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Applications of the zero-order reaction rate model and transition state theory on the intra-particle sintering of an alumina powder by using surface area measurements

Y. Sarıkaya [a,*], K. Ada [b], M. Önal [a]

[a] *Ankara University, Faculty of Sciences, Department of Chemistry, Tandoğan,06100 Ankara, Turkey*
[b] *Kırıkkale University, Faculty of Arts and Sciences, Department of Chemistry, Kırıkkale, Turkey*

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Abstract

The cylindrical compacts with the diameter of 14 mm were prepared under 32 MPa of an alumina powder having agglomeration degree of 80% and maximum surface area of 81 $m^2 g^{-1}$ after calcination at 900 °C for 2 h. Each compact was fired isothermally at a different temperature between 950 and 1150 °C for 2 h. The rate constant for each temperature was obtained from the application of the zero-order reaction rate model on the surface area measurements after sintering. Arrhenius equation for the sintering was obtained in the form: $k = (8.09 \times 10^6\ m^2\ mol^{-1}\ s^{-1})\exp(-187\,643\ J\ mol^{-1}/RT)$. Transition state theory was applied to the sintering and thermodynamic parameters of the activation were calculated. The relation of these parameters in SI units can be summarized in the forms: $\Delta H^{\#} = 178\,643 - 8.314T$, $\Delta S^{\#} = -73.6 - 8.314 \ln T$, and $\ln K^{\#} = -\Delta G^{\#}/RT = -(\Delta H^{\#} - T\Delta S^{\#})/RT = -21\,487/T - \ln T - 7.853$, where $\Delta G^{\#}$, $\Delta H^{\#}$, $\Delta S^{\#}$ and $K^{\#}$ are the Gibbs free energy, enthalpy, entropy, and equilibrium constant of activation.

Keywords: Activation parameters; Alumina; Sintering rate; Surface area; Transition state

1. Introduction

The first step of ceramics production is the preparation of the fine ceramic powders having same size and shape especially spherical as small as possible. However, most powders contain agglomerates in a great extent. Agglomerates are groups of primary simple particles can be classified as either hard or soft according to their strength. The hard and soft groups hold together by chemical bonding and van der Waals force respectively [1–3]. The hard agglomerates impair the compactibility of powders by shaping [4–8]. Agglomerated particles cause voids of different sizes in shaped compact. The voids intra- and inter-particle whose widths are smaller than 2 nm, between 2 and 50 nm and greater than 50 nm are called micropores, mesopores, and macropores respectively [9]. The last step of ceramic production is firing. The sinterability of the shaped compact by firing reduces by the increasing of the number, size, and strength of the agglomerates and also affects from porosity in the green compact [10–18]. However, agglomerates cause some difficulties to investigate of kinetics and thermodynamics for sintering.

Sintering kinetics is based on time dependent isothermal measurements of any variable at different temperatures [19,20]. Several models were reported in the literature to obtain the kinetic parameters for sintering such as rate constant, activation energy, frequency factor, and mechanism. These parameters have been obtained by the measurements of relative linear shrinkage, [21,22] density, [23–25] porosity, [26,27], and surface area [28–30]. Many relations have been derived among the relative change of these measurable quantities by sintering [30–35].

Both neck-growth sintering rate (NGSR) and *n*th-order Gaussian energy distribution (NOGD) models have been used extensively to determine the kinetic parameters for sintering [36–39]. While order (n) and activation energy ($E^{\#}$) are known to be a function of temperature in NOGD model, in NGSR model only n depends on temperature. The NOGD model has some difficulty than has NGSR model in correlating sintering data over wide ranges of time and temperature. Since the n and $E^{\#}$

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* Corresponding author. Tel.: +90 312 212 6720/1014; fax: +90 312 223 2395.
E-mail address: sakaya@science.ankara.edu.tr (Y. Sarıkaya).

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are independent from temperature, the zero-order reaction rate (ZORR) model purposed in this study is the simplest model for calculations. This model has been selected only to calculate the thermodynamic parameters of transition state easily, but has never proposed to be as an alternative model over NOGD and NGSR models. When measurable quantity taken as surface area (S) the validity limit of this model is $\Delta S/S_0 \leq 0.50$, where $\Delta S = (S_0 - S)$ is surface area reduction and S_0 is initial surface area [28–30]. For this reason, the aim of this study is the application of the ZORR model and transition state theory (TST) on the intra-particle sintering of an alumina powder by using surface area measurements in the limit of $\Delta S/S_0 \leq 0.50$.

2. Experimental

2.1. Alumina powder

Preparation and same physicochemical properties of the alumina powder selected for material in this study were investigated in our previous works [40,41]. An alumina precursor was precipitated in boiling aqueous solution contained 0.20 M Al^{3+} and excess urea. The δ-Al_2O_3 powder having the maximum surface area of 81 $m^2\,g^{-1}$ was obtained by the calcinations of the precursors at 900 °C for 2 h. The powder changes to α-Al_2O_3 above 1150 °C. The size of spherical primary particles and their agglomerates obtained from particle size distribution (PSD) are between 0.3–1.0 μm and 1.0–100 μm respectively. The PSD of powder was determined by a Mastersizer Instrument (Malvern Instruments, Model Micron) based on a light scattering technique. The PSD curves were obtained by this technique as volume percent (vol.%) against diameter (D) and its derivative. The volumetric agglomeration degree of the powder is read directly as 80% from the curve of vol.% against D in the interval of 1.0–100 μm.

