

***In-situ* Environmental TEM Study on the Activation of Ni Nanoparticles for Partial Oxidation of Methane**

S. Chenna,* and P.A. Crozier*

* School of Mechanical, Aerospace, Chemical and Materials Engineering, Arizona State University, Tempe, AZ, USA 85287-6106

Heterogeneous catalysts may undergo significant changes during a reaction (such as phase transformation, shape changes, etc.) which can affect their catalytic properties. *In-situ* environmental electron microscopy (ETEM) can allow us to probe the dynamic changes in the catalyst during gas-solid interactions providing information on morphological and chemical changes which may not be available by *ex-situ* studies. In the present work, we employ Ni nanoparticles supported on well-defined amorphous silica spheres for partial oxidation of CH₄ to syngas (CO+H₂). We performed *in-situ* ETEM studies to correlate the nanostructure changes in different gaseous environments with the catalytic activation process obtained from *ex-situ* reactor experiments.

Ni/SiO₂ catalysts were prepared by an impregnation method according to the procedures given in Banerjee et al. [1]. Catalyst measurements were carried out in an ISRI RIG-150 reactor with an online Varian gas chromatography system. *In-situ* electron microscopy studies were performed in an FEI Tecnai F20 field emission environmental transmission electron microscope (ETEM) operating at 200kV with a point resolution of 0.24nm.

Many ETEM experiments under different gas conditions must be performed to simulate the various gas-solid interactions that take place in the *ex-situ* reactor. For example, figure 1 shows the measured catalytic activity of Ni/SiO₂ during partial oxidation of CH₄. Complete combustion of up to 24% of the CH₄ takes place in the temperature range 300° C to 750°C giving CO₂ and H₂O. A further increase in temperature to 775°C resulted in a sudden increase of CH₄ conversion from 24% to 97%, with almost all the CH₄ being converted to CO and H₂. Figure 2 schematically illustrates the possible variation in gas composition along the bed over three different temperature ranges. At temperatures below 300°C, all the catalyst bed is exposed to a mixture of CH₄ and O₂ (2:1). In the temperature range of 300 to 750°C, two different regions exist in the catalyst bed, region I of the bed sees a reactant mixture of CH₄ and O₂ and region II is exposed to a mixture of CH₄, O₂, CO₂, H₂O. Above 750°C, three different regions exist in the catalyst bed, region I of the bed sees reactant gas mixture of CH₄ and O₂, region II is exposed to a mixture of CH₄/CO₂/H₂O (3:1:2) where reforming reactions take place and region III is exposed to mostly a mixture of CO and H₂ (1:2).

Our ETEM experiments show that in presence of CH₄ and O₂ (2:1) at 400°C (region I), Ni transforms to NiO voids with multiple grains (figure 3a) suggesting that NiO exists all over the catalyst bed at 400°C and is the active species for complete combustion of methane. Formation of voids can be explained by a Kirkendall mechanism [2], where diffusion of Ni along the grain boundaries in NiO is orders of magnitude greater than diffusion of O [3]. Figure 3b shows the morphology of Ni metal particle in presence of CO and H₂ (1:2 ratio) simulating to the region III in the catalyst bed. The transition from region II to region III is very important because it is associated with the dramatic increase in activity observed at 775°C. As the temperature increases in region II, the gas mixture becomes more reducing (as O₂ is consumed) and eventually NiO transforms to Ni.

Thermodynamically Ni may prefer not to stay on the surface of the nanoparticles during this reduction process. This behavior may explain the sharp rise in CO selectivity at 775°C because, as the last monolayer of NiO is reduced, the nanoparticle surface will suddenly become metallic resulting in syngas production. Evidence for this hypothesis is presented in Figure 3c which shows the presence of a thin layer on the nanoparticle surface during the final stage of NiO to Ni reduction in presence of CH₄ at 400°C. We will present ETEM observations on the intermediate stages of the NiO to Ni transformation to explain the activation of the catalyst.

References:

- [1] R. Banerjee et al., *Microsc. Microanal.* 15 (Suppl. 2) (2009) 732.
 [2] A.D. Smigellkas et al., *Trans. AIME* 171 (1947) 130.
 [3] A. Atkinson et al., *J. Mat. Sci.* 13 (1978) 427.
 [4] The support from the National Science Foundation (NSF-CBET-0553445) and the use of TEM at the John M. Cowley Center for High Resolution Microscopy at Arizona State University are gratefully acknowledged.

