

NOTE

Synthesis of ZrO₂ in Molten Salt Mixtures: Control of the Evolved Gas and the Oxide Texture

Zirconium dioxide presents considerable interest in the field of heterogeneous catalysis, due to its original acid–base and redox properties (1). Much work has been done on the preparation of high surface area zirconia, obtained either from aqueous solutions (2), thermal decomposition of basic salts (3), or sol–gel methods (4, 5). Recently, the reactions of Zr salts with molten nitrates have been successfully used for the preparation of dispersed ZrO₂ for catalytic applications (6–10). Yttrium-stabilized zirconia, obtained in molten KNO₃–NaNO₃ mixtures, showed specific surface area as high as 120–130 m²/g (9), which could be enhanced to above 200 m²/g if the reaction mixtures were doped with oxoanions such as molybdate (11) or vanadate (12). However, a disadvantage of this preparation method is the production of heavily pollutant NO_x gases during the reaction. Another problem concerns the texture of the obtained oxide. Using molten salt preparations, average pore diameters in the range of 2–3 nm were obtained, whereas a higher porosity is needed in some catalytic processes such as the hydrotreatment of petroleum fractions.

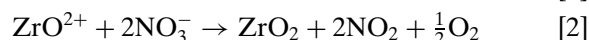
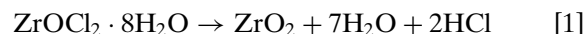
In order to solve these problems, we investigated a mixture of KNO₃–NaNO₃–Na₂CO₃ as a reaction medium. The formation of ZrO₂ in molten nitrate can be considered as an acid–base reaction in which the zirconium salt plays the role of an acid and the melt anions that of a base (13). The higher reactivity of the carbonate ion in comparison to that of nitrate could modify the reaction mechanism, and different physico-chemical properties of the resulting solid could be expected. Carbonate may also act as a textural modifier similarly to preparations performed in aqueous media (14).

The preparation procedure was as follows: hydrated zirconium oxychloride and a mixture of alkali metal salts containing a tenfold molar excess of nitrate plus carbonate relative to Zr were thoroughly mixed and placed in a Pyrex reactor. The mixtures were pretreated under a nitrogen flow at 150°C for 2 h to remove water from the precursor salts. Then the reaction was carried out at 500°C for 2 h. After cooling, the solidified melt was washed with distilled water at room temperature until a test with AgNO₃ showed no more residual chloride, then the product was dried overnight in air at 120°C. The compositions of reaction mixtures are listed in Table 1.

The gases produced during the reaction were analyzed using a mass spectrometer, Gas Trace A (Fisons Instru-

ments), equipped with a VG quadrupole analyzer working in Faraday mode. Mixtures containing ca. 1 g of salts were heated from room temperature to 550°C in a glass cell at a heating rate of 1.5° min⁻¹. A silica capillary tube heated at 180°C continuously bled off the gaseous reaction products into the spectrometer. Signals were recorded with *m/z* = 18, 30, 32, 36, 44, 46, corresponding respectively to ionized H₂O, NO, O₂, HCl, CO₂, and NO₂ molecules. X-ray diffraction patterns were recorded on a diffractometer (Siemens D500) using Ni-filtered CuK α radiation. Surface areas and pore radii distributions were measured by nitrogen adsorption. Chemical analyses of alkali metals were carried out by means of the atomic emission method. SEM images were obtained using a scanning electron microscope (Hitachi S800).

Preliminary mass spectra, discussed in Ref. (15), have shown that at least two reactions occur in the mixture of hydrated ZrOCl₂ with alkali nitrates, i.e., decomposition of hydrated ZrOCl₂ (reaction 1) and Lux–Flood acid–base interaction of the Zr salt with the molten nitrate (reaction 2):



Reaction [1] was observed mostly before the nitrate melting, whereas reaction [2] occurred in the melt. Figure 1a presents the mass spectra obtained with a mixture corresponding to the ZC0 preparation. A special care should be taken about the NO/NO₂ signals, due to the fragmentation of NO₂ in the electron beam. NO₂ is characterized by two signals of NO and NO₂ with an intensity ratio NO/NO₂ close to 10, experimentally observed using the decomposition of Pb(NO₃)₂ as a reference compound.

