Thermochimica Acta, 200 (1992) 335–347
Elsevier Science Publishers B.V., Amsterdam

Thermoanalytical study on surface reactivity and characterization of oxide powders at elevated temperatures

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(Received 30 December 1991)

Abstract

Thermoanalytical studies on the surface reactivity and characterization of oxide powders have been reviewed on the basis of the author's work between 1967 and 1992. Gas-flow DTA apparatus and the emanation thermal analysis method using ^{226}Ra as parent isotope were successfully applied for investigating the surface behavior of powders at elevated temperatures.

INTRODUCTION

A powder reaction generally starts with phase boundary reactions, followed by transport through the bulk of the newly formed phase. The importance of the phase boundary reaction that takes place in the near-surface region of powders during the initial reaction step increases with a decrease in particle size. Therefore, in order to study the reactivity of powders, especially fine powders, it is necessary to follow up the surface behavior on the basis of thermal near-surface characterization of the powder at elevated temperatures. However, discussions have been concerned with diffusion transport in the bulk phases. This is mainly because of the difficulties encountered in a study of isothermal kinetics for the initial reaction stage at high temperatures. Strictly speaking, nothing is really known about phase boundary reactions and their reaction mechanisms in solid systems. A pertinent analysis is still not available, although in some cases linear rate laws indicating phase boundary control were found when the reaction layer thickness was smaller than 1 μm [1].

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From the above standpoint, thermoanalytical studies for the initial reactivity of various oxide powders have been carried out by the use of differential thermal analysis (DTA), thermogravimetry (TG) and high temperature X-ray diffraction (HTXRD) as a non-isothermal dynamic technique. These techniques have sometimes been used as a powerful tool in investigation of the initial reaction stage, but are not adequate to follow the thermal behavior of the surface layer of the powders. Therefore, emanation thermal analysis (ETA) has been newly applied to the thermal characterization of the near-surface region of oxide powders, and to the surface reactivity study of powders in solid–solid reaction systems. ETA has provided useful information on surface characterization and on the surface processes taking place in the initial reaction stage [2].

INITIAL STAGE OF POWDER REACTION

A diffusion controlled reaction proceeding in spherical particles obeys the so-called Jander equation [3], which was originally largely developed from the study of gas–solid reactions and is based on the assumption that particles of the solid reactant are completely covered by a coherent layer of product. Many applications of this simple equation have been involved in the kinetic studies of solid–solid interactions.

For solid–solid reactions in powdery state, the two following steps are assumed: initial rapid surface reaction, and later diffusion controlled reaction which obeys Jander kinetics after completion of product layer coverage at all reactant surfaces. The Jander plots for the reactions MgO–Al_2O_3 [4], MgO–Cr_2O_3 [5] and Fe_2O_3–ZnO [6] provided straight lines, but each of the lines extrapolated to $t = 0$ intercepts the ordinate at a certain positive value. This positive intercept was considered as resulting from an initial surface reaction which proceeds rapidly. The amount of surface reaction and the thickness of the surface layer formed in the initial period of reaction were estimated for the reaction system Fe_2O_3–V_2O_5 on the basis of the modified Jander equation [7]. The surface layer thickness increased from 30 to 240 nm for $FeVO_4$ formation at 575–650°C and from 0.1 to 2 μm for $ZnFe_2O_4$ formation at 700–1000°C [6] with an increase in the reaction temperatures.

On the other hand, the zone within which reaction is most probably initiated is that at which particles of the two reactants present are in direct contact. However, the area available for chemical contact in a mixture of particles is a very small fraction of the total surface, ca. 10^{-6}. Further, bulk diffusion across a barrier layer is usually an activated process, so that interposition of product between the points of initial contact reduces the ease, and therefore the rate, of interaction.

On completion of the initial step in the reaction, the restricted zones of direct contact have undergone chemical modification, and the continuation of reaction necessitates a transport process to maintain the migration of material from one solid to a reaction surface of the other [8]. On increasing the temperature, surface migration usually becomes appreciable at temperatures significantly below those required for the onset of bulk diffusion within a product phase. It is to be expected that components of the less refractory constituent will migrate onto the surface of the other solid present. This coverage of crystallites of one reactant by the chemical constituents of the other corresponds to the complete and rapid nucleation of all the surface before occurrence of the more difficult growth step requiring bulk diffusion.

