

Understanding Sintering of Supported Metal Catalysts

Gustavo A. Fuentes*, Elizabeth Salinas-Rodríguez, Enrique Soto-Mercader, and Guillermo Rivera

Dept. of Process Engineering, Universidad A. Metropolitana-Iztapalapa, A.P. 55-534
Mexico, DF, 09340 (Mexico)

*gfuentes@xanum.uam.mx

Introduction

Sintering of supported metal catalysts is a primary cause for deactivation at high temperatures. The study of its kinetics and of the changes in crystallite size distribution has been the subject of different studies in our group [1-3], and we have been able to show that apparent inconsistencies between leading models and experimental data were caused by the use of limited solutions to the models. In particular, we have studied solutions to the Ostwald ripening model and found that the classical analytical solution, known as the LSW solution, is only a particular solution of a family of solutions. An important implication of that analysis is the observation that the particle size distributions predicted by our solutions can fit adequately the experimental distributions observed during sintering of supported metals such as Pt, Pd or Ni in a variety of supports.

Our solutions allow the analysis of both global kinetics and the experimental crystallite size distributions. They provide not only an excellent match of the experimental data, but also have sound physical foundations.

In this work we analyze the sintering of supported Pt, Pd and Ni catalysts, and discuss the conditions needed for the observed crystallite size distributions to be a truly self – similar solution within the context of the Ostwald-ripening model. The implications for the mechanism of sintering are also discussed in the light of the resulting fits.

Materials and Methods

We have based our analysis in the solution of the conservation equations using the adequate restrictions to comply with conservation of mass, probability and a criterion about the mean value of the distribution. We analyzed the experimental data reported in the literature for sintering of supported metals, and fitted those results with our equations using NLLS Marquard-Levenberg routines.

Results and Discussion

Figure 1 shows a typical fit of experimental data (7 and 15% Pd) [4,5] after being sintered during 4000 h. A second order model provides the best fit in this case, suggesting that diffusion of adatoms is the controlling process. Figure 2 provides an independent agreement with that observation, because the kinetic equation is consistent with a second order model too. It is remarkable that we are able to predict sintering after 4000 h using data from 7% Pd sintered up to 200 h

Significance

Our results are important for analyzing particle size distributions and kinetics of sintering using equations that are consistent with theory. We have found that it is possible to predict long term sintering based on data obtained during short term experiments.

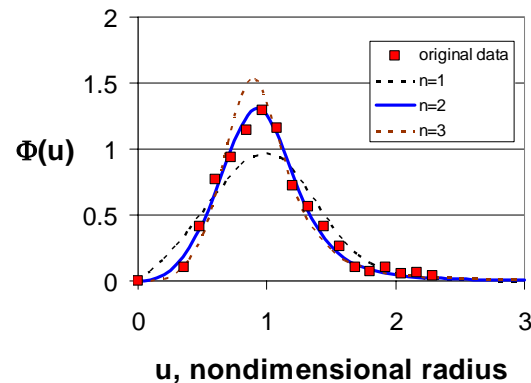


Figure 1. Particle size distribution fitted using our generalized Ostwald ripening sintering model

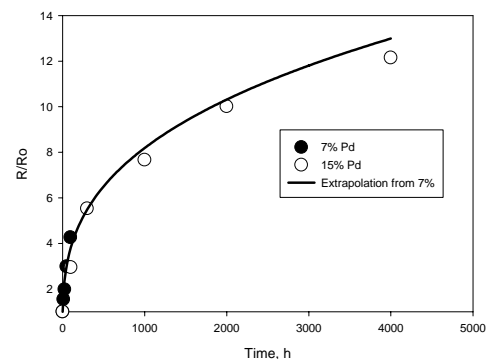


Figure 2. Prediction of the mean of the PSD and of the long term sintering kinetics based on our Ostwald ripening model

References

1. Fuentes, G.A. and Gamas, E.D., in "Catalyst Deactivation 1991", (C.H. Bartholomew and J.B. Butt, eds.), *Stud. Surf. Sci. Catal.*, vol. 68, p. 637, Elsevier, Amsterdam, 1991.
2. Anonymous, *Oil and Gas Journal* 98, 26 (2000).
3. Fuentes, G.A. and Salinas-Rodríguez, E., in "Catalyst Deactivation 2001", (J.J. Spivey, G.W. Roberts and B.H. Davis, eds.), *Stud. Surf. Sci. Catal.*, vol. 139, pp. 503, Elsevier, Amsterdam, 2001.
4. Soto-Mercader, E., M.S. (Chem. Eng.) Thesis, UAM-Iztapalapa, Mexico, 2008.
5. Datye, A. et al. *Catal. Today* 111, 59 (2006).
6. McCarty, J. et al. *JPC B* 109, 2387 (2005)