# Industrial verification of Nickel catalyst sintering models

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**Abstract:** We present results from a comprehensive study of the sintering of two commercial Nickel catalysts, that have been sintered at conditions relevant to their intended industrial operation, i.e. with steam partial pressures up to 28 bar, temperatures up to 810°C, and durations up to 6000 hrs. From the determination of the Nickel particle sizes on the sintered catalysts, sintering models based on either particle migration or Ostwald ripening were refined for the respective commercial catalysts. The refined models are then used to accurately predict the sintering of these catalysts at relevant industrial gas conditions and lifetimes.

**Keywords:** Nickel, Catalyst, Sintering, SNG.

## 1. Introduction

Supported Nickel catalysts are used widely in the chemicals industry for the generation and/or conversion of synthesis gas (syngas). For such applications, the operation conditions often combine high temperature and high steam partial pressure, two factors which are well known to promote sintering and thereby deactivation of Nickel catalysts. To size reactors and estimate catalyst lifetime in industry, it is useful to be able to accurately predict the sintering of Nickel catalysts under long term industrial operation. Numerous publications exist where catalyst sintering is investigated under conditions of atmospheric pressure, and time scales of hours or days, however such conditions cannot safely be extrapolated to industrial conditions, where Nickel syngas catalysts may be for operated for 2 to 10 years, for temperatures ranging between 300°C and 800°C, and for steam partial pressures ranging between 1 and 20 bar. It is recognized in the literature that sintering of Nickel catalysts (and other catalysts) can occur through two distinct processes: via particle migration (PMC) whereby whole Nickel nanoparticles diffuse on a carrier surface and coalesce to form larger particles, or via Ostwald ripening (OR) whereby larger nanoparticles essentially grow via transport between particles. These two sintering mechanisms have quite different signature time dependences: for PMC the development in the mean Nickel particle diameter $d_{Ni}/d_{Ni,0}$ has a time dependence $t^{1/7}$, whereas for OR $d_{Ni}/d_{Ni,0}$ has a time dependence $t^{1/3}$. For the case of Nickel nanoparticles, it is expected that these two sintering mechanisms operate under quite different regimes. For example, PMC is expected to dominate for temperatures below 570°C, whereas OR is expected to dominate for temperatures above 570°C [1] [2] [3]. With this contribution we therefore try to connect the sintering of industrial catalysts under industrially relevant conditions to the theory of these two different sintering regimes.

## 2. Experimental

For this study, we have taken two of our commercial Nickel based methanation catalysts, Catalyst A used for low temperature methanation (in Ammonia plants and at coal-to-SNG plants), and Catalyst B which is used in coal-to-SNG plants for medium and high temperature methanation processes. We have aged these catalysts in numerous laboratory and pilot experiments. For Catalyst A the aging conditions were performed for temperatures ranging up to 550°C, steam partial pressures up to 28 bar, and for durations up to 6000 hrs. For Catalyst B the aging conditions were performed with temperatures up to 810°C, steam partial pressures up to 20 bar, and for durations up to 3600 hrs. After each experiment the Nickel particle sizes of the aged catalysts were measured using X-ray powder diffraction (XRD). The combined data, Nickel particle sizes and aging condition, was then used to refine sintering models for the two different catalysts.

## 3. Results and discussion

Figure 1 below plots the normalized ($d_{Ni}/d_{Ni,0}$) Nickel particle sizes measured on the two commercial catalysts, after lab and pilot aging for the range of conditions described in the experimental section. The measured values are plotted against predicted $d_{Ni}/d_{Ni,0}$ values, the predicted values calculated using sintering models refined by the experimental data points. We plot the data for the two catalysts in separate figures, as for catalyst A, the aging temperatures were <570°C and so the sintering was modeled solely via particle migration, and for catalyst B the aging temperatures were above 570°C and so sintering was modeled solely via Ostwald ripening. In general, the data points in the figure show very good agreement between the measured and modeled Nickel particle sizes, as can be seen by the closeness of the data points to the dotted parity line. The red data points in the figure are for catalysts A and B retrieved from industry after a number of years operation – see figure caption for details – where the catalysts have been operated under conditions relevant for sintering via particle migration, or Ostwald ripening, respectively. For these industrial samples, the closeness of the data points to the parity line again demonstrates good agreement between the measured and predicted Nickel particle sizes. The data of these industrial samples was not used to tune the model, and so the good agreement between measured and modeled Nickel particle sizes reflects the high accuracy of our sintering model, even out to time scales of three years and beyond, for industrially relevant temperatures and gas conditions.