Although it is possible that surface defects may be preferentially involved in initial product formation, such zones of preferred reactivity would be of limited significance, as they would soon be covered with the coherent product layer developed by the reaction proceeding at all reactant surfaces.

The higher temperatures usually employed in isothermal kinetic studies of diffusion controlled reactions do not usually permit measurements of rates of the initial reaction steps. However, such measurements are necessary to elucidate the surface problems occurring during the initial reaction step, especially with use of fine powders smaller than 1 μm in size.

DTA AND TG STUDIES OF POWDER REACTIONS

A gas-flow DTA apparatus [9], which permits various gases to flow through a reference and the sample beds during a test, was applied to study the thermal behavior of powders in various reaction systems, single solid, solid–gas, and solid–solid. Further, powder–solid catalysis was studied thermoanalytically on the basis of the surface reactivity. TG and HTXRD were also used in part.

Single solid reactions

The thermal decomposition of $MgCl_2 \cdot 6H_2O$ was studied in five different flowing atmospheres: air, N_2, HCl, Cl_2 and steam [10]. The decomposition was greatly influenced by the atmosphere.

The effect of adding $KClO_3$ on the thermal decomposition of $CaC_2O_4 \cdot H_2O$ was studied in flowing air, N_2 and O_2 atmospheres [11]. The thermal decomposition of NH_4VO_3 was studied in N_2 and wet air atmospheres and in a vacuum [12].

Solid–gas reactions

The oxidation of UO_2 was studied in an air flow [9].

The chlorination of Mg-containing complex ores (olivine, protoenstatite and talc) with a Cl_2 gas flow was studied in the temperature range

25–1000°C [13]. In the preliminary chlorination experiments with Cl_2, the constituents of ores, MgO, FeO and Fe_2O_3, successfully showed exothermic peaks at 450, 150 and 450°C, respectively, and SiO_2 was inert towards Cl_2 up to 950°C. Only MgO required carbon as additive for the chlorination: Mg in the ores was chlorinated only when the samples were mixed with carbon.

The chlorination processes of bauxite, which consists mainly of gibbsite and hematite, were studied in the presence of active carbon. In order to examine the chlorination behavior of bauxite in more detail, the chlorination of hydrated alumina and hematite and their mixtures was carried out [14].

The chlorination processes of four hydrated aluminas, gibbsite, pseudoboehmite and boehmite, and four transition aluminates were studied in the presence of active carbon [15].

The chlorination processes of fly ash and bauxite in the presence of carbon were studied [16]. The reactivity of Al compounds estimated from DTA peak temperatures depended on the particle size, carbon content and preparation temperature of the fly ash, and was much lower than that of bauxite.

The reaction processes of solid binary metal oxides, sodium aluminate, magnesium aluminate and calcium aluminate with SO_2 were studied in order to design a new process for SO_2 recovery from polluted air [17].

TG experiments on the hydrogen reduction of Fe_2O_3 were carried out to elucidate the influence of the preparation history of the oxide on its reactivity [18].

Solid–solid reactions

The promoting effect of halides and fluorides on the formation of $MgAl_2O_4$ in the initial stage of the $MgO–Al_2O_3$ system has been studied [4].

The promoting effect of halide additives on the formation of $MgFe_2O_4$ was also studied [19]. In the case of fluoride, it seems that the reactions between the fluoride and the reactants promote $MgFe_2O_4$ formation in the initial stage, and that compounds produced by the initial reaction accelerate a diffusion in the later stage. The same promoting mechanism seems to be applicable in the case of chloride additives. The interaction between solid NaCl and solid Fe_2O_3 occurring just before melting of the NaCl seems to initiate $MgFe_2O_4$ formation.

The solid state reactions in the $MgO–Cr_2O_3$ and $ZnO–Cr_2O_3$ systems were studied under various atmospheres: O_2, N_2 and air [5]. DTA provided useful information with respect to the initial reaction stage: oxidation of Cr_2O_3 to CrO_3 in the presence of MgO or ZnO, followed by the formation of a thin layer of spinel, which consisted of an imperfect lattice, on the surface of the MgO or ZnO grains.

