14A[20]).

The absolute concentration of the paramagnetic species was determined from the integrated area of the spectra recorded at RT, using as standard the Varian strong pitch (5 $\times$ 10^{15} spin/cm). This secondary standard was accurately calibrated by a series of primary standards.[21] The standard and the samples, as powder, were placed in the EPR silica tube (i.d. 3 mm) in a weighed amount to fill the resonant cavity completely in order to have "full length geometry". In these conditions the numbers of spins/cm N of two samples *a* and *b* are related by the equation:

$$N_a = N_b \frac{g_b}{g_a} \frac{S_b(S_b + 1)A_a}{S_a(S_a + 1)A_b} \tag{1}$$

where *A* values are the integrated areas normalized for the instrumental conditions, *g* the average *g*-values, and *S* the spin. N_a was then divided by the linear density (g/cm) of the sample in the EPR tube to yield the concentration of paramagnetic species (spin/g). This value was then converted in the units reported in Table 1 and Table 2 and Figure 3. The *g* values were determined taking as reference the sharp peak at *g* = 2.0008 of the E$'_1$ center (marked with an asterisk in Figure 2a); the center was formed by UV irradiation of one of the silica dewars used as sample holder.[21]

Results and Discussion

Tmi-Doped Zirconia. *EPR Signals of Transition Metal Ions.* In ZMe samples no signal was detected from V^{4+} species.[22]

The EPR spectrum of the ZMe as prepared sample, ZMe-(383), consisted of a very weak signal (*g* = 4.3) due to Fe^{3+} ions (spectrum not reported).[9] Heating in air up to 1073 K markedly increased Fe^{3+} and caused the appearance of a strong axial signal (g$_{||}$ = 1.958 and g$_\perp$ = 1.979) and of a weaker signal at g$_\perp$ = 2.05 with a broad absorption at g$_{||}$ = 2.3, more evident in the spectrum recorded at 77 K (Figure 1a). On the basis of literature data we assign the first signal to Cr^{5+} ions[23,24] and the second one to Cu^{2+} ions.[25] The broadness of Cu^{2+} g$_{||}$ region is mainly due to the presence of several species with slightly different g$_{||}$ and A$_{||}$ parameters.

In ZMe(823) sample reduced in H_2 up to 1073 K, the Cu^{2+} signal vanished, the Fe^{3+} and Cr^{5+} signals attenuated, and a complex hyperfine structure of manganese appeared (Figure 1b). Because the hyperfine structure formed in a reducing atmosphere, we assign it to Mn^{2+} species. To analyze this complex structure and identify the site of Mn^{2+} species, we are investigating zirconia doped with a higher manganese content.

In ZMe(823) sample oxidized in O_2 at 773 K, the Cr^{5+} signal became sharper, clearly showing a small absorption-like peak at *g* = 1.997 due to most intense component of the hyperfine structure of ^{53}Cr (isotopic abundance 9.5%) (compare Figure 2a,b).

In reduced in H_2 ZMe samples, reoxidation by O_2 exposure at RT yielded the O_2^- species adsorbed on Zr^{4+} surface cation (spectrum not reported, $g_{zz} = 2.032$, $g_{yy} = 2.010$, and $g_{xx} = 2.003$).

Signal Intensity and Concentration of Paramagnetic Ions. The height of the most intense peak in first derivative spectrum was used to evaluate the signal intensity of the paramagnetic ions. Owing to the spectral features, the only signals that yielded an integrated area reliable to calculate the absolute concentration by eq 1 were those of Cr^{5+} and O_2^- species. After adsorption of O_2 at RT, in samples reduced in H_2 at increasing temperature the surface concentration of superoxide ion increased (6.0×10^{14} spin/m^2 in the sample reduced at 773 K and 24×10^{14} spin/m^2 in that reduced at 1073 K). Table 1 lists the signal intensity of the paramagnetic ions and the Cr^{5+} concentration in tmi-doped zirconia samples calcined at various temperatures and in ZMe(823) sample after redox treatments at increasing temperature.

