Formation and Surface Structure of Ti-Zn-Double Oxides and of Zn Ferrite*

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In powder mixtures of ZnO and TiO₂ the compounds Zn₂TiO₄, ZnTiO₃, and Zn₂Ti₃O₈ can be formed as a result of solid state reactions. The formation of the double oxides is essentially determined by the microstructure of the powder mixture. Furthermore, the type of the double oxide depends on the TiO₂ modification. There exist structural similarities between Zn₂TiO₄ (spinel) and TiO₂ (anatase) as well as between ZnTiO₃ and TiO₂ (rutile). Compound Zn₂Ti₃O₈ is formed only on the basis of the Zn₂TiO₄ phase. The Zn²⁺ ions on the surface of Zn₂Ti₃O₈ occupy only tetrahedral sites and not octahedral ones, like it was derived for the crystal structure of the bulk.

The formation of zinc ferrite, ZnFe₂O₄ at room temperature is possible by means of mechanical activation in a high-energy ball-milling process of a ZnO—Fe₂O₃ mixture (mechanosynthesis). The surface structure of mechanosynthesized zinc ferrite corresponds to the inverse spinel structure type. The structure of inverse spinel type is also created by means of mechanical activation of zinc ferrite of the normal spinel type.

The investigation of regenerable sorbents for the desulfurization of hot coal gases is an important task in the field of material science in connection with the development of environmentally friendly techniques of power generation from coal.

Basically, metal oxides as ZnO, Fe₂O₃, CuO, SnO₂ are suitable as sorbents for H₂S forming sulfides. The sorbents can be regenerated with O₂—N₂ mixtures which may contain also water vapour, at likewise high temperatures. The most frequently investigated sorbent for H₂S is ZnO. The use of ZnO is limited to gas temperatures lower than 900 K, because the rate of sublimation of ZnO strongly increases at higher temperatures. The undesirable loss of ZnO may be prevented to a larger extent, if mixed oxides are used instead of pure ZnO. Mixed oxides of ZnO and TiO₂ or Fe₂O₃ are proved to be universally usable. TiO₂ does not react with the components of the coal gas, but Fe₂O₃ reacts. Both substances bind ZnO and decrease its sublimation rate.

The system ZnO—TiO₂ is of interest because of the possible formation of three double oxides of different stoichiometries (Zn₂TiO₄, ZnTiO₃, Zn₂Ti₃O₈) and different TiO₂ modifications as well. Dulin and Rase [1] estimated the phase diagram ZnO—TiO₂, where above about 870 K the compounds Zn₂TiO₄ and ZnTiO₃ are thermodynamically stable. Above 1220 K the authors detected the decomposition of ZnTiO₃ to Zn₂TiO₄ and TiO₂ rutile.

The existence of the metastable compound Zn₂Ti₃O₈ was shown for the first time by Bartram and Slepetys [2] and they proposed a structure derived from the spinel type. By Wallis [3, 4] a new type of a defect spinel was derived. The crystal structure of Zn₂Ti₃O₈ can be described with a cubic close packing of oxygen ions with completely occupied tetrahedral sites (Zn²⁺ ions) and not completely occupied octahedral sites. The unoccupied octahedral sites are not arranged statistically, but they are ordered in the structure. This order leads to the decrease of the space group symmetry from Fd-3m to P4₃32.

The aim of this part of the contribution is to investigate the relation between the microstructure and the kind of the compounds in the system ZnO—TiO₂, and to investigate the surface structure of Zn₂Ti₃O₈.

The structure and properties of zinc ferrite, ZnFe₂O₄, as a result of mechanical activation in ball mills and of the thermal relaxation have been studied in previous works [5, 6]. The mechanically induced reactivity of zinc ferrite was clarified in [7, 8]. The novel synthesis pathway (mechanosynthesis) to zinc ferrite of ZnO—Fe₂O₃ mixtures is described in [9].

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The part devoted to zinc ferrite in this paper focuses on the surface structure of mechanically activated as well as mechanosynthesized zinc ferrite.

**EXPERIMENTAL**

For the preparation of zinc ferrite two synthetic routes were used, a conventional thermal method as well as a high-energy ball milling. Stoichiometric mixtures of powdered reactants (products of Merck) were used as starting materials.

