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In-Situ Environmental TEM Studies to Understand the Effect of Ru Promotion on Supported Ni Catalysts

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

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

Bimetallic catalysts sometime exhibit superior properties than the individual monometallic catalysts. Noble metals are in general highly active but they are expensive. A combination of noble metal with an inexpensive metal is an ideal case of improving the catalyst performance and at the same time keeping the materials cost low. In the present study we are performing partial oxidation of methane (POM) on SiO_2 supported Ni-Ru bimetallic catalysts for syngas ($CO + H_2$) production. The catalytic properties of the bimetallic catalysts depend on the structure and composition of the individual nanoparticles which can change significantly when they are exposed to reacting gases. It is important to understand the evolution of bimetallic nanoparticles under reacting gas conditions in order get insights into its catalytic properties. We are performing catalytic measurements in parallel with *in-situ* environmental TEM (ETEM) studies on Ni-Ru bimetallic catalysts in order to understand the effect of Ru promotion on Ni catalyst for POM reaction.

$Ni\text{-}Ru/SiO_2$ bimetallic catalysts were prepared by incipient impregnation method, according to the procedures given in Banerjee et al [1], by taking a solution containing $Ni(NO_3)_2.6H_2O$ and $RuCl_3$ together. The final metal loading of the catalyst contains 2.25 wt% Ni and 0.025 wt% Ru. Catalytic measurements were performed in an *In-Situ* Research Instruments RIG-150 reactor and the effluent gases were analyzed with an online Varian 3900 gas chromatography system. STEM and EDX analysis on bimetallic catalyst were performed in a JEOL 2010 transmission electron microscope to study the compositional variations in the individual nanoparticles. *In-situ* environmental TEM experiments were performed in an FEI Tecnai F-20 transmission electron microscope equipped with a differential pumping system to hold the gas pressures inside the environmental cell.

Figure 1a shows a Z-contrast STEM image of $Ni\text{-}Ru/SiO_2$ after the reduction step along with an EDX spectrum of a typical individual nanoparticle showing the presence of both Ni and Ru in the nanoparticle. Figure 1b shows the catalytic performance $Ni\text{-}Ru/SiO_2$ catalysts. Complete combustion of up to 19% of the CH_4 takes place in the temperature range 300 °C to 560°C giving CO_2 and H_2O. A sudden increase in CH_4 conversion and CO selectivity is observed at 585°C with an O_2 conversion of 97%. Above 585 °C both CH_4 conversion and CO selectivity gradually increase with increasing temperature. The presence of Ru has lowered the activation temperature for syngas production by 190°C compared to pure Ni catalyst [2]. From the reactor data it suggests that the gas environment around the catalyst bed varies with increase in temperature. *In-situ* ETEM experiments under variety of gas environments must be performed in order to understand the effect of Ru promotion on the catalyst performance. Figure 2a and 2b shows the *in-situ* ETEM images of $Ni\text{-}Ru/SiO_2$ at 400°C in the presence of 1 Torr of H_2 and CH_4+O_2 mixture (in 2:1 ratio) respectively. The nanoparticles transformed to void like structures when the gas composition is changed from H_2 to mixture of CH_4 + O_2. Similar observations were found in case of pure Ni catalyst, where the void-structures are NiO [2]. Figure 2c is an *in-situ* electron energy-loss spectrum from the void structure nanoparticle in the presence of CH_4 + O_2, shows the O-Kedge and Ni-$L_{2,3}$ edge. The EELS proves that the nanoparticle

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has been transformed to NiO and shows that Ru does not inhibit the formation of NiO at 400 °C in the CH_4 and O_2 atmosphere. However, at higher temperatures, Ru may facilitate reduction of NiO back to Ni permitting syngas formation at lower temperatures compared to pure Ni. We will present the *in-situ* ETEM results on the effect of Ru promotion on structure and phase of Ni nanoparticles under other reacting gas conditions and its influence on the catalysts performance will be discussed.

References

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[3] 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.

