High-Rate Synthesis of Nanostructurized Tetragonal Zirconium Oxide in Mechanochemical Apparatus

PETR N. KUZNETSOV, LYUDMILA I. KUZNETSOVA and ANATOLY M. ZHIZHAEV

Institute of Chemistry and Chemical Technology, Siberian Branch of the Russian Academy of Sciences, Ul. K. Marxa 42, Krasnoyarsk 660049 (Russia)

E-mail: kuzpn@krsk.infotel.ru

Abstract

A high-rate synthesis ofnano-crystal zirconium oxide of tetragonal modification is performed by activation of amorphous zirconium hydroxide in mechanochemical apparatus. Preliminary short-time mechanochemical treatment of the hydroxide also allows one to decrease substantially (by 150–200 °C) the temperature of subsequent crystallization of the oxide into the tetragonal form.

INTRODUCTION

Materials based on zirconium oxide ZrO_2 are widely used as construction and ion-exchange materials, selective adsorbents and catalysts due to their high thermal stability, mechanical strength and unique surface properties. Zirconium oxide exists in several crystal modifications: monoclinic (M), which is thermodynamically stable at temperatures below 1172 °C, tetragonal (T) which is stable at temperature within the range 1172–2347 °C, and cubic (C) which is stable above 2347 °C. A rhombic high-pressure ZrO_2 modification, which is metastable at usual pressure, has also been synthesized. Of special interest is metastable tetragonal ZrO_2 which is being used within the recent years as a component of acidic catalysts able to effectively catalyze many reactions of organic compounds. Discovery and development of this new family of heterogeneous acidic catalysts has been important achievement of catalysis within the recent decade [1]. These catalysts allow one to perform isomerization of *n*-paraffins at low temperature providing high yield of highly branched isomers [1–4]. In industry, acidic catalysts based on tetragonal ZrO_2 are increasingly widely used instead of less efficient zeolites or toxic and ecologically dangerous aluminium halides and liquid superacids.

The tetragonal form of ZrO_2 can be obtained by decomposition of some zirconium compounds at high temperature (above 1200 °C) followed by rapid quenching. Specific surface is very low in the case of such a procedure. Methods are known [2–5] to obtain fine dispersed tetragonal ZrO_2 at substantially lower temperature than those mentioned above; these methods are based on the use of stabilizing additives including anions and/or di- or trivalent cations of some metals. Widespread methods include obtaining a hydroxide, modifying it with SO_4^{2-}, MoO_4^{2-} and WO_4^{2-} anions and/or promotion by polyvalent cations, such as Y^{3+}, Fe^{3+}, Mn^{2+}, drying followed by annealing at temperature above 500 °C for a long time. During annealing, the promoter cations are driven into the ZrO_2 lattice thus generating oxygen vacancies. The presence of these defects is assumed [2, 6] to slow down the growth rate of tetragonal crystallites and the transformation into the stable monoclinic modification. The same role is likely to be played by the modifying anions bound at the surface of the oxide phase [3]. According to [7, 8], the formation of tetragonal ZrO_2 at low temperature as a fine dispersed phase is due to lower surface energy of its particles, in comparison with the particles of the monoclinic modification.

Methods based on pulsed mechanical action are of interest from the viewpoint of the synthesis of the tetragonal zirconium oxide. For many examples [9–15], it is demonstrated that these methods allow one to perform the synthesis of fine dispersed materials and composites as thermodynamically non-equilibrium phases. According to the data of the authors of [15], the treatment of monoclinic ZrO_2 in a ball mill at room temperature causes at first the decrease of crystallite size. After grinding for a long time (for 30 h), after the crystallite size decreases to 10 nm, a partial (45 %) phase transition into the T modification occurs. The back transition goes on much easier: the M-modification started to form from the T-modification after only 5 min, while after 1–2 h the T ® M phase transition was complete. Driving forces determining phase transition were not determined in [15]. It was assumed that one of the factors might be connected with the dimension effect.

In the present work, we report the data on mechanochemical synthesis of tetragonal zirconium oxide from the amorphous hydroxide in a centrifugal planetary mill which, in comparison with a ball mill, provides mechanical pulsed action of much higher intensity.