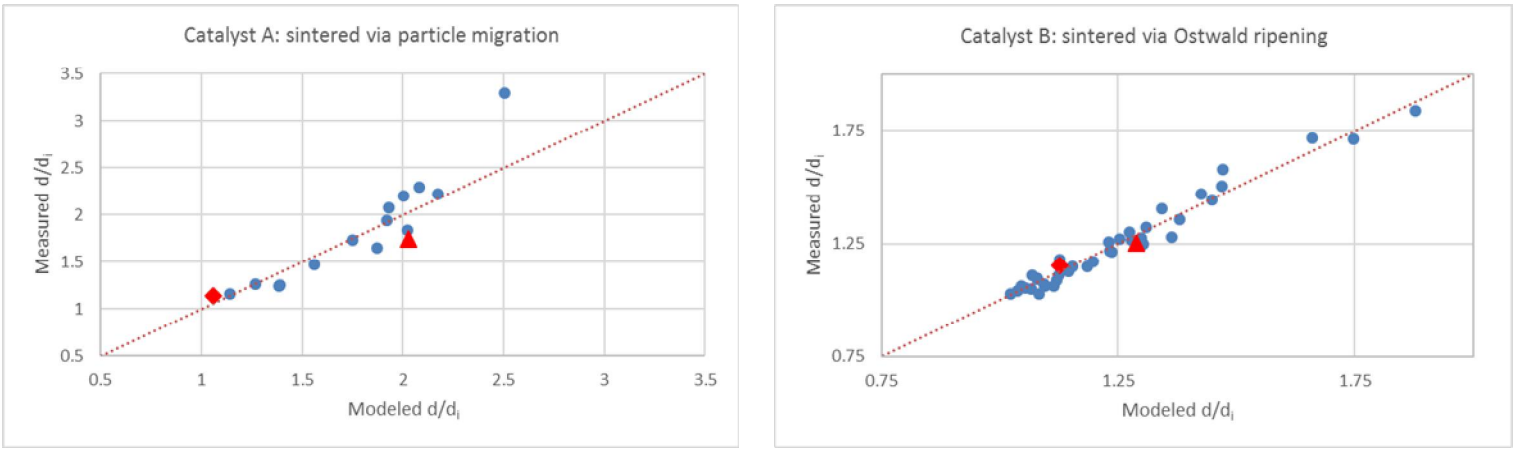


**Figure 1.** Left hand figure: Comparison of modeled and measured Nickel particle sizes for commercial catalyst A, sintered at low temperature in laboratory and pilot experiments. ♦ Industrial sample after 10 years operation in an Ammonia plant, ▲ industrial sample after 3.5 yrs operation in a coal-to-SNG plant. Right hand figure: Same comparison for commercial catalyst B sintered via Ostwald ripening. ♦ Industrial sample after 2.5 years operation at medium temperature in a coal-to-SNG plant, ▲ industrial sample after 2.5 yrs operation at high temperature in a coal-to-SNG plant.

## 4. Conclusions

We present results of a comprehensive study into the sintering of two commercial Nickel catalysts, where the catalysts have been sintered at conditions and durations relevant for their industrial operation. Analysis of the sintered samples was used to refine established sintering models for the particular catalysts, which demonstrably allows us to accurately predict the sintering and thereby deactivation of these catalysts for industrial operating conditions and lifetimes.

## References

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