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Crystallization Behavior of Zirconium Oxide Gels

Zirconia is of interest as a potentially useful catalyst support (see, for example, Iizuka *et al.* (*1*)). We report here part of our work concerning the characteristics of the zirconium oxides obtained from zirconia gels under different conditions in an attempt to understand more clearly the reasons leading to the formation of different crystalline phases.

Zirconia gel samples were prepared by precipitation with ammonia from a "zirconyl salt" solution: sample A′ was obtained from zirconyl oxychloride and sample B′ from zirconium nitrate. The resulting voluminous gels were dried in air at 110°C giving samples A and B, respectively. Portions of these two samples were treated under different conditions as indicated in Fig. 1.

Both A and B materials were gel-like and amorphous to X-ray diffraction. However, diffraction data for samples A(400) and A(500) indicated the presence of a crystalline solid that could be indexed on the tetragonal cell (*2*). On the other hand, sample A(800) was a two-phase mixture of the tetragonal (T) and monoclinic (M) ZrO_2 forms (*3*) (Fig. 2). The presence of only one diffraction line of the M form indicates that the T phase largely predominates. The A(800) sample was black and the TG curve of this sample performed in air showed a small weight gain which on the DTA curve appeared as an exothermic effect; simultaneously, as previously observed by Livage *et al.* (*4*), the sample became white. A two-phase mixture was also observed for samples AA(600) and AA(800) but the amount of the M form progressively increased until for the AA(1000) sample only the monoclinic phase was present.

In the case of the B samples (Fig. 1b), no crystalline material was observed by outgassing at 350°C for less than 30 h. After heating this sample for 30 to 70 h the T phase appeared and the sample was the more crystalline the longer the treatment, i.e., the diffraction maxima became narrower and their intensity increased with the length of the treatment at 350°C under vacuum. These facts and the results obtained in a DSC study of these samples (Fig. 3) seem to indicate that the crystallization process is reflected in the glow exotherm (glow phenomenon (*5*)) and also that, under the isothermal conditions, this crystallization occurs gradually.

The EPR spectra of the starting hydrated gels showed no signal. When sample A was heated in air at 400°C a slightly axial signal (A) with low intensity and $g_\perp = 2.004$, $g_\parallel = 2.002$ was observed. After a treatment in air at 500°C, this signal disappeared. However, after outgassing sample A at 400°C (A(400)) signal (A) appeared with a larger intensity. The height of this signal increased somewhat in the sample A(500) and grew more than 1 order of magnitude for A(800). After a treatment of this last sample in air at 600°C (A(600)) the intensity of the signal was reduced sharply, but two new signals with axial symmetry were observed namely, signal (B) with $g_\perp = 1.981$ and $g_\parallel = 1.956$ and signal (C) with $g_\perp = 2.012$ and $g_\parallel = 2.004$. For sample AA(800) signal (A) had disappeared while signals (B) and (C) maintained their intensities. The spectra of AA(1000) only showed signal (B).

A detailed study of the initial development of the EPR signals has been made with the BO.1-B70 samples. Sample B′, which after treatment at 110°C did not

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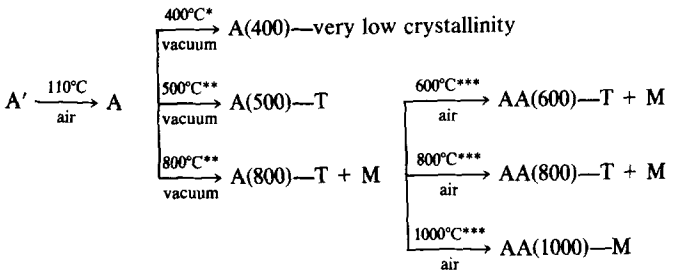
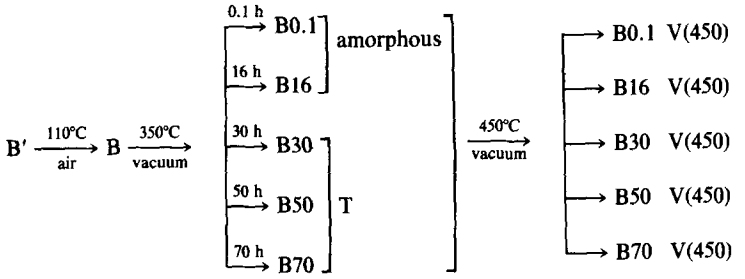


(a)



(b)

T—Tetragonal
M—Monoclinic

* These treatments were performed for 2 h.
** These treatments were performed for 10 min.
*** These treatments were performed for 6 h.