EXPERIMENTAL

Zirconium hydroxide was obtained by precipitation from the aqueous solution of zirconyl chloride (chemically pure grade) by ammonia solution at pH 9.5 ± 0.5 and room temperature. Gels obtained by precipitation were aged for 3 h and washed with distilled water. Then, they were filtered and washed till the negative reaction for Cl^- ions in washing water. The precipitate was dried first in air, then in drying chamber at 110 °C for 15 h. In some experiments, crystalline zirconium oxide of the stable monoclinic modification (pure reagent grade) was used.

Thermal activation of zirconium hydroxide was performed in a quartz reactor in air at temperatures 300–700 °C for 3 h. Mechanochemical activation was carried out in AGO-2 activator mill of the centrifugal planetary type with two tightly closed steel drums. Drums were cooled with water during the operation in order to prevent heating of the treated material. Drum rotation frequency was 1820 min^{-1}, which corresponded to the milling bodies acceleration of 600 m/s^2. The samples were activated in the form of dry powder and water suspension. Steel balls (106 g) 3 mm in diameter, and 3 g of zirconium hydroxide (or oxide) were loaded into the drum. In case of the humid activation mode, 3 ml of distilled water was added into the drum. Mechanical load was varied by changing treatment time from 5 min to 15 h.

X-ray diffraction patterns of the obtained samples were recorded with a DRON-3 diffractometer using filtered CuK_a radiation at the scanning rate of 1 deg/min. The dynamics of mechanochemical processes was characterized using the relative changes of the intensities of diffraction peaks of crystal phases. Crystallite size (the region of coherent scattering of X-rays, or coherent length) was estimated using the broadening of lines in the diffraction patterns according to the Debye – Scherrer equation. Particle size was estimated with the help of micrographs obtained with the help of the scanning electron microscope REMMA 200 M. Size distribution was calculated at the total number of particles not less than 2000. Specific surface was determined according to BET procedure (thermal desorption of argon). Mean size of particles D was estimated from the specific surface assuming their spherical (cubic) shape according to the equation $D = 6/(\rho S)$, where ρ is density $\rho = 6$ /cm^3 for tetragonal ZrO_2).

RESULTS AND DISCUSSION

Thermal crystallization of the oxide phases from X-ray amorphous hydroxide starts at a temperature of about 500 °C. Two forms of oxide are formed at first: monoclinic one, which is prevailing (most intensive reflection corresponding to d = 3.165 and 2.841), and metastable tetragonal one (the most intensive reflection being that with d = 2.96) (Fig. 1). At further temperature raise, the fraction of monoclinic modification increases while that of tetragonal one decreases. Within temperature

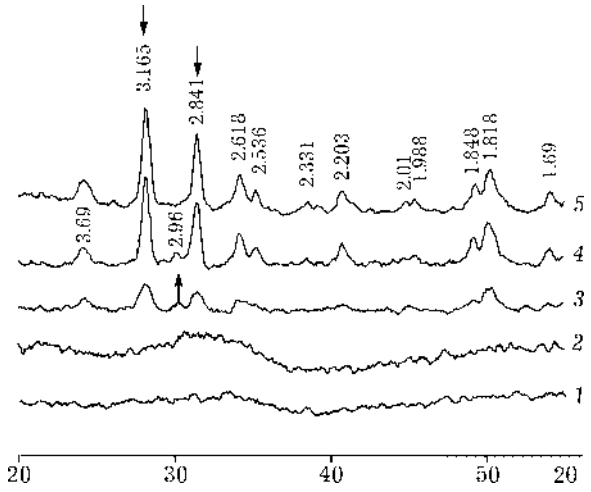

Fig. 1. Diffraction patterns of the initial zirconium hydroxide (*1*) and products of annealing at 300 °C (*2*), 500 (*3*), 600 (*4*), and 700 °C (*5*). The signs ¯ and - mark intensive and characteristic reflections of the monoclinic and tetragonal forms of oxide, respectively.

range 600–700 °C, the crystal product is represented practically by a single modification, which is monoclinic ZrO_2 (crystallite size being 20–30 nm); tetragonal modification is present at a level of minor impurity. Crystallization is accompanied by the increase of particle size, which is observed in electron microscopic images (Fig. 2). The data obtained are in agreement with the general regularities of the behaviour of the zirconium hydroxide system under thermal action [2, 3].