Interesting effects of the fluoride additives LiF, NaF and CaF_2 on the solid reactions in the $MgO–Cr_2O_3$ and $ZnO–Cr_2O_3$ systems, in N_2, were observed by DTA [20]. For the $MgO–Cr_2O_3–MF$ (M = Li, Na) systems, it was concluded that the melting of the fluoride additives plays an important role in accelerating the second reaction step at around 1000°C. On the other hand, for the $ZnO–Cr_2O_3–MF$ (M = Li, Na) systems, a marked acceleration by the additives was observed in the first step at around 700°C, a much lower temperature than the melting points of the fluorides.

The reversible reactions $MSO_4 + Al_2O_3 = MAl_2O_4 + SO_3$ ($SO_2 + 1/2O_2$) (M = Mg, Ca) were studied by means of gas-flow DTA [17].

The thermal behavior of $CaSO_4$–[oxide]$_I$ systems, where [oxide]$_I$ = MgO, CaO, ZnO, Co_3O_4, NiO or CuO, and $CaSO_4$–[oxide]$_{II}$ systems, where [oxide]$_{II}$ = Al_2O_3, SiO_2, TiO_2, Cr_2O_3, MnO_2 or Fe_2O_3, has been studied [21]. The decomposition of $CaSO_4$ was promoted by the [oxide]$_{II}$, presumably because of the formation of a binary metal oxide through some intermediates which consist of $CaSO_4$ incorporated with an oxide during the course of the reaction. However, [oxide]$_I$ had no effect.

The influence of the preparation history of TiO_2 on its reactivity in solid-state reactions in the $CaSO_4–TiO_2$ systems were studied. The reactivity of TiO_2 was dependent on structural differences due to the different preparation histories; the greater the stability of the anatase form, up to higher temperature, the higher the reactivity of TiO_2 [22].

In the initial steps, the reactions of $BaSO_4$ with anatase proceeded to $BaTi_4O_9$, of $BaSO_4$ with rutile to $BaTi_3O_7$, and of $BaCO_3$ with anatase and rutile to Ba_2TiO_4. These reactions were connected with the formation of binary metal oxide through intermediates comprising $BaSO_4$ or $BaCO_3$ incorporated with TiO_2. The reactivity of anatase was higher than that of rutile in all the reaction systems [23].

It is necessary to elucidate the effect of particle size, due to the different preparation histories, on the reactivity in further detail.

Solid catalysis

The thermal behavior of industrial vanadium catalysts for SO_2 oxidation was studied in the working state by means of gas-flow DTA [24]. The catalysts used were V_2O_5 and compositions of V_2O_5 with various promoters: Li = Li_2SO_4, Na = Na_2SO_4, K = K_2SO_4, K_1 = KOH, K_2 = $KHSO_4$, and Cs = Cs_2SO_4. Four different atmospheres, viz. air, N_2, SO_2 and SO_2 + air, were used. The DTA curves of the fresh catalysts, except for V_2O_5 and $V_2O_5–Li_2SO_4$, in SO_2–air mixtures showed an exothermic peak I at about 400°C corresponding to the activation process, the formation of complexes containing vanadium, alkali and SO_3. Another peak II at about

500°C corresponded to the catalytic oxidation of SO_2 to SO_3. Peak I disappeared in the activated catalysts. The order of the effects promoting SO_2 oxidation was estimated from the temperatures of peak II in the following manner, $(Cs) > (K) > (K_1) > (K_2) > (Na) > (Li)$. The melting points of the activated complexes, which were estimated from the DTA curves, were closely related to the thermal behavior of the catalytic oxidation. The stability of catalytic activity was tested through the observation of changes in the DTA curves with time 0–23 h.

The chemical composition change of V_2O_5–M_2SO_4 and V_2O_4–M_2SO_4 systems (M = Li, Na, K and Cs) was studied, and the relationship between the thermal behavior and catalytic activities was discussed [25]. It was estimated that M_2SO_4 compounds have the effect of promoting the reduction of V_2O_5 and the oxidation of V_2O_4, and that SO_3 adsorbed in M_2SO_4 has the effect of stabilizing the vanadium in the pentavalent state in the order $(Cs) > (K) > (Na) > (Li)$. This order corresponded to the catalytic activity estimated from DTA experiments.