TABLE 1: EPR Signal Intensity of Paramagnetic Ions and Cr^{5+} Concentrations in ZMe Samples after Heating in Air and Redox Treatments at Various Temperatures

| sample	treatment	Cr^{5+} ppm	Cr^{5+} h^a	Fe^{3+} h^a	Cu^{2+} h^a	Mn^{2+} h^a
ZMe(383)				0.1		
ZMe(823)		53	102	2.5	5.8	
ZMe(973)		37	63	2.6	5.9	
ZMe(1273)		24	41	1.7	4.4	
	O_2 773 K	43	201	2.5	4.8	
	H_2 573 K	24	116	2.2	3.4	2.5
ZMe(823)	H_2 773 K	8	50	2.0		5.4
	O_2 773 K	30	140	2.5	5.0	
	H_2 1073 K	3	14	0.7		6.8

^{a} In the first derivative EPR signal recorded at RT, the h value is the height (normalized for instrumental conditions) of the most intense component ($g_\perp = 1.978$ for Cr^{5+}, $g = 4.3$ for Fe^{3+}, and $g_\perp = 2.053$ for Cu^{2+} and the first line at low field of the hyperfine structure for Mn^{2+}).

At temperatures from 823 to 1273 K, the Fe^{3+} and Cu^{2+} signal intensities scarcely depended on the calcination temperature, whereas after heating in air at 1273 K Cr^{5+} concentration was more than halved. In the ZMe(823) sample reduced in H_2 up to 1073 K, the Cr^{5+} concentration and the intensity of Fe^{3+} and Cu^{2+} signals decreased, whereas that of Mn^{2+} increased. The order of tmi reducibility was: $Fe^{3+} < Cr^{5+} < Cu^{2+}$. After H_2 treatment at 773 K, reoxidation at the same temperature restored the initial intensities, indicating that the reductions were reversible. The highest concentration of Cr^{5+} ion measured corresponded to about 50% of the nominal chromium content. These data are essentially in agreement with that measured in ZMe and with the result previously found in diluted ($Cr \leq 0.3$ wt %) CrO_x/ZrO_2.[23] In ref 23 we showed by chemical titration that in the oxidized samples the Cr ions were present in the oxidation states 5+ and 6+ at about the same concentration. After H_2 treatments the Cr^{5+} concentration decreased to 56% at 573 K, 19% at 773 K and to 7% at 1073 K.