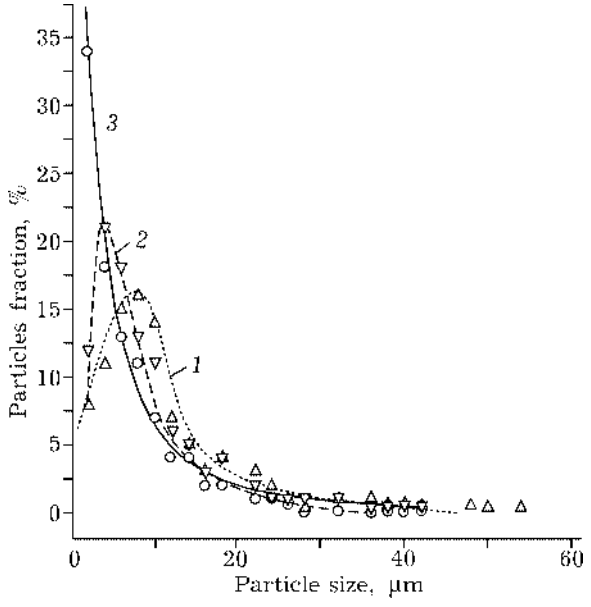

Fig. 2. Particle size distribution for the initial hydroxide (*2*), products of annealing at 600 °C (*1*) and suspension mechanically activated for 5 min (*3*).

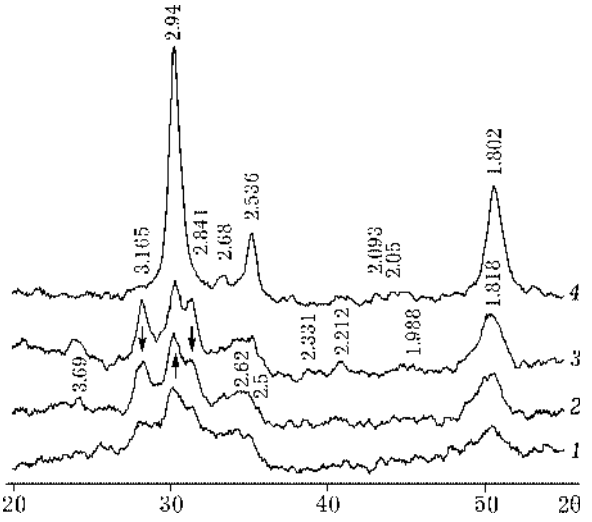

Fig. 3. Diffraction patterns of the products of mechanochemical treatment of dry zirconium hydroxide for 0.5 min (*1*), 2 (*2*), 5 (*3*), and 15 min (*4*). For designations, see Fig. 1.

Figure 3 shows diffraction patterns of the products of mechanochemical activation of a dry powder of X-ray amorphous zirconium hydroxide in centrifugal planetary mill. Even after short treatment (for 30 s), weak broadened reflections of crystal monoclinic and tetragonal oxide modifications are detected in the diffraction patterns (curve *1*). The presence of the cubic modification is also possible. A reliable identification is hindered since its diffraction picture is similar to that of the tetragonal modification, and lines are substantially broadened. An increase of mechanical load leads to the increase of crystallization degree. After 15 min, this process finishes; tetragonal ZrO_2 with crystallite size not more than 16 nm and specific surface of 19–20 m^2/g is predominant in the products (Table 1). M-modification is detected only at a level of impurity. No other crystal phases are present according to the XPA data.