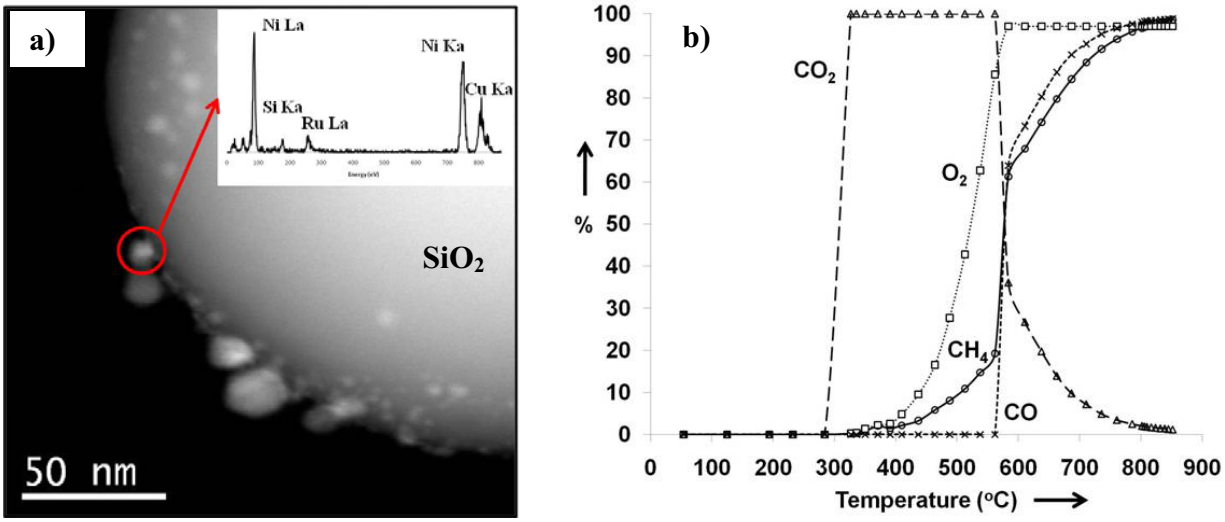

FIG. 1. a) STEM image of Ni-Ru/SiO_2 catalyst along with the EDX spectrum from individual nanoparticle showing the presence of both Ni and Ru. b) Plot showing CH_4 and O_2 conversion and its selectivity towards CO and CO_2 during the temperature ramp-up of b) Ni-Ru/SiO_2 catalyst.

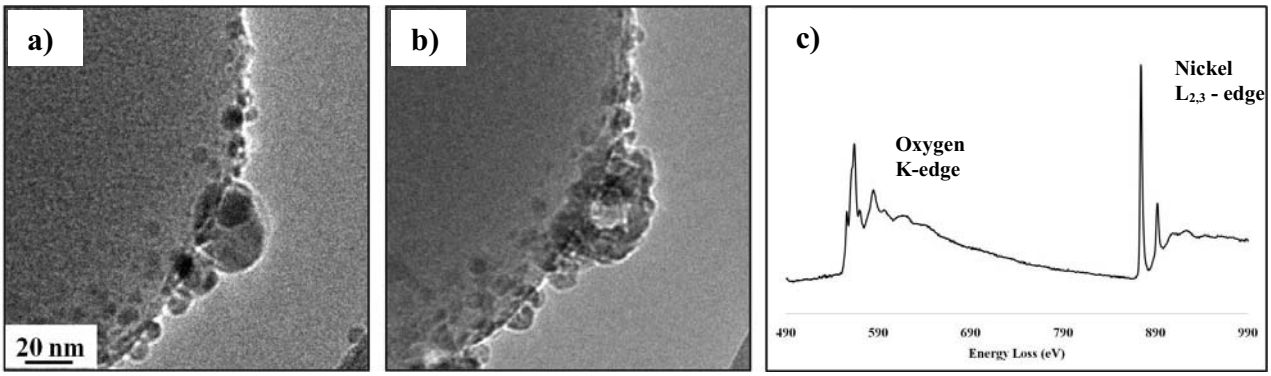

FIG. 2. a) and b) *In-situ* ETEM images of Ni-Ru/SiO_2 catalyst at 400°C in presence of 1 Torr of H_2 and CH_4 + O_2 mixture (in 2:1 ratio) respectively, c) *In-situ* EELS from a void structured nanoparticle at 400°C in the presence of CH_4 + O_2 mixture.

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