FIG. 1. Schematic representation of the preparative routes for different samples of zirconia.

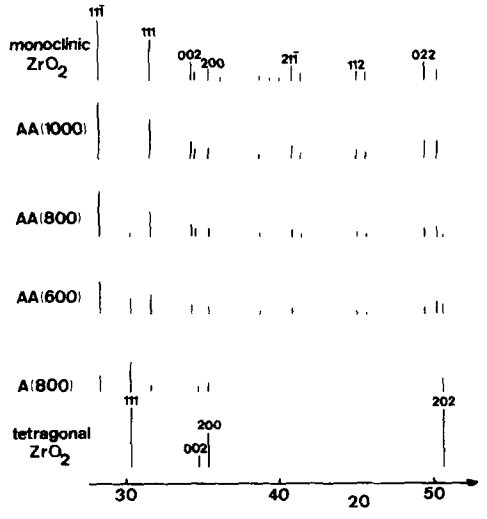


FIG. 2. Crystalline phases present in samples of the A series.

present any signal, when treated at 350°C under vacuum showed both (A) and (B) signals and their intensities changed with the heating time in the way shown in Fig. 4. Initially both signals grew in intensity but after 50 h signal (A) increased markedly while signal (B) decreased. Heating at even higher temperature enhanced this.

The three signals must be related to paramagnetic species in the bulk of ZrO_2, because they are not affected by the presence of oxygen in the gas phase at room temperature. Considering that the g values of signals (A) and (C) are close to g_e, their origin can be related to defects in the solid. Although signal (A) is not too different from the one usually observed for carbonaceous species, the line anisotropy and g-values, the synthesis conditions and its formation

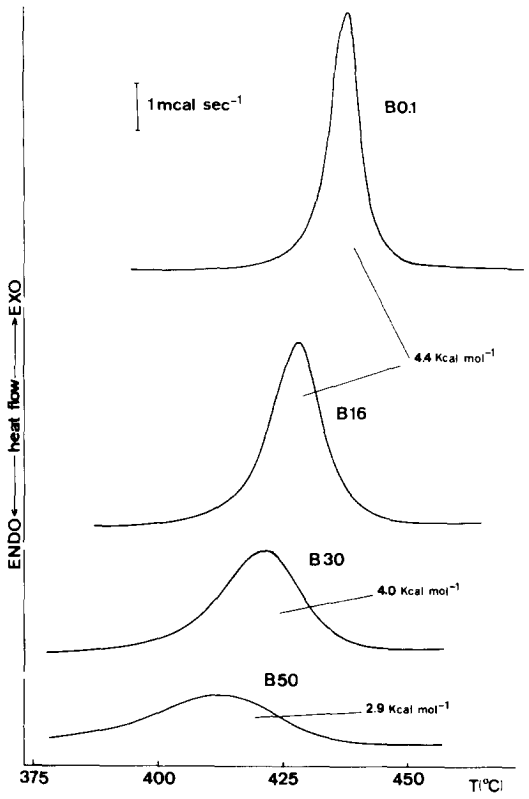


FIG. 3. DSC traces of samples of the B series.

even while treating the sample A under oxygen do not support that interpretation. As this signal appears when the glow is starting to take place, we rather assign it to trapped electrons in oxygen vacancies formed during the crystallization process. Probably the presence of these centers gives rise to the darkening of the sample. Signal (C) is only observed during the process of reoxidation and has $\langle g \rangle$ greater than g_e; both facts support the assignation of this signal to some kind of paramagnetic oxygen center. On the other hand, signal (B), with $\langle g \rangle$ much lower than g_e, is probably due to transition element ions with less than five *d*-electrons. In the present case, considering its presence in samples prepared using different materials, it can be assigned to Zr^{3+} ions, but the possibility of it being due to an impurity cannot be discarded.