Figure 4 shows X-ray diffraction patterns of the products obtained by mechanical treatment of hydroxide suspension. In the presence of a solvent, mechanically induced strain arising as a result of defect accumulation relax mainly by fragile crushing [12]. Experiments show that after mechanical treatment of the suspension, particle size distribution is shifted to smaller size, according to electron microscopic images (see Fig. 2). Specific surface in-

TABLE 1

Characteristics of the disperse state of products of the mechanochemical activation of zirconium hydroxide

Activation time, min	Activation mode	Specific surface, m^2/g	Particles size[a], nm	Size of T-crystallites[b], nm
0 (initial)	–	127	–	–
2	Dry	25	39	–
5	»	19	51	–
15	»	20	49	16
2	Wet	–	–	9
5	»	72	14	12
15	»			14

[a]Estimation from specific surface.
[b]Determined from X-ray line broadening.

creases to 72 m^2/g after treatment for 5 min, compared to 19 m^2/g after dry activation (see Table 1). According to X-ray diffraction data (see Fig. 4), the crystal product of the activation of suspension is represented at all the stages mainly by the nano-sized T-oxide, while dry activation is accompanied also by the formation of M-form at the initial stages. After 5 min, the size of T-crystallites is 12 nm, which corresponds to the mean particle size calculated using the specific surface data (14 nm) (see Table 1).

For comparison, experiments on zirconium hydroxide treatment in vibratory mill were carried out. Even after treatment for a long time (for 10 h), no formation of the oxide phases was detected according to XPA data.

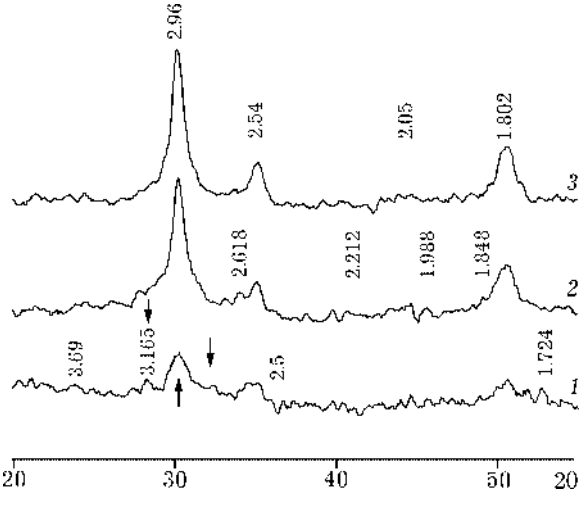

Fig. 4. Diffraction patterns of the products of mechanochemical treatment of the aqueous suspension of zirconium hydroxide for 2 (*1*), 5 (*2*), and 15 min (*3*).

The obtained results of phase analysis show that the activation of amorphous zirconium hydroxide in centrifugal planetary mill with high-power mechanical pulses causes not only dehydration and crystallization of oxide phases but also a fast phase transition of the monoclinic modification into the tetragonal one. The occurrence of M ® T transition under these conditions was confirmed by special experiments in which well-crystallized monoclinic ZrO_2 was subjected to mechanical activation. After 30 s of dry powder activation, X-ray diffraction patterns contained weak broadened reflections of the T-modification; the intensity of the peaks related to the initial modification decreased (Fig. 5). After 15 min, the M ® T phase transition was practically over; the size of the crystallites of new modification was about 10–12 nm. Continued mechanical action resulted in partial amorphization, which was exhibited by the decrease of reflection intensity. In comparative tests in a vibratory mill, phase transition did not occur even after 15 h treatment of dry powder of the monoclinic ZrO_2. Crystallite size decreased to 40 nm after treatment; the intensity of diffraction peaks was observed to decrease due to amorphization.

The effect of the conditions of mechanochemical activation on the dynamics of the accumulation of tetragonal oxide is shown in Fig. 6. The highest rate is achieved at the activation of dry monoclinic ZrO_2. Dry amorphous hydroxide gives the T-modification at lower rate. In aqueous medium, the rate slows down substantially; however, the synthesis goes on

