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MODELLING THE TITANIUM DIOXIDE SYNTHESIS BASED ON CHLORIDE PROCESS

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Abstract

Thermochemical data for intermediate TixOyClz species are calculated using quantum chemistry (mostly density functional theory) and statistical thermodynamics. By comparing results from three different density functionals, isodesmic and isogyric reactions are shown to be very important for determining standard enthalpies of formation of these species. The energy of TiOCl2, important both in the chemical mechanism and in determining standard enthalpies of other species, is determined more accurately using coupled cluster CCSD (T) calculations.It is impractical to extend the kinetic model beyond Ti2OyClz manually, so steps are taken towards automating the process. A reaction mechanism generator developed for hydrocarbons, RMG, is modified to model titanium oxychlorides.

Keywords [Titanium dioxide, Titania particle,]

1. INTRODUCTION

“Titanium dioxide is a white pigment used in everything from paint to paper. It coats the slick pages of fashion magazines. It tints suntan lotion. It colors latex hospital gloves and eye shadow. It coats synthetic fabrics so they don’t look shiny. It’s the white in plastic picnic forks. It has replaced lead in paint since 1974. It’s even the M on the M&Ms.” Savannah Morning News. Most of the titanium dioxide in the world is produced by the chloride process. In order to increase quality and cut production costs, industrial producers would like to understand the process better. Experiments are hard to perform due to the harsh conditions and short time-scales, so a computational modelling approach is useful. The process starts with chemical reactions in the gas phase, but particle processes such as coagulation are also important in determining final product properties.

2. SURFACE CHEMISTRY

TITANIUM DIOXIDE is one of the most investigated metal oxide surfaces; details can be found in a recent comprehensive review article by Diebold (2003). Nevertheless, experimental investigations of the kinetics of the surface growth of rutile TiO2 are scarce. The rate of heterogenous TiO2 surface growth was investigated at 400– 850 ◦C (Ghoshtagore, 1970) and the presented first order rate expression has been used in most modelling papers since (Pratsinis and Spicer, 1998; Spicer et al., 2002; Tsantilis and Pratsinis, 2004; Morgan et al., 2006). This extrapolation to higher temperatures should be treated with caution however, especially as a change in behaviour above 850 ◦C is reported (Ghoshtagore, 1970). A more detailed understanding of the elementary steps involved in the surface growth will help to develop a more reliable universal rate expression.

3. MODELLING APPROACHES

STUDIES of nanoparticle formation in plasmas have been undertaken for other species, such as titanium. Murphy’s (2004) theoretical study of titanium nanoparticle formation from a TiCl4 plasma used three approaches: chemical equilibrium calculations, chemical kinetic calculations, and a moment model of particle formation coupled to the gas-phase chemical kinetic scheme. It is not strictly analogous to TiO2 nanoparticle formation, as the chemistry is complicated by the addition of oxygen; however, this is roughly the approach that the following chapters will follow for the formation of titanium dioxide nanoparticles.

Akhtar et al. (1991) used DMA, SEM and XRD to characterize particles formed in a tubular flow reactor. Particle size increased with increased temperature, TiCl4 concentration, and residence time. They later used similar apparatus to measure the effects of water vapour (Akhtar et al., 1994b) and of AlCl3 (Akhtar et al., 1994a). Introducing water vapour led to rounder particles, mostly anatase, with larger aggregates but smaller primary particles. The AlCl3 doping led to rutile particles, which is its main use in industry, but also larger primary particles. They suggest that the oxygen vacancies caused by the trivalent Al dissolved in the solid titania, increases the rate of oxygen diffusion and thence phase transformation and sintering.Teleki et al. (2008) measured flame-synthesized titania particle sizes before and after high-pressure dispersion, to assess the degree of hard- and soft-aggregation. Hard aggregates consist of strongly bonded primary particles, whereas soft agglomerates break apart when forced through a nozzle at hundreds or thousands of bar pressure.

4. Developing Kinetic Model

DEVELOPING a detailed kinetic model for the gas-phase combustion of titanium tetrachloride has been the motivation for all the work described so far. In this chapter, the kinetic model is finally developed and tested. First some background theory is explained, to help the reader understand the methods described in the following sections. Next, a first kinetic model is devised. This kinetic model is then characterised near industrial reactor conditions. The flux analysis and sensitivity analysis in this characterisation are used to guide improvements to the kinetic model in §6.5. Finally, the improved kinetic model is used to simulate two sets of experiments described in the literature: a rapid compression machine and a plug flow reactor.

An elementary reaction is a chemical reaction in which one or more chemical species react directly to form products in a single reaction step and with a single transition state (IUPAC, 1997). The rate of such a reaction can be estimated using, for example, Transition State Theory (TST). In the high-pressure limit, elementary reactions are typically first order in

$$k = A\exp\left(\frac{-E_a}{k_B T}\right)$$

each of the reactants, and follow the Arrhenius form:

Although numerical simulations may be accelerated by grouping several elementary reactions (e.g. A→B, B→C, C→D) into a compound reaction (A→D), the rate expression for such a reaction will either be complicated and hard to estimate, or will fail to capture the complexity of the reaction mechanism with respect to temperature, pressure, and species concentrations. The aim of this chapter is to develop a kinetic model consisting of elementary reactions. Reduction of this complete mechanism to a smaller mechanism may be required for computationally expensive applications such as computational fluid dynamics, but this can be performed at a later date if needed (Løvås et al., 2000).

$$k = \kappa \frac{k_B T}{h} \frac{Q_{X\ddagger}}{Q_A Q_{BC}} \exp(-\Delta\epsilon_0/k_B T)$$

The partition functions according to the rigid-rotator/harmonicoscillator approximation were given in chapter 4, and can be calculated from information about the species and transition state such as moments of inertia and vibrational frequencies; these can be found through quantum chemistry calculations. The full derivation of can be found in text books such as Pilling and Seakins (1995), and an interesting account of the historical development of TST and its reception by the chemical world is given by Laidler and King (1983).

CONCLUSION

Automating the process of generating kinetic models like this is an obvious area for future research. Chapter 8 demonstrates that this is feasible, and shows one possible way forward. As detailed in that chapter, reaction templates must be found that are suitable for this system, and better Benson-style group values must be derived. Automatically starting quantum chemistry calculations looks to be within reach, but experience shows that it is not uncommon for such calculations to fail, and for these transition metal compounds the variety of reasons for failure seems unlimited.A new particle data structure, in which a computational particle contains an asymmetric binary tree of sub-particles, would allow not only better shape estimation algorithms, but also more advanced sintering models. With the knowledge of which subparticles are touching each other, mass could be redistributed between neighbors instead of randomly across all primary particles. By modelling continuous sintering between neighbouringsubparticles, two large subparticles could gradually sinter together over time, which does not happen with the current smallest-first deletion method. Sintering between neighbouringsubparticles could be modelled in terms of neck growth, rather than surface area loss, allowing direct calculation of hard- and soft-agglomerate shapes and sizes.

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