TABLE 1

Composition of the Reaction Mixtures

Sample	NaNO ₃ (g)	KNO ₃ (g)	Na ₂ CO ₃ (g)	ZrOCl ₂ · 8H ₂ O (g)
ZC0	9	11	0	3.0
ZC1	8.9	10.9	0.2	3.0
ZC2	8.7	10.7	0.6	3.0
ZC3	8.1	9.9	2.0	3.0
ZC4	6.3	7.7	6.0	3.0

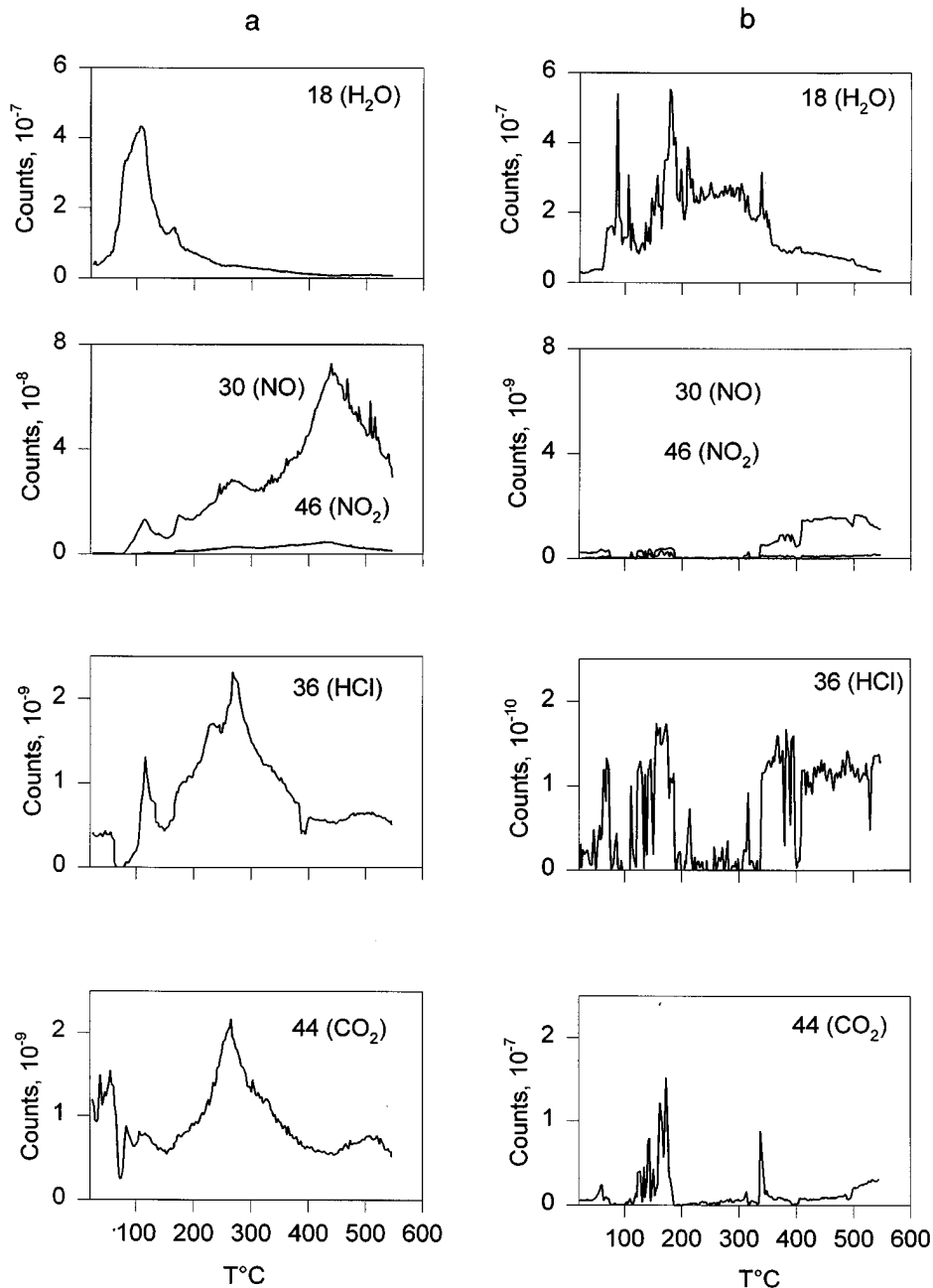


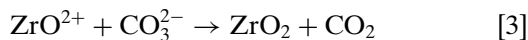
FIG. 1. Mass spectra of the gases produced upon heating in vacuum the reaction mixture $\text{K-Na-NO}_3\text{-ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ corresponding to the preparation ZC0 (a) and the reaction mixture $\text{Na}_2\text{CO}_3\text{-K-Na-NO}_3\text{-ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ corresponding to the preparation ZC4 (b).