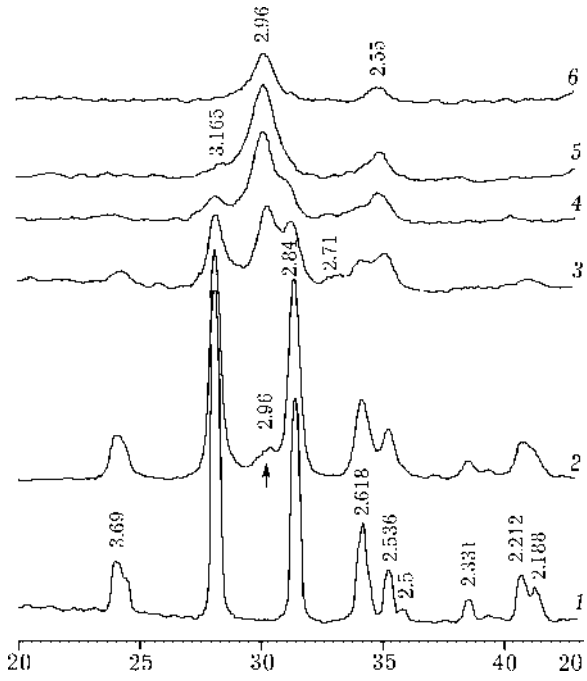

Fig. 5. Diffraction patterns of the monoclinic zirconium oxide (*1*) and products of its mechanochemical treatment in dry mode for 0.5 min (*2*), 2 (*3*), 5 (*4*), 15 (*5*), and 22 min (*6*).

selectively without the formation of M-modification as a by-product. It is important to note that the mechanochemical process of crystallization is characterized by non-monotonous dependence on the mechanical load. The dynamics of the accumulation of T-modification from dry hydroxide is most demonstrative: after a definite level of mechanical load is achieved (more than 5 min), a jumpwise growth of rate is observed, which is a characteristic feature of mechanochemical reaction.

Figure 7 shows diffraction patterns illustrating thermal behaviour of the hydroxide sample subjected preliminarily to humid short-time mechanical activation. One can see that the mechanically activated hydroxide, unlike non-activated one (see Fig. 1), is crystallized thermally at 320 °C giving mainly T-modification. At 600 °C, the degree of crystallization into T-form increases substantially. The presence of M-form remains at a level of impurity, while in the case of hydroxide not subjected to mechanical treatment M-modification was predominant at the same temperature (see Fig. 1). The size of T-crystallites increases with annealing temperature from 13 to 22 nm. No presence of other crystalline special was detected by XPA.

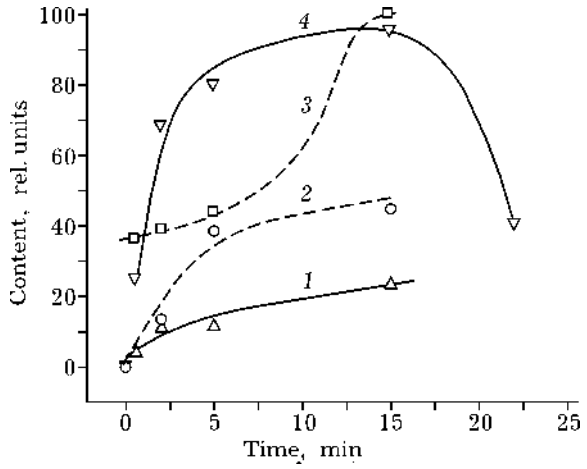

Fig. 6. The dynamics of the accumulation of tetragonal zirconium oxide during mechanochemical activation of the amorphous hydroxide (*2*, *3*) and monoclinic oxide (*1*, *4*): *1*, *2* – aqueous suspension; *3*, *4* – dry powder.

Thus, activation of amorphous zirconium hydroxide in high-power mechanochemical device stimulates fast reactions of the formation of nano-sized tetragonal oxide at low temperature. One is likely to have no reasons to assume that the observed mechanochemical reactions of the synthesis of T-form are caused by thermal activation as a result of local heating till high temperature (above 1172–1200 °C). For the treatment of suspension, when the probability of local heating decreases sharply due to heat dissipation by the liquid phase, T-modification is still formed (though at lower rate than in dry powder). but the synthesis