Assuming that a signal can be unambiguously assigned when its intensity is at least five times the background noise level, from the highest value of the height of most intense peak in first derivative spectrum we evaluated the EPR detection limit of each paramagnetic ion. The Cr^{5+} ion yielded by far the lowest detection limit (0.1 ppm vs 10 ppm for Fe^{3+}, Cu^{2+}, and Mn^{2+}); that is, it had the highest EPR sensitivity. Furthermore, of the d^1 ions investigated by EPR in zirconia matrix (V^{4+},[22] Cr^{5+},[23-24] Mo^{5+},[26] and W^{5+} [9]) Cr^{5+} alone forms without reducing treatment. In ZrO_2-based catalysts heated in air or in oxygen, these
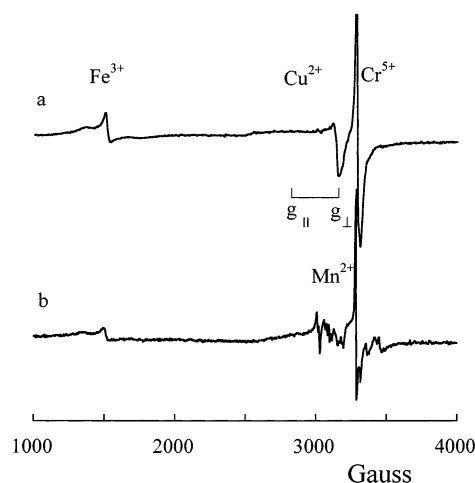
Figure 1. EPR spectra recorded at 77 of tmi-doped zirconia samples. ZMe(823) (a) and ZMe(823) reduced in H_2 at 773 K (b).
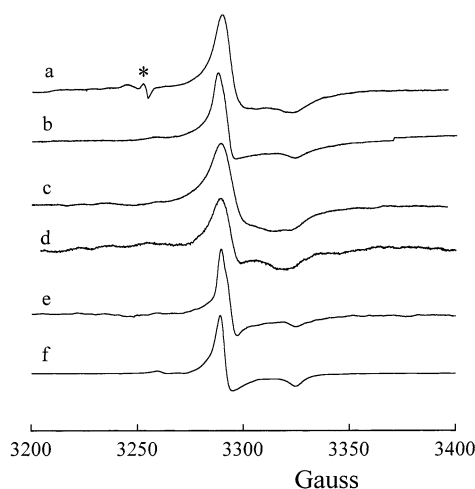
Figure 2. EPR spectra recorded at RT of doped and pure zirconia samples. ZMe(823) (a), ZMe(823) heated in O_2 at 773 K (b), ZC(823)5 (c); Z(823)A (d), Z(823)A heated in O_2 at 773 K (e), and calculated spectrum (see text) (f). The asterisk indicates the marker at $g = 2.0008$.

features often make it easy to detect the Cr^{5+} signal arising from chromium impurity.

Cr-Doped Zirconia. The spectra of ZC(823) samples consisted of two weak signals: the first one at $g = 4.3$ due to Fe^{3+}, and the second one having shape and g values similar to that of Cr^{5+} detected in ZMe sample (compare Figure 2a,c).

The absolute concentration, evaluated from the integrated area of the axial signal by eq 1, increased proportionally to the Cr content (Figure 3). In all samples the concentration corresponded to about 50% of the total chromium content, essentially in agreement with that measured in ZMe (see Table 1) and with our previous results.[23]

Pure Zirconia. *Chromium Impurity Level.* The Cr concentration determined by GFAAS was $2,0 \pm 0.1$ ppm in Z(823)A and 0.7 ± 0.1 ppm in Z(823)M. In pure zirconia prepared in our lab, the Cr impurity probably arises from $ZrOCl_2 \cdot 8H_2O$ analytical reagent grade, having a Cr impurity level ≤ 5 ppm, as certified by the manufacturer.

Surface Area. Pure and tmi-doped zirconia samples had similar surface areas. Samples slowly decomposed in a vacuum up to 773 K had the highest surface area (82 m^2/g). Heating at increasing temperature decreased the surface area: 60 m^2/g at 773 K, 29 m^2/g at 973 K, 22 m^2/g at 1073 K, and 14 m^2/g at 1273 K.

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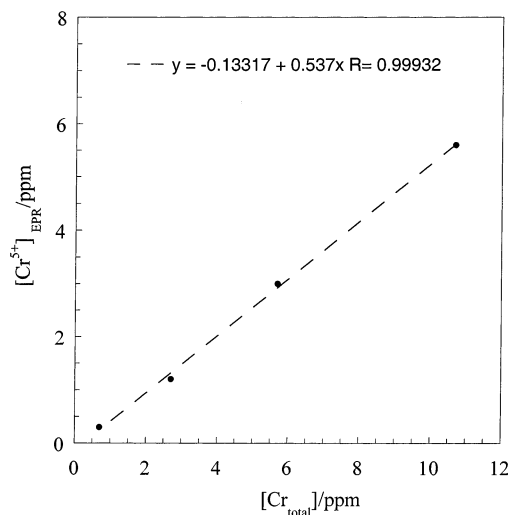
Figure 3. Cr^{5+} absolute concentration evaluated by EPR vs total Cr content in Z(823)M and ZC(823). The total Cr content corresponds to the Cr added plus the Cr present as impurity.

