

## In-Situ Synthesis of Ni-Cu/TiO<sub>2</sub> Bimetallic Catalysts

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### Introduction

Ni-Cu bimetallic catalysts exhibit better catalytic activity and selectivity than Ni monometallic catalysts [1]. This is probably due to either the enrichment of one type of metals on the surface of the particles or the modification of the electronic structure of the bimetallic particles from pure metals [2]. It was reported that Cu can dramatically lower the reduction temperature of Ni precursor during the synthesis process [3]. However, an atomic level understanding of the role of the second metal (Cu) on the catalyst synthesis and properties is not yet established. In the present work, we report an *in-situ* synthesis study of the Ni-Cu bimetallic catalysts supported on titania P-25 using environmental transmission electron microscope (ETEM). Direct atomic level evidence on Cu enhanced reducibility of the precursor material is presented. The enhanced catalyst property is also discussed in terms of the alloying/ segregation of Ni and Cu species in this bimetallic catalyst system.

### Materials and Methods

The bimetallic Ni-Cu catalyst precursors were prepared by an incipient wetness technique. Titanium dioxide powder (Degussa P-25, a mixture of about 75% anatase and 25% rutile) was impregnated by Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and Cu(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O salt solutions to generate the precursors containing 3 wt% Ni and 1 wt% Cu. The metal-loaded powder was dried in an oven in air at 120°C for 16 h. The bimetallic particles were synthesized by reducing the precursors in a Tecnai F-20 field emission ETEM at 300°C under 1.5 Torr of 20% H<sub>2</sub> / 80% N<sub>2</sub>.

### Results and Discussion

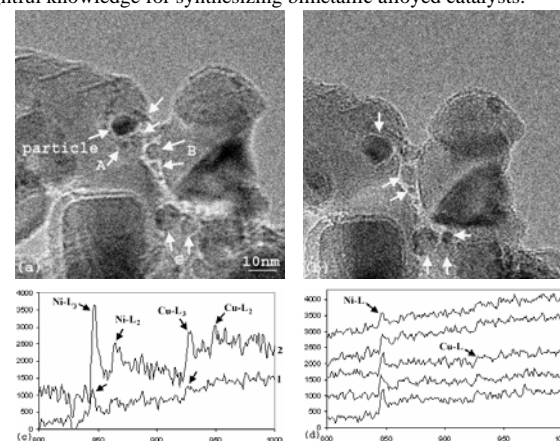
Figure 1(a) shows the formation of nanoparticles at certain surface sites (i.e., grain boundaries and surface defects) after 5 min reduction of the bimetallic precursors. Notice in Figure 1(b) that the stable, larger particle A grows at the expense of the nearby smaller particles (indicated by the white arrows). Particles B and C (shown in Figure 1(a)) merge together to form a bigger particle (indicated by an arrow in Figure 1(b)). These observations indicate that both ripening and coalescence occur during the growth of the nanoparticles in this bimetallic system. *In-situ* EELS nanoprobe analysis was performed on the nanoparticles after 120 min reduction (shown in Figure 1(c)). Approximately 87% of the nanoparticles analyzed showed similar features as that of spectrum 1. Quantitative analyses of these spectra indicate that whenever Cu is in the metallic form Ni is also in the metallic form. *In-situ* EELS nanoprobe analyses also demonstrated that Ni possesses the oxide form when Cu is not present

in the nanoparticles. This provides direct evidence of the Cu enhanced reducibility of the Ni precursor materials.

*In-situ* EELS line scan across typical nanoparticles are shown in Figure 1(d). Notice that both Ni and Cu EELS peaks are uniformly present across the whole particle, indicating a uniform alloying of the bimetallic components inside most nanoparticles. However, in a small number of nanoparticles, the Ni signal is much stronger at the particle edge even though both Ni and Cu peaks are present inside. This indicates that a small number of the Ni-Cu particles have a surface segregation of Ni. The alloying and segregation behavior of the bimetallic Ni-Cu/TiO<sub>2</sub> nanoparticles will be discussed based on the nucleation and growth mechanism of the particles and the higher reducibility of Cu ions under reducing gases.

### Significance

This is the first atomic level *in-situ* synthesis study of the Cu-Ni bimetallic catalysts prepared by incipient wetness technique. We provide direct proof of the Cu enhanced reducibility of individual Ni-Cu bimetallic nanoparticles. Detailed analyses on the alloying or segregation effects of the Ni-Cu bimetallic particles closely related to the synthesis route provide insightful knowledge for synthesizing bimetallic alloyed catalysts.



**Figure 1.** *In-situ* HREM images showing the evolution of Ni-Cu bimetallic particles on TiO<sub>2</sub> support reduced at 300°C for: (a) 5 min and (b) 60 min under 1.5 Torr of 20% H<sub>2</sub>/ 80% N<sub>2</sub>. The *in-situ* EELS probe (c) and line scan (d) analyses explore the chemical states and elemental distribution of the Ni and Cu in the Ni-Cu nanoparticles reduced after 120 min.

### References

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