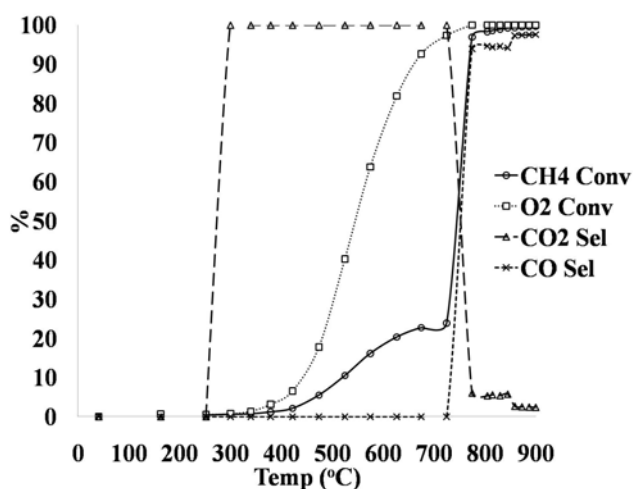


FIG 1: Plot showing conversion and selectivity during partial oxidation of methane on Ni/SiO₂ catalyst.

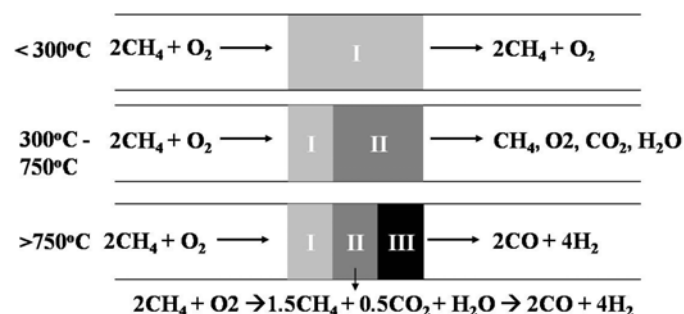


FIG 2: Schematic representation of reactor bed based on the gas compositions at different temperatures.

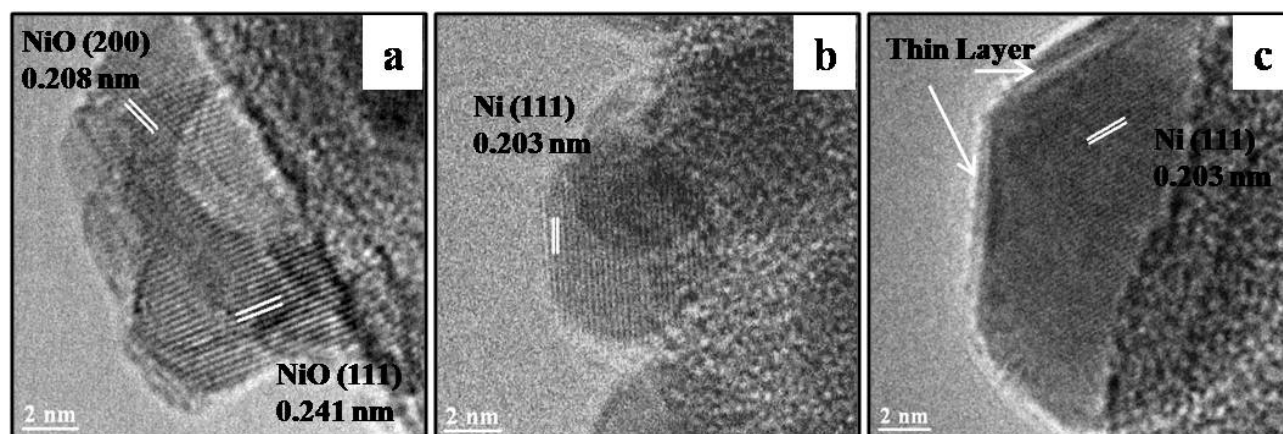


FIG 3: *In-situ* environmental TEM images of Ni/SiO₂ catalyst in presence of (a) 1 Torr of CH₄:O₂=2:1 at 400°C (b) 1 Torr of CO:H₂=1:2 at 400°C (c) 1 Torr of CH₄ at 400°C.