The experiments were carried out with powdered oxides of different particle sizes and specific surface areas $s(TiO_2)/(m^2 g^{-1})$: 9, 30, and 50; $s(ZnO)/(m^2 g^{-1})$: 3 and 70. The TiO$_2$ powders consisted of rutile or anatase or mixtures of both phases. The powdered oxides were mixed in ball mills with mole ratios $n(ZnO)/n(TiO_2) = \frac{2}{1}$, $\frac{1}{1}$, and $\frac{2}{3}$.

The milling process for the mechanical activation of crystalline zinc ferrite as well as the mechanosynthesis to zinc ferrite of Zn$_2$Ti$_3$O$_8$ powder mixtures was carried out in a planetary ball mill AGO 2 (Institute of Solid State Chemistry, Novosibirsk). A stainless steel vial (150 cm$^3$ in volume) and balls of 5 mm in diameter were used. The ball-to-powder mass ratio was 20:1. The milling was done in air.

The courses of the phase formations were investigated by temperature-dependent X-ray diffraction (XRD) methods. The initial stage of the solid state reactions was detected by in situ XRD measurements.

X-Ray diffraction patterns were collected using a URD 6 diffractometer (Seifert-FPM, Germany), a STADI P (Stoe, Germany), and a Guinier-Lenné camera (Nonius, The Netherlands). The radiations were CuKa and CoKa. Data interpretation was carried out using the database of the JCPDS with software by Stoe.

The surface analytical studies were performed by an ESCALAB 220iXL spectrometer (Fisons Instruments, Great Britain) consisting of two vacuum chambers: the analyzer and the fast entry air lock/preparation chamber. The powdered samples were fixed on a carbon tape (carbon conductive tape, Pelco International) at the top of the sample holder and transferred into the UHV. The X-ray source was monochromatic AlKα radiation (1486.6 eV) with an input power of 300 W. The emerging charge of the sample was equalized with the installed charge compensation. The final peak position was determined using the C1s peak (shifted to 285.0 eV) corresponding to absorbed carbon species. The XPS measurements were performed at a constant pass energy of 25 eV. The ESCALAB was calibrated routinely with the appropriate XPS lines of Au, Ag, and Cu as given in Ref. [10].

After background correction according to [11] the XPS spectra were described and the correct peak positions were determined by Gaussian—Lorentzian peaks if necessary with a tail function to take care of the asymmetry of the XPS signal of transition elements [12]. The information depth of these surface studies was estimated by the mean free path of electrons in solid state with approximately 7.5 nm.

**RESULTS AND DISCUSSION**

**Formation of Zn-Ti-Double Oxides and Surface Structure of Zn$_2$Ti$_3$O$_8$**

At temperatures below 1220 K mixtures of Zn$_2$TiO$_4$, ZnTiO$_3$ or Zn$_2$Ti$_3$O$_8$ are formed from ZnO

![Fig. 1. Photoelectron spectra of model substances with zinc in tetrahedral and in octahedral coordination. a) ZnO (Zn tetrahedrally coordinated), b) Zn$_2$Ti$_3$O$_8$ (Zn tetrahedrally coordinated), c) ZnTiO$_3$ (Zn octahedrally coordinated), d) Zn$_2$TiO$_4$ (Zn octahedrally coordinated). Zn$^{[4]}$ = Zn tetrahedrally coordinated, Zn$^{[6]}$ = Zn octahedrally coordinated.](image-url)
and TiO₂ as a result of solid state reactions. The formation of double oxides takes place in the temperature range between 870—1220 K. That temperature at which the solid state reaction starts decreases with an enlargement of the specific surface areas and a decrease of the particle sizes. The lowest temperatures are obtained with nanocrystalline powders and very homogeneous mixtures.

Compound Zn₂Ti₃O₈ originates only from the Zn₂TiO₄ phase. The double oxide formation with ZnO is overlapped by the transformation of the modification anatase → rutile taking place in the temperature range between 800—1100 K. The speed of transformation depends on the temperature and the particle size of the anatase powder.