Figure 4. EPR spectra recorded at RT of pure zirconia samples. Z(823)A reduced in H_2 at 1073 K (a) and Z(383)A outgassed at 773 K (b).

XRD Characterization. After heating in air, pure zirconia samples showed the reflection lines of the tetragonal (101, $2\vartheta = 30.2°$) and monoclinic (111, $2\vartheta = 28.2°$; $11\bar{1}$, $2\vartheta = 31.5°$) ZrO_2 phases. The phase composition of the samples was calculated by the method of Toraya et al.[27] Raising the calcination temperature decreased the tetragonal phase (20−40% at 823 K, 0−15% at 973 K, and absent at 1273 K).

Pure zirconia and tmi-doped zirconia samples yielded the same results, indicating that the low content of tmi did not stabilize the tetragonal phase.[19]

EPR Signals. The Z(823)A and Z(823)M samples show the same axial signal detected in ZC(823) and ZMe(823) sample (compare Figure 2a,c,d). After heating the Z(823)A in O_2 at 773 K, the signal detected in Z(823)A had identical spectral features to those detected in ZMe (compare Figures 2b,e). Yet whereas the ZMe spectrum immediately showed the satellite line at $g = 1.997$, for the Z(823)A spectrum, at least 10 accumulations were required. The satellite, though very small, is also seen in the spectrum in Figure 3 of ref 8, assigned to Zr^{3+}. Figure 2f shows the spectrum computer calculated using the following spin-Hamiltonian parameters: ^{52}Cr $g_{||} = 1.958$, $g_{\perp} = 1.979$, and ^{53}Cr (abundance of 0.095) with additional hyperfine terms $A_{||} = 42$ G and $A_{\perp} = 16$ G. These parameters are typical of six coordinate Cr^{5+} species in square pyramidal configuration.[23−24]

In addition, further spectroscopic evidence, arising from the comparison between the g values reported for d^1 ions in zirconia matrix, excludes the assignment to Zr^{3+}. As the spin−orbit coupling parameter, λ, increases progressively from $3d^1$ to $5d^1$ ions, the g values increasingly deviate from g_e. It is unlikely that the two paramagnetic species, Cr^{5+} and Zr^{3+}, having the same spectral features (line shape, line width) and relaxation times, but different λ, would have the same g values.

O_2 adsorption at RT left the axial signal appreciably unchanged, indicating that few Cr^{5+} species are exposed on the surface, and gave the signal of O_2^- species adsorbed on Zr^{4+} surface cation (spectrum not reported).

After the treatment in H_2 up to 1073 K, the spectra of all the redox treated samples showed a signal ($g = 2.002$; $\Delta H_{pp} = 4−5$ G) of Lorentzian line shape ($\Delta H_{1/2}/\Delta H_{pp} = 1.73$), due to $V_{\ddot{O}}$ (Figure 4a).