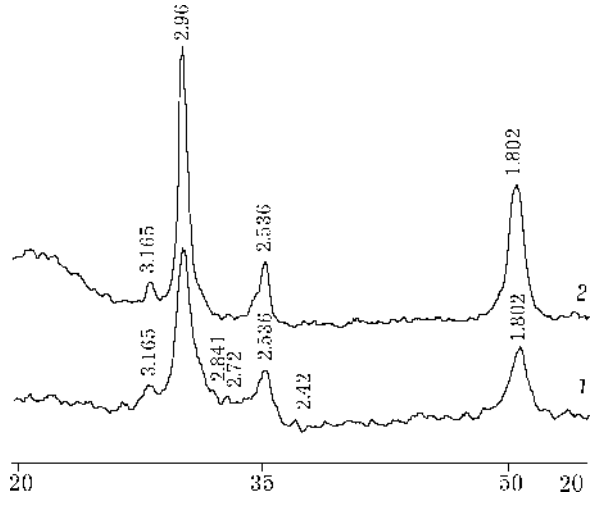

Fig. 7. Diffraction patterns of the products of annealing of mechanochemically activated hydroxide at 320 (*1*) and 600 °C (*2*).

proceeds more selectively without the formation of the M-modification. It follows from this observation that if mechanical activation makes a contribution into the development of mechanochemical crystallization under the mentioned conditions, it most likely leads to the monoclinic modification.

Many authors [7, 8] connect the formation of tetragonal modification of zirconium oxide at low temperature with its transformation into fine dispersed state. The surface energy of particles of the T-modification is much less (770 erg/cm^2 [16]) than that of the monoclinic one (1130 erg/cm^2 [8]). Because of this, at small particle size (or large specific surface), M-modification becomes less profitable from the energy viewpoint in comparison with the T-modification. As estimated [7, 8], critical crystallite size is 30 nm. The achievement of small size is provided in mechanochemical device by means of intensive mechanical dispersing; the size of crystallites in the obtained tetragonal oxide is 9–16 nm, which corresponds to the region preferable for the tetragonal modification. Thanks to intensive mechanical action, the synthesis proceeds at high rate within several minutes. For comparison, we should note that the authors of [15] observed phase transition of M-modification into T one in a ball mill at smaller crystallite size (8–10 nm). After 30 h, only 45 % of the monoclinic oxide was converted into tetragonal one; no complete transformation was achieved even after 50 h. In our experiments, we did not observe phase transition in the vibratory mill after 15 h.

Comparison shows that thermal activation of the initial hydroxide and the hydroxide mechanochemically treated for a short time resulted in different products: in the former case, stable M-modification was formed, while metastable T-modification was easily formed in the latter case (at temperature as low as 320 °C). This feature of the thermal behaviour of mechanically activated sample can be connected with its defectiveness and/or with the presence of T-modification nuclei generated by mechanical treatment. One also cannot exclude the effect of impurities from milling tools and drum on mechanochemical crystallization; however, their role is likely to be of secondary importance. In [15] cited above, monoclinic zirconium oxide was treated in a ball mill with drums and balls made of different materials (tungsten carbide, corundum, and steel). Phase transition was observed in all the three devices. In order to make a more reasonable conclusion concerning the effect of this factor on mechanochemical crystallization, a detailed analysis is necessary.

The transition of M-modification into T-modification is accompanied by the decrease of molar volume by about 7 %. One can expect that high pressure in combination with increased temperature, developed in local regions of a solid under the action of powerful mechanical pulse, can provide thermodynamic probability of the formation of T-modification. According to thermodynamic calculations [17], a linear relation between the applied external static pressure and phase transition temperature is fulfilled for the zirconium oxide system: $dT/dP = -0.032$ °C/bar. It follows from this relation that at a pressure of 2 GPa (which can be achieved in local regions of a solid in a mechanochemical apparatus, according to [12, 13]) the temperature of M ® T phase transition should decrease by 640 °C, *i. e.* to 535–565 °C. The possibility to achieve this temperature level in mechanical activation was stated by many examples [12]. Experimental data on the effect of external static pressure on phase equilibria show [18] that the transition of monoclinic ZrO_2 into dense rhombic modification (which also is metastable under normal conditions with respect to the monoclinic modification) occurs at a pressure of 2.0–2.5 GPa and a temperature of 450 °C. At pressure increased to 3.0–3.5 GPa, temperature decreases to 400 °C. At a pressure of 3.7 GPa, the transition into T-modification was observed at room temperature [19].