There are correlations between the TiO₂ modification and the formation of certain titanium-zinc-double oxides. The formation of Zn₂TiO₄ and Zn₂Ti₃O₈ is confined only in the presence of anatase, while ZnTiO₃ is only formed in the presence of rutile. Between TiO₂ anatase and Zn₂TiO₄, or Zn₂Ti₃O₈ on the one hand and TiO₂ rutile and ZnTiO₃ on the other, structural similarities could be demonstrated. The symmetries of packing of the oxygen ions (cubic close packing and hexagonal close packing) show already fundamental relationships between the structures of anatase and Zn₂TiO₄, or Zn₂Ti₃O₈ as well as rutile and ZnTiO₃ (ilmenite). The structures of TiO₂, Zn₂TiO₄, and ZnTiO₃ consist of TiO₆ octahedra which are connected over common edges. In rutile and in ZnTiO₃ the connection of the TiO₆ octahedra leads to chains and/or layers, but in anatase and in spinel (Zn₂TiO₄ and Zn₂Ti₃O₈) to three-dimensional frameworks.

Fig. 1b shows the photoelectron spectroscopic surface studies of Zn₂Ti₃O₈ in comparison to ZnO, Fig. 1a, ZnTiO₃, Fig. 1c, and Zn₂TiO₄, Fig. 1d. It is known that the Zn²⁺ ions occupy in ZnO only tetrahedral sites and in ZnTiO₃ and Zn₂TiO₄ octahedral sites. The Zn²⁺ ions in Zn₂Ti₃O₈ have the same peak position and structure of the Zn 2p₃/₂ signal like the well known ZnO with zinc only in tetrahedral positions. This is another indication of the tetrahedral coordination of zinc in the defect spinel structure of Zn₂Ti₃O₈ [3, 4].

**Formation and Surface Structure of Zn Ferrite**

ZnFe₂O₄ is formed in ZnO—Fe₂O₃ mixtures at temperatures above 1100 K. Results of the investigation of the influence of mechanical activation of ZnO—
Fe$_2$O$_3$ mixtures on the formation of zinc ferrite have shown that it is possible to achieve the mechanoynthesis of zinc ferrite (from zinc oxide and iron oxide powders) at room temperature in a planetary mill [9].

Before milling the size of the powder particles of the Fe$_2$O$_3$—ZnO mixture varies from 10 µm to 50 µm. After a relative short time of milling (8 min) the material consists of agglomerates of many small particles (1—3 µm) with a rounded shape. With further milling the powders become much finer and uniform in shape with an average particle size of about 1 µm.

XRD pattern (Fig. 2a) of the starting powder is characterized by the sharp crystalline peaks corresponding to ZnO (JCPDS 36-1451) and α-Fe$_2$O$_3$ (JCPDS 33-664). During the early stages of milling XRD reveals only a decrease of the intensity and an associated broadening of the Bragg peaks of the individual oxides.

With increasing milling time, the weak diffraction lines of both phases completely disappear and the strongest diffraction lines gradually merge together producing two broad peaks and new peaks of ZnFe$_2$O$_4$ (JCPDS 22-1012) are formed (Fig. 2b, c). The results of Mössbauer spectroscopy give an additional confirmation on the formation of ZnFe$_2$O$_4$ during the mechanical activation of the oxides at room temperature [9]. Fig. 2d shows for comparison the XRD diagram of crystalline zinc ferrite.

Under standard conditions zinc ferrite forms the structure of a normal spinel with zinc in the tetrahedral sites and iron in the octahedral sites of a cubic close packing of oxygen atoms Zn$^{[4]}$Fe$^{[6]}_2$O$_4$, shown in Fig. 3a. It is the same peak position like the tetrahedrally coordinated zinc in ZnO (Fig. 1a) and an additional peak is that with the same position like the octahedrally coordinated zinc in Zn$^{[4]}$Fe$^{[6]}_2$O$_4$.

Zn$^{2+}$ ions in mechanically activated zinc ferrite are tetrahedrally and octahedrally coordinated. This means that a part of the surface structure (< 7.5 nm) of the mechanically activated zinc ferrite corresponds already to the structure of the inverse spinel.

The mechanical activation of a mixture of zinc oxide and iron(III) oxide shown in Fig. 3c—e leads to the same result of the surface analytical studies like the mechanical activation of the normal spinel of ZnFe$_2$O$_4$ and of the coordination sphere of zinc. In the oxide
mixture (Fig. 3c) zinc is tetrahedrally coordinated, but in the mechanically activated mixture the Zn$^{2+}$ ions occupy octahedral positions (Fig. 3d, e). Zinc is octahedrally coordinated in mechanosynthesized zinc ferrite. This means that also the surface structure of mechanosynthesized zinc ferrite corresponds to the inverse spinel type.

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