Chem. Mater. **2008,** *20,* 3–4

Communications

Use of Dispersive Kinetic Models To Describe the Rate of Metal Nanoparticle Self-Assembly

Peter J. Skrdla*,† and Rebecca T. Robertson‡

640 Maple Street, Westfield,
New Jersey 07090, and Novartis Pharmaceuticals, 1 Health
Plaza, East Hanover, New Jersey 07936

Received April 23, 2007
Revised Manuscript Received June 8, 2007

In a recent publication,[1] the Finke research group proposed a mechanism for transition metal nanoparticle self-assembly which fit well the highly asymmetric, sigmoid conversion−time ($x-t$) plots for the process occurring under reductive conditions. The mechanism they proposed was a four-step one, in which a "double autocatalytic" step was used to describe the sharp "turn-on" feature typically observed after the induction period in the kinetic curves. In this communication, the authors attempt to provide an alternative description of the curves presented in ref 1, using much simpler kinetic models originally developed for solid-state applications.

Because the model proposed in the paper by Besson et al.[1] is based solely on a chemical, mechanistic interpretation of the kinetics (which is likely most useful for reactions occurring in homogeneous media), it neglects the possibility that different metal atoms may be deposited at different times (and, consequently, react with different rate constants/activation energies) simply because of their differing spatial locations inside each growing nanoparticle. This concept is core to the field of dispersive kinetics,[2] which finds application in many solid-state conversions (i.e., reactions and phase transformations).[3] Additionally, the authors believe that the curve shapes observed by Besson et al., contrary to their statement ". . .the observation of the unprecedented kinetic curves shown in Figure 1—approaching step function-like curves that have a ca. 0.4–3.0 h induction period, but then which "takeoff" very suddenly after that",[1] have routinely appeared in the solid-state kinetics literature since the advent of the Johnson−Mehl−Avrami−Erove'ev (JMAE, or, more simply, "Avrami") equations in the late 1930s/early 1940s. These models[4] have a well-established foundation in solid-state kinetics;[5–7] they were originally developed to describe nucleation rates. Also, they typically utilize only one empirical rate constant unlike the mechanistic model proposed by Besson et al., which uses a total of four rate constants to fit kinetic data trends.

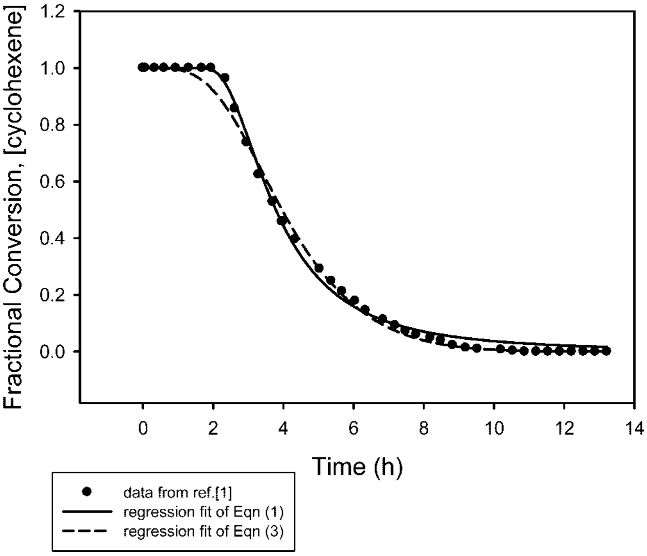

Figure 1. Conversion−time ($x-t$) transient of the cyclohexene hydrogenation "reporter" reaction used to describe a typical (isothermal) kinetic curve for the formation of metal nanoparticles; the data points were extracted from ref 1. The data is fit using the dispersive kinetic models, eqs 1 and 3; see text for details.

Data from Figure 1 in ref 1 is reproduced here in the present Figure 1 (note that because both curves were found to be essentially superimposable, only one $x-t$ transient is shown). From the figure, one can see that the simple kinetic model, below, fits the data quite well ($R^2 = 0.997$, $k = 37.6 \pm 0.8$ h^3).

$$x = 1 - e^{kt^{-3}} \tag{1}$$

(In eq 1, which can be considered a variant of one of three widely used, two-parameter, Avrami models, "A3",[4] where the time, t, exponent counts as one empirical parameter and the rate constant for the conversion, k, serves as the other, x represents the mole fraction of reagent material remaining in the system at a given t. The more general form of eq 1, with the arbitrary time exponent, n, is a known result of the dispersive kinetic treatment of Plonka, which employs the concept of fractal time.[2]) This finding demonstrates that it may be possible to explain the kinetic trends typified by the plot in Figure 1 using much simpler models than the one proposed by Besson et al. However, while eq 1 is able to fit the initial portion of the kinetic data very well (including the sharp "turn-on" feature), there is a slight deviation of the model for ~7.5 < t < 13.0 h.

---

* Corresponding author. E-mail: skrdla@earthlink.net.
† 640 Maple Street
‡ Novartis Pharmaceuticals.

