ETEM Studies of Ni Catalyst Sintering

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Introduction

Sintering is one of the most important causes of catalyst deactivation in heterogeneous catalysts. Insights into the atomic scale details of sintering would aid in understanding the phenomenon and in coming up with ways to control sintering. Previous work has relied on observed macroscopic behavior (such as sintering kinetics or particle size distributions) to arrive at mechanistic information. In this work we have used environmental transmission electron microscopy (ETEM) to monitor *in situ* the dynamics of catalytic nanoparticles.

Materials and Methods

The measurements were done using a Philips CM300 FEG ETEM[1]. We used a reactive gas environment of 3.5mbar H_2 and 3.6 mbar of 1:1 H_2/H_2O at high temperatures (500-750°C) to study the behavior of Ni particles on a high area surface support (spinel $MgAl_2O_4$). A twice-impregnated (~12wt%) Ni on spinel was used instead of a typical 1wt% Ni in order to increase the number of particles that could be analyzed and observed in profile view.

Results and Discussion

We first confirmed that the nature of the sample ageing observed *in situ* was consistent with *ex situ* observations in flowing gas. The increase in particle diameter and the overall particle size distributions (log normal) were in agreement with previous work on this catalyst system[2-3]. It is generally expected[4] that particle mobility should scale as d^{-n} where the exponent n varies from 3 to 6. Hence, one would expect the smallest metal particles to be the most mobile. Our observations were contrary to this expectation, and the small particles showed very little mobility. Rather, we can describe sintering to be dominated by Ostwald ripening, with the disappearance of the small particles as shown in Figure 1. The ETEM movies reveal abrupt disappearance of the small particles, over very short time scales (<1sec) during the first 30-60 minutes after exposure to high temperatures. Ripening events captured on movies typically lasted less than a second, and can be explained by the increasing chemical potential with decreasing particle size, leading to a rapid change in crystallite size just before it disappears.

Surprisingly, during ETEM observations, smaller particles were relatively immobile while the larger particles showed evidence for mobility, leading to coalescence events as shown in Fig. 2. The study clearly shows that Ostwald ripening is responsible for the loss of small particles leading to the observed loss in metal surface area at short times. Particle migration and coalescence becomes important as particles grow in size and we speculate that these large particles become unpinned from the support leading to events such as those shown in Fig. 2. These *in situ* experiments were reproduced on multiple samples over different time periods and with different extents of beam intensity. We found sample temperature had the greatest influence. At lower temperatures, and at similar beam intensities, we did not detect any particle mobility. Increasing the beam dose did not cause significant changes in the phenomena described here, suggesting the effect of the beam is small.

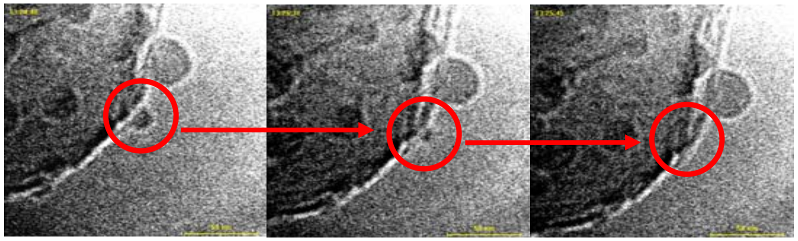

Figure 1. Series of images for a sample of $Ni/MgAl_2O_4$ heated at 750°C in 3.6 mbar of flowing H_2/H_2O. The elapsed time between images (left to right) is ~1.1sec. The smaller particle disappears very quickly via a ripening process at the beginning stages of the experiment.

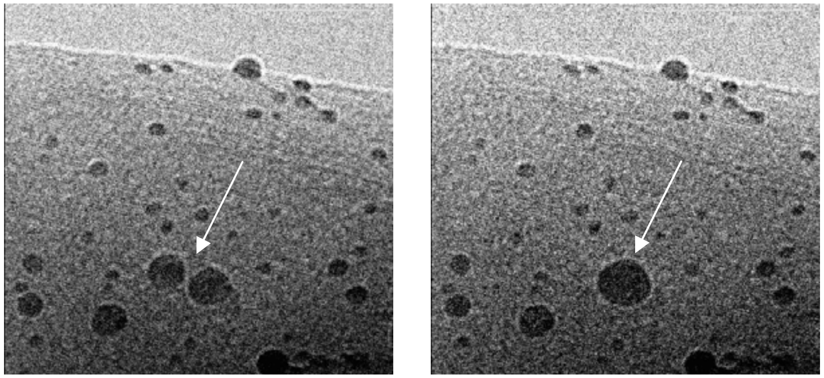

Figure 2. Migration and coalescence of two large particles captured from a series of images for a sample of $Ni/MgAl_2O_4$ heated at 608°C in 3.5 mbar of flowing H_2. The elapsed time between images (left to right) is 500 msec.

Significance

The study shows that both ripening and coalescence are operative for the sintering of the Ni/spinel catalysts. While ripening is operative for smaller particles, particle migration becomes more important for larger particles under the present ageing conditions. The combination of these two processes may lead to the long tail (toward large particle diameters) observed in the particle size distributions from these catalysts, and the observed log normal particle size distribution.

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References

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