2.2. Compaction and firing

The powder was homogeneously mixed with oleic acid (12% by mass) in a mortar [5]. The previously weighed mixtures of the powder and binder were compacted under 32 MPa by an axial press (Graseby/Specac, Orpington Kent, UK). The compacts having diameter of 14 mm were heated from room temperature to 900 °C with a heating rate of 10 K min^{-1} and held at this temperature for 2 h to ensure complete outgassing by using a furnace (Protherm Model FFL 120/7, Alser, Ankara, Turkey). The outgassed samples were then fired to different temperatures between 950 and 1150 °C with a heating rate of 5 K min^{-1} and held these temperatures for different times between 0 and 2 h by using the same furnace. At the end of firing each compact was cooled spontaneously to room temperature, without any cooling schedule.

2.3. Instrumentations

The powder and some of the fired compacts were examined by the scanning electron microscope (Model LEO 435 VP) and their SEM views were obtained. The adsorptions of nitrogen on the fired compacts were realized at liquid nitrogen temperature by using a volumetric adsorption instrument. This instrument was constructed completely of Pyrex glass and connected to high vacuum [42]. Before adsorption the samples were outgassed under vacuum at 250 °C for 4 h.

3. Results and discussion

3.1. Morphologies of the calcined and sintered particles

The SEM views for the alumina powder calcined at 900 °C and the compact fired 1150 °C are given in Fig. 1a and b, respectively. The primary particles in the powder are spherical and a lot of those are agglomerated as seen in Fig. 1a. The pores between inter-particles as seen in Fig. 1b show that the inter-agglomerates sintering did not occur by firing. On the other side, the firing compacts were almost soft and can be crushed easily by hand. However, it can be estimated that the intra-particle sintering occurs only.

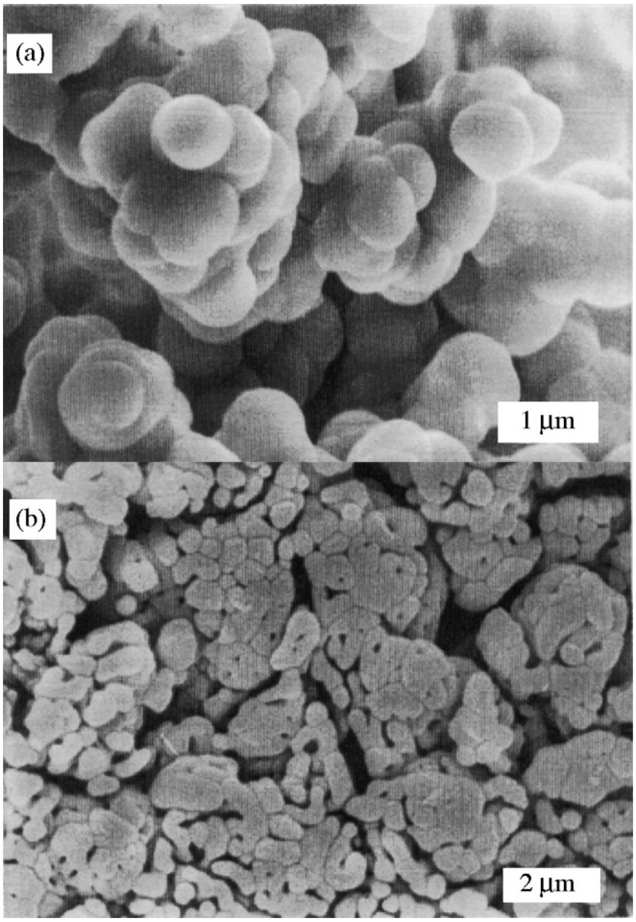

Fig. 1. The electron microscopy photographs of the powder calcined at 900 °C (a) and the compact fired at 1150 °C (b).

3.2. Applications of the zero-order reaction rate (ZORR) model

The specific surface area (S, $m^2\,g^{-1}$) for each fired compact was obtained according to the standard Brunauer, Emmett, and Teller (BET) procedure by using the adsorption data of the nitrogen in the relative adsorption equilibrium pressure range of 0.05–0.35 [43]. Time dependence of the specific surface areas for each compact at the different temperatures are given in Table 1. To use the surface area measurements for the sintering kinetics of monodisperse spherical particles the validity limit of the relative surface area reduction was reported as $\Delta S/S_0 \leq 0.50$ [28–30]. It was assumed that this limit can be validated also for the intra-particle sintering of the agglomerates composed of the spherical particles as seen in Fig. 1a. As seen from SEM view in Fig. 1a, the sizes of the spherical primary particles and their agglomerates are smaller and bigger than the 1 μm respectively. However, SEM and PSD results are congruent.