After the initial vacuum activation at 773 K, the Z(383)A sample alone yielded a signal having the same g value of $V_{\ddot{O}}$,
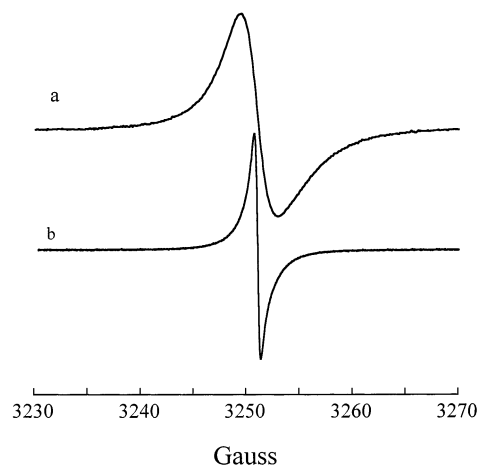
but with a different line width ($\Delta H_{pp} = 0.5−1$ G) and line shape ($\Delta H_{1/2}/\Delta H_{pp} = 3$) (Figure 4b). This signal was reversibly broadened by adsorption of O_2 at RT. In fact, in the presence of gaseous oxygen, its line width increased (4−5 vs 0.5 G) and the peak markedly decreased in height (170 vs 2700 arbitrary units), while the integrated area remained practically unchanged. After evacuation at RT the initial conditions were largely restored and a small amount of O_2^- species formed, indicating that the center is a surface species. By contrast, heating in O_2 at 773 K almost completely destroyed the signal and during the treatment in the circulation apparatus, the O_2 pressure markedly decreased, indicating a remarkable consumption of oxygen. The subsequent vacuum activation at 773 K yielded only a weak and broader ($\Delta H_{pp} = 1.4$ G) signal. During the O_2 treatment a gaseous fraction was condensed in the trap kept at 77 K. After O_2 evacuation, raising the trap temperature to 195 K evaporated this fraction, suggesting that the gas was CO_2. Carbon dioxide can be produced by the oxidation of organic material present as contaminant in the hydrous zirconium oxide precursor prepared in our laboratory. The organic contaminant probably arose from the filter paper used in the filtering and drying treatments. We therefore assign the sharp signal ($g = 2.002$; $\Delta H_{pp}=0.5−1$ G) to surface paramagnetic carbon particles. Indeed this center is the same we use as standard, Varian strong pitch. This center has been frequently observed after decomposition under vacuum of organic materials.[28] Our results suggest that the sharp signal at $g = 2.002$ detected in zirconia after vacuum activations at low temperatures (623−1073 K) and assigned to $V_{\ddot{O}}$ center[6−7,29] or after n-alkanes catalytic activation and assigned to organic radicals[9] arises from carbon impurity.

After O_2 treatment at 873 K, the carbon impurity on the Z(383)A surface was completely oxidized and the subsequent redox treatments yielded the same paramagnetic species as did the other zirconia samples.

The Concentration of Paramagnetic Species. After calcination in air at 823 K, the Cr^{5+} concentration evaluated by EPR was 0.8 ppm in Z(823)A and 0.3 ppm in Z(823)M. These amounts, equivalent to about 50% of the analytical Cr impurity level, are in agreement with those found in ZC(823) and ZMe(823).

After redox treatments at increasing temperature the Z(383)M and Z(823)M samples gave about the same concentration of the paramagnetic species formed in Z(823)A (Table 2), but a lower Cr^{5+} concentration (about one-third). In Z(823)A the Cr^{5+} species showed the same reducibility trend found in ZMe

sample: the concentration in oxidized sample (0.70 ppm) decreased to 21% after H_2 treatment at 773 K, 14% at 873 K and became lower than detection limit at 1073 K (<0.1 ppm). After H_2 treatments at 773 K, full reversibility was achieved by heating in O_2 at 873 K.

TABLE 2: Concentration of Paramagnetic Species Detected by EPR, Amount of H_2 and O_2 Reacted, and Degree of Nonstoichiometry in the Z(823)A Sample after Redox Treatments at Various Temperatures

treatment	Cr^{5+} ppm[a]	V_O', mol/g $\times10^9$	O_2^- mol/g $\times10^9$	O_2^- spin/m² $\times10^{14}$	H_2, mol/g $\times10^6$	O_2, mol/g $\times10^6$	ZrO_{2-x}, x $\times10^3$
O_2 773 K	0.70	-	-	-			
H_2 773 K	0.15	0.4			7.3		0.9
O_2 RT	0.35		33	3.8		1.9	
O_2 873 K	0.75	-	-	-		1.8	
H_2 873 K	0.12	1.3	-	-	34.2		4.5
O_2 RT	0.20		33	3.8		3.3	
O_2 873 K	0.50					16.7	
H_2 973 K	0.10	2.4	-	-	66.3		7.4
O_2 RT	0.25		30	5.8		3.0	
O_2 873 K	0.5					23.8	
H_2 1073 K	-	5.4	-	-	70.0		8.4
O_2 RT	0.1	5.4	23	7.3		1.6	
Air RT	-	5.0	-	-			

[a] 1 ppm of Cr^{5+} corresponds to 18.9×10^{-9} mol/g.