(1) Besson, C.; Finney, E. E.; Finke, R. G. *J. Am. Chem. Soc.* **2005**, *127*, 8179.

(2) (a) Plonka, A. *Sci. Rev.* **2000**, *25*, 109. (b) Plonka, A. *Annu. Rep. Prog. Chem., Sect. C: Phys. Chem.* **2001**, *97*, 91.

(3) (a) Skrdla, P. J.; Robertson, R. T. *J. Phys. Chem. B* **2005**, *109*, 10611. (b) Skrdla, P. J. *J. Phys. Chem. A* **2006**, *110*, 11494.

(4) Skrdla, P. J.; Robertson, R. T. *Thermochim. Acta* **2007**, *453*, 14.

(5) Johnson, W. A.; Mehl, R. F. *Trans. AIME* **1939**, *135*, 416.

(6) (a) Avrami, M. *J. Chem. Phys.* **1939**, *7*, 1103. (b) Avrami, M. *J. Chem. Phys.* **1940**, *8*, 212. (c) Avrami, M. J. *Chem. Phys.* **1941**, *9*, 177.

(7) Erofe'ev, B. V. *Dokl. Akad. Nauk SSSR* **1946**, *52*, 511.

10.1021/cm071092v CCC: $40.75 © 2008 American Chemical Society
Published on Web 12/08/2007

Focusing attention a previously published, "comprehensive" list of both dispersive and nondispersive (i.e., traditional) solid-state kinetic models,[4] it was found that, in addition to eq 1, the dispersive kinetic models recently developed for treating "deceleratory, sigmoid $x-t$" conversions (i.e., those processes for which the rate parameter, β, is negative[3] and the inflection point in the $x-t$ transient generally occurs closer to the beginning of the conversion than toward the end) were able to describe reasonably well the data shown in Figure 1. The best regression fit ($R^2 = 0.994$; fit not shown in the figure) was obtained using the dispersive variant of the traditional first-order (F1) model, namely,

$$x = \exp[\alpha t(e^{-\beta t^2} - 1)] \tag{2}$$

where the rate parameters,[3] α and β, have values of $0.45 \pm 0.05\ \mathrm{h}^{-1}$ and $0.031 \pm 0.005\ \mathrm{h}^{-2}$, respectively. Equation 2 was developed on the basis of the assumption of a Maxwell–Boltzmann type *activation energy distribution* for the reagent species undergoing conversion (this activation energy distribution is ultimately responsible for defining a specific functional form for the *time-dependent "rate constant"* for the overall conversion[3]), coupled with a simple "F1" reaction mechanism.[3,4] As a result of the relatively good fit of the model to the data, at least some of the kinetic complexity in the plot in Figure 1 may be attributed to molecular-level dispersion (i.e., variation) in the activation energy of the process. This dispersion occurs as a result of "system renewals" that can be considered to occur continuously over the course of the conversion,[2] producing the desired nanoparticles (which, the authors assume, are similar in size to "critical nuclei" that can be encountered in various dispersive solid-state conversions[3]). Contrastingly, in the model presented by Besson et al., the possibility of dispersive kinetics (i.e., the involvement of a molecular dynamics factor which can impact the observed kinetic trends) is ignored, in favor of a more complex view of the chemistry involved in the nanoparticle formation.

In the derivation of eq 2, a dimensionality of two (i.e., $n = 2$) was assumed[3,4] (this dimensionality is thought to best describe two-dimensional nuclei). Drawing on the earlier success using eq 1 to fit the data in Figure 1, a dimensionality of three ($n = 3$) can be introduced into eq 2 to derive a new kinetic model:

$$x = \exp[\alpha t^2(e^{-\beta t^2} - 1)] \tag{3}$$

The regression fit of eq 3 to the nanoparticle formation kinetics depicted in Figure 1 is found to be improved ($R^2 = 0.996$) relative to the fit provided by eq 2. The values of the fit parameters are as follows: $\alpha = 0.0506 \pm 0.0018\ \mathrm{h}^{-2}$, $\beta = 0.131 \pm 0.017\ \mathrm{h}^{-2}$. While the fit of eq 3 to the sharp "turn-on" feature of the curve is still not as good as eq 1 (but it is improved relative to eq 2), both eq 2 and eq 3 have a better ability to model the later stages of the conversion than eq 1.

This work demonstrates that it may be possible to utilize much simpler (i.e., containing fewer empirical fit parameters) dispersive/solid-state kinetic models to determine the kinetics of nanoparticle formation than the four-parameter, mechanistic equation described in the original work by Besson et al.[1] Here it was shown that, provided one accounts for the possibility of dispersion in the activation energy barrier of the process (a physical component of the overall kinetic description), a simple "F1-type"/exponential mechanism (a chemical component of the kinetic description) may adequately explain the $x-t$ curve shapes presented in this work. Equation 3 has not been used in kinetic modeling prior to this work, to the authors' knowledge.

CM071092V