The catalytic decomposition of $KClO_4$ by Fe_2O_3, obtained by calcination of Fe(II) salts at different temperatures, was investigated [26,27]. A sample without catalyst was found to begin fusion and decomposition simultaneously, and to form an intermediate, $KClO_3$. Addition of catalysts resulted in solid-phase decomposition before fusion of $KClO_4$. The initial decomposition temperature (T_i) increased with the temperature of preparation of the catalyst and showed a definitive relationship with the crystallite size of the catalyst. The change of T_i is discussed on the basis of the n-type semiconductive properties of the catalyst.

The effects of Fe_2O_3 and Al_2O_3 additives on the thermal decomposition of perchlorates, oxalates and hydroxides were investigated [27]. It was found that the oxides catalytically promoted the decomposition of perchlorates and resulted in a lowering of the initial decomposition temperature T_i. On the other hand, no significant effect on the decomposition of oxalates and hydroxides was shown. The catalytic effect of twelve oxides on the decomposition of $KClO_4$ was compared. Transition metal oxides such as Cr_2O_3, Fe_2O_3 and CuO markedly accelerated the solid phase decomposition. The modified catalytic mechanisms of transition metal oxides were proposed by considering the electron transfer and the oxygen-abstraction models.

Scanning electron microscopic (SEM) observation of the thermal decomposition processes of $KClO_4$, $KClO_3$, $KBrO_3$, KIO_4 and KIO_3 in the presence of Fe_2O_3 and Al_2O_3 was carried out. In order to identify the occurrence of solid state decomposition in Fe_2O_3–salt systems, SEM observations were performed for samples obtained after decomposition to various extents by heating up to various temperatures on the DTA curves. From comparison of SEM photographs of Fe_2O_3–salt systems with those of pure salts and Al_2O_3–salt systems, it was found that Fe_2O_3 shows observable indications of the solid state decomposition of the salts at the initial stage [28].

The effect of additives on the thermal decomposition of salts of halogen oxoacids ($KClO_4$, $KClO_3$, KIO_4 and $KBrO_3$), oxalates ($NiC_2O_4 \cdot 2H_2O$, $MgC_2O_4 \cdot 2H_2O$ and $CaC_2O_4 \cdot H_2O$), azide (NaN_3), permanganate ($KMnO_4$), and oxides (MnO_2 and PbO_2) was studied. The additive Fe_2O_3 exhibited a remarkable catalytic acceleration effect on the decomposition of salts of halogen oxoacids [29].

ETA STUDIES OF SURFACE REACTIVITY AND CHARACTERIZATION OF POWDERS

Emanation thermal analysis (ETA)

ETA is a dynamic technique used for detection or quantitative measurement of radioactive inert gas (radon) released from activated powders during a controlled temperature program. The ETA technique using a surface impregnation method with aqueous ^{226}Ra solution (4 μCi ml^{-1}) was applied to the thermal characterization of the near-surface region of various metal oxide powders, and to surface reactivity measurements of the solid–solid reaction systems. The parent nuclide ^{226}Ra was adsorbed on the surface and the daughter inert gas atom ^{222}Rn was formed by alpha-decay and introduced into a surface layer less than 50 nm thick [30] by the recoil energy. Before being used for ETA experiments, in both the first and succeeding runs, the dried labeled samples were stored for periods exceeding one month until a radioactive equilibrium state was reached.

In order to measure the surface reactivity of the powders in solid–solid systems, a powder mixture of labeled and non-labeled samples was prepared by mixing these powders in an agate mortar with acetone. In this mixing process, the non-labeled powder was hardly labeled by ^{226}Ra nuclide adsorbed on the surface of the labeled powder [31]. Therefore the ETA curves for the mixture are indicative of the gas-release behavior of the labeled sample in the mixture.