Multistage reaction of the zirconium salt in the K-Na-NO_3 melt can be seen in Fig. 1. The signals of m/z 30 and 46 have similar shapes, the ratio of their intensities being fairly constant. Therefore both signals can be attributed to the formation of NO_2 and its subsequent fragmentation. NO_2 appears already at ca. 120°C and its signal increases up to 450°C . At somewhat lower temperatures, the side reaction of thermal decomposition occurred and a considerable amount of HCl was observed with a maximum at ca. 270°C .

The appearance of both NO_2 and HCl confirms that the total process involves both reactions [1] and [2].

The mass spectra of hydrated ZrOCl_2 in $\text{K-Na-NO}_3 + \text{Na}_2\text{CO}_3$ were measured for the reaction mixture corresponding to the sample ZC4 (Table 1). According to the mass-spectral data (Fig. 1b) it appears that the reaction pathway was changed as a result of the addition of Na_2CO_3 . The amounts of NO_2 and HCl evolved were drastically reduced by factors of about 40 and 20, respectively, as

compared to the non-doped mixture. At the same time, strong peaks of CO_2 appear, both below and above the melting temperature (ca. 300°C). Therefore, we can conclude that carbonate addition results in a virtual change of the mechanism from reactions [1] and [2] to reaction [3].



Reaction mixtures, corresponding to the samples ZC1 and ZC2, produced CO_2 together with a considerable amount of nitrogen oxides, since the amount of carbonate in them was lower than is required by the stoichiometry of reaction [3]. The mass spectrum for mixture ZC3 which contained excess carbonate was similar to that shown in Fig. 1b. As deduced from Fig. 1b, a high degree of transformation is already obtained at 300°C . However, complementary experiments showed that a temperature of 500°C is required to achieve the complete reaction and to obtain zirconia with good textural properties.

Chemical analysis of the samples prepared at 500°C shows that all the samples contain residual alkali metals and carbonate (0.2–0.4 wt% Na; 0.2–0.6 wt% HCO_3^-), which cannot be eliminated by washing with distilled water at room temperature. The amount of chloride which comes from the ZrOCl_2 precursor is negligible. The residual nitrate level is very low, as it was in the zirconia prepared from pure nitrates (16).

It was shown earlier that the addition of multidentate chelating anions such as sulfate, molybdate (15, 17), or phosphate to the nitrate melt leads to the stabilization of the tetragonal variety of zirconia and simultaneously to a decrease of the ZrO_2 crystallite size (18, 19). Accordingly, the stabilization of tetragonal zirconia by the presence of carbonate in the melt could be expected, as well as an increase of its surface area. In agreement with this hypothesis, samples prepared with 10 and 30 wt% carbonate (ZC3, ZC4) have pure tetragonal structure, whereas the monoclinic variety was observed at low carbonate concentration (ZC1, ZC2). At the same time, the presence of carbonate ions leads to a significant increase of the mean pore size and pore volume without considerable modification of the specific surface area, though the average size of the zirconia crystallites determined by XRD was increased (Table 2). Such a behavior can be attributed to the acceleration of zirconia again in the melt due to the presence of carbonate species. The aging phenomenon, well known for aqueous precipitates and sol-gel products, consists of the growth of necks between the solid particles due to the dissolution-precipitation process. Consequently, a more open pore structure can be obtained, without appreciable decrease of the specific surface area. It is known that in aqueous media the aging of an amphoteric oxide can be strongly accelerated by the presence of acids or bases (20). By analogy with aqueous precipitates, it is proposed that

