On the Correct Solution for the Ostwald Ripening Mechanism during Sintering of Catalysts

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Introduction

Sintering of supported metal catalysts is a primary cause for deactivation at high temperatures [1]. It consists of a rearrangement of the crystallite size distribution (CSD) and is normally accompanied by a drop in activity, and frequently by changes in selectivity. In spite of its industrial importance, there are still questions concerning the underlying mechanism and of ways to stabilize the catalysts against particle coarsening.

Surface migration of adatoms is probably the most widely considered cause of sintering; it is the so-called Ostwald ripening mechanism. It has been analyzed using a variety of mathematical methods, and it is possible to find an analytical self-similar stationary solution. This was independently done for the 3-dimensional case by Lifshitz and Slyosov [2] and by Wagner [3] — the LSW solution. Chakraverty [4] was the first to address the rearrangement of a distribution of crystallites on a surface, but there were errors in his solution pointed out by Wynblatt and Gjostein [5]. All this was done within the framework of the LSW method. The problem in all cases was the fact that the predicted CSD was tailing towards small radii, whereas the tail in experimental CSD commonly points towards large radii. Brown [6] proposed a variant in the solution for the 3-dimensional case, corrected by Coughlan and Fortes [7]. Fuentes and Salinas-Rodriguez [8] extended the analysis to 2-dimensional systems. However, the generalized analytical solutions presented had still some inconsistencies that required further development.

In this work, we present the correct solutions for the stationary CSD in the case of the Ostwald ripening mechanism as it applies to supported catalyst sintering. We use them to analyze experimental PSD and show that unique fits are possible with excellent results.

Materials and Methods

The differential equation describing the evolution of the CSD was solved by the separation of variables method [7, 8]. We then imposed restrictions on the particular solutions involving conservation of mass and of probability as well as a restriction on the first moment of the distribution. Using standard numerical methods we obtained a family of solutions that depend on two parameters and that can be used to directly fit experimental distributions.

Results and Discussion

Figure 1 compares the LSW solution and one of the distributions predicted by our methodology. The particular solutions presented in this work apply to limiting cases of control by adatom emission, by migration on the surface of the support, or by capture by a crystallite. Interestingly, we could express each of the particular solutions as a function of just one parameter. This allowed us to fit experimental results readily. The restrictions imposed made it clear that only one of the three solutions applied in each case.

Significance

We prove for the first time in a mathematically consistent way that the Ostwald Ripening mechanism of sintering is compatible with experimental CSD. The methodology devised here can be readily implemented to analyze any experimental CSD. At the same time, we discuss the fundamental implications in the understanding of sintering, and in ways to use this information in the design of more stable catalysts.
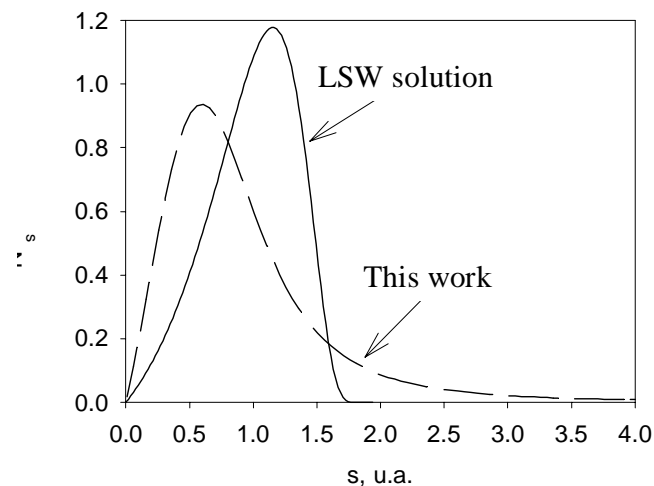

Figure 1. Comparison of the predicted crystallite size distributions using the classical LSW solution with one of the solutions using the extended method described in this work.

References

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