Interpretation of ETA curve

A comprehensive review on ETA studies was presented by Balek [32]. Balek [33] has also proposed that the release of radon from a dispersed powder with temperature rise may be separated into three parts: (a) a recoil part, E_r, due to energy that a radon atom gains during its formation by the decay of radium; (b) a diffusion part, E_p, due to the diffusion in the intergranular space, open pores, etc., of the dispersed powder; and (c) a diffusion part, E_d, due to bulk diffusion of radon in the solid matrix of the dispersed powder. The total emanating power E can be expressed as

$$E = E_r + E_p + E_d \qquad (1)$$

E_r is independent of temperature; E_p is dependent on temperature, dispersivity and morphology of the powders, but is negligible at room temperature; E_d is dependent on temperature and the effective surface of the powder.

Matzke [34] has shown that the E_d part of gas release starts at 40–50% of the absolute melting temperature T_m for a wide variety of ionic crystals with different lattice structures. The onset temperatures of gas release in the E_d part are similar to those of self-diffusion of the matrix atoms $T_s = (0.4\text{–}0.5)T_m$. The T_s was calculated at 456–639°C for Fe_2O_3 ($T_m = 1823$ K), 656–889°C for Al_2O_3 ($T_m = 2323$ K), 578–791°C for TiO_2 ($T_m = 2128$ K), etc.

Jech and Kelly [35] have demonstrated the gas release stages over the range 25–1100°C for an Al_2O_3 single crystal which was labeled by the ion-bombardment technique using ^{85}Kr.

On the basis of the useful information mentioned above, the characteristic changes in the ETA curves observed for polycrystalline powders were grouped into the following two main stages: stage I at temperatures lower than T_s, and stage II due to E_d at temperatures higher than T_s. The ETA peaks corresponding to stages I and II are hereinafter designated by peaks I and II, respectively. In many cases, peak II was split into two peaks IIa and IIb. The peak which appears at around T_s was represented as peak I′.

ETA using ^{226}Ra parent isotope was applied to various oxide powders in single and mixed systems, and the results in 1984–1987 have been summarized [2].

Surface characterization of powders

ETA was applied in the range 25–1450°C to commercial alumina powders with various preparation histories [36]. The gas-release stages in the ETA curves of Al_2O_3 prepared by a Bayer process were broadly grouped into two parts: peak I, with its maximum at 100–550°C (Ia at about 270–300°C and Ib at 450–500°C) and peak II starting at about 800°C (IIa with its maximum at 950°C and IIb at about 1200°C). The effects of Na ions, heating and grinding on the ETA behavior were discussed.

ETA was applied in the thermal characterization of the near-surface region of Fe_2O_3 powders with various preparation histories in the heating and grinding treatments [37,38]. Peaks I, II′ and II appeared at the corresponding stages. The appearance of peak I was explained by the mechanochemical effects due to the grinding treatment, and it disappeared in the repeated run. The shift of peak II from 900 to 1000°C in the repeated run was explained by the ordering effect of the crystal lattice due to the heating treatment. The behavior of peak I′ was complicated. The

ETA results using ^{228}Th solution (3 μCi ml^{-1}) showed a fundamental difference from those of ^{226}Ra solution (4 μCi ml^{-1}) [37].

The effects of heating on the surface layer of the polycrystalline powders, one basic zinc carbonate and two zinc oxides, each of which had been prepared by a different procedure, was studied by ETA [39]. The thermal behavior of the grain boundary and the mechanochemical effects were discussed.

The thermal characterization of the surface layers of the polycrystalline metal oxides NiO, CuO and MgO (which were prepared by the decomposition of their basic carbonates or hydroxides) was studied by ETA [40]. The ETA results provided useful information on the thermal behavior of grain boundaries; this could not be studied by the conventional thermoanalytical methods such as TG, DTA, HTXRD, etc.

In order to examine the effects of grinding treatment on the surface layer of powders, ETA was applied in the range 25–1200°C for characterization of the surface of five Fe_2O_3 samples with various preparation histories with regard to grinding treatment [41]. The ETA results were compared with those obtained by the conventional methods: size distribution, BET surface, XRD and SEM. The mechanochemical effects of grinding on the surface layer of the sample powders were evident as an increasing peak I and a pronounced peak IIa.