A comparison of the information obtained by EPR and X-ray diffraction of the vacuum-treated samples and their reoxidation suggests that there exists a certain parallelism between the presence of electrons trapped in oxygen vacancies (signal (A)) and the formation of the tetragonal phase. During the thermal treatment under vacuum, which produces the transition from amorphous to tetragonal ZrO_2, there must be a loss of water molecules, hydroxyl groups and even lattice oxygen that will leave oxygen vacancies in the bulk. In the absence of oxygen in the gas phase, the electrons in excess will be trapped forming Zr^{3+} or in the oxygen vacancies producing signal (A). We must bear in mind that during this transition an important amount of energy is released (see above and reference (5)) and that as zirconia is a refractory material high local temperatures can be reached (to the point that the sample glows). It could well be that this very high local temperature produces the elimination of some oxygen from the structure. In this connection it is worth recalling that, according to Aronson (6), tetragonal zirconia has a small but noticeable stoichiometry range amounting to $ZrO_{1.975}$. According to the weight gain that we have observed in reoxidation, the nonstoichiometry of our

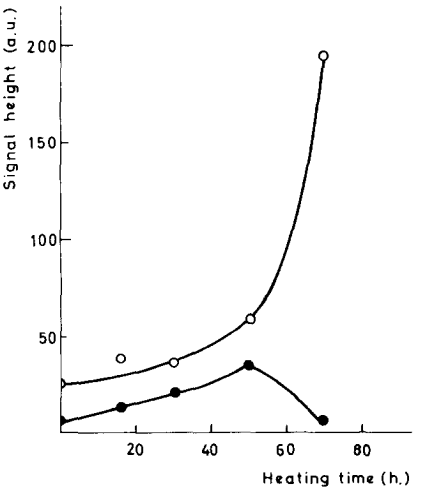


FIG. 4. Variation of the EPR signal height for ZrO_2 with heating time, at 350°C (BO.1-B70 samples). (○) Signal A; (●) signal B.

sample will amount to $ZrO_{1.97}$. Moreover, it may be that the presence of these oxygen vacancies is responsible for the existence of tetragonal zirconia at low temperature, by allowing the displacement of anions from the cubic CaF_2 structure positions along ⟨100⟩ directions. In the same way cubic zirconia can be stabilized by oxygen vacancies produced by doping it with alkaline-earth or rare-earth oxides.

It should be stressed that the trapped electron signal was also observed in the air-treated sample, although it appeared with much lower intensity and only under particular heating conditions. These conditions must correspond to a compromise between a temperature high enough to initiate the glow but not so high that all the bulk oxygen vacancies are destroyed by oxygen diffusion from the surface. On the other hand, samples prepared from "zirconium nitrate," and studied by ir spectroscopy show a certain amount of nitrate groups trapped within the gel. Previous work on these materials (*7*) has shown that hydrated zirconia oxides trap anions within the micelles forming the gel-like structure. Some of these anions are believed to be present as ligands within the tetrameric units characteristic of the so-called "zirconyl solutions." The elimination of such ionic ligands as neutral species could then be another source of the electrons that form paramagnetic centers. In fact these two alternative explanations are not mutually excluding and they can happen concurrently under appropriate circumstances.

When the tetragonal samples are treated in an oxidizing atmosphere, above 800°C, an exothermal reoxidation of the sample is produced with a weight gain, presumably oxygen gain, of 0.2%. This process includes the elimination of the oxygen vacancies that appear to be responsible for both the trapped electrons and the tetragonal structure. Consequently a transition to a more stable monoclinic phase takes place. During this process signal (C) is transitorily produced.

The presence of a small signal (B) in tetragonal and monoclinic phases seems to indicate that the Zr^{3+} ions (or other impurities) that give rise to the signal are not related with the stabilization of any particular crystalline structure of ZrO_2. These reduced centers are perhaps formed in special defect sites of the lattice and are difficult to reoxidize.

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