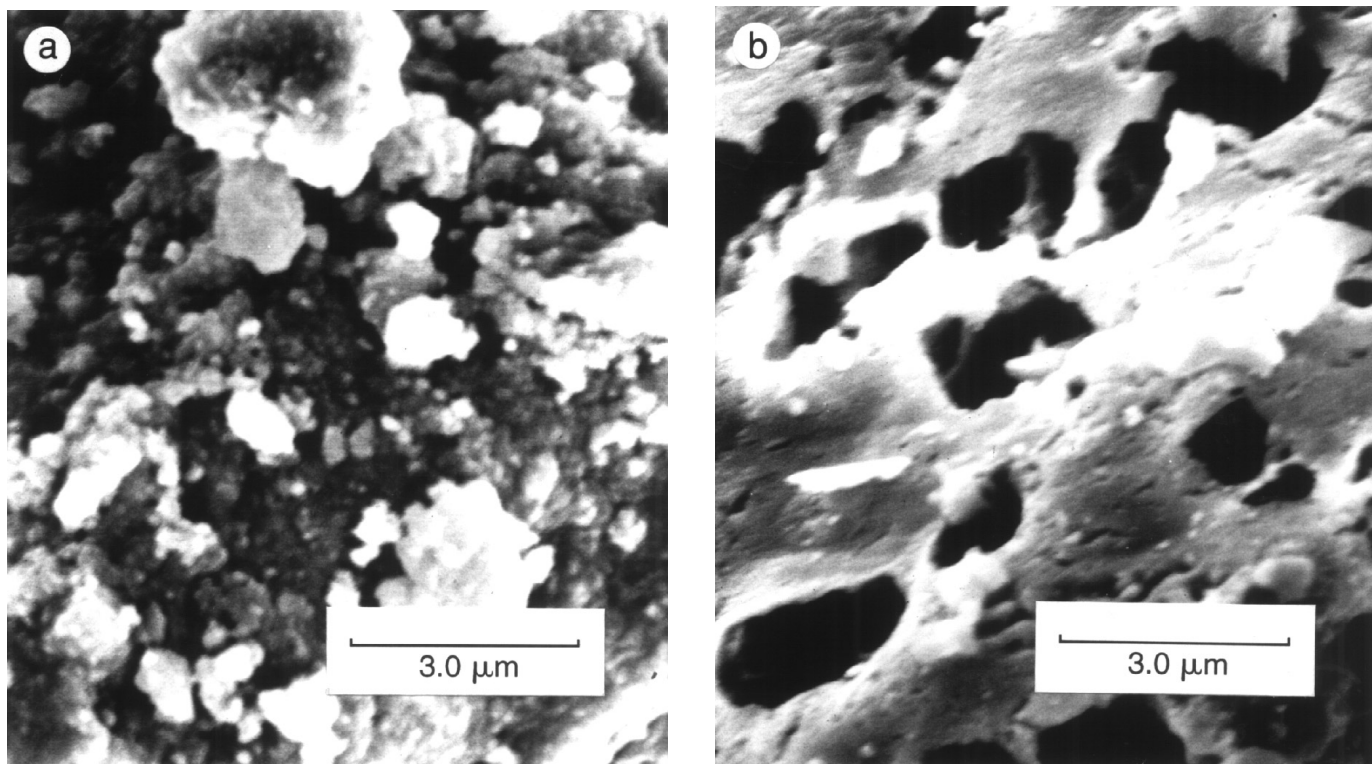


FIG. 2. SEM images of the samples ZC0 (a) and ZC4 (b).

TABLE 2

Average Pore Radius $R(p)$, Specific Surface Area S , Pore Volume $V(p)$, and Mean Crystallite Size $R(XRD)$ for Samples ZC0–ZC4

Sample	$R(p)$ (nm)	S (m^2g^{-1})	$V(p)$ (cm^3g^{-1})	$R(XRD)$ (nm)
ZC0	2.9	132	0.24	3.4
ZC1	2.9	153	0.27	3.5
ZC2	3.0	130	0.31	4.0
ZC3	3.5	140	0.30	4.5
ZC4	4.1	144	0.34	5.1

carbonate ions increase the basicity of the melt and then accelerate the mass transfer.

The influence of carbonate ions on the morphology of zirconia particles can be clearly seen on the SEM pictures. In the ZC0 sample prepared in the K–Na–NO₃ mixture (Fig. 2a) the oxide particles have a spherical morphology, typical of these preparations (16). The sample consists of spherical agglomerates having a mean diameter of ca. 1–2 μm . By contrast, the sample ZC4 exhibits a “cheesehole” morphology (Fig. 2b) which can be the result of the advanced neck growth.

Polydentate oxoanions have been applied earlier to control the properties of molten salt preparations of oxides (17). As suggested for zirconia (16), the processes determining the properties of the resulting oxide are the elimination of nitrate groups from the amorphous Zr oxonitrate, the nucleation of zirconia particles, and their extensive growth and agglomeration. Acting as a strong base, carbonate ions react chemically with the zirconium salt and accelerate the subsequent aging of the zirconia precipitate. The new reaction pathway avoids the production of pollutant gases such as HCl and NO₂. Moreover, the presence of carbonate strongly influences the morphology of the particles. It becomes possible to prepare solids with the porosity and the surface area required for some catalytic applications such as hydrotreatment.

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