Furthermore, in order to examine the effects of both grinding and sieving treatments on the surface layer of powders, ETA was applied in the range 25–1450°C for characterization of the near-surface region of 24 Al_2O_3 powders [42] and 36 TiO_2 (rutile) powders [43], each of which had various preparation histories in terms of the grinding and sieving treatments used. For Al_2O_3 powders, the effects of pulverizer material, grinding time and particle size on the ETA curves were discussed. The ETA behavior was greatly affected, in addition to grinding effects, by the dispersion phenomena of particles resulting from the sieving treatments. These results made complex the relationship between the ETA curve and the preparation history of fine powders. For TiO_2 powders, two pulverizers (planetary pulverizer and mortar grinding) and two grinding procedures (dry and wet) were used, with various grinding times. The results obtained were as follows: (i) the influence of the methods of preparation of the powders appears as a variation in the ETA peaks in the first run; (ii) the sieving effect appears mainly as an enlargement of the ETA peak IIa; (iii) the grinding effect appears markedly only in the initial grinding step; and (iv) the ETA results are supported by the scanning electron microscopy observations.

Surface reactivity of powders

The usefulness of the ETA technique was discussed for following the surface reactivity of powders on the formation of $ZnFe_2O_4$ in the Fe_2O_3–ZnO mixed systems [31].

In order to elucidate the surface reactivity of $BaCO_3$ and TiO_2 (anatase and rutile) powders, the thermal behavior of the labeled $BaCO_3$ or TiO_2 species in $BaCO_3$–TiO_2 mixed systems was monitored by means of ETA together with conventional thermoanalytical techniques, TG–DTA and HTXRD [44]. One of the most interesting aspects of the ETA behavior in this work was that, in the $BaCO_3$–TiO_2 (labeled) system, a new peak (starting at about 200°C) appeared as a result of the occurrence of surface distortion of TiO_2 powder at temperatures lower than about 700°C before the formation of the $BaTiO_3$ phase started at about 780°C. No release of CO_2 was observed at such low temperatures. This ETA result for the mixed system suggests that a phase-boundary reaction at the TiO_2 surface surrounded with $BaCO_3$ by surface migration takes place at temperatures lower than about 700°C. This hypothesis may also be supported by the ETA behavior: the surface distortion of $BaCO_3$ occurs much more easily than that of TiO_2 at low temperatures. A scheme of the surface layer in the initial reaction stage during a linear temperature increase was shown for the solid–solid reaction $A(s) + B(s) = C(s) + D(g)$.

The surface reactivity of oxide powders for solid solution formation in the system Fe_2O_3–Al_2O_3 (1:1) was studied by ETA in the temperature range 25–1450°C [45]. It was possible to consider the role of the near-surface region of the powder in the initial step: a phase-boundary reaction at the Al_2O_3 surface surrounded with Fe_2O_3 by surface migration, probably the formation of an unstable intermediate phase ($Fe_2O_3 \cdot Al_2O_3$), is initiated at about the T_s of Fe_2O_3 (456–639°C), which is lower than that of Al_2O_3 (656–889°C).

The surface reactivity of the oxide powders was examined in the solid–solid reaction systems Fe_2O_3–ZnO, Al_2O_3–ZnO and TiO_2–ZnO by ETA, on the basis of the thermal characterization of the constituent oxides [46]. The two Fe_2O_3, three Al_2O_3, two TiO_2 and two ZnO samples that were used as the starting materials were each prepared by a different procedure. It was shown that the ETA method provides useful information on the phase-boundary processes taking place in the initial reaction step under certain conditions at high temperatures. The ETA behavior observed in run 1 for the mixed systems at temperatures above T_s of the constituent oxides could be related to the reactions taking place in the surface layer of the labeled oxides. T_s is the temperature, corresponding to 40–50% of the absolute melting temperature, at which self-diffusion of the matrix atoms and the bulk diffusion of radon start simultaneously. The estimated values of T_s were 600, 800, 700 and 600°C for Fe_2O_3, Al_2O_3, TiO_2 and ZnO, respectively. For the Al_2O_3–ZnO (TiO_2–ZnO) system, the phase-boundary reaction at the Al_2O_3 (TiO_2) surface interspersed with ZnO because of surface migration that starts at about 600°C, probably with the formation of a metastable intermediate such as $Al_2O_3 \cdot ZnO$ ($TiO_2 \cdot ZnO$) followed by recrystallization to a stable $ZnAl_2O_4$ ($ZnTiO_3$), is initiated at temperatures near the T_s of Al_2O_3 (TiO_2). For the Fe_2O_3–ZnO system, surface migration of ZnO and Fe_2O_3 was initiated simultaneously at 600°C.

