

***In Situ* Observation of the Nanostructural Evolution of a Ni/SiO₂ Catalyst during the Partial Oxidation of Methane**

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Introduction

Partial oxidation of methane is an important reaction for processing fuel feed stocks. Supported Ni catalysts are of considerable interest because of their high activity and selectivity for synthesis gas production at relatively low temperatures [1-3]. To develop a deeper understanding of the functionality of these catalysts, it is necessary to understand the structure-activity relationship under reactor conditions [4]. We are performing *in situ* characterization of the nanostructure and nanochemistry of active Ni/SiO₂ catalysts during partial oxidation of methane in an environmental transmission electron microscopy (ETEM). For the same catalyst, we are also determining the methane (CH₄) conversion and carbon monoxide (CO) and carbon dioxide (CO₂) selectivities measured in a standard microreactor. By correlating information from these two approaches while varying the catalyst synthesis and operating conditions, we hope to develop a fundamental understanding of the relationship between the nanostructure and activity.

Materials and Methods

Silica spheres prepared by the Stober method [5] were impregnated with nickel nitrate hexahydrate (99.999%, Sigma Aldrich, USA) solution via the incipient wetness method to give a 5 wt% metal loading. The impregnated silica spheres were dried at 120°C for 2hrs and reduced at 400°C for 3hrs in a 5% H₂/N₂ atmosphere using an ISRI RIG 150 microreactor. Partial oxidation of CH₄ was conducted by flowing a 2:1 mixture of CH₄/O₂ in He through the catalyst bed and the output gases were analyzed in a Varian 3900 Gas Chromatograph. The catalyst nanostructure was monitored under near-reactor conditions with an FEI TECNAI F20 environmental transmission electron microscope (ETEM) equipped with a hot stage and gas reaction cell. The catalyst was reduced in 0.4 Torr H₂ in the ETM for 1 hr and then exposed to a 2:1 mixture of 1 Torr CH₄/O₂ while the temperature was increased stepwise up to 800°C. High resolution images and electron diffraction patterns were recorded in the reactive gas environment to follow the evolution of the nanostructure.

Results and Discussion

The reactor data (Fig 1) showed that the CH₄ conversion reached 90% at 720°C with a correspondingly high CO yield. CO₂ production peaked at about 500°C and decreased thereafter. *In situ* ETEM data showed that in 0.4 Torr of H₂, the Ni nanoparticles were in a predominantly metallic state (Fig 3a), were highly faceted and de-wet the silica support (Fig 2a). On exposure to 1 Torr of CH₄/O₂ at 400°C, electron diffraction showed that the metal transformed to NiO (Fig 3b) and dramatic changes occurred in the particle shape. The oxide particles assumed a dome-like structure wetting the silica as shown in Fig 2b. At still higher temperatures, the domes appeared to partially collapse and the particles compressed suggesting a possible ripening. The *in situ* electron diffraction showed that NiO was the predominant species even at 800°C.

Significance

This is the first study to correlate methane conversion and selectivity with catalyst nanostructure recorded under near reactor conditions. Detailed analyses of the nanostructures will provide insights into evolution and functioning of the catalyst.

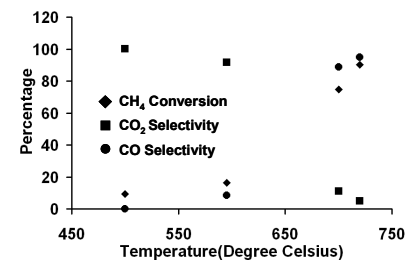


Figure 1: CH₄ conversion, CO and CO₂ selectivity.

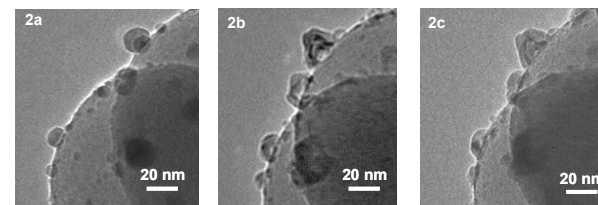


Figure 2: ETEM image of Ni nanoparticles/Silica (a) in 0.44Torr H₂ at 400°C (b) in 1 Torr CH₄/O₂ at 400°C and (c) in 1Torr CH₄/O₂ at 600°C.

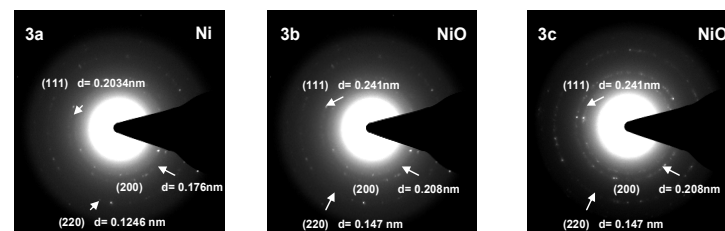


Figure 3: Electron diffraction patterns corresponding to Fig. 2a, 2b and 2c

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