After reduction in H_2 at increasing temperature up to 1073 K, the surface concentration of O_2^- formed by the subsequent O_2 exposure at RT increased from 3.8 to 7.3×10^{14} spin/m². The concentration of superoxide ion in pure zirconia was about 3 times lower than that measured in ZMe reduced at the same temperature. These results indicate that the concentration of the donor surface centers able to form O_2^- species increased with the reduction temperature and suggest a role of tmi in superoxide formation.

For O_2 adsorption and O_2^- formation we tested two temperatures (RT and 423 K). From RT to 423 K, the superoxide concentration increased about twice (data not reported in Table 2), showing that its formation is an activated process, but less pronounced than that previously reported.[10]

After reduction in H_2 at increasing temperature up to 1073 K, the concentration of V_O center increased from 0.4 to 5.4×10^{-9} mol g^{-1}. Whereas air exposure at RT destroyed the O_2^- signal, it left V_O unaffected, confirming that this center is a bulk defect.

The Degree of Nonstoichiometry. The amounts of oxygen adsorbed during the reoxidation treatments at 873 K were one-half ($\pm20\%$) of the hydrogen consumed in the reduction treatments at increasing temperature (Table 2). Reduction in H_2 up to 1073 K yielded a low degree of nonstoichiometry in ZrO_{2-x} ($x < 0.01$).

A large part of the O_2 adsorbed at RT ($\sim50\%$) was reversible, that is, was pumped off by evacuation at RT. The concentration of the O_2^- species represented always a small fraction of the O_2 irreversibly adsorbed at RT (compare column 7 with 4), suggesting a large formation of diamagnetic species (O_2^{2-} and O^{2-}). After redox treatments at temperatures higher than 773 K, the O_2 adsorbed at RT was less than 20% of that reacted at 873 K.

In all reduction steps, the amount of H_2 reacted was at least 4 orders of magnitude higher than the V_O concentrations (compare column 6 with 3). This means that most of the electrons released in the reduction at high temperature—a process

that leads to the formation of nonstoichiometric oxide, ZrO_{2-x}—occupy the conduction band and are EPR silent.

Conclusion

We conclude that the EPR axial signal ($g_\parallel = 1.953$ and $g_\perp = 1.978$), detected in zirconia activated in a vacuum or in oxygen cannot be assigned to the intrinsic center, Zr^{3+} ion. In pure and in doped zirconia the axial signal has similar spectral features, including the satellite line due to the most intense component of ^{53}Cr hyperfine structure, and the signal intensity yielded the same redox trend. In Cr-doped zirconia the concentration of the species yielding the axial signal was a constant fraction (about 50%) of the total chromium content. In pure zirconia samples, the concentration determined by EPR was also about 50% of the Cr impurity level determined by GFAAS. Compared with the other tmi investigated, Cr^{5+} has the lowest EPR detection limit in ZrO_2 matrix and it forms without reducing treatment. After the usual thermal treatment in air or in oxygen, even samples having low Cr impurity level therefore give a detectable Cr^{5+} signal. These findings attribute this signal to the extrinsic center, Cr^{5+} ion, arising from chromium impurity.

In reduced zirconia a signal of Lorentzian shape ($g=2.002$; $\Delta H_{pp}=4-5$ G) arises from the only intrinsic defect present in zirconia bulk, namely, V_O center. This signal could easily be confused with another having the same g value, but a different line width ($\Delta H_{pp} = 0.5-1$ G) and line shape, which forms in some vacuum-activated zirconia samples and arises from an extrinsic center, carbon paramagnetic impurity.

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