The effect of preparation conditions of TiO_2 powders on the reactivity for the powder reaction in TiO_2–$SrCO_3$ mixed systems was studied thermoanalytically [47]. The thermal characterization of five TiO_2 powders and one $SrCO_3$ powder was first carried out. Subsequently, the reaction behavior in the mixed systems incorporating various TiO_2 powders was followed by means of HTXRD, TG–DTA–ETA and SEM. The findings obtained were as follows: (i) the "surface migration model" at the initial reaction stage, which had been reported for TiO_2–$BaCO_3$ systems [44], is applicable; (ii) the effect of the particle size of TiO_2 is much larger than that of the crystal form or the surface state, (iii) TiO_2 prepared as fine particles of 0.2–0.3 μm diameter has a high reactivity, and (iv) an importance of the surface reaction for investigating the powder reactions was also confirmed in this reaction system.

CONCLUSIONS

Thermoanalytical studies on the surface reactivity and characterization of oxide powders have been reviewed on the basis of the author's works from 1967–1992. The main conclusions to be drawn from these results are as follows.

(1) In order to study the reactivity of powders, especially fine powders of less than about 1 μm diameter, it is necessary to follow the surface behavior, on the basis of the thermal characterization of the near-surface region of the powder at elevated temperatures.

(2) The thermoanalytical studies on the initial reactivity of various oxide powders were carried out by the use of DTA, TG and HTXRD as a non-isothermal dynamic technique.

(3) A gas-flow DTA apparatus, which permits various gases to flow through a reference and the sample beds during test, was successfully applied to monitor the thermal behavior of powders in various reaction systems, single solid, solid–gas, solid–solid and solid catalysis. TG, HTXRD and SEM were used for examining the DTA results.

(4) ETA using ^{226}Ra as parent isotope was newly applied to the thermal characterization of the near-surface region of powders, and to the surface reactivity study of powders in solid–solid reaction systems. The ETA results provided useful information on the thermal behavior of the surface layer (< 50 nm thick) during a controlled temperature program to 1500°C.

(5) The surface migration model was proposed in the initial reaction stage taking place at the temperatures above T_s (onset temperature of self-diffusion of the matrix atom) of the constituents in solid–solid systems.

(6) In powder reactions, a dominant factor increasing the reactivity is the size of the particles used, because the role of the surface reaction that

takes place in the near-surface region increases greatly with a decrease in particle size.