These data show that the formation of tetragonal ZrO_2 in a mechanochemical apparatus under the action of powerful mechanical pulse of pressure can be conditioned by the creation of thermodynamically favourable conditions (temperature and pressure) in separate regions of the solid. Rapid elimination of the pulse quenches the formed T-modification which is

non-equilibrium with respect to normal conditions. At subsequent pulses, the process can involve a substantial part of a solid and further the whole its volume. Accumulation of various defects in oxide particles can simply this process substantially.

CONCLUSIONS

Activation of the amorphous zirconium hydroxide in high-energy strain mechanochemical apparatus stimulates fast reactions of the formation of nanosized zirconium oxide of the tetragonal modification at low temperature. Its formation can be connected with dispersing particles, inducing defects, realization of thermodynamically favourable synthesis conditions in the mechanochemical apparatus (high pressure and temperature in local regions).

Mechanochemical synthesis is distinguished by its flexibility: T-modification of zirconium oxide can be prepared both from the amorphous hydroxide and from crystal oxide of the stable monoclinic modification by means of enantiotropic phase transition. Preliminary short-time mechanical treatment of the hydroxide also provides the possibility to decrease the temperature of subsequent thermal crystallization of the nanosized T-modification.

Acknowledgement

The work has been supported by the Krasnoyarsk Regional Foundation for Science (Grant No. 9F0112).

REFERENCES

1 B. H. Davis, I. Wender, *Top. Catal.*, 10 (2000) 1.
2 G. D. Yadav, J. J. Nair, *Microporous and Mesoporous Materials*, 33 (1999) 1.
3 A. V. Ivanov, L. M. Kustov, *Ros. khim. zhurn.*, XLIV, 2 (2000) 21.
4 B. H. Davis, R. A. Keogh, *Catal. Today*, 20 (1994) 219.
5 C. Morterra, G. Cerrato, L. Ferroni, L. Montanaro, *Mater. Chem. Phys.*, 37 (1994) 243.
6 P. D. L. Mercera, V. J. G. Ommen, E. B. M. Doesburgh, *J. Mater. Sci.*, 57 (1990) 127.
7 R. Gopalan, C.-H. Chang, Y. S. Lin, *Ibid.*, 30 (1995) 3075.
8 R. C. Garvie, *J. Phys. Chem.*, 69 (1965) 1238.
9 V. V. Boldyrev, *Mater. Sci. Forum*, 225–227 (1996) 511.
10 V. V. Boldyrev, Mekhanokhimicheskiy sintez neorganicheskikh veshchestv, Nauka, Novosibirsk, 1991.
11 T. F. Grigorieva, V. V. Boldyrev, *DAN*, 340, 2 (1995) 3075.
12 E. G. Avvakumov, Mekhanicheskiye metody aktivatsii khimicheskikh protsessov, Nauka, Novosibirsk, 1986.
13 G. Heinicke, Tribochemistry, Akademie-Verlag, 1986.
14 L. G. Karakchiev, E. G. Avvakumov, O. B. Vinokurova *et al.*, *Khimiya v interesakh ustoychivogo razvitiya*, 9, 1 (2001) 1.
15 J. E. Bailey, D. Lewis, Z. M. Librant and L. J. Porter, *Trans. J. Brit. Ceram. Soc.*, 71 (1972) 25.
16 D. T. Livey and P. Murray, *J. Amer. Ceram. Soc.*, 39 (1956) 363.
17 E. D. Whitney, *Ibid.*, 45 (1962) 612.
18 L. M. Lityagina, S. S. Kabalkina, T. A. Pashkina, A. Ya. Khozyainov, *Fizika tverdogo tela*, 20 (1978) 3475.
19 G. L. Ku1cinski, *J. Amer. Ceram. Soc.*, 51 (1968) 582.