REFERENCES

1 H. Schmalzried, in M.S. Seltzer and R.I. Jaffee (Eds.), Defects and Transport in Oxides, Plenum Press, London, 1973, p. 102.
2 T. Ishii, Materials Science Forum, Vol. 29, Trans. Tech. Publications, Switzerland, 1988, p. 219.
3 W. Jander, Z. Anorg. Chem., 163 (1927) 1.
4 S. Shimada, R. Furuichi and T. Ishii, Bull. Chem. Soc. Jpn., 47 (1974) 2026, 2031.
5 T. Ishii, R. Furuichi and Y. Hara, J. Therm. Anal., 11 (1977) 71.
6 S. Shimada, K. Soejima and T. Ishii, React. Solids, 8 (1990) 51.
7 R. Furuichi, T. Ishii and S. Banba, Z. Anorg. Allg. Chem., 437 (1977) 293.
8 W.E. Brown, D. Dollimore and A.K. Galway, Comprehensive Chemical Kinetics, Vol. 22, Elsevier, Amsterdam, 1980, p. 253.
9 T. Ishii, T. Furumai and G. Takeya, J. Chem. Soc. Jpn. (in Japanese), 70 (1967) 1652.
10 S. Shimada, R. Furuichi and T. Ishii, J. Chem. Soc. Jpn. (in Japanese), 74 (1971) 2006.
11 T. Ishii, K. Kamada and R. Furuichi, J. Chem. Soc. Jpn. (in Japanese), 74 (1971) 854.
12 A. Shimizu, R. Furuichi and T. Ishii, J. Chem. Soc. Jpn. (in Japanese), (1975) 39.
13 T. Ishii, R. Furuichi and Y. Kobayashi, Thermochim. Acta, 9 (1974) 39.
14 T. Ishii, R. Furuichi and K. Kudo, Netsu Sokutei, 4 (1977) 100.
15 T. Tsuchida, T. Ishii, R. Furuichi and H. Haga, Thermochim. Acta, 34 (1979) 19.
16 T. Ishii, T. Tsuchida, R. Furuichi, H. Haga and K. Kudo, Thermochim. Acta, 53 (1982) 89.
17 T. Okutani, R. Furuichi and T. Ishii, J. Chem. Soc. Jpn. (in Japanese), (1974) 2303; (1975) 275; (1975) 1153; (1975) 1485.
18 M. Shimokawabe, R. Furuichi and T. Ishii, Thermochim. Acta, 28 (1979) 287.
19 S. Shimada, R. Furuichi and T. Ishii, Bull. Chem. Soc. Jpn., 49 (1976) 1289.
20 T. Ishii, R. Furuichi, Y. Hara and S. Shimada, J. Therm. Anal., 15 (1979) 261.
21 T. Ishii, R. Furuichi and H. Matsusato, J. Appl. Chem. Biotechnol., 28 (1978) 157.
22 T. Ishii, R. Furuichi and Y. Ohshima, J. Therm. Anal., 18 (1980) 527.
23 T. Ishii, R. Furuichi, T. Nagasawa and K. Yokoyama, J. Therm. Anal., 19 (1980) 467.
24 T. Ishii, M. Aramata and R. Furuichi, J. Chem. Soc. Jpn. (in Japanese), (1972) 266.
25 T. Ishii, M. Aramata and R. Furuichi, J. Chem. Soc. Jpn. (in Japanese), (1972) 1068.
26 R. Furuichi, T. Ishii and K. Kobayashi, J. Therm. Anal., 6 (1974) 305.
27 M. Shimokawabe, R. Furuichi and T. Ishii, Thermochim. Acta, 20 (1977) 347; 21 (1977) 273.
28 R. Furuichi, T. Ishii, Z. Yamanaka and M. Shimokawabe, Thermochim. Acta, 51 (1981) 199.
29 R. Furuichi, T. Ishii, Z. Yamanaka and M. Shimokawabe, Thermochim. Acta, 51 (1981) 245.
30 T. Hashimoto, Y. Aoyagi, H. Kudo and T. Sotobayashi, J. Radioanal. Nucl. Chem., Articles, 90(2) (1985) 415.
31 T. Ishii, React. Solids, Proc. Int. Symp., 10th, 1984, Part B, Elsevier, Amsterdam, 1985, p. 959.
32 V. Balek, Thermochim. Acta, 22 (1978) 1.
33 V. Balek, J. Mater. Sci., 17 (1982) 1269.
34 H. Matzke, Can. J. Phys., 46 (1968) 621.
35 C. Jech and R. Kelly, Proc. Br. Ceram. Soc., 9 (1967) 259.
36 T. Ishii, Thermochim. Acta, 109 (1986) 227.

37 T. Ishii, J. Chem. Soc. Jpn. (in Japanese), (1984) 936.
38 T. Ishii, Thermochim. Acta, 88 (1985) 277.
39 T. Ishii, React. Solids, 6 (1988) 1.
40 T. Ishii, Thermochim. Acta, 137 (1989) 293.
41 T. Ishii, S. Nakano and A. Yada, Thermochim. Acta, 178 (1991) 109.
42 T. Ishii, T. Takemura, S. Nakano and A. Yada, Thermochim. Acta, 178 (1991) 117.
43 T. Ishii, N. Tashiro and T. Takemura, Thermochim. Acta, 180 (1991) 289.
44 T. Ishii, React. Solids, 3 (1987) 85.
45 T. Ishii, React. Solids, 4 (1988) 327.
46 T. Ishii, React. Solids, 6 (1988) 11.
47 T. Ishii and A. Yada, Mem. Tomakomai Natl. Coll. Technol. (in Japanese), 27 (1992) 1, 13.